Rheology and Thermodynamics of
Particle-stabilised Fluid Interfaces

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I would like to thank my parents and brother, who are and have been a constant source of support and encouragement throughout my life.

If I have forgotten anyone, this is solely a reflection of my poor memory and know that your contribution is appreciated.

Finally, I dedicate this thesis to the most important person in my life, Nora.

Zurich, 30th October 2017

AL
Abstract

Interfaces in foams and emulsions can be stabilised by the presence of adsorbed particles, which form a variety of structures on the surface depending on particle properties. This effect is commonly attributed to an enhancement of the rheological properties of interfaces possessing structure, but rheological models which properly account for the surface structure are severely lacking despite the explosion of interest in interfacial rheology. Our contribution takes two main forms: firstly, the development and demonstration of a general multiscale approach for formulating macroscopic rheological models from a microscopic model. Our approach is based on a nonequilibrium thermodynamic framework and guarantees thermodynamic consistency of the coarse-graining procedure. We demonstrate our approach on a toy model of hard ellipsoids adsorbed to a planar interface. Of particular note is the use of thermodynamically-guided computer simulations to aid development of the final equations. Solution of the equations yields a rich vein of nonlinear rheological behaviour, which we are able to interpret in terms of the interplay between flow, surface structure and their relation to the surface stresses. Secondly, we allow the contact angle of our ellipsoidal particles to vary. A contact angle other than $90^\circ$ results in the particle deforming the interface leading to interface-mediated interactions called shape-induced capillary interactions. Capillary interactions are multibody interactions and hence rather problematic to study in simulations, so we investigate whether pairwise interactions would be an adequate description using precise numerical calculations of the interaction energies of two- and three-particle configurations. This approximation is shown to be reasonable for the range of particle geometries and wetting angles we studied. We therefore propose a simple empirical form of the pair potential that accurately takes into account the anisotropic nature of the interaction. Since our shape-induced capillary interactions are very strong, and the bonds can be considered irreversible once formed, we employ sophisticated virtual move Monte-Carlo simulations to approximate the dynamics of self-assembly and aggregation and present for the first time large-scale simulations of the self-assembly of anisotropic particles interacting via capillary interactions.
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</tr>
<tr>
<td>$A$</td>
<td>Arbitrary functional of the state variables</td>
</tr>
<tr>
<td>$A(t)$</td>
<td>Time-dependent surface area of the interface</td>
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<td>$A_{\text{men}}$</td>
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<td>$A_1, A_2, A_3, A_4$</td>
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<td>$b$</td>
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<td>Arbitrary functional of the state variables</td>
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<td>$B_1, B_2, B_3$</td>
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<td>$B_0$</td>
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<tr>
<td>$C$</td>
<td>Arbitrary functional of the state variables</td>
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<td>$c_s$</td>
<td>Cluster size</td>
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<tr>
<td>$C, C_0$</td>
<td>Orientation tensor, reference value of the orientation tensor</td>
</tr>
<tr>
<td>$C_0$</td>
<td>Reference value of the orientation tensor</td>
</tr>
<tr>
<td>$C_4$</td>
<td>Fourth moment of the orientational distribution function</td>
</tr>
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<td>$\mathcal{C}$</td>
<td>Maximum eigenvalue of the orientation tensor</td>
</tr>
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<td>$d_{\text{ed}}$</td>
<td>Distance of closest approach between two ellipsoids</td>
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<td>$d_1, d_2$</td>
<td>Distances used to characterise 3-particle configurations</td>
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<td>$E$</td>
<td>Total energy of the system</td>
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<td>$E', E''$</td>
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<td>$E_{ij}$</td>
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<td>$f(c_i/c_i(t))$</td>
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<tr>
<td>$h$</td>
<td>Meniscus height profile</td>
</tr>
<tr>
<td>$H$</td>
<td>Hamiltonian</td>
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<tr>
<td>$i$</td>
<td>Index of a particle or imaginary unit</td>
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<tr>
<td>$I$</td>
<td>Moment of inertia</td>
</tr>
<tr>
<td>$I_n$</td>
<td>Modified Bessel function of the first kind</td>
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<tr>
<td>$j$</td>
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<tr>
<td>$\mathbf{n}$</td>
<td>Director, direction of preferred alignment</td>
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<td>$r$, $\mathbf{r}$</td>
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<td>$\mathbb{R}$</td>
<td>The set of real numbers</td>
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<td>$s_{\text{v}}$</td>
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<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature of the interfacial fluid layer</td>
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<tr>
<td>$u$</td>
<td>Internal energy density of the interfacial fluid layer</td>
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</tr>
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<td>$U_{\text{quad}}$</td>
<td>Quadrupole interaction energy</td>
</tr>
<tr>
<td>$\mathbf{u}_i$</td>
<td>Orientation of particle $i$</td>
</tr>
<tr>
<td>$\mathbf{v}$</td>
<td>Interface velocity</td>
</tr>
<tr>
<td>$\mathbf{W}$</td>
<td>Two dimensional Wiener process</td>
</tr>
<tr>
<td>$\mathbf{x}$</td>
<td>Set of macroscopic state variables</td>
</tr>
<tr>
<td>$x_{\text{rev}}$</td>
<td>Reversible parts of the equations of motion of $\mathbf{x}$</td>
</tr>
<tr>
<td>$z$</td>
<td>Dynamic scaling exponent for cluster aggregation</td>
</tr>
<tr>
<td>$z$</td>
<td>Microscopic degrees of freedom</td>
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<tr>
<td>$Z_{\Lambda}$</td>
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### Greek symbols

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<thead>
<tr>
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<tbody>
<tr>
<td>$\beta$</td>
<td>Inverse temperature, defined as $\beta = 1/(k_B T)$</td>
</tr>
<tr>
<td>$\gamma, \dot{\gamma}$</td>
<td>Shear strain, rate of shear strain</td>
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Acronyms

- DLCA: Diffusion-limited colloidal aggregation
- LB: Lattice-Boltzmann
- MC, VMMC: Monte-Carlo, Virtual move Monte-Carlo
- MD, EDM: Molecular dynamics, Event-driven molecular dynamics
- PMMA: Poly(methyl methacrylate)
- PS: Polystyrene
- SS, ST, TT: Side-side, side-tip, tip-tip
- SSS, TTT: Side-side-side, tip-tip-tip
1 Introduction

Control and understanding of the mechanical behaviour of complex fluid interfaces is a key topic in both fundamental and applied soft matter research [1]. Complex interfaces are a term coined to describe fluid interfaces containing some adsorbed ‘stuff’, which can drastically alter the mechanical properties of the interface. Examples of stuff include proteins, surfactants, polymers, fats or solid particles. Since foams and emulsions, which are composed of many fluid interfaces, are ubiquitous in our everyday lives, it must be of no surprise that they are of crucial interest for numerous industries.

In the food industry many products contain emulsions and/or foams therefore control over the interfaces within them is vitally important for processing, storage and the final product [2]. The texture of ice cream, for instance, depends on the stability of air bubbles, fat droplets and ice crystals [3]. Repeated heating and cooling cycles melts the ice crystals into water droplets, which undergo Ostwald ripening meaning that the larger droplets increase in size at the expense of the smaller. Upon refreezing, the larger ice crystals manifest themselves as a gritty, unpleasant texture. The importance of being able to stabilise the many interfaces within ice-cream cannot be understated.

In the petroleum industry, in the process of offshore oil extraction, some seawater inevitably gets mixed in with crude oil and forms an emulsion. While our everyday experience with salad dressings is that an emulsion of oil and water readily phase separates, various petroleum companies discovered that it is remarkably difficult to remove the water from a water-in-crude oil emulsion. This is an important issue since the emulsion has a higher viscosity than pure crude oil, thus increasing transportation costs, and the seawater causes corrosion of machinery and leads to sludge generation. It was finally in the 1970s that they realised the oil-water interface is complex, with adsorbed asphaltene aggregates helping to stabilise the emulsion [4, 5, 6]. We can easily also mention the importance of complex fluid interfaces in the pharmaceutical industry — particularly in drug delivery, and in the cosmetics industry — since creams and lotions are emulsions.

In this thesis, we focus on particles on fluid-fluid interfaces (particle-laden interfaces) and
consider the case when colloidal particles are irreversibly adsorbed. Generally, particles bind very strongly and irreversibly to the interface, since by doing so, they reduce the energy cost of having an interface present. A rough estimate of the binding energy for micron-sized particles onto a water-air interface gives $10^6 k_B T$ and much work has been done on adsorption pathways and detachment energies [7, 8, 9].

The discovery by Ramsden [10] and Pickering [11] that solid particles adsorbed onto the interfaces in emulsions can impart remarkable stability has led to the terms: particle-stabilised emulsion (also known as a Pickering emulsion) and particle-stabilised interface. Since their pioneering work over a century ago, there has been considerable further experimental work demonstrating this particle-stabilising effect on various foams and emulsions [12, 13] with recent exciting developments using environmentally friendly and edible materials [14, 15, 16, 17]. The stability is generally attributed to a kinetic barrier (pictured as an ‘armored bubble’) formed by the adsorbed particles, thereby preventing coalescence of droplets [2], although for very specific systems, a thermodynamically stable Pickering emulsion has been achieved [18]. However, it now seems that a sufficient condition for droplet stabilisation is a yield stress interface, which can be achieved with sub-monolayer coverage [17, 19, 20]. Furthermore, emulsion stabilisation has been demonstrated with soft, deformable microgels, which seem to have a different stabilising mechanism compared with hard particles [21, 22]. A full understanding of what constitutes necessary and sufficient conditions to achieve emulsion stability using adsorbed particles is still an open question.

To better understand the role of particles in stabilising foams and emulsions, we must take into account how the structures formed by the adsorbed particles mechanically affect the interface. We readily see that particles on interfaces can form a multitude of different structures, depending on their geometry, surface chemistry (wetting behaviour), surface charge and surface coverage, see Fig. 1.1. The different structures seen in Fig. 1.1 also reflect the good control we now have over these parameters. In fact, the self-assembly of particles on interfaces is an active area of research [23, 24], and has been exploited to form templates to fabricate particle lithography masks [25]. Aside from purely using particle properties, self-assembly can also be controlled by external electric and magnetic fields [26, 27, 28]. The surface structure must be manifest in the rheology of the interface.

Experimentally, interfacial rheology is probed by Langmuir-Blodgett troughs to study surface dilational rheology, and variations on cone rheometers and magnetic rod rheometers to study surface shear [29]. In addition, microrheological methods have also been adapted for interfacial rheology [30]. The structure of complex interfaces can be studied, either optically if the particles are large enough, or by X-ray scattering [12]. There is a reasonable body of experimental rheology of particle-stabilised interfaces [31, 32, 33, 34], with some intriguing results that suggest particle geometry to be an important factor for interfacial rheology, for equal surface coverage [17, 35].

The first constitutive model developed for interfaces is the Boussinesq-Scriven equation in
1960 [39, 40], which describes the interface as a two-dimensional Newtonian fluid. From 1960 until very recently, development of more sophisticated structure-based constitutive rheological models specifically for interfacial rheology has been severely lacking, despite the huge growth of experimental work [31, 41, 42, 43].

A possible explanation may be the complexity of the problem. Particles adsorbed at an interface experience all of the interactions that they would in the bulk, in addition to many more uniquely interface-related phenomena. Of particular note are the capillary interactions [36, 44, 45, 46], which are multibody interactions related to how the deformations of the interface due to adsorbed particles interact. Depending on the relative positions and orientations of the particles, the interface is deformed differently, leading to forces and torques between the particles as the interface attempts to reduce its surface area and hence free energy.

Physical origins of interfacial deformations include flotation forces, particle shape, surface chemistry, surface roughness and electric charge. Flotation forces are relevant for larger particles, which can reduce their gravitational potential energy by coming together, leading
to an effective attractive force — this is also the origin of the so-called ‘cheerios effect’, where floating objects (like the aforementioned breakfast cereal) are observed to aggregate [47]. This effect is, however, expected to be negligible for colloidal-sized particles [48], where wetting behaviour plays a more important role. The effect of wetting can be boiled down to a contact angle $\theta$, determined by the Young-Dupré equation

$$\sigma_1 - \sigma_2 - \sigma \cos \theta = 0 \quad (1.1)$$

where $\sigma_1$ is the surface tension between particle and fluid 1, $\sigma_2$ is the surface tension between particle and fluid 2, and $\sigma$ is the surface tension between the two fluids. Since the interface must contact the colloid at the contact angle (see Fig. 1.2), its profile must be deformed. This effect was used to help explain the shape of aggregates formed by mosquito eggs at the air-water interface [49]. Surface roughness on a particle can lead to an undulating contact line, which distorts the meniscus [45]. We note that the interface can also be deformed by the presence of charges on the particles if one of the bulk phases contains electrolytes, such as for a water-air or water-oil system [2, 46, 50, 51]. Here the physical mechanism underlying the interface deformation is related to the gathering of counterions on the electrolyte side to screen the particle charge, which results in a pressure field acting on the particle and interface, causing the interface to become deformed. The screening effect leads to a leading order dipole-dipole electrostatic repulsion at large separations [52, 53, 54].

We should also be aware of curvature effects [55, 56], bulk-interface coupling [57, 58], and the fact that the nature of bulk interparticle interactions can be drastically modified by the presence of an interface [46, 59]. It is also important to keep in mind the extended space of interfacial deformations when compared to bulk deformations, namely flows which do not preserve area (or volume, in the case of bulk flows). The change in interface area is equivalent to a change in particle surface coverage. Changing surface coverage can induce further complexity involving phase transitions in the structure, jamming of the adsorbed particles, buckling of the interface [60, 61], or pushing particles to orient out of the interface [62, 63].

Since structure formation is a direct result of particle-particle interactions, there is great interest in establishing interaction potentials between two adsorbed particles. The capillary interaction has been inferred experimentally by observing the motion of particles as they come together in [36] and measured directly using optical tweezers in [64]. The theory of capillary interactions between two particles is well developed and consists of either solving an energy minimisation problem where the free energy of the interface and particles is considered and generally consists of solving the Young-Laplace equation with non-trivial boundary conditions on the particles due to the contact angle [44, 46, 65], or by a ‘force approach’ based on mechanical equilibrium of the system [66].

However, analytic results for specific particle geometries are only generally available following simplifications (small gradients, small aspect ratio) [67] and in asymptotic limits (large sepa-
ration distance) [45, 68]. Hence the attractiveness of exact numerical methods. A frequently used piece of software for finding the equilibrium interface profile is a finite element code called Surface Evolver [69]. The interface is described by facets, the vertices of which move by gradient descent to find the optimum energy configuration, given certain boundary conditions. The interaction potential between particles can be found by solving for the interface profile at various separation distances, as was done for various particle geometries and contact angles in Refs. [70, 71, 72].

In terms of the structure formation itself, involving many particles, the difficulty lies in the separation of time and length scales. A full atomistic level Monte-Carlo or Molecular Dynamics simulation is prohibitively expensive given the particles are colloid-sized, while the solvent molecules are measured in Å. Furthermore, the structure has been observed to evolve over several days in experiments [37]. Computational fluid dynamics-type simulations of multiphase flows with solid particles at the interface are possible but also very expensive for more than a handful of particles [73]. Of note are the use of Lattice-Boltzmann methods to simulate particle-stabilised emulsions [74, 75, 76, 77] and the directed self-assembly of tilted ellipsoidal particles [78].

Nonlinear interfacial rheology seems to be a general feature of complex fluid interfaces, and is commonly encountered for even very small strains [12, 79]. Nonlinearity is associated with structural changes taking place on the interface, therefore a prerequisite to understanding interfacial rheology is an understanding of the structural changes that take place during deformations of the interface. There are very few constitutive models that link rheology to structure but one of the standout approaches is with the nonequilibrium thermodynamic framework known as the General Equation for Nonequilibrium Reversible-Irreversible Coupling (GENERIC) [80, 81, 82], which has been applied extensively to model polymer rheology [80], soft glassy rheology [83], bulk metallic glass rheology [84], nucleation [85, 86], amongst many other topics. GENERIC was recently extended to multiphase systems, with a conceptually clear bulk-interface exchange [57, 87] and the notion of local equilibrium at the interface [88]. In addition, Sagis has developed general phenomenological equations for interfacial rheology within GENERIC [41]. The strength of GENERIC lies in its foundations, where one can systematically coarse grain from the microscopic level to the macroscopic behaviour, while retaining thermodynamic consistency.

Given all the complexity detailed above, we seek to disentangle the effect of competing interactions between adsorbed particles. For this reason we begin by focusing purely on excluded volume effects. Here, we developed a general multiscale approach based on combining GENERIC with computer simulations to derive the constitutive equations [43, 89]. We demonstrate this general approach on a toy model of hard prolate ellipsoidal particles on an interface, neglecting all interactions apart from excluded volume effects and are able to systematically bridge the scales between the microscopic toy model and macroscopic rheological behaviour. Such a system corresponds to particles which are inert, electrically neutral and have a contact angle of 90° and we expect the results to be relevant in experiments where excluded volume
effects dominate, for instance at high surface coverage.

For our toy model, we neglect the effect of the bulk phases in the interests of simplicity and since we note that a coarse-grained effective pair potential between polymers at an interface is sufficient to accurately reproduce the thermodynamic and structural properties of the interfacial layer in full three-dimensional simulations including the bulk phases [90]. Furthermore, we do not expect any bulk-interface exchange of particles once they are already attached to the interface due to the aforementioned high detachment energies [7, 8].

We begin by using a systematic coarse-graining method [91, 92] to numerically determine the free energy, which we fit to a Landau-de Gennes-type expression, since at the high surface coverages and with the particle geometries typically encountered in experiments, Onsager theory is inaccurate [93, 94]. This method consists of Monte-Carlo (MC) simulations of the model in the generalised canonical ensemble, which allow us to access out-of-equilibrium states. Coupled with thermodynamic integration we can numerically obtain the free energy. Our free energy is valid for the wide range of aspect ratios, surface coverages and orientation strengths studied, and in addition it accurately predicts the location of the isotropic-nematic phase transition in systems of hard ellipses. The relaxation dynamics of the toy model are determined by coarse-graining the results from event-driven Molecular Dynamics simulations of the toy model. The numerical data is consistent with theoretical relaxation dynamics calculated by us, involving a single effective time constant (which is a function of surface coverage and orientational ordering strength). By combining the results of computer simulations and theory within the GENERIC framework, we obtain a set of time evolution equations describing the macroscopic rheology of our toy model. We solve this under various flow conditions and find that, despite the simplicity of our toy model, there is already a rich phenomenology. Since we have a full description of the system, we are able to interpret the rheological behaviour by referring to flow-induced structural changes and the interplay between various timescales.

We then turn our attention to the effect of particle geometry and capillary interactions, which are expected to be very important in structure formation. Indeed, estimates of the strength of a capillary bond between micron-sized ellipsoidal particles are around $\sim 10^6 k_B T$ [67]. Here we allow the hard ellipsoids to vary their contact angle away from $90^\circ$. This leads to the interface becoming deformed, as it must satisfy the contact angle boundary conditions on the particles while minimising its free energy. Interestingly, the interaction between ellipsoidal particle varies from attractive to repulsive depending on their relative orientation [67].

Up to now, there have been no large-scale structure formation simulations involving capillary interactions; this is something new which we will present in this thesis. Our approach consists of developing an empirical pair potential for ellipsoidal particles, fitting it to exact numerical calculations of ellipsoid pairs at different separation distances and relative orientations, which goes beyond the rather inaccurate but typically assumed quadrupolar pair potential [67]. Our pair potential is then used in sophisticated Virtual Move Monte-Carlo (VMMC) simulations to simulate structure and aggregate formation with an approximation of realistic dynamics
We study self-assembly of the particles systematically, for a range of aspect ratios, contact angles and surface coverages. Two distinct regimes are found corresponding to dilute/intermediate surface coverages, when clustering occurs and high surface coverages, where a spanning kinetically arrested gel is formed. In the dilute regime, we study the dynamics of aggregation and observe the expected scaling behaviour of cluster size growth \cite{98}. Our clusters are denser and more crystalline than the long strands seen in experiments; we believe the experimentally observed open structures are associated with the interplay between electrostatic repulsion and capillary interactions. However, at high surface coverage, our kinetically arrested final state does resemble the smectic-like structures seen in Ref. \cite{38} (c.f. Fig. 1.1(d)).

The validity of using pair potentials to describe multibody capillary interactions depends on the validity of the superposition or Nicolson approximation \cite{99}, where the interface profile is assumed to be the sum of interface profiles originating from individual particles. This is expected to be accurate for small deformations of the interface and has been used extensively in theoretical efforts to describe the interaction between two adsorbed particles, for instance, in Refs. \cite{45, 67, 68, 100}. For floating sub-millimeter spherical particles, the force between two particles calculated using the superposition approximation is accurate to within a few percent compared to the exact solution \cite{101}, although for when the interface deformation is due to electrocapillarity, the validity depends on whether the whole system is in mechanical isolation \cite{102}.

Since nearly all previous work is focused on two particle interactions (with the exception of Ref. \cite{68}, which found some multibody effects for 3 and 4 spherical particles), we investigate the use of pair potentials to describe multibody capillary interactions by considering exact numerical results for two and three particles in various configurations in order to validate the use of pair potentials in our VMMC simulations.

This thesis is organised in the following manner. In Chapter 2 we present the nonequilibrium thermodynamic framework GENERIC, that is crucial for systematic development of the constitutive equations linking structure to rheological properties and proper bulk-interface coupling. Chapter 3 demonstrates our general multiscale approach linking macroscopic behaviour to a microscopic toy model. Chapter 4 uses the results of Chapter 3 to study the rheological behaviour of our constitutive model, and Chapter 5 concerns the accuracy of the superposition approximation and structure formation of ellipsoidal particles due to capillary interactions.
Chapter 1. Introduction

The main scientific achievements described in this thesis are detailed in the publications below:


\(^1\)The sections of Chapter 3 based on this paper are the author's own work, with guidance from P. Ilg and L. M. C. Sagis.

\(^2\)The work shown in Chapters 3 and 4 based on this paper was carried out entirely by the author, with guidance from H. C. Öttinger, P. Ilg and L. M. C. Sagis. C. De Michele provided the event-driven Molecular Dynamics code for simulating the dynamics of hard ellipsoids.

\(^3\)The sections of Chapter 5 based on this paper are the author's own work, with guidance from P. Ilg and L. M. C. Sagis.
2 The GENERIC framework

Rheology, as the study of flowing matter, is inherently the study of out-of-equilibrium matter. Particle-laden interfaces enter a nonlinear regime even for very small strains [12, 79], which highlights the importance of structural changes that take place on the interface. A great advantage of the GENERIC framework is the natural incorporation of structural information into rheological models and constitutive equations in a thermodynamically consistent way.

GENERIC modelling can be either purely phenomenological, with intuition and thermodynamic and geometric considerations providing the structure of the coarse-grained equations, or based on coarse-graining from a microscopic level description, or a mixture of the two. As the GENERIC framework underpins our constitutive modelling, we provide a self-contained introduction as well as the GENERIC coarse-graining procedure. For more detail we refer the reader to Refs. [80].

We note that GENERIC has been extended to properly describe multiphase systems [87], including those with complex fluids [41]. In the following Chapters 3 and 4, we treat the interface with adsorbed particles as a two-dimensional bulk phase, therefore we do not present the extended multiphase GENERIC here but rather refer the reader to the aforementioned references. However, we do note that our results can be readily incorporated into the multiphase GENERIC framework.
Chapter 2. The GENERIC framework

2.1 Introduction to GENERIC

The first most crucial step is to identify the set of independent, macroscopic state variables $x$ that fully determine the system we wish to study at the chosen level of description. These variables are functions of the microscopic degrees of freedom $z$ of the system i.e. $x = x(z)$. The time evolution of the set of state variables is then given by the GENERIC equation

$$\dot{x} = L(x) \cdot \frac{\delta E}{\delta x} + M(x) \cdot \frac{\delta S}{\delta x}, \quad (2.1)$$

where $\delta / \delta x$ denotes functional derivatives, $L$ is the Poisson matrix and $E$ is the total energy; together they describe the reversible dynamics. $M$ is the friction matrix and together with the entropy $S$ gives the irreversible dynamics. Hence the reversible dynamics is driven by energy gradients, while the irreversible dynamics is driven by entropy gradients. The GENERIC equation (2.1) can be written equivalently in terms of brackets

$$\dot{A} = \{A, E\} + [A, S], \quad (2.2)$$

where $A$ is an arbitrary functional of the state variables. The Poisson bracket is defined as

$$[B, C] = \int \frac{\delta B}{\delta x} \cdot L \cdot \frac{\delta C}{\delta x} \, d^3r \quad (2.3)$$

where $B, C$ are also arbitrary functionals of the state variables. The underlying Poisson geometric structure imposes strict conditions on the Poisson bracket, namely antisymmetry $\{A, B\} = -\{B, A\}$, the Leibniz rule $\{AB, C\} = A\{B, C\} + B\{A, C\}$ and Jacobi identity $\{A, \{B, C\}\} + \{B, [C, A]\} + [C, \{A, B\}] = 0$. The Poisson bracket is well-studied and has been formulated for a variety of state variables, including scalars, scalar densities, vectors and tensors [80], but with the aforementioned severe restrictions, the form of the Poisson bracket is more or less set depending on the type of state variable. The dissipative bracket is defined as

$$[B, C] = \int \frac{\delta B}{\delta x} \cdot M \cdot \frac{\delta C}{\delta x} \, d^3r, \quad (2.4)$$

and simply has the properties of symmetry $[A, B] = [B, A]$ and positive semi-definiteness $[A, A] \geq 0$, which ensures that entropy production is non-negative for irreversible dynamics. The dissipative bracket describes relaxation of the state variables toward equilibrium and we note that it is less geometrically constrained than the Poisson bracket. In order to formulate it, one ideally needs some intuition and prior knowledge of the relaxation phenomena one wishes to describe. There are two supplementary degeneracy conditions

$$[A, S] = 0, \quad (2.5)$$

$$[A, E] = 0, \quad (2.6)$$

which together ensure that total energy is conserved $\dot{E} = 0$ and total entropy production is non-negative $\dot{S} = [S, S] \geq 0$, therefore guaranteeing thermodynamic consistency. In addition, the
first degeneracy condition implies reversible dynamics are entropy conserving. In constitutive
modelling, applying these degeneracy conditions specifies the form of the stress tensor and its
relationship to the state variables.

In order to construct a model using the GENERIC framework we must firstly specify the state
variables $x$, followed by the four building blocks $L, M, E, S$ (or alternatively, the Poisson and
dissipative brackets). Together, they provide a full description of the system with a closed set
of time evolution equations for the state variables $x$. Crucially, all of the building blocks can
be formulated by a systematic coarse-graining of the microscopic system [103, 104], which is
introduced in the next section.

### 2.2 Statistical physics foundations

Formally, the systematic route to coarse-grain microscopic trajectories to a macroscopic level
of description is the use of projection operators [105], where the ‘fast’ degrees of freedom are
integrated out to leave us with the ‘slow’ degrees of freedom, namely the state variables $x$. The
GENERIC framework makes use of the projection operator approach to construct the four
building blocks $L, M, E, S$ from microscopic trajectories and configurations in a thermody-
namically consistent manner.

We must begin with the microscopic variables $z$ and a nonequilibrium ensemble, for instance
the generalised canonical ensemble

$$
\rho_\Lambda = \int f_{eq}(z) e^{-\Lambda(x):\Pi(x)+\beta G(\Lambda(x))},
$$

where $\beta = 1/(k_B T)$ is the inverse temperature, $f_{eq} \sim e^{-\beta H(z)}$ is the equilibrium canonical
distribution with $H(z)$ the Hamiltonian, $\Lambda(x)$ is the Lagrange multiplier that imposes the
appropriate averages on the macroscopic variables $x = \langle \Pi(z) \rangle_{\rho_\Lambda}$ and $G(\Lambda(x))$ is the generat-
ing function, which normalises the ensemble. $\langle \ldots \rangle_\rho$ denotes an ensemble average over the
ensemble $\rho$. For the systems we are studying, involving $N$ anisotropic particles adsorbed on
an interface, the appropriate microscopic degrees of freedom of the particles are the positions
$r_i$, momenta $p_i$, orientations $u_i$ and angular momenta $l_i$, with $i = 1, \ldots, N$.

We label the total energy $E$, total entropy $S$ and Poisson matrix $L$ ‘static’ building blocks since
they only depend on microscopic configurations and not the trajectories. Hence they can be sampled using static simulation techniques, such as MC simulations in the generalised canonical ensemble (2.7). Given a microscopic Hamiltonian $H(z)$, the total energy is the usual

$$
E(x) = \langle H(z) \rangle_{\rho_\Lambda},
$$

and the Poisson matrix has the natural form

$$
L = \left\langle \frac{\partial \Pi}{\partial z} \cdot L_0 \cdot \frac{\partial \Pi}{\partial z} \right\rangle_{\rho_\Lambda} = \langle \{ \Pi, \Pi \} \rangle_{\rho_\Lambda},
$$

2.2. Statistical physics foundations
where $L_0$ is the cosymplectic matrix and we recognise the Poisson bracket of classical mechanics for the second equality. We note, however, that the reversible part of the dynamics $L \cdot \delta E/\delta x$ is typically treated analytically using the transformation behaviour of $\Pi$ (see Section 2.1 and Ref. [80]) hence we would rather focus on what is usually less well-known, and that is the macroscopic entropy, given by

$$S = -k_B \int \rho_\Lambda(z) \ln \rho_\Lambda(z) \, dz$$
$$= k_B \langle \beta G(\Lambda(x)) \rangle - k_B \Lambda(x) : x,$$

(2.10)

where the role of $\beta G(\Lambda(x)) = -\ln Z_\Lambda$ as the partition function of the generalised canonical distribution is now clear. This is indeed the quantity that must be sampled in MC simulations in order to obtain the entropy.

The friction matrix $M$ is the sole dynamic building block, so-called because it contains the material properties related to dissipative processes, examples include diffusion coefficients, relaxation timescales etc. Hence we require knowledge of the microscopic trajectories to consistently formulate it. A fluctuation-dissipation relationship in the form of a Green-Kubo formula establishes the relationship between microscopic trajectories and the friction matrix

$$M_{x,x} = \frac{1}{k_B} \int_0^{\tau_s} \langle \hat{\Pi}^f(z(t)) \hat{\Pi}^f(z(0)) \rangle_{\rho_\Lambda} \, dt,$$

(2.11)

where $\hat{\Pi}^f$ denotes the fast fluctuations of $\Pi$ and $\tau_s$ is the separating timescale between ‘fast’ fluctuations and ‘slow’ dynamics of the state variables $x$. In this approach, the fast dynamics are unresolved on the macroscopic level and are treated as noise. We can write the integrated version of Eq. (2.11) as

$$M_{x,x} = \frac{1}{2k_B \tau_s} \langle \Delta_{\tau_s} \Pi(z) \Delta_{\tau_s} \Pi(z) \rangle_{\rho_\Lambda},$$

(2.12)

where $\Delta_{\tau_s} \Pi(z) = \Pi(z(\tau_s)) - \Pi(z(0))$ is the incremental change of $\Pi$ over the time $\tau_s$. This equation can be more useful when applied to microscopic trajectories from e.g. MD simulation data. This approach was successfully applied to obtain the friction matrix numerically [104] and semi-analytically for the case of polymer melts [106].
We present a general approach based on the GENERIC framework for developing rheological models of anisotropic particles on interfaces and demonstrate our approach on a toy model. In contrast to an earlier GENERIC-based model [42], our general approach is based on and derived from a microscopic model and therefore applicable over a significant range of surface coverages and ordering strengths. This is particularly important for physical systems, which often have a high surface coverage of particles [32] and more generally, good models linking structure to rheology are indispensable for the interpretation of large amplitude oscillatory shear or dilatation results, which probe nonlinear rheology where structural changes take place.

This chapter begins by a detailed definition of our toy model, which serves as the microscopic level of description. From the microscopic degrees of freedom, we identify the relevant state variables, which should provide a full description of the macroscopic system. Thanks to the simplicity of the underlying microscopic model, the reversible dynamics are relatively straightforward. Since the irreversible dynamics lacks the geometric structure of the Poisson bracket, its formulation relies on the intuition of the researcher, or if a detailed microscopic model is available, as is our case, then we can use a systematic coarse-graining approach as described in Section 2.2. This chapter is based on published work by the author, Refs. [43, 89].

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1Any figures drawn or adapted from Refs. [43, 89] are used with permission.
3.1 The toy model

We envisage to model the rheology of a fluid-fluid interface with adsorbed anisotropic particles. Since such a system can be extremely complex (see the discussion in Chapter 1), we make a number of simplifying assumptions for our toy model:

1. **The interface is planar.** This geometry is highly relevant for experimental setups, where Langmuir-Blodgett troughs and bi-cone rheometers probe a planar interface.

2. **The particles are hard, smooth, uncharged, with a 90° contact angle and ellipsoid-shaped.** Simply an idealisation of the elongated particles used in experiments.

3. **The particles are irreversibly adsorbed onto the interface and are restricted to move and rotate within the interface.** Reasonable, given the very high detachment energies involved [7, 8, 9].

4. **There is no bulk-interface coupling.** We assume here that all the particles have adsorbed onto the interface and that the surface drag is much greater than the subphase drag so that the contributions of the bulk phases to the rheology of the interface are negligible. In terms of the Boussinesq number $Bo = \frac{\varepsilon_s}{\varepsilon_{bulk} r_0} \gg 1$, where $\varepsilon_s$ is the surface shear viscosity, $\varepsilon_{bulk}$ is the subphase viscosity and $r_0$ is the probe size.

5. **The system is homogeneous, both in temperature and surface coverage, and flows do not induce gradients in particle concentration or ordering.**

With these assumptions, the description of our toy model is complete. We essentially model the interface as a two-dimensional bulk phase comprised of a macroscopically thin fluid layer (‘the interface’) and adsorbed particles. Note, however, that our equations describing the interface can be incorporated into the more general multiphase GENERIC framework [87, 41]. Note also that our approach can handle situations where these idealisations are no longer valid — the only fundamental requirement is a well-defined microscopic model.

Our prolate ellipsoidal particles have semi-major axis length $a$, both semi-minor axis lengths are $b$, with $a > b$. The aspect ratio is defined as $k = a/b$ and the eccentricity is $\sqrt{1 - 1/k^2}$. The eccentricity is therefore small for small $k$ and equal to one in the limit of infinitely elongated ellipsoids.

3.2 Identification of the relevant variables

Given our microscopic toy model, the relevant microscopic variables associated with the adsorbed particles are the positions $r_i$, momenta $m_i$, orientations $u_i$ and angular momenta $l_i$, with $i = 1, ..., N$. From these considerations, we identify appropriate state variables

$$x = (\rho, M, u, \eta, C), \quad (3.1)$$
3.3. Reversible dynamics

where \( \rho \) is the mass density, \( M \) is the momentum density\(^2\) and \( u \) is the internal energy density of the interfacial fluid layer. The structural variables are \( \eta \) the surface coverage of the particles and \( C = \langle uu \rangle \) the orientation tensor, which describes the direction of preferred alignment as well as the ordering strength. Together, \( \eta \) and \( C \) characterise the surface structure formed by the particles.

Using the orientation tensor as the structural variable, rather than the orientation vector, is a natural way to incorporate the head-tail symmetry of ellipsoids. We further define a director \( n \), which is the eigenvector of \( C \) associated with its greatest eigenvalue and a Maier-Saupe-like order parameter \( S_2 = \sqrt{2C: C - I} \), which varies from 0 in the isotropic state, to 1 for perfect ordering. The director is the direction of preferred alignment. The surface coverage is defined as \( \eta = \frac{N \pi ab}{l_x^2} \), where the surface area of the interface is \( l_x^2 \). Note that the vector quantities are two dimensional, and that densities are area densities.

3.3 Reversible dynamics

The reversible part \( \dot{x}_{\text{rev}} = \{A, E\} \) of the time evolution equations describes how the state variables are convected by flow. In this Section we formulate two of the four building blocks: the total energy and Poisson bracket.

As the ellipsoids only interact via excluded volume, there is no particle-particle interaction energy and the total energy takes a particularly simple form

\[
E = \int \left( \frac{M^2}{2\rho} + u \right) d^2r. \tag{3.2}
\]

The first term in the integral is the kinetic energy of the system. For cases where the particles have energetic interactions, there would be an interaction term in the microscopic Hamiltonian \( H(z) \), which can be readily sampled in MC simulations to obtain \( E \) (see Eq. (2.8)). Note that the state variables are dependent on the position so that e.g. the internal energy density of the fluid \( u \) is equal to zero where particles are present. Thus the surface coverage is implicitly taken into account in the total energy (3.2). The functional derivative \( \delta E / \delta x \), which enters into the GENERIC equation (2.1) is

\[
\frac{\delta E}{\delta x} = \begin{pmatrix}
-\frac{v^2}{2} \\
v \\
1 \\
0 \\
0
\end{pmatrix} \tag{3.3}
\]

where we define the velocity \( v = M/\rho \). From consideration of the motion of rod-like particles

\(^2\)Since we use a purely hydrodynamic treatment, \( M \) measures the momentum of all mass points in the medium, including along the length of the ellipsoidal particles. We therefore do not need to introduce an additional angular momentum state variable [107, 108].
in flow [109], we find that the orientation tensor \( C \) is upper-convected, allowing us to write the Poisson bracket

\[
\{A, B\} = -\int \rho \left( \frac{\partial A}{\partial \rho} \frac{\partial B}{\partial r_j} \delta \rho - \frac{\partial B}{\partial \rho} \frac{\partial A}{\partial r_j} \delta \rho \right) d^2 r
\]

\[
-\int M_k \left( \frac{\partial A}{\partial \rho} \frac{\partial B}{\partial M_j} \delta M_k - \frac{\partial B}{\partial \rho} \frac{\partial A}{\partial M_j} \delta M_k \right) d^2 r
\]

\[
-\int u \left( \frac{\partial A}{\partial \rho} \frac{\partial B}{\partial u} \delta u - \frac{\partial B}{\partial \rho} \frac{\partial A}{\partial u} \delta u \right) d^2 r
\]

\[
-\int s_{jk} \left( \frac{\partial A}{\partial \rho} \frac{\partial B}{\partial s_{jk}} \delta s_{jk} - \frac{\partial B}{\partial \rho} \frac{\partial A}{\partial s_{jk}} \delta s_{jk} \right) d^2 r
\]

\[
+ \int C_{jk} \frac{\partial}{\partial r_j} \left( \frac{\partial A}{\partial C_{jk}} \delta C_{jk} - \frac{\partial B}{\partial C_{jk}} \delta A \right) d^2 r
\]

\[
+ \int C_{lk} \left( \frac{\partial A}{\partial \rho} \frac{\partial B}{\partial C_{lk}} \delta C_{lk} - \frac{\partial B}{\partial \rho} \frac{\partial A}{\partial C_{lk}} \delta C_{lk} \right) d^2 r
\]

\[
- \int s_{kl} \left( \frac{\partial A}{\partial \rho} \frac{\partial B}{\partial s_{kl}} \delta s_{kl} - \frac{\partial B}{\partial \rho} \frac{\partial A}{\partial s_{kl}} \delta s_{kl} \right) d^2 r
\]

\[
- \int \frac{\partial}{\partial \rho} \left( \frac{\partial A}{\partial s} \frac{\partial B}{\partial \eta} \delta \eta - \frac{\partial B}{\partial \rho} \frac{\partial A}{\partial \eta} \delta \eta \right) d^2 r,
\]

(3.4)

where we use the Einstein summation convention for the indices \( i, j, k, l \). The first four integrals form the usual Poisson bracket of hydrodynamics [80, 110] with a stress tensor \( s \) determined by applying the degeneracy condition \( \{A, S\} = 0 \). We determine the stress \( s \) once we have an expression for the total entropy \( S \). The next four integrals in Eq. (3.4) represent upper convective behaviour for the tensor variable \( C \), with the seventh integral involving the term \( (2C_{ij}C_{kl}) \) required to preserve the trace of \( C \) \([111, 112, 113]\). Physically, the trace of \( C \) must be constant because we consider hard particles, whose length cannot change in flow. The final integral describes convection of the particle surface coverage \( \eta \). All properties of the Poisson bracket are satisfied by Eq. (3.4), including the Jacobi identity [114].

### 3.4 Entropy

Onsager proposed in 1949 [93] that the entropy of infinitely long hard rods could be split into an ideal orientational part and a two-body excluded volume contribution, which is equivalent to the second virial approximation. He showed that purely entropic interactions between particles at sufficient concentration leads to a phase transition to an ordered state.

The Onsager theory is valid only in the limit of very high aspect ratio and for dilute systems.
Various attempts have been made to generalise the theory in order to study the isotropic-nematic transition in systems of anisotropic hard particles [94, 115, 116, 117], however, these fall short of accurately describing the entropy over the whole range of surface coverages and particle geometries which are practically relevant.

We therefore follow a systematic coarse-graining approach based on Section 2.2 and applied in Refs. [91, 92] to obtain the free energy for the Lebwohl-Lasher and Gay-Berne liquid crystal models. The essence is the use of MC simulations in the generalised canonical ensemble (2.7) to access out of equilibrium states and then the use of thermodynamic integration to numerically obtain the free energy. Note that the free energy of hard particle systems can be considered equivalent to the entropy (up to a factor $T$) due to the lack of inter-particle interaction energies. The numerically obtained entropy can be split into an ideal part, which we derive, and an excess excluded volume part, to which we fit a Landau-de Gennes type expression.

### 3.4.1 Coarse-graining methodology

We outline the methodology used to numerically obtain the macroscopic free energy. We begin by defining the instantaneous, two-dimensional orientation tensor

$$\Pi = \frac{1}{N} \sum_{i} u_i u_i,$$  \hspace{1cm} (3.5)

where $u_i$ is the (unit) orientation vector of particle $i$ and there are $N$ particles in total. The tensor $\Pi$ is therefore symmetric and has constant trace. From the generalised canonical ensemble (2.7), we see that in this case, the Lagrange multiplier $\Lambda$ acts like an external field which imposes an average orientation direction and strength. By normalising the distribution $1 = \int \rho_\Lambda d\mathbf{z}$ and differentiating with respect to $\Lambda$, we find that $C$ and $\Lambda$ are conjugate variables and related by

$$C = \frac{\partial (\beta G)}{\partial \Lambda}. \hspace{1cm} (3.6)$$

The thermodynamic potential $F$ corresponding to the generalised canonical distribution (2.7) is the Legendre transform of $G$ with respect to $\Lambda$

$$F(C) = -G(\Lambda(C)) + k_B T \Lambda(C) : C. \hspace{1cm} (3.7)$$

This allows us to identify the structural contribution to the entropy $S_s(N, \eta, C)$ and write

$$\frac{\partial S_s}{\partial C} = -k_B \Lambda(C). \hspace{1cm} (3.8)$$

In terms of numerics, one can perform MC simulations of hard ellipsoids for a single surface coverage and a prescribed range of $\Lambda$, and measure the average orientation tensor $C = \langle \Pi \rangle_{\rho_\Lambda}$. 

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We therefore obtain a relationship \( C(\Lambda) \), which can be inverted to give \( \Lambda(C) \). The entropy difference from a reference state defined by \( C_0 \) is given by thermodynamic integration

\[
S_s(N, \eta, C) = S_s(N, \eta, C_0) - k_B \int_{C_0}^{C} \Lambda(C') : dC'.
\] (3.9)

We hence obtain the entropy for a single surface coverage. Repeating the procedure for a range of \( \eta \) allows us to construct an entropy \( S_s(N, \eta, C) \) valid over a wide range of surface coverages and orientation strengths.

We always begin with surface coverages that have an isotropic equilibrium state i.e. \( \Lambda = 0 \) and \( C_0 = \delta/2 \), where \( \delta \) is the 2 \( \times \) 2 identity matrix. \( S(C_0) \) is then the free energy of the equilibrium isotropic state. Note the different sign in the definition of \( F \) compared to Refs. [91, 92].

3.4.2 Ideal orientational entropy

The entropy obtained using the coarse-graining methodology outlined in the previous Section 3.4.1 is the total entropy of the hard ellipsoid system

\[
S_s(N, \eta, C) = S_{id}(N, C) + S_{excl}(N, \eta, C),
\] (3.10)

where \( S_{id} \) is the ideal orientational entropy and \( S_{excl} \) is the excess entropy. The ideal entropy is the entropy of non-interacting rotators, while the excess entropy is an additional contribution due, in this case, to excluded volume effects, which limit the possible microscopic configurations in phase space.

We analytically derive the contribution \( S_{id} \) and provide a simple yet accurate interpolation formula. The ideal entropy is the macroscopic counterpart to the Boltzmann-Shannon-Gibbs ideal orientational entropy functional

\[
S_{id} = -Nk_B \int f(\Omega) \ln f(\Omega) d\Omega,
\] (3.11)

where \( f(\Omega) \) is the orientation distribution function. A general expression for the ideal part was calculated recently for an ideal gas with orientational degrees of freedom in Ref. [118] and here we extend their approach to the case of non-interacting two-dimensional planar spins.

We begin by noting that thermodynamic potentials are invariant under changes of co-ordinate system and can therefore only depend on \( C \) through its tensorial invariants. Since two-dimensional, symmetric and constant trace matrices are characterised by a single tensorial invariant, i.e. their eigenvalue, we can choose the Lagrange multiplier and order parameter without loss of generality as

\[
\Lambda = N \begin{pmatrix} \lambda + 1/2 & 0 \\ 0 & -\lambda + 1/2 \end{pmatrix}, \quad C = \begin{pmatrix} \mathcal{C} + 1/2 & 0 \\ 0 & -\mathcal{C} + 1/2 \end{pmatrix},
\] (3.12)
3.4. Entropy

where $\lambda$ characterises the strength of the Lagrange multiplier and $\mathcal{C}$ is the eigenvalue of $\mathbf{C}$. The ideal orientational entropy is then (c.f. Eq. (3.8))

$$S_{id} = \frac{G(\Lambda)}{T} - k_B \mathbf{A} : \mathbf{C}$$

$$= N k_B \left( \hat{G}(\lambda) - 2 \lambda \mathcal{C} + \frac{1}{2} \right). \tag{3.13}$$

For the ideal case of non-interacting two-dimensional spins, $\hat{G} = \ln I_0(\lambda) - 1/2$ where $I_0$ is the modified Bessel function of the first kind. This follows from the definition of $G$ as the normalisation of the generalised canonical ensemble (see Appendix A.1 for a derivation). The order parameter $S_2$ can be determined using the relationship $S_2 = 2\mathcal{C}$ and Eq. (3.6) to obtain

$$S_2 = \frac{I_1(\lambda)}{I_0(\lambda)}. \tag{3.14}$$

We can see from this expression for $S_2$ that it has an expected lower bound of 0 and an upper bound of 1 corresponding respectively to the isotropic state and to the perfectly ordered nematic state.

The exact ideal orientational entropy can be found by inverting the relationship $S_2(\lambda)$ to obtain $\lambda(S_2)$ and inserting it into Eq. (3.13). It is however, an unwieldy expression and we instead propose a simple interpolation formula for $S_{id}$ by examining the weak and strong ordering limits

$$S_{id}(N, \mathbf{C}) = N k_B \left[ \frac{1}{2} \ln(1 - S_2) + \frac{1}{2} S_2 - \frac{3}{4} (S_2)^2 + \frac{1}{6} (S_2)^3 - \frac{1}{8} (S_2)^4 + \frac{1}{10} (S_2)^5 - \frac{1}{18} (S_2)^6 \right], \tag{3.15}$$

which has good accuracy and reduces to the correct limits for strong and weak ordering. Details of the derivation and a comparison between the exact numerical solution and our proposed interpolation formula are presented in Appendix A.2.

3.4.3 Excess entropy

We first obtain the total structural entropy $S_s$ using the coarse-graining method outlined in Section 2.2. The excess entropy $S_{excl}$ is then simply the difference between the total structural entropy $S_s$ and the ideal orientational entropy $S_{id}$.

Simulation details

We perform Metropolis MC simulations in the generalised canonical ensemble of hard ellipsoids ($k = 4, 6, 8$) confined to a plane with periodic boundary conditions and $N = 1024$ particles.\footnote{No significant system size effects were found for $N = 484$ or $N = 2048$.} We begin each simulation by first setting $k$, $\eta$ and $\Lambda$, where we choose a uniaxial
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Figure 3.1 – The effect of the Lagrange multiplier $\Lambda$ on $S_2$ for various $k = 4$. Lines are guides for the eye and data for $\eta$ other than the ones shown are omitted for clarity. Inset: snapshots of part of the $k = 4$ system showing increasing alignment as $\lambda$ is increased.

Form of $\Lambda$ as in Eq. (3.12). Each MC step consists of $N$ attempted moves, split randomly between translational and rotational moves. To avoid particle overlaps we use the simple and robust Perram-Wertheim criterion [119]. The magnitude of the attempted moves is such that the acceptance ratio is about 50%. Errors are estimated by block averages and are smaller than the symbol size unless indicated otherwise. The simulations are run until a stationary state is reached, followed by $5 \times 10^5$ steps for collecting averages. The results for our equilibrium simulations with $\Lambda = 0$ are comparable to previous, fairly extensive computational studies [115, 120].

Simulation results

We present the effect of Lagrange multiplier in Fig. 3.1. One can see that at equilibrium the system is in the isotropic phase, and that nematic ordering increases with increasing strength of $\Lambda$. However, the perfectly ordered state $S_2 = 1$ can only be approached asymptotically due to the divergence of the ideal orientational entropy (3.15). We also remark that the strength of $\Lambda$ required to impose a given ordering strength $S_2$, decreases with increasing $\eta$. This is to be expected since a higher $\eta$ brings the system closer to the critical surface coverage $\eta_c$, above which the nematic phase becomes the equilibrium state.

Empirical expression

Using thermodynamic integration (3.9) on our simulation data yields the total structural entropy $S_s$. We subtract $S_{id}$ to obtain the excess entropy $S_{ex}$, and propose a simple empirical
3.4. Entropy

$$S_{\text{excl}}(N, \eta, C) = N k_B B(\eta) \left[ B_2 \left( C : C - \frac{1}{2} \right) + B_3 \left( C : C - \frac{1}{2} \right)^2 \right],$$  \hspace{1cm} (3.16)

with

$$B(\eta) = \eta + B_1 \eta^2,$$  \hspace{1cm} (3.17)

with $B_1$, $B_2$ and $B_3$ fitting parameters. We use the terms $(C : C - 1/2)$ so that in the isotropic phase $S_{\text{excl}} = 0$. We find that for moderate elongation $k = 4$, the Onsager-like second virial approximation with $B(\eta) \sim \eta$ is insufficient, however, for the higher aspect ratios $k = 6$ and $8$, which are closer to the region of validity for Onsager theory, we find that $B(\eta) = \eta$ is sufficiently accurate, hence we set the fitting parameter $B_1 = 0$ for those aspect ratios. The fitting parameters are presented in Table 3.1 and we show the fits for $k = 4$ in Fig. 3.2. From the goodness-of-fits, we conclude that the decoupling between $\eta$ and $C$ in Eq. (3.16) is valid for the range of $\eta$ we study.

![Figure 3.2](image-url)  

Figure 3.2 – The excess entropy for $k = 4$ and selected $\eta$. Solid black lines are the fits of simulation data to Eq. (3.16).

Table 3.1 – Summary of the fitting parameters of Eq. (3.16). The specified intervals indicate 95% confidence bounds.

<table>
<thead>
<tr>
<th>Aspect ratio</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$</td>
<td>$2.107 \pm 0.056$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$B_2$</td>
<td>$1.308 \pm 0.020$</td>
<td>$3.791 \pm 0.023$</td>
<td>$4.625 \pm 0.065$</td>
</tr>
<tr>
<td>$B_3$</td>
<td>$0.700 \pm 0.023$</td>
<td>$2.437 \pm 0.061$</td>
<td>$2.850 \pm 0.026$</td>
</tr>
</tbody>
</table>
Validity of the entropy

We test the validity of the structural entropy $S_s$ by seeing how well it predicts the isotropic-nematic transition in the planar hard ellipsoid system as well as the ordering strength as a function of $\eta$. The equilibrium value of $S_2$ can be calculated by finding the value of $S_2$ that maximises $S_s$ for a given $\eta$. In other words we solve \((\partial S_s / \partial S_2)_{\eta} = 0\). The results are presented in Fig. 3.3, where we compare the equilibrium value of $S_2$ obtained by maximising $S_s$, with the value of $S_2$ obtained by equilibrium MC simulations. We emphasise that we only used simulation data in the range $\eta < \eta_c$ to obtain $S_s$, so the fact that we accurately predict the isotropic-nematic phase transition [120] and have excellent agreement in the range $\eta > \eta_c$, serves to validate our expression for $S_s$.

![Figure 3.3](image-url)  
Figure 3.3 – $S_2$ obtained from equilibrium MC simulations of the hard ellipsoid system. Solid black lines are the equilibrium ordering strengths calculated from our structural entropy $S_s$.

3.4.4 Total entropy functional

To summarise the results of this Section, we can write the total entropy functional as

$$S = \int s_{\text{c}}(\rho, u) + s_{\text{id}}(\eta, C) + s_{\text{ex}}(\eta, C) \, d^2 r,$$

(3.18)

where $s_{\text{c}}(\rho, u)$ is the entropy density of the interfacial fluid layer, $s_{\text{id}}(\eta, C)$ is the ideal orientational entropy density and $s_{\text{ex}}(\eta, C)$ is the excess entropy density due to the adsorbed particles.

---

\footnote{Note that \((\partial S_s / \partial S_2)_{\eta}\) results in a 6th order polynomial expression —the correct equilibrium value of $S_2$ for a given packing fraction $\eta$ is then the one root which is physically admissible $S_2 \in \mathbb{R}$ and $0 \leq S_2 \leq 1$, and further satisfies the second derivative test to ensure that it is a local minimum. Testing other roots in the physically admissible range using the second derivative test allows us to ensure that the equilibrium value is the global minimum.}
We write \( s_{id}(\eta, C) \) and \( s_{excl}(\eta, C) \) in terms of the order parameter \( S_2 \) as

\[
s_{id} = k_B n_p \left[ \frac{1}{2} \ln(1 - S_2) + \frac{1}{2} S_2 - \frac{3}{4} (S_2)^2 + \frac{1}{6} (S_2)^3 - \frac{1}{8} (S_2)^4 + \frac{1}{10} (S_2)^5 - \frac{1}{18} (S_2)^6 \right]
\]

(3.19)

\[
s_{excl} = k_B n_p \left( \eta + B_1 \eta^2 \right) \left[ B_2 (S_2)^2 + B_3 (S_2)^4 \right]
\]

(3.20)

where \( n_p = N/\ell^2 \) is the number density of particles on the interface. The functional derivative of \( S \) is then

\[
\frac{\delta S}{\delta x} = \begin{pmatrix} -\mu / T \\ 0 \\ 1 / T \\ \partial(s_{id} + s_{excl}) / \partial \eta \\ \partial(s_{id} + s_{excl}) / \partial C \end{pmatrix}
\]

(3.21)

where we identify the temperature of the interface \( T = (\partial s / \partial u)^{-1} \) and \( \mu \) is the chemical potential of the fluid interface layer. For completeness, the remaining partial derivatives in Eq. (3.21) are

\[
\frac{\partial(s_{id} + s_{excl})}{\partial \eta} = \frac{s_{id}}{A_p} + k_B n_p (2 + 3B_1 \eta) \left[ B_2 (S_2)^2 + B_3 (S_2)^4 \right],
\]

(3.22)

\[
\frac{\partial(s_{id} + s_{excl})}{\partial C} = k_B n_p \psi(\eta, S_2) \left( C - \frac{1}{2} \delta \right),
\]

(3.23)

where

\[
\psi(\eta, S_2) = \frac{2(S_2)^3 - 5(S_2)^4 + 6(S_2)^3 - 6(S_2)^2 + 12S_2 - 12}{3(1 - S_2)} + 4(\eta + B_1 \eta^2) \left( B_2 + 2B_3 (S_2)^2 \right).
\]

(3.24)

3.5 Friction matrix — surface viscosity

There are two dissipative processes that can occur in our model: viscous heating and rotational relaxation of the particles. We treat viscous heating first, followed by rotational relaxation. Friction matrix entries for other possible dissipative processes that we have neglected such as diffusion in the presence of gradients of the structural variables, or temperature are well-known and can be found in Refs. [41] and [80].

3.5.1 Surface viscosity

This entry in the friction matrix describes viscous heating of the interfacial fluid layer due to momentum dissipation. We can use the usual hydrodynamics entry for a viscous fluid
specialised to an interface [41]

\[
[A, B]_{\text{hydro}} = \int 2\varepsilon_s T \left( \frac{\partial}{\partial r_i} \delta A \frac{\delta A}{\delta M_j} - \hat{\gamma}_{ij} \frac{\delta A}{\delta u} \right) \left( \frac{\partial}{\partial r_j} \delta B \frac{\delta B}{\delta M_i} - \hat{\gamma}_{ij} \frac{\delta B}{\delta u} \right) d^2 r + \int \varepsilon_d T \left( \frac{\partial}{\partial r_i} \delta A \frac{\delta A}{\delta M_i} - \hat{\gamma}_{ii} \frac{\delta A}{\delta u} \right) \left( \frac{\partial}{\partial r_j} \delta B \frac{\delta B}{\delta M_j} - \hat{\gamma}_{jj} \frac{\delta B}{\delta u} \right) d^2 r, \tag{3.25}
\]

where \(\varepsilon_s\) is the surface shear viscosity, \(\varepsilon_d\) is the surface dilatational viscosity and \(\hat{\gamma} = \frac{1}{2}(\kappa + \kappa^T)\) is the symmetrised velocity gradient tensor, with \(\kappa = \partial \mathbf{v} / \partial \mathbf{r}\). A bar over a tensor e.g. \(\kappa\) indicates that we are only considering the traceless, symmetric part of that tensor. Note the presence of a dilatational viscosity, which occurs due to the fact that interface area is in general not conserved.

3.6 Friction matrix —rotational relaxation

How the particles relax to their equilibrium orientations is the subject of this Section. In structural rheological models, a relaxation term is typically assumed, based on the intuition of the researcher [80]. The simplest example would be a linear relaxation with constant relaxation time [42]. However, for the related case of polymer melts, Ref. [106] showed that \(M\) depends on the structural state variables. We therefore prefer an approach similar to Refs. [104, 106], where the friction matrix entries were either semi-analytically or numerically determined.

We first analytically derive the friction matrix for rotational relaxation by assuming that the orientation of individual particles undergo random (Brownian) motion. Event-driven MD (EDMD) [121] simulations are used to validate our analytic expression and provide the relaxation timescales. We use the following form of the Green-Kubo expression (2.12) to calculate the friction matrix entries corresponding to rotational relaxation

\[
M_{\mathbf{C}, \mathbf{C}} = \frac{I_s^2}{2k_B T_s} \langle \Delta \tau, \mathbf{C} \Delta \tau, \mathbf{C} \rangle_{\rho_A}, \tag{3.26}
\]

where \(\Delta \tau, \mathbf{C} = \mathbf{C}(\tau_s) - \mathbf{C}(0)\) is the incremental change of \(\mathbf{C}\) over the time \(\tau_s\). We note that the ensemble average in Eq. (3.26) should, in principle, be taken over an appropriate distribution function \((\rho_A)\) describing the out-of-equilibrium state, hence it may not necessarily be valid in all nonequilibrium situations where this distribution function does not exist. However, in this particular case, we benefit from the isotropic-nematic transition, giving us access to equilibrium states with non-zero ordering and we further benefit from the symmetry of \(\mathbf{C}\), which has only one tensorial invariant. Therefore flow does not lead to a different tensor structure (which would break the symmetry). These considerations are important for EDMD simulations, where we can access ordered states in equilibrium simulations \((\Lambda = 0)\).
3.6. Friction matrix — rotational relaxation

3.6.1 Analytic expression for rotational relaxation

The time $\tau_s$ is an intermediate timescale separating the slow from the fast dynamics. If we assume that $\tau_s$ is sufficiently small such that there is no systematic change of an ellipsoid orientation $u$ over the timescale $\tau_s$, then any changes of $u$ are due to noise, which we model with a stochastic differential equation in the Itô prescription \[122\]

$$u(\tau_s) - u(0) = -\frac{1}{2} B^2 \tau_s u(0) + B[\delta - uu(0)] \cdot \Delta W,$$  \hspace{1cm} (3.27)

where $B = \sqrt{2k_B T/\zeta}$ is the noise amplitude of the two-dimensional Wiener process with friction coefficient $\zeta$ and $\Delta W = W(\tau_s) - W(0)$ is a Wiener increment. Note that the stochastic dynamics of Eq. (3.27) preserves the normalisation $u^2 = 1$. We can actually neglect the first term on the right hand side of Eq. (3.27) since it only contributes second and higher order terms in $(\tau_s/\tau_{rot})$ in the correlation function of Eq. (3.26). The quantity $\Delta \tau_s C$ can thus be written

$$\Delta \tau_s C = B\left(\overline{uA} - \overline{Au}\right),$$  \hspace{1cm} (3.28)

where $\overline{X} = \sum_{i=1}^{N} X_i / N$ denotes the mean of $X$, terms of order $(\Delta W)^2$ have been neglected, and we have abbreviated $u := u(0)$ and $A = (\delta - uu) \cdot \Delta W$. Note the ordering of the tensor products and the contractions. Substitution of Eq. (3.28) into Eq. (3.26) yields the following

$$M_{C,C} = \frac{B^2}{2k_B \tau_s n_p} \langle uuA + Auu + A\overline{Au} + \overline{uAu}\rangle_{\phi},$$  \hspace{1cm} (3.29)

After some algebraic manipulations and noting that $\langle \Delta W \Delta W \rangle = \tau_s \delta$ along with the definition $C = uu$ we find that

$$(M_{C,C})_{ijkl} = \frac{1}{k_B n_p \tau_{rot}} (C_{ik}\delta_{jl} + C_{jk}\delta_{il} + C_{jl}\delta_{ik} + C_{il}\delta_{jk} - 4(C_4)_{ijkl}),$$  \hspace{1cm} (3.30)

where we identify the rotational timescale $\tau_{rot} = \zeta / (k_B T)$. The constraint of constant length leads to the presence of the fourth moment $C_4 = \langle uuuu \rangle$, which we can express exactly in terms of $C$, $\delta$, $S_2$ and $S_4 = \langle \cos 4\phi \rangle$, where $\phi$ is the angle between particle orientation vector and the director. The expression for $C_4$ is rather long and therefore presented in Appendix A.3.

The values of the individual components of $M_{C,C}$ can be matched to those of the tensor in Eq. (3.26) obtained numerically via dynamical simulations. There is then a single fitting parameter, the rotational timescale $\tau_{rot}$, allowing a relationship between $\tau_{rot}$ and $\eta$ to be established.

3.6.2 Remarks on the separating timescale

The existence of $\tau_s$ is crucial to obtaining a meaningful friction matrix from simulations, therefore a small discussion of the various rotational timescales in our model is appropriate.
Chapter 3. Modelling the rheology of anisotropic particles on interfaces

Thinking about the model when there is a solvent present, the rotational dynamics of the colloidal particles is due to both Brownian motion and collisions with other colloids, which introduces two timescales: an intrinsic time for the rotation of a single particle $\tau_\text{rot}$, and the average time between collisions $\tau_\text{coll}$. It is expected and verified by our computer simulations of hard ellipsoids confined to a plane that $\tau_\text{coll}$ decreases monotonically with $\eta$, see Figure 3.4. Note that in our simulations, time is measured in units of $\tilde{\tau} = \left(\frac{1}{2\pi}\right) \sqrt{\frac{I}{k_B T}}$, where $I$ is the moment of inertia of a particle. This follows from setting the temperature of the system to $k_B T = 1$, then equipartition determines the intrinsic units of time.

We consider that $\tau_\text{rot}$ is approximately constant for dilute systems because there are few collisions and changes of orientation are caused primarily by solvent thermal fluctuations. Then $\tau_\text{rot}$ should diverge when either the nematic phase or the close packing limit is approached since it becomes increasingly difficult for the ellipsoids to reorient due to caging effects.

In our EDMD simulations, the origin of the ‘noise’ is exclusively due to multiple collisions between the ellipsoids, like in the kinetic theory of gases. The validity of a thermodynamic description requires that there is a clear separation of timescales between the fast processes (‘noise’) and systematic changes of the state variables. Therefore we can only use Eq. (3.26) to construct $M$ when the two timescales $\tau_\text{rot}$ and $\tau_\text{coll}$ are sufficiently separated i.e. when $\tau_\text{rot} \gg \tau_\text{coll}$. This condition is only satisfied for high surface coverage when $\eta > \eta_c$ (c.f. Fig. 3.4).

![Figure 3.4](image)

Figure 3.4 – The average time between collisions $\tau_\text{coll}$ for $k = 4$ hard ellipsoids confined to a plane plotted against surface coverage $\eta$. The vertical dashed line indicates the approximate position of $\eta_c$, as determined by our earlier MC simulations.

3.6.3 Friction matrix for intermediate surface coverage

For intermediate values of $\eta$, we have $\tau_\text{coll} \approx \tau_\text{rot}$ hence there is no separating timescale $\tau_s$ and we cannot use Eq. (3.26) to obtain $M_{C,C}$. We note that previous studies of the force autocorrelation function of Brownian particles suggest choosing the separating timescale $\tau_s$ to be when the autocorrelation function crosses zero for the first time [123] or to fit the (time-dependent) friction to an exponential decay form, and associate the decay constant
3.6. Friction matrix — rotational relaxation

with the friction coefficient [124]. However, we try a different approach outlined below, which we find gives more reliable results for our case.

Begin by noting that the friction matrix must be an isotropic rank-4 tensor close to the equilibrium isotropic phase due to symmetry requirements. Take the isotropic limit of Eq. (3.30) to obtain

\[
\lim_{S_j S_l \to 0} \frac{1}{C - \delta} (M_C C)_{ijkl} = \frac{1}{2k_B n_p \tau_{rot}} (\delta_{jk} \delta_{il} + \delta_{ik} \delta_{jl} - \delta_{ij} \delta_{kl}).
\]  

(3.31)

Since, close to equilibrium the entropy gradient is a linear function of \( C \), and its irreversible dynamics is given by Eq. (3.31) contracted with the entropy gradient (3.21), we expect a time evolution equation with an exponential decay solution

\[
C(t) = C(0) e^{-t/\tau} + \frac{1}{2} \delta.
\]  

(3.32)

where \( 1/\tau = 4[B_2(\eta + B_1 \eta^2) - 1]/\tau_{rot} \) is the decay constant. To test this reasoning, we perform computer experiments, in which the initial state is out of equilibrium, and we watch how the components of \( C \) relax to their equilibrium values. To construct the initial configurations, Monte-Carlo simulations of \( N = 2025 \) ellipsoids in the generalised canonical ensemble are performed, where Lagrange multipliers are used to specify the average orientation (see Section 3.4.3). The initial states have surface coverages which have an isotropic equilibrium state \( \eta > \eta_c \), but are held in an nonequilibrium ordered state by the Lagrange multipliers. For each \( \eta \) we generate 150 independent initial configurations and use our EDMD code to observe the time series of \( C \) as the configurations equilibrate. An exponential decay fits our data rather well, from which we extract the time constant \( \tau_{rot} \) for various surface coverages, see Figure 3.5. Taking inspiration from the slowing down of dynamics observed as granular materials approach jamming [125], we fit the decay constant with a power law

\[
\tau_{rot} = \tau_{visc} (1 - \eta/\eta_J)^{-1},
\]  

(3.33)

where the fitting parameters are: \( \tau_{visc} = 4.80 \pm 0.40 \) and \( \eta_J = 0.70 \pm 0.04 \). The parameter \( \tau_{visc} \) is the rotational timescale of an ellipsoid in the limit of zero surface coverage and this could be determined experimentally by observing the motion of a single adsorbed particle. We propose that \( \eta_J \) is the maximal surface coverage that could be obtained by a random packing of ellipses, which is close to the value \( \sim 0.74 \) predicted by Donev et al. [126, 127]. However, this divergence of the relaxation time cannot be observed because the isotropic-nematic phase transition occurs at a surface coverage \( \eta_{in} \sim 0.65 \), before the system can become jammed.

\[\text{5Although ellipses can randomly pack up to a surface coverage } \eta \sim 0.74, \text{ the packing is not strictly jammed since the configuration is not rigid under shear transformations [126, 127].}\]
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Figure 3.5 – Time constant of Eq. (3.32) as a function of surface coverage. It is shown with a power law fit Eq. (3.33) that diverges as jamming is approached (solid black line). Inset: Relaxation of the \( C_{11} \) tensor component. Initially the system is put into a partially ordered state and we follow its evolution to the equilibrium isotropic state. The remaining independent off-diagonal tensor component \( C_{12} = C_{21} \) is initially set to zero and remains zero.

3.6.4 Friction matrix for high surface coverage

Now we discuss the case when there is a clear separation of timescales, at high surface coverage \( (\eta > \eta_c) \) when the relaxation of C is slow compared to the microscopic timescale. Then there exists a plateau region where the entries of \( M_{C,C} \) are approximately independent of \( \tau_s \). This region exists between the fast collision timescale and the slow time for rotation of a particle \( \tau_{coll} \ll \tau_s \ll \tau_{rot} \).

We perform equilibrium EDMD simulations of the hard ellipsoids for various surface coverages in order to calculate the friction matrix entry using the Green-Kubo type formula of Eq. (3.26). Note that it is necessary to average over many independent trajectories in order to calculate the correlation function in Eq. (3.26) sufficiently accurately. Some examples of \( M_{C,C} \) extracted from simulations are shown in Figure 3.6, where a plateau region is clearly visible. We can therefore extract a value for each tensor component of \( M_{rot} \) by taking its mean value in the range \( \tau_s / \bar{\tau} \in [20, 50] \). Comparison of this with the analytic expression for \( M_{C,C} \) yields the rotational timescale \( \tau_{rot} \). We take the simulation values for \( S_2, S_4, C, C_4 \) to use in the analytic expression Eq. (3.30). Importantly, the tensor structure of \( M_{C,C} \) in Eq. (3.30) is confirmed by our simulations.

The rotational timescale as a function of the surface coverage for the nematic phase can once again be nicely fitted using a power law \( \tau_{rot} = \tau_{nem}(1 - \eta / \eta_{max})^{-\nu} \) with a dynamical critical exponent \( \nu = 4.88 \pm 0.02 \) and intrinsic timescale \( \tau_{nem} = (1.11 \pm 0.20) \times 10^2 \bar{\tau} \). The fit diverges at a significantly higher surface coverage \( \eta_{max} = \pi / \sqrt{12} \). This is the maximum possible surface coverage [128], where the ellipses are arranged regularly on a triangular lattice.
3.6. Friction matrix —rotational relaxation

Figure 3.6 – Typical form of the $(M_{C,C})_{1111}$ matrix entry calculated using Eq. (3.26) for $\eta = 0.70$ (solid red line) and for $\eta = 0.74$ (solid blue line). The dotted lines correspond to the unintegrated form of Eq. (3.26), namely Eq. (2.11). The correlation functions used to calculate these results were obtained with a moving window over a time series $0 < t/\tilde{\tau} < 200$ with timestep $dt = 0.001$ and then further averaged over 20 independent initial configurations.

The additional parameter $\tau_{\text{nem}}$ is significantly greater than the viscous rotational time $\tau_{\text{visc}}$ because in the nematic phase, rotation of a single particle requires a collective rotation of all of its neighbours. The parameter $\tau_{\text{nem}}$ should also be considered system-dependent, to be estimated by experiment. In our EDMD simulations of the quasi two-dimensional hard ellipsoid fluid, we find that $\tau_{\text{nem}}$ is approximately two orders of magnitude greater than the rotational timescale of a free ellipsoid $\tau_{\text{visc}}$.

However, a limitation of our model is that it is unlikely to accurately model interfaces with extremely high surface coverages due to the increasing possibility of ellipsoidal particles with orientations pointing out of the interface [62] as well as it being outside the range of validity of the excess orientational entropy (3.16). Finally, there is a region around the isotropic-nematic phase transition where neither method presented above produces satisfactory results for the timescale $\tau_{\text{rot}}$ due to large critical fluctuations near the transition.

We note that in comparison to Section 3.6.3, where we had to run the simulation over a timespan longer than the longest timescale in the system in order to extract $\tau_{\text{rot}}$, in this Section we see that exploiting thermodynamics results in computational efficiencies of several orders of magnitude. This is thanks to the fact that we need only simulate up to the intermediate timescale $\tau_s$, which satisfies $\tau_s \ll \tau_{\text{rot}}$, especially for high surface coverages, when collective rearrangements are slow. To summarise, the friction matrix entry for rotational relaxation is Eq. (3.30) with rotational timescale $\tau_{\text{rot}}(\eta)$ given by

$$
\tau_{\text{rot}}(\eta) = \begin{cases} 
\tau_{\text{visc}}(1 - \eta/\eta_j)^{-1}, & \text{for } \eta \leq 0.6 \\
\tau_{\text{nem}}(1 - \eta/\eta_{\text{max}})^{-\nu}, & \text{for } \eta \geq 0.7 
\end{cases}
$$

(3.34)
where the fitting parameters $\eta_J$ and $\eta_{\text{max}}$ should only depend on the particle geometries, and we expect the characteristic times $\tau_{\text{visc}}$ and $\tau_{\text{nem}}$ to be accessible experimentally or in simulations containing both particles and solvent. The fit of $\tau_{\text{rot}}(\eta)$ to our simulation data is shown in Fig. 3.7.

![Figure 3.7 – Results for the rotational timescale $\tau_{\text{rot}}$ for the isotropic and nematic phases. The blue line (red line) is the power law fit in the isotropic (nematic) phase according to Eq. (4.1). The approximate packing fraction where the isotropic-nematic transition takes place is indicated by the dashed black line. Note the use of a logarithmic scale on the $y$-axis showing the significant increase of $\tau_{\text{rot}}$ across the isotropic-nematic transition.](image_url)

3.7 Assembling the building blocks

We first apply the degeneracy condition $\{A, S\} = 0$ using our expressions for the total entropy and Poisson bracket in order to obtain the entropic contribution to the surface stress. We then put all four building blocks together according to the GENERIC equation to obtain the complete, closed set of time evolution equations describing the rheology of our toy model.

3.7.1 Surface stresses

The total surface stress is the sum of entropic contributions to the stress and viscous terms. The form of the entropic contribution to the stress $s$ is precisely specified by applying the degeneracy condition to the Poisson bracket and total entropy of Eqs. (3.4) and (3.18), giving

$$s = T \left[ \left( s - \rho \frac{\partial s}{\partial \rho} - u \frac{\partial s}{\partial u} - \eta \frac{\partial s}{\partial \eta} \right) \delta + 2 C : \frac{\partial s}{\partial C} - 2 \left( C : \frac{\partial s}{\partial C} \right) C \right]. \quad (3.35)$$

This expression for the stress can be identified with the expression for the stress in Ref. [111]. We are further able to identify the surface tension of the interfacial fluid layer $\sigma$ as

$$\sigma = u - Ts - \rho \mu, \quad (3.36)$$
3.7. Assembling the building blocks

with the contribution to the surface stress due to the structural variables given by

$$\Theta = T \left[ 2C : \frac{\partial s}{\partial C} - 2 \left( C : \frac{\partial s}{\partial C} \right) C + \eta \frac{\partial s}{\partial \eta} \delta \right]. \quad (3.37)$$

The viscous stress originates from momentum diffusion in the interfacial fluid layer described by the friction matrix entry in Eq. (3.25). We write

$$s_v = (\varepsilon_d - \varepsilon_s) \left( \frac{\partial}{\partial r} \cdot v \right) \delta + 2 \varepsilon_s \dot{\gamma}. \quad (3.38)$$

The viscous stress \( s_v \) essentially describes a two-dimensional Newtonian fluid—the linear Boussinesq model [39, 40]. The total stress \( s_{\text{tot}} \) can then be written

$$s_{\text{tot}} = - \sigma \delta + \Theta + (\varepsilon_d - \varepsilon_s) \left( \frac{\partial}{\partial r} \cdot v \right) \delta + 2 \varepsilon_s \dot{\gamma}. \quad (3.39)$$

Note that there is no energetic contribution to the total stress in our model because the particles only have excluded volume interactions. If there were other particle-particle interactions, these would be represented by a configurational internal energy density \( u_c(\eta, C) \) term in the energy functional Eq. (3.2) and an additional energetic contribution to the stress due to the structural variables, determined by the degeneracy condition stated in Eq. (2.6) [80].

3.7.2 Set of evolution equations

We put the building blocks obtained in the previous Sections 3.3, 3.4, 3.5 and 3.6 together using the GENERIC equation (2.1) to obtain the following complete set of time evolution equations describing the rheology of our toy model

$$\dot{\rho} = - \frac{\partial}{\partial r} \cdot (\rho v) \quad (3.40)$$

$$\dot{M} = - \frac{\partial}{\partial r} \cdot (v M) - \frac{\partial}{\partial r} \cdot s_{\text{tot}} \quad (3.41)$$

$$\dot{u} = - \frac{\partial}{\partial r} \cdot (u v) - s : \kappa^T + 2 \varepsilon_s \dot{\gamma} \dot{\gamma} + \varepsilon_d (\text{tr} \dot{\gamma})^2 \quad (3.42)$$

$$\dot{\eta} = - \frac{\partial}{\partial r} \cdot (\eta v) \quad (3.43)$$

$$\dot{C} = \kappa \cdot C + C \cdot \kappa^T - v \cdot \frac{\partial C}{\partial r} - 2C : \kappa^T C - \frac{1}{\tau_{\text{eff}}(\eta, C)} \left( C - \frac{1}{2} \delta \right) \quad (3.44)$$

where Eq. (3.40) is a statement of mass conservation, Eq. (3.41) contains the momentum balance terms, Eq. (3.42) is the energy balance equation and has the usual convection term and two source terms due to stress and viscous heating. Eq. (3.43) simply conserves the surface coverage \( \eta \). Eq. (3.44) describes an upper-convected \( C \), with the fourth term on the right hand side required to keep the trace of \( C \) constant (see Eq. (3.4)). For our model, \( C \) relaxes with
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effective time constant

\[
\frac{1}{\tau_{\text{eff}}(\eta, C)} = \psi(\eta, S_2)(S_4 - 1) \frac{1}{\tau_{\text{rot}}}.
\] (3.45)

An interesting consequence of such an expression for the effective time constant is that rotational relaxation is hindered both by ordering from the factor \(\psi(\eta, S_2)(S_4 - 1)\) as well as the caging effect of neighbouring particles intrinsic to the rotational timescale \(\tau_{\text{rot}}\). Recall that \(\psi(\eta, S_2)\) is given in Eq. (3.24). The remarkable occurrence of only a linear in \((C - \frac{1}{2} I)\) relaxation term in Eq. (3.44) is due to the two-dimensional nature of our system, where the tensor \(C\) only has a single tensorial invariant. However, the effective time constant \(\tau_{\text{eff}}\) is of course nonlinear in \(S_2\) and \(\eta\).

In comparison with an earlier model [42] we have corrected the upper convected behaviour of the tensor variable \(C\) so that the trace is preserved. This leads to a modification of the anisotropic part of the surface stress Eq. (3.37). Furthermore, our macroscopic, rheological model is formulated by a systematic coarse-graining of the microscopic model, which vastly improves the description of the dissipative processes. We also demonstrate the advantage of exploiting thermodynamics to efficiently bridge timescales when we are able to extract the long rotational timescale from short time dynamic simulations.

The rheology of an interface with adsorbed anisotropic particles interacting via excluded volume can now be systematically studied by solving the set of Eqs. (3.40)–(3.44) under various flow conditions, which is the subject of the next chapter.
We study the rheology of particle-laden interfaces in light of our model, Eqs. (3.40)–(3.44). In particular, we can solve the set of equations for experimentally relevant flow fields (namely shear and dilatational) and investigate the interplay between flow, structure and rheological response. It is worthwhile to emphasise that although we begin with a highly idealised microscopic model, the physical processes and constitutive equations described in our model can be considered general to complex fluid interfaces where the adsorbed components are anisotropic and can be macroscopically described with an orientation tensor.

As already discussed in the Introduction, models describing interfacial rheology from a structural point of view are severely lacking despite them being essential for the proper interpretation of nonlinear rheological data. To our knowledge, the only two examples are the work of Sagis [42] for anisotropic particles and Kralchevsky et al. [129] for crystalline monolayers formed by spherical particles. Although the work of Lishchuk [130, 131, 132] is also notable and takes a different approach by considering how particles adsorbed at the interface increase viscous dissipation in the bulk phases and thus leads to a modification of the surface shear and dilatational viscosities.

Interfacial rheology experiments typically determine shear and/or dilatational moduli by imposing an oscillatory flow and analysing the stress response [79], which is mostly interpreted in terms of a Kelvin-Voigt, Boussinesq or Maxwell model [31]. Up to now, there are not so many experiments that simultaneously study interfacial rheology and surface structure. Most relevant to us are the seminal experiments on the rheological properties of PS ellipsoid monolayers [37, 35] and on hematite ellipsoids [133]. Also worth mentioning are the studies of semi-flexible β-lactoglobulin fibrils adsorbed to an interface, which similarly to our hard ellipsoid system, also undergo an isotropic-nematic phase transition [134, 135].

For numerically solving our model equations, we must specify the model parameters. We choose the following: ellipsoid semi-minor axis length \( b = 0.025 \mu m \), semi-major axis length \( a = 0.1 \mu m \), temperature \( T = 293 K \), rotational timescales \( \tau_{\text{visc}} = 1 s \) and \( \tau_{\text{nem}} = 10^2 s \), shear viscosity \( \eta_s = 10^{-8} \text{ Pams} \) corresponding to a water-air interface [136], and we assume that
$\varepsilon_d = \varepsilon_s$. The choice of particle geometry corresponds to a particle number density of around $n_p \sim 10^{14} \text{ m}^{-2}$ for $\eta = 0.5$.

For dilatational flow, where the surface coverage can vary through the isotropic-nematic phase transition, we need a way to smoothly vary between the two regions. A simple method consists of extending the expressions for $\tau_{\text{rot}}(\eta)$ into the transition region and finding the intercept $\eta_i$. We can then write

$$\tau_{\text{rot}}(\eta) = \begin{cases} 
\tau_{\text{visc}}(1 - \eta/\eta_i)^{-1}, & \text{for } \eta < \eta_i \\
\tau_{\text{nem}}(1 - \eta/\eta_{\text{max}})^{-\nu}, & \text{for } \eta \geq \eta_i 
\end{cases} \quad (4.1)$$

We use the fitting parameters $\eta_i = 0.7, \eta_{\text{max}} = \pi/\sqrt{12}, \nu = 4.88$ as given in Sections 3.6.3 and 3.6.4.

In the following, we use the inbuilt MATLAB (Version 8.3, ode15) solver to numerically solve the set of differential equations. Initial conditions are always the equilibrium state for the initially assigned surface coverage. Results in this chapter are based on the author’s work in Ref. [43].

Remarks on nonlinear rheology

Nonlinear rheology is a hallmark of systems where an imposed flow leads to structural changes. This leads to some subtleties in the analysis methods. For a sinusoidal imposed strain $\sim \sin(\omega t)$, where $\omega$ is the angular frequency, the nonlinear stress response can be expanded

$$s_{\text{tot}}(t) = \tilde{s}_1 e^{i\omega t} + \tilde{s}_2 e^{2i\omega t} + \tilde{s}_3 e^{3i\omega t} + ..., \quad (4.2)$$

where the $\tilde{s}_1, \tilde{s}_2, \tilde{s}_3$ are the amplitudes of the harmonic components of the stress response. When a system is time-reversible so that $s_{\text{tot}}(t) = s_{\text{tot}}(-t)$, the even harmonics must disappear. The loss and storage moduli are calculated from the magnitude $|\tilde{s}_1|$ and phase lag $\delta$ of the first harmonic and neglect information contained in the higher harmonics. For highly nonlinear systems these moduli therefore do not fully characterise the rheology, but rather provide the leading order response.

A useful tool for analysis of oscillatory data is the Lissajous plot, which plots the time-dependent stress against strain. Any nonlinear behaviour e.g. shear softening or hardening is immediately apparent [138].

\footnote{Any figures drawn from Ref. [43] are used with permission.}
4.1 Linear rheological behaviour

We begin by examining the linear viscoelastic behaviour of our model for a general flow. The velocity gradient tensor can be written as \( \kappa = \kappa_0 e^{i \omega t} \), where \( \omega \) is the angular frequency of the oscillating flow. The response of the orientation tensor is then \( C = C_0 + \delta C e^{i \omega t} \), where \( C_0 \) is the orientation tensor at equilibrium and \( \delta C \) is a perturbation. Let us assume an intermediate value of \( \eta < \eta_c \) so that the equilibrium state is isotropic \( C_0 = \delta / 2 \). Substitution of these two expressions into Eq. (3.44) and neglecting second and higher order terms gives

\[
\delta C = \frac{1}{i \omega + 1/\tau} S = \delta C' - i \delta C'',
\]

where we recall \( \tau \) is the rotational relaxation timescale in the limit of zero ordering and \( S \) is the two-dimensional deviatoric rate-of-deformation tensor

\[
S = \frac{1}{2} [\kappa_0 + \kappa_0^T - \text{tr}(\kappa_0^T)]\delta.
\]

The corresponding stress response is

\[
\Theta = -2 k_B T n_p \psi(\eta, S_2 \to 0)[\delta C' \cos(\omega t) + \delta C'' \sin(\omega t)],
\]

which is simply the Maxwell model of linear viscoelasticity with an effective number density \( -n_p \psi(\eta, S_2 \to 0) \) (note that the function \( \psi(\eta, S_2) \) is negative for \( \eta < \eta_c \) and our above analysis is only valid for this range of surface coverages).

4.2 Start-up and steady shear flow

We first specialise Eq. (3.44) to the case of steady shear in the \( x \)-direction, where the only nonzero entry in the velocity gradient tensor is \( (\kappa)_{xy} = \dot{\gamma} \) with \( \dot{\gamma} \) the shear rate. The set of equations we numerically solve reads

\[
\dot{C}_{xx} = 2 \dot{\gamma} C_{xy} (1 - C_{xx}) - \frac{1}{\tau_{eff}}(C_{xx} - \frac{1}{2}),
\]

\[
\dot{C}_{xy} = \dot{\gamma} (1 - C_{xx} - 2 C_{xx}^2) - \frac{1}{\tau_{eff}} C_{xy},
\]

where due to the properties of \( C \), we also have that \( C_{yx} = C_{xy} \) and \( C_{yy} = 1 - C_{xx} \). The shear component of the total surface stress is

\[
(s_{tot})_{xy} = \varepsilon_s \dot{\gamma} - 4 n_p k_B T \psi(\eta, S_2) C_{xy} (C_{xx} - C_{xx}^2 - C_{xy}^2).
\]

We present numerical results for start-up of simple shear for a range of shear rates in Figure 4.1. For the higher dimensionless shear rates \( \dot{\gamma} \tau_{visc} \gtrsim 1 \) we observe mild stress overshoots. Unlike the model presented in Ref. [42], our properly convected structural tensor variable is well-behaved, even for large dimensionless shear rates \( \dot{\gamma} \tau_{visc} \). Note that our use of the trace-
preserving closure in Eq. (3.4) precludes any tumbling behaviour of the director in the steady state [139, 140]. The behaviour of the ordering strength $S_2$ can be interpreted as a competition between the tendency of the particles to align with the flow, and the tendency to relax to their equilibrium state, given by the maximum of the entropy $s_{id} + s_{excl}$.

Figure 4.1 – Startup simple shear for different dimensionless shear rates $\gamma \tau \nu_{visc}$, effect on ordering and shear stress. The surface coverage is $\eta = 0.5$.

Figure 4.2 – Upper panels: Steady-state simple shear solutions for the ordering strength (filled lines) and director angle with respect to the $x$-axis $\phi_d$ (dashed lines). Lower panels: Steady-state shear stress. All quantities are plotted as a function of dimensionless shear rate $\gamma \tau \nu_{visc}$.

Flow curves calculated from steady state solutions of Eqs. (4.5) are shown in Figure 4.2. Increasing the shear rate results in increased ordering, and the director aligns more closely with the flow direction. From the total surface stress, we can define the effective surface shear viscosity, which takes into account the effect of adsorbed particles as $\epsilon_{\text{eff}}^{xy} = (s_{\text{tot}, xy}) \dot{\gamma}$. We show the effective surface shear viscosity as a function of shear rate for a range of $\eta$ in Figure 4.3.
There is a Newtonian regime at low shear rates, when the flow is not sufficiently strong to cause significant changes in the alignment. Shear-thinning is behaviour typical of liquid crystals [107] and also observed in our model (cf. Figure 4.3) for all surface coverages and is caused by ordering and the alignment of particles with the flow direction. In the limit of high shear rates, when the particles are perfectly ordered in the $x$-direction, they pose no further resistance to flow and we recover the viscosity of the bare interface.

When the surface coverage is sufficiently high i.e. $\eta > \eta_{\text{in}}$, we observe a mechanically unstable regime in the flow curves where the shear stress decreases with shear rate (see lower right panel of Figure 4.2), which indicates shear banding behaviour. This behaviour is fairly widespread in complex fluids [141] and has been studied in various theoretical models of liquid crystal dynamics, which are similar to ours, see the review by Olmsted [142] and references therein. Typically, shear banding is attributed to strong shear-thinning caused by a large increase in alignment with a moderate increase in shear rate. Our model would appear to support this explanation; the unstable area of the flow curve is precisely where shear-thinning is particularly pronounced. Although, detailed numerical studies of various nematodynamic models including hydrodynamics [143] indicate that shear banding is actually a rather delicate matter with a dynamic layering of time-dependent states.

We note that the other components of the stress tensor are non-zero, meaning that our model predicts a non-zero normal stress difference for steady in-plane shear of rigid anisotropic particles

$$\sigma_{\text{tot}}^{xx} - \sigma_{\text{tot}}^{yy} = 4 k_B T \psi(\eta, S_2) (1 - 2 C_{xx})(C_{xx}^2 + C_{xy}^2 - C_{xx}),$$

which vanishes when the system is in equilibrium thanks to the factor $\psi(\eta, S_2)$. Note that this normal stress difference is in-plane and perpendicular to the direction of shear rather than out of plane.

Figure 4.3 – The effective viscosity $\epsilon_{\text{eff}}^{s}$ plotted as a function of dimensionless shear rate $\dot{\gamma} r_{\text{visc}}$ for various surface coverages showing shear thinning behaviour.
Chapter 4. Rheology of anisotropic particles on interfaces

4.3 Oscillatory shear flow

Oscillatory simple shear has \( \kappa_{xy} = \dot{\gamma} \) as the flow profile, with a time-dependent shear rate \( \dot{\gamma}(t) = \gamma_0 \omega \cos(\omega t) \), where \( \omega \) is the angular frequency and \( \gamma_0 \) is the maximum shear strain. The shear strain is defined as \( \gamma = \gamma_0 \sin(\omega t) \). Again, surface area is conserved so that \( \eta = 0 \). The set of equations is the same as Eqs. (4.5) and (4.6) but with a time dependent shear rate. In this case, the parameter space is increased to include the amplitude of shear \( \gamma_0 \), and angular frequency \( \omega \).

There are typically three regimes related to the competition between shear-induced ordering and relaxation. The characteristic flow timescale is \( \tau_{\text{flow}} \sim 2\pi/\omega \), while the effective rotational relaxation time is \( \tau_{\text{eff}} \). In the case where relaxation happens faster than shear-induced ordering, we expect mostly viscous behaviour and weak flow alignment. In the opposite case where shear-induced ordering dominates, we expect greater flow-alignment and a mostly elastic response caused by rapidly changing the alignment. These responses are apparent in the upper and lower panels of Fig. 4.4, where we present results for \( \eta = 0.5 \) — a surface coverage with an isotropic equilibrium state. More interesting behaviour is seen when both timescales are similar in value (middle panel of Fig. 4.4), where the contribution from the surface structure begins to be seen in the form of mild shear-thinning.

In Fig. 4.5, we increase the surface coverage to \( \eta = 0.75 \) (nematic at equilibrium). A higher surface coverage leads to markedly different behaviour. Rather than shear-thinning we observe shear-thickening as the shear amplitude is increased. We interpret this as being due to the fact that director is never in the optimal orientation with respect to the flow when the flow suddenly reverses. Note that \( \tau_{\text{flow}} \sim \tau_{\text{eff}} \) for the upper panels of Fig. 4.5, \( \tau_{\text{flow}} < \tau_{\text{eff}} \) for the middle panels and \( \tau_{\text{flow}} \ll \tau_{\text{eff}} \) for the bottom panels. The rheology for high surface coverage is dominated by reorientation of the already-ordered particles rather than shear-induced ordering.

We also present results for the dynamic surface shear moduli \( G' = (\langle \dot{s}_1 \rangle_{xy}/\gamma_0) \cos \delta \) and \( G'' = (\langle \dot{s}_1 \rangle_{xy}/\gamma_0) \sin \delta \). The storage modulus \( G' \) is associated with elasticity, while the loss modulus \( G'' \) is associated with viscous dissipation. The top panel of Figure 4.6 shows dynamic moduli for an inverse frequency \( \tau_{\text{flow}} \gg \tau_{\text{eff}} \). The bottom panel contains shear amplitude sweeps in the case where \( \tau_{\text{flow}} \sim \tau_{\text{eff}} \). Here, we observe a greater range of behaviours for the different surface coverages. The lowest surface coverage \( \eta = 0.4 \), exhibits dominant viscous behaviour, while increasing the surface coverage to \( \eta = 0.5 \) leads to a more elastic interface for lower shear amplitudes. As the surface coverage is increased further to \( \eta = 0.6 \), the loss modulus shows non-monotonic behaviour, that is qualitatively similar to the dynamic moduli obtained experimentally with a monolayer of ellipsoids with \( k \sim 4.6 \) [37].

The zero-shear limit of the dynamic moduli \( G'_0, G''_0 \) for a range of surface coverages and both frequencies is presented in Figure 4.7. The storage moduli is found to increase with surface coverage and we find power law behaviour for dilute surface coverages. The storage moduli peak just before \( \eta_c \) and drop to zero at the isotropic-nematic transition. The contribution
4.3. Oscillatory shear flow

Figure 4.4 – Lissajous plots of the ordering strength and shear stress for an oscillating shear flow with $\gamma_0 = 0.1, 0.2, 0.3, 0.4$, blue, red, orange and purple lines respectively. Top panel: $\omega = 0.01 \times 2\pi$ rad s$^{-1}$. Middle panel: $\omega = 0.2 \times 2\pi$ rad s$^{-1}$. Bottom panel: $\omega = 0.5 \times 2\pi$ rad s$^{-1}$. The surface coverage is $\eta = 0.5$.

Figure 4.5 – Lissajous plots of the ordering strength and shear stress for an oscillating shear flow with $\gamma_0 = 0.1, 0.2, 0.3, 0.4$, blue, red, orange and purple lines respectively. Top panel: $\omega = 0.01 \times 2\pi$ rad s$^{-1}$. Middle panel: $\omega = 0.05 \times 2\pi$ rad s$^{-1}$. The surface coverage is $\eta = 0.75$.
to the interface elasticity comes from flow-induced ordering effects, which are very weak in the nematic phase $\eta > \eta_c$, when the particles are already ordered at equilibrium. For $\eta > \eta_c$, we would therefore expect to see a loss modulus (in the limit $\gamma_0 \to 0$), which only has a contribution from the surface shear viscosity of the bare interface.

Figure 4.6 – Dynamic shear moduli plotted against shear amplitude. Left panel: $\omega = 0.01 \times 2\pi$ rad/s. Right panel: $\omega = 0.1 \times 2\pi$ rad/s.

Figure 4.7 – Zero-shear amplitude limit of the dynamic shear moduli $G'_0$, $G''_0$ plotted as a function of $\eta$ for $\omega = 0.01 \times 2\pi$ rad/s and $\omega = 0.1 \times 2\pi$ rad/s. The vertical dashed line indicates $\eta_c$. Note that the zero-shear limit of the dynamic dilational moduli $E'_0$, $E''_0$ are equivalent to $G'_0$, $G''_0$ [31].

### 4.4 Oscillatory dilatational flow

We now model the flow in a Langmuir-Blodgett trough. In this experimental technique, barriers oscillate along a single direction with angular frequency $\omega$, causing the surface area $A$ of the interface to vary in time, i.e. $A(t) = A_0[1 + \Gamma_0 \sin(\omega t)]$, where $A_0$ is the initial surface area and $\Gamma_0$ is the amplitude of deformation, measured as a fraction of $A_0$. The velocity gradient of such a flow field is therefore given by $(\kappa)_{xx} = \Gamma_0 \omega \cos(\omega t) / [1 + \Gamma_0 \sin(\omega t)]$, with the other components equal to zero. We define the strain as $\Delta A / A_0 = A(t) / A_0 - 1$. Since we assume the particles are irreversibly adsorbed on the interface, the surface coverage is time-dependent.
and varies as
\[ \eta(t) = \frac{\eta(0)}{1 + \Gamma_0 \sin(\omega t)}. \] (4.8)

Note also that the number density of adsorbed particles \( n_p \) (used in the entropy densities \( s_{id} \), \( s_{excl} \)) is also time-dependent. For dilatational flow, the relevant set of equations of motion to solve are
\[
\dot{C}_{xx} = 2(\kappa)_{xx} C_{xx}(1 - C_{xx}) - \frac{1}{\tau_{eff}} (C_{xx} - \frac{1}{2}), \quad (4.9a)
\]
\[
\dot{C}_{xy} = (\kappa)_{xx} C_{xy}(1 - 2C_{xx}) - \frac{1}{\tau_{eff}} C_{xy}. \quad (4.9b)
\]

If we take an isotropic state as the initial condition, Eq. (4.9b) is identical to zero and we are left with a single equation to solve for \( C_{xx} \). Note, however, that this is still a highly nonlinear equation due to the dependence of \( \tau_{eff} \) on both \( \eta \) and \( S_2 \).

In Figure 4.8 we show the time response of the \( xx \)-component of the surface stress to an oscillatory dilatational strain. Insets show the structure of the particles at the indicated positions. Increasing the strain amplitude \( \Gamma_0 \) results in the presence of higher harmonics in the stress response, which is manifested by an increasing deviation from purely sinusoidal behaviour — the hallmark of nonlinear rheology. We also find even harmonics in the stress response (see Fig. 4.10), which have been observed experimentally [144, 145] and are indicative of an asymmetry between extension and compression when time-reversibility is invalid [79, 146].

The corresponding Lissajous plots for the orientation tensor component \( (C)_{yy} \), ordering strength \( S_2 \) and \( xx \)-component of the surface extra stress are displayed in Figure 4.9. As expected, in compression (when the strain is negative), the particles tend to align in the \( y \)-direction, while in extension (when the strain is positive), the particles tend to align in the \( x \)-direction, although this alignment is far weaker. For small strain amplitudes (see \( \Gamma_0 = 0.02 \) in Figure 4.9), the effective relaxation time \( \tau_{eff} \) changes only a little so the flow-induced ordering is approximately symmetric in the compression and extension phases. Therefore the Lissajous plot of the stress shows no nonlinear behaviour. Upon increasing the strain amplitude, the surface coverage increases in the compression phase, with a corresponding increase in \( \tau_{eff} \). Relaxation occurs more slowly here than in the extension phase. This effect is reflected in the increased ordering in the compression phase compared with the extension phase. As a consequence of the ordering and increased surface coverage, the stress in the compression phase is significantly greater than in the extension phase. Increasing the strain amplitude even further, we find a sudden and significant resistance to compression due to the particles approaching a jammed state. The behaviour seen in our macroscopic rheological model for
dilatational flow illustrate the importance of a rotational relaxation time and entropy that varies in the correct way with \( \eta \) and \( S_2 \). The dynamic surface dilatational storage and loss

\[
\eta_0 = 0.5 \quad \text{and} \quad \omega = 0.1 \times 2\pi \text{ rad/s}.
\]

Insets: particle configurations at the positions indicated by the arrows. At high compression, the ellipsoids align preferentially along the \( y \)-axis. There is very little ordering when expanded.

Figure 4.9 – Lissajous plots corresponding to the data in Fig. 4.8. Left panel: \( C_{yy} \) (upper plots) and \( S_2 \) (lower plots). These show how the structure varies with strain. Right panel: stress response to dilatational flow. Nonlinearity and asymmetry increases with the amplitude of deformation.

moduli \( E' \) and \( E'' \) for the same numerical parameters as above are shown in Figure 4.11. Similarly to the dynamic shear moduli, \( E' \) and \( E'' \) are defined as \( E' = ((\hat{s}_1)_{xx}/\Gamma_0) \cos \delta \) and \( E'' = ((\hat{s}_1)_{xx}/\Gamma_0) \sin \delta \). For small strain amplitudes the interface is mostly viscous, however, elastic behaviour dominates when the particles in the interface approach a high surface coverage in the compression part of the flow. The compression also leads to a rapid increase of
4.5 Remarks

Despite the simplicity of our underlying microscopic toy model, we still find a rich variety of rheological behaviour. We emphasise that since we have complete information on the surface structure thanks to the closed set of time evolution equations for the macroscopic state variables (Eqs. (3.40)–(3.44)), we are able to interpret nonlinearities and asymmetries in the stress response by referring to changes in the surface structure.

The macroscopic constitutive equations formulated with the aid of nonequilibrium thermodynamics, clearly establish the important relationships between surface structure and various...
timescales in different flow conditions. Accurately modelling these relationships is shown to be crucial to understanding the interfacial rheology of particle-stabilised fluid interfaces and reproducing the rich variety of behaviours seen in experiments.

We do however, note that the magnitude of our stress responses are significantly lower than the typical values reported in experiments on ellipsoidal particles $[37, 35, 133]$, which we assume are primarily due to the limitations of our microscopic toy model and possibly the choice of numerical parameters. Despite this, the physical processes described by our model should still prove useful for the interpretation of experimental data where the rheology is dominated by flow-induced ordering transitions and realignment timescales of anisotropic particles. Furthermore, what we have done is to provide a general approach for developing constitutive equations and more realistic microscopic models can be readily treated using the general approach outlined in Chapter 3.
Capillary interactions and structure

Particles on interfaces can cause the interface to deform from its flat, undisturbed state. How these deformations interact then give rise to effective interactions between the particles, which cause the particles to self-assemble into many varied and interesting structures. These surface structures, as we have seen in the previous chapters, are fundamental to the rheological behaviour of the interface.

As a natural continuation from our work on hard ellipsoids, we now allow the contact angle $\theta$ to vary from 90°. Therefore, we only consider geometry and wetting properties (described through $\theta$). For electrically neutral colloidal-sized particles that are of interest in Pickering emulsions, the dominant capillary interaction is indeed expected to be shape-induced [147].

In this chapter we briefly review the scientific achievements in literature associated with capillary interactions and present the theoretical considerations. We use Surface Evolver to numerically solve for the interface profile of two and three particles configurations and hence obtain the interaction energies for these various configurations. We are therefore able to investigate the validity of using pair potentials to describe what is, in principle, a multibody interaction. Fortunately, we find that the superposition approximation is reasonable and we are able to develop an empirical pair potential, which fits nicely for a range of particle geometries and wetting behaviours. We then use this pair potential in advanced Virtual Move Monte-Carlo (VMMC) simulations to model structure formation of ellipsoidal particles on interfaces. VMMC simulations are indispensable to approximate realistic dynamics and avoid the unphysical kinetic traps of strongly attractive particles present in the standard single-particle Metropolis Monte-Carlo algorithm.
5.1 Theory and Literature

5.1.1 Shape-induced capillary interaction between two particles

The theory behind capillary interactions is well understood, with the main difficulty being in how to efficiently model structure formation. Meniscus deformations of a single particle due to gravity, electric charge, wettability and shape, as well as interactions between particles, have all been studied both experimentally and theoretically [44, 45, 36, 46, 56, 67, 66].

We rather focus on the effect of particle geometry and consider shape-induced capillary interactions between colloidal-sized particles that are too small for gravity to play a role. Assuming small slopes of the meniscus (which should be valid for small particles when the Bond number is small [48]), we can approximate the mean curvature of the interface with the Laplacian, hence the meniscus profile $h(r)$ satisfies the Young-Laplace equation

$$\nabla^2 h = 0,$$  \quad (5.1)

where we recall that the position vector is two-dimensional $r = (x, y)$. The contact angles of particles adsorbed on the interface provide boundary conditions for Eq. (5.1), which must be solved together with the *a priori* unknown contact line. This is already a difficult free boundary problem as the contact line must be determined self consistently using the Young-Dupré equation (1.1). Often one assumes a multipole series for $h$ so that the particle-particle interaction can be described as an interaction between multipoles [46]. An alternative to solving the free boundary problem is to minimise an appropriate free energy to obtain the equilibrium meniscus profile, contact line and particle height

$$\Delta F = \sigma \Delta A_{\text{men}} + \sum_{i=1}^{N} \left( \sigma_1 \Delta A_{1,i} + \sigma_2 \Delta A_{2,i} \right),$$  \quad (5.2)

where $\Delta A_{\text{men}}$ denotes the change in meniscus surface area, $\Delta A_{1,i}$ and $\Delta A_{2,i}$ denote the change in contact area between the particle $i$ and phase 1 and 2 respectively, and we have assumed $N$ identical particles on the interface. How this free energy behaves when the particle positions and orientations are varied gives rise to effective multibody interparticle interactions. Multibody since the interaction between two particles are affected by the presence of other particles.

We also mention the alternative approach of Domínguez et al. [66], where they use mechanical equilibrium to determine the meniscus deformation and make an analogy with two-dimensional electrostatics so that the capillary interactions are described as interactions between capillary ‘charges’. This approach is especially useful when there is a surface pressure field originating from e.g. electrically charged particles, but as this pressure field is zero for our case of shape-induced capillary interactions under the assumption of mechanical isolation, we find the energy minimisation approach to be better suited.
5.1. Theory and Literature

The superposition approximation assumes that the meniscus profile is the sum of the profiles due to each particle individually so that the contact line on each particle remains stationary and it reduces the multibody problem to pairwise interactions (see Appendix A.4). In terms of the free energy in Eq. (5.2), this means the terms $\Delta A_{1,i} = 0$ and $\Delta A_{2,i} = 0$. Clearly such an approximation cannot be valid in the near-field when the contact lines (but not contact angle) vary due to the meniscus deformation imposed by nearby particles. On the other hand, this simplifies the calculation of the pair interaction considerably and analytic results can be obtained. Notably, Stamou et al. [45] showed that an undulating contact line on a spherical particle leads to a pair interaction that is quadrupolar to lowest order

$$U_{\text{quad}} = -3\pi \sigma (\Delta u_{\text{max}})^2 \left( \frac{r_{ij}}{R} \right)^4 \cos(2\phi_i + 2\phi_j) \quad (5.3)$$

where $\Delta u_{\text{max}}$ is the maximum difference in meniscus height on the particle, $r_{ij}$ is the center-to-center separation distance, $R$ is the particle radius and $\phi_i, \phi_j$ are the orientations of particles $i$ and $j$ respectively. The monopole and dipole interactions are zero thanks to the condition of mechanical isolation. Interestingly this implies that depending on the relative orientations of the particles, the interaction can be attractive or repulsive. The far-field interaction between two ellipsoidal particles of small eccentricities ($a \approx b = R$) also reduces to Eq. (5.3) to leading order [67]. We therefore expect the most stable configuration of ellipsoidal particles to be side-to-side (SS). Indeed, quadrupolar symmetry of the meniscus deformation around a single micron-sized PS ellipsoidal particle has been observed using interferometry and optical trapping [148]. In addition, Loudet et al. [148] find that the dominant contribution to the meniscus deformation is particle shape rather than any surface heterogeneities.

The quadrupolar interaction predicts that the attractive force between two particles approaching SS or tip-to-tip (TT) both vary as $F_{\text{quad}} \sim r_{ij}^{-5}$, however, an experimental estimate [36] of the capillary force with relatively elongated ellipsoids $k \approx 4$ indicates that the force scales differently depending on whether the particles approach SS or TT. Numerically solving for the meniscus profile using Surface Evolver for ellipsoids also shows Eq. (5.3) to be inaccurate, even for moderate elongations $k = 2, 3$ [72].

The validity of the superposition approximation was investigated analytically in Ref. [102] for large inter-particle separations, but not in the near-field. Various approaches have been used to obtain the interaction potential without using the superposition approximation. An approach developed by Kralchevsky [149, 150, 151] is to solve for the pair potential between two spherical particles in bipolar coordinates, which allow to impose the exact contact angle boundary conditions on each particle. An alternative perturbative approach was recently presented by Galatola [56] for spheroidal particles of small eccentricity, who calculated that the next to leading term in the interaction potential after the quadrupole varies as $r_{ij}^{-8}$ and is always attractive.
Chapter 5. Capillary interactions and structure

5.1.2 Self-assembly and structure formation

The self-assembly of particles at interfaces leads to many different surface structures, as seen in Fig. 1.1. We begin by reviewing the experimental work concerning self-assembly of anisotropic colloidal particles on interfaces.

Curved disc particles made of gold and Nichrome investigated in Ref. [152] deform the air-water interface with quadrupolar symmetry and assemble into long chains as well as open percolating structures with preferential alignment along their axis of curvature. Loudet et al. spread PS and silica-coated PS ellipsoids of aspect ratio $k \sim 4$ onto a water-air interface, finding that the PS ellipsoids form mainly TT branched chains containing open structures, while the silica-coated particles form SS branched chains, also containing open structures, see Fig. 1.1(a) and 1.1(b). There is some polydispersity apparent in the images. They looked more closely at the effect of polydispersity in Ref. [153], where ellipsoids of different sizes assemble into stable ‘arrows’ rather the SS configuration, which becomes unstable when there is a size mismatch. Madivala et al. [37] studied the self-assembly of PS ellipsoids of both high and low surface charge, adsorbed on either an oil-water or an air-water interface. The highly charged particles have a direct electrostatic repulsion, although it may be screened somewhat by counterions in a polar fluid. Nevertheless, charged ellipsoids at low surface coverage on an oil-water interface are initially separated, although with time, capillary interactions seem to dominate and open percolating aggregates are seen [37], see Fig. 1.1(c). The low surface charge ellipsoids assemble very quickly into open percolating structures similar to Fig. 1.1(c). The surface structures also depend on the surface coverage. Ellipsoid monolayers at very high surface coverages were studied in Ref. [62]. Upon compression, a disordered jammed state was obtained, with some particles being forced to orient out of the interface. Sterically stabilised PMMA ellipsoidal particles spread on a decalin-air interface form well-defined, rigid SS chains, appearing like a two-dimensional smectic state [38]. These chains can also form more complicated morphology, see Fig. 1.1(f).

Simulation work looking at the self assembly of particles on a flat interface has either used the quadrupole approximation to describe nearly spherical particles in a MD simulation [147], or they have used the Lattice Boltzmann (LB) method coupled with an MD solver to deal with direct particle-particle interactions. Impressive LB simulations of emulsification in the presence of ellipsoidal particles were run on supercomputers, although structure formation of the particles on the interfaces was not studied here since the droplets were rather small compared to the size of the ellipsoidal particles [74, 77]. The self assembly of particles on droplets was studied in more detail in [75].

In terms of structure formation of anisotropic particles on planar interfaces, the work of Davies et al. [27, 78] is worth mentioning. Here they assumed that the ellipsoidal particles possess a magnetic moment and a magnetic field oriented normal to the interface causes the particles to tilt out of the interface. In this case the dominant capillary interaction is dipolar in nature, although they still find long SS chains in their $k = 2$, $N \sim 100$ particle simulations.
5.2 The superposition approximation

The superposition approximation excludes multibody interactions hence it implies the validity of a pairwise potential to describe capillary interactions. In our further work using pairwise interactions in VMMC simulations to observe structure formation of ellipsoidal particles, we assume the validity of this approximation, and as a justification, we investigate the error associated with neglecting multibody effects for a variety of three-particle configurations and a substantial range of particle properties $k = 2, ..., 5$ and $\theta = 30, ..., 80$.

In practice, a frequently used method to obtain the exact meniscus profile is numerically with the Surface Evolver software [69]. We use version 2.70a in the following work. The meniscus is first discretised into Lagrange elements while the contact angle boundary condition on the solid particles is modelled by a constraint energy integral along the contact line that accounts for the wetting energy, namely the contact angle and wetted area. The particle's positions and orientations are fixed. The software uses gradient descent and nonlinear Hessian steps to optimise the position of the contact line and the meniscus profile in order to minimise the free energy Eq. (5.2). In our work we use adaptive meshing and finish with second order Lagrange elements on a fine grid, allowing very precise determination of the meniscus profile and total energy of the system. Our simulation box is cylindrical and we impose a far-field (at a radius of $70a$ away from the center of mass of the particles) flat interface boundary condition, although we do allow the height of the interface to vary. This is equivalent to allowing the particle height to vary and find its optimum position with respect to the interface. Reference energies were determined by placing the particles far apart, typically $r_{ij} \approx 40a$. Our two-particle interaction energies are in accordance with Refs [72, 71] and we also observe the non-monotonic dependence of interaction strengths on contact angle.

We begin by accurately determining the interaction potentials for a variety of two-particle configurations. We then simulate a selection of three-particle configurations and compare the exact three-particle interaction energies with the sum of two-particle interaction energies. The two-particle and three-particle configurations are shown in Fig. 5.2. In addition, the side-side-side (SSS) and tip-tip-tip (TTT) configurations were simulated for different interparticle separation distances. These configurations were chosen due to their relevance in experimental work, see Fig. 1.1.\(^1\)

We characterise the error in assuming pairwise interactions by a percentage relative error, defined as $100 \times (E_3 - \sum_{i}^{3} \sum_{j=1}^{3} E_{ij})/E_3$ where $E_3$ is the three-particle multibody interaction energy and $E_{ij}$ is the pairwise interaction energy between particles $i$ and $j$. Each of these energies is determined by numerical simulations to a very high level of precision. The SSS and TTT configurations are characterised by two distances $d_1$ and $d_2$, whose meanings are made clear in Fig. 5.1. The relative error for the four different three-particle configurations is

\[^1\]In addition to these stable and metastable configurations, we also studied a selection of unstable three-particle configurations, namely STS, TST, SST and TTS. Those results are not presented here but the approximation of using pairwise energies to describe the full multibody interaction energy also appears reasonable.
Chapter 5. Capillary interactions and structure

Figure 5.1 – We characterise three particle configurations using two distances $d_1$, which is the center-to-center separation between the furthermost ellipsoids, and $d_2$, which is the center-to-center separation between the first and middle ellipsoids. Shown is the SSS three-particle configuration.

Figure 5.2 – The meniscus deformation due to ellipsoidal particles with $k = 4$, $\theta = 40^\circ$ in various configurations. Black outlines show the touching particles, white shows the removed surface area of the fluid interface. Two- and three-particle configurations (a) flower, (b) triangle, (c) SSS and (d) TTT.

Presented in Fig. 5.4 for a variety of parameters. As expected, we find that multibody effects are less pronounced for ellipsoids of smaller eccentricities and when the particles are further apart. In particular, the percentage error in the TTT arrangement seems to be consistently very low for the range of contact angles and aspect ratios we studied, due to the relatively larger center-center separation distances in such an arrangement. The triangle configuration also has very low errors, because most of the interaction energy originates from the meniscus deformation at the tips of the triangle, which is mostly an interaction between only two particles, as can be seen in Fig. 5.2(b).

The exact three-particle interaction energies are compared with the sum of pairwise interactions in Fig. 5.3. The trends in the three-particle interaction energies are clearly reproduced by the sum of pairwise interactions and, in terms of the absolute values, the two do not differ significantly (see Fig. 5.4). While we admit that our study is far from exhaustive, it does provide evidence that the superposition approximation is reasonable for the most important and frequently encountered configurations in experiments. Looking at the three-particle interactions also allows us to identify the most stable configurations — these correspond to configurations with the lowest energy. We see that across all aspect ratios and contact angles, the energetically
5.2. The superposition approximation

Figure 5.3 – Interaction energies for (a) $k = 2$, (b) $k = 3$, (c) $k = 4$ and (d) $k = 5$. Full lines: exact energies for a variety of three-particle configurations. Dashed lines: Energy calculated by summing pairwise interaction energies. We observe that the approximation of pairwise interactions faithfully follows the trends of the full multibody energy.
Figure 5.4 – Percentage errors for a variety of three-particle configurations. Legends are the same as for Fig. 5.3. The errors have a tendency to increase for higher aspect ratios, but do not change the relative stability of each of the three-particle configurations. (a) $k = 2$, (b) $k = 3$, (c) $k = 4$ and (d) $k = 5$. 
most stable configuration is the SSS, closely followed by the triangle. Note that the relative stabilities of each configuration are interaction-dependent. If the ellipsoids are charged we would expect the combined effect of shape-induced capillary interactions and electrostatic repulsion to favour a triangular configuration, which is indeed seen in experiments on charged particles [36, 37].

5.3 Our empirical pair potential

We propose an empirical pair potential, based on the distance of closest approach $d_{ecf}(\phi_i, \phi_j)$ between two hard ellipsoids. This distance was calculated analytically for arbitrary ellipsoids in Ref. [154] and was used in the development of a ‘stretched’ ellipsoid-shaped Lennard-Jones potential in Ref. [155]. A power law fit $\sim 1/r^{m_{ij}}$ for the capillary interaction energy between two ellipsoids $k = 2, 3$ was attempted in Ref. [72], however, they fitted each configuration (SS, ST, TT) separately and did not investigate a functional form for the angular dependence of the exponent $m$, nor the prefactor.

Our pair potential $U_{ij}$ contains only 4 fitting parameters and reads

$$
\frac{U_{ij}}{\sigma b^2} = -A_1 \cos(2\phi_i + 2\phi_j) \left( \frac{b}{r_{ij} - A_2 d_{ecf}(\phi_i, \phi_j) + A_3} \right)^{A_4},
$$

(5.4)

where $A_l$ with $l = 1, ..., 4$ are the fitting parameters and $r_{ij}$ is the interparticle separation. We can interpret $A_2$ as a anisotropy parameter, which characterises the eccentricity of the ellipsoid and $A_3$ as an effective particle size. The cosine term ensures that SS and TT interactions are attractive, while the ST interaction is repulsive. Note that the fitting parameters depend on both aspect ratio and contact angle.

The fitting parameters are determined by a least squares fit to the exact two-particle interaction energies in the SS, TT and ST configurations, obtained by Surface Evolver simulations. In line with the physical interpretation of the fitting parameters, we find that $0 < A_2 < 1$ and that $a < A_3 < 2a$. The angular accuracy of Eq. (5.4) is determined by comparison to exact interaction energies in configurations where $r_{ij}$ is fixed and one particle is rotated through $\pi/2$. We begin the rotation from particles initially in the SS and TT configurations. We fit Eq. (5.4) to data with $k = 2, ..., 5$ and $\theta = 30^\circ, ..., 80^\circ$. We present a selection of fits for $k = 2$ in Fig. 5.5 and for $k = 5$ in Fig. 5.6. Values of the fitting parameters are presented in Table 5.1.

Looking at Fig. 5.6, we see that Eq. (5.4) lacks the higher order multipole effects [45, 67] needed to accurately describe the angular dependence for more elongated ellipsoids, however, its simplicity and superiority, when compared to the quadrupole approximation (5.3) is clear. In particular, the ratio between SS and TT bond energies $E_{SS}/E_{TT}$ is considerably more accurate and we can therefore hope to better model the experimental structures formed by capillary interactions. 2

\[2\text{For } k = 2, \theta = 50^\circ, \text{ the exact SE data gives } E_{SS}/E_{TT} = 3.36 \text{ our empirical pair potential gives } E_{SS}/E_{TT} = 2.54,\]
Chapter 5. Capillary interactions and structure

Figure 5.5 – Fit of our empirical pair potential to the exact energies for $k = 2$. The symbols denote the exact energies and the solid lines are the fits. Upper panel: $\theta = 30$. Middle panel: $\theta = 50$. Bottom panel: $\theta = 80$.

Figure 5.6 – Fit of our empirical pair potential to the exact energies for $k = 5$. The symbols denote the exact energies and the solid lines are the fits. Upper panel: $\theta = 30$. Middle panel: $\theta = 50$. Bottom panel: $\theta = 80$. 
5.4. Self-assembly of ellipsoids at interfaces

We use VMMC simulations to study the self-assembly of ellipsoids interacting via shape-induced capillary interactions using our pair potential in Eq. (5.4). The VMMC algorithm selects clusters recursively based on gradients of interaction energies, and moves the clusters also according to gradients of interaction energies, with a move-probability satisfying detailed balance and an underlying Boltzmann distribution. Therefore internal rearrangements within a single cluster are also permitted. A detailed description of the VMMC algorithm can be found in Refs. [95, 96, 97].

Since the SS and TT bonds between particles in contact are very strong, aggregation is an irreversible process and breaks ergodicity. For this reason we begin with many independent random initial configurations and average over their time evolutions, to imitate experimental procedures where the particles are initially spread onto an interface and then allowed to self-assemble [37]. This procedure is known in the literature as a ‘rapid’ or ‘instantaneous’ quench [156, 157, 158].

The aggregation process in colloidal systems is well-studied [159], with two limiting regimes identified: diffusion-limited colloidal aggregation (DLCA), which occurs when aggregation

Table 5.1 – Parameters for our empirical pair potential for a range of $k$ and $\theta$, determined by fitting to precise numerical simulation data. Fit uncertainties are within 5% of the stated values.

<table>
<thead>
<tr>
<th>$k$</th>
<th>$\theta$</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
</tr>
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<tbody>
<tr>
<td>2</td>
<td>$A_1$</td>
<td>1.0299</td>
<td>1.5909</td>
<td>1.4142</td>
<td>1.1119</td>
<td>0.8587</td>
<td>1.2165</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>2.7713</td>
<td>2.5047</td>
<td>2.5362</td>
<td>2.6620</td>
<td>2.7758</td>
<td>2.7129</td>
</tr>
<tr>
<td></td>
<td>$A_3$</td>
<td>0.3129</td>
<td>0.4332</td>
<td>0.6029</td>
<td>0.7154</td>
<td>0.7480</td>
<td>0.3562</td>
</tr>
<tr>
<td>3</td>
<td>$A_1$</td>
<td>4.4554</td>
<td>4.0866</td>
<td>3.7970</td>
<td>3.2148</td>
<td>3.1894</td>
<td>2.4354</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>2.8946</td>
<td>2.9666</td>
<td>3.1090</td>
<td>3.2468</td>
<td>3.5717</td>
<td>4.0177</td>
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<td></td>
<td>$A_3$</td>
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<td>0.4968</td>
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<td>0.7327</td>
<td>0.7864</td>
<td>0.8009</td>
</tr>
<tr>
<td></td>
<td>$A_4$</td>
<td>4.5112</td>
<td>4.0235</td>
<td>3.8635</td>
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<td></td>
<td>$A_3$</td>
<td>0.3313</td>
<td>0.5234</td>
<td>0.6440</td>
<td>0.7235</td>
<td>0.7671</td>
<td>0.7828</td>
</tr>
<tr>
<td>5</td>
<td>$A_1$</td>
<td>7.0847</td>
<td>19.800</td>
<td>19.411</td>
<td>19.320</td>
<td>17.580</td>
<td>17.380</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>3.7345</td>
<td>4.7616</td>
<td>5.1119</td>
<td>5.5338</td>
<td>6.0607</td>
<td>7.0493</td>
</tr>
<tr>
<td></td>
<td>$A_3$</td>
<td>0.3616</td>
<td>0.5009</td>
<td>0.6024</td>
<td>0.6675</td>
<td>0.7033</td>
<td>0.7166</td>
</tr>
<tr>
<td></td>
<td>$A_4$</td>
<td>3.4187</td>
<td>3.4449</td>
<td>3.3385</td>
<td>3.3829</td>
<td>3.5284</td>
<td>3.9151</td>
</tr>
</tbody>
</table>

5.4 Self-assembly of ellipsoids at interfaces

while the quadrupole approximation is off by an order of magnitude $E_{SS}/E_{TT} = 16.1$. For higher aspect ratios the quadrupole is off by multiple orders of magnitude. (The ratios are accurate to three significant figures.)
is limited by the time taken for clusters to diffuse and encounter each other and reaction-
limited colloidal aggregation, which occurs when there is an activation barrier slowing down
aggregation. Both cases result in typical fractal cluster structures [160, 161] and scaling laws for
the cluster size distribution [162, 163, 164, 165, 166]. There is strong evidence for universality
in dilute systems, indicating that the details of the aggregation process are unimportant
[167, 168, 169]. We note that the models used to study aggregation are lattice-based [170] or
have generally only considered ‘sticky’ particles [169], which form an infinitely strong bond
upon contact so that relaxation of the particles comprising the cluster is not possible. We
expect our capillary dominated system to be more in the DLCA regime, despite the repulsion
in certain configurations, because the SS and TT bonds are so strong.

We investigate the effect of \(k\), \(\theta\) and \(\eta\) on the surface structure formed by capillary interactions.
The structures of self-assembled ellipsoids are characterised using the radial pair correlation
function \(g_2(r)\) and the angular correlation function \(g_2^2(r)\) = \(\langle \cos^2 \phi_{ij} \rangle\), where \(\phi_{ij}\) is the
angle between particles \(i\) and \(j\), and their interparticle separation is \((r - dr) \leq r_{ij} < (r + dr)\). For
the more dilute surface coverages, we also analyse the cluster size distribution \(n_{cs}(c_s)\), where
\(c_s\) is the number of particles that belong the a cluster (the cluster size) and the number of SS
and TT bonds.\(^3\) The particle parameters we studied are \(k = 2–5\), \(\theta = 30–80\) and \(\eta = 0.2–0.6\).

### 5.4.1 Simulation details

We perform VMMC simulations in a periodic square box with \(N = 512\) particles. The fitting
parameter \(A_1\) is chosen for numerical convenience such that the TT bond energy is \(E_{TT} \approx
20 k_B T\), which is sufficiently strong that thermal fluctuations will not break the bond. Since
the SS capillary bond energy \(E_{SS}\) always seems to be greater than \(E_{TT}\), the SS bond once
formed, also cannot be broken by thermal noise. Note that by setting the TT bond energy,
changing contact angle has the sole effect of changing the ratio between interaction energy
at various relative orientations. The effect of changing contact angle on the ratio \(E_{SS}/E_{TT}\) is
presented in Appendix A.5. We employ a cutoff for the capillary interaction at \(r_{cut} = 5a\), which
appears reasonable given the data in Figs. 5.5 and 5.6. Our empirical potential is then rescaled
so that it smoothly reaches zero at \(r_{ij} = r_{cut}\). Random initial configurations are formed by
running single-particle Metropolis MC for hard ellipsoids without capillary interactions. We
then turn on capillary interactions for the VMMC run. Averages are over 20–50 independent
runs. The length of the simulations for various surface coverages are summarised in Table 5.2.
Higher surface coverages result in a kinetically arrested state far more quickly than low surface
coverages.

In addition to the use of our empirical potential (5.4) for capillary interactions, we performed
simulations using the quadrupole approximation (5.3) as a comparison (all simulation details
\(^3\)Whether a particle belongs to a cluster is determined by a geometric criterion, namely if the separation distance
between two ellipsoids \(r_{ij} \leq |d_{eq}(\phi_1, \phi_2) + dr|\), where we set the small distance \(dr = b/5\). An SS bond also uses
the above geometric criterion, in addition to the angular criterion \(|u_i \cdot u_j| > 0.8\). For a TT bond, the angular criteria
read \(|r_{ij} - u_i| > 0.8\) and \(|r_{ij} - u_j| > 0.8\).
5.4. Self-assembly of ellipsoids at interfaces

Table 5.2 – Summary of the total number of MC sweeps for different surface coverages η. An MC sweep is defined as N attempted moves, and each move has a 50% chance of being either translational or rotational.

<table>
<thead>
<tr>
<th>η</th>
<th>MC sweeps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>$5 \times 10^6$</td>
</tr>
<tr>
<td>0.3</td>
<td>$5 \times 10^6$</td>
</tr>
<tr>
<td>0.4</td>
<td>$7.5 \times 10^5$</td>
</tr>
<tr>
<td>0.5</td>
<td>$5 \times 10^5$</td>
</tr>
<tr>
<td>0.6</td>
<td>$2 \times 10^5$</td>
</tr>
</tbody>
</table>

are as above). The quadrupole simulations are presented in Appendix A.6 and turn out to produce slightly different structures than those seen for our empirical potential, which is due to the bond energy ratios $E_{SS}/E_{TT}$ for the quadrupole approximation being multiple orders of magnitude too great when compared with the exact Surface Evolver results.

5.4.2 Time dependence of self-assembled structures

In the dilute regime, we observe that individual particles come together very quickly to form small clusters consisting primarily of chains of SS particles. The chains then come together via their tips to form more isotropic clusters. This process can be seen for $k = 2$ in the top rows of Figs. 5.7 and for $k = 5$ in Fig. 5.8. For intermediate surface coverages, we find the initial appearance of an almost-spanning gel-like structure formed by long strands, which then collapses into separated large clusters (see middle row). For the rather high surface coverage seen in the bottom row, the particles very quickly form a spanning cluster and subsequent dynamics are very slow when measured over the simulation timescale, hence we call this a kinetically arrested state. In this state, the particles possess local crystalline order, but at larger length scales the system appears disordered. This would indicate that gelation in our system appears due to an arrested phase separation where initial density inhomogeneities lead to the formation of a spanning cluster and subsequent arrest. The kind of structures we observe in our simulations are clearly denser than the experimentally observed open percolating structures (c.f. Fig. 1.1). This is most likely due to our assumption of uncharged particles—a uniformly charged ellipsoid would experience greatest electrostatic repulsion in the SS configuration, and when combined with an attractive capillary interaction in both SS and TT positions, an open structure would be favoured. Although our snapshots of the rather elongated $k = 5$ particles at high surface coverage do show the smectic-like structure seen for the sterically-stabilised ellipsoids of Zhang et al. [38].

We limit discussion on the time dependence of the surface structure to dilute and intermediate surface coverages $\eta \leq 0.40$ where aggregation and cluster growth is encountered. Higher surface coverages result very quickly in a kinetically arrested phase and are treated in more

\footnote{For the strong bonds formed by our particles, one would expect the final state to consist of a single spanning cluster. This point is not reached in our simulations due to slowing-down of the aggregation process as the clusters increase in size. We did however perform simulations for smaller systems of $N = 128$ and $\eta = 0.2$ and we find that to arrive at the final state with one large cluster requires $\sim 5 \times 10^7$ MC sweeps.}

\footnote{We use the term smectic-like to describe the structure in the snapshot where there is ordering in two directions. Note however, that this structure is kinetically arrested and therefore not a true smectic liquid crystal, which can flow.}
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Figure 5.7 – Snapshots of the system showing typical self-assembly and structure evolution. Number under each snapshot is the number of the VMMC sweeps when that snapshot was taken. Data for $k = 2$, $\theta = 50$, top row: $\eta = 0.2$, middle row: $\eta = 0.4$ and bottom row $\eta = 0.6$.

Figure 5.8 – Snapshots of the system showing typical self-assembly and structure evolution. Number under each snapshot is the number of the VMMC sweeps when that snapshot was taken. Data for $k = 5$, $\theta = 80$, top row: $\eta = 0.2$, middle row: $\eta = 0.4$ and bottom row $\eta = 0.6$. 
5.4. Self-assembly of ellipsoids at interfaces

Figure 5.9 – Left panel: Evolution of the average cluster size \( \langle c_s \rangle \) for various aspect ratios, contact angles and surface coverages in a log-log plot. Black line shows a power law with exponent 0.042. Right panel: Average number of SS bonds \( \langle n_{SS} \rangle \) (squares), and average number of TT bonds \( \langle n_{TT} \rangle \) (triangles). Colours correspond to the same parameters in the left panel.

detail later. Important time varying quantities are the average cluster size \( \langle c_s(t) \rangle \) and the average number of SS and TT bonds \( \langle n_{SS}(t) \rangle, \langle n_{TT}(t) \rangle \), which we present for various aspect ratios, contact angles and surface coverages in Fig. 5.9. For DLCA, the average cluster size \( \langle c_s(t) \rangle \) is predicted to vary as \( c_s(t) \sim t^{z} \) [163, 164, 165, 162] with dynamic scaling exponent \( z \), which is expected to be equal to unity in the dilute limit. Since we measure time in terms of VMMC sweeps, the value of the exponent \( z \) cannot be easily compared with physical time, nevertheless, the underlying power-law behaviour is still apparent and the fact that all data appear to have the same exponent \( z \) hints at universality in the aggregation process. In terms of the effect of different particle geometries, we find aggregation to occur faster for higher aspect ratios, and lower contact angles. The effect of \( k \) can be understood as the increased probability of more elongated particles to encounter each other. On the other hand, the effect of \( \theta \) is to change the SS bond energy (since we fix \( E_{TT} \)) and since smaller contact angles have a greater ratio \( E_{SS}/E_{TT} \), the attractive SS interaction is stronger resulting in a higher average number of SS bonds compared to TT bonds for smaller contact angles. We observe from snapshots of the simulation in Figs. 5.7 and 5.8 that smaller clusters come together to form larger clusters. This process results in the number of smaller clusters decreasing and a growth in the number of larger clusters, as can be clearly seen in the evolution of the cluster size distribution in Fig. 5.10 for one set of parameters. The universal behaviour of DLCA is manifested in the cluster size distribution, which can be collapsed onto a master curve using the scaling law [169, 166, 167, 163, 170]

\[
\frac{n_s}{N} \sim \langle c_s(t) \rangle^{-2} f\left(\frac{c_s}{\langle c_s(t) \rangle}\right),
\]

(5.5)

where \( f \) is a universal bell-shaped function. We show the cluster size distribution dynamics in Fig. 5.10 and in the inset of Fig. 5.10, demonstrate data collapse onto a master curve using the scaling law (5.5). We note that data collapse is observed across all aspect ratios and contact angles for \( \eta \leq 0.4 \), which is quite interesting given that the scaling law is in principle, only
valid for dilute systems. The cluster-size dynamics we observe indicate that the aggregation of colloids by capillary interaction fall into the universality class of DLCA.

5.4.3 Kinetically-arrested gel-like structures

We now proceed with a more quantitative analysis of the kinetically arrested states of our structures beginning with the radial and angular correlation functions, which highlight the effect of anisotropy and particle geometry have on the final structure. For all the particle geometries studied, we find the onset of a kinetically arrested state at \( \eta = 0.5 \), whereas \( \eta = 0.4 \) always results in individual clusters. An experimental study found that \( k = 4 \) PS ellipsoids form a percolating network at a much lower surface coverage of \( \eta \sim 0.25 \) \cite{17}. The discrepancy is likely due to electrostatic repulsion and capillary attraction causing the formation of open structures, which are able to form a percolating network at lower surface coverages than our denser structures.

Fig. 5.11 shows pair correlation functions \( g(r) \) and \( g_2(r) \) for \( k = 2 \) and \( k = 5 \). We see the largest peak in \( g(r) \) at \( r = 2b \). Further peaks follow at multiples of \( 2b \) and \( 2a \), corresponding to the SS and TT configurations respectively. The smaller peaks of \( g(r) \) and \( g_2(r) \) just before \( r = 4b \) for \( k = 2 \) and \( r = 10b \) for \( k = 5 \) (indicated by arrows in Fig. 5.11) is due to the ellipsoids interlocking at the tips in a crystalline structure, like zipper teeth.

We see from the plots of \( g_2(r) \) that the angular correlations are strongest when \( r \) is multiples of \( 2b \) and \( 2a \) and also that they decay slowly, indicating long-range orientational correlations. We also see that particle geometry plays a role in the characteristics of the final structures. Namely that for higher aspect ratios, the angular correlations decay more slowly and the peaks are better defined. These characteristics can be explained by the fact that higher aspect ratios cause chains of SS particles to be more rigid, as is seen in the bottom rows of Figs. 5.7 and 5.8,
where $k = 2$ ellipsoids form ‘bendier’ structures when interlocked at the tips than the straight structures favoured by the more elongated $k = 5$ ellipsoids. Indeed, the peaks corresponding to chains of $k = 5$ S5 particles are evident in Fig. 5.11. The additional rigidity is not evident in the dilute regime since there are fewer constraints on the particle chains so that the $k = 2$ ellipsoid chains are free to straighten.

5.4.4 Remarks

We study self-assembly and structure formation of ellipsoidal particles adsorbed on an interface interacting via excluded volume and shape-induced capillary interactions. We show using precise numerical solutions to find the meniscus profile and energy of various two- and three-particle configurations that the multibody capillary interaction can be well-described using pairwise potentials. Our results also touch on the relative stability of various three-particle states.

We develop a simple empirical form for the pairwise interaction, and implement it in VMMC simulations to study the self-assembly process. We are able to reproduce experimental structures at high surface coverage [38] where excluded volume and the capillary interaction dominates but not the open percolating structures comprised of triangles observed in lower surface coverages. We note that the triangle configuration is almost as energetically favourable compared to the SSS configuration when considering purely shape-induced capillary interactions but the lack of triangles in our VMMC simulations is perhaps indicative that the pathways through the free energy landscape that result in a triangle configuration are far less probable than the pathways for forming the SSS configuration. This could be remedied by the inclusion of electrostatic interactions [23, 53] (and possibly polydispersity [49, 153]), which would alter the relative stabilities of the three-particle configurations. Nevertheless, given the wide range of competing interactions present between particles adsorbed on fluid interfaces, it is important to distinguish between the effects of each and we emphasise that ours is the first study of large-scale self-assembly of anisotropic particles interacting by capillary interactions. The inclusion of an electrostatic repulsion into our approach should, in principle, be possible.
Chapter 5. Capillary interactions and structure

The simulation technique we use is able to model cluster-cluster aggregation, and we recover the dynamic scaling laws predicted for DLCA. However, we must bear in mind that the process of self-assembly depends strongly on the simulation technique, which should be chosen to mimic as closely as possible the experimentally-observed dynamics in order to obtain the correct final structures [158, 173]. We have also neglected hydrodynamic interactions, the inclusion of which increases the probability of forming open structures in systems of Lennard-Jones particles [174]. It would be beneficial to verify the structures obtained by VMMC simulations by comparison to dynamic simulation techniques such as MD, this would also allow the response of the structures to flow to be investigated.
6 Highlights and outlook

It became clear in the course of this thesis that there is a lot of work remaining to understand the structures formed by particles on interfaces, link these structures to interfacial rheology and conclusively determine the effect of interfacial rheology on the stability of Pickering emulsions. I hope to have contributed a little towards this final goal.

6.1 Highlights

We developed a multiscale approach for developing rheological models for particle-laden interfaces within the GENERIC nonequilibrium thermodynamics framework and demonstrated it on a toy model of hard ellipsoids adsorbed on a planar interface [43]. Our approach is general and only requires a well-defined microscopic model and we show the advantages and indeed, necessity, of nonequilibrium thermodynamics to consistently coarse-grain from the microscopic level of description to the macroscopic static and dynamic quantities. Particular achievements are the systematic determination of the entropy for a system of two-dimensional hard ellipsoids for various aspect ratios and a wide range of surface coverages [89], as well as the simulation-guided development of the friction matrix entries describing collective relaxation of particle orientations [43]. The physical processes governing structural changes under flow are well described and thermodynamically consistent.

By solving our model equations for various experimentally relevant flow fields, we gain great insight into the interplay between flow, structure and rheology and find a rich phenomenology. This insight can be used to help interpret large-amplitude shear and dilatational rheological experiments, which result in nonlinear behaviour. This is especially important because interfaces (in foams and emulsions) are routinely subjected to large deformations during processing. While a quantitative agreement between our model and experimental results remains elusive due to the simplistic nature of our toy model, we are confident that our general approach is capable of handling more realistic microscopic models.

We then proceeded to study shape-induced capillary interactions between ellipsoidal particles.
Precise interaction energies were calculated for a wide range of particle geometries and contact angles, in various two- and three-particle configurations in order to determine whether approximating the full multibody interaction as the sum of pairwise interactions is reasonable. For the configurations we studied, this approximation does indeed seem reasonable and the correction is small, giving us confidence to use our simple empirical pair potential in sophisticated VMMC simulations to study self-assembly and structure formation of a large number of anisotropic particles interacting via shape-induced capillary interactions for the first time.

We find distinct differences between structures formed at high and low surface coverages, and between different particle geometries. At high surface coverages and high aspect ratios, we observe smectic-like phases comprised of rigid chains of SS particles, similar to those reported in Ref. [38]. More generally, at high surface coverages the system forms a kinetically-arrested disordered state—a gel, which we have characterised using radial and angular correlation functions. For lower surface coverages we find the cluster growth proceeds via the aggregation of smaller clusters, and behaves according to the dynamic scaling laws predicted by the universality of diffusion limited colloidal aggregation [167]. We expect our results to be valid where self-assembly is dominated by shape-induced capillary interactions and it is clear that this is fulfilled in certain experimental systems [38]. However, the shape-induced capillary interaction appears insufficient to model other systems, notably where particles are charged [37, 36].

### 6.2 Outlook

There are many directions future work could take.

As our general multiscale approach linking a microscopic model to macroscopic rheology requires a well-defined microscopic model as a starting point, the development of pair potentials capable of describing the range of possible particle-particle interactions and surface structures is a necessity. Also to identify the appropriate structural variables e.g. cluster size distribution, orientation of clusters, chain length etc. for use in the GENERIC framework. These microscopic models can then be coarse-grained using static and dynamic computer simulations to help formulate the constitutive equations, as we have demonstrated for a toy model. Concretely, we would suggest as a first step the inclusion of electrostatic repulsion [175] in order to better model experimental results on charged particles [36, 37]. In the presence of a percolating network, we can expect more complex rheology, and the appearance of a yield stress. The effect of polydispersity also warrants some attention since real particles always have some degree of polydispersity, and different size ellipsoids have been shown to favor very different configurations compared with their monodisperse counterparts [153]. Dynamic simulations with some flow would be helpful to probe the effect of flow on structure and self-assembly, as well as the dissipative processes at play.

It is also important to study the interfacial rheology of other geometries, such as droplets,
since curvature modifies the particle-particle interactions [176, 177] and topology imposes constraints on the possible surface structures, for instance defects in liquid crystals (as a consequence of the hairy ball theorem) [178, 179, 180]. An additional complication of droplets, and other deformable surfaces, is the bi-directional coupling between droplet shape and surface structure (for instance when the structure imparts elasticity to the interface) [61].

Up to now, in our GENERIC model, we have neglected the effect of the bulk phases, but it is self-evident that interfaces do not exist in a vacuum and when particles are much larger than the interface thickness, they are immersed in the bulk phases and therefore coupled both to the interface and to the bulk phases. Therefore a complete description requires one to develop both bulk and interface equations, and solve the bulk equations using the interface equations as boundary conditions. Fortunately there exists a conceptually clear framework for the development of consistent bulk and interface equations [41, 87, 181]. Given the full set of bulk and interface equations, the challenge is then a numerical one, namely to solve them for the highly complex geometry of a foam or emulsion.
Bibliography


Bibliography


Bibliography


A.1 The generating function for ideal planar rotators

Ideal planar rotators are non-interacting, meaning that the Hamiltonian $H = 0$. The generalised canonical ensemble $\rho_{\Lambda}$ for two-dimensional non-interacting rotators is then

$$\rho_{\Lambda,\text{ideal}} = \exp\left(-\beta G(\Lambda) - \Lambda : \sum_{i=1}^{N} \mathbf{u}_i \mathbf{u}_i \right), \quad (A.1)$$

where $\Pi = \sum_{i=1}^{N} \mathbf{u}_i \mathbf{u}_i$ is the instantaneous orientation tensor. We use the form of the Lagrange multiplier in Eq. (3.12) and write the orientations $\mathbf{u}_i = (\cos \Omega_i, \sin \Omega_i)$. Then the normalisation of Eq. (A.1) gives

$$\beta G(\lambda) = N \ln \left( \int_{0}^{2\pi} \exp \left( -\lambda \cos(2\Omega_i) - 1/2 \right) \frac{d\Omega_i}{2\pi} \right),$$

$$= N \left[ \ln \left( I_0(\lambda) \right) - \frac{1}{2} \right]. \quad (A.2)$$

leading to

$$\hat{G}(\lambda) = \frac{G(\lambda)}{\beta N} = \ln \left( I_0(\lambda) \right) - \frac{1}{2}. \quad (A.3)$$

A.2 Interpolation formula for the ideal orientational entropy

We derive the interpolation formula for the ideal orientational entropy in Eq. (3.15) by examining weak and strong ordering limits, and interpolating between them.
Appendix A. Appendix

Weak ordering limit

For weak ordering we make a series expansion of Eq. (3.14) around $\lambda = 0$ to obtain
\[ S_2(\lambda) = \frac{1}{2} \lambda - \frac{1}{16} \lambda^3 + \frac{1}{96} \lambda^5 + \mathcal{O}(\lambda^7). \] (A.4)

This series can be inverted to give $\lambda(S_2)$
\[ \lambda(S_2) = 2S_2 + 4S_2^3 + \frac{40}{3} S_2^5 + \mathcal{O}(S_2^7), \] (A.5)

and inserted into Eq. (3.13) to give
\[ S_{id} \approx Nk_B \ln I_0 \left( 2S_2 + 4S_2^3 + \frac{40}{3} S_2^5 \right). \] (A.6)

Now take the limit $Q \to 0$ and expand Eq. (A.6) to give the orientational entropy as a function of $Q$, valid in the weak ordering limit
\[ S_{id,weak} \approx -S_2^2 - \frac{1}{4} S_2^4 - \frac{5}{36} S_2^6 + \mathcal{O}(Q^7). \] (A.7)

Strong ordering limit

We use the same approach as before to series expand Eq. (3.14) in the limit $\lambda \to \infty$ and invert the resulting series to obtain
\[ \lambda(S_2) \approx \frac{1}{2(1-S_2)} + \frac{1}{4}. \] (A.8)

Now we require an asymptotic form for $I_0(x)$ in the limit $x \to \infty$, which is obtained from Ref. [182] as
\[ I_0(x) \approx \frac{e^x}{\sqrt{2\pi x}} \left( 1 + \frac{1}{8x} \right). \] (A.9)

This gives
\[ \ln I_0(x) \approx x - \frac{1}{2} \ln(2\pi x) - \mathcal{O}(1/x), \] (A.10)

so we choose $x = [2(1-S_2)]^{-1}$, since this is the dominant term of Eq. (A.8) in the limit $S_2 \to 1$. We then insert Eqs. (A.8) and (A.10) into Eq. (3.13) to obtain the ideal entropy in the strong ordering limit
\[ \frac{S_{id,strong}}{Nk_B} \approx \frac{1}{2} \ln(1-S_2) + \frac{1-S_2}{4} + \frac{1}{2} - \frac{1}{2} \ln(\pi). \] (A.11)
A.3 Fourth moment in terms of rank two tensors

Interpolation formula

We propose the following simple and reasonably accurate interpolation formula for the ideal contribution to the orientational entropy of two-dimensional rotators

\[ S_{id} = N k_B \left[ \frac{1}{2} \ln(1 - S_2) + \frac{1}{2} S_2 - \frac{3}{4} (S_2)^2 + \frac{1}{6} (S_2)^3 - \frac{1}{8} (S_2)^4 + \frac{1}{10} (S_2)^5 - \frac{1}{18} (S_2)^6 \right], \quad (A.12) \]

This formula reduces to the correct physically admissible limit (Eq. (A.7)) for the case of weak ordering and always has a stationary point at \( S_2 = 0 \). In the strong ordering limit Eq. (3.15) has the same divergent behaviour as Eq. (A.11). We compare the interpolating formula (3.15) to the numerical solution of Eq. (3.13) in Figure A.1.

A.3 Fourth moment in terms of rank two tensors

The fourth moment \( C_4 = \langle uuuu \rangle \) can be expressed exactly in terms of the second moment and the identity tensor. From symmetry considerations \( C_4 \) can be decomposed into

\[
\begin{align*}
(C_4)_{ijkl} &= S_4 n_in_j n_k n_l + X (\delta_{ij} \delta_{kl} + \delta_{il} \delta_{jk} + \delta_{ik} \delta_{jl}) \\
&\quad + Y (n_i n_j \delta_{kl} + n_k n_l \delta_{ij} + n_i n_l \delta_{jk} + n_j n_k \delta_{il} + n_i n_k \delta_{jl} + n_j n_l \delta_{ik}),
\end{align*}
\]

(A.13)

where perms. indicates additional all permutations of the indices and we recall that \( n \) is the director. The coefficients \( X \) and \( Y \) are uniquely determined by the following properties of the second and fourth moment

\[
C_{ii} = 1 \quad \text{and} \quad (C_4)_{ijkk} = C_{ij}, \quad (A.14)
\]

Figure A.1 – Comparison between the exact expression for the ideal orientational entropy from Eq. (3.13) and our interpolating formula (3.15). Also plotted are the weak and strong ordering limits, Eqs. (A.7) and (A.11) respectively.
which when combined with the relationship
\[ C_{ij} = S_2 n_in_j + \frac{1}{2} (1 - S_2) \delta_{ij}, \] (A.15)
yields
\[ X = \frac{3 + S_4 - 4S_2}{24} \quad \text{and} \quad Y = \frac{S_2 - S_4}{6}. \] (A.16)

One can then convert Eq. (A.13) to be in terms of \( C \) and \( \delta \) rather than \( n \) and \( \delta \). Finally, the relationship between the order parameters \( S_2 \) and \( S_4 \) is expressed parameterically. We take averages with the orientation distribution function \( f(\Omega) \) (c.f. Appendix A.1) for two-dimensional non-interacting rotators
\[ f(\Omega) = \frac{1}{Z} e^{-\Lambda((\mathbf{u}\cdot\delta/2))} \] (A.17)
where \( \Lambda \) is the Lagrange multiplier, which we can choose to be \( \Lambda_{11} = -\Lambda_{22} = \lambda \) without loss of generality and \( Z = I_0(\lambda) \) is the partition function; \( I_n \) is a modified Bessel function of the first kind. The Lagrange multiplier sets the average orientation of the ensemble of rotators. Writing the orientation vector as \( \mathbf{u} = (\cos \theta, \sin \theta) \) we can calculate the ensemble averages in order to obtain the order parameters
\[ S_2 = \frac{1}{Z} \int_0^{2\pi} \frac{d\Omega}{2\pi} \cos(2\Omega) e^{-\Lambda \cos 2\Omega} \frac{I_1(\lambda)}{I_0(\lambda)}, \] (A.18)
\[ S_4 = \frac{1}{Z} \int_0^{2\pi} \frac{d\Omega}{2\pi} \cos(4\Omega) e^{-\Lambda \cos 2\Omega} \frac{I_2(\lambda)}{I_0(\lambda)}. \] (A.19)

### A.4 Pairwise interactions and the superposition approximation

In the superposition approximation, the meniscus height \( h(r) \) is the sum of the deformations of individual particles. Let \( h_i(r) \) be the meniscus profile due to particle \( i \) in the absence of any other particles. Then
\[ h(r) = \sum_i^N h_i(r), \] (A.20)
with total energy equivalent to the interfacial area (assuming small gradients)
\[ F = \frac{\sigma}{2} \int \nabla h \cdot \nabla h \, d^2r \] (A.21)
\[ = \frac{\sigma}{2} \sum_{i=1}^N \nabla h_i \cdot \sum_{j=1}^N \nabla h_j \, d^2r, \] (A.22)
A.5. Ratio of SS and TT bond energies

which can be written

\[ F = \sigma \frac{N}{2} \sum_{i=1}^{N} \sum_{j \neq i} E_{ij} + \sigma \frac{N}{2} \sum_{i=1}^{N} \int \nabla h_i \cdot \nabla h_i \, d^2 r, \]  

(A.23)

where we are able to define the pairwise interaction energy as

\[ E_{ij} = \int \nabla h_i \cdot \nabla h_j \, d^2 r. \]  

(A.24)

The second term of Eq. (A.23) is just the energy cost of the meniscus deformation of noninteracting particles. Hence the superposition approximation is equivalent to assuming pairwise interactions between the particles and neglecting multibody effects.

A.5 Ratio of SS and TT bond energies

Aside from the absolute value of the bond energies, the contact angle \( \theta \) also varies the ratio between the SS and TT bond energies. In our simulations, we set \( E_{TT} \approx 20 k_B T \), so the main effect of changing \( \theta \) is to vary the ratio \( E_{SS}/E_{TT} \). We plot the ratio \( E_{SS}/E_{TT} \) using our empirical pair potential (5.4) and the fitting parameters in Table 5.1 against contact angle in Fig. A.2. Lower contact angles result in a higher ratio \( E_{SS}/E_{TT} \).

![Figure A.2 – The effect of contact angle on ratio of the SS and TT bond energies using our empirical potential.](image)

A.6 Results of simulations with the quadrupole approximation

We briefly present results of VMMC simulations with the quadrupole approximation (5.3) and show that particularly for higher aspect ratios, the approximation yields structures very different from our more accurate potential (5.4). In particular, the SS chains are far straighter, behaving as rigid rods and we see fewer TT contacts, both are due to the far greater ratio

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$E_{SS}/E_{TT}$. This can be seen in Fig. A.3, in the left (right) panels we show typical snapshots with the quadrupole approximation (our empirical potential).

![Comparison between snapshots in VMMC simulations using the quadrupole approximation and our empirical potential.](image)

Figure A.3 – Comparison between snapshots in VMMC simulations using the quadrupole approximation and our empirical potential. The upper panels show ellipsoids with $k = 4$, $\eta = 0.3$ and $\theta = 50^\circ$ after $5 \times 10^6$ VMMC sweeps. The lower panels are at a higher surface coverage $\eta = 0.4$ after $10^6$ VMMC sweeps.
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Publications

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Physics of Soft and Biological Matter, United Kingdom, 2016
20th Symposium on Thermophysical Properties, United States, 2015
International Workshop on Nonequilibrium Thermodynamics, The Netherlands, 2015
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