

**STRUCTURE AND FORMATION
OF A GEL OF
COLLOIDAL DISCS**

Mark Kroon

Correspondence with the author of this thesis should be addressed to:

Dr. Mark Kroon
Philips Research Laboratories Eindhoven
Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands
Phone: +31 - (40) - 274 36 92, Fax:: +31 - (40) - 274 43 35
E-mail: mark.kroon@philips.com
Internet: <http://www.philips.com>, <http://www.research.philips.com>

Correspondence with the promotor of this thesis should be addressed to:

Prof. Dr. Ad Lagendijk
Van Der Waals-Zeeman Institute
Physics Department, University of Amsterdam.
Valckenierstraat 65-67, 1018 XE Amsterdam, The Netherlands
Phone: +31 - (20) - 525 56 63, Fax: +31 - (20) - 525 57 88
E-mail: adlag@phys.uva.nl, adlag@wins.uva.nl
Internet: <http://www.science.uva.nl/research/scm>

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Academische Pers B.V.
Nieuwe Herengracht 31, 1011 RM Amsterdam, The Netherlands
Phone: +31 - (20) - 623 70 73, Fax:: +31 - (20) - 626 43 71
E-mail: J.van.Kleef@acpers.nl, info@acpers.nl
Internet: <http://www.acpers.nl>

**Structure and formation
of a gel of
colloidal discs**

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Commissie : Prof. Dr. J. L. Barrat
Prof. Dr. D. Frenkel
Prof. Dr. H. N. W. Lekkerkerker
Dr. R. Sprik
Prof. Dr. J. F. van der Veen
Prof. Dr. J. T. M. Walraven

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Van der Waals-Zeeman Instituut
Universiteit van Amsterdam
Valckenierstraat 65
1018 XE Amsterdam
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Contents

1	Introduction	1
1.1	From sol to gel	1
1.2	Phase transition or structural relaxation?	2
1.3	Colloidal dispersions	4
1.4	Properties of colloidal suspensions	6
1.5	Suspensions of colloidal clay-discs	7
1.6	Structure of this thesis	9
2	Experimental procedures and techniques	11
2.1	Introduction	11
2.2	Laponite: the colloidal disc	11
2.3	Sample preparation and particle sizing	14
2.4	Some simple experiments	17
2.4.1	Samples prepared from dry powder with water	17
2.4.2	Low-viscosity state after freezing	17
2.4.3	Shear induced initial state	18
2.4.4	Swelling of a gel	19
2.5	Dynamic light scattering	20
2.5.1	Intensity fluctuations	20
2.5.2	Experimental setup	21
2.5.3	Correlation functions	24
2.5.4	Setup calibration	30

2.6	Static light and X-ray scattering	33
2.6.1	Structure and scattering	33
2.6.2	Static light scattering setup	35
2.6.3	Small angle X-ray scattering setup	35
2.6.4	Scattering with absorption	36
3	Dynamic light-scattering studies on the sol-gel transition of a suspension of colloidal discs	41
3.1	Introduction	41
3.2	Theory of dynamic light-scattering	41
3.3	Experimental	44
3.4	Results	44
3.4.1	Results for a 3.0 mass-percent sample	45
3.4.2	Results for various mass-fractions	55
3.5	Comparison with theory	57
3.6	Summary	64
4	Discrete wavelet transformation of dynamic light scattering signals	65
4.1	Introduction	65
4.2	Multi-resolution analysis	66
4.3	Discrete wavelet transformation	69
4.4	Discretely sampled traces	71
4.5	Simulations of fractional Brownian motion	77
4.6	Following the sol-gel transition	80
4.7	Spectral properties	84
4.8	Discussion	87
5	Structure and formation of a gel of colloidal discs	91
5.1	Introduction	91
5.2	Experimental	91
5.3	Results	92
5.3.1	Form factor of colloidal discs	93
5.3.2	Static structure factor	96
5.3.3	Time-dependent processes	99
5.4	Discussion	108

A	Formal theory of discrete wavelet transformation	113
A.1	Definition of the multi-resolution analysis	113
A.2	Mallatian pyramid algorithm	116
A.3	Daubechies wavelets	119
B	Accuracy and limitations of discrete wavelet transformation	125
B.1	Accuracy and limitations	125
B.2	Spectral noise	125
B.3	Heterodyne detection	128
	Bibliography	131
	Summary	143
	Nederlands Samenvatting	147
	Acknowledgements	151

Chapter 1

Introduction

1.1 From sol to gel

How can it be that a table spoon of mica-clay powder when carefully dispersed in a cup of demineralised water turns into a transparent and elastic gel in a few hours time after preparation? We might begin to answer this question by taking a look at the phenomenology of this peculiar transition, from a low-viscosity liquid-like state denoted as the “sol”, to a viscoelastic solid-like state denoted as the “gel”.

In their sol state, clay/water suspensions behave very water-like in the sense that they have a rather low viscosity and can be poured. This observation is explained by the simple fact that the majority of the volume of the system is occupied by water; only a few percent of the volume is occupied by the clay material [1, 2]. Optically the suspensions are as clear and transparent as water due to the resulting low number-density of clay particles and the relatively small size of the clay particles, of the order of only a few nanometers [2, 3, 4]. The continuous transition from sol to gel manifests itself only by an ever increasing viscosity, monitored by occasionally tumbling the batch tubes as the gelation proceeds. At the gel-point, marked down as the moment in time when the suspension ceases to flow or deform when tumbling the batch tubes, the viscosity diverges and the gel state is formed. An essential aspect of this sol-gel transition is that it occurs in time at constant temperature and density. The suspensions are never observed to phase separate into a highly diluted phase above a high-density solid phase.

During the whole process of gelation the clay suspension remains transparent and colourless. Hence the formation of dense clusters of particles by aggregation can be excluded as the driving mechanism behind the gelation process. In many of its

macroscopic properties, the gel state of the clay/water suspensions resembles the gels formed by gelatine [5], commonly encountered in food preparations. The clay gel shows an elastic response to small perturbing forces; it wiggles and behaves jelly-like. However, when subjected to shear forces above a certain threshold strength a liquid-like response (thixotropy) is observed. When left undisturbed, the sol always returns to gel state. Hence the clay gel can be brought back reversibly to a well-defined initial state under shear, provided the shear amplitude is high enough [6]. Unlike gelatine the clay/water system does not form thermotropic gels, i.e., clay gels are not reversible under temperature variation. For the clay/water suspensions shear takes the role of temperature.

1.2 Phase transition or structural relaxation?

In our everyday life we experience the three equilibrium states of matter; We breathe the gas phase of oxygen and nitrogen, we drink the liquid phase of water, and we build steel constructions with the solid phase of iron. These equilibrium states, or phases, are separated by transitions occurring as a function of the thermodynamic variables pressure, temperature, and density, which can be altered at will. For example, when a liquid is cooled quasi-statically towards the melting point, the equilibrium solid state with crystalline order is reached via a first-order phase transition [7]. However, one can reach the “undercooled” state of an ordinary liquid by cooling more rapidly than quasi-statically [8, 9, 10]. When cooling an ordinary liquid, the viscosity, and hence the characteristic time scale of density relaxation, increases exponentially with decreasing temperature. It is well known that the viscosity can increase as much as 16 orders of magnitude, without the liquid entering the equilibrium crystalline state [11]. By agreement the undercooled state of a liquid is denoted as “glassy” when the viscosity has increased beyond the limit of 10^{12} Poise [11]. By definition a glass is defined by the stationarity of its macroscopic state; within the time window of observation the thermodynamic variables that define the state remain unaltered [12]. From an experimental point of view the typical time scales of density relaxation processes then range beyond reasonable time scales of observation. The high viscosity is barring the undercooled liquid from restructuring into the equilibrium crystalline state. Hence the structure of the glass strongly resembles the disordered structure of the liquid, albeit dynamically frozen-in. It is worth mentioning that in general the transition point from liquid to glass is ill-defined and hard to obtain because the temperature at which the glassy state

is actually reached depends strongly on the history of cooling [9].

The undercooled liquid is a state of the system far from equilibrium that structurally relaxes towards the equilibrium state by means of the extremely slow process known as physical ageing [13]. For example, ordinary window glass is an undercooled ionic liquid far from equilibrium that very slowly relaxes towards the equilibrium crystal state. It is known that old church windows are thicker at the bottom side than at the top as a result of downwards viscous flow of the glassy material. For the same reason, the windows in houses of old Amsterdam, that have aged for many centuries, are separated from the runway at the top side and “hang” in a parabolic shape. Sometimes these windows have a small opening in the middle.

The clay/water system we study here appears to be off-equilibrium. It spontaneously evolves from the sol-state to the gel-state and never ceases to change, although at a much slower pace, in the gel state. With respect to molecular fluids the clay/water system consists of well-defined disc-shaped particles that are at least two orders of magnitude larger in size than ordinary molecules. Furthermore, the monocrystalline mica-like structure causes the clay particles to be charged upon dispersion and interact mainly repulsively via a screened-Coulomb potential [14, 15, 16]. Hence the gels formed by the clay/water system are “physical” gels; the rigidity of the gel does not originate from chemical bonding between constituent particles but purely from long-range electrostatic interactions. From an experimental point of view the clay/water system bears many similarities in its appearance with the glassy state encountered when sufficiently undercooling ordinary liquids; slow ageing dynamics after preparation of the system in a well-defined initial state. The observed similarities in the physical appearance combined with the clear differences in the physical character of both systems require a new interpretation.

Developing an understanding on the microscopic level of the ageing dynamics has long been a challenge. While significant advances have been made towards this goal, it is still unclear whether any existing theory or model provides a correct and complete picture for the dynamics and the related glass transition. The debate concerning whether and the extent to which the glass transition is a universal kinetic process has intensified greatly since the advent of the mode-coupling theory by Bengtzelius [18] and Leutheuser [19], and by Götze and Sjölander [20, 21]. The main premise of this theory involves non-linear coupling between pairs of density fluctuations. Increasing the strength of this coupling, either by decreasing the temperature or increasing the density, leads to a dynamic instability where the fluid structure becomes permanently frozen. At that moment the system becomes non-ergodic in the sense that during the

course of a measurement only a restricted part of the phase space available to the system is actually explored [22, 23]. The main predictions of the theory are (i) the approach to the transition from the fluid state is accompanied by the emergence of two highly non-exponential density relaxation processes with strongly diverging time-scales; (ii) arrest of the fluid structure at the transition is signalled by the vanishing of the slowest relaxation process and the emergence of frozen-in density fluctuations; and (iii) both density relaxation processes exhibit scaling properties in their characteristic time-scales.

Although much experimental and theoretical work has been carried out in order to verify the predictions of the mode-coupling theory and to understand the physical phenomenon behind the structural glass transition [24, 25, 26, 27, 28], it still remains controversial how to describe the glass transition within the framework of thermodynamics [29, 30]. Some explain the formation of a glassy state as a liquid being dynamically trapped just above a critical point [31]. Others postulate the existence of a narrowly avoided thermodynamic phase transition as a result of frustration of the system as a result of the mismatch of the structure of the equilibrium liquid and solid states [32]. New and better experiments aimed at probing different aspects of the dynamics are necessary to distinguish between the existing models and develop new ones. For this purpose we have carried out our experiments.

1.3 Colloidal dispersions

The clay/water suspensions we study are ranked as colloidal dispersions. Colloidal dispersions involve mesoscopic particles of one substance, the solute, suspended in a continuous background formed by another one, the solvent [33]. These colloidal dispersions appear in a wide variety in every day life. Dispersions consisting of either a solid or liquid phase in a gas phase are called aerosols. Natural examples are smoke and fog. Dispersions of droplets of a liquid phase in another liquid phase are called emulsions. Natural examples are milk and mayonnaise. When a gas phase is dispersed in a liquid we are dealing with a foam. Examples are encountered when shaving, washing, and extinguishing fires. Dispersions of a solid phase in a liquid phase are called sols, or complex fluids, or just suspensions. Dispersions of solids in liquids are the most abundant in nature and form the basis of a wide variety of systems of scientific and technological importance, including agricultural sprays, biological cells, ceramics, cosmetics, detergents, drilling mud's, paints, soils, toothpaste, and many

food preparations.

The scientific study of colloidal dispersions is colloid science. Colloid science dates from the early 19th century. Among the first notable investigations was that of the British botanist Robert Brown [34]. During the late 1820's Brown discovered, with the aid of a microscope, that minute particles suspended in a liquid are in continuous and random motion, envisaged best by a random walk. This phenomenon, which was later designated Brownian motion [34, 35], was found to result from the irregular collisions of colloidal particles with the molecules of the surrounding fluid. The Scottish chemist Thomas Graham [36], who is generally regarded as the founder of modern colloid science, delineated the colloidal state and its distinguishing properties. He suggested the name "colloid" from the Greek word " $\kappa ο λ λ α$ " for glue. In several works published during the 1860's, Graham observed that low diffusivity, the absence of crystallinity, and the lack of ordinary chemical relations were some of the most salient characteristics of colloids. Based on his findings he concluded that these characteristics resulted from the large size of the colloidal particles.

In colloidal suspensions, the solute units that are dispersed through the solvent are very much larger in size than the molecules of the solvent. By IUPAC definition [37] the lower limit of size for colloidal particles is roughly around 1 nanometer. With smaller particles a colloidal suspension would become indistinguishable from a molecular solution. The upper limit in size is normally set at a radius of 1 micrometer [37] in order to ensure that the particle's Brownian motion is not perturbed by external effects such as gravitational settling or convection. An advantageous feature of colloidal suspensions over atomic or molecular liquids is that the typical size of the constituent particles makes them experimentally more accessible. Submicron particle sizes allow for the use of visible light sources in experimental techniques such as light microscopy and static and dynamic light-scattering [35]. Compared to atomic or molecular liquids, the large particle size substantially slows down diffusion and density relaxation processes to characteristic time scales of the order of milliseconds to minutes. These essentially macroscopic relaxation times have important consequences for the rheology of colloidal suspensions. In an atomic fluid the experimentally attainable shear rates are much smaller than the intrinsic relaxation rate, hence the perturbation of the equilibrium structure is very small. Colloidal suspensions and colloidal solids are easily disrupted or melted by the action of relatively small forces induced by shear. The long relaxation times involved means that once distorted, a colloidal system will take a macroscopic time to return to equilibrium. During this time the non-equilibrium states and the dynamics along the trajectory towards equilibrium can be extensively studied.

1.4 Properties of colloidal suspensions

The spatial and orientational arrangement of particles in colloidal suspensions is determined by the volume fraction occupied by the particles, the interaction between the particles, and by their form and symmetry. From a theoretical point of view the equilibrium phase-diagram of colloidal suspensions of mono-disperse hard spheres is determined solely by the volume fraction. Hard-sphere systems reveal diluted gaseous phases, isotropic liquid-like phases, and solid phases at high densities [38]. A detailed experimental study on the phase behaviour of hard sphere colloids was reported by Pusey and van Megen who studied suspensions of Polymethylmethacrylate (PMMA) microspheres suspended in decalin/CS₂ mixtures [39, 40]. Suspensions of these spherical colloidal particles in a liquid show a fascinating variety of phase behaviour, ranging from equilibrium colloidal fluids to high-symmetry crystalline colloidal structures and disordered glassy phases.

The so-called “colloidal crystals” or photonic materials where the refractive index of light varies on the scale of the wavelength of visible light is expected to dramatically modify the propagation properties of light [41]. For certain crystal structures a stop gap has been observed experimentally [42]. A stop gap means that in specific directions through the crystal, dictated by symmetry, light with a wavelength in a band of frequencies can no longer propagate. The holy grail is to prepare a colloidal material where in all directions the propagation of light is no longer possible for a band of frequencies, called the “photonic band gap”. Then the radiative lifetimes of excited states of atoms or molecules with the right transition energy placed inside the colloidal structure should extend to macroscopic times.

In contrast to the high-symmetry colloidal crystals, the structure of the colloidal glass has many similarities with the colloidal liquid. The amorphous particle arrangement in the glassy state is comparable to that of the colloidal liquid. However, whereas the liquid phase is characterised by rapid motions of individual particles as a result of their large freedom of motion, in the glass these motions are much more restricted. The characteristic time-scale of the relaxation of density fluctuations becomes larger than the experimentally reasonable time-scale of observation, which actually defines the glass-state of matter [12].

The popularity of the hard-sphere system stems from the expectation, both theoretical [43] and experimental [40], that it could serve as a scaled model for simple liquids composed of spherical atoms or molecules. However, the representation of real liquids by a system of colloidal hard spheres is far from reality. First, the inter-

action between molecules in real liquids differs from the interaction between colloidal hard spheres. Actually it is softer. A convenient aspect of colloidal particles is that their mutual interaction and form can be tailored at will and independently. Soft potentials are realised by changing solvent, the concentration of salt and acids, and much more [40, 44]. In colloidal systems with soft interaction potentials the analogue of the intermediate state between liquid and glassy states encountered in real liquids, the undercooled liquid state, is predicted to occur [45]. In this respect the soft colloidal systems form a better representation of real liquids. Secondly, all molecules of real liquids possess rotational degrees of freedom, most of them are even anisotropic. Real liquids consisting of anisotropic molecules exhibit one or several liquid crystalline phases [46]. In these phases the spatial and orientational symmetry of the particle arrangement is determined completely by the shape and symmetry of the constituent molecules. When theoretically modelling these real liquids the shapes of the building blocks range from ellipsoids, cigars, and discs, to cylinders and needles. Deviation from spherical symmetry is expressed by the aspect ratio, defined as a ratio between typical particle dimensions. For example, the ratio of the lengths of axes of an ellipsoid, the diameter and thickness of a disc, and the diameter and length of a cylinder. Due to Onsager [47] we know that a system of anisotropic particles exhibits at least a nematic phase, which is characterised by long-range orientational order but short-range positional order. In colloidal systems of hard-discs many liquid crystalline-like arrangements are expected. This expectation is based on a vast amount of experimental observations on molecular liquid crystals [46], on theory [46, 47], and on numerical simulations [48, 49, 50]. For example, besides the ordinary isotropic phase at low volume fractions, Frenkel and Veerman encountered nematic, columnar, and cubatic order in their numerical simulations on the system of cut-spheres [50, 51].

1.5 Suspensions of colloidal clay-discs

The recent availability of synthetic colloidal clays, made of disc-like particles called laponite [17], promised a possible realisation of liquid crystalline phases on a mesoscopic scale. Each particle is a monocrystalline disc with an average radius of 25 nanometer and a thickness of 1.0 nanometer. Such a high aspect ratio makes the laponite system a mesoscopic model system of very thin discs. Because of its high purity and very small crystallite size, this synthetic clay forms colourless and transparent suspensions in water which are particularly suited for scattering studies. A highly

diluted suspension of laponite in demineralised water will remain a low-viscosity sol for very long periods of time (years). However, at higher volume fractions the colloidal suspensions are observed to undergo a transition in time from a low-viscosity fluid-like sol to an elastic solid-like gel, instead of entering a liquid crystalline phase [1, 2, 3, 4, 6, 52, 53, 54, 55, 56]. No evidence is observed for phase separation or density gradients over a wide range of volume fractions [1, 2]. The gelation time of the laponite system is phenomenologically observed to depend exponentially on the volume fraction [1]. This suggests that the laponite system does not have a critical volume fraction below which gelation would no longer occur, contrary to the phase diagram proposed by Mourchid *et al* [3]. The volume fractions that gelate are at least an order of magnitude lower than the location of the isotropic-nematic phase transition predicted by numerical simulations for a system of hard discs [50]. However, as a result of the underlying crystal structure the colloidal discs are negatively charged. In dilute suspensions the charged platelets separate completely and become dispersed as individual clay platelets. Charge balancing sodium cations diffuse into the surrounding polar liquid and screen the negative surface charge. As a result the particles interact via a screened Coulomb potential with a quadrupolar symmetry. Rescaling the actual volume fraction with the Debye screening length one expects the isotropic-nematic transition to take place at volume fractions in the range where actually the gel formation takes place. This is the range of our experimental study.

The phenomenologically observed sol-gel transition performed by the laponite system has already been studied quite elaborately. Rheological measurements [3, 4, 6, 53], electron microscopy and electron diffraction measurements [55], and preliminary light and neutron scattering measurements [52, 54] have been carried out. Based on these studies many structural models have been proposed in order to explain the mechanism of gel formation and the thixotropic behaviour of laponite suspensions under shear. These models range from the “house of cards” structure for the gel [57, 58], based on the attraction of the positive rim to the negative face of the clay particles, to the formation of fractal structures and clusters of particles as a result of a diffusion-limited aggregation process [4], to the formation of an equilibrium gel structure essentially by the electrostatic repulsion between charged particles [52]. Despite these experimental investigations and creative variety of proposed models, the microstructure of the gel and the nature of the sol-gel transition are still ill understood.

Motivated by these observations and by the absence of agreement between the results of different experiments we intend to determine the static and dynamic structure factor of the colloidal clay suspensions at every stage of the gelation process by means

of experiments. The goal we pursue is to determine, once and for all, the character and driving mechanism of this sol-gel transition. To achieve this goal we have performed static and dynamic light-scattering and small- and wide-angle X-ray scattering experiments [1, 2, 56].

1.6 Structure of this thesis

Chapter 2 contains a detailed discussion of the experimental procedures and techniques by which we prepare and study the colloidal suspensions of laponite [17] dispersed in demineralised water.

In Chap. 3 we present the results of an extended dynamic light-scattering study on the gelation in time of colloidal suspensions of clay discs [17]. Structure and dynamics in the neighbourhood of the transition can be studied best by using the technique of light scattering, dynamic and static. Dynamic light scattering probes the density correlation function describing the time evolution of the density fluctuations. If we consider time to be the physical control parameter, instead of temperature, the gelation has all the characteristics of a glass transition [18, 19, 20]. The measurements reveal the slowing down of the collective dynamics towards a well-defined gelation time, where the sample becomes a macroscopically immobile structure without phase separation.

In Chap. 4 we introduce the discrete wavelet transform as a quantitative tool in the interpretation of dynamic light-scattering experiments. Wavelet analysis accurately discriminates between exponential, stretched exponential and algebraic decay as the gelation occurs. From the results presented in Chap. 3 it is found that the dynamic structure factor or the related power spectrum of fluctuations is a function of time. The problem one faces is to accurately estimate the power spectrum or its functional form locally on the time axis as the system evolves. The relevant quantities to be measured are the algebraic exponents governing the relaxation of the density correlation function, and the fraction of frozen-in density fluctuations, which is considered the order parameter of the transition. However, an accurate determination of these quantities by light scattering is far from trivial [59]. One of the experimental difficulties encountered is elastic scattering in the gel-state. This static scattering is observed as “speckle” and acts as a spatially fluctuating local oscillator. The density correlation function can be extracted from the intensity correlation function under several assumptions concerning the homogeneity of the sample [1, 22, 60]. Secondly, correlation functions measured

on gel-like systems exhibit a long-time tail. The integration time used in DLS must extend beyond the longest relaxation time observed, but must be short with respect to the gelation time. This illustrates in a nutshell the experimental difficulties encountered when studying glass or gel formation. The time window of observation, the characteristic relaxation time, and the time scale of changing the external parameters (temperature gradient, shear field) that induces the glass or gel formation determines the outcome of any experiment. We believe to have overcome, at least partly, these problems by using a novel measurement procedure that analyses the intensity fluctuations locally in time. This method is the wavelet-based multi-resolution analysis, or discrete wavelet transform [61, 62, 63, 64]. The wavelet transform provides a means to reliably determine the relevant quantities describing the sol-gel transition from time-resolved recordings of the scattered intensity. Our results show that with wavelets the algebraic exponent of the power spectrum and the low and high-frequency cut-off are obtained with a higher accuracy and with a lesser computational effort compared to the conventional technique of photon correlation spectroscopy.

Chapter 5 contains a detailed account of our extended static scattering experiments performed to determine how the colloidal structure evolves as the gelation proceeds. Generally, two different types of three dimensional ordering are proposed for the gel-state. The first one, favoured by current opinion, is the "house of cards" structure for the gel [57, 58]. This conjecture is based on the physical intuition that the short-range part of the electrostatic interaction has a strong quadrupolar character. It implies the presence of T-shaped units. This may be true for gels at high particle densities. However, the observation of the existence of strong gels at low particle densities, where the colloidal discs are more than a few diameters apart, has led to the second model, a random structure for the gel. The more isotropic long-range part of the electrostatic interaction favours this structure [52, 53]. Little is known about orientational order or liquid crystalline order in this structure. Both structures are assumed to be formed by particle aggregation to form ever larger clusters in time [4]. Whether or not aggregation is the road to gel formation is one of the questions we will address in Chap. 5 of this thesis. Based on our findings we will suggest that, rather than aggregation, reorientation is the mechanism behind the phenomenon of gelation in time.

Chapter 2

Experimental procedures and techniques

2.1 Introduction

The structure and dynamics of complex fluids, where the characteristic length scales are of the order of the wavelength of light, can be studied best by light scattering techniques. Therefore, we present in this chapter the basic ingredients to derive the dynamic structure factor from dynamic light scattering and the static structure factor from small-angle X-ray scattering. The complex fluid we study is a suspension of clay discs suspended in water. In this fluid we study the transition of a low-viscosity or sol phase to a viscoelastic, glassy gel phase. Typical time scales for the transition are of the order of hours to days or longer, depending on parameters as salt concentration, volume fraction, and the initial low-viscosity state. This dependence on the initial state and the dynamical character of the transition necessitates a reproducible preparation of the initial state. Apart from some physico-chemical properties of the colloidal particles and their suspension in water we will here describe ways to prepare reproducible initial states and determine the gelation time in relation to the prepared initial state in “some simple experiments”.

2.2 Laponite: the colloidal disc

The inorganic fraction of soils and most natural sediments consists almost entirely of silica and the various silicates. The term clay is used in soil science and agriculture to mean any material of particle size less than $2\text{ }\mu\text{m}$ but the term clay mineral refers

to a specific group of silicate minerals. Some clay minerals have long been used in the ceramic industry because of their ability to bond to one another when heated to high temperatures. This makes these minerals suitable for making building bricks, earthenware, and pottery (including China). When wetted by water some clays swell and can hold-up water to a thousand times their volume. The clay-water system has thixotropic properties as one may have experienced when walking on a wet clay soil. The shear exerted by the soles of our shoes on the soil makes it slippery. The expected more or less elastic response has turned into a viscous response, tending to bring the walker out of his precarious equilibrium state. The swelling and thixotropic properties of clays can cause the famous Dutch dykes to slide at high water. These properties, however, are used on a large scale to our advantage in industry. Refined natural and synthetic clays find a wide industrial application as shear sensitive anti-settling agents in water based formulations such as paints and inks, personal care products, household products, agricultural detergents, and oil drilling fluids. Indeed, so extensive is the use of these materials in industry that clay minerals rank second to oil in terms of tonnage's used.

Most clay minerals are part of a large family of silicate minerals called *phyllosilicates* [14, 16]. As the Greek name indicates (*Phyllo* means leaf) these materials are built-up by leaves, or more precise by stacks of mineral leaves. A schematic representation of the structure of phyllosilicate minerals is depicted in Fig. 2.1. Each mineral leaf is a monocrystalline structure consisting of two-dimensional sheets of silica tetrahedra (SiO_4^{2-}) covalently bonded together. The octahedral sites in between the tetrahedral sheets are occupied by divalent or trivalent ions. The surfaces of each leaf are covered by the oxygen atoms of the silica tetrahedra and are hence negatively charged. Alkali ions like potassium K^+ , sodium Na^+ , or calcium Ca^{2+} compensate the charge and form the bonds between the leaves. Synthetic clay-minerals are generally synthesised in a sodium rich environment and the great majority of their interleaf cations are therefore sodium ions [65]. The phyllosilicate mineral structures are very easily cleaved along the surface (oxygen) plane into separate leaves, because the bonding between leaves is much weaker than the bonding between the tetrahedral sheets within each leaf.

The synthetic phyllosilicate clay-mineral laponite [17] is a swelling clay which takes up water and organic polar liquids between the mineral leaves [66]. These polar liquids can easily penetrate the interleaf regions, dissolving the interleaf cations, and separating the platelet surfaces by force. In dilute suspensions the negatively charged

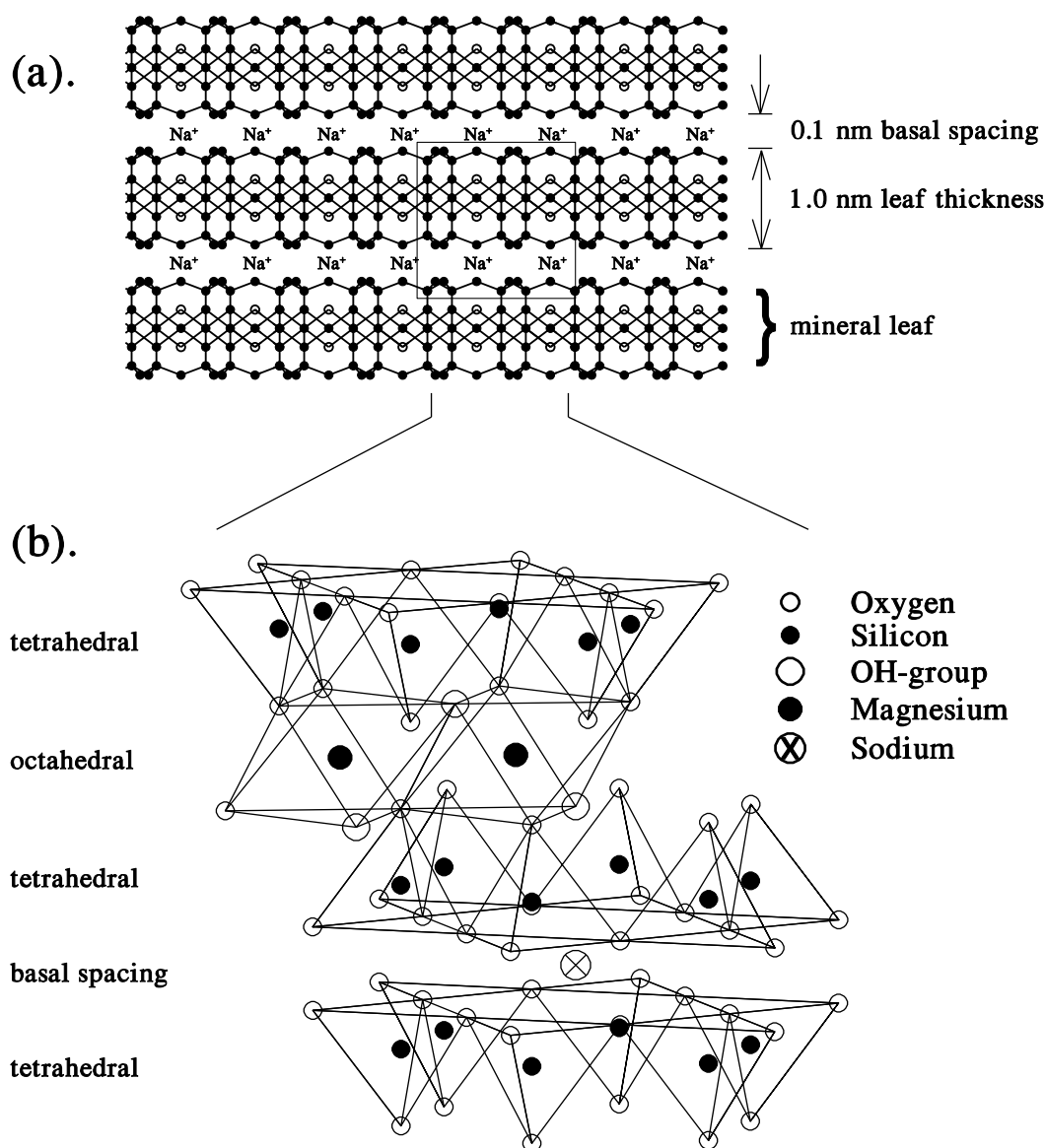


Figure 2.1: (a). Schematic representation of the layered structure of phyllosilicate minerals. Note the stacking of mineral leaves where each leaf consists of a monocrySTALLINE silicate structure. The area in the box is depicted magnified in the lower plot. (b). Idealised tri-octahedral phyllosilicate structure drawn in perspective. The legend on the right displays the elements present in the structure. Note the presence of sodium atoms in the basal spacing.

platelets separate completely and become dispersed as colloidal sized platelets, while the sodium cations diffuse into the surrounding polar liquid and screen the negative surface charge. The result is a system of uniformly charged colloidal discs surrounded by microscopic co-ions and counterions, the electrical double-layer [15]. The interaction between electrical double-layers can be represented by the Debye-Huckel potential [40],

$$V(r) = V_0 \frac{\exp[-\kappa r]}{r}, \quad (2.1)$$

where $1/\kappa$ is the Debye-screening length, and V_0 a constant. Equation 2.1 describes a spherically symmetric electrical double-layer. As a result of the build-up of an inhomogeneous and anisotropic charge distribution of counterions, the structure of the electrical double layer surrounding the colloidal discs is more complex. In that case both the Debye-screening length $1/\kappa$ as the amplitude V_0 must depend strongly on the position in space with respect to the plane of symmetry of the disc-shaped electrical double-layer. It is more convenient to write the interaction potential as a multi-pole expansion in terms of electrostatic poles [67]. The spherically symmetric monopole term is negligible because the double-layer is electrically neutral. The dipolar interaction is cancelled by the plane and rotation symmetry of the double-layer. In model calculations of Dijkstra *et al* [58] the complex interaction is reduced to a model of non-intersecting discs carrying a rigid point-quadrupole moment. These quadrupolar interactions favour edge-to-face pair configurations, or T-shaped units, that counteract the tendency of parallel or nematic alignment of bare discs at high densities. From their calculations Dijkstra *et al* [58] observe a transition from a low-density phase, where the discs assemble into elongated chain-like clusters, to a rigid gel-phase at higher densities. The gel exhibits a nearly incompressible network structure similar to the “house of cards” [57] where the T-shaped units serve as building blocks. However, the quadrupolar model is a rather drastic oversimplification of the real interaction because it totally ignores interference effects of interpenetrating electric double-layers which lead to configuration dependent many-body interactions.

2.3 Sample preparation and particle sizing

For our study we use the grade laponite RD (rapid dispersion) which is the easiest grade to disperse [17]. The laponite particle is schematically shown in Fig. 2.2, its crystal structure is shown in Fig. 2.1(b). The structure formula of laponite is

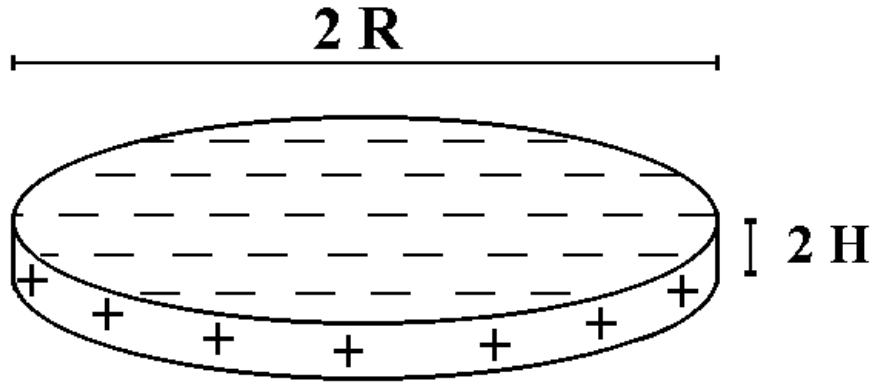


Figure 2.2: Schematic picture of the disc-like shape of the primary laponite particle. The surface charge distribution is fixed as a result of the crystalline structure of the particle as shown in Fig. 2.1(b). The thickness $2H$ denotes the thickness of a single mineral leaf as shown in Fig. 2.1(a).

$\text{Si}_8 [\text{Mg}_{5.5} \text{Li}_{0.4} \text{H}_{4.0} \text{O}_{24.0}]^{-0.7} \text{Na}_{0.7}^{0.7}$. Laponite is chemically pure because it is hydrothermally synthesised from simple salt of magnesium, lithium, and sodium silicate in the presence of mineralising agents. The synthesis is carried out at elevated temperatures and pressure to yield a precipitate which is then filtered, washed, dried, and milled to give a finely divided white powder. As a result of its high chemical purity and small particle size, laponite forms colourless and transparent suspensions which are particularly suited for light scattering studies. The natural clays on the other hand give rise to entirely opaque pink to brown dispersions in water because of mineral and transition metal impurities and their large primary particles.

For the preparation of a laponite suspension we start with demineralised and dust-free water obtained from a clean-water system (Lab-Ion Millipore *L2*, electroresistance above $10 \text{ M}\Omega\text{cm}^{-1}$). A small amount of laponite powder, typically 1 gram, is slowly mixed with the dust-free demineralised water in a certain mass fraction and stirred for 2 hours with a magnet stirrer. The suspension is then filtered using $1 \mu\text{m}$ filters (Millipore), and poured in a quartz cuvette of 10 mm diameter. After 10 hours the suspension is a charged-stabilised sol, where the light scattering entity is a single laponite particle [1, 2, 55]. The cuvette is sealed with a plastic cap in order to prevent dehydration over the time-span of all experiments discussed in this thesis (up to two years). A highly diluted suspension of laponite RD in water will remain as a low-viscosity sol for very long periods of time. However, at higher mass fraction

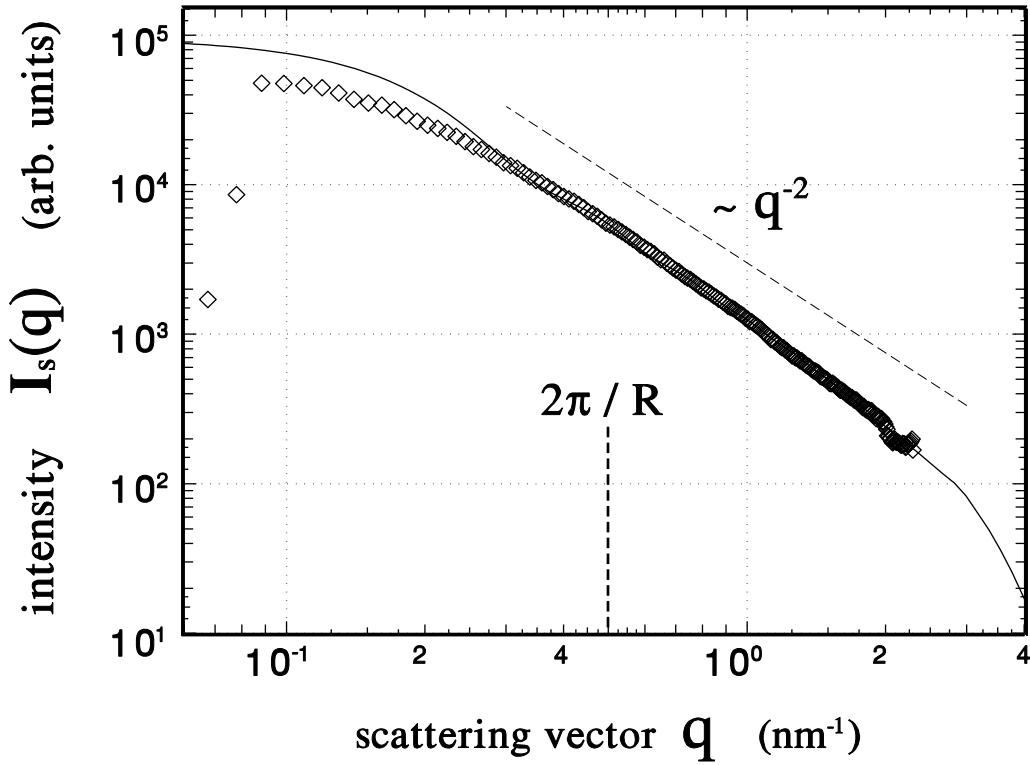


Figure 2.3: Static scattered X-ray intensity $I_s(q)$ (diamonds) of a highly diluted suspension of colloidal discs versus the scattering vector q . At large q , the intensity decays with q^{-2} (dashed line) as is expected for randomly oriented thin discs. The solid curve is the form factor calculated for randomly oriented monodisperse discs with a radius $R = 12.5$ nm and a thickness $2H = 1.0$ nm.

we observe the suspension to show an ever increasing viscosity, observed by tumbling the original batch tube as time after preparation proceeds. Finally, the suspension behaves as a macroscopically immobile structure which we call the gel. The gel does not flow nor adapts its shape when turned in the gravitational field. The suspensions remain colourless and transparent during gelation and after. We do not observe any evidence for phase separation or density gradients over a wide range of mass fractions $\varphi_m \equiv m_l/m_t$, where m_l is the partial mass of laponite in the total mass m_t [68]. In our studies the mass fraction ranges from 0.1 to 4.0 mass-percent. The limiting factor in obtaining samples at higher concentrations is the inability to fully suspend all particles individually before the suspension enters the gel state.

We estimated the single-particle dimensions from small-angle X-ray scattering measurements on a highly diluted suspension of laponite in water. These estimates are obtained by comparing the calculated theoretical expression of the form factor of

a disc-shaped particle [70] with the experimental results. In Fig. 2.3 we show this comparison, from which we estimate the colloidal discs to have an average diameter $2R = 25 \text{ nm} \pm 2.5 \text{ nm}$. The colloidal discs have a well defined thickness of $2H = 1.0 \text{ nm}$ without variance as a result of the crystal structure of the colloidal disc in the direction normal to the face. For an elaborate treatment of the theoretical form factor we refer to Sec. 2.6.1 and Chap. 5.

2.4 Some simple experiments

Besides the light and X-ray scattering experiments that will be discussed later in this chapter we have conducted several simple home-experiments with the colloidal clay suspensions in water. The aim of these experiments is to establish the preparation of a reproducible initial state and to obtain a qualitative insight in the parameters governing the gel formation.

2.4.1 Samples prepared from dry powder with water

Suspensions of laponite are prepared from dry powder and water, with mass fractions ranging from 0.4 mass-percent to 4.0 mass-percent. Gelation is followed at room temperature (20°C) and at an elevated temperature of $50^\circ\text{C} \pm 2^\circ\text{C}$ by placing colloidal samples in a hot-air oven. Suspension viscosity is monitored by occasionally tumbling the batch tubes as the gelation proceeds. The gelation time is marked down when the suspension does not flow nor adapts its shape when turned in the gravitational field, and is found to depend exponentially on the mass fraction, as shown in Fig. 2.4. This observation suggests that the laponite system does not have a critical mass-fraction below which gelation would no longer occur. This suggestion is supported by the observation of a gel formed by a 1.0 mass-percent suspension after standing alone for at least a year. Furthermore, at elevated temperatures the gelation times are up to an order of magnitude shorter than at room temperature. Apparently the gelation is a thermally driven process, where a higher temperature means a higher kinetic energy by which the process of gelation runs faster.

2.4.2 Low-viscosity state after freezing

Gelled samples are rapidly cooled down from room-temperature to a temperature of -22°C in the freezing compartment of a refrigerator. The frozen gel samples partially

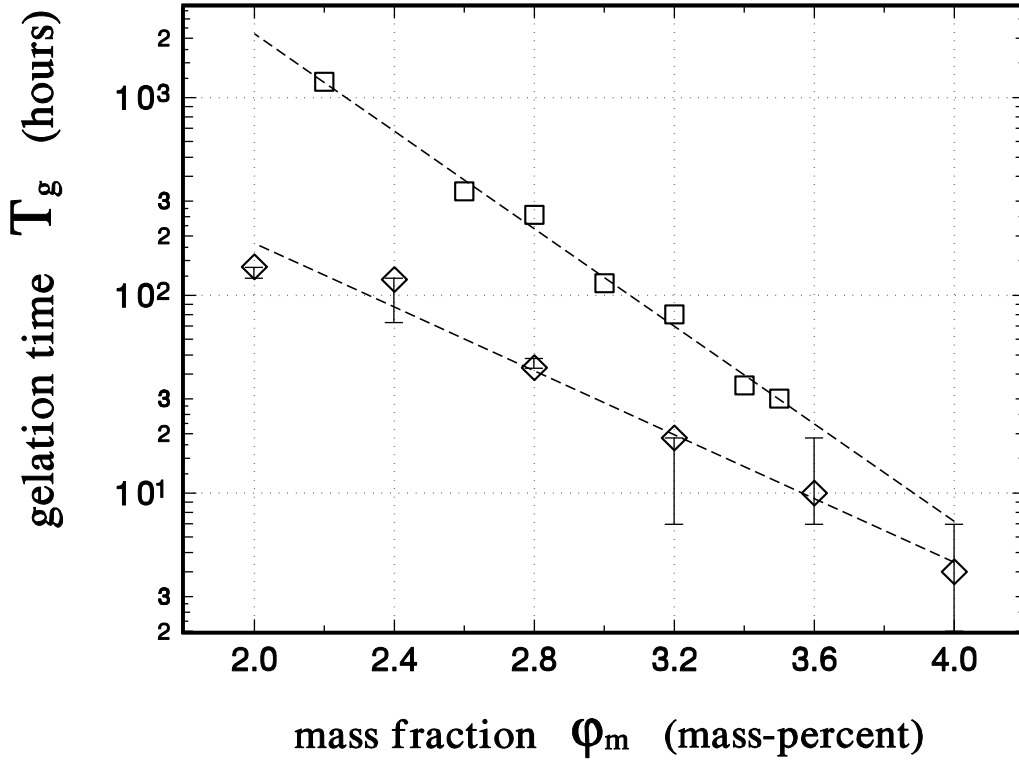


Figure 2.4: Gelation times T_g of colloidal clay suspensions prepared by mixing dry powder and water versus the mass fraction at two temperatures. The dashed lines are negative-exponential fits according to $T_g \propto \exp[-1.86 \phi_m]$ for a temperature of 50°C (diamonds), and $T_g \propto \exp[-2.83 \phi_m]$ for a temperature of 20°C (boxes).

consist of crystal clear ice and partially of opaque ice. After rapid melting by means of a warm water bath a transparent fluid is formed with an extremely low viscosity, even lower than the viscosity of samples prepared from dry powder. The samples still form gels in time, where the gelation time again depends exponentially on the mass fraction, as shown in Fig. 2.5. The gelation times, however, are typically an order of magnitude shorter with respect to samples prepared from the dry-powder state (See Fig. 2.4). Besides the method of mixing dry powder and water, the freezing and melting experiment reveals the possibility of preparing a low-viscosity initial state in a reproducing and well-defined manner.

2.4.3 Shear induced initial state

Shear measurements by Willenbacher [6] using a Couette cell reveal the possibility of preparing a low-viscosity state of laponite suspensions by applying high shear. Intense

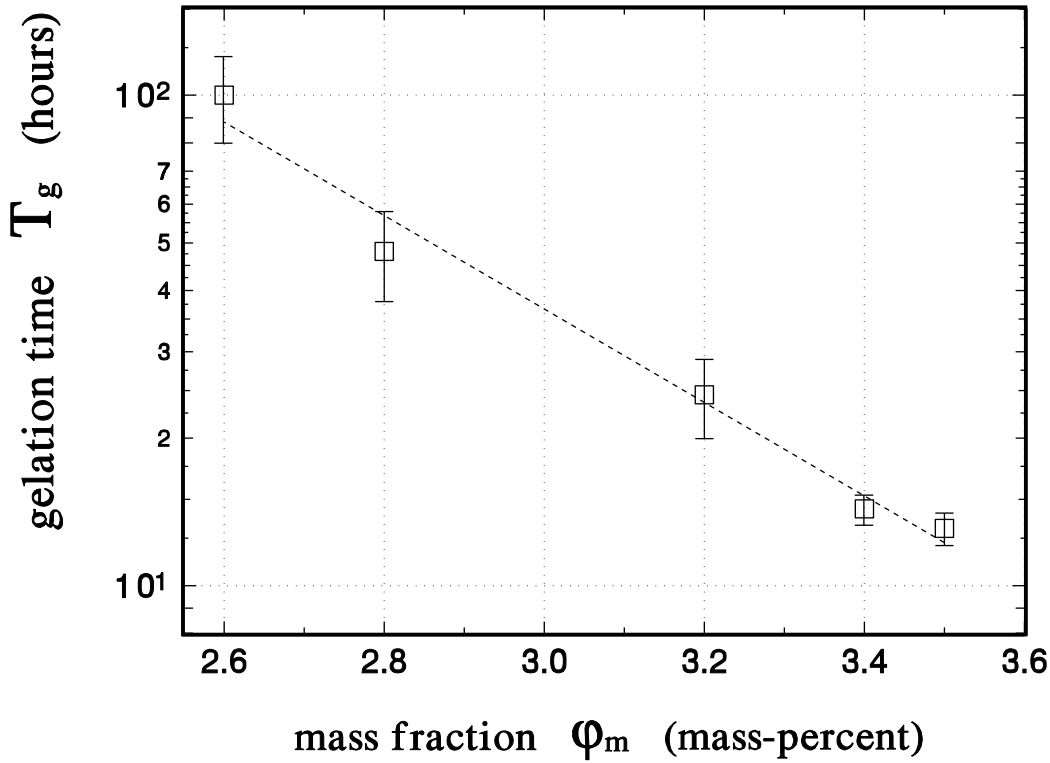


Figure 2.5: Gelation time T_g of colloidal suspensions of laponite after freezing and melting of the suspensions, where gelation is monitored at room temperature. The dashed line is a negative-exponential fit according to $T_g \propto \exp(-2.20 \phi_m)$.

stirring of a laponite gel with a magnet stirrer mildly reduces the suspension viscosity although laponite suspensions are highly thixotropic. In both cases the elastic gel-state is restored after ceasing shear, where the trajectory in time towards the gel point strongly depends on the shear history. Addition of small amounts of demineralised water while stirring results in a drastic reduction of viscosity. The slightly diluted low-viscosity suspension again forms an elastic gel which now takes substantially more time because of the dilution. The freezing method and powder-mixing method on the other hand give a better defined initial state which can be prepared in a reproducible manner. Throughout this thesis we discuss suspensions that were prepared by the powder-mixing method.

2.4.4 Swelling of a gel

On top of a gelled sample of 3.0 mass-percent and 2.0 cm height an equally thick layer of demineralised water is poured. The original gel height is visible by eye and

is marked down, the sample is sealed and left undisturbed. Over a period of a few weeks the gel height is observed to increase at least 20% while the total height of gel and water remains fixed. Although the swelling rate decreases in time, the swelling of the gel never stops where the structure remains colourless and transparent. The gel-water interface becomes blurred and in the remaining water volume density gradients are observed by eye and by laser light scattering. The latter reveals Brownian motion of single clay particles. Apparently the gel is capable of absorbing water, resulting in swelling of the gel volume. The swelling process does not result in an equilibrium or stationary state, not even in a homogeneous colloidal system within reasonable time since a characteristic time of the swelling process is at least half a year. Instead of completely breaking down into single particles and dissolving into the enlarged fluid volume, as predicted by Mouchid *et al* [3], the swollen and thus diluted colloidal structure remains to be a “glassy” viscoelastic gel.

2.5 Dynamic light scattering

2.5.1 Intensity fluctuations

Everyone who has seen a laser beam travel through dusty air has experienced the fascinating twinkling of the scattered light. These fluctuations in the intensity of scattered light stem from fluctuations in the number of scattering centres in the scattering volume V . The scattering volume is the region in space defined by the field of view of the detector and the dimensions of the incident beam of light. The intensity received at a detector placed outside the main beam fluctuates as particles move in and out of the scattering volume. Information on the number and motion of the particles can be obtained by analysis of these intensity fluctuations. In most cases of interest the relative magnitude of these number fluctuations will decrease as the mean number N of scattering centres is increased and for large enough N their effects can be neglected.

When a source emitting coherent radiation is used in a scattering experiment, fluctuations in the scattered radiation can also arise as a result of interference between fields originating from different scattering centres. The scattered field observed at a certain position in space outside the main beam is a linear superposition of the fields scattered by different scattering centres, e.g., colloidal particles. These waves have different amplitudes and a phase difference that depends on the relative particle positions only. A speckle pattern of randomly placed bright and dark areas of different intensities will be formed on the walls surrounding the scattering setup. Now consider

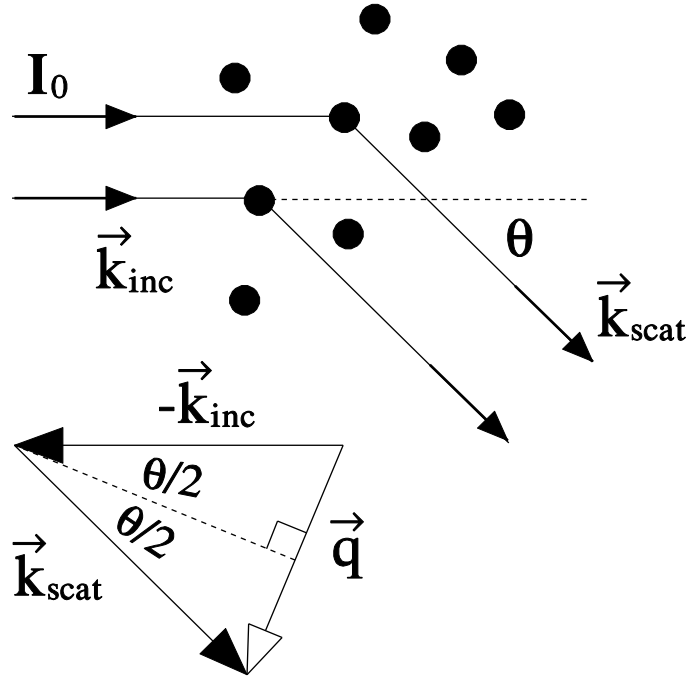


Figure 2.6: Schematic plot of a light scattering geometry, where I_0 is the intensity of incident radiation, $\vec{k}_{inc}$ and $\vec{k}_{scat}$ are the wave vectors of incident and scattered radiation, θ is the scattering angle, and $\vec{q} \equiv \vec{k}_{scat} - \vec{k}_{inc}$ the scattering vector. The solid dots represent discrete centres of scattering.

a diluted suspension of particles moving by diffusion in a fluid medium. As the particles move, the amplitude and phase differences between contributions will constantly change and the speckle pattern will fluctuate. A small detector placed at a certain position in space outside the main beam will register a fluctuating intensity whose time-dependence again provides information on the motion of the scatterers. Intensity fluctuations of this type have been named interference fluctuations.

2.5.2 Experimental setup

In Fig. 2.6 we schematically plot a light scattering geometry. The incident and scattered light field are assumed to have a plane-wave character [71] according to,

$$\vec{E}(\vec{r}, t) = \vec{E}_0 \exp(\vec{k} \cdot \vec{r} - \omega_0 t) , \quad (2.2)$$

where $\vec{E}_0$ is the polarised field amplitude, $\vec{k}$ the propagation vector, and $\omega_0 = c k/n$ the frequency, with c the vacuum speed of light and n the refractive index of the medium

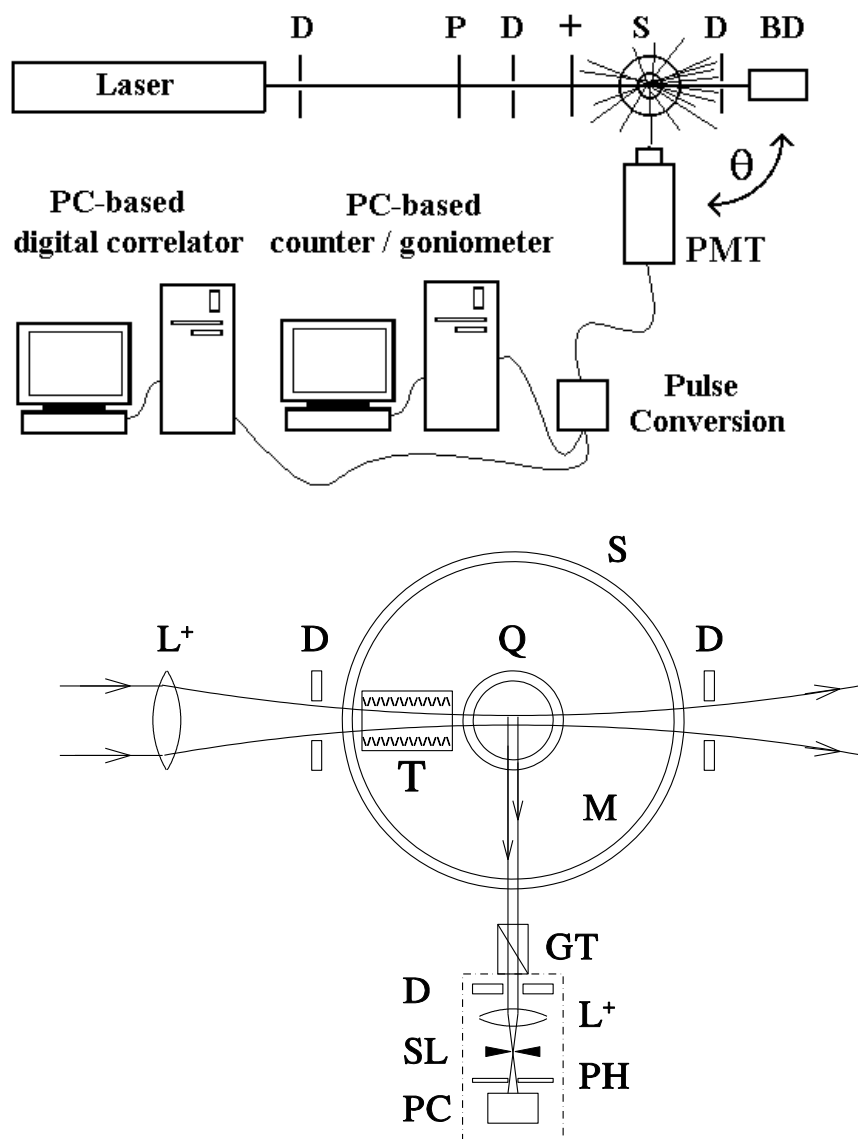


Figure 2.7: Schematic plot of the light scattering setup. Curved lines indicate electronic connections. The setup contains several diaphragms (D), a focusing lens (L), a polariser (P) defining the incoming polarisation direction, and the beam dump (BD). The scattering cell (S) contains a quartz cuvette (Q) in a refractive-index matching bath (M). Stray light scattering is suppressed by the plastic tube (T) with a rugged inner surface. Scattered light passes through the analysing Glenn-Thompson polariser (GT), a diaphragm (D), and is focused (L) on a narrow slit (SL). A pinhole (PH) of variable diameter traverses part of the speckle pattern to the photo-cathode (PC).

surrounding the scatterers. The incident and scattered light are characterised by their wave vectors $\vec{k}_{inc}$ and $\vec{k}_{scat}$, respectively. In the quasi-elastic scattering process that we are studying we assume $k_{inc} = k_{scat}$ and $\omega_{inc} = \omega_{scat} = \omega_0$. The momentum transfer q is then obtained from the conservation relation,

$$q = |\vec{k}_{scat} - \vec{k}_{inc}| = 4n\pi\lambda^{-1} \sin(\theta/2) , \quad (2.3)$$

where λ is the vacuum wavelength of incident radiation, and θ the scattering angle.

Figure 2.7 schematically shows our light scattering setup, intended for study of intensity fluctuations in scattered light. The source of laser light in our experiments is a continuous wave (CW) argon laser (Coherent Innova 100 Ar⁺ Ion laser) or a CW helium-neon laser (Melles Griot He-Ne laser). These lasers produce polarised and highly monochromatic laser light, typically $\Delta\lambda/\lambda \ll 10^{-5}$. The laser beam first passes through a polariser to define the polarisation of the incident beam and is then focused in the sample to a beam waist of approximately 50 μm . The scattering setup consists of a transparent glass beaker with a diameter of 80 mm. The beaker is filled with an index-matching fluid, either glycerol (Merck-Schuchardt, Glycerin zur synthese, C₃H₈O₃, $n_{20^\circ\text{C}} = 1.474$ [69]), toluene (Aldrich, 99.5+% spectrophotometric grade, C₆H₅CH₃, $n_{20^\circ\text{C}} = 1.496$ [69]), or cyclo-octane (Aldrich, 99+%, C₈H₁₆, $n_{20^\circ\text{C}} = 1.459$ [69]). These fluids closely match the refractive index $n = 1.4585$ of quartz [69] and help to reduce stray-light scattering. As a result of surface roughness of the low-quality beaker glass, laser light is scattered from the air-beaker interface in all directions. At small angles this flair dominates in intensity over the light scattered from the laponite sample. All care is taken to reduce stray-light scattering, as shown in Fig. 2.7. The signal to stray-light ratio is better than 10^2 over a range in the scattering angle θ from $4^\circ - 150^\circ$. The scattered light passes through an analyser which selects a given polarisation direction and finally enters a detector. The detector is a photomultiplier in single-photon counting mode measuring the intensity of the scattered light. Each light scattering measurement (dynamic and static) is performed at a randomly chosen position in the sample. To obtain the sample average of the scattered intensity distribution or to perform speckle averaging, the sample is slowly translated vertically over a distance of 5 mm through the laser beam with a home-built motorised setup while measuring the scattered intensity. The speed of sample translation is always chosen to be slow with respect to the ratio of the laser beam diameter and a characteristic time scale of the samples (See Fig. 2.8).

With this scattering setup we measure the three functions that are essential to measure the static and dynamic structure factors of a system that evolves in time. The

essential functions are: the scattered intensity or the number of scattered photons I per bin-width (sampling time), the distribution of scattered photons per bin-width $P(I)$, the photon correlation function $\langle I(0) I(\tau) \rangle$, and the cumulants and moments that can be derived from these functions. The ALV-5000 multiple-tau digital correlator [72] measures and calculates all these quantities simultaneously. In Fig. 2.8 we show an example of these quantities as measured on a standard sample. The correlation functions are measured with a bin-width of 200 nsec. The number of photons per bin-width as well as the distribution are sampled with a 6 msec integration time. In the ALV-5000 correlator the bin-width is fixed. However, in our experiments it is essential that the fluctuating intensity and the distribution of the intensity are measured with a variable bin-width. For that purpose we have a separate parallel working counter, gated with sampling times that can be varied between 100 μsec –1 sec.

2.5.3 Correlation functions

Time-dependent correlation functions of dynamical variables have been familiar for a long time in the theory of noise and stochastic processes [73]. In the last 25 years these functions have been very useful in many areas of statistical physics and light scattering spectroscopy. Parts of this section are based on the book by Berne and Pecora [35]. We start by defining the autocorrelation function of the scattered intensity $I(\vec{q}, t)$ by,

$$G(\vec{q}, \tau) = \langle I(\vec{q}, 0) I(\vec{q}, \tau) \rangle \equiv \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt I(\vec{q}, t) I(\vec{q}, t + \tau) . \quad (2.4)$$

When the time average $\langle I(\vec{q}) \rangle$ of the scattered intensity is known, it is convenient to define the deviations δI by $\delta I(\vec{q}, t) = I(\vec{q}, t) - \langle I(\vec{q}) \rangle$. Then,

$$\langle \delta I(\vec{q}, 0) \delta I(\vec{q}, \tau) \rangle = \langle I(\vec{q}, 0) I(\vec{q}, \tau) \rangle - \langle I(\vec{q}) \rangle^2 . \quad (2.5)$$

For times τ short compared to the characteristic time for the intensity fluctuations, the values $I(\vec{q}, t)$ and $I(\vec{q}, t + \tau)$ are equal and correlated,

$$\langle I(\vec{q}, 0) I(\vec{q}, 0) \rangle \equiv \langle I(\vec{q})^2 \rangle = \langle I(\vec{q}) \rangle^2 + \langle \delta I(\vec{q})^2 \rangle , \quad (2.6)$$

where $\langle \delta I(\vec{q})^2 \rangle$ is an absolute measure of the strength of intensity fluctuations. The correlation function G remains at its initial value for all times τ when $\langle \delta I(\vec{q})^2 \rangle = 0$, i.e., the scattered intensity is constant. For times τ large compared to the characteristic time for intensity fluctuations, the values $I(\vec{q}, t)$ and $I(\vec{q}, t + \tau)$ are expected to become totally uncorrelated and,

$$\lim_{\tau \rightarrow \infty} \langle I(\vec{q}, 0) I(\vec{q}, \tau) \rangle = \langle I(\vec{q}) \rangle^2 . \quad (2.7)$$

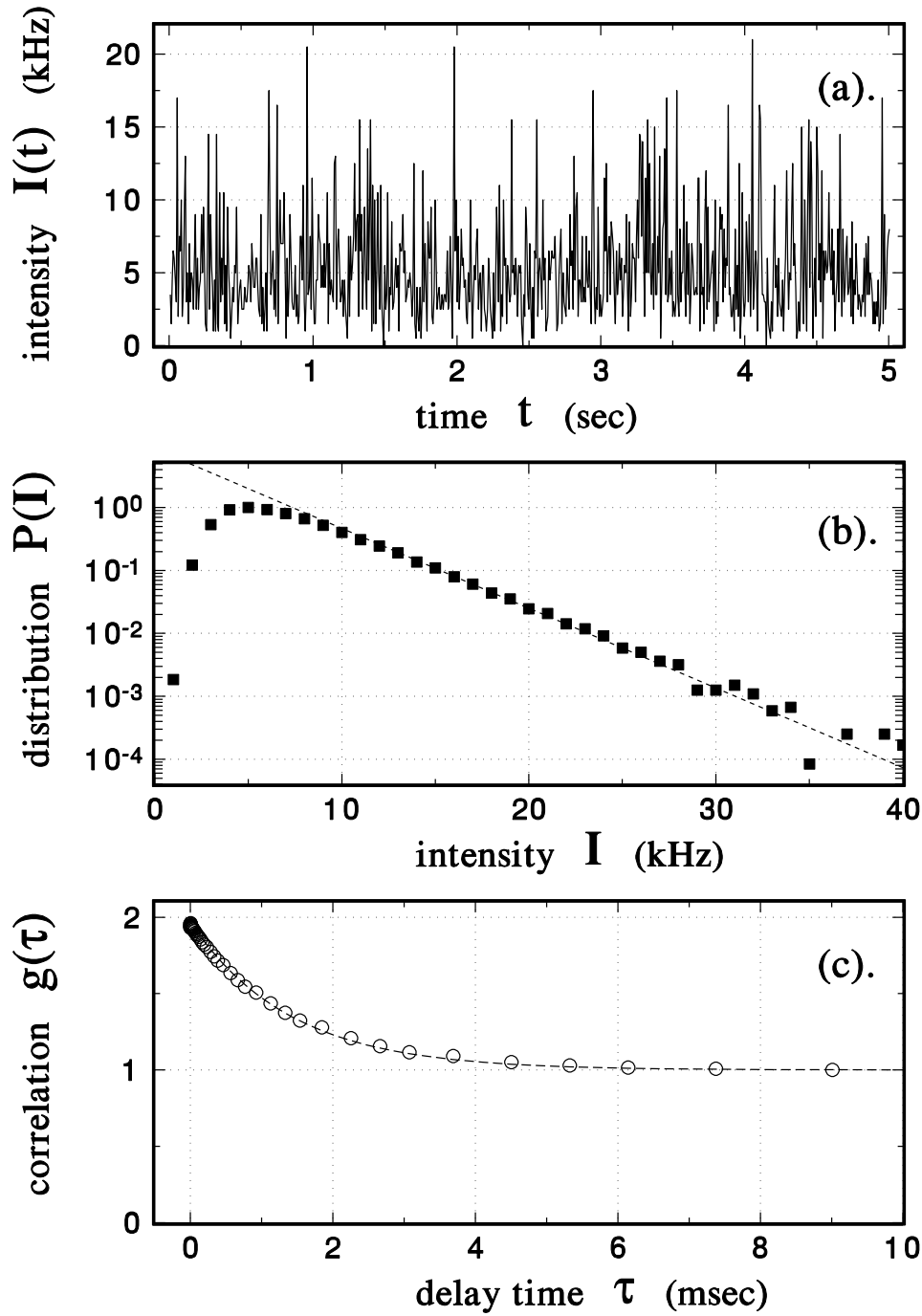


Figure 2.8: (a). Typical time-resolved scattered intensity trace $I(t)$, measured on a dilute suspension of latex microspheres in water. (b). Distribution $P(I)$ (boxes) of the scattered intensity. The dashed line is drawn according to $P(I) \propto \exp[-I/\langle I \rangle]$ where $\langle I \rangle = 3.4$ kHz. (c). Autocorrelation function $g(\tau)$ (circles) of the trace $I(t)$. The dashed line is drawn according to $g(\tau) - 1 \propto \psi \exp[-\tau/\tau_0]$ where $\psi = 0.968$ and $\tau_0 = 1.395$ msec.

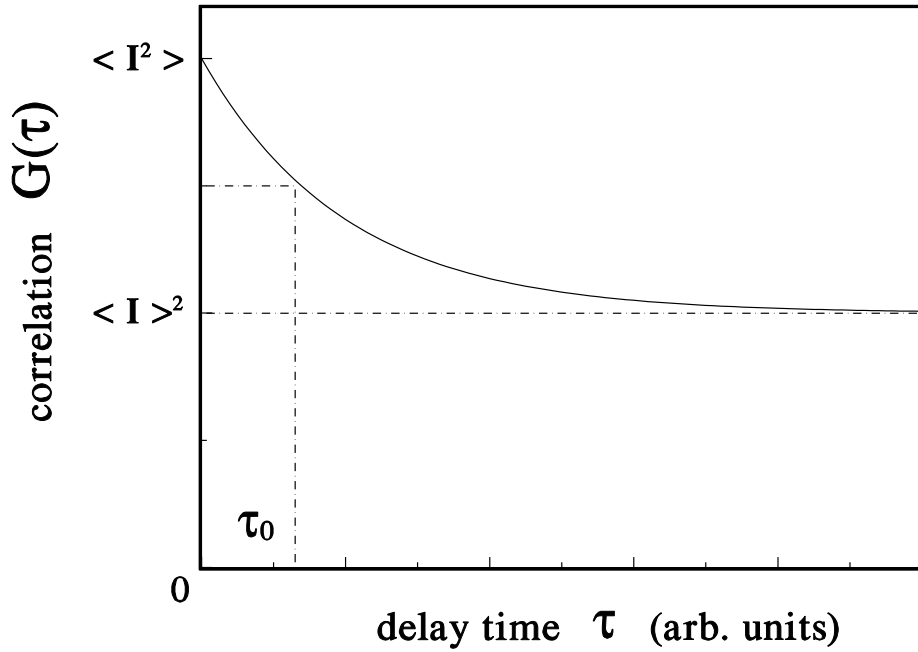


Figure 2.9: Example plot of the autocorrelation function $G(\tau)$ of the scattered intensity $I(t)$. Initially, the function starts at $\langle I^2 \rangle$. For times very long compared to a characteristic correlation time τ_0 , the correlation function decays to $\langle I \rangle^2$.

In general, the correlation function G of the non-periodically fluctuating scattered intensity decays from its initial value $\langle I(\vec{q})^2 \rangle$ to its final value $\langle I(\vec{q}) \rangle^2$ in the course of time. The characteristic behaviour of the correlation function G is illustratively shown in Fig. 2.9. For comparison purposes it is convenient to define the normalised correlation function $g(\tau)$ according to,

$$g(\tau) \equiv \frac{G(\tau)}{\langle I(\vec{q}) \rangle^2} = \frac{\langle I(\vec{q}, 0)I(\vec{q}, \tau) \rangle}{\langle I(\vec{q}) \rangle^2}. \quad (2.8)$$

The normalised correlation function reaches the limit, $g(\tau \rightarrow \infty) = 1$ for sufficiently long delay times. At the shortest delay times $g(\tau \downarrow 0)$ equals the normalised second moment or contrast $\langle I(\vec{q})^2 \rangle / \langle I(\vec{q}) \rangle^2$.

The signal produced by the detector represents the time-resolved scattered intensity, because the detector is working in photon-counting mode. However, when light impinges on matter, the electric field of the light induces an oscillating polarisation in that matter which subsequently radiates (scatters) a secondary electric field of light. Time-dependent fluctuations in the amplitude of the scattered field of light reflecting colloidal particle dynamics are measured experimentally by the fluctuating scattered intensity. Therefore it is important to establish the relationship between the field and

intensity correlation functions. For simplicity we consider a scattering volume which contains N discrete and identical particles or scatterers (See Fig. 2.6). At time t the position of the centre-of-mass of a particle labelled j is $\vec{r}_j(t)$ and the particles scatter light with a time-independent field amplitude $b(\vec{q})$. In the Rayleigh-Gans-Debye approximation [74] the incident light field is scattered by many small and individual subunits of the sample. The scattered field amplitude is calculated by merely adding the far-field part of the scattered waves with the proper phase difference according to,

$$E_s(\vec{q}, t) \equiv b(\vec{q}) \sum_{j=1}^N \exp[i\vec{q} \cdot \vec{r}_j(t) - \omega_0 t] , \quad (2.9)$$

where we assume the scattered light fields to have a plane-wave character [71], and factors independent of the particle positions have been omitted. In analogy with Eq. 2.4 the correlation function of the scattered field is given by,

$$\begin{aligned} F(\vec{q}, \tau) &\equiv \langle [E_s(\vec{q}, 0)]^* E_s(\vec{q}, \tau) \rangle \\ &= |b(\vec{q})|^2 \sum_{j=1}^N \sum_{m=1}^N \langle \exp(i\vec{q} \cdot [\vec{r}_m(\tau) - \vec{r}_j(0)]) \rangle . \end{aligned} \quad (2.10)$$

If the particles considered do not interact with each other (dilute limit) then the positions $\vec{r}_j$ and $\vec{r}_m$ are independent. The term in Eq. 2.10 in between brackets averages to zero unless $j = m$,

$$\begin{aligned} F(\vec{q}, \tau) &= |b(\vec{q})|^2 \sum_{j=1}^N \langle \exp(i\vec{q} \cdot [\vec{r}_j(\tau) - \vec{r}_j(0)]) \rangle \\ &= N |b(\vec{q})|^2 F_s(\vec{q}, \tau) , \end{aligned} \quad (2.11)$$

where the function,

$$F_s(\vec{q}, \tau) = \langle \exp(i\vec{q} \cdot [\vec{r}_j(\tau) - \vec{r}_j(0)]) \rangle , \quad (2.12)$$

represents the single-particle field correlation function. In the zero-time limit the function reaches the value $F_s(\vec{q}, \tau = 0) = 1$, and for sufficiently long delay times $F_s(\vec{q}, \tau \rightarrow \infty) = 0$. As stated previously, the observed quantity in a light scattering experiment is the scattered intensity $I_s(\vec{q}, t)$ which is defined as,

$$\begin{aligned} I_s(\vec{q}, t) &\equiv [E_s(\vec{q}, t)]^* E_s(\vec{q}, t) \\ &= |b(\vec{q})|^2 \sum_{j=1}^N \sum_{k=1}^N \exp(i\vec{q} \cdot [\vec{r}_k(t) - \vec{r}_j(t)]) , \end{aligned} \quad (2.13)$$

with Eq. 2.9. Following Eq. 2.4 the autocorrelation function of the scattered intensity becomes,

$$\begin{aligned} G(\vec{q}, \tau) &\equiv \langle I_s(\vec{q}, 0) I_s(\vec{q}, \tau) \rangle \\ &= \langle [E_s(\vec{q}, 0)]^* E_s(\vec{q}, 0) [E_s(\vec{q}, \tau)]^* E_s(\vec{q}, \tau) \rangle . \end{aligned} \quad (2.14)$$

With Eqs. 2.9 and 2.13 one finds for Eq. 2.14 the expression,

$$G(\vec{q}, \tau) = |b(\vec{q})|^4 \sum_{j,k,l,m=1}^N \langle \exp(i\vec{q} \cdot [\vec{r}_k(0) - \vec{r}_j(0) + \vec{r}_m(\tau) - \vec{r}_l(\tau)]) \rangle . \quad (2.15)$$

There are three types of non-zero contributions to Eq. 2.15; (i) $N(N - 1)$ terms for which $j = k \neq l = m$; (ii) $N(N - 1)$ terms for which $l = k \neq j = m$; (iii) N terms for which $j = k = l = m$. The term $|b(\vec{q})|^4$ is proportional to the scattered intensity squared. Summation of the non-zero contributions leads to,

$$G(\vec{q}, \tau) = \langle I(\vec{q}) \rangle^2 \left(\frac{N(N - 1)}{N^2} + \frac{N(N - 1)}{N^2} |\langle \exp(i\vec{q} \cdot [\vec{r}_j(0) - \vec{r}_j(\tau)]) \rangle|^2 + \frac{1}{N} \right) ,$$

which for $N \rightarrow \infty$ becomes,

$$G(\vec{q}, \tau) = \langle I(\vec{q}) \rangle^2 + |F_s(\vec{q}, \tau)|^2 . \quad (2.16)$$

In analogy with Eq. 2.8 we can rewrite Eq. 2.16 into the normalised form,

$$g(\vec{q}, \tau) \equiv \frac{\langle I(\vec{q}, 0) I(\vec{q}, \tau) \rangle}{\langle I(\vec{q}) \rangle^2} = 1 + |f_s(\vec{q}, \tau)|^2 , \quad (2.17)$$

quite often referred to as the Siegert relation. Equation 2.17 establishes the relationship between the field and intensity correlation functions for dilute systems and no additional stray light is detected (homodyne detection). In Chap. 3 we will treat the more general case of heterodyne detection on colloidal gels, where the relationship between field and intensity correlation functions is derived incorporating an intrinsic local oscillator.

For a dilute colloidal suspension the distribution of the amplitude of the fluctuating scattered field is without doubt a Gaussian function as a result of the central-limit-theorem [75] taking the number of scatterers $N \rightarrow \infty$. In order to prove this bold statement one has to realise that the observed quantity in our light scattering experiment is the scattered intensity. As a result of the Gaussian statistics of the scattered field one then measures a negative-exponential distribution function of the scattered intensity [75] according to,

$$P[I(\vec{q})] = \frac{1}{\langle I(\vec{q}) \rangle} \exp \left[-\frac{I(\vec{q})}{\langle I(\vec{q}) \rangle} \right] . \quad (2.18)$$

In Fig. 2.8 we show a typical time-resolved trace of the scattered intensity and the distribution $P[I(\vec{q})]$. The observation of a negative-exponential distribution function of the scattered intensity reveals the presence of Gaussian statistics of the scattered field amplitude. However, this statement only holds when the detector is monitoring only one coherence area A_{coh} of the scattered radiation and no additional stray light is detected (homodyne detection). The coherence area A_{coh} is defined as the area over which the spatial correlation function of the scattered electric field is significantly different from zero [35](p. 45). By definition different coherence areas are independent and uncorrelated. When the detector is observing a number of these coherence areas, the time-dependent fluctuations of each individual coherence area are added. The distribution of the scattered intensity is now a Poisson distribution [75] characterised by,

$$P_M[I(\vec{q})] = \frac{1}{M!} \frac{I(\vec{q})^M}{\langle I(\vec{q}) \rangle^{M+1}} \exp \left[-\frac{I(\vec{q})}{\langle I(\vec{q}) \rangle} \right], \quad (2.19)$$

where $\langle I(\vec{q}) \rangle$ is the average scattered intensity measured on a single coherence area, and $M + 1$ is the number of coherence areas observed. The second moment of the Poisson distribution, calculated to be,

$$\frac{\langle I(\vec{q})^2 \rangle}{\langle I(\vec{q}) \rangle^2} = \frac{M + 2}{M + 1} \equiv 1 + \psi, \quad (2.20)$$

where ψ is the coherence factor and $\psi^{-1} = M + 1$, yields the number of coherence areas observed by the detector. For $M = 0$ (single speckle) Eq. 2.19 yields Eq. 2.18 and the second moment Eq. 2.20 yields the value 2, equal to taking $\tau = 0$ in Eq. 2.17. With these results Eq. 2.17 becomes

$$g(\vec{q}, \tau) = 1 + \psi |f_s(\vec{q}, \tau)|^2, \quad (2.21)$$

if several coherence areas are observed simultaneously.

In a homodyne detection geometry the photo-multiplier detects the light as scattered by particles in the illuminated sample volume, of which the amplitude is given by Eq. 2.9. However, pure homodyne detection is hardly ever realised in experimental situations because scattering of small portions of coherent laser light by optical elements is almost unavoidable. Moreover, one of the experimental difficulties encountered with glassy samples is elastic scattering of the frozen-in density fluctuations. This static scattering is observed as speckle and acts as a spatially fluctuating intrinsic local oscillator. In this case, known as heterodyne detection, the light scattered towards the

detector consist of the scattered light E_s and a constant part E_c which are mixed at the detector. In the intensity correlation function the temporal fluctuations in E_s not only beat to themselves but also to the local oscillator E_c . After some algebra one obtains [1, 76],

$$g(\vec{q}, \tau) = 1 + \psi [x^2 h(\vec{q}, \tau)^2 + 2x(1-x)h(\vec{q}, \tau)] , \quad (2.22)$$

where the intensity ratio $1-x \equiv I_c/\langle I \rangle$ compares the local oscillator strength $I_c \equiv [E_c]^* E_c$ to the average scattered intensity (See Chap. 3). The function $h(\vec{q}, \tau)$ is given by Eq. 2.10 when normalised to the fluctuating intensity $x \cdot \langle I \rangle$. Deriving the density correlation function and the local oscillator strength from accurate measurements of the intensity correlation function and the moments of the intensity distribution function necessitates a precise knowledge of the coherence factor. For that purpose we have conducted light scattering experiments with a standard sample on which we report in the next section.

2.5.4 Setup calibration

An important consideration in a dynamic light scattering experiment is to ensure good optical coherence, i.e., the detector is monitoring only one coherence area A_{coh} of the scattered radiation. A number of experimental conditions must be satisfied. First the laser must work in single mode and is thus as monochromatic as possible. This can be accomplished by use of an intracavity aperture or an etalon. Secondly, the pinhole in front of the detector must be small enough to diffract only one coherence area. A useful estimate for the spatial extent of a coherence area is given by $A_{coh} \propto \lambda^2/\Omega$, where λ is the wavelength of light and Ω the solid angle subtended by the source at the detector. For our experimental setup we find $A_{coh} = 5 \times 10^{-9} \text{m}^2$, which yields a typical diameter of the coherence area of $2\sqrt{A_{coh}/\pi} = 80 \mu\text{m}$. In front of the detector a carousel of pinholes is mounted which allows the use of pinholes with diameters d ranging from $35 - 500 \mu\text{m}$. By adjusting the pinhole diameter we can choose the number of coherence areas observed simultaneously and thus optimise the optical coherence. For that purpose we have conducted light scattering experiments with a standard sample, namely, a highly diluted suspension of microspheres (latex, 200 nm diameter). These colloidal particles are performing Brownian motion [34] as a result of being constantly subjected to collisions with the molecules of the surrounding fluid. For Brownian motion Eq. 2.12 has the form,

$$F_s(q, \tau) = \exp(-q^2 D \tau) , \quad (2.23)$$

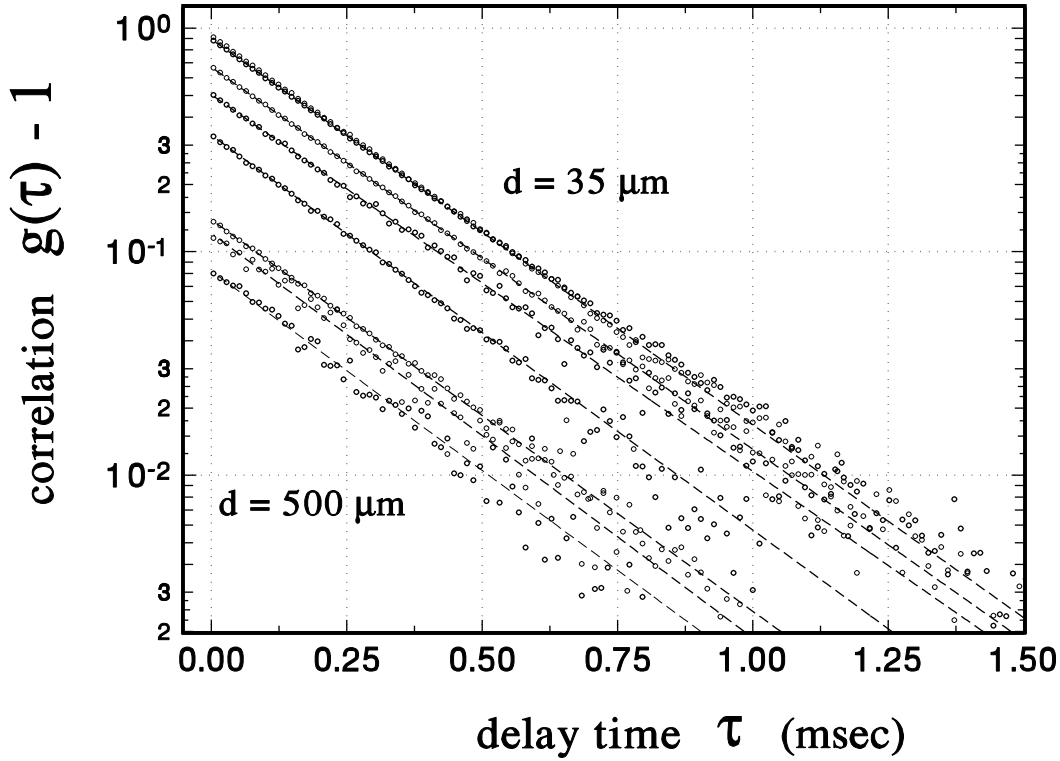


Figure 2.10: Semi-log plot of the intensity correlation function (dots) measured on a dilute sample of latex microspheres suspended in water. The plot shows $g(\tau) - 1$ for several diameters d of the pinhole in front of the detector. From top to bottom $d = 35, 50, 100, 150, 200, 300, 400$, and $500 \mu\text{m}$. The dashed lines indicate guides to the eye following Eq. 2.24.

where q is the magnitude of the wavevector $\vec{q}$, and D is the diffusion coefficient [35]. With Eqs. 2.21 and 2.23 the intensity correlation function will have the form,

$$g(q, \tau) = 1 + \psi \exp(-2 q^2 D \tau) . \quad (2.24)$$

Equation 2.24 reveals the possibility of obtaining important information on the dynamics of fluids and colloidal suspensions by light scattering measurements [77]. Here we limit the study to the coherence factor ψ . With the detector positioned under a fixed scattering angle $\theta = 90^\circ$ we perform dynamic light scattering measurements for different pinhole diameters. In Fig. 2.10 we show the results. The starting point of the correlation function $g(0) - 1 = \psi$ is observed to gradually decay as the pinhole diameter is increased, indicative of several coherence areas being observed simultaneously. For pinhole sizes ranging from $35 \mu\text{m}$ to $300 \mu\text{m}$ a linear relation between the number of coherence areas ψ^{-1} and the pinhole area πd^2 is found, as shown in Fig. 2.11. For

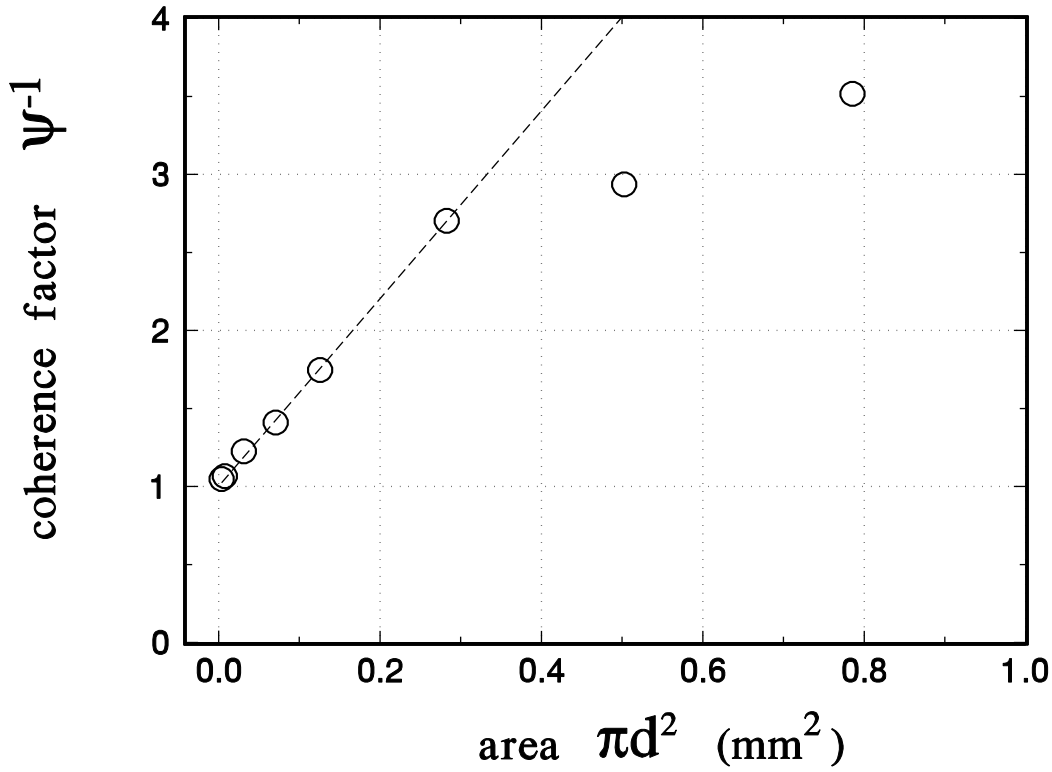


Figure 2.11: Plot of the number of coherence areas ψ^{-1} (circles) observed by the detector versus the pinhole area πd^2 . The area πd^2 determines the number of coherence areas observed by the detector. A linear dependence (dashed line) is found until a cut-off occurs at $d = 300 \mu\text{m}$ where internal optics of the detector blocks further expansion the incoming beam.

the smallest pinhole of $d = 35 \mu\text{m}$ we find a coherence factor $\psi = 0.96 \pm 0.03$, close to the optimal and maximal value of $\psi = 1.0$. With this detector setting most dynamic light scattering measurements as reported in Chap. 3 have been performed. The slope of the curves, proportional to the characteristic exponential decay-time $1/q^2 D$, is independent of the pinhole diameter. The observation of the dynamics of the colloidal system in terms of correlation functions is unperturbed by adding the contributions of several coherence areas.

2.6 Static light and X-ray scattering

2.6.1 Structure and scattering

Without going through a laborious derivation (see Refs. [74] and [38]) we simply state that the intensity of scattered electromagnetic radiation (read visible light or X-rays) per unit volume of the sample can be expressed as,

$$I_s(\vec{q}) \propto c M \overline{F^2}(\vec{q}) S(\vec{q}) , \quad (2.25)$$

where c is the mass fraction occupied by the colloidal particles, M is the mass of a single colloidal particle, and $\vec{q}$ is the wavevector. In general the dimensions of colloidal particles and the average distance between particles is much larger than the wavelength of X-ray radiation. Small-angle X-ray scattering at large q provides a means to obtain the form factor $\overline{F^2}(\vec{q})$ over a wide range in q , independent of the static structure factor $S(\vec{q})$ (See Chap. 5). Considering the dimensions of our colloidal particles and the wavelengths of commonly used laser radiation a static light scattering measurement is particularly suited to measure the static structure factor at small q independent of the form factor. With Eq. 2.25 the contributions $\overline{F^2}$ and S can then be separated in the intermediate q -regime.

The form factor $\overline{F^2}(\vec{q})$ accounts for interference of waves scattered from different parts within the scattering entity, and is formally defined as the Fourier transform of the real-space particle dimensions. The form factor of a sphere is given by [70],

$$\overline{F^2}_{sphere}(q) = \left[3 \frac{\sin(qR) - qR \cos(qR)}{q^3 R^3} \right]^2 , \quad (2.26)$$

where R is the radius of the sphere and q the magnitude of the scattering vector. At large q the form factor of the sphere decreases roughly as q^{-4} [70]. For a randomly oriented disc of infinitesimal thickness and diameter $2R$ the form factor is given by,

$$\overline{F^2}_{disc}(q) = \frac{2}{q^2 R^2} \left[1 - \frac{1}{qR} J_1(2qR) \right] . \quad (2.27)$$

The r.h.s. of Eq. 2.27 decreases as q^{-2} at large q . For a randomly oriented needle of infinitesimal thickness and length $2H$ the form factor is given by,

$$\overline{F^2}_{needle}(q) = \frac{Si(2qH)}{qH} - \frac{\sin^2(qH)}{q^2 H^2} , \quad (2.28)$$

where the function,

$$Si(x) \equiv \int_0^x \frac{\sin(t)}{t} dt . \quad (2.29)$$

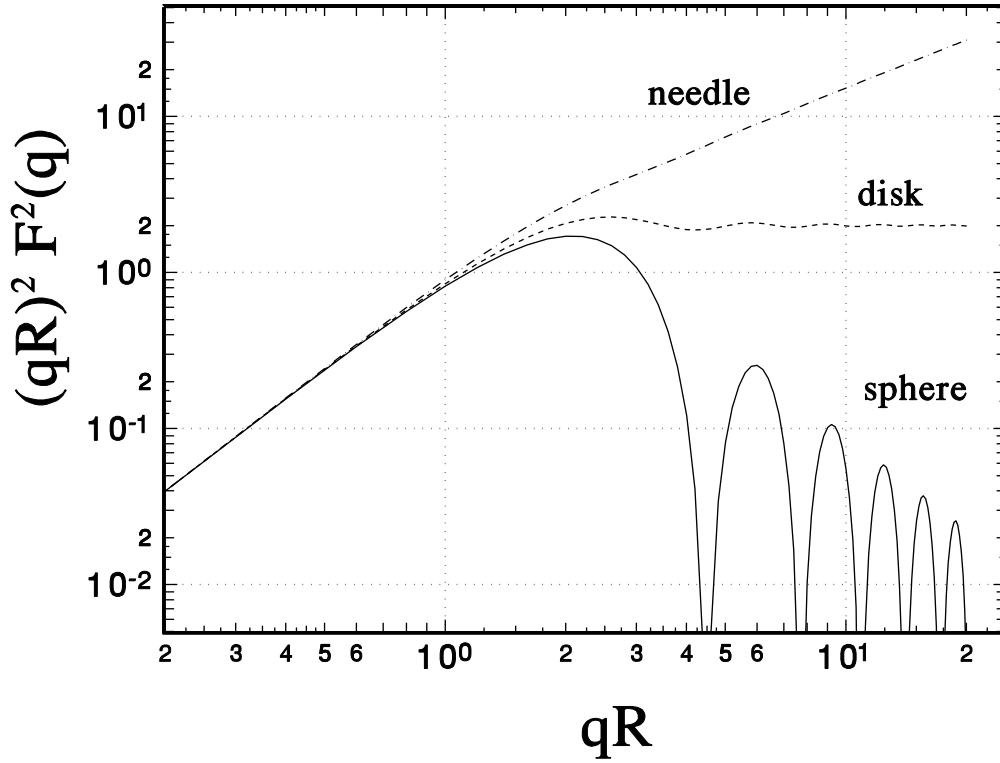


Figure 2.12: Guinier plot of the form factor of several elementary shapes; from top to bottom the thin needle (dash-dotted), the thin disc (dashed), and the sphere (solid). For the disc and the needle a random orientation is assumed.

At large q the form factor of the thin needle decreases as q^{-1} . In general the form factor reaches the limiting value $\overline{F^2}(q=0) = 1$. In Fig. 2.12 we plot the form factor of several basic shapes of particles, where we have assumed a random particle orientation. The depicted functions are multiplied by $(qR)^2$, where R is a characteristic particle dimension.

The static structure factor $S(\vec{q})$ in Eq. 2.25 accounts for interference of waves scattered from different regions in the colloidal structure, and thus describes the spatial arrangement of the colloidal particles which are acting as scatterers. Formally, the static structure factor is defined as,

$$S(\vec{q}) - 1 \equiv 1/N \sum_{i \neq j} \langle \exp[-i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)] \rangle_s, \quad (2.30)$$

where $\vec{r}_i$ and $\vec{r}_j$ are the positions in space of particles i and j , respectively. The angular brackets $\langle \cdots \rangle_s$ in Eq. 2.30 indicate an average over an ensemble of particle configurations. Equation 2.30 shows that a scattering experiment can probe the structure factor

when the length scale q^{-1} is substantially larger than typical particle dimensions, because then the form factor $\overline{F^2}(q) = 1$. The structure factor reaches the limiting value $S(q \rightarrow \infty) = 1$.

2.6.2 Static light scattering setup

The experimental static light scattering setup is exactly the same as the dynamic light scattering setup as shown in Fig. 2.7. Scattered light is detected in VV geometry with a photo multiplier that is mounted on the arm of a Philips goniometer. In principle the scattering angle θ ranges from 0° – 180° , but in practice θ ranges from 4° – 150° , with an accuracy of $1/800^\circ$. The effective range in q is $9.2 \times 10^{-4} \text{ nm}^{-1}$ to $2.6 \times 10^{-2} \text{ nm}^{-1}$. The signal to stray light ratio is better than 10^2 for this range.

2.6.3 Small angle X-ray scattering setup

At a synchrotron radiation facility a beam of electrons is travelling close to the speed of light in a high-vacuum storage ring. As the electron beam passes through bending magnets and wigglers, electromagnetic radiation is generated over a wide and continuous spectrum ranging from hard X-rays through the visible way into the infra-red. A simplified scheme of a synchrotron radiation facility is shown in Fig. 2.13. After passing through a system of monochromators, consisting of plates of germanium which are cut along a crystal axis, the X-ray beam enters the user hutch via a vacuum chamber window. Small angle X-ray scattering experiments are performed at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France) on the high brilliance beam line ID2/BL4 [78], and at the Daresbury (United Kingdom) Synchrotron Radiation Source (SRS) on station 8.2 [79]. At the ESRF the wavelength of the radiation is set at $\lambda = 0.0988 \text{ nm}$. The scattering vector q ranges from $1.0 \times 10^{-2} \text{ nm}^{-1}$ to $5.3 \times 10^{-1} \text{ nm}^{-1}$. A two-dimensional gas-filled detector is employed which allows the study the (an)isotropy of the scattering. At the SRS the wavelength of the radiation is set at $\lambda = 0.154 \text{ nm}$. Here the scattering vector q ranges from $9.9 \times 10^{-2} \text{ nm}^{-1}$ to 2.3 nm^{-1} . A gas filled quadrant X-ray detector is employed, which compensates for the decrease in scattering intensity towards higher q by the use of larger collecting elements a higher angles. The beam cross-section is $1 \times 0.5 \text{ mm}^2$ in size at both facilities.

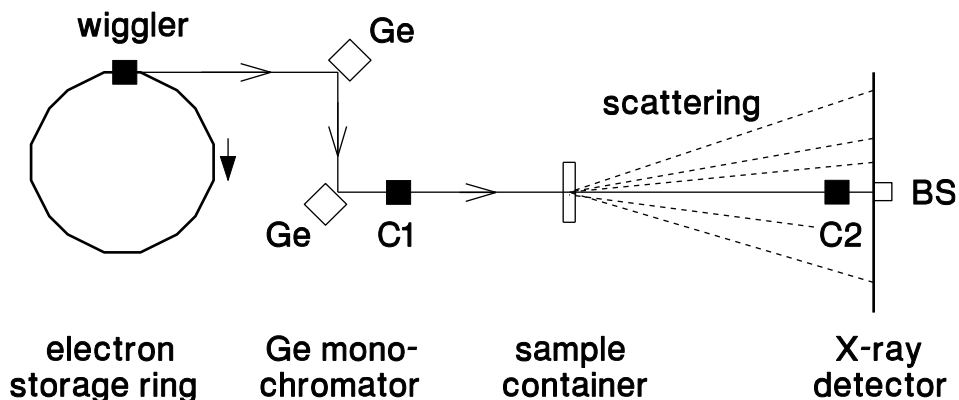


Figure 2.13: *Simplified scheme of the Daresbury and Grenoble synchrotron radiation facility. The ion chambers C_1 and C_2 keep track of the incoming and transmitted intensities. Unscattered X-rays are absorbed by a beam stop (BS).*

2.6.4 Scattering with absorption

The sample containers used in the X-ray scattering measurements are made of a brass frame ($1 \times 4 \text{ cm}^2$) acting as a spacer of 0.5 mm thickness. Windows of Kapton (Polyimide Film, Goodfellow Cambridge Ltd., thickness 0.05 mm) or Mica (Muscovite Mica, Goodfellow Cambridge Ltd, thickness 0.025 mm) are glued on both sides. The colloidal suspensions are inserted through sealable holes. We use such thin containers in the X-ray scattering experiments as a result of the strong absorption of X-rays by water (absorption coefficient $\mu \sim 10^3 \text{ m}^{-1}$). This problem is not encountered when performing light scattering experiments on laponite suspensions with visible light frequencies (absorption coefficient $\mu \sim 10^{-3} \text{ m}^{-1}$). In turn, the thin plane parallel geometry of the X-ray cell is impractical to use in light scattering. The strong scattering from the window interfaces and the relatively low scattering from the laponite suspensions prohibits the use of the same cell.

The scattering geometry of the small angle X-ray scattering experiments is shown schematically in Fig. 2.14. The X-ray beam passes through the sample container where scattering occurs on all the components present in the beam. The window materials scatter the X-ray radiation with a certain pattern $x(\theta)$, water in the colloidal samples yields a pattern $z(\theta)$, and scattering of X-rays by the laponite particles yields a pattern $y(\theta)$. The aim of this section is to derive the pattern $y(\theta)$ from the total scattered intensity pattern when taking into account the severe absorption of X-rays by water. In

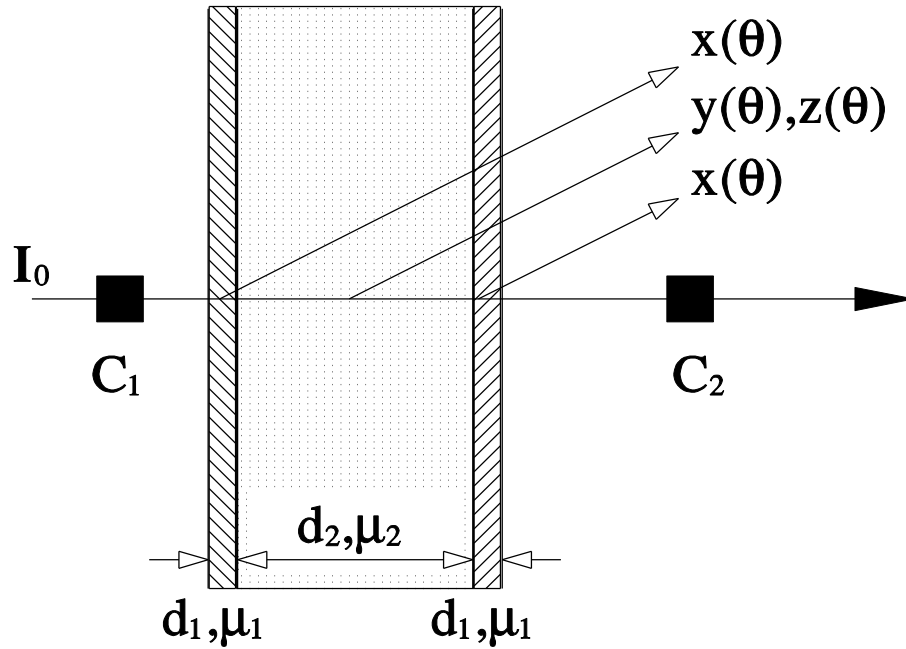


Figure 2.14: *Basics of the small angle X-ray scattering setup at the Daresbury SRS and the Grenoble ESRF. We refer to the text for further explanations.*

these derivations we take into account a possible variation in the thickness of different samples with respect to the empty and water-filled reference samples. We assume absorption of X-rays by water to dominate over the losses as a result of scattering, and the absorption of X-rays by laponite to be comparable to water as a result of the comparable oxygen concentration.

The scattering process can be divided up into three parts: First the incoming beam with intensity I_0 will be exponentially attenuated by absorption according to,

$$I(x) = I_0 \exp(-\mu x) , \quad (2.31)$$

where μ is the absorption coefficient and the x-axis represents the propagation direction of incoming X-rays. Simultaneously the material involved scatters X-rays with the pattern $z(\theta)$ by,

$$\Delta I(\theta, x) = I(x) z(\theta) \Delta x . \quad (2.32)$$

The scattered X-rays are attenuated along the remaining optical path through the scattering geometry. The scattering angle θ is assumed to be small enough to approximate

the total beam path with the sample thickness d . Then,

$$\Delta I(\theta, x, d) = \Delta I(\theta, x) \exp(-\mu[d - x]) . \quad (2.33)$$

The total intensity scattered under an angle θ is calculated by integration of the scattering process along the beam path through the sample,

$$\begin{aligned} I(\theta, d) &= \int_0^d I_0 \exp(-\mu x) z(\theta) \exp(-\mu[d - x]) dx \\ &= I_0 d z(\theta) \exp(-\mu d) . \end{aligned} \quad (2.34)$$

From the empty cell, from here on referred to as “(ec)”, we record contributions from both windows. The scattering pattern from the first window is exponentially attenuated by the second window, and vice versa,

$$I_{d_1}^{ec}(\theta) = 2 I_0 x(\theta) d_1 \exp(-2\mu_1 d_1) , \quad (2.35)$$

where d_1 is the window thickness and μ_1 the absorption coefficient of the window material. The reference sample filled with water only, from here on referred to as “(hc)”, gives contributions from both windows and the water. Here we have to keep clear track of the attenuation.

$$I_{d_2}^{hc}(\theta) = I_0 [2d_1 f(\theta) + d_2 z(\theta)] \exp(-2\mu_1 d_1 - \mu_2 d_2) , \quad (2.36)$$

where d_2 is the thickness of the water region in between the windows and μ_2 is the absorption coefficient of water. When the cell is filled with the colloidal suspension, from here on referred to as “(lc)”, we must allow for the possibility of this sample to have a different thickness d_2' with respect to the water filled cell. Laponite adds a pattern $y(\theta)$ to the scattered intensity,

$$I_{d_2'}^{lc}(\theta) = I_0 \{2 d_1 x(\theta) + d_2' [z(\theta) + y(\theta)]\} \exp(-2\mu_1 d_1 - \mu_2 d_2') . \quad (2.37)$$

From here on we need to manipulate the expressions to obtain the scattering pattern $y(\theta)$ of laponite. In Eqs. 2.35, 2.36, and 2.37 we recognise the same exponential attenuation term, only with different path lengths. We define the following transmission coefficients,

$$\begin{aligned} T_{d_1}^{ec} &= \exp(-2\mu_1 d_1) , \\ T_{d_2}^{hc} &= \exp(-2\mu_1 d_1 - \mu_2 d_2) , \\ T_{d_2'}^{lc} &= \exp(-2\mu_1 d_1 - \mu_2 d_2') , \end{aligned} \quad (2.38)$$

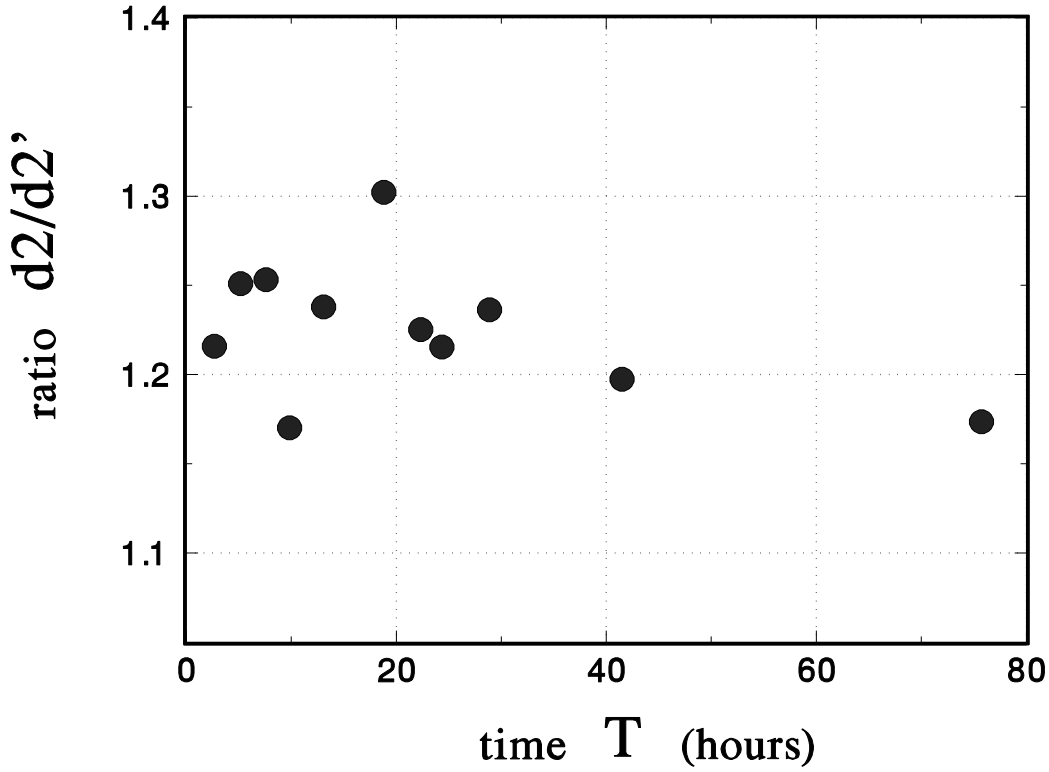


Figure 2.15: Ratio of the laponite sample thickness d_2' and the water reference sample thickness d_2 as a function of time after filling. The ratio does not decay much because the samples have been carefully sealed to prevent leakage.

and divide the scattered intensity patterns by these transmission coefficients and the incoming intensity, according to,

$$\begin{aligned}
 I_{d_1}^{ec}(\theta)/I_0 T_{d_1}^{ec} &= 2 d_1 x(\theta) , \\
 I_{d_2}^{hc}(\theta)/I_0 T_{d_2}^{hc} &= 2 d_1 x(\theta) + d_2 z(\theta) , \\
 I_{d_2}^{lc}(\theta)/I_0 T_{d_2}^{lc} &= 2 d_1 x(\theta) + d_2' [z(\theta) + y(\theta)] .
 \end{aligned} \tag{2.39}$$

Subtraction of the empty-cell contribution and recollection of the remaining terms leads to the following expression for the scattering pattern $y(\theta)$,

$$y(\theta) = \frac{1}{d_2'} \left(\frac{I_{d_2}^{lc}(\theta)}{I_0 T_{d_2}^{lc}} - \frac{I_{d_1}^{ec}(\theta)}{I_0 T_{d_1}^{ec}} \right) - \frac{1}{d_2} \left(\frac{I_{d_2}^{hc}(\theta)}{I_0 T_{d_2}^{hc}} - \frac{I_{d_1}^{ec}(\theta)}{I_0 T_{d_1}^{ec}} \right) . \tag{2.40}$$

The absolute value of the thickness of the samples is not known beforehand. However, we can calculate the ratio of d_2' and d_2 with the definitions of the transmission. From Eq. 2.38 we obtain,

$$\ln(T_{d_1}^{ec}) = -2\mu_1 d_1 ,$$

$$\begin{aligned}
\ln(T_{d_2}^{hc}) &= -2\mu_1 d_1 - \mu_2 d_2 \ , \\
\ln(T_{d_2'}^{lc}) &= -2\mu_1 d_1 - \mu_2 d_2' \ .
\end{aligned}
\tag{2.41}$$

By subtraction and division we find for the ratio of thickness,

$$\frac{d_2'}{d_2} = \frac{-\mu_2 d_2'}{-\mu_2 d_2} = \frac{\ln(T_{d_2'}^{lc}) - \ln(T_{d_1}^{ec})}{\ln(T_{d_2}^{hc}) - \ln(T_{d_1}^{ec})} \ .
\tag{2.42}$$

The electron current in the storage ring of a synchrotron shows a continuous decay because of use of the beam energy and scattering of electrons on atmospheric particles in the high-vacuum system. During the scattering experiments the measurement system keeps track of the incoming and transmitted intensities via two ion-chamber readouts (See Fig. 2.14). The incoming beam intensity is monitored by the first ion chamber and yields a proportional voltage C_1 . The incoming intensity attenuated by the sample is monitored by the second ion chamber which yields a proportional voltage C_2 . The sample transmission is retrieved by $T = a C_2/C_1$, where a is the ratio C_1/C_2 of the ion chamber readouts without a sample cell mounted in the setup. Possible changes in the incoming beam intensity and sample transmission are automatically compensated for in Eq. 2.40 by division of the scattered intensity pattern with the reading of the second ion chamber. In Fig. 2.15 we show as a function of time after preparation the ratio of thickness d_2'/d_2 for a measurement run. The ratio is always larger than unity because the viscosity of laponite suspensions is larger than the viscosity of clean water. Therefore the samples of laponite are filled with slightly more force.

Chapter 3

Dynamic light-scattering studies on the sol-gel transition of a suspension of colloidal discs

3.1 Introduction

In this chapter, we present the results of a dynamic light-scattering study on the sol-gel transition of a suspensions of disc-shaped colloidal particles, called laponite [17], in water. When dispersed in water, laponite forms a unique system amidst the mesoscopic gel or glass formers. Preparing the system in a low-viscosity sol-like state, it becomes more viscous as time progresses until in the gel state it behaves elastically at small shear rates. Unlike some polymeric gel formers the gel formation is reversible in the sense that it can be brought reproducibly in a well-defined initial state under shear [6]. This sol-gel transition in the time domain has the characteristics of the thermodynamic glass transition [20]. Preliminary experimental evidence points to an ageing phenomenon, i.e., the out of equilibrium evolution of a system quenched into a glassy state. The purpose of the experimental work presented in this chapter is to gain a better understanding of the phenomenon of gelation in time.

3.2 Theory of dynamic light-scattering

Suspensions of laponite remain colourless and transparent during and after gelation, which makes them ideally suited for a light-scattering study. Dynamic light-scattering probes the density fluctuations of the medium present in the scattering volume [35].

In recent years dynamic light-scattering has been applied to, among others, colloidal glasses [25, 27], polymer gels [5, 80, 81, 82], silica gels [76], and gelating clay suspensions [1, 53, 52, 56]. These systems share the common feature that they solidify under certain circumstances. When this solidification has occurred, the local time-averaged properties are observed not to be equal to the sample-averaged properties. Local properties are measured at one particular position in the sample. Sample-averaged properties are obtained by sampling many different positions in the samples and taking the average afterwards [23]. The constituent particles are thought to be localised near a fixed time-averaged position around which only small-amplitude motions can be executed [22]. Then the field amplitude $E(\vec{q}, t)$ as scattered by the medium undergoing density fluctuations can be written as,

$$E(\vec{q}, t) = E_f(\vec{q}, t) + E_c(\vec{q}) , \quad (3.1)$$

where the zero-mean complex variable E_f results from the remaining but restricted particle motion, and $\vec{q}$ is the scattering vector. The constant part E_c is scattered off the frozen-in density fluctuations. In the fluid-like state the system the constant part is absent because here the particle motion is diffusive. In the solid-like state, however, the local configuration of fixed time-averaged particle positions, and thus the contribution of the constant part to the scattered field, is nowhere the same. This spatial dependence explains the difference between locally obtained and sample-averaged properties.

The observed quantity in our light-scattering experiment is the scattered intensity, defined as $I(\vec{q}, t) \equiv [E(\vec{q}, t)]^* E(\vec{q}, t)$. Calculating the scattered intensity with Eq. 3.1 yields,

$$I(\vec{q}, t) = I_f(\vec{q}, t) + 2\text{Re}\{[E_f(\vec{q}, t)]^* E_c(\vec{q})\} + I_c(\vec{q}) , \quad (3.2)$$

where $\text{Re}(A)$ denotes the real part of the complex variable A . The quantity $I_f \equiv [E_f]^* E_f$ denotes the fluctuating intensity. The quantity $I_c \equiv [E_c]^* E_c$ denotes the static scattering. Relevant quantities in describing the statistical character of the scattered intensity are the time-averaged first and second moment of the observed intensity distribution Using Eqs. 3.1 and 3.2 and assuming a Gaussian distribution for the fluctuating part E_f , one finds for these moments [75],

$$\langle I(\vec{q}) \rangle = \langle I_f(\vec{q}) \rangle + I_c(\vec{q}) , \quad (3.3)$$

$$\langle I^2(\vec{q}) \rangle = 2\langle I(\vec{q}) \rangle^2 - (I_c(\vec{q}))^2 , \quad (3.4)$$

where $\langle I \rangle \equiv t^{-1} \int_0^t I(t) dt$ denotes an average over time t , typically during 2 hours. For a fluid-like sample, where the static scattering is absent, we find $\langle I \rangle = \langle I_f \rangle$

and $\langle I^2 \rangle = 2\langle I \rangle^2$. With Eqs. 3.3 and 3.4 we can obtain the static scattering and the time-averaged fluctuating intensity from the time-averaged moments of the observed intensity distribution by,

$$I_c(\vec{q}) = [2\langle I(\vec{q}) \rangle^2 - \langle I^2(\vec{q}) \rangle]^{\frac{1}{2}}, \quad (3.5)$$

$$\langle I_f(\vec{q}) \rangle = \langle I(\vec{q}) \rangle - I_c(\vec{q}). \quad (3.6)$$

A single dynamic light-scattering measurement provides an estimate of the time-averaged intensity correlation function $g(\vec{q}, \tau)$, defined as [35],

$$g(\vec{q}, \tau) \equiv \frac{\langle I(\vec{q}, 0) I(\vec{q}, \tau) \rangle}{\langle I(\vec{q}) \rangle^2}. \quad (3.7)$$

For sufficiently long delay times τ the system has evolved to a state which is completely uncorrelated with its initial state. In that case the intensity correlation function reaches the limit, $g(\vec{q}, \tau \rightarrow \infty) = 1$. At the shortest delay times $g(\vec{q}, \tau \downarrow 0)$ equals the normalised second moment or contrast of the scattered intensity (See Eq. 3.4). With the constant part acting as the intrinsic local oscillator one finds with Eqs. 3.1 and 3.7 [60, 76],

$$g(\vec{q}, \tau) = 1 + x^2 h(\vec{q}, \tau)^2 + 2x(1 - x)h(\vec{q}, \tau). \quad (3.8)$$

In Eq. 3.8 the intensity ratio $x \equiv \langle I_f \rangle / \langle I \rangle$, thus $1 - x$ compares the local oscillator strength to the local scattering strength. The function $h(\vec{q}, \tau)$ is the correlation function associated with the fluctuating field component and is defined as,

$$h(\vec{q}, \tau) \equiv \frac{\langle [E_f(\vec{q}, 0)]^* E_f(\vec{q}, \tau) \rangle}{\langle I_f(\vec{q}) \rangle}. \quad (3.9)$$

The correlation function reaches the limit, $h(\vec{q}, \tau \rightarrow \infty) = 0$, for sufficiently long delay times. At the shortest delay times, $h(\vec{q}, \tau \downarrow 0) = 1$. Solving Eq. 3.8 for the correlation function h results in,

$$h(\vec{q}, \tau) = 1 + x^{-1}([g(\vec{q}, \tau) - g(\vec{q}, 0) + 1]^{\frac{1}{2}} - 1). \quad (3.10)$$

In the next section we will experimentally show that the local time-averaged quantities $\langle I_f \rangle$, I_c and h are the relevant quantities describing the sol-gel transition. We will experimentally show that the fluctuating intensity and the correlation function h are equal to their sample-averaged values. The experimental verification of the sample homogeneity for the dynamic properties is an essential condition for both the method presented here as the method presented in Ref. [22].

3.3 Experimental

We describe the experimental setup shortly: Our light source is a CW Ar^+ laser producing 25 mW laser light with vertical polarisation at a wavelength $\lambda = 514.5$ nm. The laser beam is focused in the sample to a beam waist of $50\text{ }\mu\text{m}$. Scattered light with vertical polarisation is detected with a photo multiplier under a fixed scattering angle (fixed q) of 90° . The coherence factor $\psi = 0.98$, measured on a dilute sample of latex micro spheres, where ψ^{-1} is the number of speckle spots observed by the detector [35]. The gelation is followed using a gated counter for time resolved measurements of the scattered intensity, and an ALV-5000 digital correlator [72] for dynamic light-scattering measurements. Each measurement is performed at a randomly chosen fixed position in the sample. The progress of the gelation is denoted by the time T , where T starts directly after sample preparation. We use τ and t to denote time variables associated with the decay of density fluctuations that are observed in dynamical measurements. The integration over time t of the time-averaged quantities is continuously increased over the gelation process to efficiently capture the complete spectrum (all time scales) of the fluctuations, and is roughly adjusted to 5 times the longest correlation time observed in the intensity correlation function. In the gel this integration time is typically 2 – 4 hours. The time scale τ , the time difference argument in the correlation functions, ranges from 10^{-6} to 10^{+3} seconds. To obtain the sample-scattered intensity distribution, the sample is slowly ($8\text{ }\mu\text{m/s}$) translated vertically over a distance of 5 mm through the laser beam with a motorised setup, while measuring the scattered intensity. We refer to Chap. 2 for a detailed description of the experimental details.

3.4 Results

In later sections we will discuss the results obtained with several mass-fractions ranging from 2.2 to 3.5 mass-percent. The gelation times of these samples varied between 24 hours to well over a few weeks depending on the mass fraction. These times are long enough to accurately measure correlation functions which reveal the mesoscopic dynamics of the system. As an illustrative example we will first discuss the results obtained with the 3.0 mass-percent sample, a mass fraction at which a gel is formed in 100 hours.

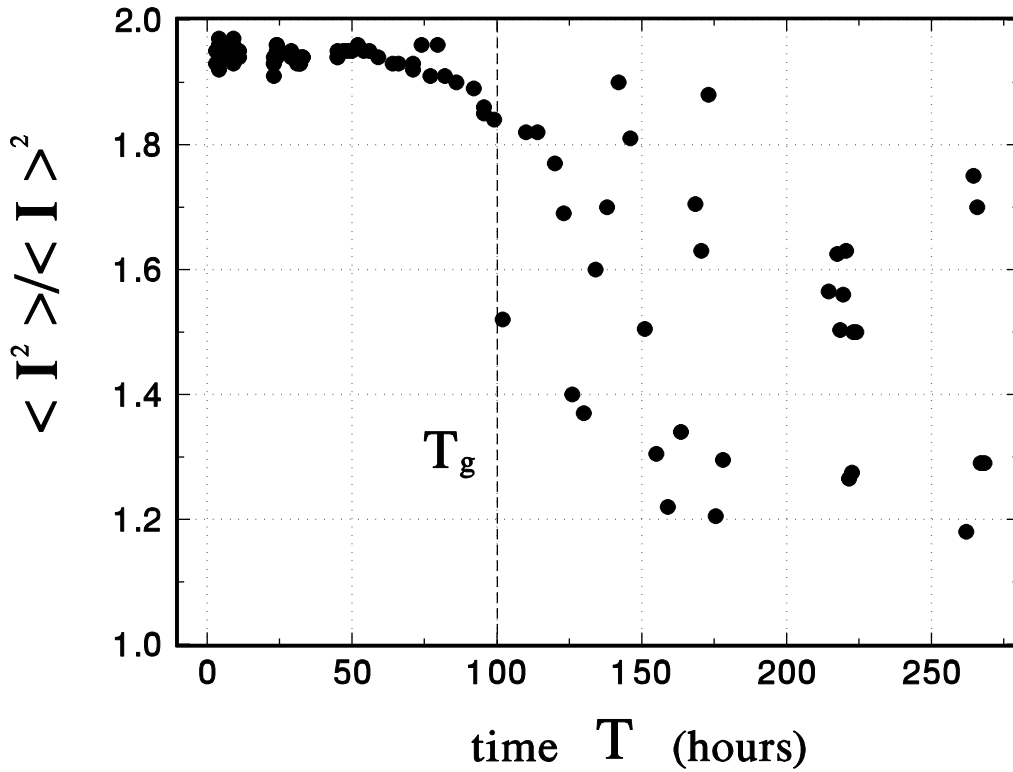


Figure 3.1: Measured time-averaged normalised second moment $\langle I^2 \rangle / \langle I \rangle^2$ of the scattered intensity as a function of time T after preparation of a 3.0 mass-percent sample. Each point represents a local time-average of the second moment where local properties are measured at a fixed location in the sample. The dashed line indicates the location of the gel-point $T_g = 100$ hours for this sample.

3.4.1 Results for a 3.0 mass-percent sample

In Fig. 3.1 we show the observed normalised second moment of the scattered intensity as a function of time T after sample preparation. At early times the second moment is nearly equal to the ideal value of 2 for a fluid-like sample, which shows that the particles are performing “free” Brownian motion. Each data point in Fig. 3.1 is measured at a different location in the sample, chosen at random. At a certain time, from here on referred to as T_g , the smooth behaviour changes abruptly into a wide scatter of values. We take this point in time as the definition of the gelation time. The wide scatter in values stems from the appearance of a speckle pattern, which is the Fourier image of the static structure of the illuminated sample. The speckle pattern will change when we illuminate the sample under a different angle or at a different position. The coherence area A_{coh} , roughly equal to the size of a speckle spot as observed by the naked eye, is

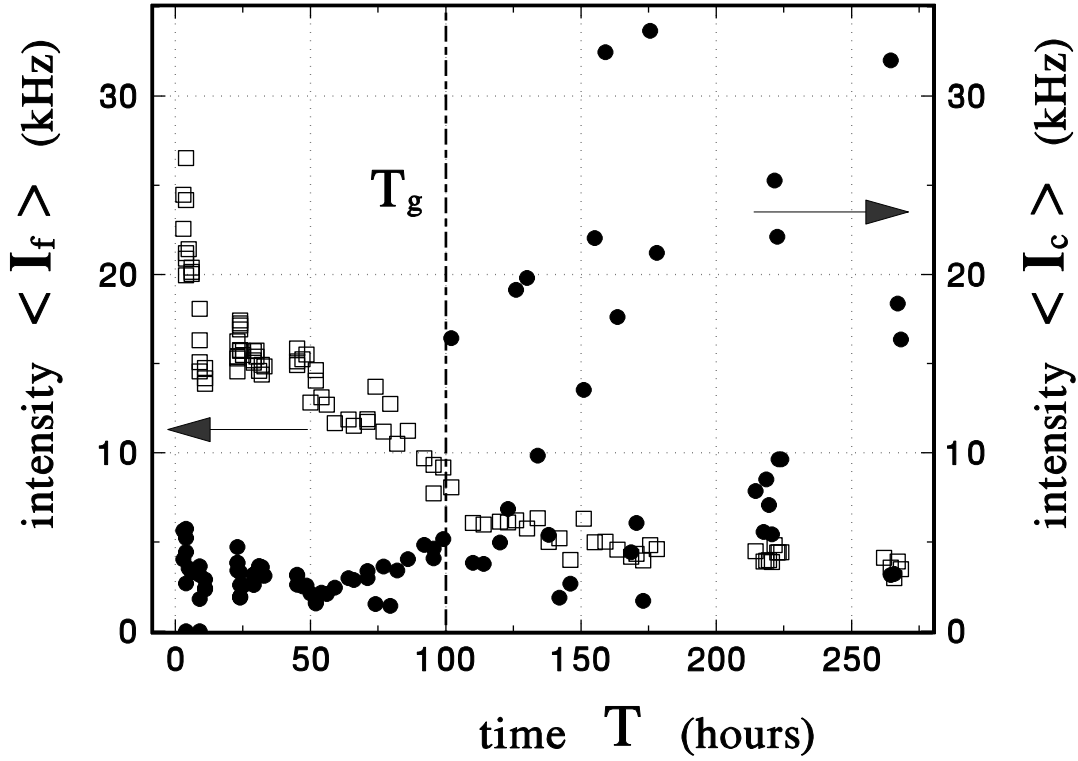


Figure 3.2: *Fluctuating intensity $\langle I_f \rangle$ (squares) and static intensity I_c (circles), versus the time T after preparation of the 3.0 mass-percent sample. Each point represents a local time-average. Note the abrupt change in the static intensity at the gelation time T_g .*

formally defined as the area over which the spatial correlation function of the scattered electric field is significantly different from zero [35](p. 45). For our experimental setup we find $A_{coh} = 5 \times 10^{-9} \text{m}^2$, which yields a typical diameter of the coherence area of $2\sqrt{A_{coh}/\pi} = 80 \mu\text{m}$ (See Chap. 2). In all experiments we used a detector aperture of $35 \mu\text{m}$ in diameter. Because this aperture is smaller than the coherence area, the scatter in measured intensities on a Brownian sample will be of the same order as its average, i.e., the second moment equals 2.

Beyond the gelation time T_g we observe that the second moment is lower than its value of 1.96 as observed in the sol state. If we now separate the fluctuating and static intensity according to Eqs. 3.5 and 3.6, this implies the presence of a static intensity. In Fig. 3.2 we show as a function of time T this observed static intensity and the time-averaged fluctuating intensity obtained with Eqs. 3.5 and 3.6. The value of $\psi = 0.96$ causes the static intensity to be non-zero in the sol state. Beyond the gelation

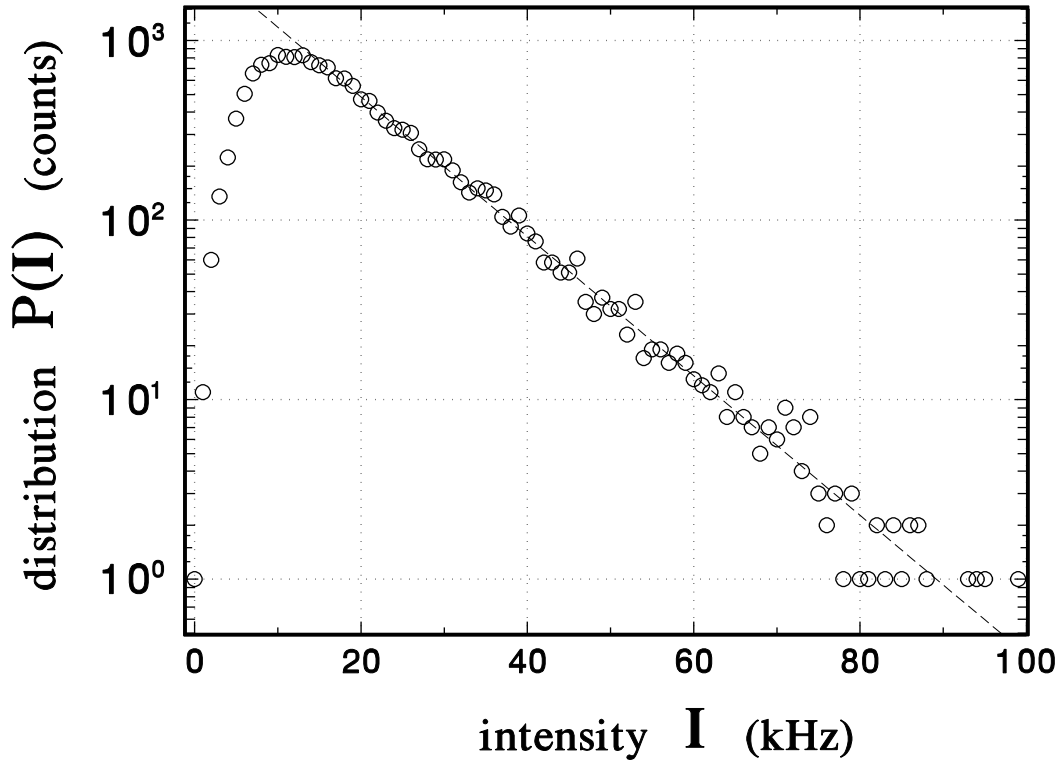


Figure 3.3: *Distribution $P(I)$ (circles) of the locally-measured scattered intensity measured early in the gelation process ($T/T_g = 0.1$) in the 3.0 mass-percent sample with a sampling time of $100 \mu\text{sec}$. The dashed line represents a negative-exponential fit to the observed distribution given by $A \cdot \exp(-I/\langle I \rangle)$, where $A = 2890 \pm 195$, and $\langle I \rangle = 11.2 \pm 0.2$. It fully represents the fluctuating intensity distribution.*

time the smooth behaviour of the static intensity changes to a wide scatter of values, which explains the observed behaviour of the second moment as depicted in Fig. 3.1. This wide scatter in the static intensity reflects the position dependence of the local oscillator, because each (time-averaged) data-point depicted in Fig. 3.2 is measured at a different location in the sample. The results depicted in Figs. 3.1 and 3.2 point to the existence of an immobile colloidal structure beyond the gelation time. The fast decrease of the fluctuating intensity just after preparation is assigned to a remnant of the dissolving process of particle clusters into the homogeneous suspension [55]. By eye it is observed as a fading of the initially opaque appearance. The fluctuating intensity remains a smoothly decreasing function of time T , although each data point depicted in Fig. 3.2 reflects a measurement at a different location in the sample.

In Fig. 3.3 we show the observed distribution of the scattered intensity measured early in the gelation process with a sampling time of $100 \mu\text{s}$. The initial upsurge of the

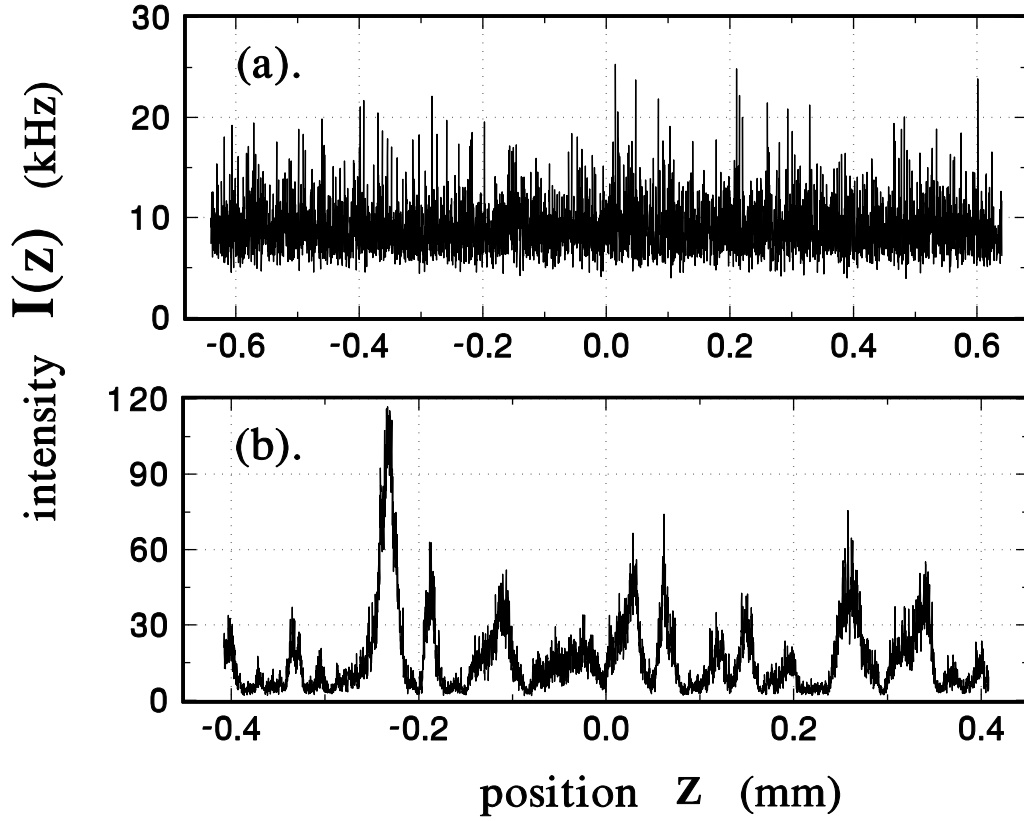


Figure 3.4: Scattered intensity $I(z)$ measured as a function of the position z of the scattering volume v in the 3.0 mass-percent sample early in the gelation (a. $T/T_g = 0.1$) and far beyond the gelation time T_g (b. $T/T_g = 1.8$). The speckle pattern in Fig. 3.4(b) is accurately and reproducibly resolved because of the slow scanning speed of $8 \mu\text{m/s}$ and the sampling time of 10 ms , which integrates out most of the temporal fluctuations.

distribution and the small horizontal offset are caused by integration over the fastest fluctuations during the sampling time. We observe a negative-exponential distribution which is attributed to the fluctuating intensity only, because early in the gelation process the second moment is nearly equal to 2 (See Fig. 3.1). The observation of a negative-exponential distribution together with the position-independent character of the fluctuating intensity confirm the previously assumed Gaussian and position-independent character of the fluctuating part $E_f(t)$. The spatial fluctuations observed in the static intensity (speckle) are uncorrelated with the temporal fluctuations (the fluctuating intensity). These observations provides the experimental evidence for the homogeneity of the gel-samples for the dynamical properties.

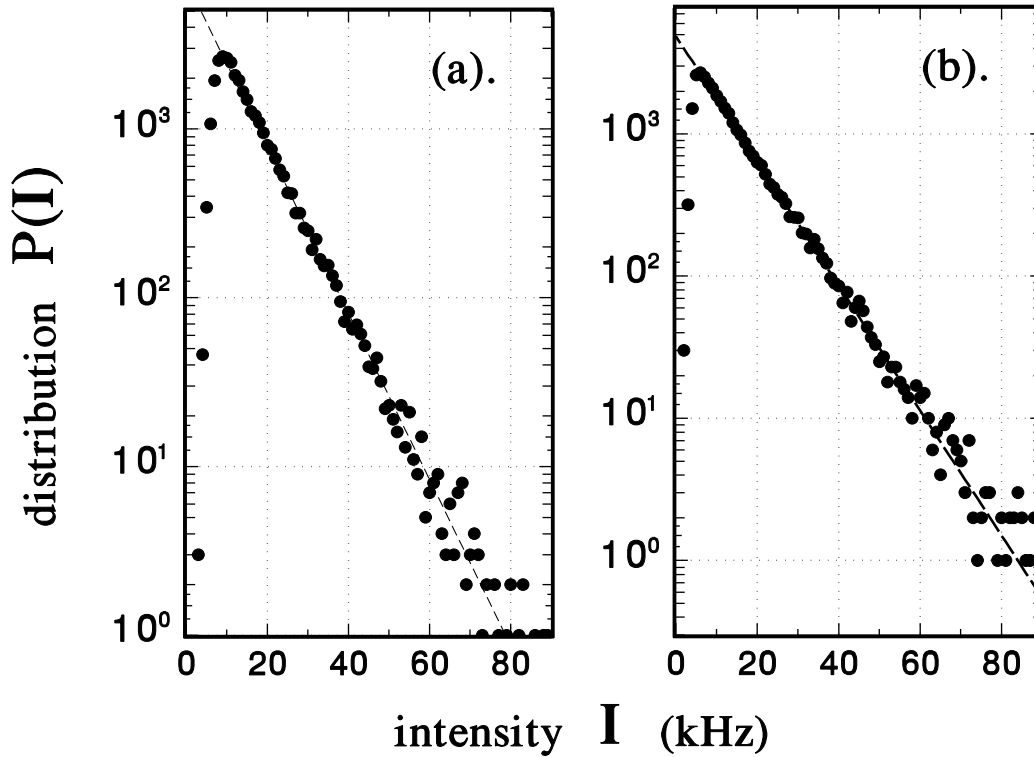


Figure 3.5: Distribution $P(I)$ (dots) of the observed scattered intensity $I(z)$ as depicted in Fig. 3.4. The dashed lines represent a negative-exponential fit, $A \cdot \exp(-I/\langle I \rangle)$, with (a) $A = 8145 \pm 550$ and $\langle I \rangle = 8.6 \pm 0.1$ and (b) $A = 4840 \pm 225$ and $\langle I \rangle = 9.9 \pm 0.1$. The observation of a negative-exponential distribution shows a sufficient sampling of independent locations in the sample.

In Fig. 3.4 we show an example of the observed spatial fluctuations in the scattered intensity measured as a function of z , the relative position in the sample. The counter is gated with a sampling time of 10 ms. A large part of the high-frequency temporal fluctuations are integrated over resulting in the offset of the trace in Fig. 3.4(a). In the gel state the scattered intensity is dominated by the static scattered intensity. Hence the scattered intensity pattern as depicted in Fig. 3.4(b) is almost fixed and reproducible. On the walls surrounding the setup it is observed as speckle. In Fig. 3.5 we show the observed distribution of the scattered intensity as depicted in Fig. 3.4. The observed distribution is a negative-exponential function during the entire gelation process, which shows that a sufficient amount of independent locations in the sample have been sampled by moving the scattering volume.

Formally the fraction of frozen-in density fluctuations $f(\infty)$ is defined as the spatially or sample-averaged static intensity normalised to the sample-averaged inten-

sity,

$$f(\infty) \equiv \frac{\langle I_c \rangle_s}{\langle \langle I \rangle \rangle_s}, \quad (3.11)$$

where $\langle \cdots \rangle_s$ denotes an average over the sample. We obtain the sample-averaged intensity $\langle \langle I \rangle \rangle_s$ by slow vertical translation of the sample while measuring the scattered intensity with the gated counter. The fraction of frozen-in density fluctuations is equivalent to the well-known Debye-Waller factor [83], which is considered as the order parameter of the sol-gel transition followed. We can rewrite the sample-averaged static intensity using the observed position-independent character of the time-averaged and locally-measured fluctuating intensity. Taking $\langle I_f \rangle = \langle \langle I_f \rangle \rangle_s$, as shown in Fig. 3.2, and $\langle \langle I \rangle \rangle_s = \langle I_f \rangle + \langle I_c \rangle_s$, we find with Eq. 3.11,

$$f(\infty) = 1 - \frac{\langle I_f \rangle}{\langle \langle I \rangle \rangle_s}. \quad (3.12)$$

In Fig. 3.6 we show the observed fraction of frozen-in density fluctuations and sample averaged scattered intensity versus the time T after preparation. Each data point results from an average over the sample. Comparing Fig. 3.6 with Fig. 3.2 we observe that the sample-averaged scattered intensity and the fluctuating intensity have the same dependence on time T at early times. The fast decrease of the sample-averaged scattered intensity just after preparation is again assigned to a remnant of the dissolving process. Beyond gelation time T_g the sample-averaged scattered intensity shows minor fluctuations between successive measurements. The fluctuating intensity and the fraction of frozen-in density fluctuations show the same, though opposite dependence on the time T , which is explained by Eq. 3.12. In soft solids like our gels it is questionable whether the structure will ever come to full arrest. On time scales, an order of magnitude longer than the gelation time, the fluctuating intensity and the fraction of frozen-in density fluctuations have changed minute amounts. They seem to approach values different from 0 and 1 respectively. Just as for glasses, the gel is considered locally in equilibrium on realistic time scales. The remaining temporal fluctuations then originate from collective fluctuations of the gel network.

In Fig. 3.7 we show a typical series of correlation functions h measured at different locations in the sample during the gelation process. The correlation function measured on dilute laponite suspensions consist of two superposed exponential functions, where the characteristic exponential relaxation times differ more than an order of magnitude. The observation of this double-exponential relaxation can be explained by the disc-like shape and cylinder symmetry of the primary particles [35]. We observed

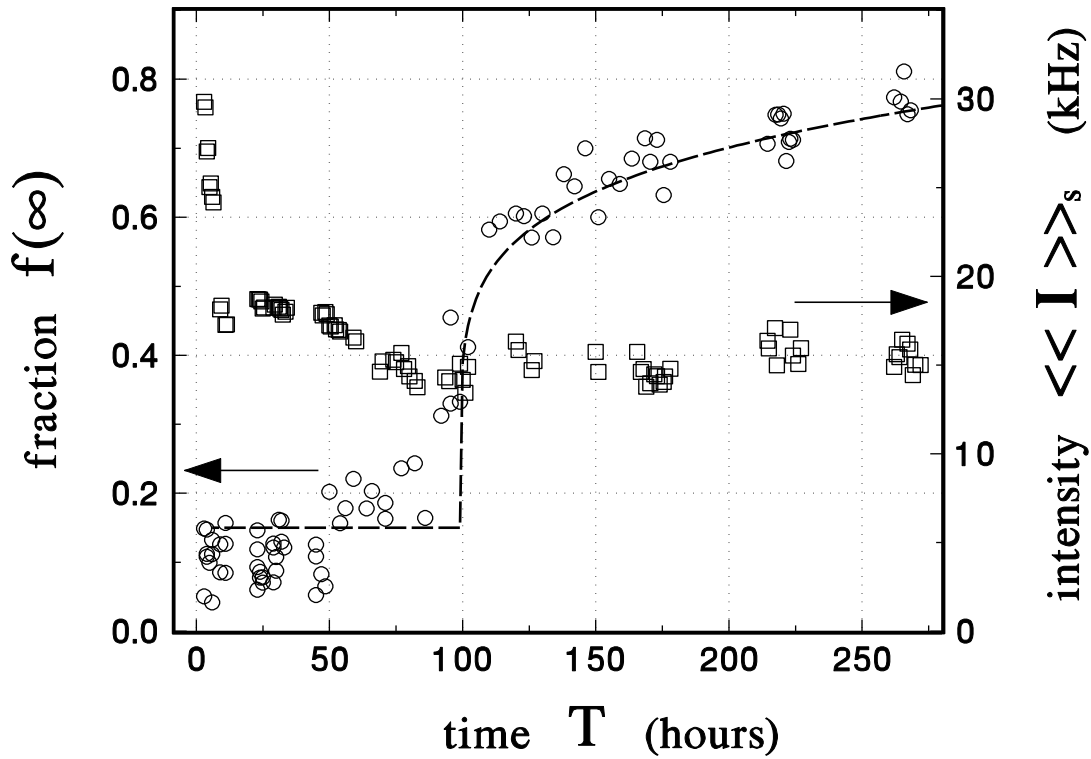


Figure 3.6: Sample-averaged scattered intensity $\langle\langle I \rangle\rangle_s$ (squares) and the fraction of frozen-in density fluctuations $f(\infty)$ (circles) versus the time T . The dashed line represent the function, $f(\infty) = f_c(q) + A((T - T_g)/T_g)^\varphi$, where $f_c(q) = 0.15$, $A = 0.55$, and $\varphi = 0.18$ (See Sec. 3.5 for further explanation).

a q^2 dependence for the longest relaxation time, where q is the momentum transfer or scattering vector. Thus this part of the correlation function reflects translational diffusion of particles. The shorter relaxation time showed no q^2 dependence, and is thus designated as rotational diffusion. The latter was verified by measurements under various scattering angles on dilute suspensions under VV and VH polarisation.

At early times T , the intensity scattered on the suspension consists predominantly of a fluctuating term as depicted in Fig. 3.2. Then the intensity ratio $\kappa = 1$ and Eq. 3.8 reduces to the Siegert relation [35]. As the gelation proceeds we observe that the short time behaviour of the correlation function h , designated as the rotational diffusion, remains unchanged. Apparently the particles in the network formed are allowed to perform free rotational motion around at least one axis. The translational exponential (long time behaviour) shows a stretching over more than five order in time as the gelation proceeds, until finally the correlation function shows a power-law decay, $h(\tau) \propto \tau^{-a}$. Beyond the gelation time T_g we hardly observe changes in the correlation

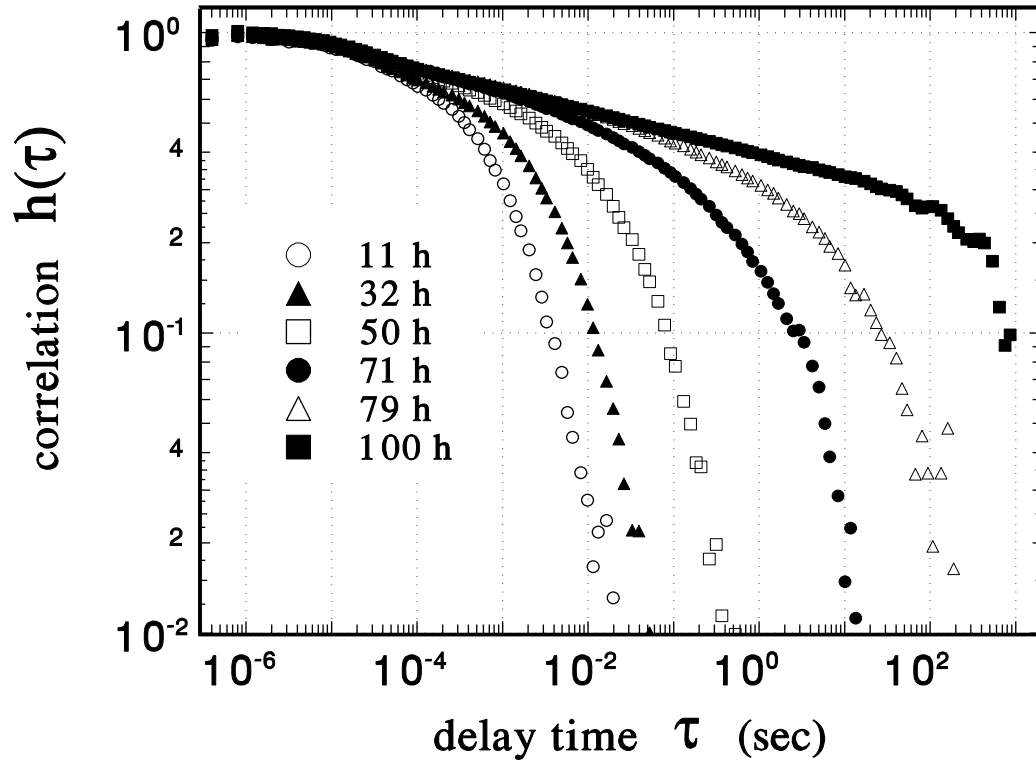


Figure 3.7: Typical series of the correlation function $h(\tau)$ measured during the gelation of the 3.0 mass-percent sample. The legend shows the symbols relating the time T to the measured functions.

function, although the laponite system is known to show ageing effects [52]. In Fig. 3.8 we show the correlation function h measured at $T/T_g = 1.7$. After a fast exponential decay designated as rotational diffusion we observe a power-law decay over more than five orders in time τ with an exponent of $a = 0.14 \pm 0.03$.

Beyond the gelation time T_g , the shape of the intensity correlation function g shows a strong dependence on the position of measurement in the sample. The latter is explained by the presence of the position-dependent static scattering and described by Eqs. 3.4 and 3.8. The locally-obtained correlation function h show absolutely no position dependence, which is explained by the position-independent character of the fluctuating part E_f . Hence the locally-obtained and time-averaged correlation function h represents the sample-averaged value $\langle h(\tau) \rangle_s$. Under these conditions Pusey and van Megen [22] already pointed out that one can express the locally-obtained and time-averaged correlation function h in terms of the (sample-averaged) intermediate

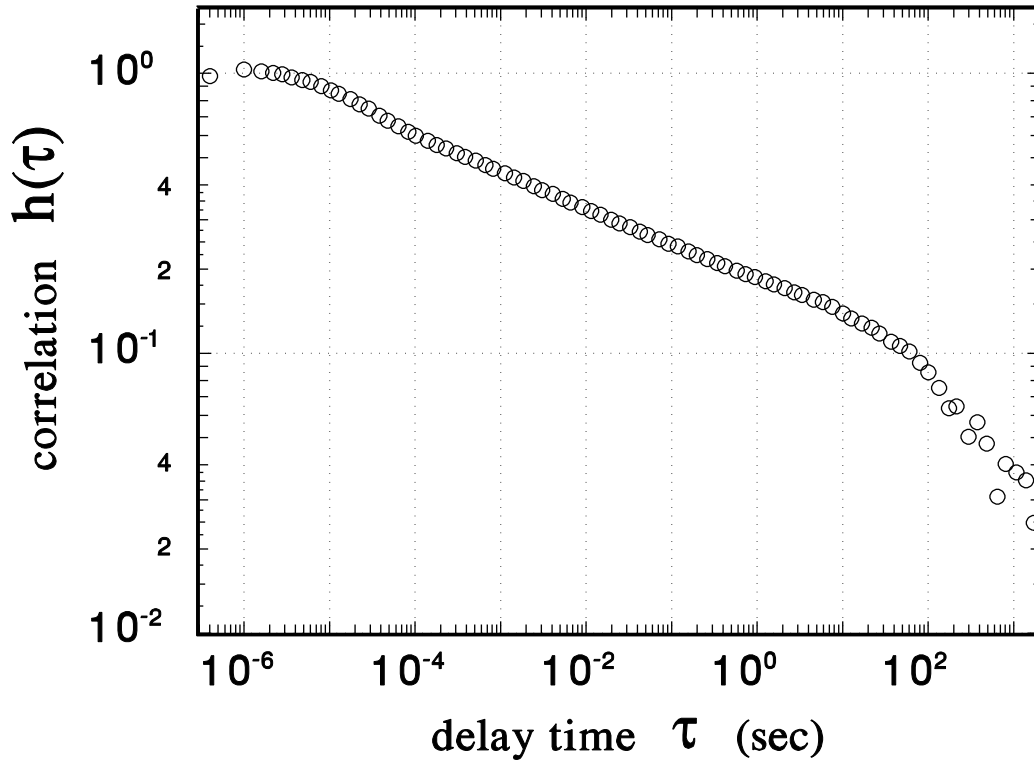


Figure 3.8: Correlation function $h(\tau)$ at $T/T_g = 1.7$ in the 3.0 mass-percent sample. Beyond the time scale of the rotational diffusion, the correlation function shows a power-law decay $h(\tau) \propto \tau^{-a}$ over more than five orders in time τ with an exponent of $a = 0.14 \pm 0.03$.

scattering function $f(\tau)$. The latter is defined as [22],

$$f(\tau) \equiv \langle \langle E(0)E(\tau) \rangle \rangle_s / \langle \langle I \rangle \rangle_s . \quad (3.13)$$

In Ref. [22] Pusey and van Megen derive the following equations relating the intermediate scattering function f and the fraction of frozen-in density fluctuations $f(\infty)$ to the locally-obtained and time-averaged correlation function g ;

$$f(\tau) = \frac{y-1}{y} + \frac{1}{y} [g(\tau) - g(0) + 1]^{\frac{1}{2}} , \quad (3.14)$$

$$f(\infty) = \frac{y-1}{y} + \frac{1}{y} [2 - g(0)]^{\frac{1}{2}} , \quad (3.15)$$

where $y \equiv \langle \langle I \rangle \rangle_s / \langle I \rangle$ compares the local scattering strength to the sample-averaged scattering strength. Strong similarities between Eqs. 3.14 and 3.15 of Pusey and van Megen and our Eq. 3.10 are expected and can be explained. Application of Eq. 3.1 to

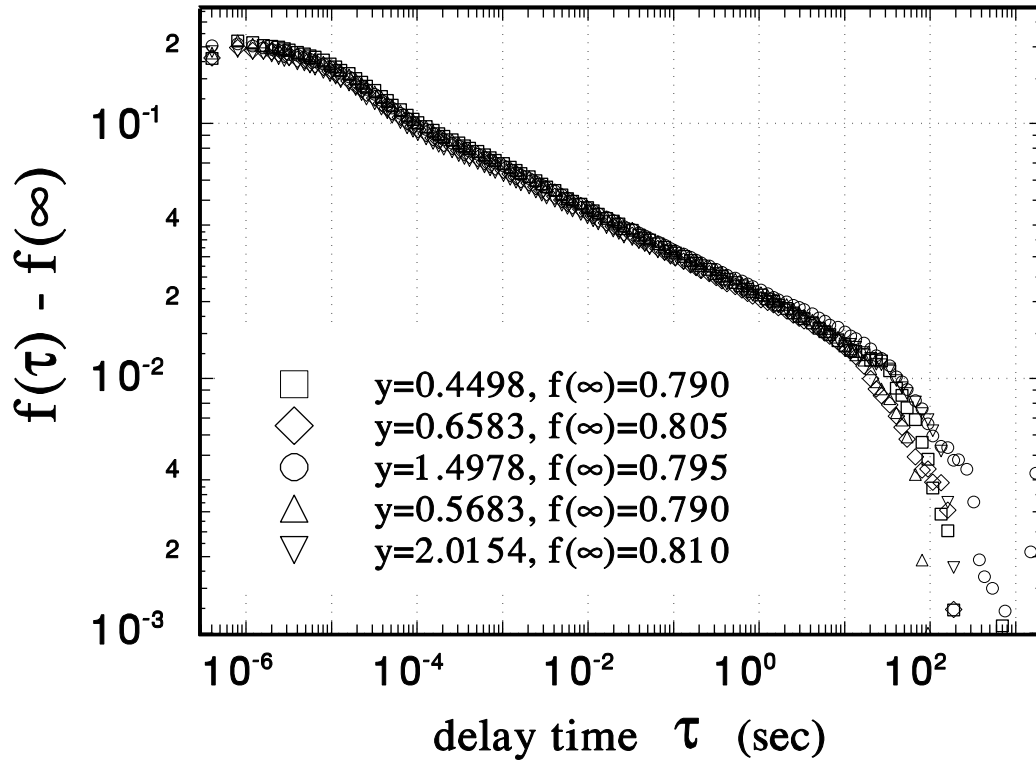


Figure 3.9: Sample-averaged intermediate scattering function $f(\tau)$ minus the fraction of frozen-in density fluctuations $f(\infty)$, measured at different locations z in the 2.2 mass-percent gel at $T/T_g = 2.4$. Note that there are five curves brought to overlap over the entire time window. The experimental inaccuracy in $f(\infty)$ allows adjustment to obtain optimal overlap. The variation of the local oscillator strength with position z is expressed in terms of y .

Eq. 3.13 with Eq. 3.9 and some algebra yields the connection,

$$h(\tau) = \frac{y}{x} [f(\tau) - f(\infty)] . \quad (3.16)$$

With these definitions the intensity ratio $x = [1 - f(\infty)]y$. In Fig. 3.9 we show the function $f(\tau) - f(\infty)$ measured at different locations z in the 2.2 mass-percent gel. The local oscillator strength is expressed in terms of y . The intermediate scattering function and the fraction of frozen-in density fluctuations are obtained from single local measurements of the intensity correlation functions and the sample averaged scattered intensity with Eqs. 3.14 and 3.15. The spread in the values of the fraction of frozen-in density fluctuations is more than 5 percent. This allows all five correlation functions depicted in Fig. 3.9 to come to complete overlap by adjusting $f(\infty)$ within this error.

The observed algebraic decay of the locally obtained correlation function h on the gel state will also be observed in the sample averaged function $f(\tau) - f(\infty)$. In order to accurately determine the exponent of the algebraic decay, one has to estimate the value of $f(\infty)$ with an accuracy of at least 10^{-2} . Otherwise, $f(\tau) - f(\infty)$ can take any desired shape to match to theoretical predictions. The accuracy of sample averaging is limited by the available spatial range, the finite time window of averaging, and the stability of our light scattering setup. Gel-like systems show fluctuations on all time scales and therefore require local averaging times of hours. Approaching the gel-point, the intrinsic non-stationarity of the continuously evolving particle system limits the available averaging time to the integration time used when evaluating local time-averaged properties. Estimating sample-averaged properties with the required accuracy on slowly evolving particle systems is therefore difficult.

The method we used here requires no such sample averaging. Apart from the accuracy in the measured intensity correlation function, the accuracy in determining the correlation function h from the intensity correlation function is given only by the accuracy in the intensity ratio x . As a matter of fact, this is the accuracy in the measured second moment of the intensity distribution from which the ratio x is calculated. The second moment is integrated simultaneously with the intensity correlation function over at least multiples of the typical correlation time. In comparison with the sample-averaging procedures [22, 23], the method we used here assures the highest experimental accuracy in the relevant quantities describing the sol-gel transition

3.4.2 Results for various mass-fractions

We have followed the gelation of laponite suspensions in water at different concentrations, or mass fractions φ_m . Beforehand it was noticed that suspensions with a higher mass-fraction showed a much more rapid solidification, and one could wonder whether the development of the gelation depends on the used mass-fraction. The limiting factor in obtaining samples at high mass-fractions is the inability to fully suspend all clusters of particles before the system shows the phenomenological observation of gelation. The remaining clusters can not be broken down by forceful stirring. Samples with a mass fraction lower than 2.0 mass-percent show a gelation time T_g larger than 2000 hours. We therefore limited the study to mass fractions in between 2.2 and 3.5 mass-percent.

The observed behaviour of the correlation function h , the fluctuating intensity $\langle I_f \rangle$ and the static intensity I_c over the gelation at several mass-fractions are not dif-

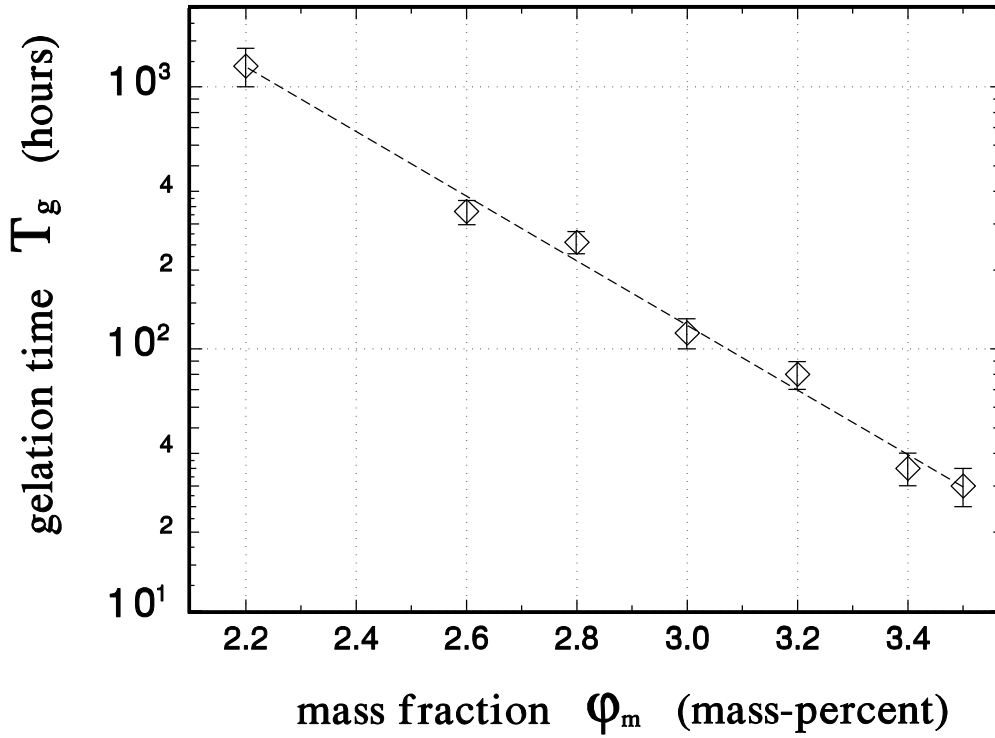


Figure 3.10: Gelation time T_g as a function of the mass fraction ϕ_m (expressed in mass-percent) of laponite in the suspensions investigated. The dotted line represents a negative-exponential fit, according to $T_g \propto \exp(-2.83 \phi_m)$.

ferent from the results that were shown in Figs. 3.2 and 3.7. In all mass fractions the fluctuating intensity shows a smooth decrease whereas the static intensity shows a transition to a wide scatter of values beyond a certain time T_g . The observed gelation time T_g shows a nearly exponential dependence on the mass fraction ϕ_m , as depicted in Fig. 3.10. This suggests that the laponite system does not have a critical mass-fraction below which gelation would no longer occur, as argued by Mourchid *et al* [3]. Furthermore, a suspension of 1.0 mass-percent showed a gel structure after standing alone for at least a year. No indication for phase-separation or density gradients could be found. The same holds for all other mass-fractions studied. If there is a critical mass-fraction, it is assumed to be small, at least smaller than 0.5 mass-percent. The exponent of the correlation function h as measured well in the gel state reveals a surprising and nearly linear dependence on the mass fraction, as depicted in Fig. 3.11. With increasing mass-fraction the average inter-particle distance decreases. Subsequently, the interaction strength between particles increases and the gel structure formed is observed to be more rigid. A fluctuating mode is less subject to disturbing

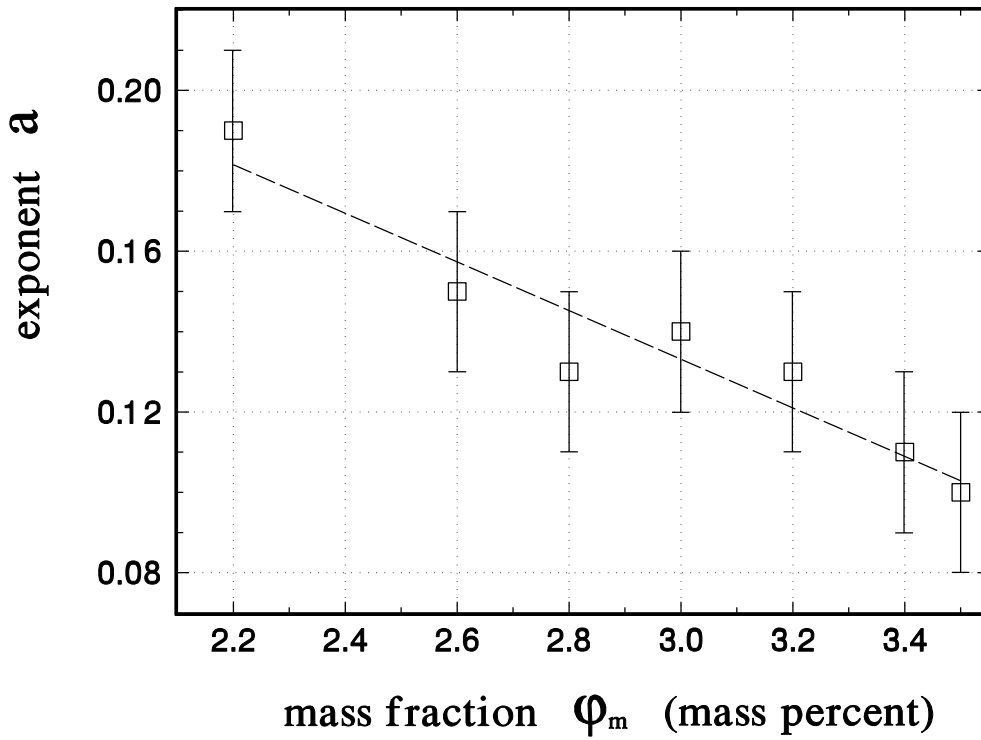


Figure 3.11: Exponent a of the correlation function $h(\tau)$ as a function of the mass fraction ϕ_m of laponite in the suspensions investigated. The exponents and error margins are extracted from a power-law fit to $h(\tau) \propto \tau^{-a}$ in the gel state of each sample. The dashed line serves as a guide to the eye.

thermal fluctuations and shows a less rapid decay of the algebraic time-correlation.

3.5 Comparison with theory

In complex systems such as colloidal suspensions several correlation functions are characterised to describe the dynamics the system. The spectrum of dynamics involves, among others, thermally driven fluctuations in density, and transverse and longitudinal currents. The idea of mode-coupling is that damping of such modes occurs by the decay of one mode into two or more modes of the same (similar) type. In the case of the glass transition the density-density correlation function is important when characterising the dynamics. In the solid or glass state of the system energy can be dissipated by phonons, but the density fluctuations are frozen-in because diffusion becomes negligible.

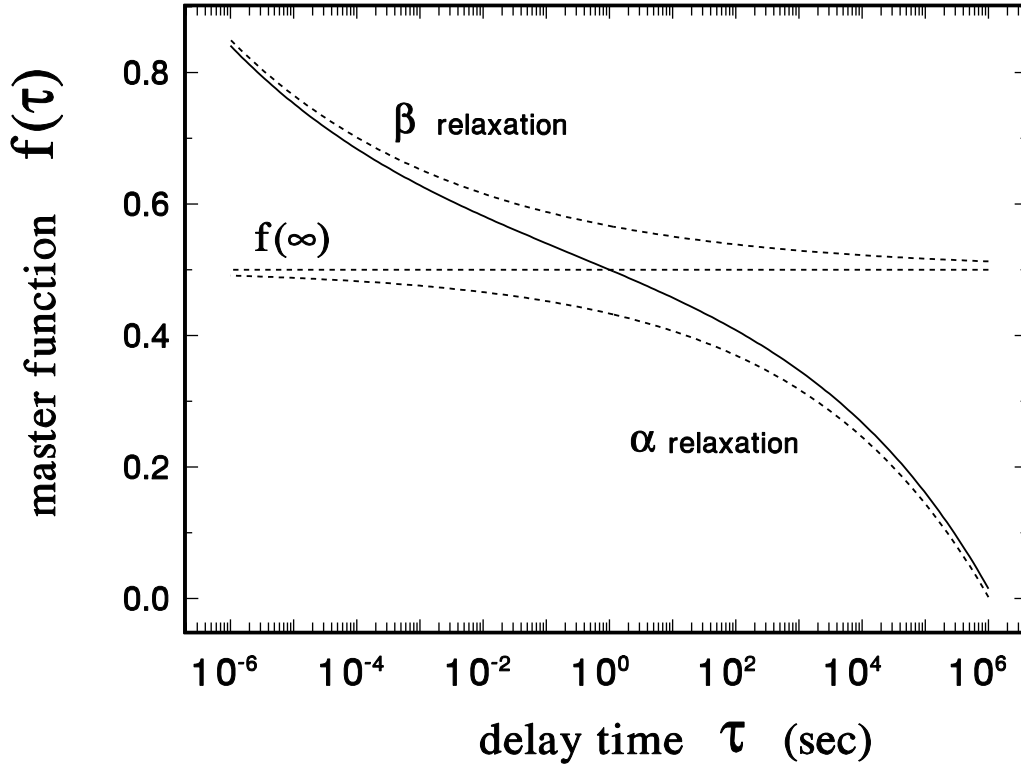


Figure 3.12: *Illustrative picture of the predictions of the mode-coupling theory, following Eqs. 3.18 and 3.20. The plateau $f(\infty)$ is formed in the glass state only (See Fig. 3.6) and represents the fraction of frozen-in density fluctuations. In the glass state the α relaxation is frozen-in and the β relaxation dominates the entire time window.*

In the past decade the mode-coupling theory has produced several predictions for the glass transition in terms of the density-density correlation function. Master functions for the intermediate scattering function $f(q, \tau)$ have been derived, and have been self-consistently calculated for a system of hard spheres [20]. The theory identifies two relaxation processes for glassy systems beyond the region of microscopic motion; α and β relaxation. Close to the glass transition these relaxations span over ten orders in time with well separated time-scales τ_α and τ_β . The scaling of the time-scales τ_α and τ_β with the control parameter ϵ is predicted to be different for the two processes, yet interconnected in the theory. The control parameter ϵ , that records the distance to the transition point, is defined as, $\epsilon = (\xi - \xi_g)/\xi_g$, where ξ is taken as the density, temperature or volume fraction and ξ_g its value at the transition. If we take for ξ the time T , the experimental results show strong similarities with the structural glass transition.

Prior to the structural glass transition the intermediate scattering function $f(q, \tau)$

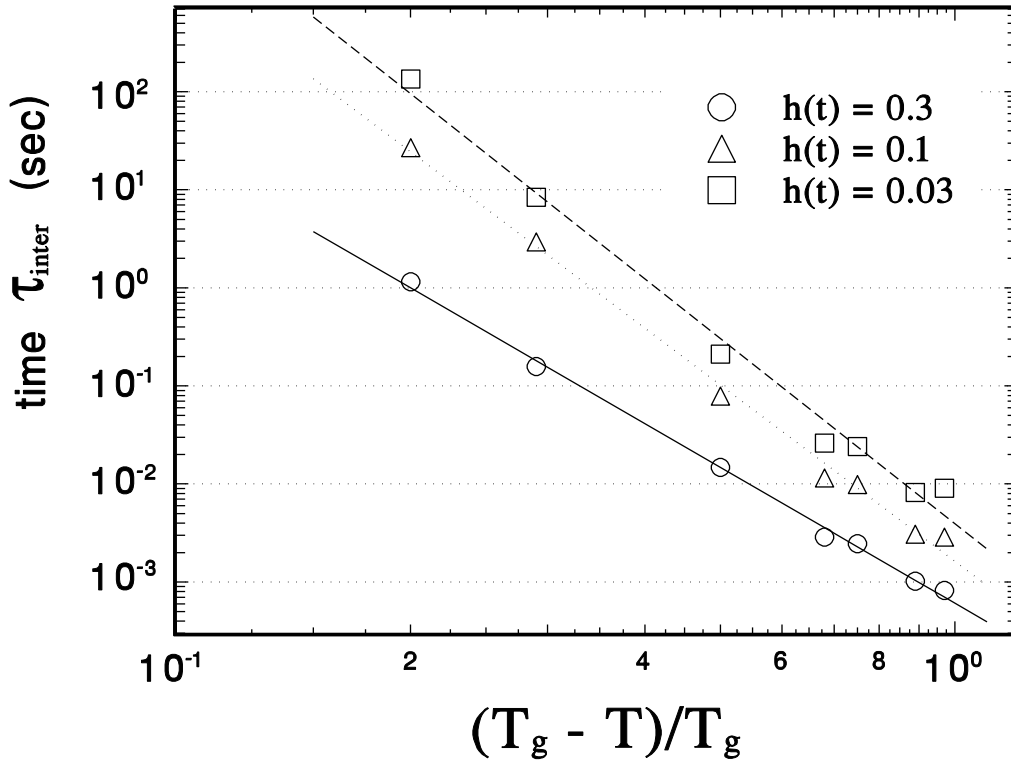


Figure 3.13: Interception time τ_{inter} of the correlation function $h(\tau)$ depicted in Fig. 3.7 with several levels of correlation, as a function of $(T_g - T)/T_g$, where $T_g = 100$ hours. The legend shows the correlation level at which the interception was followed. The straight lines drawn are power-law fits to the data of which the exponent ranges from -4.6 [solid line, $h(\tau) = 0.3$] to -6.3 [dashed line, $h(\tau) = 0.03$].

shows a two-step decay. First an algebraic decay towards a plateau, β relaxation, followed by the slower α relaxation. Approaching the glass transition, the characteristic time of the slower α relaxation, and thus the time window spanned by the β relaxation, widens until it is stretched to infinity at the transition. After the transition to the gel or glass state only the β relaxation remains, and the intermediate scattering function decays to a plateau. The value of the plateau is given by the static structure factor and increases as the square root of the distance from the transition point [20, 27]. The plateau value is also referred to as the non-ergodicity parameter [22], or Debye-Waller factor [83], and is considered as the order parameter for the transition. Close to the transition the mode-coupling theory gives the explicit form of the intermediate scattering function and its algebraic behaviour. The prevailing prediction of the glass transition gives the following form for the master function, the relevant algebraic

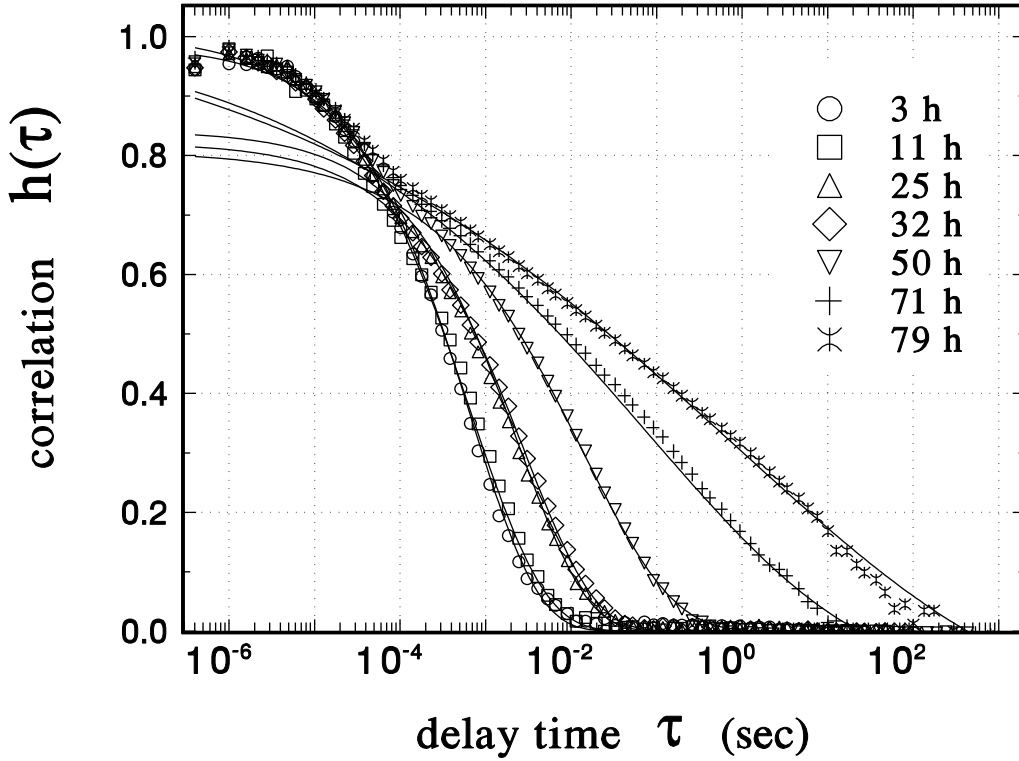


Figure 3.14: Matching the empirical Kohlrausch function to the correlation functions of Fig. 3.7. The solid lines are the fits. The legend shows the symbols related to the time T . Note the scatter of amplitudes at short times τ .

exponents and their relations,

$$f(q, \tau) = f(q, \infty) + s(q, \epsilon) m\left(\frac{\tau}{\tau_\epsilon}\right), \quad (3.17)$$

where $f(q, \infty)$ represents the fraction of the structure that is frozen-in at the transition point ($\epsilon = 0$). The amplitude of the β process is $s(q, \epsilon) = c_\epsilon S(q)$, with $c_\epsilon = c_0 |\epsilon|^{\frac{1}{2}}$, c_0 a material-dependent constant, and $S(q)$ the static structure factor. The characteristic time τ_ϵ diverges with a power of $|\epsilon|$ depending on the process. For the β relaxation the scaling goes as $\tau_\beta = \tau_0 |\epsilon|^{-1/(2a)}$, where τ_0 is a material-dependent microscopic time scale. For the α process the characteristic time goes as $\tau_\alpha = \tau_0 |\epsilon|^{-\gamma}$, where $\gamma = 1/(2a) + 1/(2b)$. The function m in Eq. 3.17 is the master function depending on the rescaled time τ/τ_ϵ only. The explicit expressions are,

$$\begin{aligned} m(\tau) &= (1/\tau^a) + \dots, & \tau_0 \ll \tau \ll \tau_\alpha, \\ m(\tau) &= -B\tau^b + \dots, & \tau_\beta \ll \tau \ll \tau_\alpha, \end{aligned} \quad (3.18)$$

where $B > 0$ and the dots denote higher order terms. The non-universal exponents a

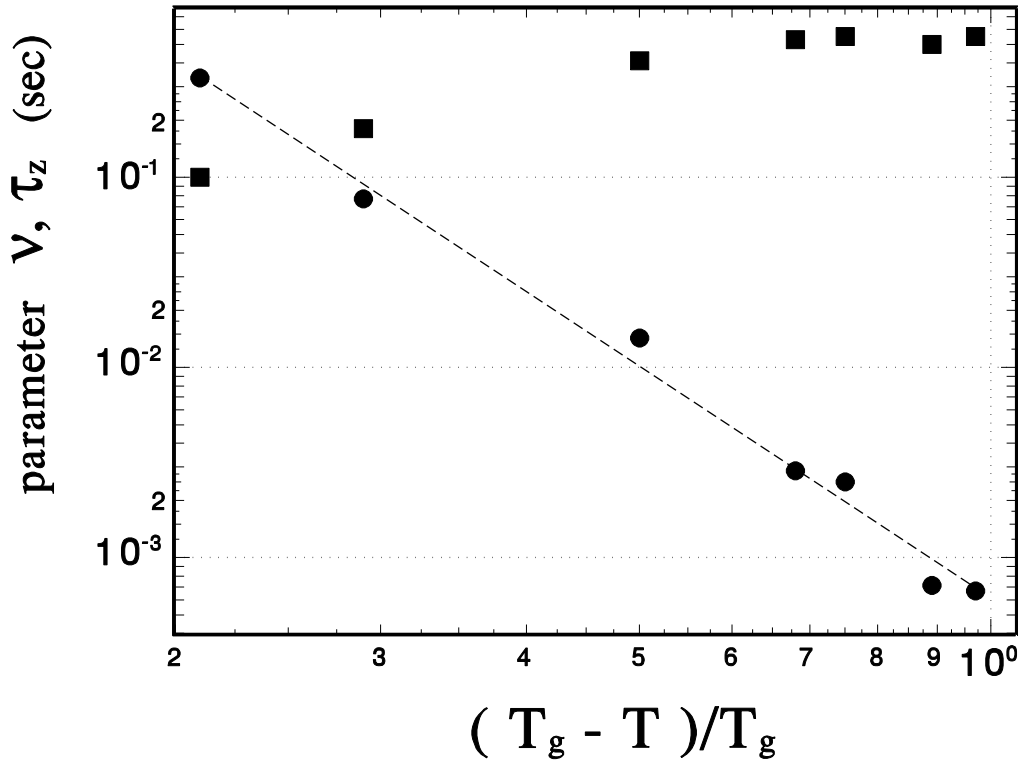


Figure 3.15: Time-parameter τ_z (circles) and scaling parameter ν (squares) of the empirical Kohlrausch function as a function of the reduced time $(T_g - T)/T_g$, for the functions shown by the solid lines in Fig. 3.14. The dashed curve represents a power-law fit to τ_z , according to, $\tau_z = K |(T_g - T)/T_g|^{-\phi}$, with $\phi = 4.0$, $K = 6 \cdot 10^{-4}$, where $T_g = 100$ hours.

and b , whose values lie in the range of $0 < a < 1/2$ and $0 < b < 1$, are specified by the exponent parameter λ [20]. The exponents are related by the following transcendental equation,

$$\frac{\Gamma^2(1+b)}{\Gamma(1+2b)} = \lambda = \frac{\Gamma^2(1-a)}{\Gamma(1-2a)} . \quad (3.19)$$

The plateau value to which the correlation function decays in the gel state is the fraction of frozen-in density fluctuations, $f(\epsilon, q, \infty)$, which is predicted to obey [28],

$$f(\epsilon, q, \infty) = f_c(q, \infty) + \begin{cases} h(q)\sqrt{\epsilon} + O(\epsilon) , & \epsilon > 0 , \\ O(\epsilon) , & \epsilon < 0 . \end{cases} \quad (3.20)$$

The constant $f_c(q, \infty)$ and the critical amplitude $h(q)$ are related to the amplitude of the β process. On the macroscopic time scale $\tau \simeq \tau_\alpha$ the dynamics on the fluid side of

the transition are governed by the α process. In the glass state the α process is completely arrested but the β process persists and saturates at long times. An illustrative picture of the mode-coupling master function and the plateau formed by the fraction of frozen-in density fluctuations is shown in Fig. 3.12.

The master function m in Eq. 3.17 is a function of the rescaled time τ/τ_ϵ , where τ_ϵ diverges with a power of ϵ depending on the process. As the normalised distance towards the transition point ϵ approaches zero, the master function preserves its mathematical shape. A practical approach to study the scaling divergence of the slower α relaxation is to follow a certain level of correlation or height in the correlation function h as a function of ϵ . Application of this practical approach to the gelation of laponite means drawing a horizontal line in Fig. 3.7 and mark down the interception time τ_{inter} of this level with the correlation function h at different times in the gelation. In Fig. 3.13 we plot the interception time τ_{inter} versus the normalised distance ϵ . Clearly a scaling $\tau_{inter} \propto |\epsilon|^\xi$ is present at the chosen correlation levels. However, the exponent ξ ranges from $\xi = -4.6$ for the level $h(\tau) = 0.3$, to $\xi = -6.3$ for the interception with $h(\tau) = 0.03$.

A second practical approach which is widely used for glasses to describe the shape of the master function prior to the glass transition is the empirical Kohlrausch function or stretched exponential, $F(\tau)$ [27, 24], according to

$$F(\tau) = A \exp[-(\tau/\tau_z)^\nu] . \quad (3.21)$$

For certain values of the exponents a and b it is stated that this function accurately describes the master function for the α process. For the hard sphere system the master functions have been calculated numerically [26] and it was found that they could be well parametrised by the Kohlrausch function. Other workers [5, 25, 27, 81, 82] have utilised the Kohlrausch function to analyse colloidal glasses [25, 27] and polymer gels [5, 81, 82] in terms of the glass transition. As it turned out we were also able to match the empirical Kohlrausch function to the correlation functions measured on laponite. In Fig. 3.7 we showed a typical series of correlation functions h as measured during the gelation of the 3.0 mass-percent sample. In Fig. 3.14 we show the comparison of our data measured prior to the gelation time with the empirical Kohlrausch function. The short time decay of the correlation function h is excluded from the fitting procedure because this part is attributed to the particle rotation. In Fig. 3.15 we show the typical relaxation time τ_z and the scaling parameter ν versus ϵ . The time parameter τ_z reveals a scaling relation with ϵ , according to $\tau_z \propto |\epsilon|^{-4.0}$. However, the ν parameter could not be held constant and must be continuously and significantly altered in the vicinity

of the gelation time T_g . The amplitude A of the Kohlrausch function shows a wide scatter of values which is completely uncorrelated with T or ϵ . Therefore we doubt the applicability of the Kohlrausch function.

In the gel state the master function of the mode-coupling theory is easily matched to the measured correlation function h . We only have to take into account the first algebraic term of the series expansion given by Eq. 3.18. Then the exponent $a = 0.140 \pm 0.03$, and we find $\lambda = 0.960 \pm 0.002$ and $b = 0.176 \pm 0.005$. For the exponent of the β and α relaxation we then find $1/(2a) = 3.58 \pm 0.07$, and $\gamma = 1/(2a) + 1/(2b) = 6.42 \pm 0.16$, respectively. Evaluation of the interception time τ_{inter} at the higher correlation levels is dominated by the presence of the β relaxation process, while lower levels are likely to be influenced by stability and accuracy. The exponent of τ_z as used in the Kohlrausch function approaches the prediction for the β relaxation time-scale closely, although this estimate is strongly interconnected with the continuously adjusted ν parameter. Neither of the two approaches can explain the scaling behaviour of the diverging time-scales obtained from our data.

Finally we tried to match the prediction of the mode-coupling theory on the behaviour of the fraction of frozen-in density fluctuations with $f(\infty)$ as presented in Fig. 3.6. As it turned out we were not able to match $f(\infty)$ with the prediction in the form of Eq. 3.20. From a power-law fit to $f(\infty) - f_c(q)$ versus ϵ we obtained an exponent ranging from 0.12 to 0.19 for values of $f_c(q)$ ranging from 0.1 to 0.2. The dashed line in Fig. 3.6 represent the best fit, $f(\infty) = f_c(q) + A[(T - T_g)/T_g]^\varphi$, where $A = 0.55$, $f_c(q) = 0.15$ and $\varphi = 0.15$. The smearing of the theoretically predicted cusp in the actual measured value of $f(\infty)$ is a discrepancy between theory and the experiment. This discrepancy was previously measured by Li *et al* [28] on the ionic glass CaKNO_3 , and was already pointed out by Götze in Ref. [21]. We therefore conclude that our observations are not quantitatively described by the mode-coupling theory. The correlation functions as measured in the fluid region only show qualitative agreement with the predicted behaviour.

3.6 Summary

We have presented a dynamic light-scattering study on the sol-gel transition of a suspension of disc-shaped colloidal particles in water. The measurement of the constant part of the scattering combined with the dynamic light-scattering results reveals a slowing down of the dynamics of a homogeneous sol until the gelation time T_g . Beyond the gelation time T_g the sample becomes a space-filling, macroscopically immobile, solid-like structure. This slowly, collectively relaxing network gives rise to the observed speckle pattern. Provided the gelation process is slow and the dynamics independent of position in the sample we can derive the true intermediate scattering function from the dynamic light-scattering measurements. The physical picture emerging from the correlation functions is a fast local rearrangement of particles followed by the slower collective rearrangement over larger and larger distances. This physical picture and the qualitative features of the correlation functions match rather well with the predictions of mode-coupling theory for the structural glass transition. We have qualitatively observed many of the characteristics of the glass transition; an algebraic decay in the gel state, a stretching of the long-time cut-off, and a smeared cusp in $f(\infty)$. However, in the framework of the mode-coupling theory we need a multi-parameter master function to derive the desired parameters quantitatively. Even then the results can not decide between pure β relaxation or the combined α - β relaxation picture of Götze.

Chapter 4

Discrete wavelet transformation of dynamic light scattering signals

4.1 Introduction

Discrete wavelet transformation [61, 62, 63, 64] is a relatively new tool in the analysis of signals in general. The method is especially suited for the analysis of signals from systems with non-stationary processes, like glass or gel formation [1, 5, 60, 27], or processes with intermittent dynamic behaviour, like turbulence [84, 85], earthquake recordings [86], and geomagnetic jerks [87]. In these processes the dynamic structure factor or the power spectrum of fluctuations will in general be a function of time. The problem one faces is to accurately estimate the power spectrum or its functional form locally on the time axis as the system evolves. It is evident that classical Fourier analysis does not solve the problem. The sine and cosine functions used are delta functions in frequency space but span the whole of time space. Wavelet analysis uses functions that are defined locally in time and frequency space as much as possible. The local nature of the analysing functions promises and, as we will show, provides information about the functional form of the power spectrum locally on the time axis. Wavelet analysis as used here provides information about the scaling behaviour of the moments of the power spectrum. However, it is not a panacea. Some of the information is lost.

In Chap. 3 we have presented the correlation functions of a colloidal clay system gelating in 100 hours [17]. The results show that the observation time (the time to measure a correlation function) and a characteristic time of the correlation functions are both short with respect to the gelation time and the time scale of the ageing pro-

cesses after gelation. Thus the measured correlation functions will be good estimations of the true functions at that particular point in time. Under these conditions the use of wavelets may seem an unnecessary and superfluous exercise. However, the correlation functions show a fast exponential decay, followed by an algebraic tail that is cut off at long times by again a more or less exponential decay. This complicated function is difficult to model and hence the relevant parameters are model dependent. Given a model it is difficult to rigorously determine the relevant parameters. Wavelet analysis enables us to accurately determine the algebraic exponent and both the short and long time cut-offs of the algebraic tail, without the use of any model. These results indicate both the power and the limitations of the method, because any information about exponential relaxation processes is lost.

4.2 Multi-resolution analysis

The backbone of the discrete wavelet transformation is formed by the multi-resolution analysis, which was inspired on schemes for analysis and reconstruction of digital visual data [88]. Understanding the principles and results of discrete wavelet transformation necessitates a thorough introduction to the multi-resolution analysis. For that purpose we sketch the “Mallatian Pyramid algorithm” originally devised by Mallat [61] and perform some calculations. The interested reader is referred to App. A where we present a more formal treatment of the multi-resolution analysis. We start with a trace of discrete data points, for example the trace of positive integer numbers as shown in Fig. 4.1(a). The idea behind the multi-resolution analysis is to define successive approximations of the original trace of discrete numbers and to encode the difference in information between the approximations. The original trace of discrete numbers, labelled $I^{(0)}$, is transformed into the approximation trace, labelled $I^{(1)}$, in the following elegant way [88],

$$I_k^{(1)} = \sum_n I_n^{(0)} w_{n-2k} , \quad (4.1)$$

where the coefficients w_j are weighting factors satisfying the condition $\sum_j w_j = \sqrt{2}$. In the example depicted in Fig. 4.1 we use two non-zero coefficients $w_0 = w_1 = \sqrt{2}/2$. Following Eq. 4.1 the trace $I^{(1)}$ is obtained in two steps; first multiply the trace $I^{(0)}$ with $\sqrt{2}/2$, and then rebin the trace by pair-wise addition of elements. For example; the elements $I_1^{(0)}$ and $I_2^{(0)}$ yield $5\sqrt{2} + 3\sqrt{2} = 8\sqrt{2} = I_1^{(1)}$, the elements $I_3^{(0)}$ and $I_4^{(0)}$ yield $4\sqrt{2} + 2\sqrt{2} = 6\sqrt{2} = I_2^{(1)}$, and so on. The trace $I^{(1)}$ is shown in Fig. 4.1(b) and

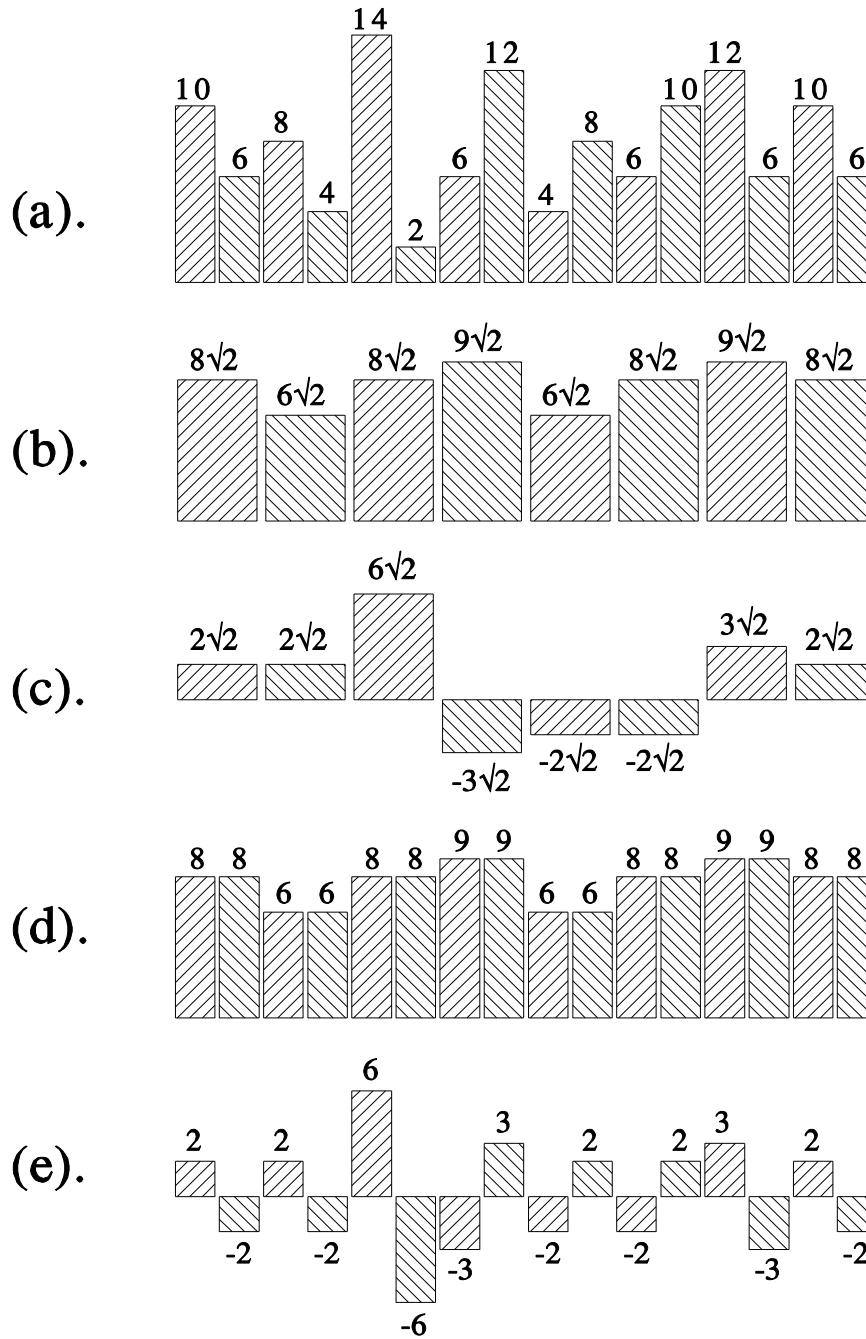


Figure 4.1: Numerical example of a multi-resolution analysis of a trace of discrete numbers following the “Mallatian Pyramid algorithm”. From top to bottom; (a) the original trace $I^{(0)}$, (b) the approximation trace $I^{(1)}$ (Eq. 4.1), (c) the detail trace $d^{(1)}$ (Eq. 4.2), (d) the reconstructed trace $\tilde{I}^{(0)}$ (Eq. 4.3), and (e) the reconstructed trace $\tilde{d}^{(0)}$ (Eq. 4.4). Addition of (d) and (e) yields the original trace (a).

represents the structure of the original trace on the scale $s_1 = 2^1 s_0$, twice as large as the bin-width s_0 of the original trace. The operation in Eq. 4.1 consists of a convolution and a decimation because (i) the original trace is convoluted with the weighting factors and (ii) the number of elements in the approximation trace is half the number of elements of the original trace. To encode the difference in information between the traces $I^{(0)}$ and $I^{(1)}$ we construct the detail trace, labelled $d^{(1)}$, in analogy with Eq. 4.1 by,

$$d_k^{(1)} = \sum_n I_n^{(0)} g_{n-2k} , \quad (4.2)$$

where the coefficients g_m are weighting factors satisfying the conditions $\sum_j g_m = 0$ and $g_m = (-1)^m w_{1-m}$ [61, 89]. In our numerical example we now have the coefficients $w_0 = w_1 = \sqrt{2}/2$ and $g_0 = -g_1 = \sqrt{2}/2$. Following Eq. 4.2 the trace $d^{(1)}$ is obtained in two steps; first multiply the trace $I^{(0)}$ with $\sqrt{2}/2$, and then subtract the elements of the trace $I^{(0)}$ in a pair-wise manner. For example; the elements $I_5^{(0)}$ and $I_6^{(0)}$ yield $7\sqrt{2} - \sqrt{2} = 6\sqrt{2} = d_3^{(1)}$, the elements $I_7^{(0)}$ and $I_8^{(0)}$ yield $3\sqrt{2} - 6\sqrt{2} = -3\sqrt{2} = d_4^{(1)}$, and so on. The trace $d^{(1)}$ is shown in Fig. 4.1(c) and contains information on the differences between the elements of the original trace, though represented on the larger scale s_1 .

The original trace of discrete numbers can be completely reconstructed by inversion of the averaging operations Eqs. 4.1 and 4.2. First we construct the trace $\tilde{I}^{(0)}$ by inversion of the operation in Eq. 4.1 using the same weighting factors,

$$\tilde{I}_n^{(0)} = \sum_k I_k^{(1)} w_{n-2k} . \quad (4.3)$$

Following Eq. 4.3 the trace $\tilde{I}^{(0)}$ is obtained by splitting up each element of the trace $I^{(1)}$ into two elements and multiply these by $\sqrt{2}/2$. For example; the element $I_1^{(1)}$ yields $\tilde{I}_1^{(0)} = \tilde{I}_2^{(0)} = 8\sqrt{2}/\sqrt{2} = 8$, the element $I_2^{(1)}$ yields $\tilde{I}_3^{(0)} = \tilde{I}_4^{(0)} = 6\sqrt{2}/\sqrt{2} = 6$, and so on. The trace $\tilde{I}^{(0)}$ is shown in Fig. 4.1(d) and contains the pair-wise average of the original trace on the original scale. Then we construct the trace $\tilde{d}^{(0)}$ by inversion of the operation in Eq. 4.2 using the same weighting factors,

$$\tilde{d}^{(0)}_n = \sum_k d_k^{(1)} g_{n-2k} . \quad (4.4)$$

Following Eq. 4.4 the trace $\tilde{d}^{(0)}$ is obtained by splitting up each element of the detail trace $d^{(1)}$ into two elements and multiply these by $\sqrt{2}/2$ (odd index) or $-\sqrt{2}/2$ (even index). For example; the element $d_3^{(1)}$ yields $\tilde{d}_5^{(0)} = -\tilde{d}_6^{(0)} = 6\sqrt{2}/\sqrt{2} = 6$, the element $d_4^{(1)}$ yields $\tilde{d}_7^{(0)} = \tilde{d}_8^{(0)} = -3\sqrt{2}/\sqrt{2} = -3$, and so on. The trace $\tilde{d}^{(0)}$ is shown in

Fig. 4.1(e) and contains the detail structure of the original trace on the scale s_0 , which was lost by the averaging procedure Eq. 4.1. The original trace is now recovered simply by addition of the constructed traces following $I^{(0)} = \tilde{I}^{(0)} + \tilde{d}^{(0)}$ to yield $I_5^{(0)} = 8 + 6 = 14$, $I_7^{(0)} = 9 - 3 = 6$, and so on.

Generalising Eqs. 4.1 and 4.2 the transformation of the discrete approximation trace $I^{(p)}$ on the scale $s_p = 2^p s_0$ to the next approximation trace $I^{(p+1)}$ and the accompanying detail trace $d^{(p+1)}$ on the scale $s_{p+1} = 2^p s_0$ is achieved by,

$$\begin{aligned} I_k^{(p+1)} &= \sum_n I_n^{(p)} w_{n-2k} , \\ d_k^{(p+1)} &= \sum_n I_n^{(p)} g_{n-2k} , \end{aligned} \quad (4.5)$$

where the integer p keeps track of the number of transformations completed. The trace $I^{(p)}$ can be recovered completely by (i) constructing $\tilde{I}^{(p)}$ from $I^{(p+1)}$ in analogy with the operation Eq. 4.3, (ii) constructing $\tilde{d}^{(p)}$ from $d^{(p+1)}$ in analogy with the operation Eq. 4.4, and then simply add these traces.

4.3 Discrete wavelet transformation

In the formal definitions of the ‘‘Mallatian Pyramid algorithm’’ a trace of discrete numbers is developed as a vector on a high-dimensional basis of orthonormal functions. The family of orthonormal functions forming these bases are scaled and integer-translated versions of a generating function ϕ defined by,

$$\phi_{p,k}(x) \equiv 2^{-p/2} \phi(2^{-p}x - k) . \quad (4.6)$$

Orthonormality of the basis functions under integer translation is expressed by the condition $\langle \phi_{p,k} | \phi_{p,n} \rangle = \delta_{k,n}$ where the integral,

$$\langle \phi_{p,k} | \phi_{p,n} \rangle \equiv 2^{-p} \int_{-\infty}^{\infty} \phi(2^{-p}x - k) \phi(2^{-p}x - n) dx = \langle \phi_{0,k} | \phi_{0,n} \rangle \quad (4.7)$$

Hence we require the generating function to form an orthonormal basis under integer translation. The vector representation of the approximation trace $I^{(p)}$ is given by an expansion on the orthonormal basis of functions by,

$$\mathbf{I}^{(p)} \equiv \sum_k I_k^{(p)} \phi_{p,k} . \quad (4.8)$$

Successive approximations containing less detail are obtained by projections of this vector trace onto lower-dimensional bases. From Eqs. 4.8 and 4.6 it follows directly

that the weighting factors encountered in these projections, formulated by the multi-resolution analysis algorithm Eq. 4.5, are given by overlap integrals of translated versions of the generating function which differ only one step in scale,

$$w_{n-2k} = \langle \phi_{p+1,k} | \phi_{p,m} \rangle = \langle \phi_{1,k} | \phi_{0,n} \rangle. \quad (4.9)$$

In principle, there are a countless number of candidates for the generating function, but only a small subset of these can meet the stringent conditions required to give an accurate and preserving representation of the trace under investigation. Formulations of such requirements and the specific functions adhering these conditions, known as wavelets, can be found in the excellent books by Newland [63] and Kaiser [64]. As generating functions we use here the special class of wavelet functions originally devised by Daubechies which are known as Daubechies wavelets [61, 62, 63, 64]. One of the main reasons for the popularity of Daubechies wavelets is their ability to form orthonormal basis of compactly supported wavelets with as much locality and smoothness as desired. With these specific functions the number of non-zero weighting factors as introduced in the example is limited, even, and equal to the order N ($= 2, 4, 6, \dots$) of the Daubechies wavelet. Using these “wavelet-based” weighting factors in the multi-resolution example as presented in the previous section defines a wavelet-based multi-resolution analysis or discrete wavelet transformation. Furthermore, Daubechies wavelets are constructed such that the moments of the generating function defined by,

$$\langle x^m \rangle \equiv \int x^m \phi(x) dx = 0, \quad (4.10)$$

for integers $m = 0 \dots N - 1$. Calculations of moments and cumulants of measured signals are then never polluted by the moments and cumulants of the analysing wavelet. Finally, Daubechies wavelets are defined both locally in time and frequency space as much as is allowed, i.e., Daubechies wavelets are bandwidth limited functions. As contracted versions of the generating functions have a reduced spatial range, their range in frequency increases proportionally. The price to pay for this enhanced spatial resolution is a proportional decrease of the frequency resolution, and vice versa. A wavelet representation can be tuned from excellent spatial resolution to premium frequency resolution by appropriate dilation of the wavelet function. For completeness and insight we present in App. A several examples of Daubechies wavelet functions together with exact values of weighting factors.

4.4 Discretely sampled traces

In our experiments a discretely sampled trace of integer numbers is obtained by repeatedly counting the number of scattered photons during the sampling time t_0 according to,

$$I(k) = I_k^{(0)} = \int_{k t_0}^{(k+1) t_0} I(t) dt , \quad (4.11)$$

where $I(t)$ is the intensity of laser-light scattered by a colloidal clay suspension and measured with a photomultiplier. We refer to Chap. 2 for a more detailed description of the experimental procedures and techniques. The results we discuss here are obtained with the 3.0 mass-percent sample, a mass fraction at which a gel is formed in 100 hours. The discretely sampled trace represents a time-resolved recording of the scattered intensity $I(t)$ sampled on the time-scale t_0 . Actual time is replaced by the discrete time $t_k = k t_0$. Furthermore, the trace has a specified length $K_0 = 2^M$, where the integer M is typically of the order of 16. An example of a discretely sampled intensity trace recorded on the colloidal gel is shown in Fig. 4.2. The recorded trace can be considered stationary on a time-scale of minutes, which is sufficient to characterise the spectrum. Figure 4.2 clearly demonstrates the presence of intensity fluctuations on all scales, from the finest scale set by the sampling time of the counter, to the entire duration of the trace. In Fig. 4.3 we show the power spectrum $S(\omega)$ of the trace depicted in Fig. 4.2. The power spectrum $S(\omega)$ denotes the intensity of fluctuations at a frequency ω and is obtained by,

$$S(\omega) \equiv |I(\omega)|^2 , \quad (4.12)$$

where $I(\omega)$ is the Fourier transform [90] of the time-resolved intensity trace. The power spectrum of Fig. 4.3 spans more than three orders of magnitude in frequency and shows an algebraic behaviour $S(\omega) \propto \omega^{-\gamma}$ where the spectral exponent $\gamma = 0.82 \pm 0.06$. The accuracy of estimating the spectral exponent from this very noisy data is rather poor. These simple observations reveal one of the experimental difficulties encountered in glassy systems such as colloidal clay gels; a wide frequency spectrum of fluctuations, i.e., a wide range of time-scales of fluctuations. Results of photon correlation spectroscopy are reliable only when the correlation functions are measured during periods of time at least an order of magnitude longer than the inverse of the low-frequency cut-off [5, 60, 27]. However, the integration time must be short with respect to the gelation time. Considering the long correlation times involved one may wonder if this condition will ever be met.

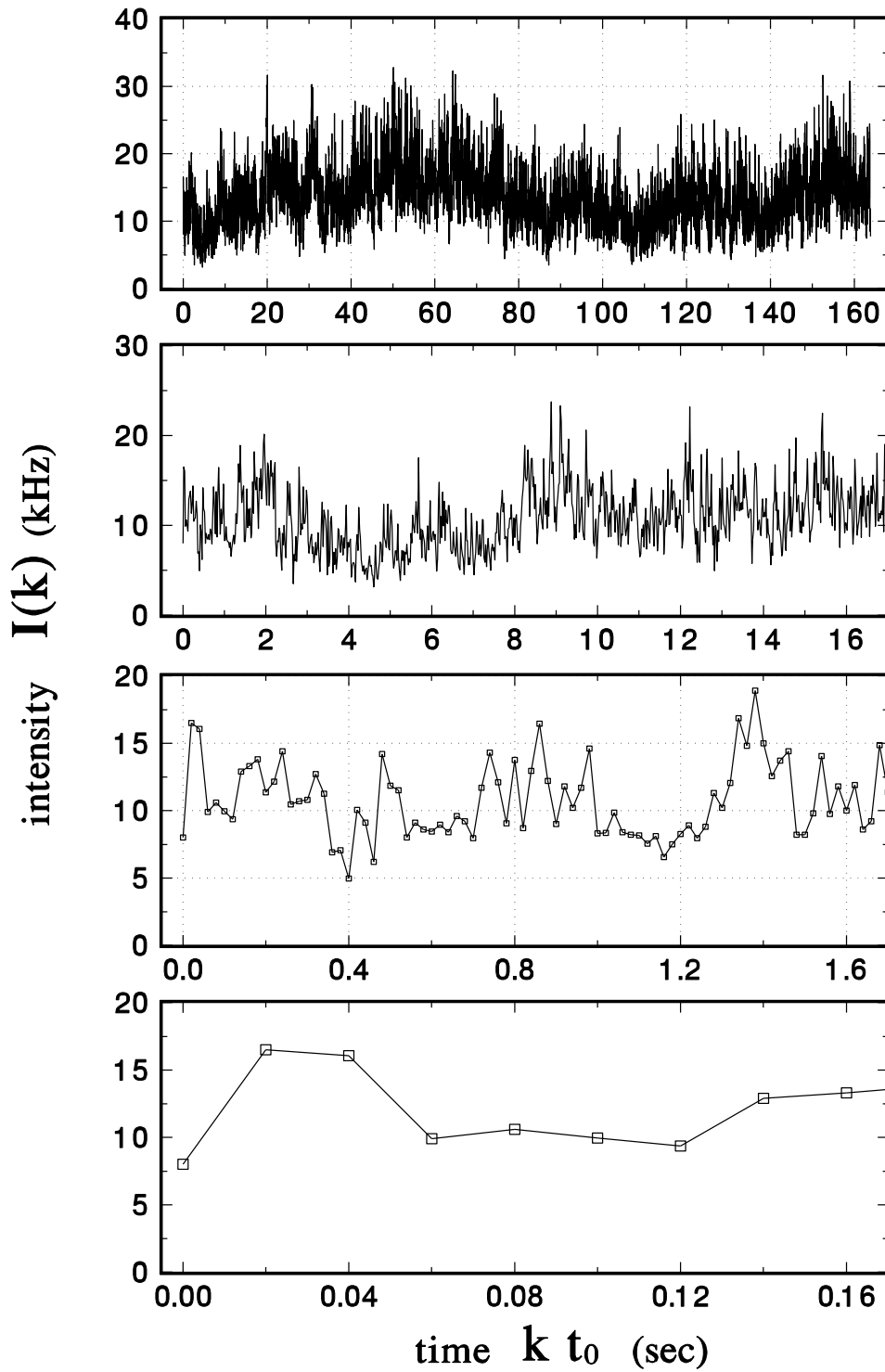


Figure 4.2: Typical measured time-resolved trace $I(k)$ of the scattered intensity as recorded on the colloidal gel. Time is replaced by $k t_0$ where t_0 is the sampling time. From top to bottom the plots zoom-in on the data and, although decreasing their apparent amplitude, reveal the presence of fluctuations on all scales.

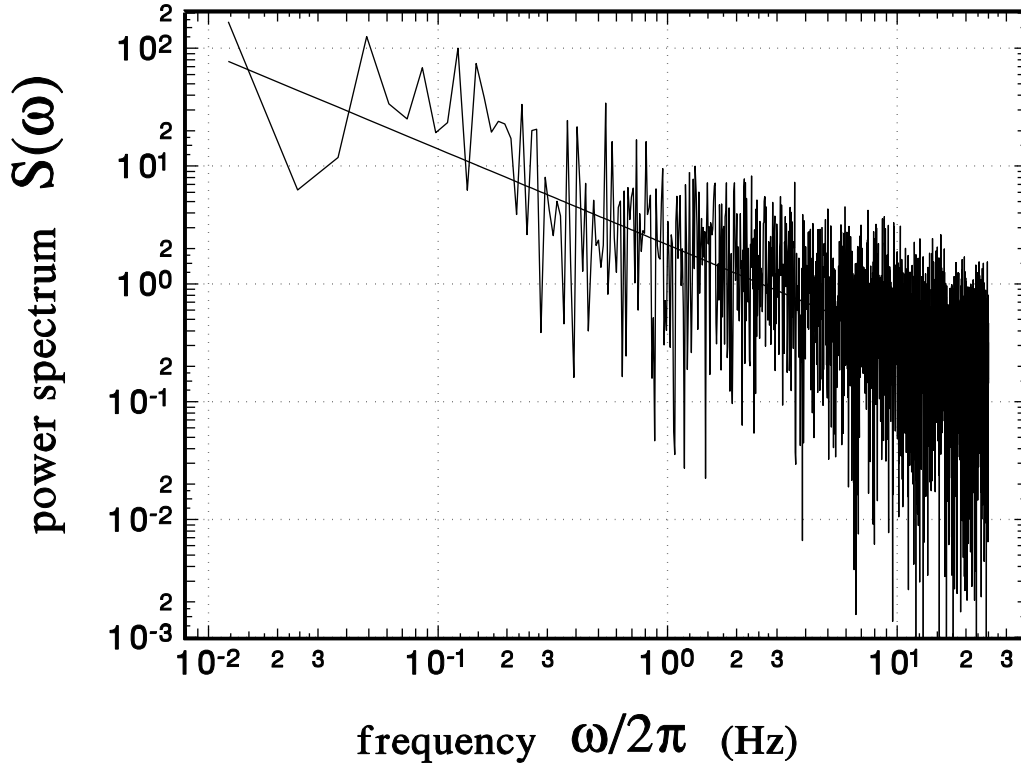


Figure 4.3: Power spectrum of the time-resolved intensity trace as shown in Fig. 4.2. The solid line shows a power-law fit $S(\omega) \propto \omega^{-\gamma}$. The high amount of noise inhibits an accurate determination of the spectral exponent $\gamma = 0.82 \pm 0.06$.

The observations presented above reveal the opportunity to characterise the measured intensity trace with wavelet analysis. Wavelet analysis has proven to be the natural tool to analyse non-stationary and chaotic signals locally in time without any prejudice to the scale of fluctuations [61, 84, 86]. Application of the transformations Eqs. 4.1 and 4.2 to the intensity trace of Fig. 4.2. yields the approximation trace $I^{(1)}$ and the detail trace $d^{(1)}$ of reduced length $K_1 = 2^{M-1}$ on a coarser time-scale $\tau_1 = 2^1 t_0$. Recursive application of the transformations Eq. 4.5 builds a hierarchy of approximations $I^{(1)}, I^{(2)}, \dots, I^{(p)}$ and details $d^{(1)}, d^{(2)}, \dots, d^{(p)}$ of reduced length $K_p = 2^{M-p}$ on coarsening resolution $\tau_p = 2^p t_0$. The integer p keeps track of the number of transformations completed where we limit the number of transformations $p \leq M - 5$ to warrant statistical accuracy. In Fig. 4.4 we plot on the l.h.s. a number of approximations of the intensity trace. The large-scale structure of the original trace remains conserved although frequency components higher than $\omega_p \propto \tau_p^{-1}$ are stripped off at every stage p of the transformation. On the r.h.s. in Fig. 4.4 we plot the removed detail at several stages of the transformation. Note that the detail trace contains

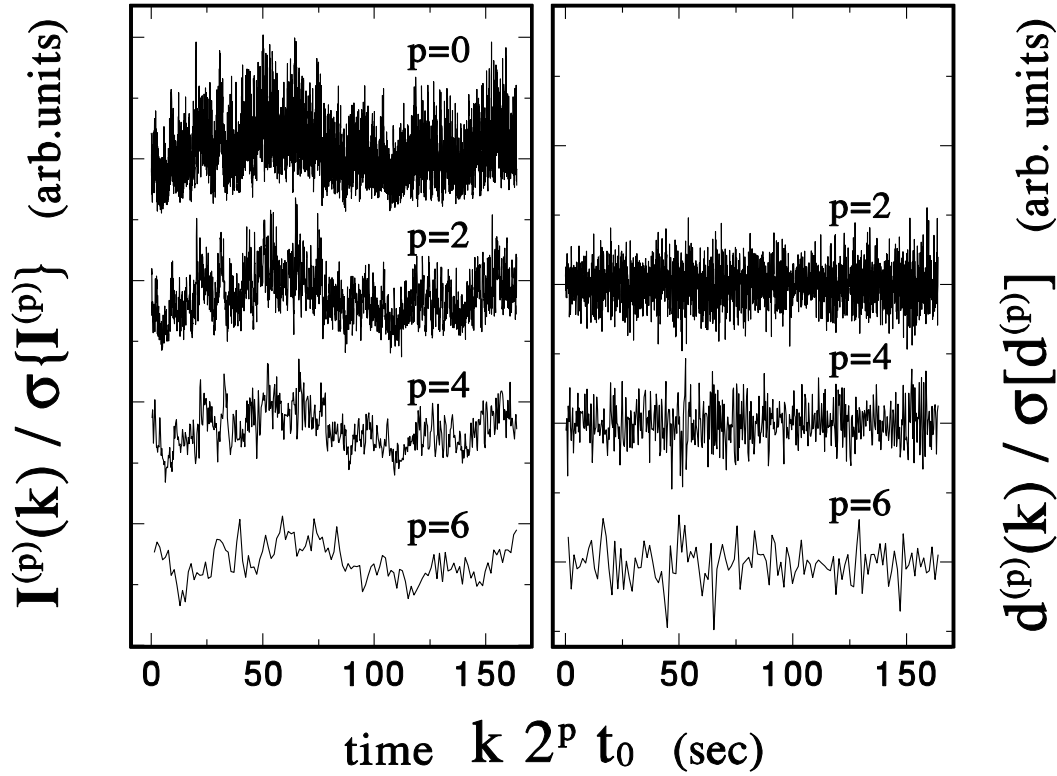


Figure 4.4: Results of subsequent discrete wavelet transformations on the intensity trace of Fig. 4.2. Actual time is represented by $k 2^p t_0$ where the integer p denotes the level of approximation. For graphical convenience the approximation trace (l.h.s.) and the removed detail trace (r.h.s.) are depicted for even p only. The results are normalised with respect to their variance σ .

no information regarding the long-time (low-frequency) structure of the self-similar intensity trace.

It has been argued and proven by Kaplan *et al* [89] that the moments of the removed detail $d^{(p)}$ represent the moments of the spectral distribution of fluctuations exactly on the time-scale τ_p related to the frequency scale τ_p^{-1} . To exemplify this statement we show in Fig. 4.5 the application of discrete wavelet transformation with $N = 2$ to a specific discrete trace. The first transformation by Eqs. 4.5 yields the traces of Fig. 4.5(b). Although the number of datapoints is halved, the structure of the trace remains intact and no detail is lost. The approximation trace in Fig. 4.5(b) has become an alternating series of numbers, similar to a cosine function being sampled at twice its frequency. The very next transformation of this specific trace moves all the information present exactly at that scale from the approximation trace to the detail

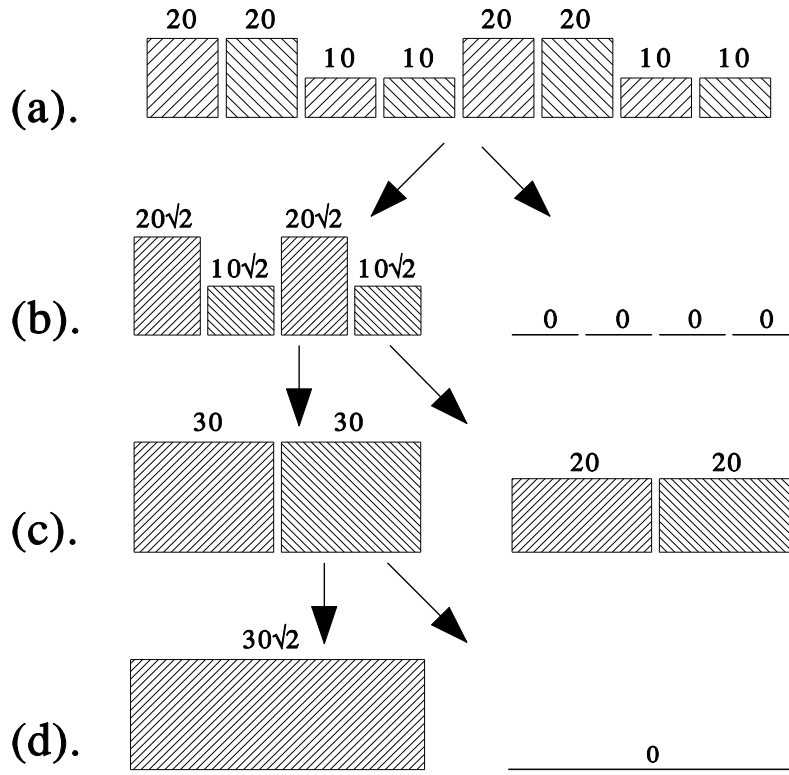


Figure 4.5: Numerical example of discrete wavelet transformation with $N = 2$ applied to a special series of discrete numbers. From top to bottom; (a) the original trace $I^{(0)}$, and on the l.h.s the traces (b) $I^{(1)}$, (c) $I^{(2)}$, and (d) $I^{(3)}$, on the r.h.s the traces (b) $d^{(1)}$, (c) $d^{(2)}$, and (d) $d^{(3)}$.

trace as shown in Fig. 4.5(c). Subsequent transformations (See Fig. 4.5(d)) can never extract information on the previous scale because it was lost by the previous transform. Indeed frequency components higher than $\omega_p \propto \tau_p^{-1}$ are stripped off at every stage p of the transformation and stored in the detail trace. Frequency components lower than $\omega_p \propto \tau_p^{-1}$ progress to the next approximation. Algebraic behaviour of the power spectrum $S(\omega)$ is revealed by the second moment or variance of the removed detail as a function of the time-scale by,

$$^2\log(\sigma\{d^{(p)}\}) = ^2\log(\sigma_0) + ^2\log(\tau_p/t_0) \gamma, \quad (4.13)$$

where γ is the spectral exponent and the variance σ_0 is proportional to the variance of the original trace $I^{(0)}$ sampled on the finest time-scale t_0 . Equation 4.13 is known as the variance progression [89]. In Fig. 4.6 we plot the variance of the detail trace versus

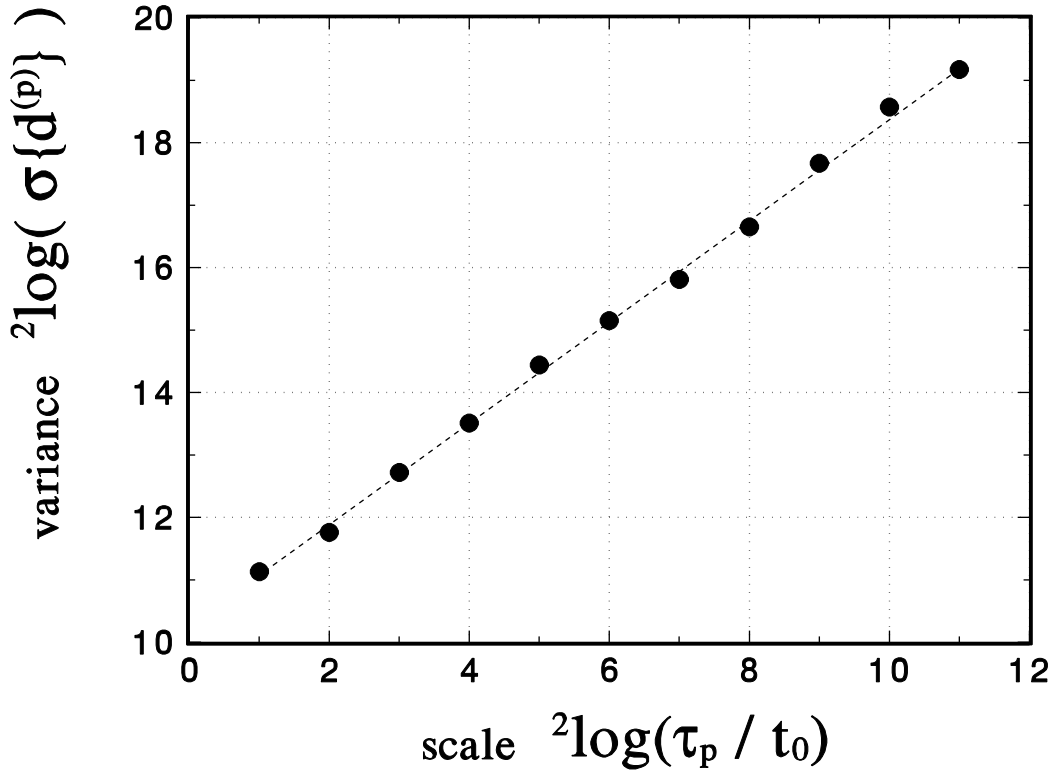


Figure 4.6: Progression of the variance $\sigma\{d^{(p)}\}$ of the removed detail $d^{(p)}$ plotted in Fig. 4.4 versus the scale τ_p . Matching Eq. 4.13 to the results (dashed line) yields the spectral exponent $\gamma = 0.82 \pm 0.01$.

the time-scale of the analysis. The substantial number of discrete data-points in the original intensity trace has been reduced tremendously to no more than 11, the number of wavelet transformations. With Eq. 4.13 we find for the spectral exponent a value $\gamma = 0.82 \pm 0.01$. Because the moments of Daubechies wavelets are zero up to the order N of the wavelet, the signal processing carried out with Eqs. 4.1 and 4.2 conserves the true moments of the sampled signal. Wavelet analysis identifies the predicted algebraic power spectrum underlying the sampled intensity trace through the variance progression. The increased accuracy of the estimate of the spectral exponent illustrates the power of wavelet analysis over Fourier analysis. Moreover, determining the power spectrum and spectral exponent with wavelet analysis requires at least a factor of 5 less calculation power with respect to Fourier transformation. Results obtained with different order N of the Daubechies wavelets are similar within experimental accuracy. Therefore we adopt $N = 12$ for the remainder of this chapter.

4.5 Simulations of fractional Brownian motion

To study the power and accuracy of the discrete wavelet transformation we have performed simulations of time sequences of fractional Brownian motion and applied the wavelet analysis to the simulated data traces. The concept of fractional Brownian motion (fBm) was introduced by Mandelbrot and van Ness [91] as a generalisation of normal Brownian motion. Fractional Brownian motion represents a non-stationary stochastic process that exhibits significant correlation over long times. The time sequence describing this type of motion has a power spectrum of the form,

$$S(\omega) \propto |\omega|^{-\gamma}, \quad (4.14)$$

where γ is the spectral exponent. A time sequence of fractional Brownian motion can be simulated by an efficient algorithm; one takes the square root of the power spectrum of the form Eq. 4.14 as the amplitude of the fractional Brownian motion at a certain frequency, and multiplies this amplitude by the cosine of a random phase. Fourier transformation then gives a time sequence whose power spectrum is given by Eq. 4.14. In our simulations the interval in frequency $\omega \in [-0.5, 0.5]$ with a frequency resolution $\delta\omega = 2^{-M}$ where the integer M is typically 16. Hence the effective length of 2^{M-1} data points of the simulated time sequence covers an interval $t = 2^{M-2}$ in time. In Fig. 4.7(a) we show several time sequences of fractional Brownian motion for different values of the spectral exponent. As the spectral exponent is increased, the amplitude of short-time fluctuations decreases in favour of long-time fluctuations, as expected. According to Eq. 4.12 the time sequence of fractional Brownian motion can be considered a representation of the time-resolved scattered intensity. However, because of the observation of algebraic decay of the density correlation function measured on the gel-state of our colloidal suspensions (See Chap. 3) we are not interested in the power spectrum of the scattered intensity but more in the power spectrum of the scattered field as the primary variable. The time sequence of fractional Brownian motion can also be considered a representation of the time-resolved scattered field where the underlying power spectrum is given by Eq. 4.14. The variance progression of the model signals of Fig. 4.7(a) falls on perfect straight lines, as is dictated by Eq. 4.13 and depicted in Fig. 4.7(b). Since the second and fourth moment of a Gaussian distributed zero-mean variable are simply related, the variance progression Eq. 4.13 will hold for both interpretations of the simulated time sequences. In Fig. 4.8 we show the results of an extensive series of simulations from which the limitations in γ of the combination “fractional Brownian motion-wavelet analysis” are readily seen. For the

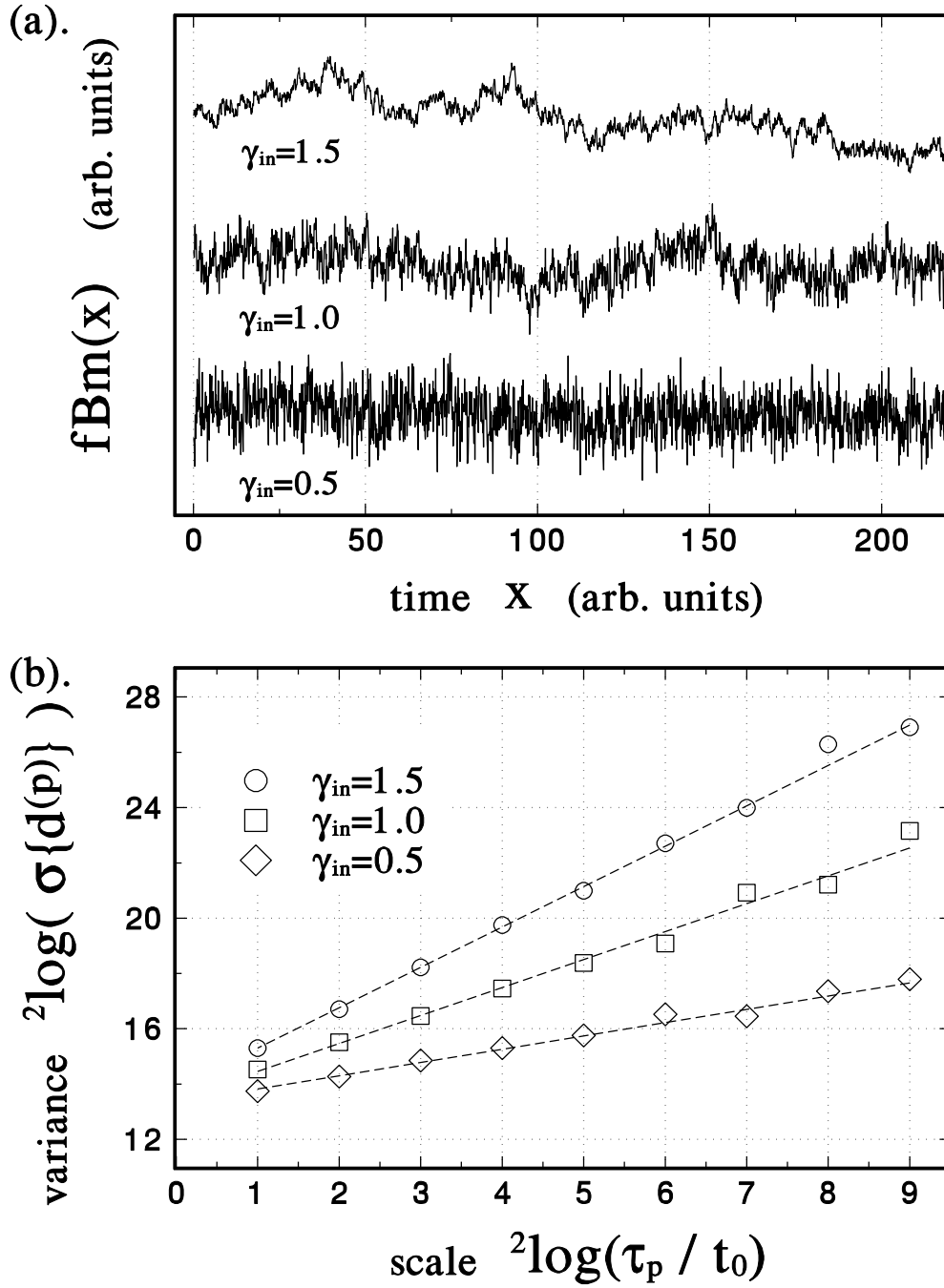


Figure 4.7: (a). Time sequences of simulated fractional Brownian motion $fBm(x)$ for different value of the spectral exponent γ_{in} implemented in the simulations. (b). Variance progression for the model signals depicted in (a). Matching Eq. 4.13 to the results (dashed lines) yields (from top to bottom) the estimates $\gamma_{out} = 1.46(\pm 0.02)$, $\gamma_{out} = 1.01(\pm 0.05)$, and $\gamma_{out} = 0.48(\pm 0.03)$.

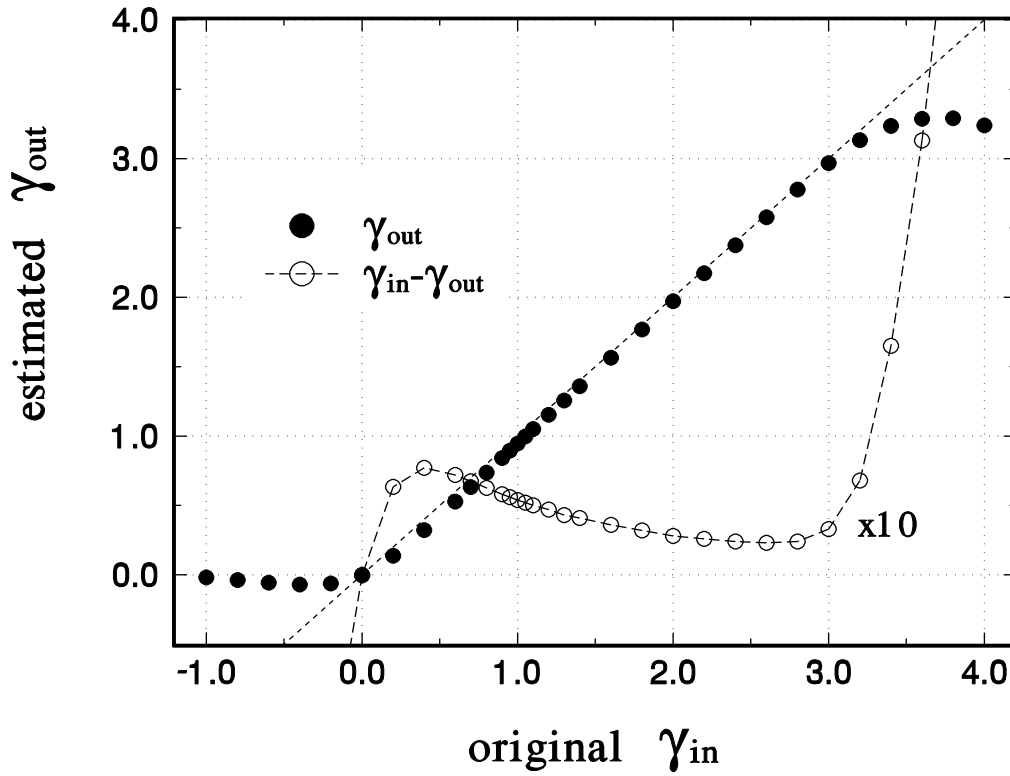


Figure 4.8: Spectral exponent γ_{out} recovered with wavelet analysis (dots) from simulated time sequences of fractional Brownian motion versus the value of the spectral exponent γ_{in} implemented in these simulations. The dashed line indicates the relation $\gamma_{in} = \gamma_{out}$. The difference $\gamma_{in} - \gamma_{out}$ (circles) reveals a structural underestimate of the spectral exponent by wavelet analysis.

range $\gamma \in [0, 3]$ wavelet analysis accurately recovers the spectral exponent, although the analysis structurally underestimates its value. On the other hand, an accuracy better than 5×10^{-2} for individual estimates is quite impressive. Any modification of the time sequence of fractional Brownian motion, in terms of taking absolute values and taking roots and powers, drastically diminishes the accuracy of individual estimates of the spectral exponent and the good agreement between entered and recovered spectral exponent displayed in Fig. 4.8. The results depicted in Fig. 4.8, however, remain unaltered by the addition of a zero-frequency contribution to the fractional Brownian motion, i.e., addition of a constant background. Further simulations performed to study the limitations and accuracy of wavelet analysis are presented in App. B.

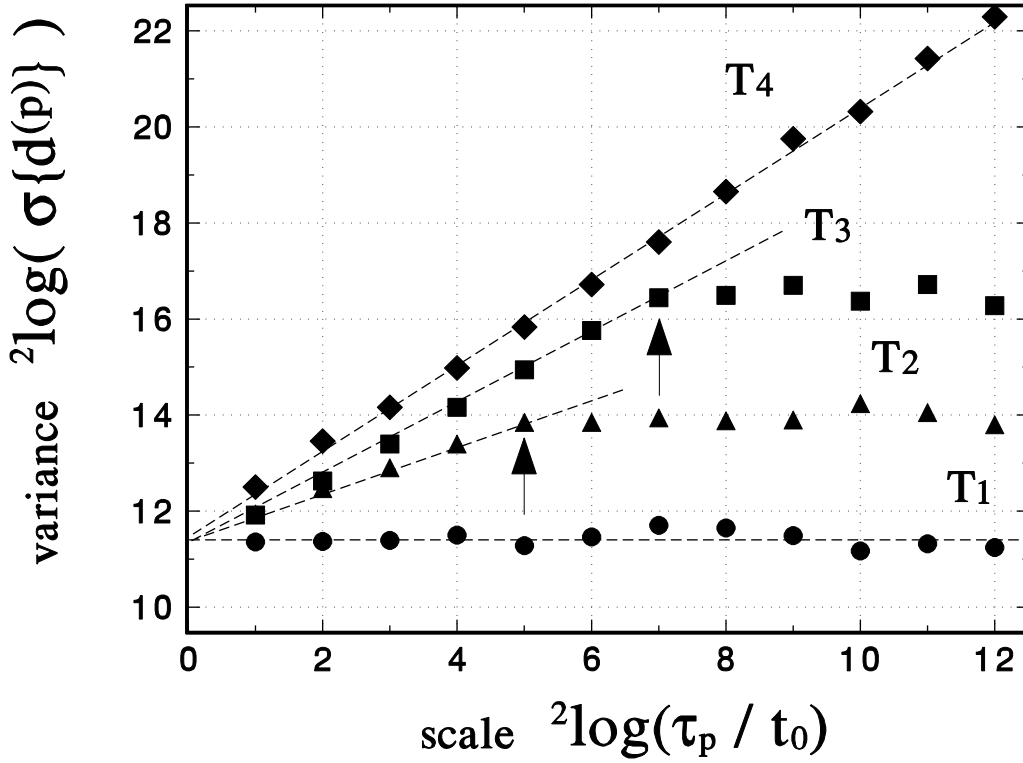


Figure 4.9: Evolution of the variance progression $\sigma\{d^{(p)}\}$ versus the time-scale τ_p over the gelation of a colloidal clay suspension. The symbols T_i denote well-separated regions in the gelation process and are related to Fig. 4.10(a). The arrows indicate the end of the range τ'_p of algebraic decay.

4.6 Following the sol-gel transition

The results presented so far have been measured on the stable gel-phase of our colloidal clay suspension. We have also measured time-resolved recordings of the scattered intensity as the gelation of our colloidal suspensions proceeds. In Fig. 4.9 we depict the variance progression at well separated moments T_i in the gelation process. Here the time-resolved intensity trace is sampled with a sampling time $t_0 = 20$ msec. Just after sample preparation (region T_1) the variance progression is flat over the entire range in time-scales covered. In region T_2 we observe the first few points of the variance progression to fall on a straight line which bends off at a certain time-scale τ'_p , denoted by arrows in Fig. 4.9. Beyond this time-scale, or below its inverse (frequency) scale $\omega'_p = (\tau'_p)^{-1}$, the algebraic decay ceases. Therefore the scale τ'_p denotes the range of algebraic decay in the variance progression. With Eq. 4.13 we extract the spectral exponent in this range. As the gelation proceeds we observe the spectral exponent and

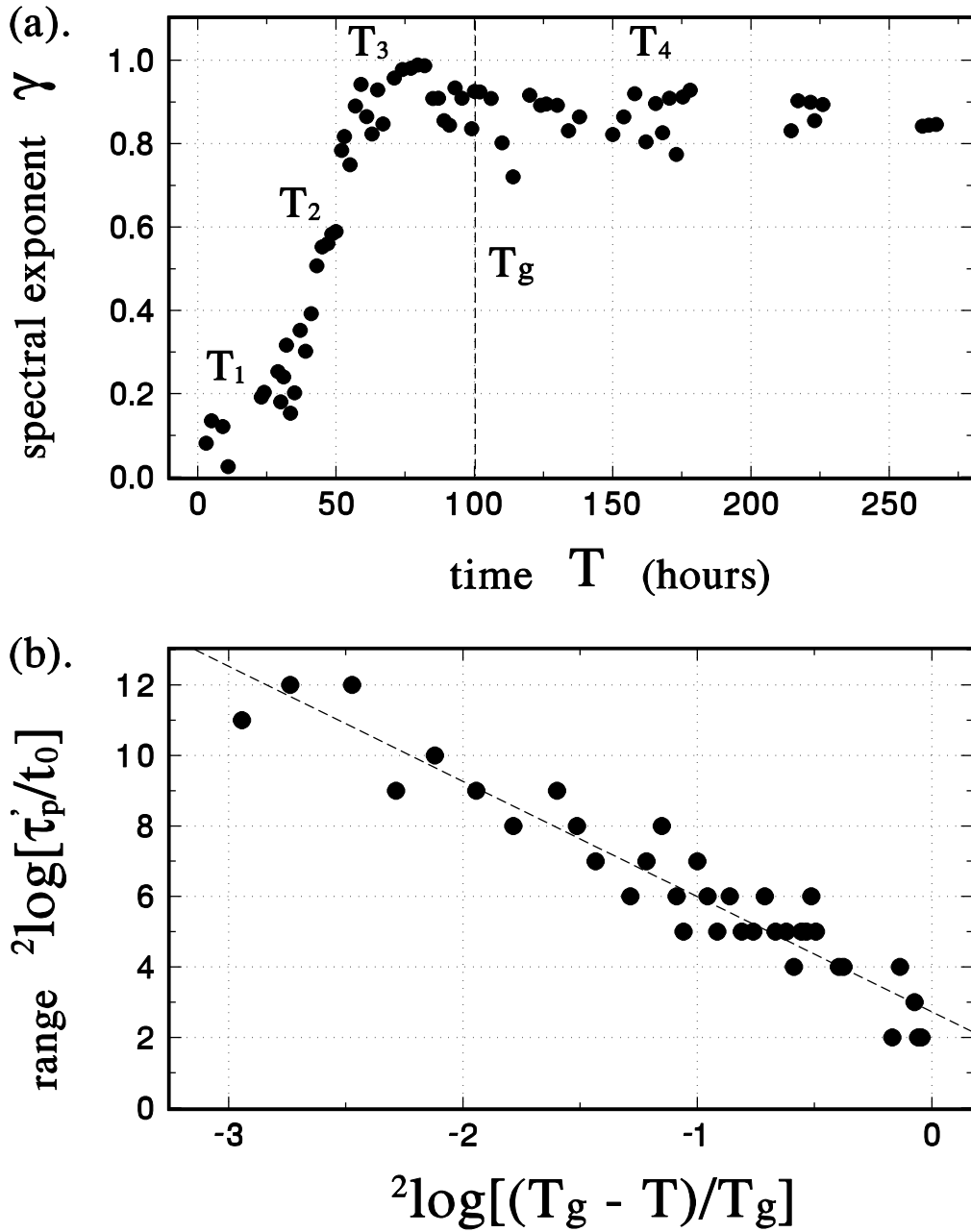


Figure 4.10: (a). Spectral exponent γ as a function of time T in the gelation process, obtained by Eq. 4.13 as the slope of the algebraic decay in Fig. 4.9. The symbols T_i denote well separated regions in the gelation process, and the dashed line indicates the gel point $T_g = 100$ hours. (b). The algebraic range τ'_p versus the normalised distance to the gel-point $\epsilon = (T_g - T)/T_g$. The dashed line shows a power-regression fit according to $\tau'_p \propto \epsilon^{-\alpha}$ where $\alpha = 3.3 \pm 0.1$.

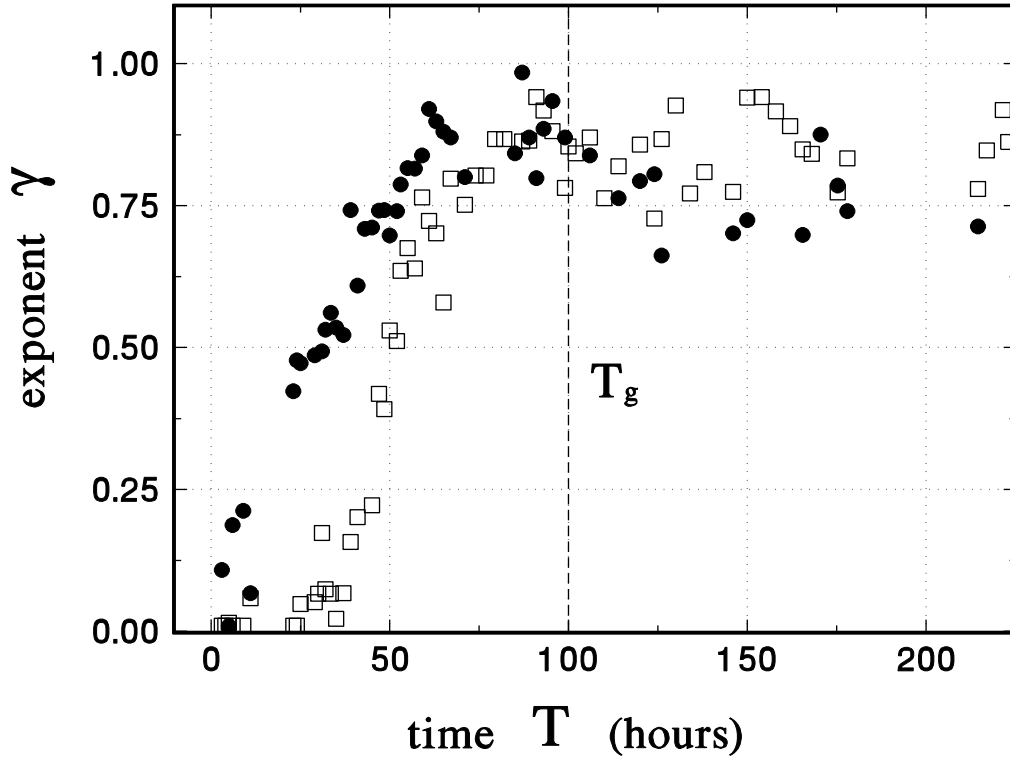


Figure 4.11: Spectral exponent versus the time T after preparation for two different sampling times (a) $t_0 = 2$ msec (circles) and (b) $T_0 = 40$ msec (boxes). The dashed line denotes the gel-point $T_g = 100$ hours.

the algebraic range to increase, as is shown in Figs. 4.10. Finally, in the gel (region T_4) we observe an algebraic decay of the variance progression over the entire range in time-scales covered by the analysis. Here the spectral exponent has settled at a relatively constant value of $\gamma = 0.86 \pm 0.04$. In Fig. 4.10(b) we depict the algebraic range τ'_p versus the normalised distance to the gel-point $\epsilon = (T_g - T)/T_g$, where the gel-point $T_g = 100$ hours [1]. Approaching the gel-point, we observe the algebraic range to “stretch” to infinity according to a simple power-law $\tau'_p \propto \epsilon^\alpha$ where the critical exponent $\alpha = -3.3 \pm 0.1$. As a result of the restricted time duration of the recorded trace the stretching of the algebraic range is obtained over a limited range in time-scales. A wider range in time-scales requires either shorter sampling times or longer trace measurements, the latter endangers the condition of stationarity for the recorded spectra.

The sampling time combined with the length of the recorded intensity trace sets an upper and lower limit for both the time and frequency window of observation. To in-

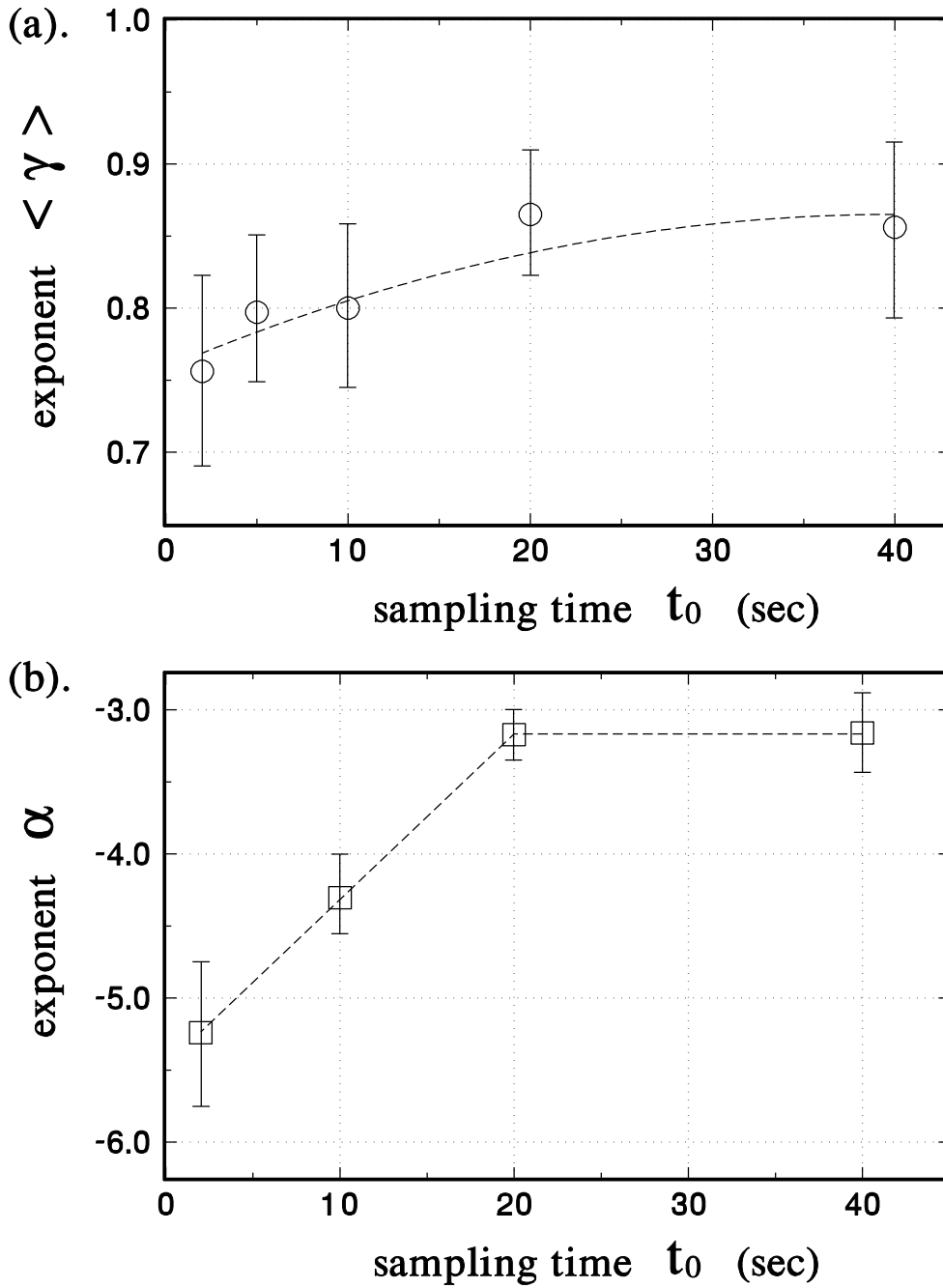


Figure 4.12: (a). Average value of the spectral exponent γ for times $T > 150$ hours versus the sampling time of photon counting. The dashed curve is given by the relation $\langle \gamma \rangle = 0.86 - [(t_0 - 40)/120]^2$ and serves as a guide to the eye. (b). Exponent α of the algebraic range τ'_p depicted in Fig. 4.10(b) versus the sampling time of photon counting. The dashed lines serve as guides to the eye.

investigate these limits we have varied the sampling time t_0 when recording the intensity traces during gelation. Figure 4.11 depicts the development of the spectral exponent for two different sampling times. When using the short sampling time the maximum value of the spectral exponent is reached early in the gelation process, whereas with longer sampling times the rise in the $\gamma - T$ curve is delayed and becomes much more steep. Despite the difference in shape the curves plotted in Fig. 4.11 can be more or less brought to overlap merely by shifting the curves with respect to the horizontal axis. This operation is allowed and successful as a result of the relatively small difference in sampling times. Approaching the gel-point T_g the algebraic range is always observed to “stretch” to infinity according to a simple power-law. However, the critical exponent describing this stretching varies with the sampling time, as shown in Fig. 4.12(b). Hence the exponent describing the critical divergence of the algebraic range depends on the frequency window captured by wavelet analysis. In the gel (region T_4) the spectral exponent reaches a relatively constant value, mildly subjected to slow processes like ageing. However this final value strongly depends on the sampling time, as is shown in Fig. 4.12(a). Starting low the average spectral exponent rises when increasing the sampling time and saturates at a value 0.86 ± 0.04 .

4.7 Spectral properties

Previously, in Sec. 4.5, we showed that wavelet analysis can recognise the underlying algebraic power spectrum of time sequences of fractional Brownian motion through the variance progression and accurately reproduces the exponent, regardless of deliberately added spectral noise (See Fig. B.2 in App. B). Supported by these findings the wavelet analysis predicts an algebraic power spectrum in the gel-phase of our clay suspensions. Then the autocorrelation function of the scattered intensity, related to the power spectrum by Fourier transformation [90], must show algebraic decay, which is indeed observed (See Chap. 3). However, the results of dynamic light scattering measurements, presented in Chap. 3, reveal drastic changes in the shape of the correlation functions as the gelation proceeds which must be accompanied by similar changes in the power spectrum. At this point we must answer the question whether wavelet analysis is able to recognise other than algebraic spectra and whether wavelet analysis can discriminate between different spectra. Therefore we have performed simulations of time sequences of fractional Brownian motion based on different underlying power spectra. A very popular spectrum originating from the theory of Götze [20] for the

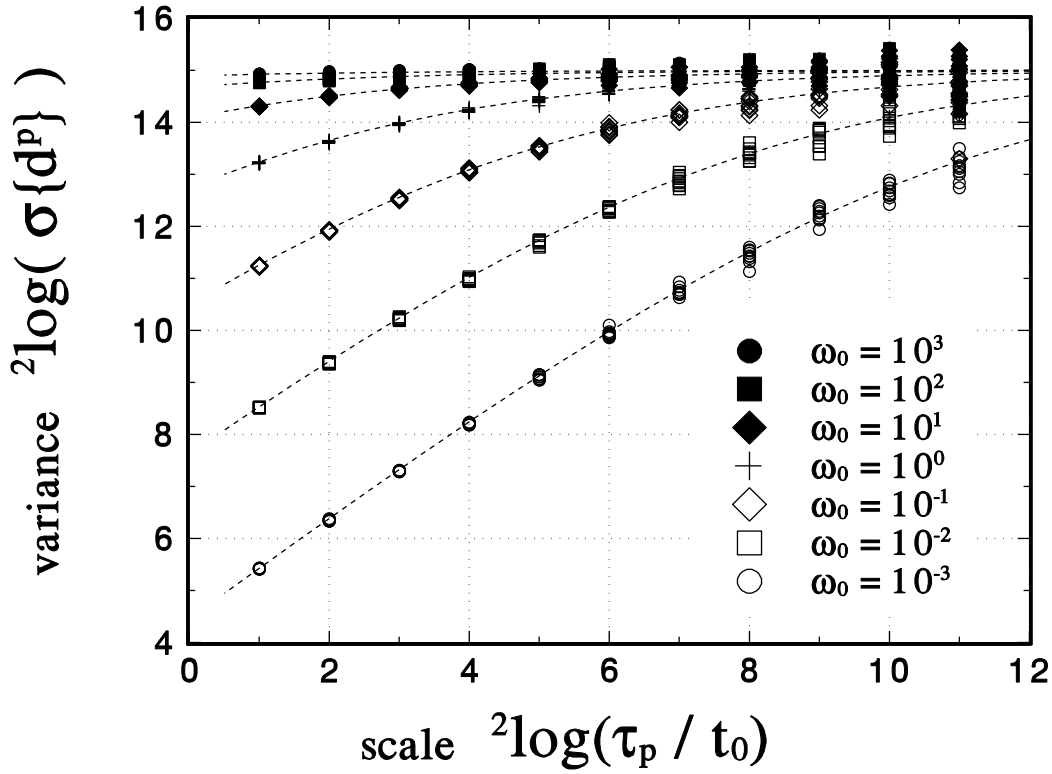


Figure 4.13: Variance progression for simulated time sequences of fractional Brownian motion based on the power spectrum Eq. 4.15 generated for several values of the frequency parameter ω_0 . For every ω_0 the results of ten simulations are plotted. The dashed lines represent Eq. 4.15 when frequency is given by $\omega_p/\omega_0 = \tau_0/\tau_p$.

structural glass transition is given by,

$$S(\omega, \omega_0) \equiv \left[1 + \left(\frac{\omega}{\omega_0} \right)^\gamma \right]^{-1}, \quad (4.15)$$

where the spectral exponent γ and the frequency ω_0 characterise the spectrum. In Fig. 4.13 we plot the variance progression for time sequences of fractional Brownian motion based on Eq. 4.15 generated for several values of ω_0 . For large ω_0 the spectrum Eq. 4.15 represents white noise, hence the variance progression is flat. In the limit $\omega_0 \downarrow 0$ the spectrum Eq. 4.15 is algebraic and the variance progression yields a straight line with the correct slope. Intermediate values of ω_0 yield curved results which appear indecisive. However, the dashed lines drawn in Fig. 4.13 represent the actual power spectra defined by Eq. 4.15 when we relate the “frequency-axis” of the simulated power spectrum to the “scale of analysis-axis” according to the surprisingly simple relation $\omega_p/\omega_0 = \tau_0/\tau_p$, or $2 \log[\tau_p/\tau_0] = -2 \log[\omega_p/\omega_0]$. Thus wavelet ana-

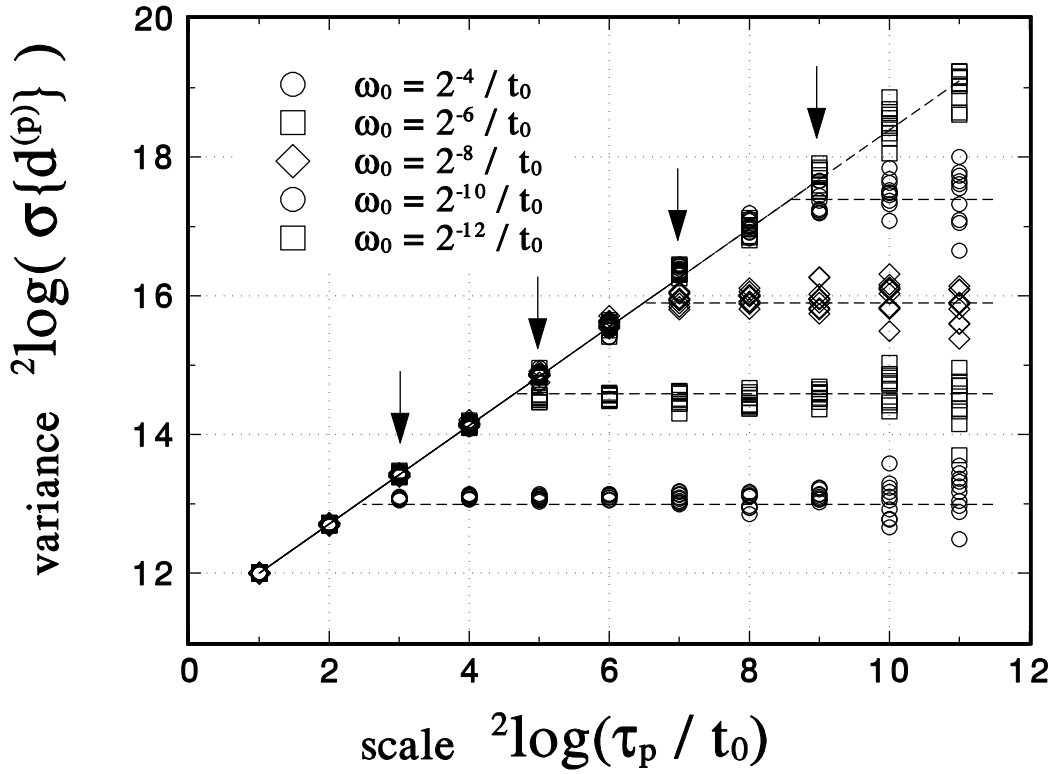


Figure 4.14: Variance progression for simulated time sequences of fractional Brownian motion based on the power spectrum defined by Eq. 4.16 generated for several values of the parameter ω_0 . The results of ten simulations are plotted for every ω_0 . Dashed lines represent guides to the eye following Eq. 4.16. Arrows indicate the end of the algebraic range (cf. Fig. 4.9).

lysis maps out the power spectrum by the variance progression. More precisely, in Fig. 4.13 the horizontal axis is a reversed frequency axis. Therefore the results displayed in Fig. 4.9 are reliable and map the state of the clay suspension in the process of gelation. From Fig. 4.13 it is also clear that conclusions drawn for the functional form of the power spectrum depend on the choice of the frequency window monitored by wavelets, i.e., the number of wavelet transforms denoted by p . The power spectrum is characterised as algebraic following Eq. 4.14 when one limits the discussion to small p . At large p , however, the results are curved on all scales and suggest the presence of a distribution of spectral exponents, i.e., a stretched exponential form of the density correlation function characterised by a distribution of time scales of relaxation.

The spectrum Eq. 4.15, however, does not reproduce the results of Fig. 4.9 ob-

tained on the gelation. A more appropriate but unrealistic spectrum [92] is given by,

$$S(\omega, \omega_0) \equiv \begin{cases} 1 & , \quad 0 \leq \omega \leq \omega_0 \\ (\omega_0/\omega)^\gamma & , \quad \omega_0 \leq \omega \leq 1 \end{cases} \quad (4.16)$$

where the frequency ω_0 determines the location of the cross-over point in the spectrum. In Fig. 4.14 we plot the variance progression for time sequences of fractional Brownian motion based on Eq. 4.16 generated for several values of the frequency ω_0 . For large ω_0 the power spectrum is predominantly of white-noise nature and yields a flat variance progression. As ω_0 becomes smaller the algebraic part of the power spectrum extends and the cross-over point moves to higher scale τ_p . Again the simulated power spectra can be drawn in perfect agreement with the wavelet results of Fig. 4.14. Moreover, the wavelet results for this spectrum are again insensitive to deliberately added spectral noise. The results of the simulations based on the spectrum Eq. 4.16 and shown in Fig. 4.14 closely mimic our experimental findings on the gelation process presented in Fig. 4.9. Relating the cross-over frequency $\omega_{0,p} \propto 2^{-p}/t_0$ applied in Eq. 4.16 to the algebraic range τ'_p denoted by arrows in Fig. 4.14 yields the relation $2 \log[\tau'_p/t_0] \approx p - 1$. Hence the algebraic range is inversely proportional to the cross-over frequency of the model spectrum Eq. 4.16.

4.8 Discussion

For an assessment of the results presented in this chapter it is important to note that wavelet analysis is an accurate tool to discriminate between different types of correlation functions, i.e., different functional forms of the power spectrum of fluctuations. Early in the gelation (region T_1) and later on at long delay times (beyond the algebraic range) scaling ceases as shown in Fig. 4.9. A line with zero slope means an exponentially decaying correlation function. The correctness of this interpretation is beared out by our simulations. For the gelating laponite system the algebraic decay goes over rather abruptly in an exponential decay. Then the long time cut-off is clear and unambiguous. This is in contrast to spectra or correlation functions that are algebraic in their asymptotic limits, as shown in Fig. 4.13. In the double logarithmic plot of variance versus scale, the cut-off is ill-defined. Seen within a finite time or frequency window the variance plot corresponds to that of a process with a stretched exponential correlation function. In this case the variance progression is curved on any scale. The use of a stretched exponential to describe the correlation function before the gelation point, as

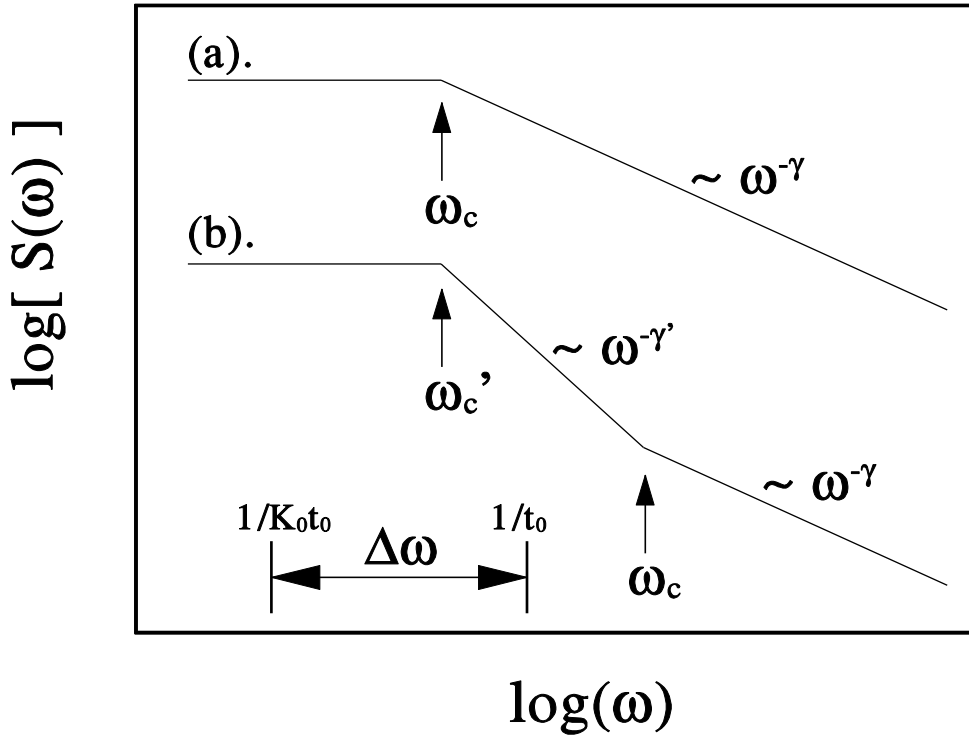


Figure 4.15: Schematic representation of power spectra of density fluctuations for the suspensions of colloidal clay in water. Spectrum (a) is based on the experimental observations with wavelets. Spectrum (b) is predicted by the theory of Götze [20] on the structural glass transition. The range $\Delta\omega$ denotes the frequency window monitored by wavelet analysis. The position and width of this range can be adjusted at will by changing the sampling time t_0 and length K_0 of the recorded traces.

argumented by Refs. [20, 27], is therefore justified only as a phenomenological fitting tool.

The physical picture that we can derive from the results presented in this chapter is schematically illustrated in Fig. 4.15(a). The spectrum of density fluctuations $S(\omega)$ is composed of two distinct regions. The high-frequency region of the power spectrum is characterised by a power-law relation $S(\omega) \propto \omega^{-\gamma}$ where ω denotes frequency and γ the spectral exponent. At a certain frequency ω_c this high-frequency region goes over into the low-frequency region characterised by either a Lorentzian representing exponential decay in the time domain, or something else that wavelet analysis distinguishes from scaling. We will assume that here the spectrum is flat, as wavelet analysis does not give any clue to its exact form. The cross-over frequency ω_c marks an important point in the spectrum: the onset of algebraic dependence. Early in the gelation process

the time-scale $\tau_c = 1/\omega_c$ lies inside the sampling time of photon counting, i.e., outside the frequency window monitored by wavelet analysis. The variance progression picks up the flat part of the spectrum. As the gelation proceeds the cross-over frequency shifts to ever lower frequencies, the cross-over time extends beyond the sampling time, and photon counting picks up the intensity fluctuations. The power-law characteristic of the high-frequency region starts to dominate over an ever larger range in frequency, which is reflected by the increase of the algebraic range. Approaching the gel-point the algebraic range diverges, which is consistent with the cross-over frequency critically approaching zero. In the final gel-state the spectrum of density fluctuations is fully characterised by the algebraic relation with frequency, an experimental fact supported by the simultaneous observation of an algebraic tail in the density correlation function.

Measurement of the intensity trace using a different sampling time merely tends to shift the results as shown in Fig. 4.10 with respect to the horizontal axis only for a limited range in sampling times. The sampling time combined with the length of the recorded intensity trace sets an upper and lower limit for both the time and frequency window of observation; the sampling time sets the high-frequency cut-off of the analysis, whereas the length of the sampled trace sets the low-frequency cut-off. In all our experiments we have kept the trace length constant. With larger sampling times the occurrence of algebraic decay in the power spectrum will be seen at a later stage in the gelation process because the frequency window monitored by wavelet analysis is shifted to lower frequency in Fig. 4.15. Similarly, the development of the spectral exponent towards the relatively constant value reached in the gel phase will be more and more delayed. The stretching behaviour of the low-frequency cut-off, i.e., the algebraic range increasing towards lower and lower frequencies, is observed for every sampling-time. The algebraic range defines the characteristic time range in the development of the gel, and the spectral exponent defines the state of the suspension in the process of gelation. However, the spectral exponent changes, though at a much slower pace, beyond the gelation point. A spectral distribution corresponding to this situation is shown in Fig. 4.15(b). Now the spectrum consists of a flat part and two algebraic parts with different spectral exponents. Approaching the gel-point both cross-over frequencies ω_c and ω'_c approach zero, though at a different pace. This spectral distribution passes through the necessarily finite frequency window used in the wavelet analysis. The estimated spectral exponent changes from zero in the sol-phase, to an intermediate value determined by the spectral exponent of the low-frequency part of the spectrum. Beyond the gel point the second part of the spectrum shifts into the observation window. With a short sampling time, resulting in a high frequency location

and small width of the frequency window, one first encounters the value γ' and then γ for the spectral exponent. Moreover, wavelets analysis picks up the "stretching" of the time-scale $1/\omega_c$. A longer sampling time shifts the frequency window of observation to lower frequencies and therefore measures the exponent γ' and the time-scale $1/\omega_c'$ over the entire duration of the experiments. In the gel-state the spectral exponent evolves from γ' to the final value γ only by the tediously slow process of ageing. After sufficient time has passed (multiples of the gelation time) two cross-over time-scales are sometimes observed, although highly irreproducible.

The spectrum of the density fluctuations, which is measured by light scattering, changes continuously when the colloidal system is going through the transition. It shows an algebraically decaying part between a high and low frequency cut-off, the latter is approaching zero frequency at the transition. These characteristics can be addressed quantitatively with wavelet analysis and are obtained without the bias of a presupposed model to analyse the data with. With correlation functions the bias is introduced by the necessity to use a functional form, on the basis of a model or as a practical phenomenological tool, to obtain the characteristic parameters. Moreover the correlation functions can be measured only with any reliability, when the evolution of the spectral distribution is a few orders slower than the inverse of the low frequency cut-off. Wavelet analysis does not suffer from these drawbacks. It is fast and efficient and can be used as a valuable tool in analysing non-stationary signals, physical systems in non-stationary states, such as glass or gel-formation. However, advantage and loss go together. Wavelet analysis only analyses the fluctuations in a signal. The constant part of the intensity, a characteristic parameter in the gel formation, cannot be assessed. This shortcoming also holds for those fluctuations that possess a non-algebraic power spectrum.

Chapter 5

Structure and formation of a gel of colloidal discs

5.1 Introduction

In this chapter, we present results on static scattering experiments on the transition from a fluid-like sol to a solid-like gel of a suspension of disc-shaped charged colloidal particles in water. Suspensions of these charged colloidal discs are observed to undergo a sol-gel transition in time, instead of entering a liquid crystalline phase. The picture emerging from our dynamic light-scattering measurements is one of frustration of the particle motion [1, 56]. This frustration is a result of the increasing viscosity [6] and is barring the colloidal suspension from entering a crystalline state, just as in the glass transition [20]. Static light-scattering and small-angle X-ray scattering techniques have been used to investigate the time-evolution of the structure and the degree of liquid crystalline order. The combination of the results of static light-scattering and small-angle X-ray scattering probes more than three orders of magnitude in the scattering vector q . This allows us to investigate the state of the colloidal suspensions from sub-particle length scales to the large length-scale colloidal arrangement.

5.2 Experimental

We describe the experimental setup shortly: In the static light-scattering setup a He-Ne laser is producing a 10 mW beam with vertical polarisation. The laser beam is focused in the sample to a beam waist of $50\text{ }\mu\text{m}$. The sample is contained in a cylindrical 10 mm diameter quartz cuvette which is immersed in an index-matching toluene bath

of 80 mm diameter. Scattered light is detected in VV polarisation geometry with a photo multiplier that is mounted on a goniometer arm. The signal to straylight ratio is better than 10^2 over the experimentally accessible range in q . Speckle averaging is performed by slow vertical translation of the sample through the laser beam with a motorised setup, while measuring the scattered intensity. Small-angle X-ray scattering experiments were performed at the European synchrotron radiation facility (ESRF) in Grenoble [78] and at the Daresbury synchrotron radiation source [79]. The sample containers used here are made of a brass frame of $1 \times 4 \text{ cm}^2$ acting as a spacer of 0.5 mm thickness. Windows of kapton or mica are glued on both sides. The suspensions are inserted through sealable holes. We have to use such thin containers in the small-angle X-ray scattering experiments as a result of strong X-ray absorption by water (absorption coefficient $\mu \sim 10^3 \text{ m}^{-1}$). In turn, the thin flat-plate cell geometry of the X-ray cell was impractical to use in light scattering. We refer to Chap. 2 for a more elaborate discussion of the experimental procedures and techniques.

5.3 Results

In Fig. 5.1 we show an overall view of the static scattered intensity $I_s(q)$ as obtained with the different scattering set-ups. The scattered intensities as shown in Fig. 5.1 have been measured on a stable gel, and have been scaled to merge. (i) At the smallest q , between 10^{-3} nm^{-1} and 10^{-2} nm^{-1} , a steep decrease in the scattered intensity is observed. In this range of q the measured intensity is proportional to the static structure factor $S(q)$ of the colloidal arrangement. (ii) There is a plateau at intermediate q values, between 10^{-2} nm^{-1} and 10^{-1} nm^{-1} . The corresponding length scale is of the order of the average interparticle distance. (iii) At the largest q values, between 10^{-1} nm^{-1} and 10^0 nm^{-1} , the scattered intensity roughly follows a q^{-2} power-law decay, which is consistent with the form factor $\overline{F^2}(q)$ of randomly oriented thin discs [70].

We adopt the usual assumption that the knowledge of the relative positions of two particles on no way modifies the probabilities of their different orientations (Ref. [70], p. 30). Hence the scattered intensity is separated into two factors by,

$$I_s(q) \propto \rho I_0 S(q) \overline{F^2}(q) , \quad (5.1)$$

where $\rho = N/V$ is the number density of individual scatterers and I_0 is the incident intensity. The single-particle form factor $\overline{F^2}(q)$ accounts for the interference of radiation scattered from different parts within one particle. The static structure factor $S(q)$

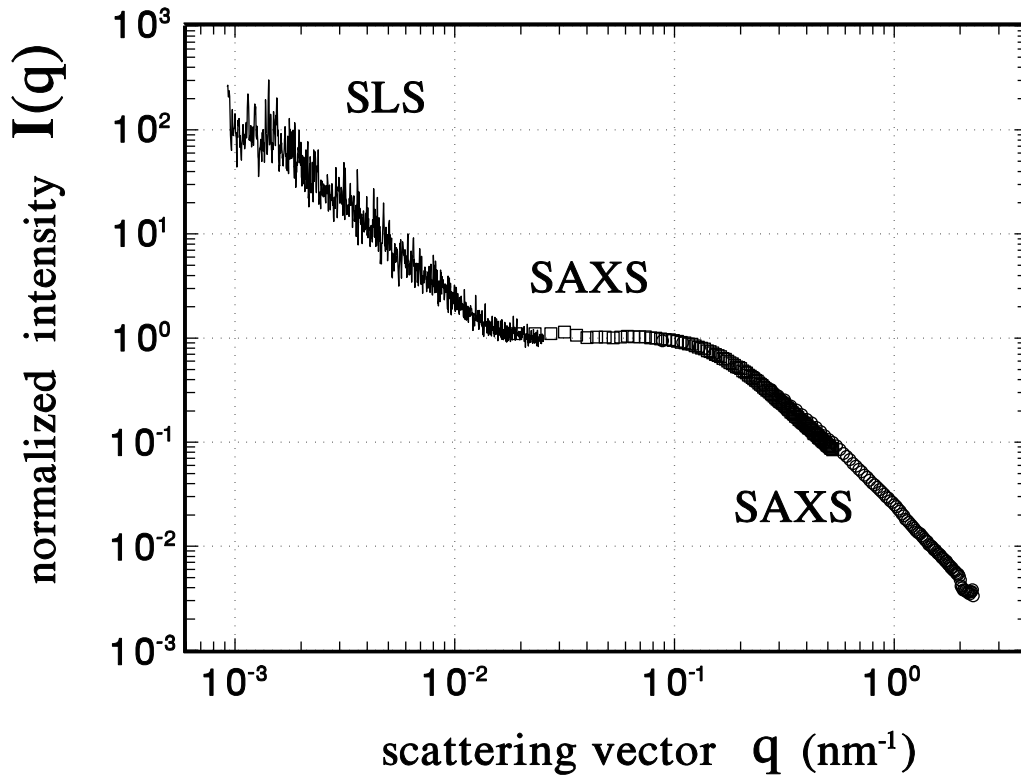


Figure 5.1: Overview of the static scattered intensity $I_s(q)$ as obtained from three static scattering experiments. The smallest q regime, between 10^{-3} nm^{-1} and 10^{-2} nm^{-1} is captured by static light-scattering (SLS). The intermediate q regime, between 10^{-2} nm^{-1} and 10^{-1} nm^{-1} , and the largest q regime, between 10^{-1} nm^{-1} and 10^0 nm^{-1} , are captured by small-angle X-ray scattering (SAXS).

accounts for the interference of radiation scattered from different discs in the colloidal structure.

5.3.1 Form factor of colloidal discs

In order to measure the form factor $\overline{F^2}(q)$ of the colloidal discs, we have performed small-angle X-ray scattering measurements on a dilute non-gelating colloidal suspension in water, with a mass fraction $\varphi_m = 0.1$ mass-percent. The results are shown in Fig. 5.2. For a thin disc the scattered field $F(q; H, R, \theta)$ is given by [70],

$$F(q; H, R, \theta) = \frac{\sin(qH \cos \theta)}{qH \cos \theta} \times \frac{2J_1(qR \sin \theta)}{qR \sin \theta}, \quad (5.2)$$

where θ is the angle between the normal to the disc plane and the scattering vector q , $2R$ is the disc diameter, $2H$ is the thickness of the disc, and J_1 is the first order Bessel

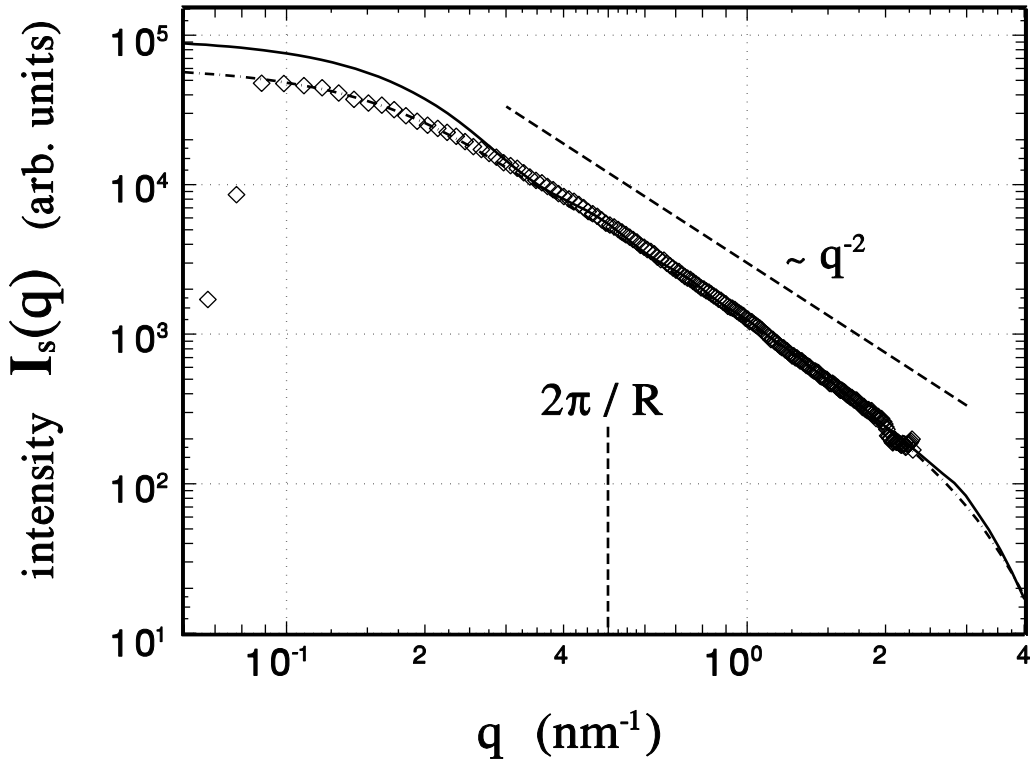


Figure 5.2: Static scattered intensity $I_s(q)$ (diamonds) of a dilute, non-gelating suspension of colloidal discs in the range of the form factor. At large q , the intensity decays with q^{-2} (dashed line) as expected for randomly oriented thin discs. The solid curve is the form factor calculated for randomly oriented monodisperse discs with a radius $R = 12.5 \pm 0.25$ nm and a thickness $2H = 1.0 \pm 0.1$ nm. The dash-dotted curve is the form factor calculated for randomly oriented discs with the same dimensions and with a Gaussian polydispersity in the radius of 4 ± 1 nm.

function. The form factor becomes,

$$\overline{F^2}(q; H, R) = \int_0^{\pi/2} |F(q; H, R, \theta)|^2 P(\theta) \sin \theta d\theta, \quad (5.3)$$

where $P(\theta)$ is the orientational distribution function. If the discs are randomly oriented then $P(\theta) = 1$, and the form factor decreases as q^{-2} at large q [94]. In Fig. 5.2 we show a comparison of the measured small-angle X-ray scattered intensity I_s with the form factor $\overline{F^2}(q; R, H)$. Here we assumed $P(\theta) = 1$ because the measured intensity roughly follows a q^{-2} power-law decay. From this comparison we estimate $R = 12.5 \pm 0.25$ nm and $2H = 1.0 \pm 0.1$ nm. These numbers are in good agreement with the values reported previously [3, 52, 53, 54, 55]. The comparison as shown in Fig. 5.2 confirms that the diluted suspension is a dispersion of randomly oriented

colloidal discs. In the gel phase at higher mass fraction, the same results are obtained for the form factor and the particle dimensions. The gel is therefore also a collection of randomly oriented colloidal discs.

Surprisingly, previous workers [3, 52, 53, 54, 55] have not considered the polydispersity of the particle sizes in the interpretation of their experimental results, whereas polydispersity is usually an important consideration when dealing with colloids in general [40, 95, 96]. Inhomogeneity in either the shape or size (polydispersity) of the particles leads to an ambiguity in the interpretation of the angular dependence of the static scattered intensity. Since the measured form factor is a (distribution of size) weighed average over the form factors of all the scattering particles, it is hardly possible to fully characterise polydisperse samples with the limited amount of information available. However, if the shapes of the particles is uniform and known, certain features of the distribution of size can be assessed. In the case of laponite, the crystal structure of the colloidal disc in the direction normal to the face is well-known and comparable to mica and other montmorillonites [17]. Therefore the colloidal discs have a well defined thickness of $2H = 1.0$ nm without variance, which was checked by us by wide-angle X-ray scattering measurements. The disc radius, however, is determined by the complicated process of synthesis of the mineral mix and the raw mechanical process of milling [17]. Hence a substantial polydispersity in the disc radius is to be expected. We have calculated the effect of a polydispersity in the radius by convoluting Eq. 5.3 with a normalised Gaussian distribution,

$$\Psi(\mathcal{R}) = (\Delta\sqrt{\pi})^{-1} \exp[-(\mathcal{R} - R)/\Delta]^2) , \quad (5.4)$$

where $\mathcal{R}$ is the radius and the standard deviation Δ is the polydispersity parameter. The best fit with $R = 12.5 \pm 0.25$ nm and $\Delta = 4 \pm 1$ nm, as shown in Fig. 5.2, agrees much better with the experimental data than the previous monodisperse models. Estimates of the error in the average radius R and the polydispersity Δ can be made separately. The model of the form factor (Eq. 5.3) is very sensitive to the average radius R , especially at large q values, hence the precise value of R . The polydispersity parameter Δ has only a moderate influence on the calculated form factor, mainly at small q values. Therefore the Δ parameter is less accurately constrained

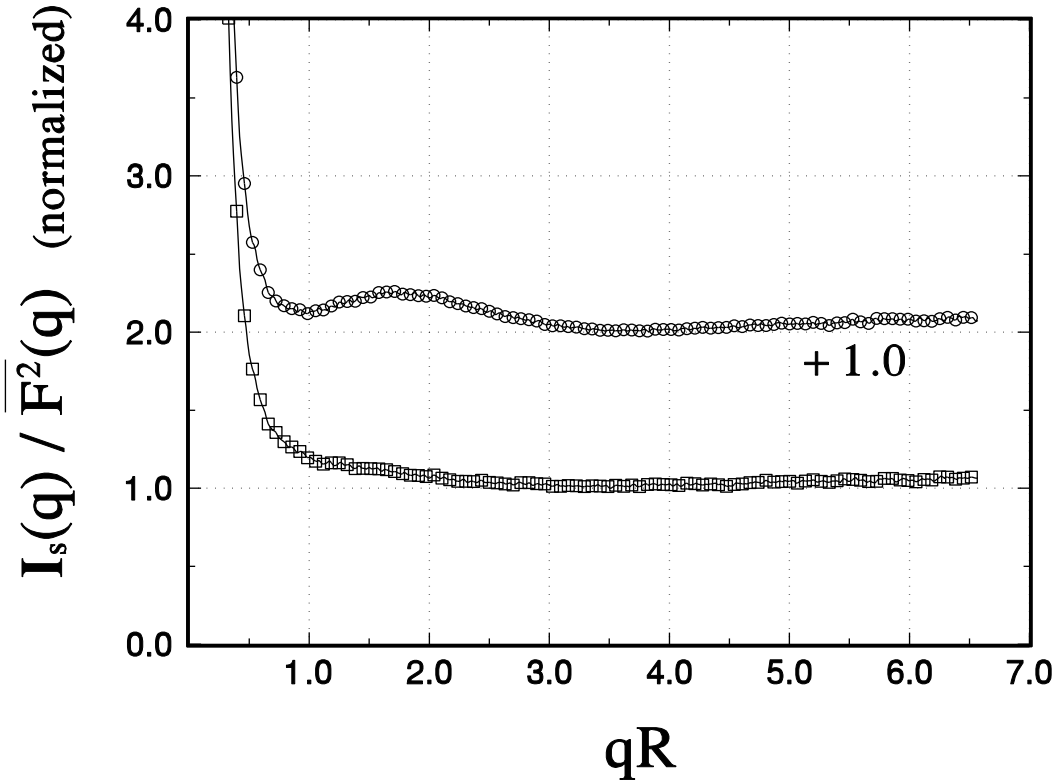


Figure 5.3: Static structure factors of a sol (circles) and a gel (squares) in the intermediate regime in qR . The measured intensity patterns have been divided by the polydisperse form factor and scaled to unity at the minimum. The upper curve has been shifted for clarity. The sol-phase shows a peak that corresponds to nearest-neighbour correlations, which is absent in the gel phase. Both curves show a strongly increased structure factor at small qR .

5.3.2 Static structure factor

The static structure factor $S(q)$ is depicted in Fig. 5.3. The static structure factor is obtained from Eq. 5.1, by dividing the measured scattered intensity by the polydisperse form factor. In Fig. 5.3 we take a closer look at the intermediate regime in qR . The upper curve was measured on the low-viscosity sol right after sample preparation. A peak around $qR = 2.0$ is visible, suggesting an average interparticle distance of $a = 2\pi/q = 39$ nm. This length scale is rather close to the effective distance of $a_{\text{eff}} = (1/\rho)^{1/3} = 34$ nm between the centers of hard-spheres in a random structure. Here $\rho = 2.45 \times 10^{22} \text{ m}^{-3}$ is the number density of colloidal particles corresponding to the mass fraction $\varphi_m = 3.0$ mass-percent. Although nearest-neighbour correlations exist, the approach by a random structure is valid because these correlations are rather

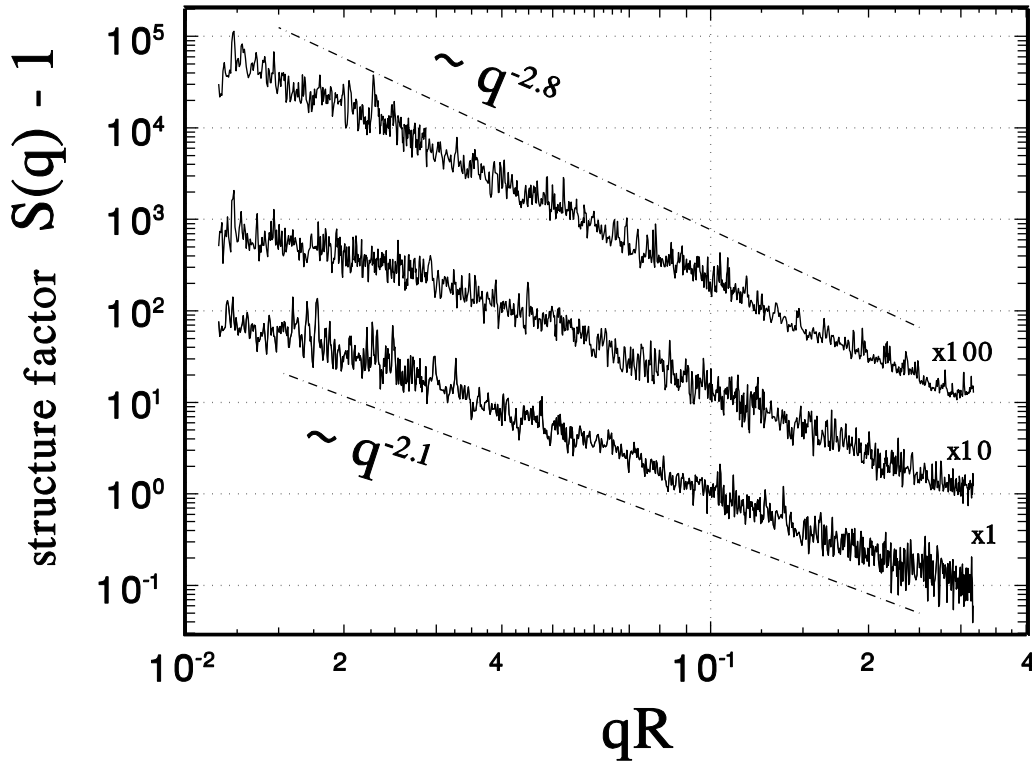


Figure 5.4: Time series of the static structure factor $S(q) - 1$ versus qR as measured on the colloidal suspension of discs with a mass fraction $\varphi_m = 3.0$ mass-percent in water, depicted in the following order (from top to bottom); $T = 2.5$ hours, 98 hours, and 1.5 years. The dash-dotted lines denote an algebraic dependence with qR characterised by an exponent d , that decays from $d = 2.83(\pm 0.01)$ at $T = 2.5$ hours to $d = 2.09(\pm 0.01)$ at $T = 1.5$ years.

small. Thus the structure factor of the sol in the intermediate regime reminds of a low-density hard-sphere liquid. The lower curve in Fig. 5.3 was measured on a gel in which no significant time-dependent changes were observed anymore. Clearly no such nearest-neighbour particle correlations exist in the gel.

With the static light-scattering setup we can probe the static structure factor in the regime $qR = 10^{-2} - 3 \times 10^{-1}$. In this regime the scattered intensity is proportional to the static structure factor because the form factor equals unity. The static light-scattering results are shown in Fig. 5.4 at different stages of the transition from sol to gel. We have studied the suspension of colloidal discs in water with a mass fraction $\varphi_m = 3.0$ mass-percent, a fraction at which a gel is formed in 100 hours [1]. The measured scattered intensity shows an algebraic decay with qR at the larger qR values. This is typical for a structure with self-similar, or fractal, properties [97] as we will

now show. The self-similarity reflects the quantity that the structure looks the same on any length scale, i.e., there is no characteristic size. A quantitative description of the density distribution in real space is given by the van-Hove distribution function $G(r)$,

$$G(r) \equiv \langle \rho(0) \rho(r) \rangle_s / \langle \rho \rangle_s^2, \quad (5.5)$$

where $\rho(r)$ is a number density function, $\langle \rho \rangle_s$ is the average number density N/V in the sample volume V , and $\langle \cdots \rangle_s$ denotes an average over the sample. The van-Hove function is related to the radial distribution function $g(r)$ by,

$$G(r) = \delta(r) + \langle \rho \rangle_s g(r), \quad (5.6)$$

where the delta-function $\delta(r)$ is the “self-correlation” function. The radial distribution function expresses the probability density of finding a particle at a distance r away from a particle at an arbitrary position in space. For a self-similar or fractal structure the definition of $G(r)$ must be treated with some caution to avoid edge effects. In general, the fractal description applies only in an intermediate range for which both inequalities $qR \ll 1$ and $q\xi \gg 1$ are fulfilled. Here ξ is a correlation length, which can in principle be infinite but which is in practice limited by the sample dimensions. Scale invariance is introduced by a particular form of $G(r)$, which is insensitive to a magnification factor m . We can formally write,

$$G(mr) = m^{-\eta} G(r). \quad (5.7)$$

Taking $m = 1/r$ results in,

$$G(r) = G(1) / r^\eta. \quad (5.8)$$

The mass within a fractal structure is related to $G(r)$ via,

$$M(\xi) = \int_0^\xi d^3r G(r) \propto \int_0^\xi r^2 G(r) dr \propto \xi^{3-\eta}, \quad (5.9)$$

where ξ is the radius of the sphere inside the fractal structure. By definition the mass within a fractal structure $M(\xi) \propto \xi^{d_f}$. Then $\eta = 3 - d_f$ and,

$$G(r) = G(1) r^{d_f-3}. \quad (5.10)$$

The static structure factor is related to the particle pair-correlation function by,

$$S(\vec{q}) \equiv \int d^3x (G(x) - \langle \rho \rangle_s^2) \exp(-i\vec{q} \cdot \vec{x}). \quad (5.11)$$

In an isotropic system Eq. 5.11 takes the form,

$$S(q) = 1 + 4\pi \langle \rho \rangle_s \int dr |g(r) - 1| r^2 \frac{\sin(qr)}{qr} . \quad (5.12)$$

For an infinite fractal structure one finds [98], $\langle \rho \rangle |g(r) - 1| \propto r^{d_f-3}$ and,

$$S(q) - 1 \propto 4\pi q^{-d_f} \int_0^\infty (qr)^{d_f-3} \frac{\sin(qr)}{qr} (qr)^2 d(qr) . \quad (5.13)$$

With some algebra [98] it follows that,

$$S(q) - 1 \propto Aq^{-d_f} , \quad (5.14)$$

where A is a constant. In general this description applies only in an intermediate range for which both inequalities $qR \ll 1$ and $q\xi \gg 1$ are fulfilled. Here ξ is a correlation length of the colloidal structure, which can in principle be infinite but which is in practice limited by the sample container dimensions. Equation 5.14 predicts that with increasing q the static structure factor decays towards a plateau value, which is shown in Fig. 5.1. The intensity curves measured along the gelation process started roughly at the same plateau value A . Therefore we have normalised the measured intensity to A and subtracted unity. Matching Eq. 5.14 to the resulting scattered intensity reveals the existence of a power-law decay over the experimental qR range accessible by SLS, as shown in Fig. 5.4. At $T = 2.5$ hours the exponent $d = 2.8$. Then, as the gelation proceeds evolves we see after 12 hours that the exponent has decreased to $d = 2.2$. In later stages the static structure factor hardly changes and the exponent seems to converge to a value of 2.1. Measurements on a year old gel, where the exponent indeed equals 2.1, support this finding.

We have seen that the large length-scale structure of the sol is observed to be the similar in the gel. Therefore the sol is not comparable to a simple liquid but can be considered a low-viscosity precursor of the elastic gel.

5.3.3 Time-dependent processes

The viscosity of the colloidal gels can be tremendously reduced by shear forces. Shear measurements by Willenbacher [6] reveal the possibility of preparing a low-viscosity initial state of the laponite suspension in a reproducible manner. Phenomenologically it is then observed that the immobile arrangement of colloidal discs, macroscopically observed as the gel, is always restored. The question is now how this final state is reached, and whether or not this is a stable state of the suspension. Therefore we have

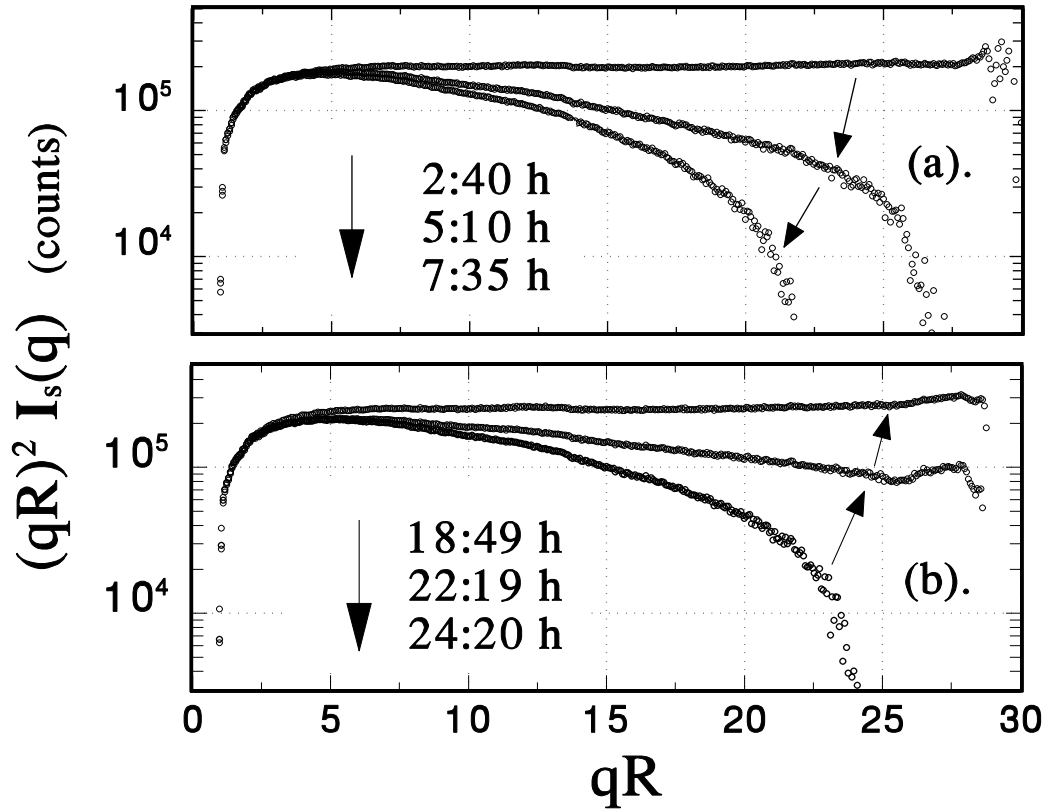


Figure 5.5: Typical series of small-angle X-ray scattering intensity patterns (obtained at Daresbury) after inserting the suspension into the sample container. In this Guinier plot the original intensity patterns have been multiplied with $(qR)^2$. (a). At first the curve tends to decrease in time at the larger qR -values. (b). After 10 hours this process is reversed and the original signal is obtained after 40 hours. The tendency observed is independent of the initial state before shear (sol or gel).

performed small-angle X-ray scattering measurements while this restoring process was taking place. We inserted the colloidal suspensions with great force in between the narrowly spaced container windows (aspect ratio > 100). After application of the resulting shear forces to the suspensions, we have observed the presence of relaxation processes, on which we will report in the next two sections.

5.3.3.1 Large qR -regime ; form factor

In Fig. 5.5 we show a typical series of small-angle X-ray scattering intensity patterns obtained at Daresbury for the colloidal disc suspension in a kapton windowed container. In this Guinier plot we have rescaled the vertical axis with $(qR)^2$, because the

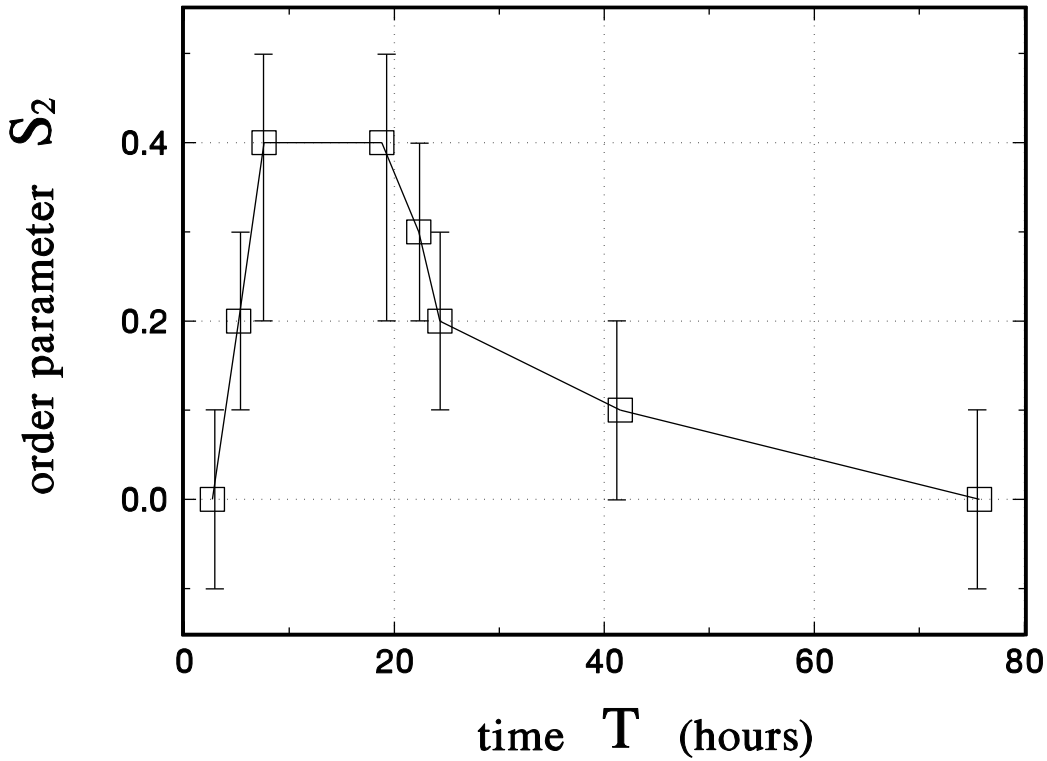


Figure 5.6: Time dependence of the nematic order parameter S_2 characterising the distribution function of the disc orientation, fitted to the data of Fig. 5.5. The positive value of S_2 indicates a preferential ordering of the colloidal discs as facing the container walls.

form factor of randomly oriented discs decays as q^{-2} . In such a plot deviations from such a behaviour are readily seen. Right after inserting the colloidal sample we observe that $(qR)^2 \overline{F^2}(q)$ is a constant. The starting situation is indeed a collection of randomly oriented discs, as expected for a sol. Within a few hours, however, the form factor decreases faster than $(qR)^2$. This suggests that the discs are preferentially oriented with their faces perpendicular to the X-ray beam (See below). After 8 hours this process is reversed, and after 40 hours an almost constant signal is measured indicating that the gel state also has a random orientation of the discs. The whole process occurred on the same time scale regardless of whether the suspension was inserted into the sample container as a sol or as a gel. Thus, after the application of shear the suspension has lost all memory of its history. In addition, we find no differences between using kapton or mica as window materials, although these materials are quite different. Mica closely resembles the chemical composition of the clay particles. Kapton is a plastic and quickly acquires a static electric charge when handled.

We interpret our data in terms of a preferential disc orientation as a result of flow of the suspension under shear forces. The integration of Eq. 5.3 is performed over a well-defined orientational distribution function $P(\theta)$ [46]. Nematic ordering is characterised by the nematic order parameter S_2 according to,

$$P(\theta) = 1 + \frac{5}{4} S_2 [3 \cos^2 \theta - 1] . \quad (5.15)$$

We will limit the study to the nematic part because the scattered intensity I_s measured with the one-dimensional detector at Daresbury can not give reliable information on the higher order orientational terms. In Fig. 5.6 we show the time dependence of the nematic order parameter S_2 , obtained by comparing the results of the integration with the results as shown in Fig. 5.5. First S_2 tends to increase. This indicates a preferential ordering of the colloidal discs parallel to q , i.e., orthogonal to the incident X-ray beam. As time proceeds the order parameter decreases and reaches zero again, i.e., the isotropic distribution is restored. The error bars on S_2 in Fig. 5.6 are mainly determined by background corrections, which become increasingly important at the large qR .

5.3.3.2 Intermediate qR-regime ; structure factor

The small-angle X-ray scattering intensity patterns obtained at the ESRF are recorded with a two-dimensional detector. From the recorded patterns we do not only obtain information as a function of the scattering vector q but also as a function of the azimuthal angle α . The azimuthal angle α is defined in the detector plane as the angle between a unit vector in this $y - z$ plane and the z -axis. In the experimental geometry, the y and z -axis are chosen as the horizontal and vertical axis in the detector plane, respectively, and the x -axis is parallel to the incoming X-ray beam. Thus one has the opportunity to investigate the presence of ordering effects, both positional and orientational, in the colloidal structure. Orientational ordering will be reflected as an anisotropy in α in the scattered intensity pattern in the two-dimensional plane of detection.

In Fig. 5.7 we show the scattered intensity pattern right after injection of the colloidal suspension into the sample container. In order to analyse the variations in detail, we have divided all measured intensity patterns by the last pattern measured. This last pattern is independent of the azimuthal angle α and was recorded after a few days [99] when no changes were observed any longer. After integration over the azimuthal angle α , the scattered intensity pattern exactly fits the form factor measured on the dilute sample discussed above (except for the region of $qR < 5 \cdot 10^{-2}$ where the intensity

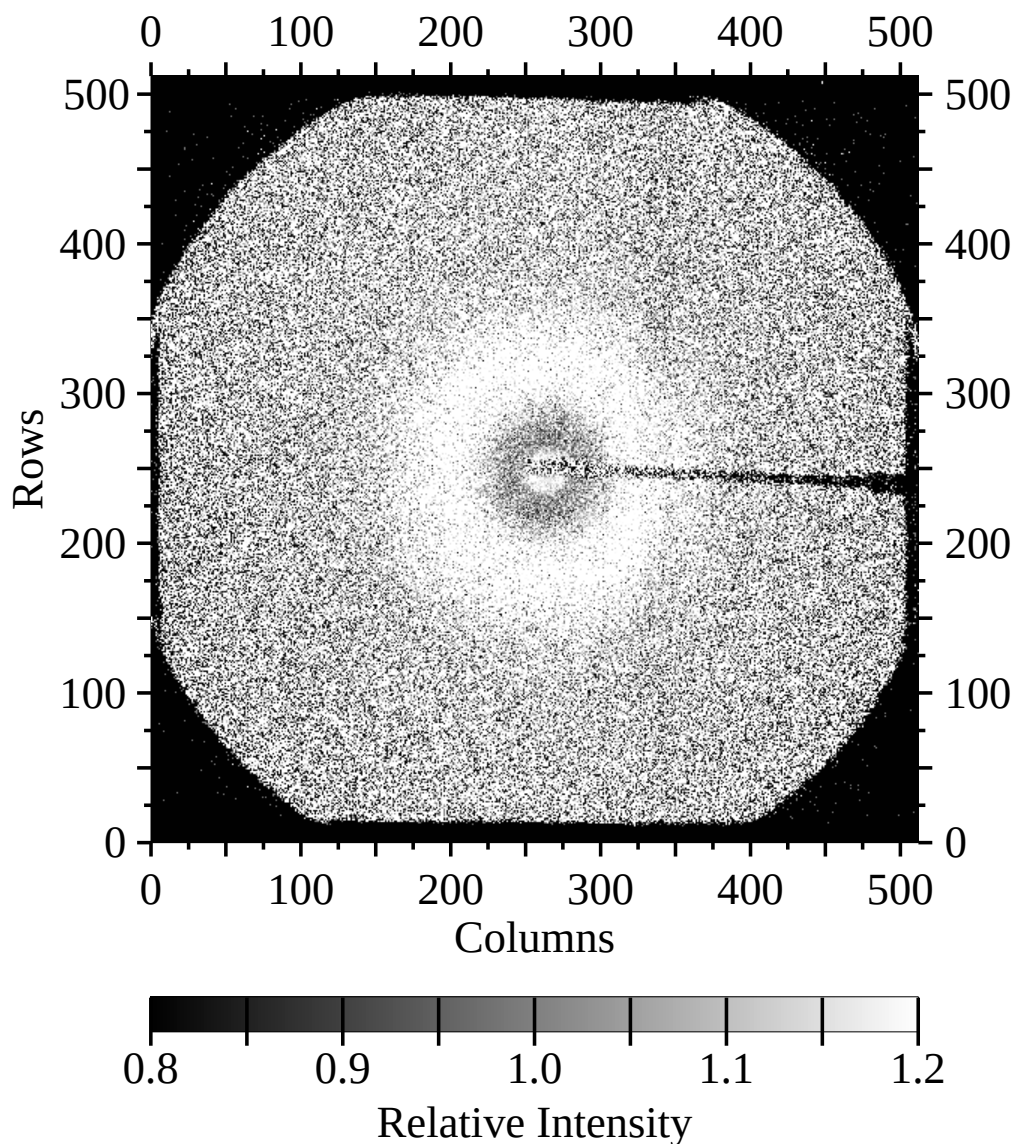


Figure 5.7: Two-dimensional small-angle X-ray scattering pattern right after inserting the gel-state suspension into the sample container. On the horizontal and vertical axis the number of the detector channel is depicted. The shadow of the beam stop is seen as the black stripe from the right to the center of the plot. A prominent feature is the presence of a ring, caused by nearest-neighbour correlations. The ring and other features are observed to have an almost perfect rotational symmetry and are independent of the sample orientation with respect to the incident X-ray beam.

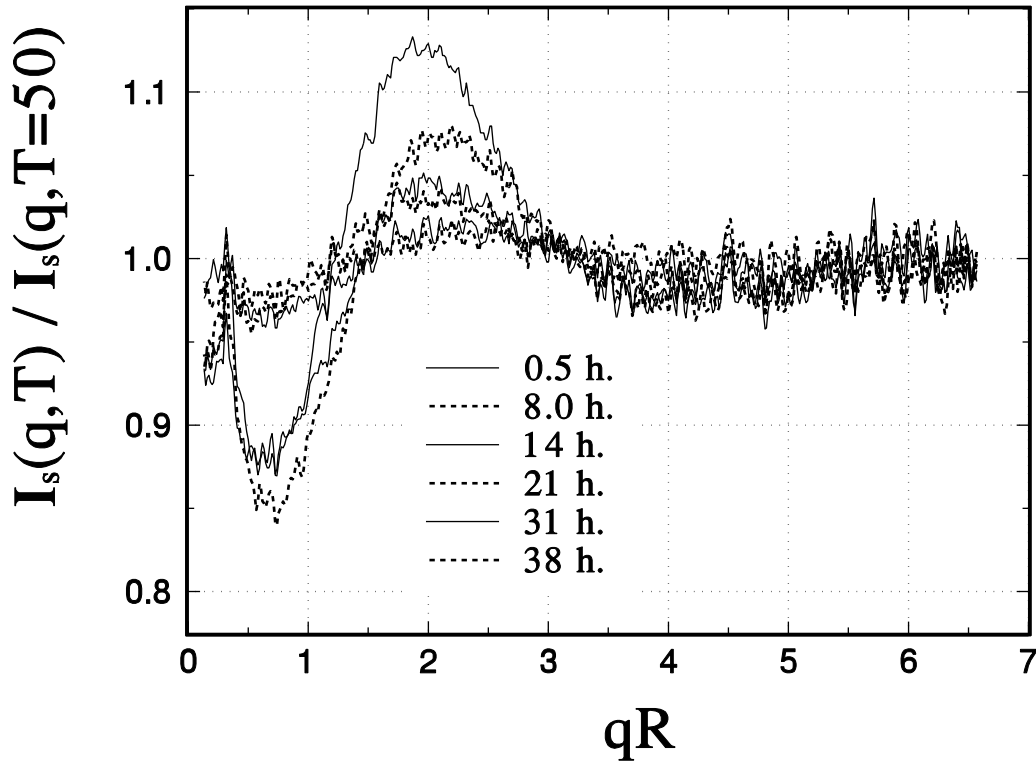


Figure 5.8: Typical series of integrated (one-dimensional) small-angle X-ray scattering intensity patterns when divided by the stationary pattern measured after 50 hours. Specifically at the region of the plateau of Fig. 5.1 the relative signal shows significant changes in the first few hours after inserting the suspension. The peak at $qR = 2.0$ corresponds to the ring as shown in Fig. 5.7. Note the drastic decrease in depth of the crest at $qR = 0.5$ between $T = 14$ hours and $T = 21$ hours.

increases with a power-law as observed in the light-scattering data). The prominent feature in Fig. 5.7 is the presence of a ring, corresponding to the average interparticle separation (cf. Fig. 5.3). Integrating these two-dimensional scattered intensity patterns over the azimuthal angle α yields the familiar one-dimensional structure factor as shown in Fig. 5.8. At early times the results depicted in Fig. 5.8 has a form that one expects for a low-density hard-sphere liquid or a dense gas. As time progresses the first peak shifts to somewhat higher values, broadens, and eventually disappears. The variance in the average nearest-neighbour distance increases until the distribution merges with the low-wavevector distribution.

At first sight the two-dimensional pattern depicted in Fig. 5.7 appears to be independent of the azimuthal angle α . However, a plot of the measured intensity on the

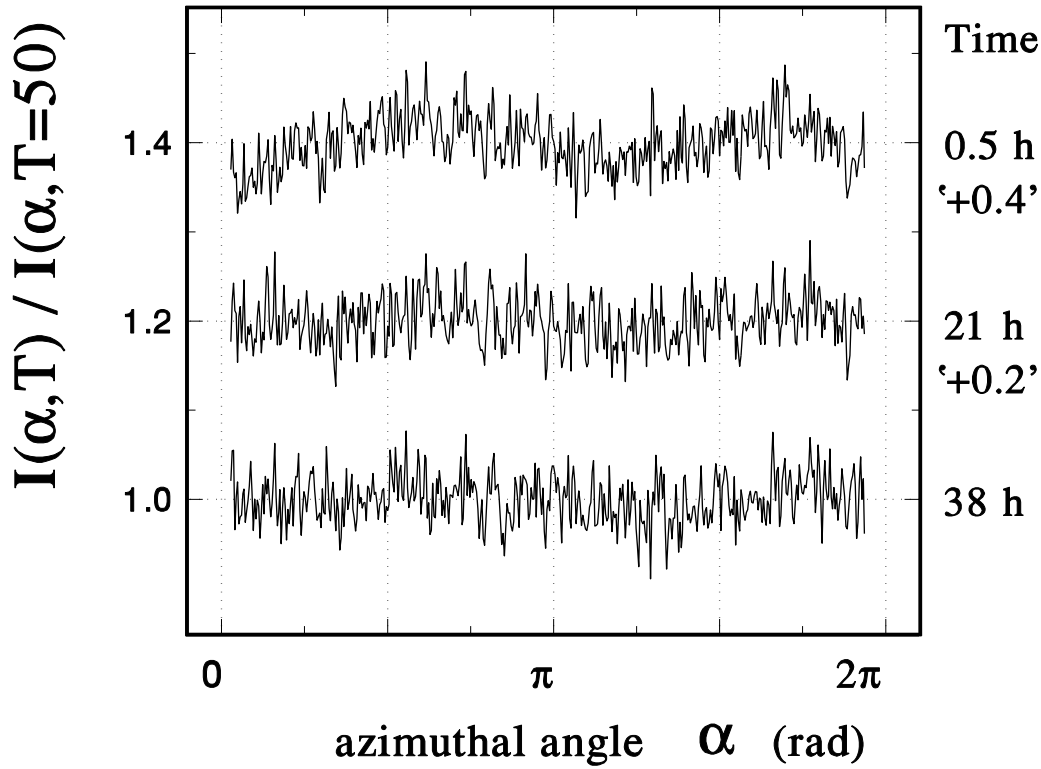


Figure 5.9: Static scattered intensity $I_s(\alpha, T)$ as a function of the azimuthal angle α extracted from the data as shown in Fig. 5.7. The data have been averaged over a range $qR \in [1.56, 2.19]$ and reflect the behaviour of $I_s(\alpha, T)$ at the location of the ring-shaped feature as seen in Fig. 5.7 at different times T . In time the angular variations are observed to gradually decay.

ring as a function of α reveal a slight sinusoidal variation. In Fig. 5.9 we show the measured intensity pattern on the ring as a function of the azimuthal angle α at several moments in time after sample preparation. Again the scattered intensity patterns have been divided by the pattern measured after a few days. The small variation observed gradually decays in time. The signal to noise ratio is such that a quantitative determination of an order parameter cannot be reliably made. The observed sinusoidal variation is independent of sample orientation with respect to the incident X-ray beam, and the state of the suspension before insertion.

In order to get an idea of the amount of orientational order responsible for the variations shown in Fig. 5.9, we have performed experiments on a completely orientationally ordered sample. Such a sample was prepared by slowly drying a gel sample which was contained in a long cylindrical stock tube, until a hard transparent dime of a few millimetre thickness formed. For this sample we have recorded two-dimensional

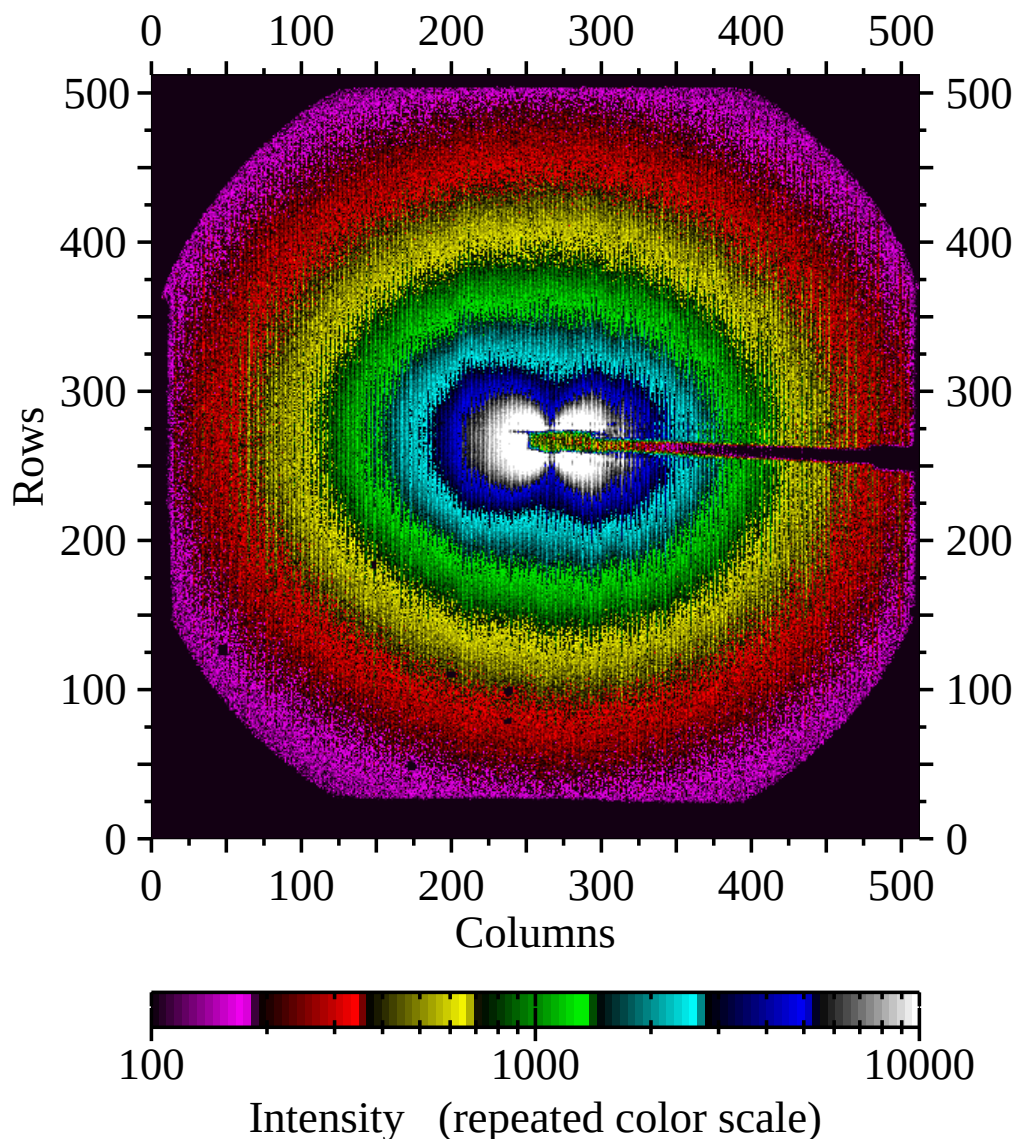


Figure 5.10: Typical two-dimensional small-angle X-ray scattering pattern recorded on a dried out gel, with the normal to the face of the dime under 45° orientation with respect to the incoming X-ray beam. At 0° orientation, the intensity $I_s(q)$ falls off exponentially with q in every direction. The use of a repeated colour scale on this logarithmic plot then yields a set of perfect circles. Changing the angle of orientation leads to a drastic deformation of the rings to the depicted ellipsoids.

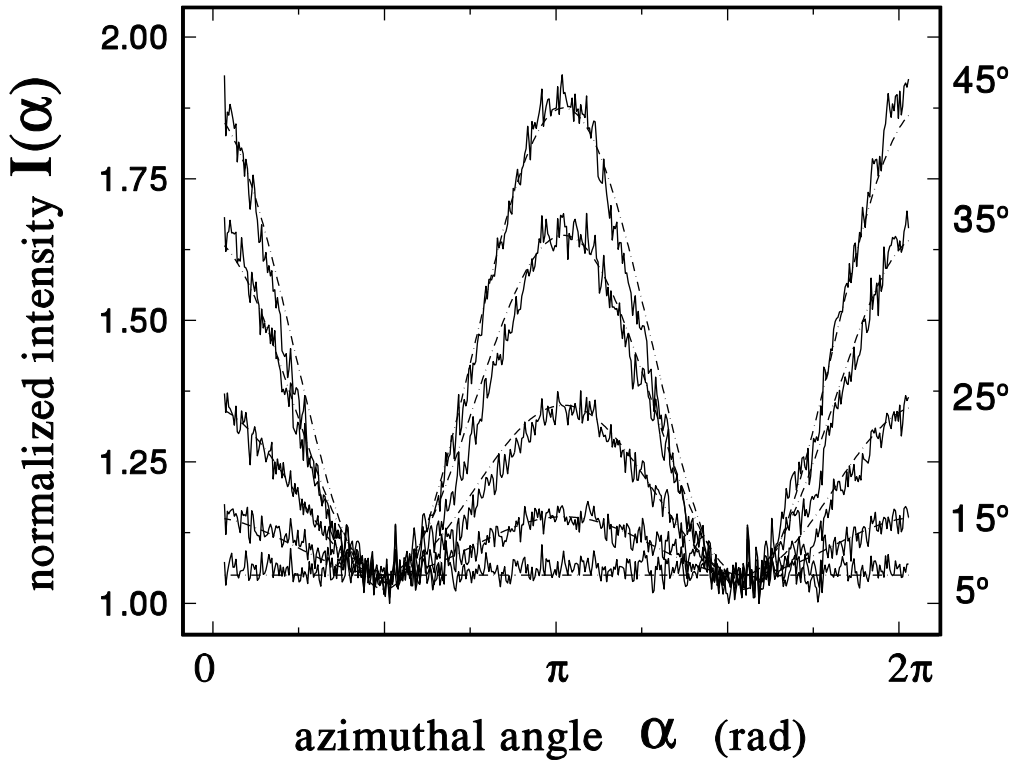


Figure 5.11: Static scattered intensity $I_s(\alpha, \xi)$ as a function of the azimuthal angle α of the data as shown in Fig. 5.10 for different orientation of the dime denoted by the angle ξ . The data have been averaged over a range in $q \in [1.56, 2.19]$ centred around the position of the peak observed in Fig. 5.8. All curves can be perfectly matched to a simple cosine function (dash-dotted curves).

small-angle X-ray scattering intensity patterns with the normal to the face of the dime under various angles with respect to the incoming X-ray beam. At an angle of 0° a two-dimensional pattern is observed that is independent of the azimuthal angle α . By changing the angle between the normal and the incoming beam to 45° , the measured pattern as shown in Fig. 5.10 is a text-book example of an orientationally ordered sample [46, 100]. In Fig. 5.11 we plot the scattered intensity as a function of the azimuthal angle. The data have been averaged over a small range in q centred around the position of the peak observed in Fig. 5.8. The results as shown in Fig. 5.11 reflect a perfectly aligned nematic arrangement of discs with long-range orientational order. The dehydrated sample consists of stacked layers of colloidal discs. In these layers the discs are translationally disordered with their surface normal directed perpendicular to the layer stacking. Comparing the results of the ordered dehydrated sample with the gelating suspension in Figs. 5.11 and 5.9, it is obvious that the gelating suspension shows a

trifle amount of liquid-crystalline order limited to a short-range. In the static structure factor at intermediate qR we have not observed any signature of persistent long-range order. At large qR we have seen strong effects in the form factor, indicating that single discs are indeed oriented. Taking these considerations into account we conclude that the colloidal suspension of discs has not entered a liquid-crystalline state or that the isotropic-nematic phase transition has taken place.

5.4 Discussion

In this chapter we have presented static scattering experiments on the transition from a fluid-like sol to a solid-like gel of a suspension of disc-shaped charged colloidal particles. This gelation proceeds in time at constant density and temperature, and is not driven by an aggregation process. In the regime $qR < 0.5$, a characteristic algebraic wavevector dependence of the structure factor is measured right from the start of the entire gelation process. The value of the algebraic exponent $d = 2.1$ in the final gel-state corresponds to the value for the fractal dimension d_f of gels of spherical particles and polymers formed via an aggregation process [101, 102, 103]. In these gels the fractal dimension of 2.1 is considered to be the dimension of a structure formed by a diffusion (or chemically) limited aggregation process, where clusters with a characteristic density grow as a function of time. In contrast to the aggregated gels of spherical particles and polymers the gelation studied here is not an aggregation process. There is not a preferred length scale observed at any time during the gelation process. We do not observe a maximum in the structure factor, which might point to a characteristic size of a cluster that grows as the gelation proceeds. Neither do we observe a low-wavevector cut-off that defines a correlation length. If there is a correlation length it must be longer than the maximum length of 6000 nm as probed by our light-scattering measurements. This length corresponds to at least 170 times the average interparticle distance, or 240 times the average radius of the disc. At first sight this result contradicts the results of a similar study by Pignon *et al* [4], who have observed a characteristic correlation length in a gel of colloidal discs. However, Pignon *et al* studied samples with mass fractions so high that the gelation times are of the order of the time necessary to disperse the discs. When the gelation and dispersion processes overlap in time, undissolved stacks of colloidal discs may be present, giving rise to the observed correlation length.

The static structure encountered in the final gel-state corresponds rather to the

class of fractal materials described by Maynard [104]. Like aerogels [105], these materials are founded on hierarchical structures, in contrast to percolating networks or aggregates with filaments and dangling bonds (occupied sites that do not contribute to the structure and rigidity of the network). Following the arguments of Maynard [104] and Courtenis [105] we have calculated the spectral dimension γ of the spectral density $S(\omega) \propto \omega^{-\gamma}$ for a structure of plates with a fractal dimension $d_f = 2.1$ without any dangling bonds. An additional exponent σ is required, which relates the elasticity of the network to the density and is set to unity [104, 105]. The resulting value of $\gamma = 1.0$ is close to the value of $\gamma = 0.86$ observed by dynamic light-scattering on the laponite suspensions [1, 56]. A lower value for γ can possibly be explained by assuming a certain amount of dangling bonds and consequently a less rigid structure. Thus we find for the gel-phase a close correspondence of the dynamic and static scaling behaviour with the propositions of Ref. [104] and Ref. [105]. We may extrapolate this description to the low-viscosity sol-phase. There we have found a spectral exponent $\gamma = 0$ from wavelet analysis [56]. This is consistent with even less rigidity. In the picture sketched here we have monitored the transformation of a structure that has many dangling bonds and no rigidity at all into a structure with a low amount of dangling bonds and a high rigidity.

Since the gelation is not an aggregation process, which involves changes in the positional correlations, one may still wonder if aggregation of orientationally correlated clusters accompanies the gelation process. Measurement of the form factor after applying shear to the suspensions reveal an initially random orientation of the discs. Within a few hours, however, an orientational ordering of the discs is observed. After reaching a maximum in the order parameter S_2 , the suspensions reveal a restoring of the random orientation of the colloidal discs until the highly viscous, elastic gel-state is reached. At first sight it seems surprising that the colloidal discs tend to order orientationally before returning to a state with random orientations. However, when squeezing a gel in between two plates, Pignon *et al* have observed thin low-viscosity boundary layers through which the bulk of the gel is sliding through [106]. In our case, a thin low-viscosity boundary layer with presumably high liquid crystalline order exists close to the walls of the sample cell, surrounding an elastic gel in the middle. The observed growth of nematic order is induced by particle interactions from the boundary layer inwards. As a result the liquid-crystalline ordered layer becomes thicker as time progresses. However, local reorientation driven by thermal motion breaks down the orientational order and eventually leads to the observed random gel-state. This conjecture explains the behaviour of the order parameter S_2 as a function of time.

Nowhere along the gelation, however, did we observe the presence of long-range orientational correlations. If there is a correlation length associated with the orientational order, this length only extends to the nearest neighbours and in time becomes shorter, as the measurements of the structure factor in Figs. 5.8 and 5.9 indicate. In Fig. 5.8 we observe a structure factor one would expect for a normal liquid. The first peak at $qR = 2.0$ corresponds to an interparticle separation of 39 nm, substantially larger than the average diameter of the discs of 25 nm. One would expect this structure factor for a hard-sphere fluid consisting of spheres with a diameter of 34 nm. The volume of this sphere is roughly equal to the volume cut out by the colloidal disc taking into account an estimate of the Debye screening length of an orientationally averaged screened Coulomb potential [15]. In this regime of qR we look at mutual orientation ordering. The measurements reveal that the T-shaped configuration, the favoured unit in the suggested “house of cards” structure for the gel, is absent. This configuration of discs would show up in the structure factor at shorter length scales [58]. Dijkstra *et al* [58] showed that the quadrupolar character of the screened Coulomb potential is essential in the formation of the gel phase. In their Monte Carlo study they used a collection of infinitely thin discs with a point quadrupole moment. The model carries the essential features of the interparticle interaction of the real colloidal disc system. Without the quadrupolar interaction the model of discs exhibits the isotropic to nematic phase transition according to the Onsager criterion [47, 49, 50]. With the quadrupolar interaction turned on they show that the model-collection of discs undergoes a transition from a low density phase, where the discs assemble into elongated chain-like clusters, to a rigid gel-phase at higher densities. The gel exhibits a nearly incompressible network structure similar to the house of cards structure thought to be typical of clay gels. At these high densities the quadrupolar interaction favours edge-to-face pair configurations (T-shaped units) that counteracts the parallel alignment of bare hard discs.

In the real colloidal disc system gel formation occurs at lower mass fractions (or related volume fractions) than studied by Dijkstra *et al* [58]. The measurements indicate that the formation and growth of orientational clusters is not the cause of gelation. There is no orientational order left in the gel phase. The behaviour of the form factor after applying shear to the suspensions does suggest that local reorientations are essential in the transformation of the fractal structure. We have experimentally monitored a dynamic process where a fractal structure with many dangling bonds and low elasticity transforms into a fractal structure with a low amount of dangling bonds and a high rigidity. This transition is made possible by continuous local reorientation of the

colloidal discs, which allows more and more particles to become part of the network. In time the rigidity and elasticity of the colloidal structure increases, the viscosity diverges, and the solid phase is formed in close analogy with the glass transition.

Appendix A

Formal theory of discrete wavelet transformation

A.1 Definition of the multi-resolution analysis

A multi-resolution analysis of a function f consists of a hierarchy of approximations of the function f , which are defined as averages on different scales. This scale is related to the accuracy or resolution of the approximation; the finer the scale, the better the approximation. More precisely, one has a hierarchy of subspaces of the space $L^2(C)$ of squared-integrable functions according to,

$$\cdots \subset V_{-2} \subset V_{-1} \subset V_0 \subset V_1 \subset V_2 \subset \cdots , \quad (\text{A.1})$$

such that the cross section of these subspaces contains the zero element only and addition of these subspaces forms the space $L^2(C)$ by,

$$\cap_{p \in Z} V_p = \{0\} \quad , \quad \cup_{p \in Z} V_p = L^2(C) \quad , \quad (\text{A.2})$$

where Z is the collection of integer values. The *scaling aspect* of a multi-resolution hierarchy is expressed by the condition,

$$g(x) \in V_p \Leftrightarrow g(2x) \in V_{p+1} \quad , \quad (\text{A.3})$$

for any element g of subspace V_p . A *translation invariance* is imposed by,

$$g(x) \in V_p \Leftrightarrow g(x - k) \in V_p \quad \forall k \in Z \quad . \quad (\text{A.4})$$

Finally, the zero element is defined such that an arbitrary function $g(x) \in V_p$ is invariant under addition of the zero element,

$$\exists ! \{0\} \in V_p \mid g(x) \in V_p \Leftrightarrow g(x) + \{0\} = g(x) \in V_p \quad . \quad (\text{A.5})$$

The definitions as stated in Eqs. A.1 to A.5 are the basic requirements for a linear space of functions. In order to derive a measure or norm in a linear space one generally defines an inner product according to,

$$\langle f | g \rangle \equiv \int_{-\infty}^{\infty} \overline{f(x)} g(x) dx , \quad (\text{A.6})$$

where $\overline{f}$ represents the complex conjugate of f . With Eq. A.6 the norm of an arbitrary function g is defined by,

$$\| g \|^2 \equiv \langle g | g \rangle = \int_{-\infty}^{\infty} |g(x)|^2 dx . \quad (\text{A.7})$$

The elements of the space $L^2(C)$ are functions with a finite norm, i.e., these functions are squared integrable following Eq. A.7 and hence can be normalised to unity.

To simplify computations it is convenient to define a set of functions which form an orthonormal basis for a linear space. Elements of the linear space, being functions, can then be represented as vectors on that basis. Here we set the requirement that there exists some function $\phi \in V_0$ such that the family of integer translates,

$$\phi_k(x) \equiv \phi(x - k) \quad \forall k \in Z , \quad (\text{A.8})$$

forms an orthonormal basis for the subspace V_0 according to,

$$\langle \phi_k | \phi_n \rangle = \delta_{k,n} \quad \forall k, n \in Z . \quad (\text{A.9})$$

Hence, an arbitrary function $g \in V_0$ can be expanded on the orthonormal basis according to,

$$g(x) \equiv \sum_{k \in Z} c_k \phi_k(x) , \quad (\text{A.10})$$

where,

$$c_k \equiv \langle \phi_k | g \rangle = \int_{-\infty}^{\infty} dx \overline{\phi(x - k)} g(x) . \quad (\text{A.11})$$

The measure of the function g becomes the length of the vector representing g on the orthonormal basis of the linear subspace V_0 ,

$$\| g \|^2 = \sum_{k \in Z} |c_k|^2 . \quad (\text{A.12})$$

We now require that for arbitrary integer p there exists some function $\phi_p \in V_p$ such that the family of integer translates,

$$\phi_{p,k}(x) \equiv 2^{p/2} \phi(2^p x - k) , \forall p, k \in \mathbb{Z} , \quad (\text{A.13})$$

forms an orthonormal basis for the subspace V_p . The scale or range s_p of the function $\phi_{p,k}$ is given by $s_p = 2^{-p} s_0$ where s_0 is the scale or range of the function $\phi \in V_0$. The set of functions $\phi_{p,k}$ defined by Eq. A.13 indeed constitutes an orthogonal basis for the linear space V_p because,

$$\begin{aligned} \langle \phi_{p,k}(x) | \phi_{p,n}(x) \rangle &= 2^p \int_{-\infty}^{\infty} dx \overline{\phi(2^p x - k)} \phi(2^p x - n) \\ &= \int_{-\infty}^{\infty} dy \overline{\phi(y - k)} \phi(y - n) \\ &= \delta_{k,n} \quad \forall k, n \in \mathbb{Z} , \end{aligned} \quad (\text{A.14})$$

where we have changed variables $y = 2^p x$. Equation A.14 shows that the norm of the basis vector $\phi_{p,k}$ equals the norm of the generating function ϕ . Hence the family of functions $\phi_{p,k}$ constitutes an orthonormal basis for the linear subspace V_p .

With the functions defined by Eq. A.13 we can write the multi-resolution hierarchy of approximations of a function f as vectors on orthogonal bases and establish relations between the successive approximations. For a given function f a multi-resolution approximation of scale s_p can be defined as an orthogonal projection $P_p f$ on the subspace V_p of the vector representing f according to,

$$P_p f(x) \equiv \sum_{k \in \mathbb{Z}} c_{p,k} \phi_{p,k}(x) , \quad (\text{A.15})$$

where in analogy with Eq. A.11 the coefficient,

$$c_{p,k} \equiv \langle \phi_{p,k} | f \rangle . \quad (\text{A.16})$$

When subsequently decreasing the scale parameter $p < 0$, the vector f is represented by a function $\phi_{p,k}$ of which the scale (or range) has increases a factor 2^p with respect to the generating function ϕ . Not being able to represent the fine scale details of the vector f these projections suffer from partial loss of details with respect to the original vector f . The difference in information between two successive approximations $P_{p+1} f$ and $P_p f$ is given by the orthogonal projections $Q_p f$ onto the orthogonal complement W_p of V_p . We define the orthogonal complement W_p of V_p by,

$$\begin{aligned} W_p &\perp V_p , \\ V_p \oplus W_p &= V_{p+1} , \\ Q_p f &= P_{p+1} f - P_p f . \end{aligned} \quad (\text{A.17})$$

Here we set the requirement that there exists some function $\psi_p \in W_p$ of finite norm such that the family of integer translates,

$$\psi_{p,k}(x) \equiv 2^{p/2} \psi(2^p x - k) \quad \forall p, k \in \mathbb{Z} \quad , \quad (\text{A.18})$$

forms an orthonormal basis for the space W_p . The required orthonormality of the functions $\psi_{p,k}$ is accomplished when, in analogy of Eq. A.9 for the function ϕ , the function ψ is presumed orthonormal under integer translation. However, the orthogonal complements W_p do not form a hierarchy of subspaces. Information contained in the orthogonal complement W_p , obtained by the difference between the projections $P_{p+1} f$ and $P_p f$, is never found in the orthogonal complement W_{p-1} . Therefore the spaces W_p are mutually orthogonal and generate the space $L^2(C)$ only by addition,

$$\begin{aligned} W_p &\perp W_{p'} \quad p \neq p' \quad , \\ \bigoplus_{p \in \mathbb{Z}} W_p &= L^2(C) \quad . \end{aligned} \quad (\text{A.19})$$

For this purpose the basis functions $\psi_{p,k}$ must also be orthonormal at different scale,

$$\langle \psi_{p,k} | \psi_{m,n} \rangle = \delta_{p,m} \delta_{k,n} \quad . \quad (\text{A.20})$$

At this point it suffices to say that the functions $\phi_{p,k}$ and $\psi_{m,n}$ are scaled and integer translated versions of the generating functions ϕ (scaling) and ψ (analysing), respectively. The required orthonormality of integer translates defines the first of a set of conditions which the generating functions have to fulfil. Additional requirements for the generating functions will limit the available choice of functions to finite-sized wave-like functions, called wavelet functions or wavelets. In Sec. A.3 we present the Daubechies wavelets and show some examples of these remarkable functions. Next we discuss the multi-resolution analysis when applied to discrete sets of numbers instead of functions.

A.2 Mallatian pyramid algorithm

Based on the multi-resolution analysis of functions as treated in the previous section, Mallat developed the Mallatian pyramid algorithm for sets of discrete numbers [61]. The idea behind the Mallatian pyramid is to define a hierarchy of successive approximations of an original set of discrete numbers. These approximations are defined as averages on coarser scales. First we write the original set of discrete numbers $I^{(0)}$ as a

vector $\mathbf{F}_0$ according to,

$$\mathbf{F}_0 = \sum_n I_n^{(0)} \phi_{0,n} , \quad (\text{A.21})$$

where the function $\phi_{p,k}$ is given by Eq. A.13. The vector $\mathbf{F}_0$ can be decomposed into an approximation $\mathbf{F}_{-1}$ on a twice as large scale and a vector $\mathbf{D}_{-1}$ containing the information which is lost as a result of the increase of scale. Each of these vectors can be developed on an orthogonal basis of scaling and analysing functions according to,

$$\mathbf{F}_0 = \mathbf{F}_{-1} + \mathbf{D}_{-1} , \quad (\text{A.22})$$

$$\mathbf{F}_{-1} \equiv \sum_k I_k^{(1)} \phi_{-1,k} , \quad (\text{A.23})$$

$$\mathbf{D}_{-1} \equiv \sum_k d_k^{(1)} \psi_{-1,k} , \quad (\text{A.24})$$

where the function $\psi_{p,k}$ is given by Eq. A.18. With the definition of the inner product Eq. A.6 and the orthonormality relations Eqs. A.14 and A.20, we can find from the foregoing Eqs. A.22, A.23, and A.24,

$$I_k^{(1)} = \langle \phi_{-1,k} | f_0 \rangle = \sum_n I_n^{(0)} \langle \phi_{-1,k} | \phi_{0,n} \rangle \equiv \sum_n I_n^{(0)} w_{n-2k} , \quad (\text{A.25})$$

$$d_k^{(1)} = \langle \psi_{-1,k} | f_0 \rangle = \sum_n I_n^{(0)} \langle \psi_{-1,k} | \phi_{0,n} \rangle \equiv \sum_n I_n^{(0)} g_{n-2k} . \quad (\text{A.26})$$

Generalising Eq. A.25 defines the Mallatian pyramid algorithm by which successive approximations at coarsening scales of the original discrete set of numbers can be obtained,

$$I_k^{(p+1)} = \sum_n I_n^{(p)} w_{n-2k} . \quad (\text{A.27})$$

Generalising Eq. A.26 defines the algorithm by which the loss of information between successive approximations can be found,

$$d_k^{(p)} = \sum_n I_n^{(p-1)} g_{n-2k} . \quad (\text{A.28})$$

Furthermore, we have defined the filter coefficients w_{n-2k} and g_{n-k} by the overlap integrals,

$$w_{n-2k} = \langle \phi_{-1,k} | \phi_{0,n} \rangle = \int_{-\infty}^{\infty} 2^{-1/2} \overline{\phi(2^{-1}x - k)} \phi(x - n) dx , \quad (\text{A.29})$$

$$g_{n-k} = \langle \psi_{-1,k} | \phi_{0,n} \rangle = \int_{-\infty}^{\infty} 2^{-1/2} \overline{\psi(2^{-1}x - k)} \phi(x - n) dx . \quad (\text{A.30})$$

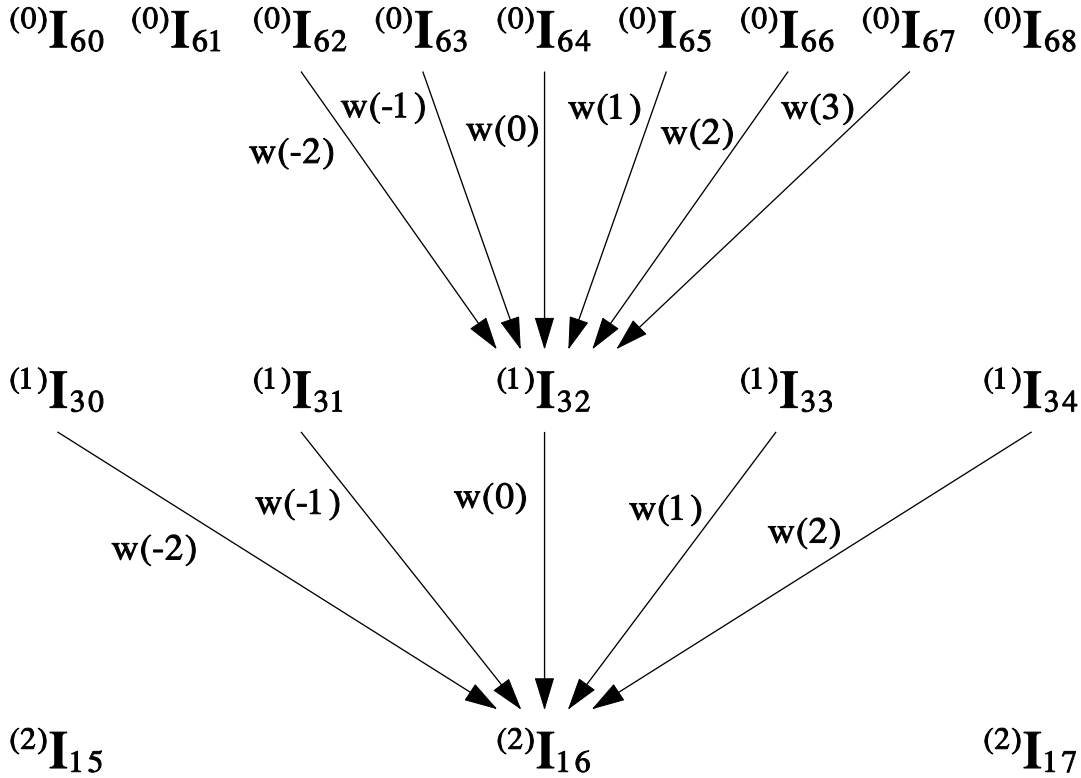


Figure A.1: Schematic representation of the Mallatian pyramid algorithm as formulated in Eq. A.27. In this representation we assume that six filter coefficients are different from zero. Note the drastic reduction of the number of discrete points after each successive transformation.

In Fig. A.1 we show a schematic representation of the transformation as formulated in Eq. A.27. The scale s_p accompanying the approximation $I^{(p)}$ is given by $s_p = 2^p s_0$ where the scale s_0 is the resolution of the set $I^{(0)}$. Equations A.27 and A.28 both consist of a convolution of the discrete set of numbers $I^{(p)}$ with the set of averaging coefficients w_j and g_j , respectively. Moreover, Eq. A.27 performs a decimation of the number of discrete points contained by the next approximation by a factor 2. In this convenient scheme the operations Eqs. A.27 and A.28 are both acting on the original set f_0 according to,

$$I^{(p+1)} = W I^{(p)} \quad , \quad d^{(p+1)} = G I^{(p)} \quad , \quad (\text{A.31})$$

where W and G are matrix-operators defined by Eq. A.27 and Eq. A.28. In Fig. A.2(a) we show a schematic representation of the transformations as formulated in Eq. A.31. The reconstruction operators W^* and G^* can be defined by inversion of Eq. A.31 (See

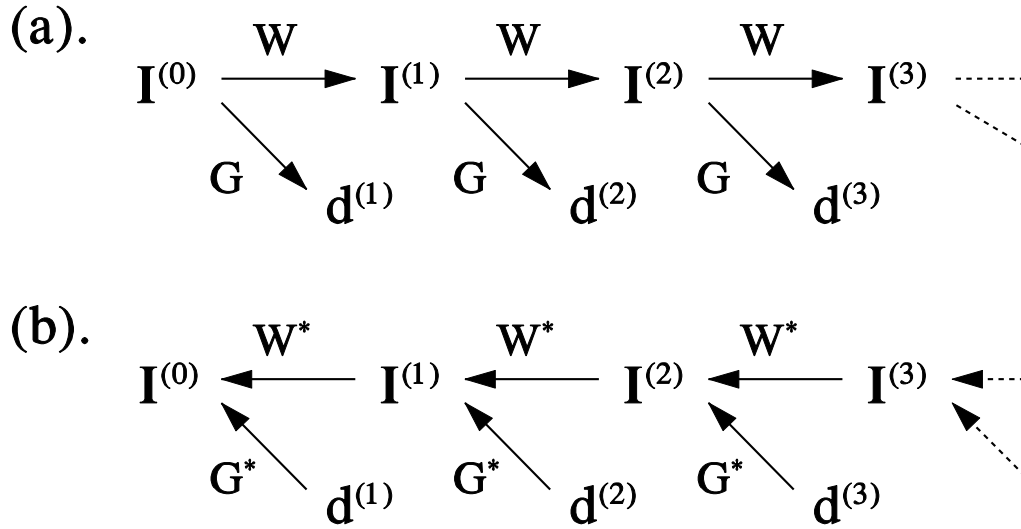


Figure A.2: Mallatian pyramid algorithm for trace decomposition (a) and reconstruction (b) in the operator representation Eq. A.31.

Ref. [61] for details) to obtain,

$$I^{(p)} = W^* I^{(p+1)} + G^* d^{(p+1)} . \quad (\text{A.32})$$

After p transformations following Eqs. A.27 and A.28 one obtains a collection of approximations $I^{(1)}, I^{(2)}, \dots, I^{(p)}$ and details $d^{(1)}, d^{(2)}, \dots, d^{(p)}$. The original set of discrete numbers can be fully reconstructed by repeated application of Eq. A.32 as shown in Fig. A.2(b).

A.3 Daubechies wavelets

The absolute values of filter coefficients in the Mallatian pyramid algorithm depend on the choice of the scaling and analysing generating functions ϕ and ψ , respectively. In principle there are an infinite number of candidates for these functions but only a small subset of these meet the conditions that are necessary if the analysis is to give an accurate representation. The important task Daubechies has fulfilled is to find a class of functions which fulfil these conditions and more. These functions turn out to be finite-sized wave-like functions, known as *wavelet* functions. Daubechies wavelets are orthonormal under the dilation and scaling operations, and form orthonormal bases with as much locality and smoothness as desired. The unexpected existence of such bases is one of the reasons why wavelet analysis has gained widespread popularity.

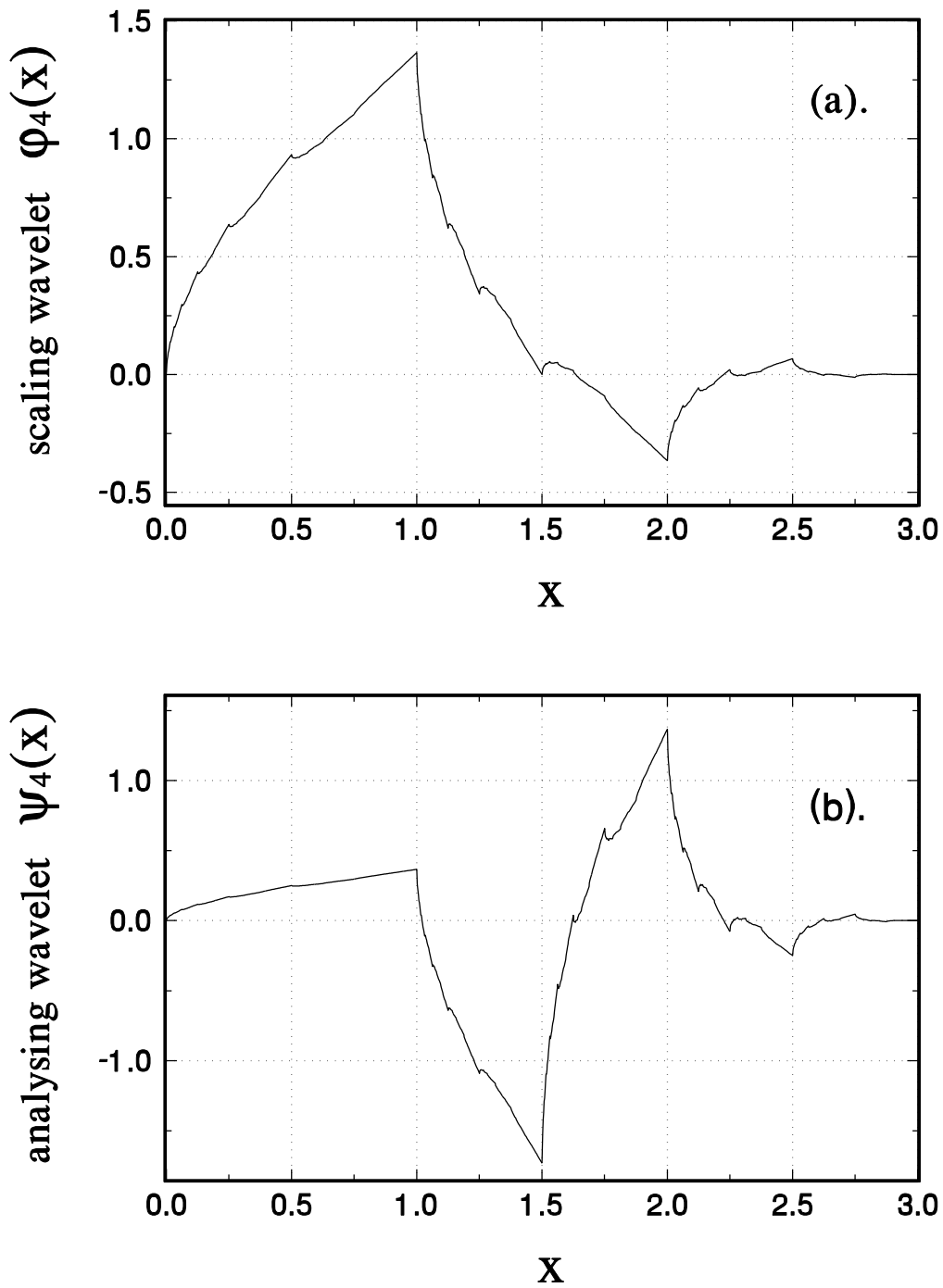


Figure A.3: (a) Scaling and (b) analysing Daubechies wavelet functions of order $N = 4$. The wavelet functions have a fractal nature, i.e., when drawn to larger scale the irregular outline of the functions remains.

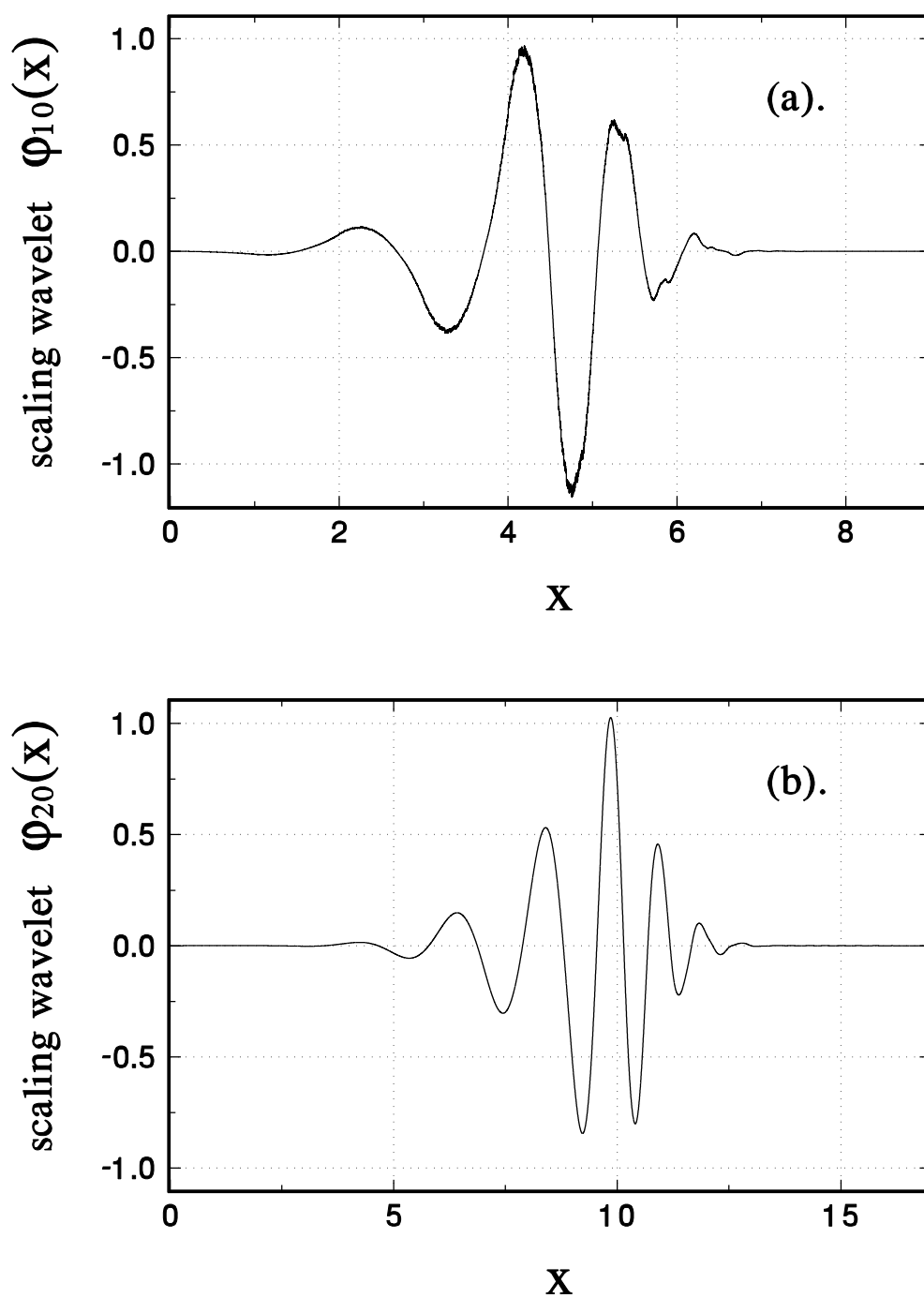


Figure A.4: Scaling Daubechies wavelets of order $N = 10$ (a) and order $N = 20$ (b). The functions depicted here and in Fig. A.3 are certainly rather surprising functions to serve as basis generating functions.

The construction of the Daubechies wavelets begins by recognising a salient feature of Eqs. A.29 and A.30; the filter coefficients w and g are defined as overlap integrals between integer translated versions of the generating wavelets which differ one step in the scale parameter p . Because these functions themselves form an orthonormal basis, it is natural to define the generating wavelet ϕ by the expansion,

$$\phi(x) \equiv w_0 \phi(2x) + w_1 \phi(2x - 1) + \dots + w_{N-1} \phi(2x - N + 1) . \quad (\text{A.33})$$

Equation A.33 is known as the dilation equation [63]. Following Eq. A.29 the coefficients w_k are exactly the filter coefficients as used in the transformation algorithm Eq. A.27. The number of coefficients used in the dilation equation defines the order N of the generating wavelet ϕ . For simplicity we write Eq. A.33 as,

$$\phi(x) = \sum_{k=0}^{N-1} w_k \phi(2x - k) . \quad (\text{A.34})$$

The generating wavelet ϕ can define a family of orthogonal wavelets according to Eq. A.13 when the coefficients w_k fulfil specific conditions. The generating wavelet ψ can be constructed from the wavelet ϕ following a similar type of dilation equation,

$$\psi(x) = \sum_{k=0}^{N-1} (-1)^k w_k \phi(2x + k - N + 1) , \quad (\text{A.35})$$

which defines a family of wavelets according to Eq. A.18. The definitions Eq. A.34 and Eq. A.35 then provide two orthonormal functions. Elaborate discussions of the requirements which these functions have to fulfil and the conditions imposed on the set of filter coefficients can be found in Ref. [61] and in the excellent books by Newland [63] and Kaiser [64]. For completeness and insight we list in Table A.1 a number of Daubechies wavelet coefficients. More wavelet coefficients, up to $N = 20$, can be found in Ref. [93].

As an illustration we show in Fig. A.3 the scaling and analysing Daubechies wavelet functions of order $N = 4$, numerically generated with Eq. A.33 when starting from a block function that equals unity for $x \in [0, 1]$ and equals zero everywhere else (See Ref. [63]). The irregular and fractal functions ϕ and ψ as depicted in Fig. A.3 are certainly rather surprising functions to serve as a basis for signal analysis. In order to obtain smoother wavelet functions, it is necessary to include more terms in the dilation equation Eq. A.33 as is shown in Fig. A.4 where we depict the scaling Daubechies wavelet functions of order $N = 10$ and $N = 20$. Daubechies wavelet functions have a finite spatial range $\Delta x = N - 1$ where N is the order of the wavelet function (See

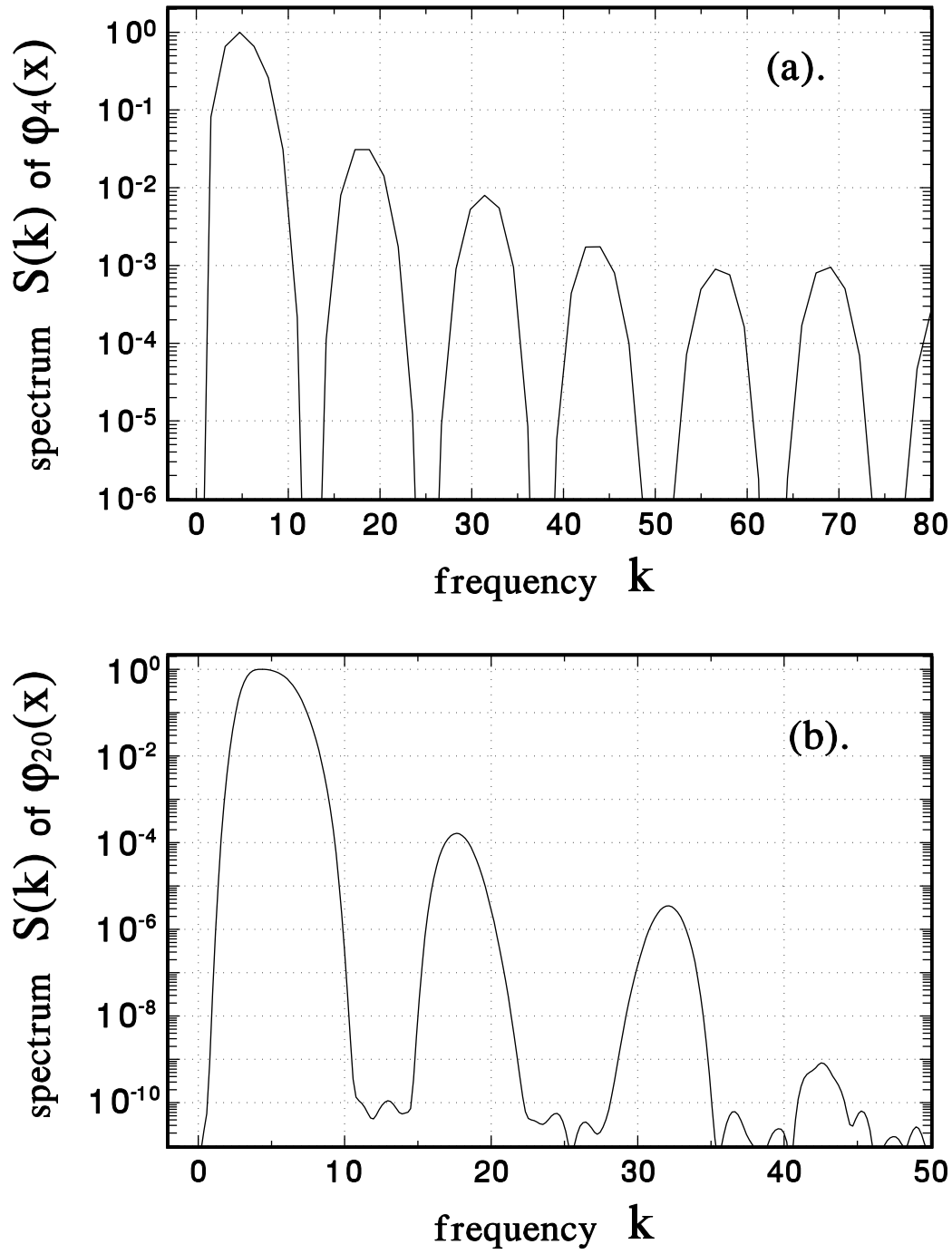


Figure A.5: *Fourier Transforms of Daubechies scaling wavelets of order $N = 4$ (a) and order $N = 20$ (b) where $k \equiv 2\pi/x$. Note the repeated occurrence of zero's in the power spectrum, resulting from the requirement of zero moments.*

wavelet order	wavelet coefficient
$N = 2$	$w_0 = 1/\sqrt{2}$ $w_1 = 1/\sqrt{2}$
$N = 4$	$w_0 = (1 + \sqrt{3})/4\sqrt{2}$ $w_1 = (3 + \sqrt{3})/4\sqrt{2}$ $w_2 = (3 - \sqrt{3})/4\sqrt{2}$ $w_3 = (1 - \sqrt{3})/4\sqrt{2}$
$N = 6$	$w_0 = (1 + \sqrt{10} + \sqrt{5 + 2\sqrt{10}})/16\sqrt{2}$ $w_1 = (5 + \sqrt{10} + 3\sqrt{5 + 2\sqrt{10}})/16\sqrt{2}$ $w_2 = (5 - \sqrt{10} + \sqrt{5 + 2\sqrt{10}})/8\sqrt{2}$ $w_3 = (5 - \sqrt{10} - \sqrt{5 + 2\sqrt{10}})/8\sqrt{2}$ $w_4 = (5 + \sqrt{10} - 3\sqrt{5 + 2\sqrt{10}})/16\sqrt{2}$ $w_5 = (1 + \sqrt{10} - \sqrt{5 + 2\sqrt{10}})/16\sqrt{2}$

Table A.1: Wavelet coefficients of Daubechies wavelets for even order N . The special case of $N = 2$ is known as the Haar wavelet and is used as an example in Sec. 4.2. For $N > 6$ the coefficients have to be calculated numerically.

Figs. A.3 and A.4). By definition the Fourier transform of Daubechies wavelet functions has a finite range $\Delta k \propto 1/(N - 1)$ in its frequency representation. Hence the Daubechies wavelets are bandwidth limited functions in the sense that $\Delta k \Delta x$ is constant and finite. As contracted versions of the generating functions have a reduced spatial width, their range in frequency increases proportionally. The price to pay for an increase of spatial resolution is a proportional decrease of the frequency resolution, and vice versa. In Fig. A.5 we depict the Fourier transform of Daubechies wavelet functions of order $N = 4$ and $N = 20$ to illustrate this feature. The spectral range is obtained from the decay of the envelope. By extending the numerical generation of the wavelets the depth of the crests, in theory equal to zero, can be further reduced. Calculation power and memory limitations inhibit more accurate generations of the wavelet functions. In our experiments we analyse time-resolved recordings of the scattered intensity, i.e., the variable x in Figs. A.4 and A.3 represents actual time. Hence the variable k in Fig. A.5 represents frequency.

Appendix B

Accuracy and limitations of discrete wavelet transformation

B.1 Accuracy and limitations

In Sec. 4.5 we have performed simulations of fractional Brownian motion and applied the wavelet analysis to simulated data traces to study the power and accuracy of the discrete wavelet transformation. Here we study the dependence of the value and accuracy of the estimated spectral exponent in terms of the sequence length and wavelet order. Therefore we have generated an fractional Brownian motion sequence with a length of 2^{18} points, and extract the spectral exponent from an array of 2^P points as a function of the array length characterised by P , the array position, and the number of weighting coefficients N equal to the order of the Daubechies wavelet. In Fig. B.1(a) we show the results for $P = 16$ for different order N where we implemented a value $\gamma = 2.0$ for the spectral exponent. Variations in the spectral exponent as a function of the array position hardly depend on the wavelet order N . Therefore we adopt $N = 12$ for the analysis performed in this appendix. However, with increasing block size the spectral exponent slowly converges to the entered value while the spread in values reduces, as shown in Fig. B.1(b). Therefore we adopt $P = 15$ in this chapter and appendix.

B.2 Spectral noise

An important difference between the experimentally obtained power spectrum of Fig. 4.3 and the power spectrum defined by Eq. 4.14 for simulated fractional Brownian motion sequences is the absence of spectral noise in the latter. It is precisely this noise

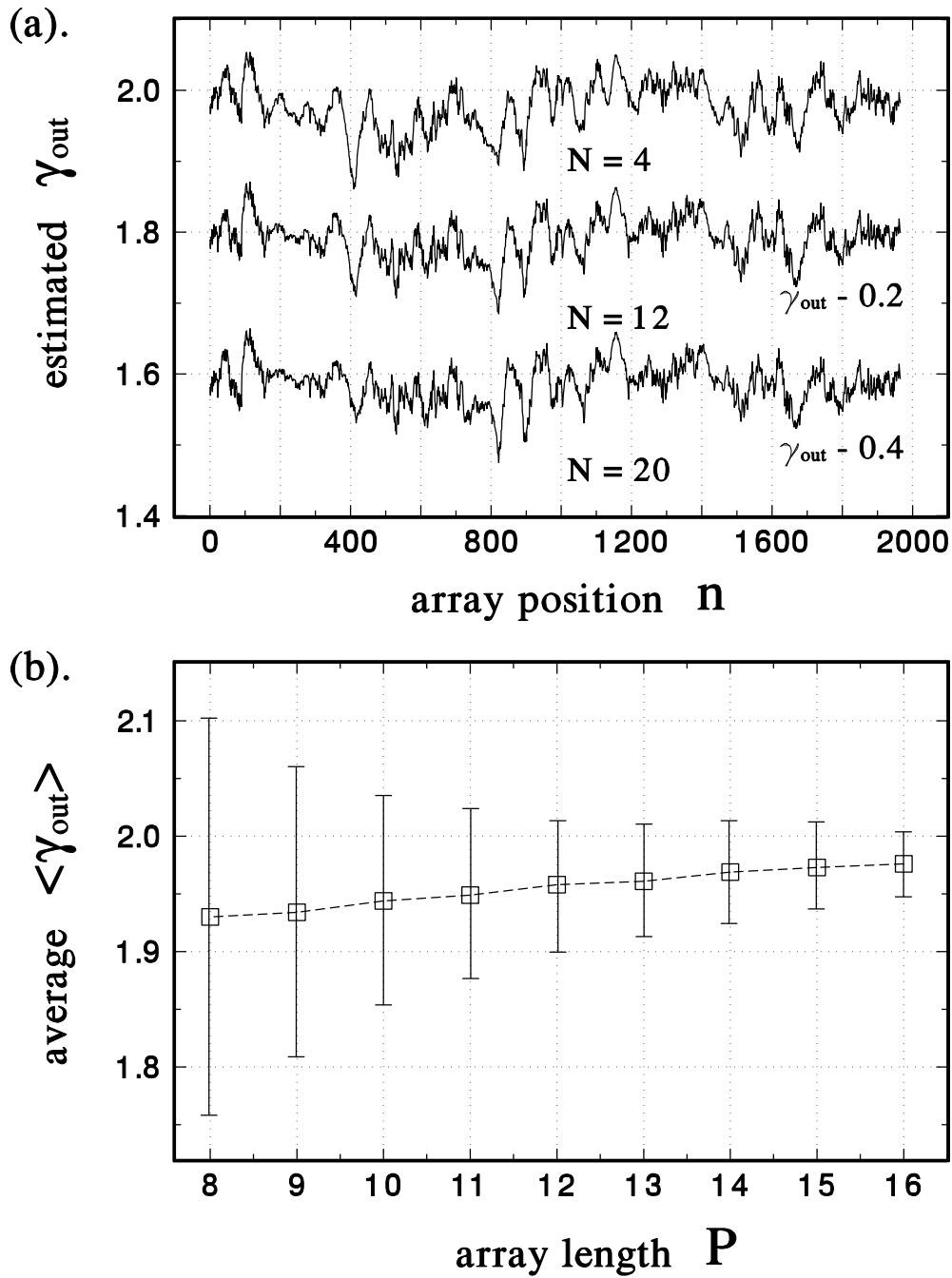


Figure B.1: (a). Spectral exponent γ_{out} estimated from an array of length 2^{16} points as a function of the array position on a simulated fractional Brownian motion sequence of length 2^{18} points for several numbers of weighting coefficients N . (b). Convergence of the average spectral exponent versus the array length 2^P for $N = 12$. The error bars indicate the spread in spectral exponent values.

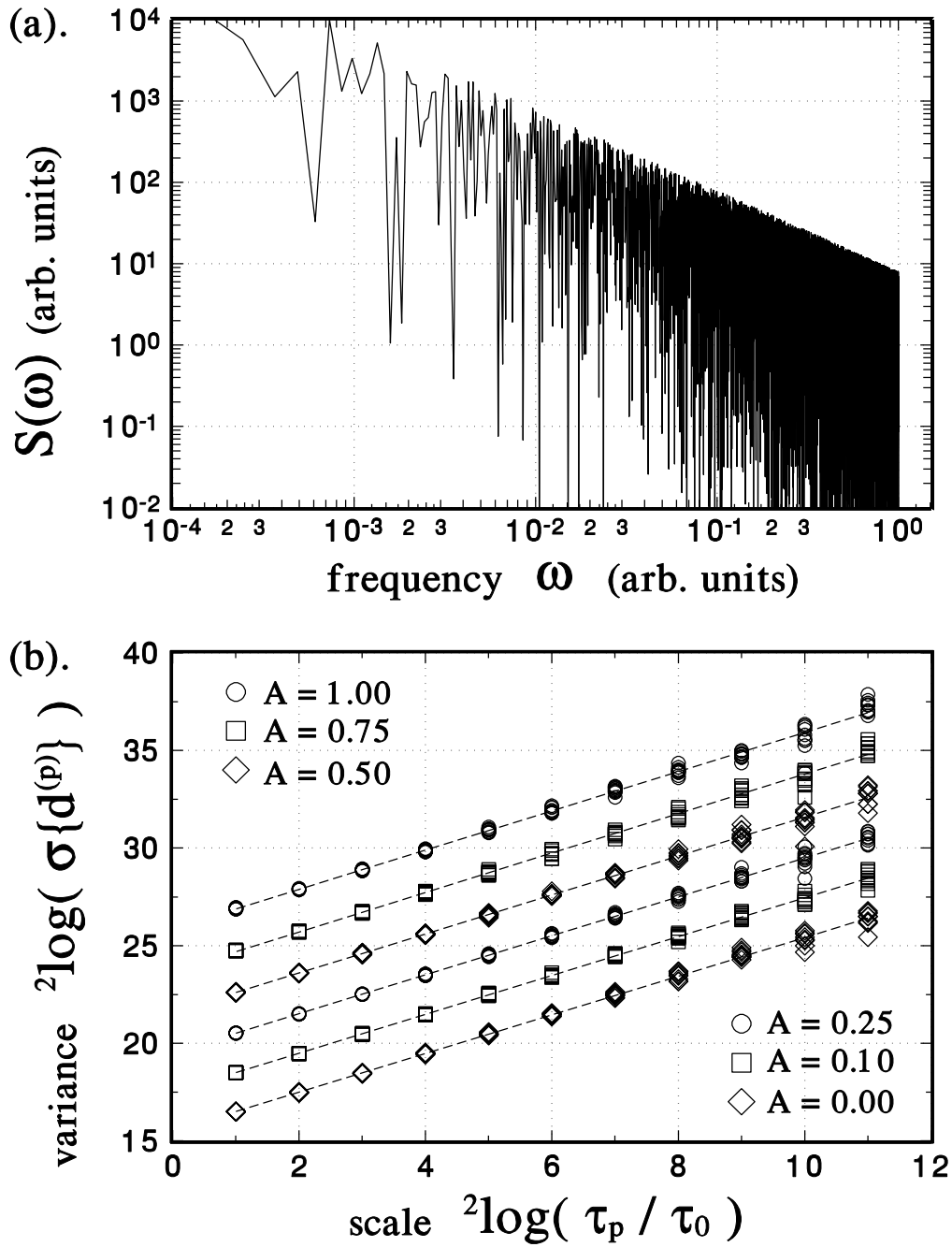


Figure B.2: (a). Power spectrum of a simulated fractional Brownian motion sequence based on Eq. B.1 for the parameters $\gamma_{in} = 1.0$ and $A = 1$. (b). Variance progression of simulated sequences for different noise levels. When matching these results to Eq. 4.13 we find the estimates (from top to bottom) $\gamma_{out} = 0.994(\pm 0.005)$, $0.996(\pm 0.004)$, $0.997(\pm 0.003)$, $0.998(\pm 0.007)$, $1.011(\pm 0.012)$, and $1.005(\pm 0.015)$.

which causes the inaccuracy in the spectral exponent when estimated from the power-spectrum of Fig. 4.3. Therefore we have performed simulations of fractional Brownian motion sequences with a noisy power spectrum generated by,

$$S(\omega) \propto |\omega|^{-\gamma} [1 + \text{rnd}(A)] , \quad (\text{B.1})$$

where the function $\text{rnd}(A)$ generates random numbers between $[-A, A]$ while filling the frequency array. Figure B.2(a) shows the power spectrum of a fractional Brownian motion sequence based on Eq. B.1 for $A = 1$ which bears many features of the experimentally obtained power spectrum depicted in Fig. 4.3. The variance progression of fractional Brownian motion sequences simulated from power spectra based on Eq. B.1 is shown in Fig. B.2(b) for various noise levels. Wavelet analysis completely ignores the spectral noise and recovers the spectral exponent with an unaltered accuracy, irrespective of its value.

B.3 Heterodyne detection

Photon correlation experiments on the gelation of our colloidal clay suspension revealed the slowing down of the dynamics of a homogenous sol until at the gel-point a slowly and collectively relaxing network gives rise to an observed speckle pattern. In the gel phase the scattered field amplitude consists of a fluctuating part $E_f(t)$ as a result of the remaining particle motion [25, 22] and a static part E_c scattered off the frozen-in degrees of freedom. The static scattering acts as an intrinsic and spatially varying local oscillator. In the intensity correlation function the temporal fluctuations beat to themselves (homodyne) and to the local oscillator (heterodyne) and yields (See Chap. 3 and [1, 76],

$$g(\tau) = 1 + x^2 h(\tau)^2 + 2x(1 - x)h(\tau) , \quad (\text{B.2})$$

where $1 - x$ expresses the local oscillator strength, $h(\tau)$ is the density correlation function, and the heterodyne parameter $x = 1 - I_c/\langle I \rangle$, where the static scattering $I_c = [E_c]^* E_c$. Because the Fourier transform of the intensity correlation function is the power spectrum as sampled by wavelet analysis, a valid question to be asked is the role of the local oscillator in wavelet analysis. The necessary corrections on the exponent γ as a result of heterodyne detection can be derived from simulations, done by us along the lines set out by Mandelbrot [91] and Kaplan [89].

Beyond the gel point T_g we observe the density correlation function to show a power-law decay $h(\tau) \propto \tau^{-a}$ where the exponent $a = -0.14 \pm 0.01$. In the glassy

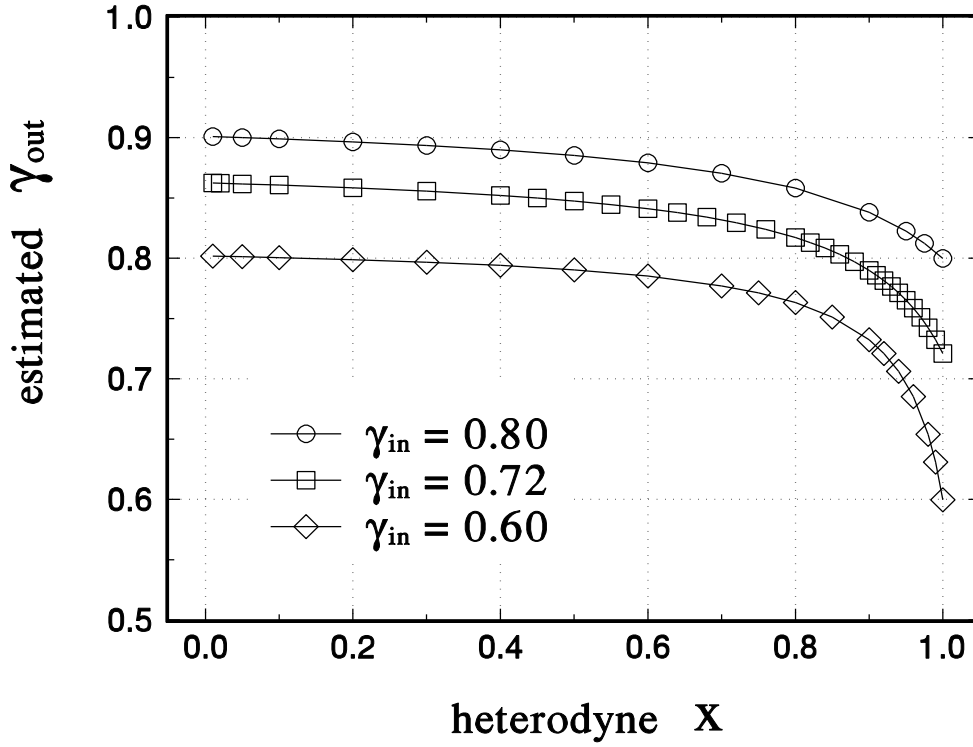


Figure B.3: Estimated exponent γ_{out} versus the heterodyne parameter x where $1 - x = I_c / \langle I \rangle$ which denotes the local oscillator strength. Simulations are performed with $\gamma_{in} = 2a + 1$ where a characterises an algebraic decay of correlation functions.

phase most measurements are performed in the limit $x \leq 0.5$ where the long-time tail of the intensity correlation function is dominated by the algebraic tail of the density correlation function $g(\tau) \propto 2x(1-x)h(\tau) \propto \tau^{-a}$. Fourier transformation of the correlation function Eq. B.2 yields two terms of the form of Eq. 4.14, hence the spectral exponent γ is expected to depend on the heterodyne parameter. We generated fractional Brownian motion representations of which the complex square root serves as a representation of the fluctuating field $E_f(t)$ as scattered off our colloidal gel. Addition of a real valued stationary background E_c to the simulated field $E_f(t)$ and multiplying this trace with its complex conjugate yields a representation of the scattered intensity trace $I(t)$. We show in Fig. B.3 a summary of the results obtained with several values of H as a function of x . With our approach the estimated spectral exponent is observed to gradually shift from the homodyne value $\gamma = 2a + 1$ to the heterodyne value $\gamma = a + 1$ as the local oscillator strength is increased ($x \downarrow 0$). In the gel phase we are always close to heterodyne limit with $x \leq 0.5$. Then the result for γ from wavelet analysis are comparable in value and accuracy with the results from photon correlation

spectroscopy. For example, the value $a = -0.14 \pm 0.01$ obtained from the density correlation function measured in the gel-phase yields a value $\gamma = 0.86 \pm 0.01$ for the spectral exponent which is remarkably similar to the results obtained with wavelet analysis (See Fig. 4.12(a)). However, the time needed for an accurate measurement of the intensity correlation function is at least an order of magnitude larger. The overall corrections are found to be small and will lead to a somewhat steeper rise in the value of γ as shown in Fig. 4.10. From the simulations presented in this appendix and in Sec. 4.5 we obtain a fairly good insight in the power of wavelet analysis and in the accuracy and limitations of estimates made with the variance progression. Results obtained from experiments can be compared to and supported by these findings.

Bibliography

- [1] M. Kroon, G. H. Wegdam, and R. Sprik, *Dynamic light scattering studies on the sol-gel transition of a suspension of anisotropic colloidal particles*, Phys. Rev. E **54**, 6541 (1996).
- [2] M. Kroon, W. L. Vos, and G. H. Wegdam, *Structure and formation of a gel of colloidal discs*, Phys. Rev. E **57**, 1962 (1998).
- [3] A. Mourchid, A. Delville, and P. Levitz, *Sol-gel transition of colloidal suspension of anisotropic particles of laponite*, Faraday Discuss. **101**, 275 (1986).
- [4] F. Pignon, J. M. Piau, and A. Magnin, *Structure and pertinent length scale of a discotic clay gel*, Phys. Rev. Lett. **76**, 4857 (1996): F. Pignon, A. Magnin, J. M. Piau, B. Cabane, P. Lindner, and O. Diat, *Yield stress thixotropic clay suspension: investigations of structure by light, neutron, and X-ray scattering*, Phys. Rev. E **56**, 3281 (1997).
- [5] S. Z. Ren, W. F. Shi, W. B. Zang, and C. M. Sorensen, *Anomalous diffusion in aqueous solutions of gelatin*, Phys. Rev. A **45**, 2416 (1992): S. Z. Ren and C. M. Sorensen, *Relaxation in gels: analogies to α and β relaxation in glasses*, Phys. Rev. Lett. **70**, 1727 (1993).
- [6] N. Willenbacher, *Unusual thixotropic properties of aqueous dispersions of laponite RD*, J. Colloid Interface Sci. **182**, 501 (1996).
- [7] C. Kittel and H. Kroemer, *Thermal Physics* (Freeman, San Fransisco, 1980).
- [8] H. Bässler, *Viscous flow in supercooled liquids analysed in terms of transport theory for random media with energetic disorder*, Phys. Rev. Lett. **58**, 767 (1987).
- [9] R. S. Miller and R. A. MacPhail, *Ultraslow nonequilibrium dynamics in supercooled glycerol by stimulated Brillouin gain spectroscopy*, J. Chem. Phys. **106**, 3393 (1997).

- [10] Undercooling of a liquid is not something that always happens if one just cools rapid enough. (i). The rate of cooling is strongly material dependent. Furthermore, several other conditions in terms of pressure and temperature must be obeyed. (ii) With ordinary liquids we denote almost all liquids except for water.
- [11] C. A. Angell, *Formation of glasses from liquids and biopolymers*, Science **267**, 1924 (1995).
- [12] N. E. Cusack, *The physics of structurally disordered matter* (Adam Hilger, Bristol and Philadelphia, 1987).
- [13] I. M. Hodge, *Physical ageing in polymer glasses*, Science **267**, 1945 (1995).
- [14] R. J. Hunter, *Foundations of colloidal science* (volume I, Clarendon Press, Oxford, 1986)
- [15] E. Trizac and J. P. Hansen, *Free energy of electric double layers around finite particles*, J. Phys.: Cond. Matt. **8**, 9191 (1996).
- [16] Laponite technical bulletin, L104.90/A, *Laponite - structure, chemistry and relationship to natural clays* [17].
- [17] Laponite (RD) is manufactured by Laporte Absorbents, P.O. Box 2, Cheshire, UK.
- [18] U. Bengtzelius, W. Götze, and A. Sjölander, *Dynamics of supercooled liquids and the glass transition*, J. Phys. C.: Solid State Phys. **17**, 5915 (1984).
- [19] E. Leutheusser, *Dynamical model of the liquid-glass transition*, Phys. Rev. A **29**, 2765 (1984).
- [20] W. Götze and L. Sjögren, *β relaxation at the glass transition of hard sphere colloids*, Phys. Rev. A **43**, 5442 (1991).
- [21] W. Götze, in *Liquids, freezing and glass transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn Justin, (North Holland, Amsterdam, 1991), pg. 464.
- [22] P. N. Pusey and W. van Meegen, *Dynamic light scattering by non-ergodic media*, Physica A **157**, 705 (1989).
- [23] J. Z. Xue, D. J. Pine, S. T. Milner, X. J. WU, and P. M. Chaikin, *Nonergodicity and light scattering from polymer gels*, Phys. Rev. A **46**, 6550 (1992).

- [24] F. Mezei, W. Knaak, and B. Farago, *Neutron spin-echo study of dynamical correlations near the liquid-glass transition*, Phys. Rev. Lett. **58**, 571 (1987).
- [25] W. van Megen, S. M. Underwood, and P. N. Pusey, *Nonergodicity parameters of colloidal glasses*, Phys. Rev. Lett. **67**, 1586 (1991); W. van Megen and S. M. Underwood, *Dynamic light scattering study of glasses of hard colloidal spheres*, Phys. Rev. E **47**, 248 (1993); W. van Megen and S. M. Underwood, *Glass transition on colloidal hard spheres: mode-coupling theory analysis*, Phys. Rev. Lett. **70**, 2766 (1993); W. van Megen and S. M. Underwood, *Glass transition in colloidal hard spheres: measurement and mode-coupling theory analysis of the coherent intermediate scattering function*, Phys. Rev. E **49**, 4206 (1994).
- [26] M. Fuchs, I. Hofacher, and A. Latz, *Primary relaxation in a hard-sphere system*, Phys. Rev. A **45**, 898 (1992).
- [27] E. Bartsch, M. Antonietti, W. Schupp, and H. Sillescu, *Dynamic light scattering study of concentrated microgel solutions as mesoscopic model of the glass transition in quasiatomic fluids*, J. Chem. Phys. **97**, 3950 (1992); E. Bartsch, V. Frenz, J. Baschnagel, W. Schärfl, and H. Sillescu, *The glass transition dynamics of polymer micronetwork colloids: a mode-coupling analysis*, J. Chem. Phys. **106**, 3743 (1997);
- [28] G. Li, W. M. Du, J. Hernandez, and H. Z. Cummins, *Locating the nonergodicity-parameter anomaly near the liquid-glass cross-over temperature in CaKNO_3 by Brillouin scattering*, Phys. Rev. E **48**, 1192 (1993).
- [29] Th. M. Nieuwenhuizen, *To maximise or not to maximise the free energy of glassy systems*, Phys. Rev. Lett. **74**, 3463 (1995); Th. M. Nieuwenhuizen, *Solvable glassy system: static versus dynamical transition*, Phys. Rev. Lett. **78**, 3491 (1997); Th. M. Nieuwenhuizen, *Ehrenfest relations at the glass transition: solution to an old paradox*, Phys. Rev. Lett. **79**, 1317 (1997).
- [30] M. Alexanian and T. W. Haywood, *Thermodynamic aspect of the glass transition*, Physica A **157**, 797 (1989).
- [31] J. P. Sethna, *Speculations on the glass transition*, Europhys. Lett. **6**, 529 (1988).
- [32] D. Kivelson, S. A. Kivelson, X. Zhao, Z. Nussinov, and G. Tarjus, *A thermodynamic theory of supercooled liquids*, Physica A **219**, 27 (1995).

- [33] “Colloids” Britannica CD. Version 97. Encyclopedia Britannica, Inc., 1997.
- [34] “Brownian motion” Britannica CD. Version 97. Encyclopedia Britannica, Inc., 1997.
- [35] B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).
- [36] “Thomas Graham” Britannica CD. Version 97. Encyclopedia Britannica, Inc., 1997.
- [37] *IUPAC manual of symbols and terminology for physicochemical quantities and units*, Appendix II, part I, edited by D. H. Everett, (Butterworth, London, 1972).
- [38] P. M. Chaikin and T. C. Lubensky, *Principles of condensed matter physics* (Cambridge University Press, Cambridge, 1995).
- [39] P. N. Pusey and W. van Megen, *Phase behaviour of concentrated suspensions of nearly hard colloidal spheres*, *Nature* **320**, 340 (1986).
- [40] P. N. Pusey, in *Liquids, freezing and glass transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn Justin, (North Holland, Amsterdam, 1991), pg. 765.
- [41] D. V. van Coevorden, R. Sprik, A. Tip, and A. Lagendijk, *Photonic band structure of atomic lattices*, *Phys. Rev. Lett.* **77**, 2412 (1996).
- [42] W. L. Vos, R. Sprik, A. Lagendijk, G. H. Wegdam, A. van Blaaderen, and A. Imhof, in *Photonic band gap materials*, edited by C. M. Soukoulis, (Kluwer, Amsterdam, 1996), pg. 107, *Influence of optical band structures on the diffraction of photonic colloidal materials*: W. L. Vos, M. Megens, C. M. van Kats, and P. Bösecke, *Transmission and diffraction by photonic colloidal crystals*, *J. Phys.: Cond. Matt.* **8**, 9503 (1996); W. L. Vos, R. Sprik, A. van Blaaderen, A. Imhof, A. Lagendijk, and G. H. Wegdam, *Strong effects of photonic band structures on the diffraction of colloidal crystals*, *Phys. Rev. B* **53**, 16231 (1996).
- [43] L. Onsager, in *The collected works of Lars Onsager*, edited by P. C. Hemmer , H. Holden, and S. Kjelstrup Ratkje (World Scientific, Singapore, 1996): Article; *Theory of concentrated electrolytes*, *Chem. Rev.* **13**, 73 (1933).
- [44] N. Verhaeg, Thesis, *Structure and kinetics of phase separating colloidal suspensions*, University of Utrecht, Utrecht, The Netherlands (1996).

- [45] Y. A. Berlin and A. L. Burin, *Hierarchically constrained dynamics of the configurational co-ordinate for rate processes in complex systems*, Chem. Phys. Lett. **267**, 234 (1997).
- [46] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon, Oxford, 1993).
- [47] L. Onsager, in *The collected works of Lars Onsager*, edited by P. C. Hemmer, H. Holden, and S. Kjelstrup Ratkje (World Scientific, Singapore, 1996): Articles; *Viscosity and particle shape in colloid solutions*, Phys. Rev. **40**, 1028 (1932); *Anisotropic solutions of colloids*, Phys. Rev. **62**, 558 (1942); *The effects of shape on the interaction of colloidal particles*, Ann. NY Acad. Sci. **51**, 627 (1949).
- [48] R. Eppenga and D. Frenkel, *Monte Carlo study of the isotropic and nematic phases of infinitely thin hard platelets*, Mol. Phys. **52**, 1303 (1984).
- [49] D. Frenkel, in *Liquids, freezing and glass transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn Justin, (North Holland, Amsterdam, 1991), pg. 689.
- [50] J. A. C. Veerman and D. Frenkel, *Phase behaviour of disc-like hard-core mesogens*, Phys. Rev. A **45**, 5632 (1992).
- [51] Cut-spheres are prepared by slicing off the top and bottom caps of a sphere. Hence the aspect ratio is adjustable from unity, describing ideal spheres, to nearly zero, describing thin discs.
- [52] J. D. F. Ramsey, *Colloidal properties of synthetic hectorite clay dispersions: I. rheology*, J. Colloid Interface Sci. **109**, 441 (1986).
- [53] R. G. Avery and J. D. F. Ramsey, *Colloidal properties of synthetic hectorite clay dispersions: II. light and small-angle neutron scattering*, J. Colloid Interface Sci. **109**, 448 (1986).
- [54] L. Rosta and H. R. von Gunten, *Light scattering characterisation of laponite sols*, J. Colloid Interface Sci. **134**, 397 (1990).
- [55] D. W. Thompson and J. T. Butterworth, *The nature of laponite and its aqueous dispersions*, J. Colloid Interface Sci. **151**, 236 (1992).
- [56] M. Kroon, G. H. Wegdam, and R. Sprik, *Analysis of dynamic light scattering signals with discrete wavelet transformation*, Europhys. Lett. **35**, 621 (1996).

- [57] H. van Olphen, *Clay colloid chemistry*, 2nd ed. (John Wiley, New York, 1977).
- [58] M. Dijkstra, J. P. Hansen, and P. A. Madden, *Gelation of a clay colloid suspension*, Phys. Rev. Lett. **75**, 2236 (1995); M. Dijkstra, J. P. Hansen, and P. A. Madden, *Statistical model for the structure and gelation of smectite clay suspensions*, Phys. Rev. E **55**, 3044 (1997).
- [59] X. C. Zeng, D. Kivelson, and G. Tarjus, Phys. Rev. Lett. **72**, 1772 (1994), Comment on W. van Megen and S. M. Underwood, *Glass transition on colloidal hard spheres: mode-coupling theory analysis*, Phys. Rev. Lett. **70**, 2766 (1993).
- [60] J. G. H. Joosten, E. T. F. Geladé, and P. N. Pusey, *Dynamic light scattering by nonergodic media: Brownian particles trapped in polyacrylamide gels*, Phys. Rev. A **42**, 2161 (1990); J. G. H. Joosten, J. L. McCarthy, and P. N. Pusey, *Dynamic and static light scattering by aqueous polyacrylamide gels*, Macromolec. **24**, 6690 (1991).
- [61] I. Daubechies, in *Wavelets, time-frequency methods and phase space; proceedings of the international conference, Marseilles, 1987*, edited by J. M. Combes, A. Grossmann, and Ph. Tchamitchian. (Springer-Verlag, 1989).
- [62] C. K. Chu, *An introduction to wavelets* (Academic press, New York, 1992).
- [63] D. E. Newland, *Random vibrations, spectral and wavelet analysis* 3rd ed. (Wiley, New York, 1993).
- [64] G. Kaiser, *A friendly guide to wavelets* (Birkhäuser, Berlin, 1994).
- [65] R. Perkins, R. Brace, and E. Matijević, *Colloid and surface properties of clay suspensions: I. laponite CP*, J. Colloid Interface Sci. **48**, 417 (1974).
- [66] N. C. Lockhart, *Electrical properties and the surface characteristics and structure of clays: I. swelling clays*, J. Colloid Interface Sci. **74**, 509 (1980).
- [67] D. J. Griffith, *Introduction to electrodynamics* (Prentice Hall, New Jersey, 1989).
- [68] The mass fraction φ_m of the suspensions can be converted to the volume fraction φ_v by $\varphi_v = \varphi_m([1 - \varphi_m]\rho_l\rho_w^{-1} + \varphi_m)^{-1}$. The volume fraction $\varphi_v \equiv v_l/v_t$ where v_l is the volume occupied by laponite in the total volume v_t . The density of laponite $\rho_l = 2.2 (\pm 0.1) \times 10^3 \text{kg/m}^3$ as estimated by Thompson [55], and

resembles the density of mica. The density of pure water under standard pressure and temperature $\rho_w = 0.998 (\pm 0.001) \times 10^3 \text{ kg/m}^3$ [69].

- [69] *Handbook of chemistry and physics*, 67th edition (CRC press, Boca Raton, 1987).
- [70] A. Guinier and G. Fournet, *Small-angle scattering of X-rays* (Wiley, New York, 1955); A. Guinier, *X-ray diffraction, in crystals, imperfect crystals, and amorphous bodies* (Dover, New York, 1994).
- [71] In principle the scattered field has a spherical wave character of which the amplitude decays linearly with the distance to the scattering cell. At the location of the detector this distance is large compared to the average distance of particle motion and the wavelength of the scattered light. Therefore the scattered wave is approximated by a plane-wave, which drastically simplifies calculations.
- [72] K. Schätzel, *Noise in photon correlation and photon structure functions*, *Optica Acta* **30**, 155 (1983); K. Schätzel, in *Optical measurements in fluid mechanics*, Proceedings of the VIth international conference on photon correlation and other techniques in fluid mechanics: Article; *New concepts in correlator design*, pg. 175 (Adam Hilger, Bristol and Philadelphia, 1985); K. Schätzel, *Dead time correction of photon correlation functions*, *Appl. Phys. B* **41**, 95 (1986); K. Schätzel, *Correlation techniques in dynamic light scattering*, *Appl. Phys. B* **42**, 193 (1987); K. Schätzel, M. Drewel, and S. Stimac, *Photon correlation measurements at large lag times: improving statistical accuracy*, *J. Mod. Opt.* **35**, 711 (1988).
- [73] N. Wax, *Selected papers on noise and stochastic processes* (Dover, New York, 1954).
- [74] B. Chu, *Laser light scattering, basic principles and practice*, 2nd ed. (Academic press, New York, 1991).
- [75] J. W. Goodman, in *Laser speckle, and related phenomena*, edited by J. C. Dainty, (Springer-Verlag, New York, 1989).
- [76] B. J. Frisken and D. S. Cannell, *Critical dynamics in the presence of a silica gel*, *Phys. Rev. Lett.* **69**, 633 (1992).
- [77] According to the Stokes-Einstein relation [35] the diffusion coefficient is given by $D = kT/6\pi\eta a$, where k is the Boltzmann constant, T the temperature, η the viscosity of the fluid medium, and a is the typical particle radius. Combined

with other results, the technique of photon correlation spectroscopy permits an accurate determination of fluid viscosity, macro-molecular weights and particle size distributions.

- [78] P. Bösecke, O. Diat, and B. Rasmussen, *High-brilliance beamline at the European Synchrotron Radiation Facility*, Rev. Sci. Instrum. **66**, 1636 (1995).
- [79] W. Bras *et al*, *Simultaneous time-resolved X-ray scattering experiments in the small- and wide-angle region*, J. Phys. IV, C8 (France), Suppl. J. Phys. I **3**, 447 (1993).
- [80] T. Tanaka, L. O. Hocker, and G. B. Benedek, *Spectrum of light from a viscoelastic gel*, J. Chem. Phys. **59**, 5151 (1973).
- [81] M. Adam, M. Delsanti, and L. P. Munch, *Dynamical studies of polymeric cluster solutions obtained near the gelation threshold: glass-like behaviour*, Phys. Rev. Lett. **61**, 706 (1988): D. Durand, M. Delsanti, M. Adam, and J. M. Luck, *Frequency dependence of viscoelastic properties of branched polymers near gelation threshold*, Europhys. Lett. **3**, 297 (1987).
- [82] J. E. Martin, *Slow aggregation of colloidal silica*, Phys. Rev. A **36**, 3415 (1987): J. E. Martin and J. P. Wilcoxon, *Critical dynamics of the sol-gel transition*, Phys. Rev. Lett. **61**, 373 (1988): J. E. Martin, J. P. Wilcoxon, and J. Odinek *Decay of density fluctuations in gels*, Phys. Rev. A **43**, 858 (1991).
- [83] N. W. Ashcroft and N. D. Mermin, *Solid state physics* (Saunders College, Philadelphia, 1987), pg. 792.
- [84] F. Argoul, A. Arneodo, G. Grasseau, Y. Gagne, E. J. Hopfinger, and U. Frisch, *Wavelet analysis of turbulence reveals the multifractal nature of the Richardson cascade*, Nature **338**, 51 (1989): J. F. Muzy, E. Bacry, and A. Arneodo, *Wavelets and multifractal formalism for singular signals: application to turbulence data*, Phys. Rev. Lett. **67**, 3515 (1991).
- [85] P. H. J. van Dam and G. H. Wegdam, *The role of small coherent structures in turbulent drag-reduction*, Appl. Sc. Res. **51**, 155 (1993): P. H. J. van Dam and G. H. Wegdam, *Distribution of turbulent velocity fluctuations in a drag-reducing solution*, J. Phys. Chem. **98**, 1939 (1994): P. H. J. van Dam and G. H. Wegdam, *The structure of turbulence in a dilute polymer solution*, J. Non-Newtonian Fluid Mech **53**, 215 (1994).

- [86] P. Goupillaud and J. Morlet, *Decomposition of Hardy functions into square-integrable wavelets of constant shape*, SIAM J. Math. Anal. (1984): P. Goupillaud, A. Grossmann, and J. Morlet, *Cycle-octave and related transforms in seismic signal analysis*, Geop exploration **23**, 85 (1984).
- [87] M. Alexandrescu, D. Gibert, G. Hulot, J. L. Le Mouél, and G. Saracco, *World-wide wavelet analysis of geomagnetic jerks*, J. Geophys. Res. **101**, 21975 (1996).
- [88] P. Burt and E. Adelson, *The Laplacian pyramid as a compact image code*, IEEE Trans. Comm. **31**, 582 (1983): P. Burt and E. Adelson, *A multi-resolution spline with application to image mosaics*, ACM Trans. Graph. **2**, 217 (1983).
- [89] L. M. Kaplan and C. C. Jay Kuo, *Fractal estimation from noisy data via discrete fractional Gaussian noise (DFGN) and the Haar basis*, IEEE Trans. Sig. Proc. **41**, 3554 (1993).
- [90] R. N. Bracewell, *The Fourier transform and its applications*, 2nd ed. (McGraw-Hill, New York, 1986).
- [91] B. M. Mandelbrot, J. W. V. Ness, *Fractional Brownian motions, fractional noises and applications*, SIAM Rev., Volume 10, Oct 1968: B. Mandelbrot, *The fractal geometry of nature* (Freeman, San Francisco, 1982).
- [92] Why is the spectrum Eq. 4.16 non-physical? No system in nature at a finite temperature has such a sharp transition or cross-over in its density of states. If modes are allowed to exist due to very stringent conditions and only delta functions were to survive (cavity modes for example) still thermal and inhomogeneous broadening effects would smear the spectrum.
- [93] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical recipes in Fortran*, 2nd ed. (Cambridge, New York, 1992).
- [94] In the limit $H \rightarrow 0$ the first factor on the right hand side of Eq. 5.2 becomes equal to unity. In the limit of large q , Eq. 5.3 can be rewritten as an integral over the decaying Bessel function squared. This gives a constant divided by the remaining factor q^2 .
- [95] H. G. Barth and S. T. Sun, *Particle size analysis*, Anal. Chem. **65**, 55R (1993).

- [96] M. Megens, C. M. van Kats, P. Bösecke, and W. L. Vos, *In situ characterisation of colloidal spheres by synchrotron small-angle X-ray scattering*, *Langmuir* **13**, (Nov. 12, 1997).
- [97] *On growth and form, fractal and non-fractal patterns in physics*, edited by H. E. Stanley and N. Ostrowsky, (Kluwer, Dordrecht, 1986).
- [98] J. Teixeira, in *On growth and form, fractal and non-fractal patterns in physics*, edited by H. E. Stanley and N. Ostrowsky, (Kluwer, Dordrecht, 1986), pg. 145.
- [99] We have divided all one-dimensional static scattered intensity patterns by the last pattern recorded, because (i) the scattered intensity spans almost three orders of magnitude which obscures small variations, (ii) uncertainties in the background level and local detector overload introduce additional inaccuracies when dividing the static scattered intensity by the form factor, (iii) a few days is well beyond the restoring time of the gel thus the figure shows the relative deviation from the constant (relaxed) signal.
- [100] A. J. Leadbetter, in *The molecular physics of liquid crystals*, edited by G. R. Luckhurst and G. W. Gray, (Academic Press, New York, 1979), pg. 296.
- [101] M. Kolb, R. Botet, and R. Jullien, *Scaling of kinetically growing clusters*, *Phys. Rev. Lett.* **51**, 1123 (1983).
- [102] D. W. Schaeffer and K. D. Keefer, in *Fractals in physics*, edited by L. Pietronero and E. Tosatti, (Elsevier, Amsterdam, 1986), pg. 39.
- [103] P. W. Rouw and C. G. de Kruif, *Adhesive hard-sphere colloidal dispersions: fractal structures and fractal growth in silica dispersions*, *Phys. Rev. A* **39**, 5399 (1989).
- [104] R. Maynard, *Elastic and thermal properties of hierarchical structures: application to silica aerogels*, *Physica A* **157**, 601, (1989): G. Deutscher, R. Maynard, and O. Parodi, *Simple model of the elasticity of heterogeneous materials: application to silica gels*, *Europhys. Lett.* **6**, 49 (1988).
- [105] E. Courtens, J. Pelous, J. Phalippou, R. Vacher, and T. Woignier, *Brillouin-scattering measurements of phonon-fracton cross-over in silica aerogels*, *Phys. Rev. Lett.* **58**, 128 (1987): E. Courtens and R. Vacher, *Structure and dynamics of fractal aerogels*, *Z. Phys. B: Condensed Matter* **68**, 355 (1987): E. Courtens, in

Fractals in physics, edited by A. Aharony and J. Feder, (North Holland, Amsterdam, 1989).

- [106] F. Pignon, A. Magnin, and J. M. Piau, *Thixotropic colloidal suspensions and flow curves with minimum: identification of flow regimes and rheometric consequences*, J. Rheol. **40**, 573 (1996).

Summary

Laponite, the monocrystalline colloidal disc we disperse in demineralised water, forms a unique system amidst the mesoscopic gel or glass formers. The gel formation is reversible in the sense that it can be brought back reproducingly to a well-defined initial state under shear, provided the shear amplitude is high enough. Polyelectrolytes like gelatine form thermotropic gels that are reversible under temperature variation. Unlike polymers, the laponite particle has a well-defined disc-like shape of nanometer dimensions with a high aspect ratio. Hence the laponite system is a mesoscopic model system of very thin discs. The charge density on the discs is fixed due to the underlying crystalline structure; a layered silicate which closely resembles the natural clay mineral hectorite in both structure and composition. As a result of the presence of charge balancing ions the clay platelets interact via a screened-Coulomb potential with a quadrupolar symmetry. The range of this interaction can be varied reproducibly by varying the salt concentration.

Preparing the system in a low-viscosity sol state, it becomes more and more viscous as the time after preparation progresses until in the gel phase the suspension behaves elastically at small shear rates. In this thesis we have followed and characterised this sol-gel transition in the time domain by measurements of the dynamic and static structure factor by experimental light scattering and small-angle X-ray scattering. The physical picture emerging from the dynamic structure factor is a fast local rearrangement (re-orientations) of particles followed by the slower collective rearrangement (translations) over larger distances. As the gelation proceeds only the translational component slows down considerably, at least five orders of magnitude in time, until at the gelation point the sample becomes an elastic gel. We are able to define the gelation point unambiguously as the point in time where a fixed speckle pattern is formed by the laser light scattered from the gelating system. The amplitude of the speckle pattern, fixed in space but growing with the distance beyond the gel-point, can be considered the order parameter of the transition.

The algebraic behaviour of the dynamic structure factor around the gel point showed a clear signature of the structural glass transition: an algebraic decay with a long-time cut-off that stretches towards infinity as the gel-point is approached. However, in the framework of modern theories we need a multi-parameter master function in order to derive the desired physical parameters quantitatively. Even then the results are not decisive in discriminating between pure β relaxation or the combined α - β relaxation picture of Götze. For that purpose we have used a novel measurement procedure, called wavelet analysis, that analyses the detected intensity fluctuations locally in time. Wavelet analysis enables us to accurately determine the exponent related to the algebraic decay of the dynamic structure factor and follow the critical divergence of both the short and long-time cut-offs of the algebraic decay, without the use of any model. We were the first to establish experimentally the relations between the associated exponents, postulated in the theories of the glass transition. Wavelet analysis proved to be not just a valuable tool in dynamic light scattering experiments, but in this case an essential and necessary tool to extract the desired physical parameters accurately, without the bias of a model fit to the data. The results of wavelet analysis refuted the assumption of stretched exponential decay of the correlation functions for the first time.

Measurement of the static structure factor over four orders of magnitude in length-scale, from the single particle dimensions to a hundred times the interparticle separation, showed the absence of clusters of particles. Right from the start of the entire gelation process a characteristic algebraic wavevector dependence of the static structure factor is measured, where in time only the exponent decreases continuously. The large length-scale structure of the sol is observed to be the similar in the gel phase; the sol is not comparable to a simple liquid but can be considered a low-viscosity precursor of the gel. There is not a preferred length scale observed at any time during the gelation process. The gelation therefore cannot be one of aggregation, where in time a distribution of clusters grow in size.

We have shown unambiguously that the gel is a fractal network with random particle orientation and not, as has been suggested, with short-range orientational order which one expects from the quadrupolar symmetry of the interaction. Measurement of the form factor after applying shear to the suspensions reveals an orientational ordering of the colloidal discs parallel to the flow field. However, this orientational order disappears on a time-scale comparable to the gelation time. Hence the nematically ordered is not the equilibrium state. Based on our findings we have suggested that, rather than aggregation, local reorientation is the mechanism behind the phenomenon

of gelation in time. Local reorientation releases stress by means of density fluctuations while at the same time the viscosity diverges. The continuous reorganisation of the clay network can be interpreted as a co-operative self-delaying process that freezes the system in the glassy phase before entering the liquid crystalline phase.

The sol-gel transition in the time domain has all the characteristics of the structural glass transition. Here mechanical shear is the external field, in contrast to temperature, pressure, or density. The experimental evidence points to an ageing phenomenon, i.e., the out of equilibrium evolution of a system quenched into a glassy state, a phenomenon encountered with spin glasses and undercooled liquids. There is now a renewed interest from theoretical side for this ageing process and the relation with the glass transition. This system of colloidal discs looks very promising to study experimentally this relation and the glass transition in general.

Nederlandse Samenvatting

Laponite is een synthetisch klei in poedervorm verkrijgbaar bestaande uit monokristallijne kleischijfjes van colloïdale afmetingen. Een suspensie, of dispersie, van deze deeltjes in gedemineraliseerd water vormt een uniek systeem temidden van de mesoscopische gel of glasvormers. Suspensies van laponite vertonen na preparatie een continue ontwikkeling in de tijd, van een laagvisceuze sol-toestand naar een elastische vaste stof. Dit gelatieproces is omkeerbaar in de zin dat de gel op een reproduceerbare manier kan worden teruggebracht naar een welgedefinieerde begintoestand door middel van afschuifkrachten, onder de voorwaarde dat de sterkte van deze afschuifkrachten groot genoeg is. Polyelectrolieten zoals gelatine daarentegen vormen thermotropische gels welke kunnen worden teruggebracht naar een welgedefinieerde begintoestand door verhogen van de temperatuur boven een zekere waarde. In tegenstelling tot polymeren hebben de kleideeltjes van laponite een goedgedefinieerde schijfvorm met nanometer afmetingen en een zeer hoge aspectratio (diameter-dikte verhouding van 25). Dit maakt het laponite-in-water-systeem tot een mesoscopisch modelsysteem van dunne schijfjes, of dunne plaatjes. De ladingsverdeling aan het oppervlak van de kleischijfjes wordt bepaald door de onderliggende kristalstructuur van de deeltjes; een gelaagde silicaat welke qua structuur en samenstelling sterk lijkt op het natuurlijke kleimineraal hectoriet. Ladingscompenserende ionen, aanwezig in de suspensie, omringen het geladen kleideeltje waardoor de kleiplaatjes wisselwerken volgens een zogenaamde “afgeschermd Coulomb-potentiaal” met een quadrupolaire symmetrie. Het bereik van deze interactie kan nauwkeurig worden gevarieerd door de concentratie zouten in de oplossing aan te passen.

Nadat het klei-water systeem nauwkeurig is geprepareerd in de laagviskeuze sol-toestand wordt de suspensie steeds viskeuzer naarmate de tijd na preparatie verstrijkt, totdat de geltoestand is bereikt waar de suspensie zich gedraagt als een elastische vaste stof. Deze “sol-gel overgang” in het tijdsdomein hebben wij gevolgd en gekarakteriseerd door experimentele meting van de dynamische en statische struc-

tuurfactor met lichtstrooiing en kleine-hoek Röntgenstrooiing. Het fysische beeld dat volgt uit de gemeten dynamische structuurfactor is op korte tijdschalen een locale herrangschikking van de kleischijfjes (reorientatie) gevolgd door een veel tragere collectieve beweging van de deeltjes (translatie) over langere afstanden. Terwijl het gelatiepocess voortschrijd in de tijd wordt alleen een toename waargenomen van de karakteristieke tijdschaal van de translationele component van de dynamische structuur factor. Deze tijdschaal neemt toe met minimaal vijf ordes van grootte, totdat het gelatiepunt wordt bereikt. We zijn erin geslaagd om dit gelatiepunt onweerlegbaar vast te stellen als het tijdstip na preparatie vanaf waar op de muren rondom de opstelling een stilstaand “speckle”-patroon is waar te nemen zoals gevormd door het verstrooide laserlicht. De amplitudo, of beter, het contrast van het spikkelpatroon groeit met de tijd en kan worden gezien als de ordeparameter van de overgang.

Het algebraïsch gedrag van de dynamische structuurfactor rond het gelpunt is een duidelijke weerspiegeling van de structurele glasovergang: een algebraïsch verval welke drastisch wordt afgekapt bij de lange correlatietijden. Dit afkappunt divergeert naar oneindig wanneer het gelpunt nadert. Echter, om de gewenste fysische parameters van de overgang kwantitatief vast te leggen binnen het raamwerk van de moderne theorieën hebben we een modelfunctie nodig met meerdere aanpasbare parameters. Zelfs in dat geval kunnen de resultaten geen onderscheid maken tussen een zuivere β -relaxatie of de combinatie van α en β -relaxatie zoals voorgesteld door Götze. Speciaal voor dat doel hebben we een nieuwe analysemethode toegepast, bekend als de wavelet-analyse, welke fluctuaties in de gemeten intensiteit van het verstrooide laserlicht lokaal op de tijd-as analyseert. Wavelet-analyse stelt ons in staat om gedurende het gehele tijdstraject van gelatie de exponent van het algebraïsch vervallende deel van de dynamische structuurfactor nauwkeurig vast te leggen, en tegelijkertijd de kritieke divergentie van zowel de korte als lange tijdsafkap van het algebraïsche deel te volgen zonder gebruik te maken van enig model of fitfunctie. We zijn er als eerste in geslaagd om de relaties tussen de gerelateerde exponenten, zoals gepostuleerd door de moderne theorieën van de glasovergang, experimenteel hard vast te leggen. Wavelet-analyse bleek niet alleen een waardevolle techniek te zijn in dynamische lichtstrooi experimenten in het algemeen. In dit geval bleek wavelet-analyse een essentiële methode te zijn om de gewenste fysische parameters nauwkeurig te bepalen zonder gebruik te maken van vergelijkingen van modelfuncties met de gemeten data. De geldigheid van de beschrijving van de dynamische structuurfactor zoals gemeten vlak voor het gelpunt met de zogenaamde “stretched exponential decay” is door ons met overtuigende argumenten voor het eerst verworpen. Deze argumenten zijn verkregen met wavelet-analyse.

De combinatie van experimentele statische lichtstrooi metingen en Röntgen strooi metingen bestrijkt meer dan vier orden van grootte in de ruimtelijke schaal, van de afmetingen van een enkel kleischijfje tot meer dan honderd maal de gemiddelde afstand tussen de deeltjes. Metingen van de statische structuurfactor brachten voor het eerst de afwezigheid van pakketjes van kleideeltjes aan het licht. Alreeds vanaf het begin van het gehele gelatieproces wordt in de statische structuurfactor een algebraïsche relatie met de golfvector gemeten. Alleen de gerelateerde exponent blijkt in de tijd een continu neerwaarts gedrag te vertonen. We hebben waargenomen dat bij de langere lengteschalen de structuur van de sol-toestand dezelfde is als de structuur van de gel-toestand; de sol-toestand is dus niet vergelijkbaar met een simpele vloeistof maar moet worden gezien als een laagviskeuze voorloper van de onvermijdelijke gel. Tijdens het gelatieproces wordt er nimmer een karakteristieke lengteschaal in het colloïdale systeem waargenomen. Dientengevolge kan de gelatie van onze klei-water suspensies niet verklaard worden door een aggregatieproces, waarbij in de tijd clusters van deeltjes groeien door het aankleven van deeltjes.

We hebben onweerlegbaar aangetoond dat de gel een fraktaal netwerk van colloïdale deeltjes is waarbij de kleischijfjes willekeurig georiënteerd staan en niet, zoals door anderen gesuggereerd, een orientationele ordening vertonen. Deze waarneming staat in tegenstelling met een kortedrahts orientationele ordening zoals werd verwacht op basis van de quadrupolaire symmetrie van de elektrostatische interactie. Nadat er afschuifkrachten aan het werk zijn geweest op de suspensies tonen metingen van de vormfactor aan dat de kleideeltjes zich orientationeel ordenen parallel aan het stromingsveld. Echter, deze ordening is geen eeuwig leven beschoren en verdwijnt op tijdschalen welke vergelijkbaar zijn met de gelatietijd. De nematisch geordende toestand is dus niet de evenwichtstoestand. Op basis van onze waarnemingen hebben wij gesuggereerd dat, anders dan aggregatie, de locale reorientatie van de colloïdale kleideeltjes het mechanisme is achter het fenomeen van gelation in de tijd. Deze locale reorientatie bevrijdt het systeem van spanningsvelden en frustratie door middel van dichtheidsfluctuaties maar laat tegelijkertijd de viscositeit divergeren. Het continue herrangschikken van het netwerk van kleideeltjes kan worden gezien als een gezamenlijk en zelfvertragend mechanisme dat er zorg voor draagt dat het systeem invriest in de glastoestand nog voordat de geordende “vloeibaar-kristallijne” toestand kan worden bereikt.

De sol-gel overgang zoals waargenomen in het tijdsdomein vertoont alle karakteristieke weerspiegelingen van en sterke gelijkenissen met de structurele glasovergang. In het geval van laponite wordt het externe veld gevormd door afschuifkrachten,

in tegenstelling tot systemen waar de temperatuur, druk of dichtheid het externe veld vormt. De resultaten verkregen uit fysische experimenten duiden op een verouderingsproces zoals wordt waargenomen aan de zogenaamde spinglazen en aan onderkoelde vloeistoffen. Bij een verouderingsproces neemt men de ontwikkeling waar van een systeem dat plotseling buiten evenwicht is geplaatst en zich vanaf dat moment bevindt in een glasachtige toestand. Vanuit de theoretische wereld is er een vernieuwde belangstelling voor dit verouderingsproces en de relatie met de glasovergang. Het door ons bestudeerde systeem van colloïdale kleiplaatje-in-water belooft een goede kandidaat te zijn om deze relatie, en de glas overgang in het algemeen, experimenteel te bestuderen.

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