Evolution of structure in electromagnetic suspensions

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Evolution of structure in electromagnetic suspensions

Konstantinos Manikas
Evolution of structure in electromagnetic suspensions

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus prof.dr.ir. F.P.T. Baaijens, voor een commissie aangewezen door het College voor Promoties, in het openbaar te verdedigen op woensdag 24 juni 2020 om 16:00 uur

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“All I know is that I know nothing”
Socrates
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Summary

Suspensions of particles have been attracting scientific interest since the beginning of the 20th century, as they exhibit fascinating properties and promising applications in many fields, e.g. the food industry, cosmetics, medicine, water treatment, paint, and ceramics. If particles have a dielectric or magnetic dipole moment, either permanent or induced, their behavior can be externally controlled by exposing them to an electric or magnetic (EM) field; the particles interact and eventually form structures of particles. Depending on field conditions, the particles can form strings (unidirectional constant field) that evolve and aggregate in the course of time, planes, or networks (unidirectional time-dependent field). The time period over which these different structures can be formed depends on the viscosity of the suspending medium that hinders, through friction, the structure formation of the particles. The formed structures can be used for the effective enhancement of the transport properties of the medium, e.g. dielectric permittivity, magnetic susceptibility, and thermal and electrical conductivity. The control of the structure formation, by tuning parameters like the strength and time dependence of the imposed field, enables the user to tailor the evolution and the eventual structure formed. While the structure formation occurs when the suspending medium is liquid, it is desirable to fixate the structure by solidifying the suspending medium, so that the formed structure persists even in the absence of an imposed field. A possible medium for fixating the structure is a photo-reactive resin. Such resins polymerize when exposed to UV-light, which increases their viscosity, whereby the dynamics is arrested and the structure is fixated. These resins are widely used for stereolithography – a 3D-printing technique, in which every layer is sequentially cured by a light source. The combination of responsive to an external field particles with photo-reactive resins is the primary interest of this thesis. The goal is

- To identify the effect of the relevant physical parameters (e.g.
particle size, field strength, dielectric permittivity, medium viscosity) on the structure formation under an external EM field, which we seek to achieve by way of the following tools:

- To quantitatively characterise the resulting structures, e.g. strings, thick strings, planes, and networks of particles, and
- To identify the dimensionless groups that govern the dynamics, and to eventually benefit from time scaling (even inhomogeneous).

The physical effects included in our model for particle-structure formation are dipole-dipole interactions, excluded volume interactions, Stokes-drag forces, and thermal fluctuations. This many-particle model is solved by means of Brownian Dynamics simulations. The structures that we expect to create are either strings of particles or networks, and combinations of string-like with network-like clusters. To quantitatively characterise string structures, we need to acquire information about their orientation, anisotropy, size, and percolation. We achieve this by organizing particles into clusters (by connectivity) and quantifying the average orientation of their inter-particle vectors (second Legendre polynomial), size of particle clusters, anisotropy of the gyration tensor of every cluster, and the existence of (cluster) percolation. In contrast, the characterisation of network-like structures requires a quantification in terms of branchpoints (number density, degree) and branches (thickness, orientation) of the network. In this thesis, a combination of graph-theory tools with 3D-image analysis techniques, particularly skeletonization, is used to obtain this information, as described in the first part of the thesis.

A procedure has been developed for the systematic simplification and quantitative characterization of structures formed by particles, with a particular interest in networks with thick branches and branch points. Starting from a structure consisting of thick components, the simplification provides a thin skeleton with minimal connectivity. The procedure is composed of five steps. First, the structure given by the Cartesian coordinates of the particles is transformed into a discretized binary 3D image in terms of cubic voxels, from which small cavities are eliminated. After applying the actual skeletonization process, the resulting skeleton is simplified with respect to the branch points in terms of connectivity reduction and triangle elimination. Finally, the fully simplified skeleton is characterized in terms of branch points (i.e. number density, degree), branches (i.e. thickness, orientation), number density of clusters, and existence of percolation.
Unidirectional constant fields are used to study the formation of structures of particles. Both the magnitude of the ratio between the strength of the electric field and the thermal fluctuations, and the volume fraction of particles are varied and the structural evolution of the system is followed. The results show that the characteristic time-scale calculated from the interaction of only two dipoles is also the characteristic time-scale for the collective dynamics emerging from many-particle simulations. If time is appropriately scaled, the ratio between field strength and thermal fluctuations in the range of values we investigate influences only the magnitude of the fluctuations around but not the average behaviour itself. Keeping the ratio between field strength and thermal fluctuations constant and varying the volume fraction of the dispersed particles, we observe that the main characteristics (number density of branch-points, thickness of branches) of the network are increasing monotonously with the volume fraction.

Then, the effect of time-dependent external fields on the structure formation is studied. The strength of the field is increased in one direction and then kept constant for a certain amount of time, with the structure formation being influenced by the slope of the field strength. This effect can be partially rationalized by inhomogeneous time re-scaling with respect to the field strength, however, the presence of thermal fluctuations makes the scaling at low field strength inappropriate. After the re-scaling, one can observe that the lower the slope of the field increase, the more network-like and the thicker the structure is. In a second part of the study, the field is also rotated instantaneously by a certain angle, and the effect of this transition on the structure is studied. It is found that, for small rotation angles ($\theta \leq 20$) the clusters rotate but stay largely intact, while for large rotation angles ($\theta \geq 80$) the structure disintegrates and then reforms, due to the nature of the interactions (parallel dipoles with perpendicular inter-particle vector repel each other). For intermediate angles ($20 < \theta < 80$), it seems that, during rotation, the structure is altered towards a more network-like state, as a result of cluster fusion (larger clusters).

The solidification of the suspending medium, which mimicks the curing of the photo-reactive resin, is represented in our simulations by increasing the viscosity of the suspending medium. It is shown that the effect of the time-dependence of the viscosity can be rationalized conveniently by re-scaling the time in the Fokker-Planck equation, if the time-dependence of the viscosity is given a-priori. Specifically, since the viscosity of the curing resin is a positive and monotonously increasing function, as observed experimentally, one can study the effects of the viscosity increase by time re-scaling, akin to the time-temperature superposition principle, but here also in the presence of noise. Therefore, instead of
performing simulations with a continuously increasing viscosity, we advocate performing simulation at a constant (low) viscosity and subsequently rescale time (inhomogeneously) for re-interpretation of the simulation results. In practice, the viscosity increase is so drastic that further evolution of the particle structure can be considered as arrested after the characteristic transition-time of the viscosity is reached.
Chapter 1

Introduction

1.1 Background

Suspensions of particles exhibit intriguing properties and have a lot of applications, e.g. in the food industry [1], cosmetics [2], medicine [3], water treatment [4], paint [5], and ceramics [6]. This is one of the reasons they have been a topic of scientific interest since the beginning of the 20th century [7, 8]. Their microstructure is interesting both from a scientific and an industrial point of view, and determines the macroscopic properties of the suspension, especially the mechanical ones [9, 10].

One particular group of suspensions is the electromagnetically active suspensions. An external electric or magnetic field affects a suspension of electromagnetically active particles (e.g. dielectric, magnetic) by inducing dipoles to the particles, due to the difference in the dielectric permittivity or magnetic susceptibility between them and the medium [11]. The induced dipoles interact [11] and structures of particles are formed [12]. The particles can form different structures depending on the field conditions, e.g. strings [13], that evolve and aggregate in time [13], planes [14], and networks [15].

Several studies concerning the characteristics of electromagnetically active suspensions have been performed. The arrangement of particles into structures can enhance the properties of the composite material, especially in the direction along the structure formed [14, 16]. The transport properties are affected considerably by the structures formed, due to percolation paths and in general smaller inter-particle distances between the particles [15]. The suspensions that contain filler particles responsive to an external field are called electro-
Chapter 1. Introduction

/magneto-rheological fluids. The structure formation occurs on $O(1\text{s})$ time scales and results in an increase of the viscosity [12, 17–20]. The response of these systems under shear has been extensively investigated [21, 22]. The effect of the Mason number [23], which is the ratio of viscous to magnetic forces, has been explored with respect to mixing on micrometer scales [24–26] with a rotating field.

One of the most influencing factors for the behaviour of such systems is the suspending medium. Most studies focus on the behaviour of the system in a liquid suspending medium, as the structure formation is accessible under experimental conditions. However, it is desirable to fixate the structure by solidifying the suspending medium, so that the formed structure persists even in the absence of an imposed field. The fixation of the structure could be achieved using a photo-reactive resin as a medium [27, 28]. The polymerization of such resins is triggered when exposed to UV-light, increasing their viscosity, whereby the dynamics is arrested and the structure is fixated. These resins are widely used for stereolithography (SLA) [29], a 3D-printing technique in which every layer is sequentially cured by a UV-source. The low viscosity of the resins before curing makes the structure formation possible within the usual time-scales ($O(1\text{s})$) of 3D-printing. In this thesis, the combination of photo-reactive resins with responsive to an external field particles is of primary interest.

Additive manufacturing (or 3D-printing) has been a topic of extensive research for a long time [30] and it still is an active research field [31]. The materials used include metals [32], polymers [33], ceramics [34] and combinations of them [31]. The range of applications is wide: aerospace applications (cabin interiors) [35], medicine [36], anthropology [37], and design [38]. In this thesis, the feasibility of 3D-printing electromagnetic suspensions is explored.

The combination of photo-reactive resins with electromagnetic particles for 3D-printing could amount to interesting applications for polymer-composite materials, and functionalized 3D-printed objects. In the polymer-composite route, the incorporation of dielectric, magnetic or conductive functionality to the matrix material [39–41] is always a challenging application. Additionally, specific structures of particles can be selectively formed inside a complex geometry by the controlled use of an external electric or magnetic field. In terms of 3D-printed objects, personalized hearing aids [42], flat lenses with a gradient of concentration of particles that have the functionality of their curved counterparts [43], piezoelectric or Hall effect sensors [44], and direction-specific thermally or electrically conductive composites [15] could be achieved.

The structural evolution of electromagnetic suspensions in an external field greatly depends on the motion of particles through the suspending fluid, and can
be simulated with a variety of methods depending on the effects (e.g. hydrodynamic interactions) and scales (length, time) that one desires to resolve, e.g. in ascending length-scale Molecular Dynamics [45], Dissipative Particle Dynamics [46], Stokesian Dynamics [17], Brownian Dynamics [47, 48], Lattice-Boltzmann method [49] or Finite Element Method [24, 50]. The system we are interested in exhibits disparity in length- and time-scales, as it consists of monomers of the liquid matrix, with the size of its constituents on the order of nm, and suspended particles on the order of µm. A simulation technique suitable for this situation is Brownian Dynamics (BD) [51], where the equations of Newton are solved in the overdamped limit, so no acceleration is present (i.e. correlations in velocity vanish within a single timestep of the integration) [52] and interaction (e.g. dipole-dipole [11, 12, 53]) and thermal forces are taken into account. BD can resolve spatial effects on the order of the size of the particle and on macroscopically relevant time scales [11, 12, 53].

1.2 Objective of the dissertation

The objective of this dissertation is the formulation of semi-quantitative design rules for making the desired electromagnetically active structure. Therefore, the main goal is:

- To identify the effect of the relevant physical parameters (e.g. particle size, field strength, dielectric permittivity, medium viscosity) on the structure formation under an external electric or magnetic field,

which we seek to achieve by way of the following tools:

- To quantitatively characterise the resulting structures, e.g. strings, thick strings, planes, and networks of particles, and

- To identify the dimensionless groups that govern the dynamics and to eventually benefit from time scaling (even nonlinear).

1.3 Overview of the dissertation

For achieving these objectives, we use a computational approach, where the physical effects included in our model for particle motion are dipole-dipole interactions, excluded volume interactions, Stokes-drag forces, and thermal fluctuations. This many-particle model is solved by means of BD simulations. The
expected structures are ranging from strings to networks, and combinations of them (e.g. string-like and network-like clusters). String structures can be quantitatively characterised, if knowledge concerning their orientation, anisotropy, size, and percolation is acquired. The realisation of this arises by the organisation of particles into clusters (by connectivity) and quantifying the average orientation of their inter-particle vectors (second Legendre polynomial), size of particle clusters, anisotropy of the gyration tensor of every cluster, and the existence of (cluster) percolation. The characterisation of networks and network-like structures is considered much more complicated as one has to quantify the branch-points (number density, degree) and branches (thickness, orientation) of the network. In this thesis, a combination of graph-theory tools with 3D-image analysis techniques, particularly skeletonization, is used to obtain this information, as described in the first part of the thesis.

In Chapter 2, a procedure is developed for the systematic simplification and quantitative characterization of structures formed by particles, with a particular interest in networks with thick branches and branch points. The simplification is applied on a structure of thick constituents and extracts a thin skeleton with minimal connectivity. In particular, a discretized 3D-binary image is created based on the Cartesian coordinates of the particles. Small cavities between the particles are eliminated. The skeletonization process is applied to the image, and the resulting skeleton is simplified with respect to the branch points in terms of connectivity reduction and triangle elimination. Finally, the fully simplified skeleton is characterized in terms of branch points (i.e. number density, degree), branches (i.e. thickness, orientation), number density of clusters, and existence of percolation.

In Chapter 3, unidirectional constant fields are used to study the formation of structures of particles. The volume fraction of particles and the ratio between the thermal fluctuations and the strength of the external field are varied, and the effect on the structure formation is investigated. The characteristic time-scale resulting from the pair-interaction between dipoles is found to agree with the one emerging from the collective dynamics of many-particle simulations. The average behaviour of the structure formation is independent of the ratio between the thermal fluctuations and the field strength, when the time is scaled properly; the magnitude of the fluctuations around the observed behaviour, however, is influenced. We observe that the main characteristics (number density of branch-points, thickness of branches) of the network are increasing monotonously with the volume fraction, if the ratio between field strength and thermal fluctuations is kept constant and only the volume fraction of the suspended particles is altered.
In **Chapter 4**, the effect of time-dependent external fields on the structure formation is studied. The field-strength is increased linearly until, after a certain transition time, the field is kept constant. The structure formation is influenced by the transition time. The time-dependent field-strength is used to non-linearly transform the time to map the various transition-time cases to the constant-field case for the purpose of reducing the complexity, see Fig. 1.1, however, this transformation is of limited use when thermal fluctuations are relevant. In terms of transformed time, one can observe that the lower the slope of the field increase, the more network-like and the thicker the structure is. In a second part of the study, the orientation of the field is altered instantaneously by a certain angle and the effect of this transition on the structure is studied. The formed clusters are found to rotate remaining largely intact for small rotation angles ($\theta \leq 20$), while for large rotation angles ($\theta \geq 80$) the structure disintegrates and then reforms, due to the nature of the interactions (parallel dipoles with perpendicular inter-particle vector repel each other). For intermediate angles ($20 < \theta < 80$), cluster fusion is taking place, resulting in larger clusters and more network-like structures.

In **Chapter 5**, the viscosity of the suspending medium is increased to emulate the solidification occurring during the curing of a photo-reactive resin, e.g., in 3D-printing. It is shown that the effect of the time-dependence of the viscosity on the structure formation can be rationalized by a non-linear transformation of time, if the time-dependence of the viscosity is given a-priori, akin to
the time-temperature superposition principle, but here also in the presence of noise. Therefore, instead of performing simulations with a continuously increasing viscosity, we advocate performing simulation at a constant (low) viscosity and subsequently transform time (nonlinearly) for re-interpretation of the simulation results, see Fig. 1.1. In practice, the viscosity increase is so drastic that further evolution of the particle structure can be considered as arrested after the characteristic transition-time of the viscosity is reached.

In Chapter 6, a discussion of the presented results, as well as some suggestions for further research are presented.
Chapter 2

Characterization of structures of particles

Abstract

A methodology for the characterization of particle structures, especially networks, is developed. This scheme combines 3D image analysis techniques with graph theory tools for the simplification of a structure of thick agglomerates to its skeleton. The connectivity graph of the initial structure is compared with the one of the corresponding skeleton, as a measure of simplification. Examples are used to illustrate the effectiveness of our scheme. Particle structures obtained by Brownian Dynamics simulations are characterized qualitatively and quantitatively. Instead of looking at the characteristics of the structure at the level of the individual particles or neighborhoods of particles, our scheme results in quantitative measures of the network, e.g. the number density of branch-points, the degree of branch-points, and the thickness and the orientation of the branches.

2.1 Introduction

Suspensions of particles have been a matter of scientific interest since the beginning of the 20th century [7, 8]. These systems have a lot of applications, e.g. in the food industry [1], cosmetics [2], medicine [3], water treatment [4], paint [5], and ceramics [6]. Their microstructure is interesting both from a scientific and an industrial point of view. The microstructure determines the macroscopic properties of the suspension, especially the mechanical ones [9, 10]. In the following, we focus on the characterization of the microstructure of this kind of systems, and especially of network structures.

Many techniques have been used for the characterization of the arrangement of the suspended particles in a suspension, often using only two-particle correlations. The most common is the pair-correlation function, \( g(r) \) [54–59], and related to that the fractal dimension [60, 61]. The radial pair-correlation function is a powerful tool that quantifies the distribution of the inter-particle distances, which, however, give an accurate description only if the structure is homogeneous and spherically symmetric. The cylindrical pair-correlation function in two dimensions is another example [13, 16]. To quantify the orientation of the connector vector between any two bonded particles, the second Legendre polynomial, \( S_2 \) [16], is used, which quantifies the orientation of the bond direction with respect to an external (imposed) direction.

The information obtained by studying the relative arrangement of only two particles is many times insufficient, so a variety of techniques have been developed concerning the nearest neighbors (\( \mathcal{O}(10) \)) of particles. The Voronoi tessellation is a characterization technique, which is used in various kinds of systems [62–66], particularly, for the characterization of glass forming polymers [67] and in the context of self assembly [68]. For the Voronoi polyhedra, one can quantify their coordination number, the so-called isoperimetric quotient, and the principal moments of inertia [69], which in turn are used for defining measures for prolateness, oblateness, and sphericity/uniformity. The Voronoi tessellation, in combination with its dual Delaunay tessellation [70], is used for determining voids, between atoms or particles [71, 72]. Furthermore, adaptive common neighbor analysis in combination with neighbor distance analysis are used mainly for crystalline systems [73], where the Voronoi polyhedra are highly perturbed by slight alternations of the coordinates. Another technique that provides information about the heterogeneity of networks particularly on intermediate length-scales is the Minkowski functionals or quermass integrals [58], based on integral geometry. With this technique, the heterogeneity and the pore-size distribution can be analyzed on different length-scales. Another
analysis technique is based on the gyration tensor [16, 74], calculated for certain clusters of particles, as one can extract information about the size, shape [74], and main orientation [16] of the cluster. Particularly, for analyzing the arrangements of particles in colloidal gels, various other techniques have been employed, namely, the distributions of bond angle [56], angles in bonded triangles [56, 73], length of straight paths [75], pore size [76], and the contact distributions [59].

All the above methods require the positions of the particles, although they are not always accessible experimentally. For low-volume fractions, the characterization of colloidal-particle structures can be performed by electron microscopy [77–80] or by static scattering techniques [81, 82], where the latter are directly related to the pair-correlation function, $g(r)$. In denser systems, multiple scattering is observed, which needs to be eliminated or at least limited, e.g. by cross-correlation techniques [83, 84], index matching [85], or complementary small-angle neutron scattering [86, 87]. The pore-size distribution can be measured in solids, and even under certain conditions in fluids (Cryo-SEM) [57, 88]. The most detailed local structural and dynamical information in dense systems has recently been obtained with confocal laser scanning microscopy. This direct visualization technique has been used to study colloidal gels and glasses [89–92] via time-resolved determination of the three-dimensional positions of the particles.

Many characteristics of the particle arrangement can be obtained by the techniques summarized before, however, in networks other features are of interest as well. Networks are observed in colloidal suspensions [56], neural systems [93], polymers [94] and elsewhere [95]. The characterization of colloidal networks could give some insight about the microscopic characteristics that govern the properties of network as a whole, i.e. mechanical properties [9], and transport properties through the network itself [15] and through the suspending medium [96]. For networks, the amount of branch-points (BP), the degree of BP (how many branches emerge from a BP), the thickness of the branches, the existence of percolation, and the number of clusters are key features. These features can be assessed qualitatively by visual inspection (“pattern recognition”), however, it is difficult to perform a quantitative analysis of networks with thick branches and BP in an automated way. To identify the essence of the structure by exploring the characteristics of the neighborhoods of particles (Voronoi) or by cluster analysis turns out to be cumbersome, if not impossible, due to the extensive thickness of the structures (too many particles, with Voronoi cells of small volume and isotropic shape); the essential features of the structure are actually blurred by the multitude of particles. It is proposed in this chapter to analyze such thick structures by a combination of an image analysis technique
called skeletonization [95, 97], and a connectivity graph analysis [98]. Analysis techniques for connectivity graphs have been developed and used extensively in the past [99, 100], however, rather than simplifying the connectivity graph of the structure, we apply a simplification on the actual structure. Given the 3D image of a structure, the skeletonization technique makes use of a parallel medial thinning algorithm [101] for the reduction/thinning of the structure to an infinitely thin representation. The characterization of osteocytes has already been performed with this kind of techniques [95, 97], although it is also used for other applications, e.g., testing the geometry of porous media obtained by 3D printing [102]. Assessment of the local thickness of particle-structures is possible, defined in terms of the sphere of maximum radius that fits in the structure at that point [103]. The connectivity of the final structure can be simplified using tools of connectivity-graph analysis. The simplification can result to a totally simplified graph, highlighting the essential connectivity between the nodes/particles. As totally simple graph, we define the graph that has zero global and local clustering coefficients.

In this work, an effort towards the complete quantitative characterization of particle networks is made, especially when thick sub-structures are present. The full detail on the particulate level is going to be translated to the network level, leading to a simplified skeleton where BP and branches can be quantified easily. This chapter is organized as follows. First, our scheme for structure simplification is introduced in Sec. 2.2, discussing in detail also the pre- and post-processing of the structure. After introducing characterization tools for the skeletonized network-structure in Sec. 2.3, the procedure is validated on some characteristic examples in Sec. 2.4. The effect of resolution when converting the particle-structure into a 3D binary (voxel) representation is examined in Sec. 2.5. In Sec. 2.6 configurations obtained by Brownian Dynamics (BD) simulations [52] with different interaction potentials are analyzed and compared. Conclusions are drawn in Sec. 2.7.

2.2 Method of simplification of thick networks

In this section, we introduce a technique for the reduction of a network of particles to the bare skeleton of the actual structure. For that purpose, we employ an already developed method called skeletonization [95]. In this section, we describe the methodology we use, with all the steps presented in the flowchart in Fig. 2.1. The procedure includes some pre-processing steps, the creation of a 3D binary image, and the actual skeletonization process, where the actual
2.2. Method of simplification of thick networks

![Flowchart](image)

Figure 2.1: Flowchart of the basic steps of our methodology.

reduction of the structure happens, see Subsec. 2.2.1. The result of this process is a skeleton (backbone of filled voxels) in the form of a 3D binary image. This skeleton is subjected to refining or simplification, see Subsec. 2.2.2, before the actual quantitative characterization of the network takes place.

### 2.2.1 Skeletonization

In this section, the 3D image creation and skeletonization of our structures is described. Our purpose is to characterize structures of particles obtained by particle-based simulations. However, the method can be also applied to configurations obtained by experimental techniques [77, 95]. In the rest of this section, the steps that are necessary for numerically-obtained structures are discussed, and a distinction is made as far as the experimental configurations is concerned.

Initially, an empty 3D mesh tessellating the simulation box is drawn and a blank (all voxels set equal to zero) binary image is created. For the discretization, the voxel size is chosen such that the radius of the particles $R_p$ is commensurate to 10 voxels, i.e., $R_p = 10 a_{\text{vox}}$, with $a_{\text{vox}}$ being the edge length of the voxel. The volume of a particle is represented by the voxels whose cen-
Figure 2.2: (a) Schematic representation of the initial structure of particles (blue), in a cubic grid. (b) Configuration of the particles (blue circles), and binary representation (squares). The blue squares are part of a particle and the red ones part of a bond. (c) Same configuration as in (b), where the pixels belonging to a cavity have been filled (green squares).

...ters are separated from the center of the particle by less than $1.10 R_p$, see Fig. 2.2b. Additionally, particles that are bonded (condition for a bond between particles $i$ and $j$ is $|r_{ij}| \leq 2.20 R_p$ in our case, where $r_{ij}$ is the inter-particle vector) are represented by an additional cylinder of diameter $2.20 R_p$, between the bonded particles, see Fig. 2.2b. The reason for choosing the diameter of the particles slightly larger than the actual value is to create sufficiently solid necks between bonded particles. Empty voxels between bonded particles are unwanted, as such empty voxels would result in artifacts, since the thinning process (in the skeletonization) is initiated from the empty voxels next to the surface. All the bond-cylinders are introduced to avoid empty voxels between closely packed particles, e.g., close random packing. The intention is that closely packed particles appear as one body in the skeletonization process, to avoid any empty voxels between the particles. Another reason for choosing this bond-length originates from the interaction potential used to generate the structure: the ratio $U_{\text{exv}}/k_B T$ is lower than 10% at a distance of $2.2R_p$, where $U_{\text{exv}}$ is the excluded volume potential and $k_B T$, the thermal energy. In case of polydisperse systems, the above procedure would have to be amended. For any pair of particles with radii $R_{p,i}$ and $R_{p,j}$, a bond should be identified if the inter-particle distance satisfies the condition $|r_{ij}| \leq 1.10 (R_{p,i} + R_{p,j})$. And, the cylinder representative of the bond should have a diameter equal to the diameter of the smaller of the two particles.

There is still a chance of finding empty voxels between closely packed particles in the form of cavities, a cavity being a domain of empty voxels that is...
2.2. Method of simplification of thick networks

smaller in extent, in every direction, than the size of the periodic simulation box. Cavities inside the structure create a surface of voxels after the skeletonization. Despite the fact that cavities are of large topological significance [104–106], in the systems studied in this chapter (i.e., colloidal particles structures) only cavities between particles in close distances are expected. As this is not of interest in this chapter, these cavities are filled, see Fig. 2.2c. In order to assess the severity of filling the cavities, their number density and volume fraction are quantified,

\[ n_c = \frac{N_c}{N_p}, \]  
\[ \phi_c = \frac{V_c}{V}, \]

before actually applying the filling. Here, \(N_c\) is the total number of cavities and \(N_p\) is the number of primary particles, while \(V_c\) is the total volume of all the cavities and \(V\) is the volume of the box. Normalized in this way, the quantities are defined in a way that they are independent of the size of the box.

As already mentioned, the steps necessary for processing experimentally obtained structures are also discussed. The only step that is necessary for experimental results is the last one concerning the filling of the cavities. This step is related to the technique with which the structure has been measured, and an appropriate choice needs to be made with respect to the filling of cavities. The reason cavities are unwanted during the skeletonization process were mentioned earlier. Another experimental issue is the noise of the image, and small artefacts created by the method with which the image is obtained [95].

After representing the actual structure as a 3D binary image, we use a 3D medial axis thinning algorithm [101] for reducing it to a one-voxel-thick skeleton. This technique is used to determine network structures in biological systems [95, 97]. It was developed for non-periodic systems. However, we intend to use it for configurations that comply with periodic boundary conditions. To avoid issues of periodicity, we use as an input an image that has an edge length of \(2L\), where \(L\) is the box-length or the primary structure. Our primary box is located exactly in the middle of the image, and it has an extra layer of \(L/2\) thickness in every direction which is created by using periodic images of the primary box. The effect of choosing the thickness of the extra layer different from \(L/2\) is not studied further in this chapter, because the structures we will be analyzing have their characteristic features on length scales significantly smaller than \(L/2\), and so this choice is not expected to lead to any limitation. The output of the skeletonization is a 3D binary image, where the skeleton is represented by the
2.2.2 Simplification of a skeleton

As already mentioned, the skeleton needs post-processing after the skeletonization. Of highest importance in a network is the existence and location of branch-points (BP). To this end, we identify the neighboring voxels by applying a distance criterion for defining bonds, \( r_{\text{cut}} = 1.05 \sqrt{3} a_{\text{voxel}} \). To locate the neighboring voxels of a skeleton voxel, one should check if some of the 26 neighboring voxels (implied by the grid) also belong to the skeleton. The criterion thus covers the neighbors with a common face, edge, or corner (maximum distance of \( \sqrt{3} a_{\text{voxel}} \)). However, there are some issues arising from this, admittedly natural, choice of a distance criterion. The problem is that if two branches emanate from a common point, there is a high probability that the first voxels of the branches heading out from the BP are also neighbors to each other. This means that there will be small triangles of bonded voxels. This is unwanted, as this would eventually result in more than one branch-point on the length scale of one primary particle’s radius, i.e. voxel length. Therefore, one must post-process the skeleton to simplifying it in this respect.

Identification of the BPs proceeds along the following steps. First, we determine the voxels that have more than two bonds, and the connectivity between these voxels, see Fig. 2.3. If there are connected components in this graph, we replace them by one voxel at the position of the center of mass of the voxels that belong to that component. This new voxel inherits the connectivity/bonds from its “parents”, where “parents” are the voxels that it is replacing. Then, we reproduce the skeleton with the updated voxels and bonds. The reproduced skeleton may contain triangles of voxels, which relate to a few voxel branches attached to BPs of the skeleton. If there are triangles in the graph, we replace them with one voxel in their center of mass. This new voxel inherits the connectivity/bonds from its “parents”. In the case that long bonds are created by the replacement process, we try to shorten these bonds. For this purpose, we add voxels in the middle of the inter-voxel separation vector (bond), if \( r_{\text{bond}} > 2 a_{\text{voxel}} \), so that \( r_{\text{bond}} \leq \sqrt{3} a_{\text{voxel}} \). Finally, one does not want several BPs in a volume occupied by a single primary particle, so an additional step is needed for the proper quantification of the BPs, see Sec. 2.3.

In the end, three smoothing steps are applied to the resulting skeleton, where
Figure 2.3: Example of immediate connectivity between branch-points of a skeletonized structure. Only the branch-points and the connections between them are depicted, while the rest of the voxels are ignored in this graph. The colors indicate the different clusters of connected branch-points.
the position of all the particles that have two bonds is altered according to

\[ r_i^{\text{new}} = w r_i + (1 - w) \frac{r_{i-1} + r_{i+1}}{2}, \quad \text{(2.3)} \]

where \( i \pm 1 \) denotes the connected particles, and \( w \) is the weight of the smoothing step, in our case \( w = 1/3 \). If \( w = 0 \), the position of the voxel moves exactly in between the two particles, and if \( w = 1 \), the particle stays at its original position. The reason why one should apply some smoothing steps is that the position of the skeleton voxels is dictated by the grid of the binary image used during skeletonization. The smoothing steps help to get rid of unnatural kinks in the skeleton. However, a large number of smoothing steps would result in shrinkage of closed structures, as for example circles, and other unwanted distortions of the structure.

### 2.2.3 Quantification of simplification

Before we proceed with applying the simplification, we introduce the global and local clustering coefficients for estimating the complexity of the connectivity graph. The global clustering coefficient is defined by the number of triangles divided by the number of triads present in the graph [107, 108]. The local clustering coefficient of a node is the number of connections between its neighbors, divided by the amount of potential connections between its neighbours. It becomes unity on a fully connected graph (every vertex is connected to every other vertex) and has typical values ranging from 0.1 to 0.5 in many small-world real-life networks [109].

By following the simplification procedure presented in Secs. 2.2.1,2.2.2, we obtain a skeleton of the simplest possible connectivity, i.e., there are no parallel edges, triangular connections, etc. All the closed triangles, and interconnected 3-bonded voxels have been simplified. The effectiveness of the simplification is investigated with the global clustering coefficient and the bonds per particle/voxel. The global clustering coefficient, and also the local clustering coefficient of the nodes, has a finite value on the initial connectivity graphs of the structures. However, after the application of our simplification scheme these measures (both global and local clustering coefficient) drop to zero, which corresponds to the disappearance of triangles or complex connections, between the nodes. So our final connectivity is far simpler than the initial one. The bonds per voxel is reduced in comparison to the bonds per particle, as a result of the simplification.
2.2.4 Particle-to-voxel transition

The structures targeted for simplification are structures of particles of certain size. However, for turning the structure to a 3D-binary image, a certain resolution, $a_{\text{voxel}}$, has to be chosen. This resolution should be capable of capturing the characteristics of the structure microscopically, and be able to roughly represent the spherical surfaces in terms of general shape (i.e., multiple voxels per surface of one particle). To this end, the resolution of the binary image should be much finer than the particle-size, which means that multiple voxels in a row are needed to span the diameter of a primary particle. Conclusively, the resulting simplified skeleton has significantly more voxels in absolute numbers than primary particles. That being said, one should note that the skeletonized structure is less complex than the original one, as the reduction of the clustering coefficients shows (see Subsec. 2.2.3).

2.3 Characterization of a simplified skeleton

The structure of the totally simplified, and thus easier to characterize, skeleton described in Sec. 2.2 is quantified in terms of branch-points (BP) (number density, degree), branches (thickness, orientation), existence of percolation, and number of clusters. Details concerning these characteristics are given in the following.

The BPs are identified by the number of their bonds to neighboring voxels in the simplified skeleton. Every voxel bearing three or more bonds is identified as a BP. As already mentioned in Subsec. 2.2.2, it is unphysical to have more than one BP in a volume occupied by a single primary particle, however, this artefact can arise due to the skeletonization procedure (during the reduction of the medial surface to the medial axis, the paths created depend on the resolution and the noise of the medial surface) [101]. To avoid such unphysical situations, we proceed as follows. We identify the BPs that have $|r_{I,J}| \leq 2R_p$, where indices $I,J$ refer to BPs, and we introduce bonds between these BPs. We neglect the rest of the skeleton (voxels that are not BPs), and then the independent clusters of this new connectivity graph are counted as BPs. This step is needed due to the nature of the technique and the structures of particles. Similarly it has been found [101] that when a noisy binary image is skeletonized, first one obtains the medial surface, and then this can be reduced to the medial axis, although the medial axis for different resolution is influenced by the noise on the surface. Therefore, a plane where all the voxels have one of the three coordinates $(x, y, z)$
equal, will be reduced to one branch, however, the same surface with noisy voxel positions is going to create multiple branches. This problem is more prominent when curved planes are present. In this chapter, only the medial axis is used, and not the medial surface. After this BP-reduction step, the number density of branch points per volume is given by

\[ n_{\text{BP}} = \frac{N_{\text{BP}}}{N_p}, \]  

(2.4)

where \( N_{\text{BP}} \) is the absolute number of BPs, and \( N_p \) is the again amount of primary particles. By way of its normalization, \( n_{\text{BP}} \) is independent of system size. In addition, also the average degree of the BPs can be studied, \( \langle d_{\text{BP}} \rangle \). The degree of a BP, \( d_{\text{BP}} \), is defined as the number of bonded voxels in the simplified skeleton. For the BPs that are replaced during the final step (several BPs inside a primary particle), we use the average degree of the replaced BPs as the degree of the new BP. The difference of the average degree of the replaced BPs with the actual degree of the new BP is insignificant for the structures studied in this chapter. These numbers could differ in some specific cases, e.g. a BP with large volume and few branches emerging from it; in this situation, the averaged degree would be larger due to the complicated connections emerging from the skeletonization of the BP, while the degree of the replaced BP would be the number of branches emerging from it.

The characterization of the branches of a network has two components. The first one concerns quantifying the local orientation of the branch, and the second is the estimation of its thickness. The orientation is defined as \( \hat{\mathbf{e}}_i = (\mathbf{r}_{i-2} - \mathbf{r}_{i+2})/|\mathbf{r}_{i-2} - \mathbf{r}_{i+2}| \) for every voxel \( i \), where \( i \) is neither a BP nor directly connected to a BP, and the notation \( i \pm 2 \) refers to the next-nearest neighbors along the branch. This definition of the orientation is such that is forward-backward symmetric. Also, it is good to avoid defining orientations based on the directly bonded voxels, since then only 26 discrete directions (13 orientations) would be possible due to the representation on a cubic grid. Choosing voxels that are four bonds apart alleviates this problem substantially. The resulting orientation is an approximation of the tangent of the skeleton at the specific point. For the estimation of the thickness of a branch, we consider the orientation \( \hat{\mathbf{e}}_i \) of the branch at that specific point on the skeleton \( \mathbf{r}_i \); in the plane perpendicular to that orientation, we search (starting from the center, i.e., the point on the skeleton) for the edge of the primary image/structure, an idea similar to [110]. Specifically, a grid with voxel size \( a_{\text{voxel}} \) is created on the plane. The pixels on the plane/grid obtain their values with respect to the nearest voxel belonging to the initial binary image, see Fig. 2.4. The nearest
2.3. Characterization of a simplified skeleton

Figure 2.4: (a) Example of skeleton structure (red), where specific particle of skeleton (black) are indicated together with the orientation vector defined by the skeleton at this point (green). (b, c) Zoomed-in view of the indicated particles, with the plane normal to skeleton-orientation vector.

to $\mathbf{r}_i$ empty voxel is located, and the thickness of the branch $d_B(i) = 2d_{\text{min},i}$ is calculated for every $i$, where $d_{\text{min},i}$ is the distance between $\mathbf{r}_i$ and the nearest empty pixel. The average of all the values, i.e. for all voxels belonging to a branch, will give the average branch thickness, $\langle d_B \rangle$. This quantity will be measured in units of $R_p$.

The orientation vector defined above and used for the determination of the branch thickness can also be used, obviously, to quantify the orientation distribution, namely in terms of the second Legendre polynomial, $S_2$, defined as

$$S_{2,\hat{u}}(\hat{n}) = \frac{3}{2} \left\langle (\hat{n} \cdot \hat{u})^2 \right\rangle - \frac{1}{2},$$  \hspace{1cm} (2.5)

with orientation vectors $\hat{n}$ of the skeleton and reference orientation $\hat{u}$, both of unit length. $S_2$ is an average measure of the orientation with respect to a reference orientation $\hat{u}$. It takes the value $-0.5$ if the distribution of the orientation vector $\hat{n}$ contains only vectors perpendicular to $\hat{u}$, it is zero if the distribution of the orientation vector is isotropic, and it equals unity for a distribution of orientation which contains only vectors parallel to $\hat{u}$. Often, the reference orientation is taken one of the main directions $x, y, z$. 

One could assume that, once the BP-reduction has been applied, also the branches themselves would need to be reduced. However, since the need for BP-reduction originates from noise in the medial surface, the reduction of branches is not necessary, as they already belong to the medial surface. As a consequence, we argue that the results concerning thickness and orientation of the branches will not be altered by reducing the branches. For more details on this point, see Sec. 2.5.

The existence of percolation in each direction of the box is also investigated. One tries to establish in-box pairing between any two voxels that are close to two opposite faces of the simulation box ("close to" implying that they have a bond crossing that respective face of the box).

The number density of the number of clusters, $n_{cl}$, is defined by identifying the number of independent components in a connectivity graph of the skeleton. This quantity is reported again with the same normalization as BP number density, Eq. 4.12.

## 2.4 Validation of the proposed procedure

Some example structures are used to explore the suitability of the technique. The examples are chosen to prove that the procedure outlined above can handle the issues described in Introduction (i.e., the existence of thick branches, thick BPs). Also, the possible existence of cavities is covered in one of the examples. The conclusions of this section serve as validation of the proposed procedure for reducing particle-structures only, and no further measurements or quantitative results about the resulting skeleton are presented in this Section.

For the example structures, an FCC crystal structure is used to create them. Initially, the whole box is filled in with an FCC crystal structure of points. The different structures are then created with a distance criterion from a line or circle. The resulting structures of particles are a thick chain of particles, two hollow structures: a ribbon with a tunnel in the middle and a chain with a cavity in the middle, and finally a multi-structure of a torus and a rounded cylinder. All the structures presented in this Section are not obtained by simulations of a physical system. They were created as example structures to which our procedure can be applied for testing.

All our structures have periodic boundary conditions. However, some of the structures are smaller than the box, i.e. they do not span the box in any direction.
2.4. Validation of the proposed procedure

2.4.1 Thick chain

A simple example, c.f. Fig. 2.5, is used to demonstrate the technique. Indeed, the skeletonization technique manages to reduce a thick chain of particles to a thin line of voxels, as expected. One can observe the final skeleton together with the initial image in Fig. 2.5b.

2.4.2 Hollow structures

A more complicated example of a ribbon with a tunnel, see Fig. 2.6, is used to further test the technique. One can observe the final skeleton in Fig. 2.6b. The structure is successfully simplified, and the closed loop is preserved.

An example of a cylinder with a cavity inside, see Fig. 2.7, is used to illustrate the importance of filling cavities. The resulting skeletonized structure contains a blob of voxels around the (original) cavity in the middle. This structure is unwanted for the characterization of the skeleton, as explained earlier. This problem is solved by filling the cavities that are not connected to the planes of the box, i.e., by using the procedure described in the previous section.
Figure 2.6: Hollow structure. (a) Original arrangement of particles (dark blue). (b) Corresponding skeleton (dark blue), with superposed original particles (light blue).

Figure 2.7: Thick chain with a cavity in the interior. (a) Original arrangement of particles (dark blue). (b) Corresponding skeleton (dark blue) if cavity-filling is not employed, with superposed original particles (light blue); particles with more than two bonds in the skeletonised structure are colored green.
2.4. Validation of the proposed procedure

2.4.3 Torus and rounded cylinder

One can see three more complicated examples in Fig. 2.8. These examples contain a torus structure (thick ring of particles) and a rounded cylinder structure. These structures can be seen as separate structures in Fig. 2.8a, in contact at four different points in Fig. 2.8b, and in total contact in Fig. 2.8c.

One can observe the difference in the final skeleton between the different initial images. In Fig. 2.8a, one can see the two disconnected components of the skeleton. The first is the simplification of the rounded cylinder structure, and the second of the torus structure. The shape of the skeleton thus properly represents the initial image. In Fig. 2.8b, one can see the same components of the skeleton inter-connected. The connections are located on the points of contact. In Fig. 2.8c, one can observe only a thin chain of voxels as skeleton. This happens because the two structures (torus and cylinder) are expanded in such a way, that the whole structure is a big agglomerate of voxels with no empty voxels, neither tunnels nor cavities. This example is also a sign that one should be careful with the creation of the initial image. The increase of the radius of the particles should be done with care, since the structure may be altered as in this case. The solution we propose is, as detailed in the previous section, a slight increase of the radius of the particles to avoid small gaps due to the geometry of our primary particles, the introduction of cylinders to the particles we consider as bonded, and the coverage of the cavities of the structure.

Figure 2.8: Torus with cylinder. Original particle arrangement (light blue) and skeleton (dark blue), in different states of contact: (a) totally separated, (b) four-point contact, and (c) total contact.
2.5 Resolution analysis

In this section, we use a structure of an anisotropic network structure, to examine how the results of the structure quantification change upon variation of the number of voxels used per particle radius. In particular, an initial assessment of the region of trust for the resolution is made by computing the accessible volume. Afterwards, in addition to the resolution levels of 2, 5, 10 reported above, also the resolutions of 15, 20 and 25 voxels per particle radius ($R_p$) are studied.

The accessible or free volume of the structure is the space that is not covered by a particle and is quantified in an analytic/exact way by using the method developed by Dodd et al. [111], and is then compared with the computed accessible volume (based on empty voxels) from binary images of different resolutions (2-30 voxels/radius) created from the same snapshot (studied in this section), in order to determine a region of trust for the resolution, see Fig. 2.9. It is found that beyond a resolution of 10 voxels/radius, the value for the accessible volume of the discretized image converges to a value really close to the one calculated analytically. The variations after a resolution of 10 voxels/radius are small deviations originating from representing spherical particles on a cubic grid. Therefore, a small deviation (of $O(0.01\%)$) of the numerical from the analytical result is to be expected, and can not be gotten rid of by increasing the resolution further.

The results concerning the filling of the cavities can be found in Fig 2.10, for the BP (number density, degree) in Fig 2.11, for the branches (thickness,
2.5. Resolution analysis

Figure 2.10: Effect of changing the resolution, in terms of the number of voxels per particle radius, on the number density $n_c$ (a), and volume fraction $\phi_c$ of cavities (b), for the anisotropic network structure. The grey area depicts the region of trust.

orientation) in Fig. 2.12, and for percolation and number of clusters.

One can observe in Fig 2.10 that higher resolution results in a higher number density of cavities, because smaller gaps between the particles become apparent at higher resolution. However, higher resolution leads to a lower volume fraction of cavities, because the cavities close to the surface of the structure find paths to connect with the outside; the smaller gaps found at higher resolutions are quite small, leading to a decrease in the volume fraction. The result is that the number density is increased, although the volume fraction decreases and convergence is reached after 10 voxels/radius for the volume fraction and after 20 voxels/radius for the number density of cavities.

Fig. 2.11 shows that the number density and average degree of the BPs converge as the resolution is increased. The ratio between subsequent resolutions confirms this fact. The increase observed in number density upon increasing the resolution (at low resolutions) occurs because smaller pores (not cavities) in the structure become visible, resulting in more short branches with simpler connectivity (lower degree). The results of Fig. 2.11 refer to the case when BP-reduction has been applied. To illustrate the significance of the BP-reduction, we present in Appendix A a regular grid with a known amount of BPs; it is observed that the number density of BPs increases, and does not converge in the absence of BP-reduction, which is unphysical.

The results in Fig. 2.12 show that the average thickness of the branches re-
Figure 2.11: Effect of changing the resolution, in terms of the number of voxels per particle radius, on the number density $n_{BP}$ (a), and average degree $\langle d_{BP} \rangle$ of BPs (b), for the anisotropic network structure. The grey area depicts the area of trust.

Figure 2.12: Effect of changing the resolution, in terms of the number of voxels per particle radius, on the thickness $\langle d_B \rangle$ (a) and orientation in different directions $S_{2,i}$ (b) of branches, for the anisotropic network structure. The grey area depicts the area of trust.
mains quite constant for resolutions equal to or higher than 5. In this range, the differences are quite small, namely on the order of \( R_p/20 \), which is comparable to the pixel-edge length. The orientation becomes stronger the higher the resolution, however, the variations being relatively small. This slight variation in orientation can be interpreted by the fact that more branches are present at higher resolution, and the effect of orientation is more pronounced for more detailed skeletons. This issue could be resolved with removing the smaller branches.

We study percolation and number density of clusters for a resolution of 2, 5, 10, 15, 20 and 25 voxels per particle radius. The structure is percolating in \( x- \), \( y- \), and \( z- \) directions for every resolution, and the number density of clusters is \( 4.0 \times 10^{-3} \) for a resolution of 2, and \( 3.0 \times 10^{-3} \) for the rest of the resolution values. This suggests that the procedure of getting a binary representation of the actual structure with the bonds being represented by cylinders is robust.

In conclusion, one observes that all the presented measures converge when the resolution is increased. Our technique is producing more nodes in the connectivity graphs due to the finer resolution of the voxels compared to the particles, however, this fact is not influencing our measures or the complexity of our graphs in terms of global clustering coefficient. The choice of resolution depends on the structure characteristics one wishes to resolve. If one wishes to fully resolve the cavities in terms of their number density, one should use a resolution of 20 voxels/radius. However, if one wishes to resolve only the network characteristics, i.e. BPs, degree, thickness, orientation, a resolution of 10 voxels/radius is sufficient. The resolution of 10 voxels/radius is used for the rest of this chapter.

The image analysis was implemented in MATLAB (MATLAB 2018b, Mathworks), while the network analysis was implemented in python using the Graph tool package [112]. The analysis of a single structure with volume fraction 30% of 1000 particles and resolution of 10 voxels/radius takes less than 12 min on two Intel i5 (i5-8259U) 2.3 GHz CPU and consumes about 1 GB RAM. It is mentioned that not all parts of the code run in parallel.

2.6 Application to real structures

The general scheme presented above is now applied to four different structures of different dynamic systems. The structures are thin chains, thick chains, an isotropic network, and an anisotropic network. The thin chains, thick chains, and the anisotropic network are configurations obtained from BD simulations.
of dielectric particles in a constant and uniform electric field in the $z$-direction [113], with dipole-dipole interactions [11, 24]. The resulting structures are strongly anisotropic in the direction of the external field. In contrast, the isotropic network was obtained again by BD simulations of particles interacting via short-range DLVO-interactions [56]. An important parameter for these structures is the volume fraction of particles, $\phi$. The different configurations to be analyzed have $\phi = 0.05$ for thin chains, $\phi = 0.10$ for thick chains, $\phi = 0.20$ for the isotropic network, and $\phi = 0.30$ for the anisotropic network. In general, one tries to establish a relation between the physics included in the simulation and the structures obtained from that simulation. The method presented in this chapter bridges this gap, offering quantitative information about the characteristic features of the structure, based on the Cartesian coordinates of the particles.

All the structures that are going to be used have periodic-boundary conditions. It should be mentioned that in the connectivity graphs the effect of the periodic-boundary conditions is large. For example, this can be seen for strings that span the box, which will be represented in the connectivity graph as closed loops, due to boundary-crossing bonds between particles on opposite sides of the simulation box (see Fig. 2.14b).

### 2.6.1 Cavities

Before presenting the results about the quantification of the actual structures, the presence of (to-be-filled) cavities is assessed in terms of their number density and volume fraction; the results are listed in Table 2.1.

We expect the thin chains to have the lowest number density and volume fraction of cavities. This is justified by the fact that this structure is the one with the lowest $\phi$ (0.05) and the least local clustering. The thick chains, in contrast, are expected to have more cavities, although still less than the other structures, i.e., the networks. The isotropic network is expected to have more cavities due to the nature of its short-range potential [56, 58], and the higher complexity in terms of the form of particle-paths. The volume fraction of cavities is expected to be strongly dependent on the volume fraction $\phi$ of particles, so the isotropic network is expected to have a lower volume-fraction of cavities than the anisotropic network. The anisotropic network is expected to have the largest number density and volume fraction of cavities, the main reason being the volume fraction. In addition, the nature of the interactions (repulsive in direction perpendicular to the external field direction), could promote large-volume cavities. One can see in Table 2.1, that there is large variation on the
Table 2.1: Scaled number density, see Eq. (2.1), and volume fraction of cavities, see Eq. (2.2) of all structures.

<table>
<thead>
<tr>
<th>structure</th>
<th>$n_c$</th>
<th>$\phi_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>thin chains</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>thick chains</td>
<td>$1.600 \times 10^{-2}$</td>
<td>$2.90 \times 10^{-5}$</td>
</tr>
<tr>
<td>isotropic network</td>
<td>$1.996 \times 10^{-1}$</td>
<td>$6.48 \times 10^{-4}$</td>
</tr>
<tr>
<td>anisotropic network</td>
<td>$6.900 \times 10^{-2}$</td>
<td>$1.05 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

measures depending on the structure, the variation being in agreement with the expectation. The thin chains structure has no cavities. The thick-chains structure has the least (non-zero) amount of cavities, and volume fraction, in comparison to the networks. The isotropic network has a one order of magnitude larger number density and volume fraction of cavities. Finally, the anisotropic network shows the highest volume fraction.

### 2.6.2 Structures

The structures under consideration are presented in Figs. 2.13, 2.14, 2.15, and 2.16, for the thin chains, thick chains, isotropic network, and anisotropic network, respectively. In these figures, there are four subfigures for all structures, representing the initial structure of the primary particles (a), the final structure of the skeleton (c), and the connectivity of the particles in a 2D projection of the initial structure (b) and of the final skeleton (d). The connectivity graphs are not related to the actual 3D Cartesian positions of the particles/voxels. For all the structure simplification presented in the following, the term “the skeletonization procedure” refers to the entire procedure discussed above, including filling of the cavities and simplification based on the connectivity graph.

One can observe in Figs. 2.13a and 2.13c that the initial structure is preserved, i.e. it is not altered significantly by the skeletonization procedure. This close resemblance of the skeletonized to the initial structure occurs because the structure itself is simple. The only difference is visible in the connectivity graphs, Figs. 2.13b and 2.13d which shows that the structure is indeed simplified, as desired. It shows that even the few complex connections in the initial structure are transformed to simple ones by our procedure. It should be mentioned that the procedure results in more nodes in the connectivity graph of the skeleton than initially present. This happens due to the detailed voxel representation, i.e., since the side length of a voxel is 20 times smaller than
the particle diameter, Subsec. 2.2.4. The simplification is verified by the fact that the global clustering coefficient drops from a value of 0.1224 for the initial structure to 0 in the final skeleton. The number of bonds is 1.93 per primary particle; in contrast, the number of bonds is 1.99 on the level of (filled) voxels. This increase is reasonable since the voxel-level gives more emphasis to the branches (many filled voxels are part of a branch) than to the BPs and branch-ends, as compared to the primary-particle level. Therefore, the finer the voxel-representation, the more the number of bonds per (filled) voxel approaches the value 2 (i.e., branch-dominated).

For the structure with thick chains, Figs. 2.14a, and 2.14c show that the initial structure is significantly simplified by the skeletonization scheme. The connectivity graphs, Figs. 2.14b and 2.14d, are simplified in terms of bonds per particle/voxel and the local clustering coefficient [107, 114]. The connectivity graph is significantly simplified also visually, since the thick rings in Fig. 2.14b, representative of thick strings, are transformed into single-voxel thick rings in Fig. 2.14d. The simplification is verified by the fact that the global clustering coefficient drops from a value of 0.3680 for the initial structure to 0 in the final skeleton. The number of bonds is 4.26 per primary particle; in contrast, the number of bonds is 2.03 on the level of (filled) voxels.

Considering the isotropic network, the complexity of the structure in Fig. 2.15a still allows a reasonable simplification, see Fig. 2.15c. The connectivity graphs, Figs. 2.15b and 2.15d, are also simplified in terms of bonds per node, and local clustering coefficient [107, 114]. However, the simplification cannot be discerned by visual inspection, since the original structure is quite simple already, and only little changes are to be expected from our scheme. The scheme is essentially producing more voxels in the connectivity graph, whereby thin branches are getting longer in the connectivity graph. Also, bonds are crossing and the graph seems rather complicated, although it is fully simplified in terms of global clustering coefficient, which drops from a value of 0.4519 for the initial structure to 0 in the final skeleton. The number of bonds is 1.98 per primary particle; in contrast, the number of bonds is 1.86 on the level of (filled) voxels. The lower ratio of bonds per voxels in the final state is based on the amount of ends present. The skeletonization produces small branches when a structure has small imperfections (see also [101]), resulting to more ends. In the literature, this effect is dealt with a technique called thresholding [95], where the small branches are basically chopped off.

For the anisotropic network, the simplification of the structure is similar to the case of the isotropic network, see Figs. 2.16a and 2.16c. The skeletonization procedure simplifies the connectivity graph, see Figs. 2.16b and 2.16d, in terms
Figure 2.13: Structure of thin chains. Initial configuration in real space (a) and its connectivity graph (b); the ratio of bonds per particle is 1.93. Simplified skeleton in real space (red) (c) and its connectivity graph (d); the ratio of bonds per voxel is 1.99. The color in the connectivity graphs indicate different clusters of particles or voxels. In (a), the size of the particles is reduced by a factor of 2 to increase the visibility of the structure.
Figure 2.14: Structure of thick chains. Initial configuration in real space (a) and its connectivity graph (b); the ratio of bonds per particle is 4.26. Simplified skeleton in real space (red) (c) and its connectivity graph (d); the ratio of bonds per voxel is 2.03. The color in the connectivity graphs indicate different clusters of particles or voxels. In (a), the size of the particles is reduced by a factor of 1.5 to increase the visibility of the structure.
Figure 2.15: Isotropic network. Initial configuration in real space (a) and its connectivity graph (b); the ratio of bonds per particle is 1.98. Simplified skeleton in real space (red) (c) and its connectivity graph (d); the ratio of bonds per voxel is 1.86. The color in the connectivity graphs indicate different clusters of particles or voxels.
Table 2.2: Number density and average degree of BP.

<table>
<thead>
<tr>
<th>structure</th>
<th>$n_{BP}$</th>
<th>$\langle d_{BP} \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>thin chains</td>
<td>0.0230</td>
<td>3.0000</td>
</tr>
<tr>
<td>thick chains</td>
<td>0.0430</td>
<td>3.1561</td>
</tr>
<tr>
<td>isotropic network</td>
<td>0.1866</td>
<td>3.5027</td>
</tr>
<tr>
<td>anisotropic network</td>
<td>0.0820</td>
<td>3.2955</td>
</tr>
</tbody>
</table>

of bonds per node, and local clustering coefficient [107, 114]. Our procedure is capable of reducing this complex particle structure to its essence, which was the main goal of this chapter. The simplification is verified by the fact that the global clustering coefficient drops from a value of 0.3120 for the initial structure to 0 in the final skeleton. The number of bonds is 6.43 per primary particle; in contrast, the number of bonds is 2.10 on the level of (filled) voxels.

The simplified skeletons we obtain from the four structures presented above are further analyzed, to give a more quantitative characterization of these structures.

2.6.3 Branch-points

The results concerning the number density and degree of BP are reported in Table 2.2. One can observe the differences between the structures. The thin chains have the lowest number density of BP and the lowest degree. This was to be expected as the structure is without significant bifurcations, see Fig. 2.13. The BPs that do appear are leading to small branches and no connection paths are present between the chains. The degree of the BPs supports this statement, since the value of 3.0 is the absolute minimum value of degree a BP can have (by the definition of a BP).

The structure with thick chains has a number density of BP that is almost twice as large as for the thin chains, although it still has a rather low value with respect to the total number of particles. The average degree is slightly higher than for the thin chains. These observations support the existence of more branches and inter-connections between chains.

The isotropic network has the highest values of all four structures for the number density and for the average degree per BP. In the isotropic network, the number density is one order of magnitude higher than for the chain-structures, implying that the structures have a lot of bifurcations, and thus (on average) shorter branches with their thickness being influenced by the volume fraction.
Figure 2.16: Anisotropic network. Initial configuration in real space (a) and its connectivity graph (b); the ratio of bonds per particle is 6.43. Simplified skeleton in real space (red) (c) and its connectivity graph (d); the ratio of bonds per voxel is 2.10. The color in the connectivity graphs indicate different clusters of particles or voxels. In (a), the size of the particles is reduced by a factor of 1.2 to increase the visibility of the structure.
Table 2.3: Average thickness $\langle d_B \rangle$ and orientation of branches in different directions, $S_{2,i}$.

<table>
<thead>
<tr>
<th>structure</th>
<th>$\langle d_B \rangle$</th>
<th>$S_{2,x}$</th>
<th>$S_{2,y}$</th>
<th>$S_{2,z}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>thin chains</td>
<td>3.2851</td>
<td>-0.4612</td>
<td>-0.4563</td>
<td>0.9175</td>
</tr>
<tr>
<td>thick chains</td>
<td>3.4951</td>
<td>-0.2499</td>
<td>-0.2867</td>
<td>0.5366</td>
</tr>
<tr>
<td>isotropic network</td>
<td>3.9143</td>
<td>0.0140</td>
<td>0.0113</td>
<td>-0.0253</td>
</tr>
<tr>
<td>anisotropic network</td>
<td>5.5863</td>
<td>-0.1398</td>
<td>-0.1172</td>
<td>0.2570</td>
</tr>
</tbody>
</table>

The anisotropic network has a number density and average degree of BP higher than the thin- and thick-chain structures, but lower than the isotropic network. The anisotropic network has double the amount of branch points as compared to the thick-chain structure, but half as compared to the isotropic network.

2.6.4 Branches

The results concerning the characteristics of the branches, namely their thickness and orientation, are shown in Table 2.3. The thin chains show the lowest thickness and highest orientation along the $z$-direction. From the measurements of the thickness we understand that there are mostly one- or two-particle-thick chains. The structure with thick chains shows higher thickness, obviously, meaning there are more two- or more particle thick chains. The difference in thickness between the thin and thick chains is rather low, due to the fact that the thick-chain structure looks more like curved sheets than thick cylinders. The orientation with respect to the $z$-direction is weaker. The isotropic network shows thicker branches, almost two-particle thick on average. The orientation is indeed random, since all three values $S_{2,i}$ are close to 0. This was expected as the structures have been created with a spherical potential, and there is no preferable direction as for the rest of the structures. The anisotropic network structure shows by far the thickest branches, also because this structure has the highest volume fraction. The orientation is weak with a preference for orientation in the $z$-direction.

2.6.5 Percolation and number of clusters

The results concerning percolation and the number density of clusters are reported in Table 2.4. The thin chains percolate only in the $z$-direction, which is
Table 2.4: Percolation in different directions and number density of clusters, \( n_{cl} \).

<table>
<thead>
<tr>
<th>structure</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>( n_{cl} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>thin chains</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>( 4.8 \times 10^{-2} )</td>
</tr>
<tr>
<td>thick chains</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>( 1.2 \times 10^{-2} )</td>
</tr>
<tr>
<td>isotropic network</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>( 7.5 \times 10^{-4} )</td>
</tr>
<tr>
<td>anisotropic network</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>( 3.0 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

the direction of the external electric field, and has the highest number density of clusters, as was to be expected. The thick chains also percolate the box only in the \( z \)-direction. This structure has less clusters than the thin-chain structure because more particles make bonds with each other. Both the isotropic and the anisotropic networks percolate in all three directions. The amount of clusters differs significantly. The isotropic network is a result of a diffusion-dominated process. The number of clusters is the lowest of all structures. So all the particles have found their way to a larger structure.

2.7 Summary and discussion

A procedure has been developed for systematic simplification and quantitative characterization of structures formed by particles, with a particular interest in networks with thick branches and branch points. Starting from a structure consisting of thick components, the simplification provides a thin skeleton with minimum connectivity. The procedure can be described in five steps. First, the structure given by the Cartesian coordinates of the particles including bonds is transformed into a discretized binary 3D image in terms of cubic voxels, from which cavities are eliminated. After applying the actual skeletonization process, the resulting skeleton is simplified with respect to the branch points in terms of connectivity reduction and triangle elimination. Finally, the fully simplified skeleton is characterized. In the skeletonization scheme, several numerical parameters can be tuned, which is discussed below.

The choices that must be made in the skeletonization procedure concern the pre- and post-processing steps. For the pre-processing, the resolution must be chosen. This choice should be such that it is fine enough to resolve the characteristics of the structure, i.e. accessible volume, but not making the computational cost intractable, because of too many voxels in a the skeleton analysis. Further-
more, one needs to decide whether to eliminate the cavities. One could choose to apply the skeletonization without eliminating the cavities and deal with them in the post-processing steps. The structures investigated in this chapter have a low volume fraction of cavities, and we consider them of minor importance for the network structure; in general, one should be critical about the importance of cavities in the structure [105]. In addition, one can decide about including the cylinders representing the bonds. The definition of whether two particles are bonded is based on the fulfillment of a distance criterion, that has to be set. Choosing the critical value for the center-to-center distance slightly above the sum of the two particle radii ensures that particles are bonded when represented in the binary 3D image. The critical values can be rationalized on the basis of the interaction potential used to acquire these structures, as explained earlier. In the determination of the thickness of the branches, one should make choices concerning the orientation of the normal vector of the plane, the resolution of the grid on the plane, and the definition of the thickness in this plane. For the orientation, one could choose to use the orientation vector of the bond, instead of the next-nearest neighbours orientation, to determine the plane. The resolution of the grid on the plane can be finer or coarser. And, the thickness can be defined in ways different from our approach, e.g. identification of two empty voxels in opposite directions of the voxel in study, or determining maximum sphere fitting on this point of the image [103].

Standard methods for particle detection require a resolution of approximately 5-20 voxels per diameter of the visualized object, for extracting the particle coordinates [115, 116]. If one wishes to apply the thinning algorithm presented in this chapter to experimental data, one should use a slightly higher resolution to properly image the characteristics of the structure, since the measures of the network characteristics (e.g. BPs) can be trusted for a resolution that is higher than 10 voxels/radius, or even 20 voxels/radius for the number of cavities. Experimental imaging often results in different resolution in the different spatial directions, the resolution in depth typically being worse than the lateral resolution. In our technique, there is no fundamental reason for the voxels to be cubic, and so parallelepiped voxels of unequal edge lengths can be used in principle. In case the voxels are strongly anisotropic, e.g. much longer in the depth-direction than laterally, one can choose to subdivide the voxel along its depth-direction, thereby generating voxels that are nearly cubic.

Needless to say that the proposed procedure also has some disadvantages. First, choices need to be made in relation to the pre- and post-processing steps, as discussed above. Being able to make choices is in principle not a problem, however, these choices must be conscious and well-thought of. Second, at higher
volume fractions ($\phi \geq 0.40$), the technique is rather unsuitable, as the unoccupied space is rather low. And third, the application of the technique to a periodic system is cumbersome. One should be mindful about the how think an extra layer to choose around the primary box, since this is related to the characteristic length scale of the structure.

This skeletonization and analysis procedure was developed for structures obtained via particle-based simulations (e.g., Brownian Dynamics), although it is fully applicable to experimental structures as well. Also in this case, care should be taken with the creation of the image, since additional pre-processing may be needed. Depending on the form of the initial structure, and the way it was obtained, the image may need cavity filling [95]. An advantage of our scheme is its universality, since it can be applied to structures obtained either experimentally or numerically. Being able to use one and the same procedure for analyzing structures of different origin is beneficial for comparing them consistently.
Chapter 3

Structure formation in suspensions under uniform electric or magnetic field

Abstract

The structure formation of particles with induced dipoles dispersed in a viscous fluid, under a spatially and temporarily uniform external electric or magnetic field, is investigated by means of Brownian Dynamics simulations. Dipole-dipole interactions forces, excluded volume forces and thermal fluctuations are accounted for. The resulting structures are characterized in terms of average orientation of their inter-particle vectors (second Legendre polynomial), network structure, size of particle clusters, anisotropy of the gyration tensor of every cluster and existence of (cluster) percolation. The magnitude of the strength of the electric field and the volume fraction of particles are varied and the structural evolution of the system is followed in time. The results show that the characteristic time-scale calculated from the interaction of only two dipoles is also valid for the collective dynamics of many-particle simulations. In addition, the magnitude of the strength of the electric field in the range of values we investigate influences only the magnitude of the deviations around the average behavior. The main characteristics (number density of branch-points and thickness of branches) of the structure are mainly affected by the volume fraction. The possibility of 3D printing these systems is explored.

This chapter is based on: K. Manikas, G.G. Vogiatzis, M. Hütter, P.D. Anderson, Structure formation in suspensions under uniform electric or magnetic field. To be submitted. (2020).
3.1 Introduction

When dielectric or conductive particles are exposed to an external electric or magnetic field, dipoles are induced to the particles due to the difference in the dielectric permittivity or magnetic susceptibility between them, and the medium [11]. Due to these dipoles, the particles interact [11] and the result of this interaction is the formation of structures of particles [12]. Depending on the field conditions, the particles can arrange into strings [13], that evolve, and aggregate in time [13], planes [14], or networks [15]. In addition, the short-time aggregation dynamics has been studied [117, 118], as well the manipulation of a single particle [119]. The enhancement of the properties of the material in the direction along which the structures are created originates from the arrangement of the particles [14, 16]. The transport properties are greatly affected by the structures formed, due to enhancement by percolation paths [15]. The suspensions that contain filler particles responsive to an external field, are called electro-/magneto-rheological fluids and have been a subject of research due to their unique characteristics. Their rheological response occurs in $O(1s)$ time-scales and is exploited in force-feedback sensors [120] and in robotics [121]. The rapid viscosity increase in the direction perpendicular to the applied field has also been widely investigated in the past [12, 17–20, 122]. The response of these systems under shear has been a topic of extensive research [21, 22]. The effect of the Mason number [23], which is the ratio of viscous to magnetic forces, has been studied for the investigation of mixing on micrometer scales [24–26] with a rotating field. The structures created in a spatially uniform external field have also been studied at large time-scales both athermally (no Brownian motion) [13], and thermally (including Brownian motion) [123].

Additive manufacturing is nowadays a subject of extended research [31], although it has been on the surface for a long time [30]. The materials used include metals [32], polymers [33], ceramics [34] and combinations of them [31]. Printing of polymer-matrix composite materials is used for various purposes such as rapid prototyping (temporary substitutes for parts of higher mechanical performance) [41], or topology optimization (introduction of shape memory in a passive matrix) [124]. They have a wide range of applications: aerospace applications (cabin interiors) [35], medicine (mimics of living tissue) [36], anthropology (reconstruction of medieval skulls) [37] and design (spatially-dependent elasticity) [38]. Another reason for using composite systems is the incorporation of dielectric, magnetic or conductive functionality to the matrix material [39–41]. Additionally, if the microstructure of the composite can be controlled during printing by the use of an external electric or magnetic field, one can
achieve specific structures of particles inside a complex geometry. This can be an important application of this work, especially if photo-reactive resins [125] filled with electrically or magnetically active particles are concerned. Resins are widely used as media for particles [27, 28], so that the structure of the particles is captured with the solidification of the resin. The low viscosity of the resins before curing makes the structure formation possible within the usual time-scales ($O(1\text{s})$) of 3D-printing. The targeted technique is stereolithography (SLA) [29]. Potential uses of these systems in applications include personalized hearing aids [42], flat lenses with a gradient of concentration of particles that have the functionality of their curved counterparts [43, 126], piezoelectric or Hall effect sensors [44], and direction-specific thermally or electrically conductive composites [15, 127]. In the following, we focus on the physical behavior of these systems, in terms of structural evolution.

The motion of particles serving as dipoles inside a fluid can be simulated with a variety of methods depending on the effects (hydrodynamic interactions) and scales (length or time) that one desires to resolve. The most accurate technique is molecular dynamics, as it simulates the motion of the atoms [45, 66] by integrating the (frictionless) Newton’s equations of motion. However, the system we are interested in, exhibits disparity in length- and time-scales, as it consists of monomers of the liquid matrix whose average size is on the order of nm and particles whose size is on the order of $\mu\text{m}$. Molecular Dynamics can resolve the nano-scales in time and space. The effect of the matrix on the particles is governed by the collision of the monomers on the surface of the particle, and can be effectively represented by thermal fluctuations on the $\mu\text{m}$ scale. Stokesian Dynamics [17] is another option for simulating these systems and especially resolving the hydrodynamic interactions at close distances. One of the best known techniques is the Brownian Dynamics (BD) [51], where the equations of Newton are solved in the overdamped limit, so no acceleration is present (i.e. correlations in velocity vanish within a single timestep of the integration) [52]. However, the great advantage with respect to the system in discussion is the incorporation of thermal fluctuations. BD can resolve spatial effects on the order of the size of the particle and times of up to $O(10\text{s})$. The Finite Element method [24, 50] is also suitable for solving the equations describing the problem, although with this method the system is treated either as a macroscopic medium, or at a much finer spatial resolution than the size of the particles. The macroscopic approach is totally neglecting the microstructure, i.e. solving the equations of Maxwell for resolving the electromagnetic response of the material and/or the Navier-Stokes equations for the rheological response. The finer resolution approach solves the same equations implementing the mass and momentum
balance equations, but also resolves the local effects of non-uniformities of the electromagnetic field and/or the flow field, respectively. The downside of this method is the “limited” number of particles that can be studied due to the computational cost. In order to study the structures in short/intermediate time-scales, the BD technique is used. The motion of the particles is mainly affected by the dipole-dipole interactions [11, 12, 53].

Our method results in a structure of particles, and our characterization depends on the nature of these structures. As already mentioned, one can get various structures depending on the field conditions, like strings [13], planes [14], or networks [15]. The goal of characterizing such structures is to extract their main features and to describe these features in a quantitative manner. For example, for strings one should know the size, orientation, thickness and correlations between these measures, for planes the size and orientation, and for networks the number density of branch-points (BP), the degree of BP, the thickness of the branches, the number of clusters present, and the existence of percolation. There are a lot of techniques used for the characterization of an ensemble of points/particles, like studying their gyration tensor (eigenvalues and eigenvectors) [74] and Voronoi tesselation [62]. The Voronoi tessellation is widely used in the characterisation of disordered systems [128], polymers [66–68, 71], colloidal gels [92], and granular materials [65]. Other techniques like the (radial or cylindrical) pair-correlation function, bond-angle distribution [56], and quermass integrals [58] have also been developed for the characterization of the structure of networks. Here, the gyration tensor of clusters, the Voronoi polyhedra, and a previously developed skeletonization method [95, 97, 129] are employed for the quantitative characterization of the structures.

In this chapter, we use BD with dipole-dipole interactions to simulate the motion of particles (dipoles) within a fluid under a spatially uniform field. The characterization of the structures is performed by grouping particles in clusters and by reducing the structure to its skeleton (skeletonization). Our goal is to identify the most relevant physical parameters, and relate the corresponding physical input with the structure and eventually the transport properties, specifically the thermal conductivity of the material. The chapter is organized as follows. Sec. 3.2 provides the basic methodological tools that were used for the production of the structures. Moreover, we present a dimensionless analysis with all the relevant dimensionless groups. In Sec. 3.3, we introduce the tools we use to characterize the obtained structures. In Sec. 3.4, we present the structural evolution in time in dimensionless terms, and the characteristic features of our formed structures. Finally, the chapter is concluded with a discussion in Sec. 3.5.
3.2 Methodology

In this section, our methodology is discussed, including the simulation details and dimensionless analysis. Our system consists of particles with particle radius $R_p$ and volume fraction $\phi$, and the monomeric fluid that serves as medium with constant viscosity $\eta$ in a finite box of edge-length $L$, where periodic boundary conditions are applied in all three spatial directions. The system is influenced by an external field that is applied to the system. In the current chapter, the system consists of particles that have dipoles induced by a uniform external electric or magnetic field. The interactions governing the dynamics are the dipole-dipole interactions [11, 12]. One can define the potential energy of $N$ particles with induced dipoles under an external field [11, 24],

$$U_{em} = -\sum_{i}^{N} \left[ p_i(r_i) \cdot E_e(r_i) \right] - \frac{1}{4\pi\epsilon_m} \sum_{i=1}^{N-1} \sum_{j>i}^{N} p_j(r_j) \cdot C(r_{ij}) \cdot p_i(r_i),$$  \hspace{1cm} (3.1)

where $p_i$ is the dipole moment of particle $i$, defined in Eq. (3.2), $E_e(r_i)$ is the field intensity at the position $r_i$, $\epsilon_m$ is the dielectric permittivity of the medium, $C(r) = \nabla r \nabla \frac{1}{r} = \frac{1}{r^2} \left( \frac{3}{r^2} rr - I \right)$ is the second derivative of the position with $r = |r|$, and $r_{ij} = r_i - r_j$ is the inter-particle separation vector. The appearance of dipole moments is a result of the polarization induced by the external field [11]

$$p_i(E_e) = 4\pi\epsilon_m KR_p^3 p_e,$$  \hspace{1cm} (3.2)

where $K = \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m}$ is the Clausius-Mossotti constant [130], with $\epsilon_p$ the dielectric constant of the particles.

The gradient of the potential energy with respect to the position $r_i$, results in the expression for the forces

$$F_{i}^{em} = -\frac{\partial U_{em}}{\partial r_i} = \nabla_{r_i} \left[ p_i(r_i) \cdot E_e(r_i) \right] + \frac{1}{4\pi\epsilon_m} \sum_{j\neq i}^{N} \nabla_{r_i} \left[ p_j(r_j) \cdot C(r_{ij}) \cdot p_i(r_i) \right].$$  \hspace{1cm} (3.3)

In Eq. (3.3), one can observe that dipole $i$ is different from dipole $j$, however, in our study we only considered dipoles that are induced by the field, so all the dipoles are identical ($p_i = p_j = p$) since no local polarization is considered,
only a spatially uniform field is studied, and only particles are used that are identical in size, shape, and dielectric permittivity (or magnetic permeability). For the rest of this chapter, we are using different indices for different dipoles, as it corresponds to the general case.

The presented form of the energy, Eq. (3.1), is the point-dipole approximation [26, 131]. The validity of this approximation depends on the dielectric mismatch $\epsilon_p/\epsilon_m$, and the volume fraction [132]; the lower these two values, the better is the approximation. In the current chapter, we neglect the multipolar interactions [11, 131] that become significant at close distances ($r_{ij} < 4R_p$). At these distances the dipole approximation is not adequate, as it neglects the spatial variation of the field around the particles, which at close distances is significant and the importance of higher-order multipoles increases. The dipole approximation is also ignorant of the polarization arising from the neighboring dipoles; the dipoles can influence the field intensity locally, causing an alternation of the polarization of the neighboring dipoles. Mathematically, this is considered in the mutual dipole approximation [131], where the dipole moments depend on their relative positions of the dipoles within the system. Despite the limitations of Eq. (3.1), it is still used in this chapter to simulate the structure formation of particles under a spatially uniform field for two reasons. First, the systems considered in this chapter have a low dielectric mismatch, which will be absorbed in a dimensionless group further below. And second, this approximate interaction is appropriate at the low volume fractions studied here, while at the higher values of volume fraction it nevertheless can give a qualitative picture of the overall behavior of the many-particle system. Also, it is mentioned in the literature that the calculation of the multipole interactions is computationally inefficient with respect to the accuracy obtained in comparison to the simple dipole approximation [131].

In Eq. (3.1), we present the potential energy in terms of electric dipoles. However, if one uses magnetic dipoles, $\mu$, the equivalent expression of the field intensity, $H$, and adjusts the prefactor of the second term of the right-hand side of the equation [11], then one has the equivalent for magnetic dipoles in the presence of a magnetic field. The nature of the interactions is similar, and in terms of dimensionless parameter the difference between the two cases becomes trivial. One should be careful with ferromagnetic behavior [133], as it is not included in the potential energy presented in Eq. (3.1).

Due to the finite size of the simulation box, every interaction is truncated at a certain cut-off radius, $r_{\text{cut}} < L/2$, with $L$ being the edge-length of the simulation box. The problem of finite truncation of interactions is dealt with by calculating the forces neglected outside the sphere of radius $r_{\text{cut}}$, and correcting
3.2. Methodology

the final result (tail corrections). If one deals with electrostatics or pairwise potentials that have \( n < 4 \) in \( 1/r^n \) in terms of energy, c.f. Eq. (3.1), then the neglected energy is infinite and one should account for long-range corrections with other methods; the same translates to the forces as well. In the case of the presence of partial charges, this problem is known for almost a century [134], and has been dealt with the method of Ewald summation. The Ewald summation resolves the issue by turning part of the forces (and/or potential) in the reciprocal space with a Fourier transform, taking advantage of the periodicity of the system. No estimations are made, the solution results from an analytical transformation. Other techniques have been developed like the reaction field method or the Wolf summation [54, 135], however, these techniques treat the system as a medium making approximations in the calculation of the quantities, which exhibit systematic errors [54]. In reciprocal space the sum converges much faster with the use of wave-vectors. Studies about the accuracy of the method have been performed both for charges [121, 136, 137], and dipoles [138]. In this chapter, the Ewald summation method is used to account for the long-range corrections to the forces, and we use the parameter \( \alpha = 7.5 \, L^{-1} \) that defines the split between real and reciprocal space, where \( L \) is the box length, and \( k = 10 \), where \( k \) is the amount of wave-vectors used.

The potential that was chosen is purely attractive and there is need for an extra force that will prevent the particles from overlapping. This problem was encountered in the past [12]. The choice is usually made between a power law \( (1/r^{12}) \), and an exponential \( e^{-\kappa(r_{ij}/(2R_p)-1)} \). Our choice is the exponential, Eq. (3.4), and has to do with the particle configurations observed experimentally. The power law alters the potential in close distances preventing particles from forming chains that are thicker than one time the particle diameter [12]. The form of the force for preventing particles from overlapping is

\[
F_{exv}^i = -\frac{3\rho^2}{32\pi \epsilon_m R_p^4} \sum_{j \neq i} e^{-\kappa \left( \frac{r_{ij}}{2R_p} - 1 \right)} \hat{r}_{ij}, \tag{3.4}
\]

where \( \kappa = 30 \), is a constant that determines the interaction range of the excluded volume, while the pre-exponential factor defines the overall strength of the interaction [24], and \( \hat{r} \) is the unity vector of \( r \). One can observe that the softness of the particles (hard particles are difficult to handle numerically) depends on the magnitude of the dipole moments, which is rather unexpected due to the different physical origin of the excluded volume and dipole-dipole interactions. This forcefield has been used extensively in other studies in the literature.
As the excluded-volume force (3.4) depends on the dipole moments, it vanishes for infinitely weak dipole moments; however, the expression (3.4) is suitable for the cases in this chapter, where dipole moments always have finite values, because there is always an imposed external field that induces the dipoles. Additionally, the magnitude of the excluded volume force is always larger than the other physical phenomena, i.e., Brownian and dipole-dipole interaction forces; therefore, it produces results very similar as if an alternative excluded-volume force was used.

The motion of a particle inside a fluid is influenced by friction forces, originating from the collisions of the molecules of the surrounding fluid with the particle. These forces can be incorporated by a drag force,

\[
\mathbf{F}_d^i = -\zeta \mathbf{v}_i = -6\pi \eta R_p \mathbf{v}_i, \tag{3.5}
\]

where \( \zeta = 6\pi \eta R_p \) is the friction coefficient, and \( \mathbf{v}_i \) is the velocity of particle \( i \). In our case, we use the Stokes drag force \[139\], while many-particle hydrodynamic interactions are neglected. The reason for neglecting the latter is that otherwise the computational cost would be prohibitive, in particular, since the main goal of this chapter is to conduct an extensive study of the effect of dipole-dipole interactions and thermal fluctuations on the structure evolution and to resolve the physical behavior of the system. We expect that correctly accounting for hydrodynamics will influence primarily the time scale, however, there could also be an effect of hydrodynamic interactions on the structure formed. Lubrication forces are much larger than those predicted by Stokes’ law, but are only important at small particle-separations where the particles are already locked into their local structure by the dipole-dipole forces. Hence, lubrication effects are not expected to significantly influence the structures formed \[12\].

The Brownian force is given by

\[
\mathbf{F}_B^i = \sqrt{2k_B T \zeta} \frac{d\mathbf{W}_i}{dt}, \tag{3.6}
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( \mathbf{W} \) is a Wiener process and \( d\mathbf{W} \) its increment \[47\]. This has the properties \( \langle d\mathbf{W}(t) \rangle = 0 \) and \( \langle d\mathbf{W}(t)d\mathbf{W}(t') \rangle = \delta(t-t') \). So its increment can be expressed as \( d\mathbf{W}_i = \sqrt{dW} \mathbf{\xi}_i \), where \( \mathbf{\xi}_i \) is a vector whose components are drawn from a random-number distribution with mean value of 0 and standard deviation of 1. The realization of the thermal noise through a Wiener process is such that the Brownian force has a mean value of zero, and it is uncorrelated in time.

For all the above, we have chosen to use Brownian dynamics (BD) simulations \[52\]. This kind of simulations is an approach to the mathematical modeling
of molecular systems by the use of stochastic differential equations [47]. The effect of inertia is considered negligible for systems where the relaxation time for the particle velocity, \( \tau_p = m/\zeta \), with \( m \) being the mass of the particle and \( \zeta \) the friction coefficient, is much smaller than the other time-scales. Using \( m = 24.57 \times 10^{-15} \) kg \( (\rho \sim 5.5 \text{g/cm}^3 \) [140]), \( R_p = 1 \mu \text{m} \), and \( \eta = 0.5 \text{ Pa s} \), one finds \( \tau_p = 2.607 \times 10^{-9} \text{s} \ll \tau_{\text{pot}} \sim 1 \text{s} \), where \( \tau_{\text{pot}} \) is the characteristic time-scale for structure formation \( t_{\text{pot}} = 8\pi^2 \epsilon_m \eta R_p r_c^5 / \rho_c^2 \) (see further details below, Eq. (3.12)). For values of \( r_c \), Eq. (3.8), corresponding to \( \phi = 1 - 30\% \), \( \epsilon_m = 4\epsilon_0 \), and \( R_p = 1 \mu \text{m} \), the timescale is on the order of \( \mathcal{O}(1 \text{s}) \). BD describe a system of \( N \) particles and positional coordinates \( r = r(t) \) with the stochastic differential equation [47, 48]

\[
dr_i = (F_{\text{em}}^i + F_{\text{exv}}^i) / \zeta dt + \sqrt{2 k_B T / \zeta} dW_i. \tag{3.7}
\]

In Eq. (3.7), the index \( i = 1, \ldots, N \) indicates the particle. The differential equation Eq. (3.7) is solved with the predictor-corrector algorithm of first order [47].

In order to reduce the set of physical parameters that influence the behavior of the system, and to introduce dimensionless quantities with physical meaning, we re-write Eq. (3.7) in dimensionless form. The procedure that is followed begins by introducing scaling quantities for the principal variables of the problem,

\[
r_i^* = \frac{r_i}{r_c}, \quad r_c = \frac{1}{\sqrt[3]{n_d}}, \tag{3.8}
\]

\[
p_i^* = \frac{p_i}{p_c}, \quad p_c = 4\pi \epsilon_m K R_p^3 E_c, \tag{3.9}
\]

\[
E_c = \sqrt{\langle E^2(r) \rangle_{\text{sp}}}, \tag{3.10}
\]

\[
t^* = \frac{t}{t_c}. \tag{3.11}
\]

Here, \( n_d \) is the number density, and the index “sp” refers to the spatial average over the simulation box. For the length scale \( r_c \), our choice is based on the system properties. We would like the length scale to be independent of the system size (box length), and the size of the particles (radius or diameter), so we select the third root of the average volume per particle in the system.
This quantity is a measure of the inter-particle distances in the system, and independent of extensive variables of the system. For the scaling of the dipole moments, we choose the dipole moment that corresponds to an induced dipole with the characteristic field intensity value. For the characteristic value of $E$, we choose the spatially (“sp”) averaged field intensity in the simulation box. Finally, the time scale is chosen such so that the electromagnetic effects occur on a dimensionless time-scale of order unity in Eq. (3.7), so the prefactor of this term is set to 1 [141], see Eq. (3.12). It has to be noted that the excluded volume forces have the same scaling with the dipole-dipole interactions (square of the magnitude of the dipole moment). The characteristic time-scale is thus given by

$$t_c = \frac{8\pi^2 \varepsilon_m \eta R_p r_c^5}{p^2 c}.$$ (3.12)

As a result, Eq. (3.7) turns into [47, 48]

$$d\mathbf{r}_i^* = (\mathbf{F}_{i}^{\text{em}*} + \mathbf{F}_{i}^{\text{exv}*}) dt^* + B^* \sqrt{dt^*} \xi_i,$$ (3.13)

with

$$\mathbf{F}_{i}^{\text{em}*} = \sum_j \frac{1}{r_{ij}^4} \left[ \hat{\mathbf{r}}_{ij} (\mathbf{p}_i^* \cdot \mathbf{p}_j^*) - 5 \hat{\mathbf{r}}_{ij} (\mathbf{p}_i^* \cdot \hat{\mathbf{r}}_{ij})(\mathbf{p}_j^* \cdot \hat{\mathbf{r}}_{ij}) ight]$$

$$+ (\mathbf{p}_i^* \cdot \hat{\mathbf{r}}_{ij}) \mathbf{p}_j^* + (\mathbf{p}_j^* \cdot \hat{\mathbf{r}}_{ij}) \mathbf{p}_i^* \right],$$ (3.14)

$$\mathbf{F}_{i}^{\text{exv}*} = -\frac{r_c^4}{8 R_p^4} \sum_{j \neq i} e^{-r_{ij}^2 r_c^{-1}} \hat{\mathbf{r}}_{ij},$$ (3.15)

$$B^* = \sqrt{\frac{2k_B T t_c}{\zeta r_c^2}}.$$ (3.16)

If there was an externally imposed flow, e.g. imposed simple-shear deformation, another characteristic timescale associated with that flow would enter the analysis. However, imposed flow is not considered in this study. Furthermore, we neglect hydrodynamic interactions, i.e., the effect of the flow created...
3.2. Methodology

The BD algorithm employed in our work has already been used in several studies before [142–145], without the dipole interactions. Here, the dipole-dipole interactions are tested by considering some limiting cases. The alignment of two particles in the absence of Brownian forces is tested and compared with the analytical solution. In Fig. 3.1, one can see the interparticle distance versus time for an attractive (interparticle vector aligned with external field) and a repulsive case (interparticle vector perpendicular to the external field) for a simulation of two particles with no Brownian motion and no excluded volume interactions. Good agreement between the BD simulations and the analytical solutions is obtained. In Appendix C, the simulation of many particles is shown in the absence of dipole-interaction, but with Brownian motion and excluded volume interactions included. The obtained structures agree with the expectation.

For solving Eq. (3.13), one should use time discretization, with a finite value for the time increment \( dt \). The timestep is set, so that important information of the fastest physical process is preserved. In the current study, the fastest process is governed either by the dipole-dipole interactions or the excluded volume interactions. At large distances the forces decay, so one should consider
only the case with the largest forces, which is the case of particles at small distance. In this case, we are going to consider $r_{ij}^\ast = 1.9R_p$, in view of thermal fluctuations. For determining which of the two interactions is dominant, we check Eqs. (3.14), (3.15). If one calculates the characteristic time-scales for the two effects[141], one gets $t_{c,\text{dip}}^\ast = r_{ij}^4$ and $t_{c,\text{exv}}^\ast = 8R_p^4/(r_{ij}^4 e^{\kappa *0.05})$. If one estimates these time scales for $\phi = 30\%$, and the chosen value of $r_{ij}^\ast$, then one gets $t_{c,\text{dip}}^\ast = 3.87607 \times 10^{-1}$ and $t_{c,\text{exv}}^\ast = 5.30915 \times 10^{-2}$. The time scale concerning the excluded volume interaction is faster, so one should consider the excluded volume effect for the choice of timestep. In the dimensionless form of the model used here, the resulting time-scale corresponding to the excluded volume depends on the average characteristic distance between the particles, so one should estimate the time-scale value for different volume fractions. Taking this fact into account, we select a timestep of $dt^\ast = 2.4 \times 10^{-4}$, which is sufficient for all volume fractions considered in this study. The details of this choice are presented in Appendix B.

### 3.3 Morphology characterisation

In this section, we are discussing the measures employed for the morphology characterisation, which we categorize with respect to the amount of particles participating in the calculation of these quantities. Structures similar to our resulting structures of particles have been studied before [13, 15, 28]. It has to be mentioned, that the tools we apply only need the position vectors (Cartesian coordinates) of the particles.

Most measures concern two particles, see Subsection 3.3.1. Although, most of the times two-particles measures are not enough to resolve the whole structure characteristics, so one can look either in the neighbourhood (nearest neighbours), see Subsection 3.3.2, or clusters/structures of particles, see Subsection 3.3.3. If one has in mind particles organised in strings, then one would think in terms of touching particles (bonded) creating an anisotropic structure. This characteristic of the structure led to the distinction of the particles to clusters. The condition for characterising two particles as bonded is $r_{ij} \leq 2.2R_p$. This choice was based on the ratio $U^{\text{exv}}/k_B T$, where at distance of $2.2 R_p$ this ratio is lower than 10%. This means that the effect of the excluded volume has ceased and the displacement due to Brownian motion is dominant at this limit.
3.3.1 Measures for pairs of particles

There exist a lot of measures concerning two-particle properties, the most well known being the pair-correlation function [54]. However, due to the nature of our structures (anisotropic) in this chapter we discuss a measure of the orientation of the inter-particle direction, $S_2$, with respect to an external direction, that being the external field, $\hat{E}$

$$S_2 = \frac{3}{2} \left\langle (\mathbf{r}_{ij} \cdot \hat{\mathbf{E}})^2 \right\rangle - \frac{1}{2}.$$  \hspace{1cm} (3.17)

This is the second Legendre polynomial for every pair of particles in the system independent of the distance between them, however, periodic boundary conditions are applied and only the primary image is considered. Eq. (3.17) is sensitive to the orientation of the inter-particle distances with respect to the direction of the field. $S_2$ measure has a value of 1 if the average orientation is parallel to the external direction, a value of 0 if there is a random orientation with respect to the direction of the field, and a value of $-1/2$ if the orientation is perpendicular to the external direction. If two, parallel with the field, one-particle-thick strings are present, then the value depends on the distance between them. However, despite the fact that they are ideally oriented the value of the measure is lower than 1, as the inter-particle vectors between particles belonging to different strings are also considered.

3.3.2 Measures for first neighbours of a particle

If a neighbourhood of particles is to be considered, then the average volume per particle comes up naturally. The Voronoi polyhedron of a particle is uniquely defined by the positions of its neighbours. This quantity is the essence of the calculation of the Voronoi polyhedra [62].

The Voronoi tessellation is widely used in the literature [66–68, 74, 128]. The result of the tessellation is polyhedra. The volume, shape (number of faces), and orientation of these polyhedra can give us insight on characteristic features of the underlying particle structure. The characteristics of the polyhedra depend on the relative positions of their first neighbours. We choose to use Mitrich’s method [146], to calculate the gyration tensor of the polyhedra, and extract information as the main direction of the polyhedron and the shape of it. The gyration tensor [74]

$$\mathbf{S}_k = \left\langle (\mathbf{r}_i - \mathbf{r}_{cm,i})(\mathbf{r}_i - \mathbf{r}_{cm,i})^\top \right\rangle_k,$$  \hspace{1cm} (3.18)
where the brackets indicate the arithmetic average over the vertices \( k \) of the polyhedron of particle \( i \), and \( r_{cm,i} \) is the position of the center of mass of the Voronoi polyhedron of particle \( i \). The gyration tensor defines an ellipsoid \([74]\). The relative magnitude of the eigenvalues of the gyration tensor give the relative difference in size of the three axes of the ellipsoid.

The measures that will be used for characterising the polyhedra out of the gyration tensor and conclusively the structures, are the volume of the polyhedron, \( V_i \), and the relative shape anisotropy \([68, 74]\)

\[
\kappa^2 = \frac{b^2 + \frac{3}{4}c^2}{(\lambda_1 + \lambda_2 + \lambda_3)^2}, \tag{3.19}
\]

where \( b = (\lambda_1 - \frac{1}{2}(\lambda_2 + \lambda_3)) \) is the asphericity of the ellipsoid defined by the gyration tensor, \( c = (\lambda_2 - \lambda_3) \) is the acylindricity, and the eigenvalues of the gyration tensor \( S \) are in descending order, \( \lambda_1 \geq \lambda_2 \geq \lambda_3 \). The value of \( \kappa^2 \) for a sphere is 0, for an infinitely long rod is 1, and for a flat disk is 1/4.

### 3.3.3 Measures for clusters/networks of particles

Here, we discuss morphology measures concerning clusters/structures of particles. First, we introduce the gyration tensor for clusters of particles \([74]\)

\[
S_I = \left\langle (r_i - r_{cm,I})(r_i - r_{cm,I})^\top \right\rangle_i, \tag{3.20}
\]

where the brackets indicate the arithmetic average over the particles \( i \), the index "\( I \)" indicates the cluster number, and \( r_{cm,I} \) is the position of the center of mass of the particles belonging to the cluster \( I \). The gyration tensor defines an ellipsoid \([74]\), and its geometrical features can give insight about the structure of the clusters.

The first measure is the same as in Eqn. (3.17), the only difference being that the average is limited to the particles belonging to the same cluster

\[
S_{2,I} = \frac{3}{2} \left\langle (\hat{r}_{ij} \cdot \hat{E})^2 \right\rangle_I - \frac{1}{2}, \tag{3.21}
\]

where the index \( I \) denotes the cluster index, so for cluster \( I \) the average is defined as the average of the particles that participate in \( I \).

The second measure quantifies the anisotropy of each cluster. For that we calculate the gyration tensor \([74]\). The gyration tensor is calculated per cluster, so each cluster can be described as an ellipsoid \([74]\), where the eigenvalues of
the gyration tensor give the relative difference in size of the three axes of the ellipsoid. So we introduce a measure that quantifies anisotropy,

$$\lambda^*_I = 1 - \text{det}(S_I)\lambda_{\text{max},I}^{-3},$$

(3.22)

where $\lambda_{\text{max}}$ is the largest eigenvalue of the gyration tensor, and $\text{det}(S_I)$ is the determinant of the gyration tensor of cluster $I$. This measure has a value of 1 if the anisotropy is high, and a value of 0 if the system is isotropic (sphere). Note that this measure does not depend on the direction of the anisotropy.

The third measure that we pick, has to do with the size of the cluster. This measure is,

$$N^*_I = \frac{N_I}{N_L},$$

(3.23)

where $N_I$ is the number of particles that belong to the cluster $I$, $N_L$ is the minimum amount of particles that stacked together can span the edge-length of the box in one direction. This measure has a value of $N^* < 1$ if the cluster size is smaller than the $N_L$, and a value of $N^* \geq 1$ if the particle-string has enough particles to span the box, even if the box is not actually spanned in that specific configuration (floculates). A schematic representation of the described measures can be found in Fig. 3.2.

The averages of the measures $S^*_2, \lambda^*_I,$ and $N^*_I$ are reported in the following, and these averages will be denoted by the same symbol as their per-cluster counterparts, but without the cluster index. The size of the cluster serves also
as a weighting factor for these averages, so that every particle of the structure has equal effect on the measured quantity. However, it is much different from calculating these quantities for the entire system.

In previous work of ours [129], we introduced a method to characterise large structures of particles, including networks. That method uses a 3D-binary image of the initial structure, and thins out this structure to an infinitely thin skeleton. This procedure is called skeletonization [95], and it results to an ensemble of voxels (skeleton); there are still complex connections in the skeleton representing the abstract connectivity inherent to the actual structure provided as input. This issue is tackled by several post-processing steps that result in a topologically equivalent skeleton with essentially the same connectivity [129]. The whole scheme we described, results to a simplified, and easier to characterise skeleton structure. The simplified skeleton is characterised in terms of:

- branch-points (BP) (number density, degree)
- branches (thickness)
- existence of percolation

Details concerning these points follows.

The BPs are identified by the number of their connections to neighboring voxels in the simplified skeleton. Every voxel bearing three or more connections is accounted for as a BP. So one can identify the number of BPs. A BP-reduction step is required to prevent unphysical results of BPs lying in neighboring voxels. This step concerns BPs located inside the volume of a single primary particle, when BPs like the ones described are identified they are grouped together as one BP. Then the number density of branch points per volume is given

\[ n_{BP} = \frac{N_{BP}}{N_p}, \]

(3.24)

where \( N_{BP} \) is the absolute number of BPs, and \( N_p \) is the amount of primary particles. Except the number density, also the average degree of BPs can be studied, \( \langle d_{BP} \rangle \). The degree is defined by counting the bonds of all the BPs in the simplified skeleton, and then taking their average.

The average thickness of the branches is calculated by cutting a slice of the initial binary image at the position of each voxel and taking as the normal vector the orientation of the skeleton at this point (tangent of the skeleton) [129]. The percolation in each direction of the box is also checked. One tries to establish in-box pairing between any couple of particles each of them being
close to two opposite faces of the simulation box (“close to” implying they have a bond crossing that respective face of the box).

3.4 Results

The results of particle-based simulations using the tools mentioned in Sec. 3.3, will be reported. At this point, we would like to note that the error-bars in this section will always refer to different random numbers sequences. Our system consists of 1000 particles, and our protocol indicates that we use three simulations with different random numbers sequences to produce the error-bars. In the rest of the section, we discuss the effect of the variation of random initial configurations, see Subsection 3.4.1, the $B^*$ variation, see Subsection 3.4.2, and the $\phi$ variation, see Subsection 3.4.3.

3.4.1 Initial configuration variation

In this subsection, we study the effect that different random initial configurations have on the structure with the measures introduced before. We obtain the initial configurations by setting the particles to a simple cubic lattice, and letting them re-arrange into the box. We use a Brownian Dynamics scheme and the deterministic part for the equilibration loop consists of the repulsive part of a Lennard-Jones potential [147, 148] with $\sigma = 2R_p/r_c$, and $\varepsilon = 1$. This randomness of the structure has been investigated by examining the number density of particles in a tessellated box and the pair correlation function. The box contains 1000 particles, it is tessellated in 125 cubic boxes, and the number density is defined as the average number of particles that appear in the cubic box. The average number density over the cells is constant by definition, so we look at the standard deviation of this measure over the cells and through (dimensionless) time of $90t_c$. The samples are equilibrated, until the standard deviation between the cells shows a plateau with a value smaller than 0.2, so that a homogeneous distribution over the cells is reached. At the same point the pair-correlation function is calculated and has the same characteristics as a Lennard-Jones fluid [54]. The details can be found in Appendix C.

Once these random configurations are obtained, we study the impact of varying them in the structure evolution in terms of $S_2$, $\lambda^*$, and $N^*$. We choose these measures mainly because they are applied to the primary structure and no transformation of the structure has to occur (skeletonization). We used four different random initial configurations, each of them evolved by three simula-
Figure 3.3: A random configuration of particles (red) is presented with their Voronoi cells (blue) produced by using the Voro++ library [149].

3.4.2 $B^*$ variation

The variation of the single physical dimensionless parameter, $B^*$, will be discussed in this subsection. The variation of the parameter $B^*$, has to do with varying physical parameters like the field intensity or temperature and many-particle simulations are needed to investigate these effects.

Different $B^*$ = 0.01, 0.0316, 0.1, 0.316 and $\phi = 1\%, 2\%, 5\%, 10\%, 20\%$, and 30% values were used to unveil the effect of the only dimensionless parameter to the structure formation. The response of the system in terms of our measures ($S_2$, $\lambda^*$, and $N^*$), is expected to depend on the value of the parameter $B^*$, as $B^*$ defines the magnitude of the thermal noise, see Eq. (3.13). However, $B^*$
is a parameter introduced based on two-particle interactions and we expect to observe some deviations in the generalisation to many-particle systems. In Fig. 3.4, one can see the response over dimensionless time for $\phi = 10\%$, is overlapping to a single curve independent of the $B^*$. This means that the characteristic timescale concerning two-particle dynamics is of relevance also for systems with many particles, and no adaptation of the $B^*$ is needed to study the structure formation, so the thermal noise can be neglected in the regime we investigated. In the rest of this chapter, we are going to use the value of $B^* = 0.01$. Only one value of $\phi$ is presented here, although we used the same $B^*$ values for $\phi = 1\%, 2\%, 5\%, 10\%, 20\%, \text{ and } 30\%$, we display some characteristic values of low and high $\phi$ in Appendix D.

If one would increase the value of $B^*$ further, e.g., to values as high as order unity, one should expect to see “deviations” from the pattern of Fig. 3.4, the reason for these “deviations” being the following. In order for the scaling with $t_c$ to collapse the simulation results obtained under different conditions, it is assumed that the dipole-dipole interactions are dominant over the thermal fluctuations; if this does not hold, the structure formation will be changed qualitatively. No hard limits can be defined, however, we believe that for $B^* > 0.5$ the thermal fluctuations dominate, and a straightforward collapse of the results by scaling can not be achieved anymore.

It should be noted that the simulations presented in Fig. 3.4, were completed in dimensionfull units. The difference in dimensionless time comes from the fact that equal overall dimensionfull times were used. One should expect equal simulation times in $t^*$ for the different $B^*$-values, however, our simulations results were independent of the $B^*$-value, as they overlap onto a single curve. To this end, we concluded that conducting additional simulations would not be a significant contribution to the essence of this chapter.

### 3.4.3 Volume fraction variation

In this subsection, we would like to focus on the $\phi$ variation and its impact on the structure. Our goal is to determine the structures created in different systems, and explore the applicability of our dimensionless analysis, and morphology tools. The goal of this study is the determination of structure-formation time-scales and structure that can be achieved.
Figure 3.4: Morphology measures $S_2$ (a), $\lambda^*$ (b), and $N^*$ (c) plotted against the dimensionless time, $t^*$. Different lines correspond to different values of $B^*$ (0.01, 0.0316, 0.1, 0.316) for $\phi = 10\%$. 
Cluster characterisation

The volume fraction, $\phi$, was varied (1%, 2%, 5%, 10%, 20%, and 30%) for the minimum $B^*$ value (0.01). We expect that structure formation will occur at the same dimensionless time as $\phi$ increases. This occurs due to the lower inter-particle distances met in higher $\phi$-values, the time scale is decreasing, see Eq. (3.11). However, we also expect significant differences among different $\phi$-values as our scaling was performed for two-particle interactions and in this subsection we study many-particle systems with different inter-particle distances. In Fig. 3.5, one can observe that all the $\phi$ values used show initial response in our measures at $t^* \sim 0.05$. That means that our expectation was correct and the structure formation for higher $\phi$ in terms of time is resolved from the scaling analysis. The difference observed for different $\phi$ implies that the two-particle scaling is not enough to resolve the structural evolution of many-body systems when the inter-particle distances are modified. That means that more complex physics take place. We also observe a significant drop in our measures as time increases especially for $\phi > 10\%$. This can be justified by the fact that our measures are applied to whole clusters, and all the particles create a single cluster in higher $\phi$, see Fig. 3.5c. For this purpose further investigation is required, to this end we are going to explore the neighbourhoods of particles.

At this point, it should be mentioned that the structure formation occurs in $O(1s)$ for all $\phi$-values, Eq. (3.12). This timeframe is suited for applications like 3D-printing, and more specifically stereolithography. In recent studies [150], it has been observed that the gel-point of acrylate systems is reached at times within the same order of magnitude.

Neighbourhood characterisation

We study the neighbourhoods of particles through the Voronoi tessellation technique for the same configurations we investigated before. Except for the Voronoi volume distributions, the relative shape anisotropy of the cells, defined in Eq. (3.19), is also explored.

The main issue of our tools is the insufficiency for identifying the main characteristics of a structure that is formed by one cluster (probable network). We expect that the Voronoi cells of the particles are going to distinguish the core of the structure ($V_{cor} < \langle V_{vor} \rangle$ and isotropic shape). We speculate that particles belonging to the external layer of the structure will exhibit $V_{ext} > \langle V_{vor} \rangle$, and pretty anisotropic shape (distant neighbours). Although, conclusions can be drawn about the structure, no identification of the core was made. In Fig. 3.6,
Figure 3.5: Morphology measures $S_2$ (a), $\lambda^*$ (b), and $N^*$ (c) plotted against the dimensionless time, $t^*$. Different lines correspond to different values of $\phi = 1\%$, 2\%, 5\%, 10\%, 20\%, and 30\%.
one can see that the evolution of the structure in time, and the distributions are far from random (broader), no quantitative identification of the characteristics (BP, branches) is possible. A well-known [55, 62, 128] technique in many different fields [63, 65–68, 71, 92] has proven inefficient for the quantitative characterisation of our systems.

**Skeleton characterisation**

Since, our attempt at identifying the main structure characteristics concerning networks or late stages of the structure formation did not yield the desirable results, we will focus at transforming our structure to its bare skeleton with our previously introduced [129] skeletonization methodology. This technique gives us the possibility to identify the main characteristics of the structure and create a skeleton from which we can extract all the important information (BPs, thickness of branches, existence of percolation).

Here, we discuss the results obtained from the skeletonization of our structures. This technique uses a 3D-binary image as an input, in this image the cavities are filled in for avoiding complications. The results concerning the filling of the cavities [129], are presented in Appendix E for all $\phi$, and $B^* = 0.01$. The number density, and degree of BPs are presented in Fig. 3.7. The average thickness of branches for all $\phi$ used are presented in Fig. 3.8.

We expect to find an initial increase of BPs due to the initial structure formation and then a decreasing amount of BPs for increasing $t^*$. The particles create a structure at early stages, and after they rearrange microstructurally to the optimal configuration with respect to the potential (more compact, less short branches). One can observe in Fig. 3.7a, that for $\phi = 10\%$ our expectation is verified, as after an initial increase until $t^* = 2$, $n_{BP}$ decreases and eventually reaches a plateau. We also expect the plateau value of $n_{BP}$ to increase with increasing $\phi$, as the smaller the inter-particle distances the more network-like structures created. Our expectation is confirmed in the final structure ($t^* = 10$), the $n_{BP}$ is increasing with increasing $\phi$.

As the structure is formed we expect more complex pathways being present initially, and the degree of BPs to be reduced as thicker components and simpler pathways are formed over time. In Fig. 3.7b, for $\phi = 10\%$ we observe an initial increase following the same trend as $n_{BP}$, and after that a plateau around its minimum value (three) is reached within errorbars. We also expect the degree to be unaffected for varying $\phi$, as the structure at advanced times is evolved and the complex pathways has been replaced by thicker components of the structure. In Fig. 3.7b, no significant influence of $\phi$ is observed for the degree at the final
Figure 3.6: (a) The distribution of scaled Voronoi volumes is plotted as a function of dimensionless time for a system of $\phi = 10\%$ and $B^* = 0.01$. The scaling is performed with the average Voronoi volume of the configuration. The distribution of scaled Voronoi volumes (b), and relative shape anisotropy (c) are plotted for dimensionless time $t^* = 10t_c$ and $\phi = 1\%, 2\%, 5\%, 10\%, 20\%$, and $30\%$. The distributions of a random configuration of particles, and of an isotropic network (isonet) are also plotted for comparison.
3.4. Results

structure \((t^* = 10)\) as expected.

The evolution of the structure is expected to be followed by increasing thickness in time. In Fig. 3.8, for \(\phi = 10\%\) we observe an initial increase until the structure is formed \((t^* = 1)\), and then deviates around a plateau value. An exemption is observed for \(\phi = 30\%\); the thickness is increasing until dimensionless time of approximately 4, and then decreases to approximately a stable value. This decrease is related with the filling of the cavities shown in Appendix E, as the volume of cavities filled decreases an order of magnitude at \(t^* > 4\) the average distance of a skeleton voxel to an empty voxel is decreased as the percentage of empty voxels is larger in the box. So thinner branches are present. We also expect an increasing thickness for increasing \(\phi\), as the higher the \(\phi\) the smaller the inter-particle distances and the thicker the structures formed. In Fig. 3.8, for \(t^* = 10\) one can observe that indeed the thickness is increasing proportionally to \(\phi\).

The existence of percolation is also checked. It is expected to achieve percolation along a single direction at the same time, as \(N^*\) reaches a value of one. Percolation occurs for lower \(\phi\) (1%, 2%, 5%, 10%) at time of 1 in the direction of the field \(z\). Percolation in not reached in the other directions \((x, y)\), in the limit we investigate in this chapter. On the contrary, the higher \(\phi\) (20%, 30%), reach percolation in \(z\) at \(t = 1\) and in \(x, y\) at \(t = 2\). This is explained by the fact that the unoccupied space in larger \(\phi\) is limited and results to the creation of percolation paths also on the \(xy\) plane, which is perpendicular to the main direction of anisotropy.

**Thermal conductivity**

At this point, we would like to present Fig. 3.9, where the enhancement factor of the thermal conductivity of the medium for the principal directions for the \(\phi\) used in this article is shown. We did not develop this theoretical analysis [16], but we use it to demonstrate the enhancement that one can achieve by aligning the particles in a medium. This analysis of the thermal conductivity of composites produced under an external field (magnetic or electric) shows that the particle structuring could improve thermal transport, however, other transport properties have isomorphic behavior (e.g. electrical conductivity, dielectric permittivity) [15]. This theory is an adaptation and extension of the Maxwell theory that takes into account spatial correlations between particles [151], it originates from the equivalent theory concerning the magnetic susceptibility [14]. In Fig. 3.9, one can see how much the thermal conductivity coefficient \(K_{\text{eff}}\) can be enhanced by the alignment of particles compared to random addi-
Figure 3.7: (a) Number density of branch-points for $\phi = 1\%, 2\%, 5\%, 10\%, 20\%,$ and 30% is plotted against time. (b) Degree of branch-points is plotted against time for the same $\phi$.

Figure 3.8: The average thickness of branches is plotted against time for $\phi = 1\%, 2\%, 5\%, 10\%, 20\%,$ and 30%.
Figure 3.9: Thermal conductivity enhancement factor [15] against $\phi$ for final configuration.

The enhancement ratio is calculated as [16]

$$\frac{K_{\text{eff},w}}{K_{\text{poly}}} = 1 + \frac{3\phi}{1 - \phi - \delta_w \psi_z},$$

where the subscript $z$ refers to the direction of the external field, $w$ is an index that indicates any of the three principal axes, $x$, $y$, or $z$, of the sample, $\delta_x = \delta_y = 1$, and $\delta_z = 2$. This expression differs from the Maxwell theory only by the structural order parameter

$$\psi_z = -\frac{1}{N} \sum_{j=1}^{N} \sum_{i \neq j} (2R_p/r_{ij})^3 P_2(\hat{r}_{ij} \cdot \hat{E}),$$

where $P_2(x) = \frac{3}{2}x^2 - \frac{1}{2}$ is the second Legendre polynomial.

We use Eq. (3.25), developed in [16], to relate the actual structure with the thermal conductivity, as an example of the enhancement of transport properties due to the structure formation. A more direct way of calculating the thermal conductivity would be performing full finite-element method (FEM) calculations, solving the energy balance [152]. Another way of obtaining the thermal conductivity from simulations would involve the Fluctuation Dissipation Theorem which relates thermodynamic response functions to the appropriate time-autocorrelation functions. The thermal conductivity is related to
the time-autocorrelation function of the heat-flux operator. The effective contribution of particles towards the overall thermal conductivity of the system is calculated using the appropriate Green-Kubo relation in relation to the heat-flux operator. Once this contribution to the thermal conductivity is obtained, the parallel model of thermal conductivity is used to calculate the effective conductivity as described in Bhattacharya et al. [153].

3.4.4 Comparison to literature

In this chapter, a relation between the physical input and the final structure of suspensions under a uniform external field is made. Our numerical results can be compared to experimental findings as follows. The formation of strings in the direction of the external field is observed in our simulations, and it has also been observed experimentally both for a few particles [154, 155] and many particles [156]. Beyond such a general agreement, we would also like to compare experiments with our numerical results in the regime of volume fractions for which our model is most appropriate, $\phi \leq 10\%$. In this regime, it is observed in experiments (at $\phi \sim 2\%$, see [157]) that chains form, which then might percolate depending on the magnitude of the field and the time the suspension is exposed to this field. This behavior is analogous to the regime of structure formation $t^* \leq 1$ of our suspensions in Fig. 3.5. The thickening of the clusters observed in our simulations has also been observed experimentally [158], where the chains aggregate over time and form thicker chains. Additionally, taking the experimental parameters studied in [158] and using them in the calculation of the characteristic timescale according to our procedure, one obtains indeed the times that correspond to the structure formation observed experimentally in [158]. This supports our hypothesis that two-particle scaling is appropriate for describing many-particle dynamics.

3.5 Summary and discussion

The structure formation and evolution of electro/magnetically (EM) active particles under a spatially uniform external electric or magnetic field was studied. EM active particles create dipoles when exposed to an external field. When two dipoles are sufficiently close, their interaction results in the formation of structures, e.g. chains. The physical parameters of relevance for this formation were organized in dimensionless groups, and the effect of these dimensionless numbers on the structure evolution was investigated. The possibility of 3D-printing
these systems with stereolithography [159] was explored in terms of the relevant time-scales. In this section, the results concerning the physical behavior of the system presented in Sec. 3.4, are discussed.

We used BD simulations to track and characterize structures of particles under a spatially uniform external field. We simulate the electro-magnetic interactions with the simple dipole approximation, the Stokes drag and Brownian force are used for the interaction with the surrounding medium. A method was presented to capture the structural dynamics of these systems, with special attention to the effect of the dipole-dipole interactions on the structure formation and evolution. We introduced a combination of measures for quantifying the evolution of the structure in time.

In Subsection 3.4.1, the initial configuration of the system was varied, and exhibited a larger impact on the results than the effect of the variation in random numbers sequence. The variation of the initial structure is required for the observation of the structural evolution of such systems. One should be careful with that observation, as an initial configuration with specific structure (e.g. FCC crystal structure) could have a large impact on a study of this kind.

The observations about $B^*$-variation were the following. Our scaling concerned only two-particle interactions, so our parameters like $B^*$ and $t_c$ are based on that assumption. This scaling should be obeyed for simulations of two-particle systems. However, a generalization to many-particle systems cannot be performed easily, as it is not clear if the same scaling is obeyed. To this end, we performed simulations of 1000 particles with various values of $B^*$, where we observed that the scaling is obeyed for many-particle systems as well, and the magnitude of the thermal fluctuations can be considered negligible in the regime we investigated, the only effect being that the fluctuations around the average increase.

Additionally, one can identify three main regimes, in Fig. 3.4. During the increase of $S_2$ in Fig. 3.4a, we have the formation of the chains. After that and until dimensionless time of 10, the anisotropy stays at the maximum level, Fig. 3.4b. The orientation measure $S_2$ reaches a maximum and then decreases to a plateau, as it is sensitive to thickening of the strings that are being formed. This conclusion is based on Fig. 3.4c, were at the same time the increase begins $t^* \sim 0.1$, the chains span the box in length, $N^* \sim 1$, after that the chains keep growing and the $S_2$ drops due to the thickening. At larger times, $t^* > 8$, it seems that the system reaches an equilibrium state, where $S_2$ exhibits a plateau.

The $\phi$-variation was performed in steps. The first step involved the same three measures we used before: $S_2$, $\lambda^*$, and $N^*$. There, we identified that different $\phi$-values exhibit different behavior, as our two-particle scaling is not
enough to resolve this variation. However, one can see that with increasing $\phi$, the $S_2$ and $\lambda^*$ decrease to really low values indicative of isotropy, at similar values of dimensionless time. From $N^*$ we observe that at high volume fractions of particles, $\phi > 20\%$, all particles of the system belong to the same cluster. These big aggregates are not characterized well by the above measures. The reason is that these measures were developed for string-like structure and at this point we do not have distinct strings. The structures look more like a network. To characterize them, we focused on the investigation of neighbourhoods of particles using the Voronoi tessellation. Although, some qualitative observations were made, one could not distinguish particles that belong to the core of the structure by the characteristics of their Voronoi cells. The main reason is that too many particles belong to the layer surrounding the core layer, resulting to large fraction of particles with the characteristics we are seeking for.

At high volume fractions, attention was paid on transforming the structure into a form that is easier to characterize, namely a skeleton with simplified connectivity. In this way, we were able to calculate the branch points (BPs), the thickness of branches, and the existence of percolation in all three directions and study their evolution in time. After the formation of the structure at early times, the local rearrangement of particles results in more compact structures as time advances. The BPs and thickness of branches seem to be mainly affected by the volume fraction $\phi$, the higher $\phi$ the higher the number density of BPs and the thickness of branches. The existence of percolation and the anisotropy of the structure were investigated. For $\phi > 10\%$, the structures formed percolate in all three directions ($x, y, z$). A lower values of $\phi$, the structure percolates only in the direction of the external field, $z$.

The thermal conductivity is calculated by way of a theoretical analysis, and it appears to be effectively increased by the structuring of the particles (see Figure 3.9). The relative enhancement ratio increases monotonously with the volume fraction for the final configurations of our structures. In addition to that, the thermal conductivity in all directions ($x, y, z$) is enhanced in relation to the random arrangement of particles. It has to be noted that this enhancement is significantly larger if polydispersity is introduced to the system, as the inter-particle distances are decreasing and the effective thermal conductivity coefficient is growing, Eq. (3.25). In this chapter, the thermal conductivity is presented, however, other effective properties such as the magnetic susceptibility, dielectric permittivity, and electrical conductivity exhibit isomorphic behaviour [15].
Chapter 4

Structure evolution of suspensions under time-dependent electric or magnetic field

Abstract

The effect of time-dependent external fields on the structure formation of particles with induced dipoles dispersed in a viscous fluid is investigated by means of Brownian Dynamics simulations. Dipole-dipole interactions forces, excluded volume forces and thermal fluctuations are accounted for. The resulting structures are characterised in terms of average orientation of their inter-particle vectors (second Legendre polynomial), network structure, size of particle clusters, anisotropy of the gyration tensor of every cluster and existence of (cluster) percolation. The strength of the external field is increased in one direction and then kept constant for a certain amount of time, with the structure formation being influenced by the slope of the field-strength increase. This effect can be partially rationalized by inhomogeneous time re-scaling with respect to the field strength, however, the presence of thermal fluctuations makes the scaling at low field strength inappropriate. After the re-scaling, one can observe that the lower...
the slope of the field increase, the more network-like and the thicker the structure is. In the second part of the study, the field is also rotated instantaneously by a certain angle, and the effect of this transition on the structure is studied. For small rotation angles ($\theta \leq 20$) the clusters rotate but stay largely intact, while for large rotation angles ($\theta \geq 80$) the structure disintegrates and then reforms, due to the nature of the interactions (parallel dipoles with perpendicular inter-particle vector repel each other). For intermediate angles ($20 < \theta < 80$), it seems that, during rotation, the structure is altered towards a more network-like state, as a result of cluster fusion (larger clusters).

4.1 Introduction

An external electric or magnetic field is affecting a suspension of dielectric or conductive particles by inducing dipoles to the particles, due to the difference in the dielectric permittivity or magnetic susceptibility between them and the medium [11]. The presence of the dipoles cause the particles to interact [11] and the result of this interaction is the formation of structures of particles [12]. The particles under different field conditions can form strings [13] that evolve and aggregate in time [13], planes [14], or networks [15]. In addition, the short-time aggregation dynamics has been studied [117, 118]. The additional enhancement of the properties of the material in the direction along which the structures are created comes as an effect of the arrangement of the particles [14, 16]. The transport properties are greatly affected by the formed structures, due to the existence of percolation paths [15]. The suspensions that contain fillers particles responsive to an external field, are called electro-/magneto-rheological fluids and have been a subject of research due to their unique characteristics. Their rheological response occurs in $\mathcal{O}(1s)$ time scales and is exploited in force-feedback sensors in robotics [121]. The rapid viscosity increase in the direction perpendicular to the applied field has also been widely investigated in the past [12, 17–20, 122]. The response of these systems under shear has been a topic of extensive research [21, 22]. The structures created in a spatially uniform external field have also been studied on large time-scales both athermally (no Brownian motion) [13], and thermally (including Brownian motion) [113, 123].

Additive manufacturing has been a subject of scientific interest for a long time [30], although it is nowadays a subject of extended research [31]. Different kinds of materials are used including metals [32], polymers [33], ceramics [34] and combinations of them [31]. Printing of polymer-matrix composite materials is used for various purposes such as rapid prototyping (temporary substitutes
for parts of higher mechanical performance) [41], or topology optimization (introduction of shape memory in a passive matrix) [124]. They have a wide range of applications: aerospace applications (cabin interiors) [35], medicine (mimics of living tissue) [36], anthropology (reconstruction of medieval skulls) [37], and design (spatially-dependent elasticity) [38]. The incorporation of dielectric, magnetic or conductive functionality to the matrix material [39–41] is another advantage of composite materials. Additionally, if the microstructure of the composite can be controlled during printing via the use of an external electric or magnetic field, then one can achieve specific structures of particles inside a complex geometry. This can be an important application of this work, especially if photo-reactive resins [125] filled with electrically or magnetically active particles are concerned. Resins are widely used as dispersing media for particles [27, 28], so that the structure of the particles can be captured with the solidification of the resin; the low viscosity of the resins before curing makes the structure formation possible within the usual time-scales (\(O(1s)\)) of 3D-printing. The targeted technique is stereolithography (SLA) [29]. Potential uses of these systems in applications include personalised hearing aids [42], flat lenses with a gradient of concentration of particles that have the functionality of their curved counterparts [43], piezoelectric or Hall effect sensors [44], and direction-specific thermally or electrically conductive composites [15]. In the following, we focus on the physical behaviour of these systems, in terms of structural evolution under a time-dependent field.

A combination of electromagnetic suspensions and curable resins with application to SLA would be possible with sufficient knowledge of the structure formation under time-dependent fields. Different kinds of structures can be obtained by time-dependent fields, more network-like structures are obtained if the field is increasing gradually [14]. The effect of this slope with respect to the characteristic time-scales of structure formation [113] is investigated in this chapter. The multidirectional external fields are interesting due to the transitions of the fields either inside a layer or from layer to layer during 3D-printing, if one wants to create a path of particles inside a layer or a 3D structure of particles inside the printed object. In the literature, the effect of rotating fields have been studied before. The effect of the Mason number [23], which is the ratio of viscous to magnetic forces [24–26], is studied in a system with a rotating field. In this chapter, an already formed structure is subjected to a rotated, with respect to the initial field orientation, field and the structure evolution is followed.

In this chapter, we use Brownian Dynamics (BD) simulations with dipole-dipole interactions, to simulate the motion of particles (dipoles) in a fluid under
a time-dependent and spatially uniform field. Our method results in a structure of particles, and the characterisation depends on the nature of these structures. As already mentioned, one can get various structures depending on the field conditions, like strings [13], planes [14], or networks [15]. The goal of characterizing such structures is to extract their main features and to describe these features in a quantitative manner. For example, for strings one should know the size, orientation, thickness and correlations among these measures, for planes the size and orientation, and for networks the number density of branch-points (BP), the degree of BP, the thickness of the branches, the number of clusters present, and the existence of percolation. There are a lot of techniques used for the characterisation of an ensemble of points/particles, like investigating their gyration tensor (eigenvalues and eigenvectors) [74] and the Voronoi tessellation technique [62]. The Voronoi tessellation is widely used in the characterisation of disordered systems [128], polymers [66–68, 71], colloidal gels [92], and granular materials [65]. Other techniques like the (radial or cylindrical) pair-correlation function, bond-angle distribution [56], and quermass integrals [58] have also been developed for the characterisation of the structure of networks. Here, the gyration tensor of clusters, and a previously developed skeletonization method [95, 97, 129] are employed for the quantitative characterisation of the structures.

The goal of this chapter is twofold. In the first part, we investigate the effect of unidirectional time-dependent fields on the structure formation, and compare it with the case of a constant field [113]. In the second part, we investigate the effect of rotating the field on the structure evolution. The chapter is organised as follows. Sec. 5.2 provides the basic methodological tools that were used for the production and characterisation of the structures. In Sec. 5.3, we present the structural evolution in time in dimensionless terms, and the characteristics features of our formed structures for both uni- and multidirectional fields. Finally, the chapter is concluded with a discussion in Sec. 4.4.

4.2 Methodology

In this section, the simulation details and morphology characterisation are discussed. Our system consists of particles with particle radius $R_p$ and volume fraction $\phi$, and the dispersing fluid with viscosity $\eta$, in a finite box of edge-length $L$, where periodic boundary conditions are applied in all three directions. The system is influenced by an external field. In the current chapter, the system consists of particles with induced dipoles due to the mismatch in the dielectric
permittivity of the matrix, $\epsilon_m$, and the particles, $\epsilon_p$, under a time-dependent external field.

### 4.2.1 Simulation details

In our model, we include dipole-dipole interactions [11, 12], excluded volume interactions, and thermal fluctuations. For reducing the physical and numerical parameters of our model to the minimum, we introduce characteristic scales for length, dipole moment, and time. The positions of the particles are scaled with the characteristic length-scale, $r_c = 1/\sqrt[3]{n_d}$, where $n_d$ is the number density of particles, and the dipole moments with the characteristic dipole moment magnitude, $p_c = 4\pi\epsilon_m K R_p^3 E_c$, with $E_c$ the maximum value of the electric field and $K$ the Clausius-Mossotti constant [11]. The time is scaled with the characteristic time-scale introduced in Manikas et al. [113],

$$t_c = \frac{8\pi^2 \epsilon_m \eta R_p r_c^5}{p_c^2}.$$  (4.1)

The corresponding dimensionless time is denoted by

$$t^{(1)} = \frac{t}{t_c}. \quad (4.2)$$

To simulate the system, we use Brownian Dynamics (BD) [47, 48] simulations of the following evolution equations, in dimensionless form,

$$d\mathbf{r}_i^* = (\mathbf{F}_{i}^{\text{em}*} + \mathbf{F}_{i}^{\text{exv}*}) dt^{(1)} + B^* \sqrt{dt^{(1)}} \xi_i, \quad (4.3)$$

with

$$\mathbf{F}_{i}^{\text{em}*} = \sum_j \frac{1}{r_{ij}^{*4}} \left( ((\mathbf{p}_i^* \cdot \mathbf{p}_j^*) - 5(\mathbf{p}_i^* \cdot \hat{\mathbf{r}}_{ij})(\mathbf{p}_j^* \cdot \hat{\mathbf{r}}_{ij}))\hat{\mathbf{r}}_{ij} 
+ (\mathbf{p}_i^* \cdot \hat{\mathbf{r}}_{ij})\mathbf{p}_j^* + (\mathbf{p}_j^* \cdot \hat{\mathbf{r}}_{ij})\mathbf{p}_i^* \right), \quad (4.4)$$

$$\mathbf{F}_{i}^{\text{exv}*} = -\frac{r_c^4}{8R_p^4} \sum_{j \neq i} p_i^* p_j^* e^{-\kappa \frac{r_{ij}^* r_{ij}}{2m_p}} \hat{\mathbf{r}}_{ij}, \quad (4.5)$$
\[ B^* = \sqrt{\frac{2k_B T t_c}{\zeta r_c^2}}. \]  

(4.6)

While \( \xi_i \) are statistically independent vectors whose components are drawn independently from a Gaussian random-number distribution with mean value of 0 and standard deviation of 1, \( \mathbf{F}_i^{\text{em}*} \) is the force due to the dipole-dipole interactions, \( \mathbf{F}_i^{\text{exv}*} \) is the force preventing the particles from overlapping, \( \mathbf{p}_i^* \) is the scaled dipole moment of particle \( i \) which may depend on \( t^{(1)} \), however, this dependence is omitted from Eq. (4.4) for clarity, the notation \( \mathbf{r}_i^* = \mathbf{r}_i / r_c \) is used to denote the position vectors \( \mathbf{r}_i \) and difference vectors \( \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j \) in rescaled form, and \( \hat{\mathbf{r}} \) is the unit vector, \( \mathbf{r} = \mathbf{r} / r \), where \( r = |\mathbf{r}| \); this notation is used for all quantities in the rest of the paper for scaled vectors, unit vectors and magnitude of vectors. The parameter \( \kappa = 30 \) is a constant that determines the interaction range of the excluded volume, while the pre-exponential factor defines the overall strength of the interaction [24]. The Boltzmann constant is denoted by \( k_B \), the temperature by \( T \), and the friction coefficient is \( \zeta = 6\pi\eta R_p \). The Ewald-summation technique is used for the long-range corrections of the dipole-dipole interactions [138].

### 4.2.2 Morphology characterisation

In this subsection, we introduce the measures that we are going to use for the rest of this chapter. We discuss morphology measures concerning clusters/structures of particles. The first measure concerns the orientation of the inter-particle direction with respect to an external direction, that being the external field, \( \hat{\mathbf{E}} \),

\[ S_{2,I} = \frac{3}{2} \langle (\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{E}})^2 \rangle_I - \frac{1}{2}, \]  

(4.7)

where the index \( I \) denotes the cluster index, so for cluster \( I \) the average is defined as the average of the particles that participate in \( I \). Eq. (4.7) is the second Legendre polynomial for the pairs of particles that belong to the same cluster \( I \), however, periodic boundary conditions are applied and only the primary image is considered. Eq. (4.7) quantifies the orientation of the inter-particle distances with respect to the direction of the field. \( S_2 \) has a value of 1 if the average orientation is parallel to the external direction, a value of 0 if there is random orientation with respect to the direction of the field, and a value of \(-1/2\) if the orientation is perpendicular to the external direction.
4.2. Methodology

The second measure quantifies the anisotropy of each cluster, and for that we calculate the gyration tensor [74],

\[ S_I = \left\langle (r_i - r_{cm,I})(r_i - r_{cm,I})^T \right\rangle_I , \]  
\[ (4.8) \]

where the superscript “T” denotes the transpose, \( N_I \) is the number of particles that belong to the cluster \( I \), and \( r_{cm,I} \) is the position of the center of mass of the particles belonging to the cluster \( I \). The gyration tensor defines an ellipsoid [74]. The eigenvalues of the gyration tensor give the relative difference in size of the three main axes of the ellipsoid. As a measure that quantifies anisotropy, we introduce,

\[ \lambda_I^* = 1 - \text{det}(S_I)\lambda_{\text{max},I}^{-3} , \]  
\[ (4.9) \]

where \( \lambda_{\text{max}} \) is the maximum eigenvalue of the gyration tensor, and \( \text{det}(S_I) \) is the determinant of the gyration tensor. This measure has a value of 1 if the anisotropy is high, and a value of 0 if the system is isotropic (sphere). Note that this measure does not depend on the direction of the anisotropy.

The third measure that we use has to do with the size of the cluster,

\[ N_I^* = \frac{N_I}{N_L} , \]  
\[ (4.10) \]

where \( N_L \) is the minimum amount of particles that are needed to span the box-length in one direction. This measure has a value of \( N^* < 1 \) if the cluster size is smaller than the \( N_L \), and a value of \( N^* \geq 1 \) if the string has enough particles to span the box, even if the box is not spanned (flocs).

The averages over all clusters of the measures \( S_{2,I} \), \( \lambda_I^* \), and \( N_I^* \) are reported in the following, and these averages will be denoted by the same symbol, but without the cluster index. The weighted-average is given by

\[ A = \frac{1}{N_p} \sum_{I=1}^{N_{cl}} N_I A_I , \]  
\[ (4.11) \]

where \( A \) is any quantity of interest, \( N_{cl} \) is the number of clusters, \( N_I \) is the number of particles in cluster \( I \), and \( A_I \) is the value of the quantity \( A \) for the cluster \( I \).

The rest of the characterisation techniques do not subdivide the particles into clusters, but concern all the particles.

In previous work of ours [129], we introduced a method to characterise large structures of particles, in particular networks. This method uses a 3D-binary
image of the initial structure, and thins out this structure to an infinitely thin skeleton. This procedure is called skeletonization [95], and it results in an ensemble of voxels (skeleton). Since there are still complex connections in the skeleton, post-processing steps are used that result in a totally simplified skeleton with the essential connectivity [129], which is easier to characterise. The simplified skeleton is characterised in terms of branch-points (BP) (number density, degree), branches (thickness), and existence of percolation, as follows.

The BPs are identified by the number of their bonds to neighboring voxels in the simplified skeleton. Every voxel bearing three or more bonds is accounted as a BP. The number density of branch points per volume is given by

\[ n_{BP} = \frac{N_{BP}}{N_p}, \]  

(4.12)

where \( N_{BP} \) is the absolute number of BPs, and \( N_p \) is the amount of primary particles. Also the average degree of BPs can be studied, \( \langle d_{BP} \rangle \). The degree is defined by counting the bonds of all the BPs in the simplified skeleton, and calculating the average. The average thickness of the branches is calculated as explained by Manikas et al.[129]. The percolation in each direction of the box is also checked. One tries to establish in-box pairing between any two particles each of them being close to two opposite faces of the simulation box ("close to" implying they have a bond crossing that respective face of the box). If there is no percolation in any of the three orthogonal directions (\( x, y, z \)), there is no percolation in the system.

### 4.3 Results

In this section, we present simulation results concerning suspensions under unidirectional time-dependent fields, and multi-directional time-dependent fields. Our system consists of 1000 particles, with three simulations with different random numbers sequences, and three different random initial configurations to generate the error-bars [113]. In all simulations, the ratio between the thermal fluctuations and the strength of the electric field, \( B^* \), and the characteristic time-scale \( t_c \) are kept constant, only the time-dependence of the field-strength of the electric field is varied through the simulations. This means that the magnitude of the thermal fluctuations relative to the final field strength remains constant throughout the simulations and only the deterministic part in Eq. (4.3), is varied.
4.3. Results

4.3.1 Uni-directional time-dependent fields

For uni-directional time-dependent fields, we use a spatially constant field with variation of its strength over time. The re-scaled time $t^{(1)}$, Eq. (4.1), is used to characterise the time dependence of the field strength: increasing field strength over the interval $[0, t_s^{(1)}]$ until the field reaches the maximum value, and then it remains constant for 10.0 units of time $t^{(1)}$ (see Fig 4.1); $t_s^{(1)} = 0.1, 1.0, \text{ and } 10.0$ are used.

The field magnitude is given by

\begin{align}
E^*(t^{(1)}) &= \frac{1}{t_s^{(1)}} t^{(1)}, \quad t^{(1)} < t_s^{(1)}, \quad (4.13) \\
E^*(t^{(1)}) &= 1, \quad t^{(1)} \geq t_s^{(1)}. \quad (4.14)
\end{align}

In Fig. 4.2, one can observe the measures $S_2$, $\lambda^*$, and $N^*$ for $t_s^{(1)} = 0.0, 0.1, 1.0, \text{ and } 10.0$. As one can observe, the initial response of the measures presented depends strongly on $t_s^{(1)}$, so the constant $t^{(1)}$-scaling is not optimal for this case. We would like to scale the time corresponding to the field value at each point in time. This can be achieved by introducing

\begin{equation}
\tilde{t}^{(2)} = \int_0^{t^{(1)}} E^{*2} \left(t^{(1)}\right) \, dt^{(1)}, \quad (4.15)
\end{equation}

Figure 4.1: Dimensionless uni-directional time-dependent field $E^*(t^{(1)})$, with transition time $t_s^{(1)}$. 
where for a field of the type presented in Fig. 4.1, one finds,

\[ t^{(2)} = \frac{t^{(1)^2}}{3t^{(1)^2}} , \quad t^{(1)} < t^{(1)s} , \]  
\[ t^{(2)} = t^{(1)} + \frac{2t^{(1)s}}{3}, \quad t^{(1)} \geq t^{(1)s}. \]  

(4.16) \hfill (4.17)

Departing from Eq. (4.3), one finds

\[ d\mathbf{r}_i^* = (\mathbf{F}_{\text{em}}^{**} + \mathbf{F}_{\text{exv}}^{**}) dt^{(2)} + B^{**} \sqrt{dt^{(2)}} \xi_i, \]  

(4.18)

with

\[ \mathbf{F}_{\text{em}}^{**} = \sum_j \frac{1}{r_{ij}^4} \left( (\hat{p}_i \cdot \hat{r}_{ij}) - 5(\hat{p}_i \cdot \hat{r}_{ij})(\hat{p}_j \cdot \hat{r}_{ij}) \right) \hat{r}_{ij} \]
\[ + (\hat{p}_i \cdot \hat{r}_{ij}) \hat{p}_j + (\hat{p}_j \cdot \hat{r}_{ij}) \hat{p}_i, \]  

(4.19)

\[ \mathbf{F}_{\text{exv}}^{**} = -\frac{r_{ij}^4}{8\rho_{ij}} \sum_{j\neq i} e^{-\kappa \left( \frac{r_{ij}}{2\rho_{ij}} \right)} \hat{r}_{ij}, \]  

(4.20)

\[ B^{**} = \sqrt{\frac{2k_B T t_c}{\zeta r_c^2 E^* \left( t^{(2)} \right)}}, \]  

(4.21)

where the dipole moments \( \hat{p}_i \) are unit vectors. The deterministic term in Eq. (4.18) is of order unity, however, the stochastic term depends on the value of the field strength \( E^* \), see Eq. (4.21). That means that if there were no thermal fluctuations, the cases for different \( t^{(1)s} \) were indistinguishable in the \( t^{(2)} \)-representation, the latter representing the case of a time-independent field. However, this is not the case in this chapter, as thermal fluctuations are included in our model. Thermal fluctuations are relevant particularly at early times, where the field strength is small and \( B^{**} \) is large (see Eq. (4.21)). The \( t^{(2)} \)-scaling is only accurate if the dipole interactions are dominant over the thermal fluctuations (\( B^{**} \) close to 0). \( B^{**} \) ranges from zero, where the thermal fluctuations are absent and our \( t^{(2)} \)-scaling is sufficient, to a large value, where the thermal fluctuations dominate over the dipole-dipole interactions. In our
4.3. Results

Figure 4.2: Morphology measures $S_2$ (a), $\lambda^*$ (b), and $N^*$ (c) versus dimensionless time $t^{(1)}$. The colour indicates the different values of $t_s^{(1)}$. 
case, we start with a large value for $B^{**}$, which then decreases gradually to a constant value. One needs to define a transition value, below which the $B^{**}$-value is low enough for the field to be dominant over the thermal fluctuations, so that the formation of clusters occurs at the same dimensionless time. To that end, we shift the curves such that we “neglect” the time before the strength of the field reaches $E^*_\text{negl} = 0.4933$. If one substitutes this value in Eq. (4.21), then a value of $B^{**} = 0.0203$ is obtained, meaning that the prefactor of the dipole-dipole interactions is almost 50 times larger than the one of the thermal fluctuations. The shift is the third time-transformation we apply and present it as $t^{(3)}$,

$$
t^{(3)} = t^{(2)} - c_{\text{negl}}t_s^{(1)} = \frac{t^{(1)} - t_s^{(1)}}{3t_s^{(1)}} - c_{\text{negl}}t_s^{(1)}, \quad t^{(1)} < t_s^{(1)} \quad (4.22)
$$

$$
t^{(3)} = t^{(2)} - c_{\text{negl}}t_s^{(1)} = t^{(1)} - \frac{2t_s^{(1)}}{3} - c_{\text{negl}}t_s^{(1)}, \quad t^{(1)} \geq t_s^{(1)} \quad (4.23)
$$

where $c_{\text{negl}} = E^*_\text{negl}^3/3 = 0.04$, and originates from the value of $t^{(2)}$ when $E^* = E^*_\text{negl}$. For the sake of simplicity, we will refer to the different conditions of electric field in terms of the value of $t_s^{(1)}$ (i.e., in scaling level $t^{(1)}$ rather than in scaling level $t^{(3)}$).

In Fig. 4.3, one can see the results presented in Fig. 4.2 after the transformation of time to $t^{(3)}$. The initial increase of the cluster measures occurs at the same time, meaning that our scaling works as expected. So the evolution of the structure due to the dipole-dipole interactions is actually suppressed until the field is strong enough to dominate over the thermal fluctuations. However, our $t^{(3)}$-scaling is still not ideal, as the transition between the two regimes described (large versus zero $B^{**}$-value) occurs gradually with a finite $t_s^{(1)}$-value. If a higher $t_s^{(1)}$-value is used, then the $B^{**}$ decreases slower in comparison to a lower $t_s^{(1)}$-value. So, the higher $t_s^{(1)}$, the slower the structure evolution becomes. If one dealt with a sharp transition, then the $t^{(3)}$-scaling should cause overlap of the curves for the different $t_s^{(1)}$-values.

The skeletonization measures are also examined for the same set of simulations. We expect that with higher $t_s^{(1)}$ the structure becomes more network-like rather than string-like, because if the thermal fluctuations are stronger relative to the dipole-dipole interactions, the particles are arranging in a more isotropic way. Our expectation is verified by the higher number density of BPs achieved with higher $t_s^{(1)}$, see Fig 4.4a. The degree of BPs is approximately the same
4.3. Results

Figure 4.3: Morphology measures $S_2$ (a), $\lambda^*$ (b), and $N^*$ (c) against dimensionless time, the colour indicates the different $t_s^{(1)}$ used (0.0, 0.1, 1.0, and 10.0).
for all $t_s^{(1)}$, i.e., no significant difference in the complexity of the pathways is observed, Fig. 4.4b. However, the standard deviation of the degree is clearly larger for the time-dependent cases, except the case of $t_s^{(1)} = 1.0$. The thickness is also influenced by $t_s^{(1)}$; the higher $t_s^{(1)}$, the higher the thickness, see Fig. 4.5. It is also observed that larger variations in thickness occur, in comparison to the constant-field case [113]. The observed decrease of thickness for $t_s^{(1)} = 0, 0.1$ is related to the volume of cavities filled, as the volume of cavities decreases an order of magnitude from the rearrangements of particles after the structure formation occurs ($t^{(3)} > 2$) [113]. The average distance of a skeleton voxel to an empty voxel is decreased as the volume of filled (entrapped) cavities decreases. The gradual increase of the field allows for a better rearrangement of the particles during the early stages of structure formation, which justifies the absence of this decrease for higher $t_s^{(1)}$.

In Fig. 4.6, one can see our measures for $t_s^{(1)} = 1.0$, and different $\phi$-values (1%, 2%, 5%, 10%, and 20%). We expect that structure formation will occur at the same dimensionless time, since a major effect of $\phi$ has already been taken into account when re-scaling towards $t^{(1)}$. In Fig. 4.6, one can observe that all the $\phi$ values used show an initial response in the structure measures at $t^{(3)} \sim 0.1$, however, different behavior between the $\phi$-values is observed thereafter. The difference observed for different $\phi$ implies that the two-particle scaling,
4.3. Results

The average thickness of branches is plotted against time for \( \phi = 5\% \), and \( t_s^* = 0.0, 0.1, 1, \) and 10.

Figure 4.5: The average thickness of branches is plotted against time for \( \phi = 5\% \), and \( t_s^* = 0.0, 0.1, 1, \) and 10.

on which Eq. (4.1) and (4.2) are based, is not sufficient for collapsing the structural evolution of many-body systems for different \( \phi \) [113]. That means that more complex physics take place than what could be anticipated based on a two-particle picture. We also observe a significant drop in \( S_2 \) and \( \lambda^* \) as time increases, especially for \( \phi > 10\% \), which implies the formation of isotropic structures. The measures presented here are calculated as cluster averages, see Eq. (4.11). In the presence of clusters comparable to the total amount of particles of the system for \( \phi > 10\% \), no orientation/anisotropy can be detected as the measures account for the whole system at once.

The \( \phi \)-study is extended to the skeletonization measures. We expect to find an initial increase of BPs due to the initial structure formation and then a decreasing amount of BPs for increasing \( t^{(3)} \). The particles create a structure at early stages, and thereafter they rearrange microstructurally to the optimal configuration with respect to the interaction (more compact, less short branches).

One can observe in Fig. 4.7a that for \( \phi \leq 20\% \) our expectation is verified, as after an initial increase, \( n_{BP} \) decreases and eventually reaches a plateau. For \( \phi = 30\% \), the number of BPs is increasing gradually over time; due to the lower interparticle distances thicker branches are formed that are less mobile and the connections between different branches take more time to form. We also expect the final value of \( n_{BP} \) to increase with increasing \( \phi \), since for the smaller interparticle distances more network-like structures are created. Our expectation is confirmed in the final structure, the \( n_{BP} \) is increasing with increasing \( \phi \).

As the structure is formed we expect more complex pathways to be present.
Figure 4.6: Morphology measures $S_2$ (a), $\lambda^*$ (b), and $N^*$ (c) against dimensionless time for $t_0^{(1)} = 1.0$. The colour indicates the different volume fraction values $\phi$ used (1%, 2%, 5%, 10%, 20%, and 30%).
4.3. Results

Figure 4.7: (a) Number density of branch-points and (b) degree of branch-points is plotted against time for the $t_{s}^{(1)} = 1.0$. The colour indicates the different volume fraction values $\phi$ used (1%, 2%, 5%, 10%, 20%, and 30%).

Initially, and the degree of BPs to be reduced as thicker components and simpler pathways are formed over time. In Fig. 4.7b, for $\phi = 5\%$ we observe an initial increase following the same trend as $n_{BP}$, and after that a plateau around a value of 4 is reached. In Fig. 4.7b, no significant influence of $\phi$ is observed on the degree at the final structure ($t_{s}^{(3)} \sim 9$).

The initial formation of the structure is expected to be followed by increasing branch thickness over time, as well as that the final value for the thickness would increase monotonically with $\phi$, due to the lower inter-particle distances. In Fig. 4.8, for all $\phi$ we observe an initial increase until the structure is formed, and then fluctuations around a plateau value, as expected. It seems that for $\phi = 1\%, 2\%, 5\%$ the time needed for reaching the plateau is lower than for $\phi = 10\%, 20\%, 30\%$. This is connected with microstructural rearrangements leading to thicker components due to elimination of small gaps between the particles that are more difficult to occur when the free space is smaller and the particles are being trapped. In Fig. 4.8, for $t_{s}^{(3)} \sim 9$ one can observe that indeed the final value for the thickness is increasing monotonically with increasing $\phi$. 
Figure 4.8: The average thickness of branches is plotted against time for $\phi = 1\%, 2\%, 5\%, 10\%, 20\%, \text{ and } 30\%$.

**Transforming back to real time**

In Subsection 4.3.1, our results are presented in terms of transformed time, $t^{(3)}$. However, one could translate the results to a “real” time, $t^{(1)}$. The relation between $t^{(1)}$ and $t^{(3)}$ is given by

\[
t^{(1)} = \sqrt{\frac{3}{2}} \left( t^{(3)} + c_{\text{negl}} t^{(1)} \right), \quad t^{(1)} < t^{(1)}_{s},
\]

\[
t^{(1)} = t^{(3)} + \left( \frac{2}{3} + c_{\text{negl}} \right) t^{(1)}_{s}, \quad t^{(1)} \geq t^{(1)}_{s},
\]

which are Eqs. (4.22) and (4.23) inverted. In Fig. 4.9, one can see how the transformation from $t^{(3)}$ to $t^{(1)}$ looks like.

The main difference between the $t^{(1)}$- and $t^{(3)}$-representations is the amount of time the system spends at $B^{**}$-values higher than $B^{**} = 0.01$. Our transformation reduces this discrepancy by scaling each moment in time with the time scale corresponding to the instantaneous field strength value. So the time it takes for reaching the maximum field-strength is basically compressed, see Figs. 4.2a, 4.3a. If one transforms back to $t^{(1)}$, then the higher the $t^{(1)}_{s}$ the more time it takes the structure to form.
Figure 4.9: The relation between the transformed time $t^{(3)}$ and real time $t^{(1)}$ is plotted for different values of $t^{(1)}$.

4.3.2 Multi-directional time-dependent fields

For multi-directional time-dependent fields, we use a configuration obtained by applying a constant in time and space field for time of $t^{(1)} = 10.0$, then rotate the field instantaneously to a different direction and follow the structure evolution for time of $t^{(1)} = 5.0$. The reason that we use $t^{(1)} = 5.0$ is that we are interested in the main transition, rather than the evolution after that; a time of approximately 5.0 should suffice for providing this information, as the characteristic time for two particles to touch is 1.0 and the structure formation occurs at the same time [113]. We use an angle $\theta$ to determine the rotation of the field around the $x$-axis; the initial field orientation is the $z$-axis. The $\theta$-values we use are ranging from $\theta = 10^\circ$ to $\theta = 90^\circ$ in steps of $10^\circ$. Note that the $S_2$ reported in this subsection always uses as reference direction the field-orientation before the rotation, which is the $z$-direction.

The expectation about the physical evolution of the system is based on the interaction potential. The radial component of the interaction force turns negative at an angle of 54.7$^\circ$ between the external field and the interparticle vector. This implies that two particles initially aligned with the external field would rotate trying to align their interparticle vector with the new orientation of the external field if $\theta_c < 54.7$, and would repel each other and reform their contact if the angle is larger. So we expect to have rotation until the described angle, while disintegration and reformation in the new orientation are expected for larger angles.
Figure 4.10: Morphology measures $S_2$ (a), $\lambda^*$ (b), and $N^*$ (c) against dimensionless time for different rotation angles $\theta$. The triangles indicate the closest value to the $S_2(\theta)$, for every rotation angle.
The effect of rotation angle of the field orientation on the structure evolution is investigated for a system of $\phi = 5\%$, see Fig. 4.10. The values of $S_2(\theta)$ are depicted with triangles in Fig. 4.10. For low angles $\theta < 20^\circ$, we observe a constant plateau initially for $S_2$ in Fig. 4.10a, and then a decrease indicating thickening of the clusters, see Fig. 4.10c. The anisotropy remains at high levels throughout the process, a fact that indicates the presence of anisotropic clusters (chains), see Fig. 4.10b. In Fig. 4.10c, one can observe that the size of the clusters does not decrease, indicative of the rotation of the clusters. For large angles ($\theta > 80^\circ$), we observe that the orientation reaches the value of $S_2(90^\circ)$ and then reaches a plateau. We interpret this fact as disintegration of the clusters/strings to smaller string-shaped clusters that rotate and create larger string clusters in the new field-orientation. Our explanation is supported by the anisotropy results, see Figs. 4.10b, 4.10c, where a drop is observed. The drops indicate smaller and less anisotropic string-shaped clusters, minimum ($\sim 0.6$) is quite large for isotropic clusters. For intermediate angles ($20^\circ \leq \theta \leq 80^\circ$), we observe intermediate situations, where the $S_2(\theta)$ is reached, but not maintained as the clusters are increasing in size. The anisotropy, $\lambda^*$, remains in high levels ($\lambda > 0.8$) for these angles, thus the anisotropic shape is maintained. For the same range of $\theta$, we also observe that the size decreases initially and then increases. The decrease depends on $\theta$ in a monotonic way: higher $\theta$ means larger decrease in size. For $\theta > 60^\circ$ substantial decomposition occurs, see Fig. 4.10c. After the decrease, the size increases again, however, the structure is formed in another direction, see Fig. 4.10a. This increase in size is greatly influenced by the rotation as merging of rotating clusters occurs for $20^\circ \leq \theta \leq 80^\circ$, see Fig. 4.10c.

The effect of the rotation angle of the field orientation on the structure formation is studied for low $\phi$-values; the final values (after $t(1) = 5.0$) of our measures for different $\phi$ are plotted against the field orientation $\theta$, in Fig. 4.11. We expect that the higher $\phi$, the less space available for the clusters to move and so cluster merging will result in more network-like structures, while for low $\phi \leq 2\%$ we expect rotation of the clusters. The orientation $S_2$ of $\phi = 1\%$ and $\phi = 2\%$ exhibit almost perfect alignment with the $\theta$-value (close to $S_2(\theta)$), see Fig. 4.11. The anisotropy $\lambda^*$ maintains the high value and the size $N^*$ also remains constant, so our expectation of rotating chains is met for low $\phi$-values. The 5% and 10% show similar behavior at low and high angles. However, at intermediate angles ($20^\circ \leq \theta \leq 80^\circ$), $S_2$ seems independent of the rotation angle, showing a plateau at almost random orientation, $S_2 \sim 0.15$, see Fig. 4.11a. This effect is related to the fusion of clusters, since larger clusters result in isotropic $S_2$-values [113]. The anisotropy remains high for all $\phi$, except certain angles
for $\phi = 10\%$. The $\phi = 10\%$ data show two dips at $30^\circ$ and $60^\circ$ angles, that are related to fusion of clusters resulting in larger clusters. Correspondingly, one can see $N^*$ indicating two maximums at the same angles, Fig 4.11. For $\phi = 1\%, 2\%, 5\%$, the size depends on $\phi$, the higher the $\phi$ the higher the size.

As far as the skeletonization measures are concerned, we expect simpler structures when rotation or disintegration and reformation occurs, and more complex when partial disintegration and cluster fusion occurs. In Fig. 4.12b, one can observe that the number of BPs depends only weakly on $\theta$ and, with the exemption of $\phi = 10\%$, increases with increasing $\phi$. For $\phi = 2\%$ and $\theta = 30^\circ$, there is a higher value, which may be due to the number of BPs strongly depending on local fusion of clusters. The lower BP-values of $\phi = 10\%$ in comparison to $\phi = 5\%$ can be explained on the basis of the resulting structure as follows (see Fig. 4.14): after rotation, the sample at $\phi = 5\%$ forms interconnected chains, while the sample at $\phi = 10\%$ forms sheet-like structures[14], resulting in less BPs. The complexity of the BPs, see Fig. 4.12b, does not exhibit any significant systematic trend over $\theta$ and $\phi$, which indicates that the structures created are highly dependent on incidental local cluster fusion; the errorbars are relatively large. In Fig. 4.13, one can observe the thickness over time, where the thickness seems almost independent of $\theta$ within errors. The thickness increases monotonously with increasing $\phi$, which is expected as less space is available for higher $\phi$. One has to note that the deviations of the thickness are large relative to the average.

One can see the results concerning percolation in Table 4.1. For $\phi \leq 10\%$, we expect percolation to occur only in the direction of the field before the switch, and then eventually to occur instead along the final direction of the field. For $\phi = 1\%, 2\%, 5\%, 10\%$, our expectation is met for the $10^\circ$, $20^\circ$, $80^\circ$ and $90^\circ$ degrees of rotation, as we have percolation in $z$ direction for $10^\circ$ and $20^\circ$, and percolation in $y$ direction for $80^\circ$ and $90^\circ$. No percolation in any direction is observed for all other angles for $\phi = 1\%, 2\%$, as the clusters formed are not large enough to span the box in any direction. For $\phi = 5\%$, percolation is observed in both $y$ and $z$ directions for $30^\circ$, $40^\circ$, $50^\circ$, $60^\circ$ and $70^\circ$ degrees of rotation in the final state. For $\phi = 10\%$, for $\theta = 30^\circ$, $60^\circ$ percolation occurs in every direction ($x$, $y$, $z$), which is related to the large clusters formed at these angles. For $\theta = 40^\circ$, $50^\circ$, $70^\circ$, percolation is exhibited in $z$ and $y$ directions, but not in $x$ direction. It is noted that the behavior for $\phi = 10\%$ is non-monotinous; percolation is a binary measure that strongly depends on local rearrangements/paths, so this non-monotinous behavior may be caused by poor statistics.
4.3. Results

Figure 4.11: Morphology measures $S_2$ (a), $\lambda^*$ (b), and $N^*$ (c) against rotation angle $\theta$ for volume fractions $\phi = 1\%$, $2\%$, $5\%$, and $10\%$. The dashed blue line in (a) indicates the function $S_2(\theta)$. 
Figure 4.12: (a) Number density of branch-points is plotted against time for different volume fractions $\phi = 1\%$, 2\%, 5\%, and 10\%. (b) Degree of branch-points is plotted against time for the same angles.

Figure 4.13: The average thickness of branches is plotted against time for different volume fractions $\phi = 1\%$, 2\%, 5\%, and 10\%.
Figure 4.14: Final configurations for $\phi = 5\%$ (a) and $\phi = 10\%$ (b), after rotating the field by $\theta = 20^\circ$.

Table 4.1: Existence of percolation for different $\theta$- and $\phi$-values.

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4.4 Summary and discussion

The structure formation and evolution of electro/magnetically (EM) active particles under a unidirectional or a rotated time-dependent external electric or magnetic field was studied. EM active particles create dipoles when exposed to an external field. When two dipoles are sufficiently close, their interaction results in the formation of structures, e.g., chains. The physical parameters of relevance for this formation were organized in dimensionless groups with respect to the external field, and the effect of these dimensionless numbers on the structure evolution was investigated.

BD simulations have been used to track and characterize structures of particles under a unidirectional time-dependent or a rotated external field. We simulated the electro-magnetic interactions with the simple dipole approximation, and the Stokes drag and Brownian force are used for the interaction with the surrounding medium. A method was presented to capture the structural dynamics of these systems, with special attention to the effect of the dipole-dipole interactions on the structure formation and evolution. A combination of measures introduced before [113] was applied for quantifying the evolution of the structure in time under different conditions.

The effect of using a unidirectional time-dependent field on the structure formation was investigated. A spatially constant field with increasing field strength is used. The rate of increasing is determined by the time it takes to reach its maximum value \( t_\text{s}^{(1)} \), after the increase the field is kept constant at its maximum value for \( t^{(1)} = 10.0 \). The \( t_\text{s}^{(1)} \)-values used are 0.1, 1.0, and 10.0. The dynamics are re-mapped nonlinearly in time in such a way as to scale out the time-dependence on the field-strength, however, this transformation is not ideal due to the presence of thermal fluctuations. Our mapping would work perfectly in the absence of thermal fluctuations, or, more generally, if the dipole interaction dominates over the thermal fluctuations. To make this more apparent in the transformed time, the transformed time is also shifted to ensure that the field is dominant over the thermal fluctuations, \( B^{**} < 0.0203 \) (dipole-dipole interactions 50 times larger than thermal fluctuations). Our mapping would also work if the transition from the initial \( B^{**} \)-value to the final one was occurring instantaneous, however, we deal with a gradual decrease of \( B^{**} \).

Our results after the time-transformation exhibit delay in structure formation for larger \( t_\text{s}^{(1)} \). Additionally, more isotropic configurations of particles are created, that result in more network-like structures than the ones formed under a constant-in-time field [113]. For larger \( t_\text{s}^{(1)} \), more network-like structures with
thicker branches are achieved, as well as more deviations of the local structures are observed, i.e., larger standard deviations observed in comparison to $t_s^{(1)} = 0$. The variation of $\phi$ revealed that after the formation of the structure at early times, the local rearrangement of particles results in more compact structures as time advances, especially for higher $\phi$-values.

An already formed configuration is used and the field is rotated by different angles $\theta$, keeping it constant thereafter for time of 5.0. This imposed rotation results in either rotation of the formed substructures, e.g. chains, at low angles ($\theta < 20^\circ$) or decomposition and reformation for large angles ($\theta > 80^\circ$). At the intermediate angles, we observe cluster merging and partial decomposition and reformation of the formed strings. The effect of varying the volume fraction of particles $\phi$ was also studied.

A time-dependent multi-directional field was used. The structure evolution strongly depends on the rotation angle, however, it is possible to take advantage of an already formed structure for creating a new structure in a different direction. This possibility may benefit the potential 3D-printing practitioner aiming for different orientation from layer to layer or inside a layer. Structure characteristics that were not observed in unidirectional field [113] can be generated, as rotating an already formed structure could result in more network-like structures for low volume fractions of $\phi \leq 10\%$, or percolation in multiple directions can be achieved. Additionally, the structure can be rotated preserving the desired characteristics if the rotation angle is small enough.
Chapter 5

Solidification during structure formation in electromagnetic suspensions

Abstract

For suspensions, it is investigated how the solidification of the suspending liquid affects the structure that is formed by the suspended particles. This work on solidification is motivated by and applicable to the curing of a photo-reactive resin in stereolithography processes. The particles under consideration interact by way of electric (or magnetic) dipole-dipole interactions. Brownian Dynamics simulations are used for studying the formation of particle structures, in which the solidification is represented by a continuously increasing viscosity of the suspending liquid with time, in agreement with experimental observations for curing photo-reactive resins. It is shown that one may study the effects of the viscosity increase by a transformation of time, akin to the time-temperature superposition principle, but here also in the presence of thermal noise, i.e., Brownian motion of the particles. Therefore, instead of performing simulations with a continuously increasing viscosity (computationally inefficient), we advocate performing simulations at a constant (low) viscosity and subsequently transforming time (nonlinearly) for re-interpretation of the simulation results. In practice, the viscosity increase is that strong that further evolution of the particle struc-
ture is basically absent after the characteristic transition-time of the viscosity is reached. Semi-quantitative rules of thumb are formulated for the 3D-printing practitioner.

5.1 Introduction

Additive manufacturing is a topic of scientific interest for a long time [30, 31]. Different kinds of materials are used including metals [32], polymers [33], ceramics [34] and combinations of them [31]. In this chapter, we are interested in polymer-matrix composite materials used in stereolithography (SLA) [29, 160] of UV-curable resins. Printing of polymer-based materials is currently used for various purposes such as rapid prototyping [41], or topology optimization [124]. There is a range of applications: aerospace (cabin interiors) [35], medicine (mimics of living tissue) [36], anthropology (reconstruction of medieval skulls) [37], and design (spatially-dependent elasticity) [38]. The use of composites in SLA is possible as multi-materials including suspensions are already being printed [161], however, challenges are still present [162]. The incorporation of dielectric, conductive or magnetic functionality to the printed object [39–41, 163] has been investigated by the usage of electromagnetically active particles. The microstructure of the composite can be controlled during printing via the use of an external electric or magnetic field, in order to achieve specific structures of particles inside a complex geometry. These systems can be used in applications like personalised hearing aids [42], flat lenses with a gradient of concentration of particles that have the functionality of their curved counterparts [43], piezoelectric or Hall effect sensors [44], and direction-specific thermally or electrically conductive composites [15].

The behaviour of such systems is highly influenced by the suspending medium. When an external field is used, the particles create structures [12]. The behaviour during structure formation is mostly investigated in a liquid suspending medium, as the structure formation is accessible under experimental conditions [125, 164]. However, in SLA the medium is irradiated and as a result it solidifies. This process could be used to fixate the structure, so that the formed structure persists even in the absence of an imposed field. Photo-reactive resins are used in SLA [165], and also as suspending medium [27, 28]. The polymerization of such resins is initiated by energy input from a UV-source, and solidification is envisioned as an increasing viscosity, which results in the arrest of the dynamics and fixation of the structure. The low viscosity of the resins before curing makes the structure formation possible within the usual time-scales ($O(1s)$) of
3D-printing. In this chapter, the effect of the solidification of the suspending medium on the structure formation is investigated.

To this end, Brownian Dynamics (BD) simulations are used with dipole-dipole interactions, to simulate the motion of particles (dipoles) within a fluid under an external field. This method provides the evolution of the particle arrangement, and the structure created is characterised. One can achieve various structures of particles depending on the particles, suspending medium and field conditions, e.g. strings [13], planes [14], and networks [15]. The main features of the structure can be identified and quantified. For example, for strings one should know the size, orientation, and thickness, for planes the size and orientation, and for networks the number density of branch-points (BP), the degree of BP, the thickness of the branches, the number of clusters present, and the existence of percolation. Various techniques have been used for the characterisation of a structure of particles or points, like the characteristics of the gyration tensor [74], or the Voronoi tessellation technique [62, 66]. Voronoi polyhedra have proven useful in the characterisation of many systems, e.g. disordered systems [128], polymers [67, 68, 71], colloidal gels [92], granular materials [65]. The (radial or cylindrical) pair-correlation function, bond-angle distribution [56], and quermass integrals [58] are alternative methods for the characterisation of the structure of particles. In previous work, we presented a combination of graph theory tools with the image analysis technique called skeletonization [95, 97, 129] for the quantitative characterisation of the structures, particularly networks. In this chapter, the previously presented cluster measures [113] for orientation, anisotropy and size are used to illustrate the effect of solidification on structure formation.

The goal of this chapter is to investigate how the solidification of the suspending liquid affects the formation of structures of the suspended particles, so that the most relevant parameters of a prototypical viscosity profile are identified and semi-quantitative rules for the 3D-printing practitioner can be formulated. To this end, in Sec. 5.2 we prove analytically with two different procedures that the effect of an increasing viscosity over time on the structure formation of particles can be studied by means of time transformation. In Sec. 5.3, a viscosity profile representative of the solidification of a photo-reactive resin [150] is introduced, and employed for re-interpretation of previously obtained constant-viscosity BD simulation results [113] in terms of a continuously-increasing viscosity scenario, as an illustrative example. The chapter is summarised and the results are discussed in Sec. 5.4.
5.2 Methodology

In this section, the methodology is discussed, including the simulation details, and morphology measures. The system consists of particles with radius $R_p$ at volume fraction $\phi$ of the suspension, and the monomeric fluid that serves as suspending medium with viscosity $\eta(t)$, where $t$ is the time in a finite box of edge-length $L$, where periodic boundary conditions are applied in all directions. BD simulations are used to simulate the system. For the rest of this chapter, we present quantities in dimensionless terms. The positions of the particles are scaled with the characteristic length-scale, $r_c$ [113], and time is scaled with the characteristic time-scale, $t_c$ [113],

$$t^{(1)} = \frac{t}{t_c}.$$  \hspace{1cm} (5.1)

In Subsection 5.2.1, a viscosity profile of the form

$$\eta^*(t^{(1)}) = \frac{\eta(t^{(1)})}{\eta_c},$$ \hspace{1cm} (5.2)

will be used, where $\eta_c$ is a characteristic value for $\eta$. It will be shown in the following, that the solidification of the suspending liquid described by an appropriate time-dependent viscosity can be studied without the need for additional, i.e. increasing-viscosity simulations. Note that in Eq. 5.2 it is assumed that the viscosity does not depend on the particle positions; the time-dependence originates from physical or chemical processes within the suspending liquid itself. Any positive and monotonically increasing function $\eta(t^{(1)})$ can be used in the procedure described in the following, once it is turned into dimensionless form, see Eq. 5.2.

5.2.1 Non-linear transformation of time

When one refers to BD, one considers a stochastic differential equation (SDE) describing the dynamics. The system can be described also by the corresponding Fokker-Planck equation, which describes the evolution of the distribution function of the microscopic state of the system. These two approaches are equivalent [47].
Procedure 1: Stochastic Differential Equation

If one considers a SDE of the form

$$dX_{t^{(1)}} = \frac{1}{\eta^*(t^{(1)})} \hat{A}(X_{t^{(1)}}) dt^{(1)} + \frac{1}{\sqrt{\eta^*(t^{(1)})}} \hat{B}(X_{t^{(1)}}) dW_{t^{(1)}}, \quad (5.3)$$

where $t^{(1)}$ is the time with a varying viscosity, $X_{t^{(1)}}$ is the state at time $t^{(1)}$, $\hat{A}(X_{t^{(1)}})$ and $\hat{B}(X_{t^{(1)}})$ are functions depending on the state, $dW_{t^{(1)}}$ are increments of Wiener processes, and $\eta^*(t^{(1)})$ is the time-dependent viscosity. In the following, it is assumed that the viscosity function is known, does not depend on $X_{t^{(1)}}$, is positive, and is increasing monotonously with time. Eq. (5.3) can be simplified by using

$$dt^{(2)} = \frac{dt^{(1)}}{\eta^*(t^{(1)})}, \quad (5.4)$$

i.e.

$$t^{(2)} \big(t^{(1)}\big) = \int_0^{t^{(1)}} \frac{1}{\eta^*(t)} dt,$$ \quad (5.5)

where $t^{(2)}$ is the rescaled time. If Eq. (5.3) was an ordinary differential equation, the transformation of time would be straightforward. However, the stochastic term, i.e. the Wiener processes, complicates the procedure. When one rescales time, one should consider the condition of Wiener processes being uncorrelated in time,

$$\langle dW_{t^{(1)}} dW_{t^{(1)\prime}} \rangle = \delta \left(t^{(1)} - t^{(1)\prime}\right) dt^{(1)} dt^{(1)\prime} 1, \quad (5.6)$$

where $t^{(1)}$ and $t^{(1)\prime}$ are two moments in time. If one performs the time rescaling of Eq. (5.6) with the help of Eq. (5.4), and uses

$$\delta \left(t^{(1)} - t^{(1)\prime}\right) = \delta \left(t^{(2)} - t^{(2)\prime}\right) / \eta^*(t^{(2)} \big(t^{(1)}\big)),$$ \quad (5.7)

one obtains

$$\langle dW_{t^{(1)}\big(t^{(2)}\big)} dW_{t^{(1)\prime}\big(t^{(2)\prime}\big)} \rangle =$$

$$\delta \left(t^{(2)} - t^{(2)\prime}\right) \eta^* \left(t^{(2)} \big(t^{(1)}\big)\right) dt^{(2)} dt^{(2)\prime} 1. \quad (5.7)$$

If one rescales Eq. (5.3), with the help of Eqs. (5.4) and (5.7), one gets

$$dX_{t^{(2)}} = \hat{A}(X_{t^{(2)}}) dt^{(2)} + \hat{B}(X_{t^{(2)}}) dW_{t^{(2)}}, \quad (5.8)$$
where \( dW_{t(2)} = dW_{t(1)}(t(2))/\sqrt{\eta^*)(t(1)(t(2)))} \). Eq. (5.8) resulted from the transformation of time from a time-dependent viscosity to a constant viscosity. Therefore, Eq. (5.8) is equivalent to BD simulations in dimensionless form like the one presented in ref. [113]. One can simulate a system of varying viscosity (e.g. solidifying resin) by means of nonlinear time-mapping of constant-viscosity simulations.

**Procedure 2: Fokker-Planck Equation**

In the previous procedure, we worked on the stochastic differential equation; here, the same conclusion is derived on the basis of the Fokker-Planck equation (FPE). In terms of the FPE, Eq. (5.3) is represented as

\[
\frac{\partial t(1)p}{\partial t} = -\partial_x \left( \frac{1}{\eta^*} \hat{A}p \right) + \frac{1}{2} \partial_x \partial_x : \left( \frac{1}{\eta^*} \hat{B} \cdot \hat{B}^T p \right).
\]  

(5.9)

Since \( \eta^* \) is independent of \( x \), one can write

\[
\eta^* \frac{\partial t(1)p}{\partial t} = -\partial_x \left( \hat{A}p \right) + \frac{1}{2} \partial_x \partial_x : \left( \hat{B} \cdot \hat{B}^T p \right).
\]  

(5.10)

The left-hand side of Eq. (5.10) is equal to \( \partial t(2)p \), as \( \partial p/\partial t(2) = (dt(1)/dt(2)) \left( \partial p/\partial t(1) \right) = \eta^* \partial p/\partial t(1) \). Eq. (5.10) is compatible with the SDE of Eq. (5.8).

**5.3 Application of the general procedure**

In Section 5.2, two procedures were presented with which the time-dependence of the viscosity function can be rationalized conveniently by a transformation of time. This can be exploited practically in the following sense: Instead of studying the dynamics of the particles with an increasing-in-time viscosity of the suspending liquid, one may instead study the system with a constant (low) viscosity and then re-interpret the results by an appropriate transformation of time. In this section, a prototypical viscosity-function is used to illustrate this principle. To this end, results obtained by constant-viscosity simulations are re-interpreted as if simulations of a solidifying suspending liquid were performed. The prototypical viscosity, the simulation details, the measures for the structure quantification, and the transformed results are presented, and semi-quantitative guiding principles are formulated.
5.3. Application of the general procedure

\[ \eta^* \left( t^{(1)} \right) = \eta^* + \frac{\Delta \eta^*}{2} \tanh \left( \frac{t^{(1)} - t_0^{(1)}}{\tau} \right), \]  

(5.11)

where \( \eta^* = (\eta^*_0 + \eta^*_\infty) / 2 \) and \( \Delta \eta^* = \eta^*_\infty - \eta^*_0 \geq 0 \), with \( \eta^*_0 \) and \( \eta^*_\infty \) the values of the initial and final plateaus, respectively, \( t_0^{(1)} \) indicates the mid-point of the transition, and \( \tau \) represents the width of the transition, see Fig. 5.1. The entire viscosity function has already been scaled with \( \eta_c \), see Eq. (5.2). For the rest of this chapter, \( \eta^*_0 = 1 \) will be used, meaning that the dimensional viscosity at \( t \sim -\infty \) is equal to \( \eta_c \).

If one uses Eq. (5.4) in combination with Eq. (5.11), one obtains

\[ t^{(2)} = \frac{\eta^* t^{(1)}}{\eta^*_0 \eta^*_\infty} \cdot \frac{\Delta \eta^* \tau}{2 \eta^*_0 \eta^*_\infty} \ln \left( \frac{\eta^*_0 e^{-t_0^{(1)} + t^{(1)}} + \eta^*_\infty e^{t^{(1)} - t_0^{(1)}}}{\eta^*_0 e^{t_0^{(1)}} + \eta^*_\infty e^{-t_0^{(1)}}} \right). \]  

(5.12)

Figure 5.1: The viscosity function based on a shifted hyperbolic tangent with the parameters \( \eta^*_0, \eta^*_\infty, t_0^{(1)}, \) and \( \tau \).

5.3.1 Time-dependent viscosity during solidification

For transforming time, one needs a viscosity function representative of the curing process. Experimental observations [125, 164] indicate that this function has an initial and final plateau, and a transition of certain width in between. The initial plateau value corresponds to the viscosity of the monomeric resin, and the final plateau to the cured sample [150]. To this end, we pick a hyperbolic tangent of the form

\[ \eta^* \left( t^{(1)} \right) = \eta^* + \frac{\Delta \eta^*}{2} \tanh \left( \frac{t^{(1)} - t_0^{(1)}}{\tau} \right), \]  

(5.11)
Figure 5.2: The relative error of the two functions is plotted against the ratio \( \frac{(t^{(1)} - t_0^{(1)})}{\tau} \).

The ratio \( \frac{(t^{(1)} - t_0^{(1)})}{\tau} \) is increasing with increasing \( t^{(1)} \), so one can observe that the exponential functions will cause numerical problems at high \( t^{(1)} \)-values. To this end, we make the approximation to neglect the first term of the denominator in the logarithm of Eq. (5.12), leading to

\[
t^{(2)}_{\text{app}} = \frac{t^{(1)}}{\eta_\infty^*} - \frac{\Delta \eta^*}{2 \eta_0^* \eta_\infty^*} \left( \tau \ln \left( \frac{\eta_\infty^*}{\eta_0^* e^{-\frac{t^{(1)} - t_0^{(1)}}{\tau}} + \eta_\infty^* e^{-\frac{t^{(1)} - t_0^{(1)}}{\tau}}} \right) - t_0^{(1)} \right). \tag{5.13}
\]

However, Eq. (5.13) is not valid for the whole range of \( t^{(1)} \). We choose to use a combination of Eqs. (5.12) and (5.13): Eq. (5.13) is used for large \( t^{(1)} \) if the relative error \( \frac{(t^{(2)} - t^{(2)}_{\text{app}})}{t^{(2)}} \) is smaller than \( 10^{-4} \). In Fig. 5.2, one can see the relative error plotted against the ratio \( \frac{(t^{(1)} - t_0^{(1)})}{\tau} \).

Our intention is to transform the dynamics from the \( t^{(2)} \)-representation to the \( t^{(1)} \)-representation, i.e. from an existing constant-viscosity simulation to a time-dependent viscosity situation. Therefore, one needs to determine \( t^{(1)} \) from \( t^{(2)} \), which means solving Eqs. (5.12) and (5.13), using \( t^{(2)} \)-values corresponding to constant-viscosity simulations. In the case of Eq. (5.13), one can solve
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towards \( t^{(1)} \) analytically, however, for Eq. (5.12) this is non-trivial, and the Newton-Raphson method [166] is thus used for solving Eq. (5.12) numerically.

In the following, the dependence of the \( t^{(1)} - t^{(2)} \) relation on the parameters of the viscosity function, see Eq. (5.11), is explored. The parameters to be varied are \( \eta^*_\infty \), \( t_0^{(1)} \), and \( \tau \). The results can be found in Fig. 5.3. First, we choose the values for the study of the \( \eta^*_\infty \)-variation, Fig. 5.3a, such that they are representative of the real process, namely \( \eta^*_\infty = 10^2, 10^3, 10^5 \), which correspond to the values obtained for different light intensities [150]. The values for the other parameters are \( \tau = 0.1 \) and \( t_0^{(1)} = 3.0 \). Afterwards, we choose the values for the transition time \( t_0^{(1)} \)-variation with respect to the crossing point of \( G' \) and \( G'' \) observed experimentally \((t_0^{(1)} \sim 2.5) \) [150]; the values are \( t_0^{(1)} = 1.0, 3.0, \) and \( 10.0 \), Fig. 5.3b. The values for the two additional parameters are \( \tau = 0.1 \) and \( \eta^*_\infty = 10^5 \). The transition time has limitations in our case, as we attempt to use a compact mathematical function to represent the real viscosity function. The limitation has to do with the existence of the initial plateau depicted in Fig. 5.1; if one uses a low \( t_0^{(1)} \)-value and high \( \tau \)-value, then at time \( t^{(1)} = 0 \) the transition will be taking place already. This effect is unphysical and for this reason we choose \( t_0^{(1)} \) such that at time \( t^{(1)} = 0 \) the viscosity has a value as close as possible to 1.0. The values for the variation study of \( \tau \) are \( \tau = 0.1, 0.5, \) and \( 1.0 \), see Fig. 5.3c. The values for the other parameters of the function are \( \eta^*_\infty = 10^5 \) and \( t_0^{(1)} = 5.0 \).

In Fig. 5.3, one can observe the relation between the time \( t^{(1)} \) and the time \( t^{(2)} \) for a viscosity function given by Eq. (5.11). In Fig. 5.3a, one can see the dependence on \( \eta^*_\infty \), mainly affecting the final time for completing the structure formation. The final time is increased monotonically with increasing \( \eta^*_\infty \). The transition is quite steep, see inset Fig. 5.3a, as the transition time \( \tau \) is low and the viscosity difference \( \eta^*_\infty - \eta^*_0 \) large. In Fig. 5.3b, one can see the dependence on \( t_0^{(1)} \), which defines the time at which the behaviour deviates from the no-transition case \( t^{(1)} = t^{(2)} \). In the inset of Fig. 5.3b, one sees the steepness of the transition, which is mainly affected by the transition time \( \tau \), which is low, and the viscosity difference \( \eta^*_\infty - \eta^*_0 \), which is large. In Fig. 5.3c, one can see the dependence on \( \tau \). This parameter controls the duration of the transition in the \( \eta^*-\)function, however, here it seems to affect also the deviation from the no-transition case \( t^{(1)} = t^{(2)} \), as the transition starts earlier if the \( \tau \) is larger. The fact that \( \tau = 1.0 \) starts from a higher value of \( t^{(1)} \) is based on \( \tau \) not being significantly lower than \( t_0^{(1)} \), and the viscosity has a value quite higher than \( \eta^*_0 \) already at \( t^{(2)} = 0 \). One can observe that for \( \tau = 1.0 \), the transition exhibits
a smoother behaviour (smoother increase) compared to the other values, as it lasts longer.

5.3.2 Simulation details

Considering the many-particle system, one uses $x = (r_1, r_2, ..., r_n)$, where $r_i$ is the center position of particle $i$. These particles have induced dipoles due to the mismatch in the dielectric permittivity of the matrix, $\epsilon_m$, and the particles, $\epsilon_p$, under an external field. The interactions governing the structure formation are the dipole-dipole interactions [11, 12]. Here, BD simulations [47, 48] are used in dimensionless form; including the nonlinear re-mapping in relation to the time-dependent viscosity, one obtains (see ref. [113] for the $t^{(1)}$-representation)

$$dr_i^* = (F_i^{\text{em}} + F_i^{\text{exv}})dt^{(2)} + B^* \sqrt{dt^{(2)}} \xi_i,$$

with

$$F_i^{\text{em}} = \sum_j \frac{1}{r_{ij}^{*4}} \left( \left( (p_i^* \cdot p_j^*) - 5(p_i^* \cdot \hat{r}_{ij})(p_j^* \cdot \hat{r}_{ij}) \right) \hat{r}_{ij} + (p_i^* \cdot \hat{r}_{ij})p_j^* + (p_j^* \cdot \hat{r}_{ij})p_i^* \right),$$

$$F_i^{\text{exv}} = -r_c^4 \sum_{j \neq i} \frac{p_i^* p_j^*}{8R_p^4} e^{-\kappa \left( \frac{r_{ij}^* r_c^*}{2\eta_T} - 1 \right)} \hat{r}_{ij},$$

$$B^* = \sqrt{\frac{2k_B T \tau_c}{\zeta \tau_c^2}},$$

where $F_i^{\text{em}}$ is the force due to the dipole-dipole interactions, $F_i^{\text{exv}}$ is the force preventing the particles from overlapping (excluded volume), and $p_i^*$ is the scaled dipole moment of particle $i$. The parameter $\kappa = 30$ is a constant that determines the interaction range of the excluded volume, while the pre-exponential factor defines the overall strength of the interaction [24]. The Boltzmann constant is denoted by $k_B$, the temperature by $T$, and the friction coefficient by $\zeta = 6\pi \eta_c R_p$. The positions of the particles are scaled with the characteristic length-scale, $r_c = 1/\sqrt{n_d}$, and the dipole moments with the characteristic dipole moment, $p_c = 4\pi \epsilon_m K R_p^3 E_c$ with $E_c$ the constant value of the field strength. The time in the $t^{(1)}$-representation is scaled with the characteristic time-scale introduced in ref. [113], $t_c = 8\pi^2 \epsilon_m \eta_c R_p \tau_c^5 / p_c^2$. 
Figure 5.3: The dimensionless time $t^{(1)}$ (no variation of $\eta$ considered) is plotted against dimensionless time $t^{(2)}$ for different values of (a) $\eta^*_\infty$, $\tau = 0.1$, $t_0^{(1)} = 3.0$, (b) $t_0^{(1)}$, $\tau = 0.1$, $\eta^*_\infty = 10^5$ and (c) $\tau$, $\eta^*_\infty = 10^5$, $t_0^{(1)} = 5.0$. 
5.3.3 Morphology characterisation

In this subsection, we introduce the measures for morphology characterisation that we are going to use for the rest of this chapter. We discuss morphology measures concerning clusters/structures of particles. The first measure concerns the orientation of the inter-particle direction with respect to an external direction, that being the external field,

\[ S_{2,I} = \frac{3}{2} \left\langle (\hat{r}_{ij} \cdot \hat{E})^2 \right\rangle_I - \frac{1}{2}, \tag{5.18} \]

where the index \( I \) denotes the cluster index, so for cluster \( I \) the average is defined as the average of the particles that participate in \( I \). This is the second Legendre polynomial for the pairs of particles that belong to the same cluster \( I \), however, periodic boundary conditions are applied and only the primary image are considered. \( S_2 \) has a value of 1 if the average orientation is parallel to the external direction, a value of 0 if there is random orientation with respect to the direction of the field, and a value of \(-1/2\) if the orientation is perpendicular to the external direction.

The second measure is a measure to quantify the anisotropy of each cluster. For that purpose, we calculate the gyration tensor [74],

\[ S_I = \left\langle (r_i - r_{cm,I})(r_i - r_{cm,I})^\top \right\rangle_I, \tag{5.19} \]

where the index “\( I \)” indicates the cluster index, and \( r_{cm,I} \) is the position of the center of mass of the particles belonging to cluster \( I \). The gyration tensor defines an ellipsoid [74]. The eigenvalues of the gyration tensor give the relative difference in size of the three axes of the ellipsoid. We introduce a measure that quantifies the anisotropy,

\[ \lambda^*_I = 1 - \det(S_I)\lambda_{\text{max},I}^{-3}, \tag{5.20} \]

where \( \lambda_{\text{max}} \) is the maximum eigenvalue of the gyration tensor, and \( \det(S_I) \) is the determinant of the gyration tensor. This measure has a value of 1 if the anisotropy is high, and a value of 0 if the system is isotropic (sphere). Note that this measure does not depend on the direction of the anisotropy.

The third measure has to do with the size of the cluster,

\[ N^*_I = \frac{N_I}{N_L}, \tag{5.21} \]

where \( N_I \) is the number of particles that belong to cluster “\( I \)”, and \( N_L \) is the minimum amount of particles that are needed to be stacked together for
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spanning the box-length in one direction. This measure has a value of $N^* < 1$ if the cluster size is smaller than the $N_L$, and a value of $N^* \geq 1$ if the string has enough particles to span the box, even if the box is not spanned (flocs).

The averages over all clusters of the measures $S_{2,I}$, $\lambda^*_I$, and $N^*_I$ are reported in the following, and these averages will be denoted by same symbol, but without the cluster index. The size of the cluster serves as a weight for these averages,

$$A = \frac{1}{N_p} \sum_{I=1}^{N_{cl}} N_I A_I,$$

(5.22)

where $A$ is any quantity of the ones referring to clusters, $N_{cl}$ is the number of clusters, $N_I$ is the number of particles in cluster $I$, and $A_I$ is the value of the quantity $A$ for the cluster $I$.

### 5.3.4 Results for unidirectional constant field

As an illustrative example, the nonlinear transformation of time is applied here to identify the most important parameters for structure formation in a suspension with a solidifying suspending liquid. The results concern suspensions of particles that are exposed to a unidirectional and spatially constant field [113], which results in induced dipoles in the particles and therefore interaction between them. We use the measures introduced in Subsec. 5.3.3 for monitoring the structure formation. The study of the parameters in the viscosity function (5.11) allows for the construction of rules of thumb concerning their effect on the structure formation.

The results of BD simulations with (low) constant viscosity obtained in previous work [113] are interpreted here as $t^{(2)}$-representation results, and transformed in order to obtain the structure formation with a prototypical time-dependent viscosity, i.e. the $t^{(1)}$-representation. The system consists of $10^3$ particles at volume fraction $\phi = 10\%$, and three simulations with different random numbers sequences, and different random initial configurations are used to generate the error-bars [113]. In all simulations, the $B^*$ and $t_c$ are kept constant.

We use the results obtained in ref. [113], which are constant-viscosity simulations in representative of $t^{(2)}$-dynamics, and re-interpret them by transforming to the $t^{(1)}$-representation for exploring the influence of the solidification on the structure formation.

In Fig. 5.4, one can observe the three measures versus $t^{(1)}$ for different values of $\eta^*_\infty$, namely $\eta^*_\infty = 1.0, 10^2, 10^5, 10^8$, with $t_0^{(1)} = 3.0$ and $\tau = 0.1$. It is clear that when the transition happens the time is extended by some orders
of magnitude with respect to the constant viscosity case. This deceleration depends strongly on the \( \eta^*_\infty \)-value, since it affects the effective freezing of the structure formation.

In Fig. 5.5, the influence of the transition time \( t_0^{(1)} \) is explored on the three measures for \( t_0^{(1)} = 1.0, 3.0, 10.0 \), with \( \eta^*_\infty = 10^5 \) and \( \tau = 0.1 \). The transition time seems to be a rather important parameter, since after this time-value the structure formation is slowed down significantly (orders of magnitudes). The difference with the \( \eta^*_\infty \)-variation is that the amount of deceleration of the dynamics is constant (constant \( \eta^*_\infty \)), while \( t_0^{(1)} \) controls the moment when this deceleration will occur.

The variation of the last parameter \( \tau \) can be seen in Fig. 5.6, for values \( \tau = 0.1, 0.5, \) and \( 1.0 \), with \( t_0^{(1)} = 5.0 \) and \( \eta^*_\infty = 10^5 \). This parameter determines how swiftly the deceleration occurs. One has to note that this parameter is not affecting how much the dynamics are decelerated or when it happens, however, it affects the way the structure formation is decelerated before and after the transition time.

5.4 Summary and discussion

In this chapter, it has been proven that a suspension of particles in a solidifying suspending liquid can be studied by means of a nonlinear transformation of time of constant-viscosity dynamics. The only assumptions are (i) that the solidification is described in terms of a viscosity that increases monotonically with time, and (ii) that the viscosity increase is due to physical or chemical processes within the suspending liquid itself and thus does not depend on the positions of the particles. The described procedure is equivalent to the time-temperature superposition principle, however, in our case in the presence of thermal noise, i.e., Brownian motion of the suspended particles.

In Sec. 5.3, a viscosity function that is representative of the experimentally observed solidification of a photo-reactive resin [150] has been used for re-interpreting constant-viscosity simulations of suspensions in terms of simulations with an increasing viscosity. For the sake of an illustrative example with the most characteristic features but only a few parameters, the viscosity function has been assumed to have the form of a shifted hyperbolic tangent. The relation between the two scalings of time, \( t^{(1)} \) and \( t^{(2)} \), has been investigated with respect to variations of the parameters of the viscosity function, \( \eta^*_\infty, t_0^{(1)} \) and \( \tau \).
Figure 5.4: Morphology measures (a) $S_2$, (b) $\lambda^*$, and (c) $N^*$ against dimensionless time, the colour indicates the different $\eta^*_\infty$-value, while $t_0^{(1)} = 3.0$ and $\tau = 0.1$. 
Figure 5.5: Morphology measures (a) $S_2$, (b) $\lambda^*$, and (c) $N^*$ against dimensionless time, the colour indicates the different $t_0^{(1)}$-value, while $\eta_\infty^* = 10^5$ and $\tau = 0.1$. 
Figure 5.6: Morphology measures (a) $S_2$, (b) $\lambda^*$, and (c) $N^*$ against dimensionless time, the colour indicates the different $\tau$-value, while $t_0^{(1)} = 5.0$ and $\eta_*^{\infty} = 10^5$. 
The competition between the formation of particle structures and the solidification of the suspending liquid, realized by an increasing viscosity, has given rise to some rules of thumb for the 3D-printing practitioner with an interest in photo-curable resins. The effect of \( \eta^* \) is found to alter how much the formation of particle structures is decelerated; the effective freezing of the structure can be controlled. The parameter \( t_0^{(1)} \) has the most important effect, to the best of our knowledge, as it defines the moment when the deceleration occurs; it can be tuned such that the desired structure, which might be transient, is arrested. The last parameter \( \tau \) describes how swiftly the deceleration is switched on.
Chapter 6

Conclusions and recommendations

6.1 Conclusions

In this thesis, the structural evolution of electromagnetic suspensions was studied for the construction of semi-quantitative design rules for 3D-printing such systems, concerning the relation between the structure and the actual physical input, e.g. volume fraction, external field, curing kinetics. To this end, a method was developed for the quantitative characterisation of structures of particles in Chapter 2. The evolution of the structure was investigated under unidirectional constant field in Chapter 3, and under time-dependent uni- and multi-directional field in Chapter 4. The effect of the solidification of the suspending medium on the structure formation was studied in Chapter 5. The main conclusions are:

- The higher the volume fraction of the system, the more network-like is the structure.

- A uni-directional time-dependent field, which increases linearly to a maximum field-strength value equal to the one of the uniform field case and is then kept constant for a certain amount of time, produces more network-like structures for the same time-interval and the same volume fraction.

- A multi-directional time-dependent field, realised by rotation of a uniform field already applied for a certain period of time by an angle $20^\circ \leq \theta \leq 80^\circ$,
produces more network-like structures for low volume fractions.

- The structure formation is significantly decelerated by the solidification of the matrix, so the desired structure should be formed already before the onset of the viscosity increase in the curing procedure.

In this dissertation, time-transformation is used extensively for the simplification of the dynamics and the reduction of either the number of the parameters (i.e. numerical, physical) or for avoiding the need for additional simulations. The benefit of a proper time-transformation is proven to be significant for the system studied. The reduction of the number of parameters that has been performed by dimensionlizing the evolution equations is already a significant advantage as one has only the dimensionless parameters $B^*$ and $\phi$ to investigate. The time-transformation used in Chapters 4 and 5 were beneficial for the better interpretation of results, eliminating (some of the) time-dependencies such as $E(t)$ and $\eta(t)$, and the lack of need for new simulations for investigating the solidification process.

We formulated general conclusions concerning the whole thesis. In the rest of this Chapter we are going to formulate some more detailed conclusions concerning each chapter separately.

A method to quantitatively characterise structures of particles was introduced in Chapter 2. The procedure that has been developed for systematic simplification and quantitative characterization of structures formed by particles, with a particular interest in networks. The initial structure is transformed to a 3D-binary image, and then skeletonized. The resulting skeleton is further simplified in terms of connectivity and branch-points. A resolution analysis is applied and the measures studied are converging. The technique is applied to different structures, e.g. thin chains, thick chains, isotropic and anisotropic network, and the differences between the structures are identified. The procedure effectively simplifies the targeted structure, especially if thick branches and branch-points are concerned.

Simulations of electromagnetically active particles under a unidirectional constant field were performed in Chapter 3. Brownian Dynamics simulations were used. The physical and numerical parameters of the problem were re-organised in dimensionless groups based on the two-particle interaction potential. The scaling of two-particle interaction was found to hold also for many-particle interactions. The results showed that the higher the volume fraction the more network-like the structure.

In Chapter 4, simulations of time-dependent fields were performed. Firstly, uni-directional time-dependent fields were used to demonstrate their effect on
structure formation. After the transformation of time for mapping the time-dependency of the field to the constant-field case, it was found that the structure formation is delayed, if the field strength is increased gradually. The structure formation is essentially prohibited by the thermal fluctuations, until the strength of field is high enough to dominate over the thermal motion. The structures are found more network-like and with thicker branches with respect to constant field. In a continuation of the above, a rotated field was used to investigate the transition of a formed structure to a new field-orientation. The structures are rotating at small angles ($\theta \leq 20^\circ$), and decompose and reform at large angles ($\theta > 80^\circ$). Rotation of the structures at intermediate angles ($10^\circ < \theta < 90^\circ$) results in fusion of clusters, and more network-like structures.

The effect of solidification on the structure evolution under an external field is investigated in Chapter 5. We assume that the solidification process can be simply simulated by an increase of the matrix viscosity. It is proven that the structure formation in a matrix with a monotonically increasing viscosity function can be studied by means of nonlinear time-transformation. The transformation maps prototypical time-dependence of the viscosity profile to the constant-viscosity case. A prototypical viscosity profile is used to represent the experimental observations, and the structure formation under a constant field is re-interpreted to the equivalent time-range in case of solidifying matrix. It is found that the particle structure can be considered as arrested after the characteristic transition-time of the viscosity is reached.

## 6.2 Recommendations

The work presented in this dissertation is focused on the effect of the physical input on the structure formation for 3D-printing of electromagnetic suspensions. The findings of this work encourage further research to address the issues that remain open, so the following recommendations are given. This section is divided into extension of the current work, and experimental realisation of it.

- In this dissertation, the hydrodynamic interactions, except the single-particle Stokes drag force, are neglected. However, their effect has proven to be non-trivial [17], so one should investigate the influence of them on the structure formation.

- The external field used in this thesis is spatially constant. The exploration of spatially non-uniform fields is not extensively investigated in the
literature. The control of structure formation (no static structure is obtained with non-uniform fields) could result in great benefits, e.g. gradient concentration of particles.

- Additionally, alternative field protocols can be used for the formation of different structures, e.g. planes, honeycomb structures [15], and paths of particles.

- Polydispersity could also be a nice extension of the current work.

- In Chapter 2, a characterisation technique for structures of particles is presented. This technique takes advantage of the transformation of the structure to its skeleton to quantitatively characterise a structure. This fact can be seen as a drawback, so a characterisation technique acting directly on the primary structure is desirable. One could try to start from the primary structure and detach particles that belong to the surface of the structure, until a structure equivalent to the skeleton will emerge. In this way, no transformation will be needed.

- In this thesis, a connection between the physical input of the system and the resulting structure is made. A natural extension of this work would be establishing the connection between the structure and the final properties of the material. This connection could be accomplished using only the resulting structures in a finite element framework and using an external stimulation to track the response of the material. Then one would establish a connection between the physical input and the final properties of the material. This point could also be realised experimentally.

- In our approach, we use a box with periodic boundary conditions, which translates to simulations of the bulk of the material. However, 3D-printing and more specifically SLA, the length scales involved are comparable to the height of the simulation box, since typical layer thickness is in the range 25µm – 100µm [167, 168], and our particle radius is 1µm. The simulation of SLA would become more realistic if periodicity was kept in the $x$ and $y$ directions only, but not on the height direction. In this direction, one side should be considered solidified, i.e. particles are frozen in an already formed configuration, as it represents the previous layer. The opposite side should either be free, i.e. air, or have a hard boundary, i.e. side of the resin tank.
6.2. Recommendations

The work presented in this thesis is purely computational and no quantitative validation has been established with experimental results. Some suggestions for heading in this direction are given in the following:

- One could retrieve the positions of the particles in 3D [89–92], for the same field protocols used in Chapters 3 and 4 using particles of the same properties and apply the exact same measures used in this dissertation, e.g., \( S_2, \lambda^*, N^*, n_{BP}, d_B \) to make a one-on-one comparison of the experimentally acquired structures with the ones obtained in this thesis. This way the practitioner would have a better physical insight for the experiments and establish the validity of the simulations results.

- One should validate the results of the dimensionless analysis presented in Chapters 3-5 also in the context of experiments. The time scale can be retrieved either by the time it takes for two particles to come into contact or from the many-body structure formation. If one has access to the 3D coordinates of the particles, then the overlap between different \( B^* \)-curves could be validated.
Chapter 6. Conclusions and recommendations
Appendix A

Branch-points on a regular grid (Chapter 2)

A regular grid of 64 intersections is created with 9460 particles. The branches of it are thick FCC structures like the ones presented in Sec. 2.4, see Fig. A.1a. The grid is analysed in terms of BPs for different resolutions, and the results concerning the number density of BP and degree of BP are presented in Table A.1. The results about the skeleton before the final reduction (BPs inside the diameter of a particle) are also presented, $n_{\text{BP, before}}, d_{\text{BP, before}}$. One can observe that for the BPs before the BP-reduction, at resolution of 20, additional BPs are identified, however, they are reduced with the elimination of BPs inside a primary-particle diameter. In Fig. A.1, one can observe the initial and final configuration of the regular grid, as well as the BPs before and after the BP-reduction. It is obvious that BPs are present in closer distances in higher resolution.
Table A.1: Effect of changing the resolution, in terms of the number of voxels per particle radius, on the number density \( n_{\text{BP}} \) and average degree \( \langle d_{\text{BP}} \rangle \) of BPs, for the regular-grid structure. The index “before” refers to before the reduction of BPs inside the diameter of a primary particle.

<table>
<thead>
<tr>
<th>resolution</th>
<th>( n_{\text{BP}} )</th>
<th>( \langle d_{\text{BP}} \rangle )</th>
<th>( n_{\text{BP, before}} )</th>
<th>( \langle d_{\text{BP, before}} \rangle )</th>
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<td>( 6.7653 \times 10^{-3} )</td>
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<tr>
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<td>( 6.8710 \times 10^{-3} )</td>
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<td>20</td>
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<td>( 5.7672 )</td>
<td>( 7.9281 \times 10^{-3} )</td>
<td>( 5.4533 )</td>
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</tbody>
</table>

Figure A.1: (a) Initial configuration of regular grid with noise (blue). (b) Final skeleton of regular grid with noise (red). (c) The BPs are depicted without the rest of the skeleton for resolution of 20. The red color indicates the new BPs obtained from the BP-reduction step, whereas green represents the BPs present before the reduction step.
Appendix B

Timestep convergence (Chapter 3)

In Fig. B.1, one can see our measures \( S_2 \), \( \lambda^* \) and \( N^* \) for various timesteps. The system that is used is of \( \phi = 10\% \), and \( B^* = 0.01 \). The timesteps used in dimensionless units (scaled with Eq. (3.12)) are \( dt^* = 7.1 \times 10^{-6}, 3.6 \times 10^{-5}, 7.1 \times 10^{-5}, 2.4 \times 10^{-4}, 2.4 \times 10^{-4}, 3.6 \times 10^{-4}, 7.1 \times 10^{-4}, 3.6 \times 10^{-3} \) and \( 7.1 \times 10^{-2} \). The largest timestep that our simulation continues without large overlaps of the particles, that result in rather large increments in the next steps, can be seen in the measures as a continuous curve with no discontinuities for \( 2.4 \times 10^{-4} \).

The failure of the simulations occurs, because of really large forces produced by large overlaps between the particles. This forces cannot be resolved with longer timesteps than the one calculated by \( t_{c,exv}^* \).
Figure B.1: Evolution of the morphology measures ($S_2$, $\lambda^*$ and $N^*$) with time for the same configurations under different level of discretization in time. The errorbars correspond to different random number seeds.
Appendix C

Initial configurations (Chapter 3)

The protocol followed for the creation of equilibrated initial configuration will be presented here. Initially, we work with a system of 1000 particles in $\phi = 40\%$, so if the configuration is equilibrated for this system it will be also for every system with the same positions of the particles and lower volume fraction. We initially place the particles in a simple cubic lattice. Then, we let them equilibrate with a repulsive part of a Lennard-Jones potential. On top of that, we use a higher temperature $T = 493K$, so that the diffusion timescale reduces. The equilibration is checked with the standard deviation value of the number density of particles per cubic cell. We observe the standard deviation, which drops with time, Fig. C.1a. Our criterion for terminating the equilibration loop is the standard deviation to reach a value lower than 0.2. For further checking this assumption we calculate the radial distribution function, Fig. C.1b, and one can observe that it looks like a Lennard-Jones fluid with excluded volume interaction [45].

As we obtained these random initial configurations, we studied the effect on the structure formation. The volume fraction of the selected system for study is $\phi = 10\%$. In Fig. C.2, we present the measure introduced in the previous section for four different initial configurations, indicated by different colours.

One could observe that in one dimensionless unit of time the difference in the measured quantities is low compared to the values of the measures, but visible. If one compares with the variation of the random numbers (error-bars), the variation of the initial configurations has a larger impact on the measured quantities.
Figure C.1: (a) Standard deviation as a function of equilibration time for number density per cell $n$, and (b) radial distribution function for the same configuration after $t^* = 90$. 
Figure C.2: Morphology measures $S_2$ (a), $\lambda^*$ (b), and $N^*$ (c) plotted against the dimensionless time, $t^*$. Different colour indicates different initial configurations.
Appendix D

Variation of $B^*$ and volume fraction (Chapter 3)

In this part, we present the results for different $B^*$, and $\phi$. These results correspond to the same values used in subsecs. 3.4.2 and 3.4.3 for $B^* = 0.01, 0.0316, 0.1, 0.316$. One can see that the results for different $\phi$'s presented collapse to a single master curve as in Fig. 3.4. The three measures $S_2$, $\lambda^*$, and $N^*$ are presented for $\phi = 1, 30\%$ in Fig. D.1 and D.2 respectively. In Table D.1, one can find all the values of $B^*$ and $\phi$ used in Chapter 3 and their relevant position in this Appendix.

Table D.1: Place of appearance for results concerning the values of $B^*$ and $\phi$ used in Chapter 3.

<table>
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<th>$\phi/B^*$</th>
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<td>-</td>
<td>-</td>
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<td>Subsection 3.4.2</td>
<td>Subsection 3.4.2</td>
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</tr>
<tr>
<td>20%</td>
<td>Subsection 3.4.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure D.1: Morphology measures $S_2$ (a), $\lambda^*$ (b), and $N^*$ (c) for $\phi = 1\%$ plotted against dimensionless time, $t^*$. 
Figure D.2: Morphology measures $S_2$ (a), $\lambda^*$ (b), and $N^*$ (c) for $\phi = 30\%$ plotted against dimensionless time, $t^*$. 
Appendix D. Variation of $B^*$ and volume fraction (Chapter 3)
Appendix E

Filling of cavities (Chapter 3)

When an image is processed to its skeleton all closed cavities (cavities that do not connect to the side of the simulation box with empty voxels) are represented as surfaces of voxels, to avoid this artefact of the technique it is common to fill the cavities before processing [95, 97]. These cavities are characterized in terms of number density and volume fraction with respect to the simulation box, as they are being part of the structure. In Fig E.1, one can see that the $\phi$ dominates both the number density (normalized with number density of primary structure), and volume fraction of cavities. The number density shows an initial increase, which is interpreted with the structure formation happening. The general trend is the decrease of both number density, and volume fraction of cavities are decreasing in a consistent way, until they reach a plateau and fluctuate around this plateau.
Figure E.1: (a) Number density of cavities for different volume fractions, $\phi = 1\%, 2\%, 5\%, 10\%, 20\%, \text{ and } 30\%$ is plotted against time. (b) Volume fraction of cavities is plotted against time for the same value of $\phi$. 
References


The work presented in this thesis is the result of four years of hard work. However, it would be a great omission, if I was not expressing my gratitude to those who made it possible and/or helped me develop in any way possible.

First and foremost, I would like to thank Markus for all the help, guidance and support throughout these years. I am grateful to you for being available when I needed help and hearing me out even when I was being unreasonable. This thesis would not be completed without you. Thank you for teaching me to be simple, efficient and critical and these are values I will never forget. I am also grateful to my promotor Patrick, thank you for providing advice and encouragement. I enjoyed our discussions and I was inspired by you.

I would also like to thank my former supervisors Doros and George. You introduced me to the world of particle-based simulations. George, thank you also for all your time spent on answering my dumb questions.

These four years became more enjoyable due to all the colleagues in the Polymer Technology group. Thank you all for the nice discussions. My office mates Christos, Frank, Priyam, Debarshi, Jessica, Mick and Roy, thank you for bearing me in the office and making it a comfortable place. Special thanks to lunch/fuit-time mates Kalouda, George and Wing-Hin, it was a pleasure. I am also grateful to all my friends for their support. Antonis, Petros, EMP group, Themis and my basketball family, you have been a true stress-reliever.

The gratitude to my family is unspeakable. As my mother, father and brother have loved me, supported me and believe in me even when I was unbearable. I will try to make it up for you. To my grandparents, you fed my hunger for knowledge and became guidance and inspiration.

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