Edited by
Gerhard Gompper, Michael Schick

Soft Matter

Volume 2
Complex Colloidal Suspensions

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Cover illustration
The picture shows a polarization light
micrograph of colloidal boehmite rods during
isotropic-nematic phase separation. Blue color
indicates the isotropic, red color the nematic
phase. The nematic droplets sink to the
bottom because their density is slightly larger.
The schematic picture in the front shows the
orientational ordering of colloidal rods in the
nematic phase. (Original pictures courtesy of
J. Dhont and Z. Dogic).

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Preface

The study of Soft Matter is concerned with understanding the properties of materials which have structural length scales in the range of a few nanometers to several micrometers, and which are strongly affected by thermal fluctuations. Several interesting properties follow immediately from these seemingly simple conditions. For example, the long length scales imply that small external fields can lead to large perturbations, which is the origin of the name "Soft Matter". Similarly, long length scales and an energy scale on the order of the thermal energy $k_B T$ imply large structural relaxation times. Therefore, phenomena far from thermal equilibrium play a very important role.

Most soft-matter components are macromolecules which exhibit polymeric, colloidal, or amphiphilic properties. Although these materials have been studied for a long time, it has been realized only in the last two decades that these systems share many properties, so that a large synergy arises from a unification of these subfields. In recent years, this unification has become more urgent due to the fact that many biological systems and biomaterials simultaneously contain several components with different polymeric, amphiphilic and colloidal character. One example, in which all these properties are united in a single macromolecule, is provided by membrane proteins. They consist of a linear chain of amino acids, and are therefore hetero-polymers, have hydrophobic and hydrophilic parts to favor localisation in a lipid bilayer membrane, and are therefore amphiphilic, and behave in some of their properties like a cylindrical barrel, and are therefore colloidal.

The first volume of this Soft Matter series focused on system in which the polymeric properties were dominant. In this second volume, our attention is turned to systems in which the colloidal character prevails. In Chapter 1, Zvonimir Dogic and Seth Fraden provide an excellent overview of the surprising variety of structures which self-assemble in the apparently simple system consisting of a mixture of colloidal spheres and rods. In addition, the system contains non-adsorbing polymers, which serve to induce an effective attractive interaction between the colloidal components. This "depletion in-

teraction" arises from the change of accessible conformations of a polymer in the vicinity of surfaces. The theoretical description of the colloid-polymer interaction is the topic of Chapter 2 of Erich Eisenriegler, who employs the very powerful tools developed for critical phenomena to extract the universal properties of these systems. Finally, in Chapter 3, Jan Dhont and Wim Briels authoritatively describe the behavior of rod-like colloids in shear flow. This chapter addresses some of the very interesting phenomena arising in systems far from thermal equilibrium. While such non-equilibrium dynamics play an important role in all soft matter systems, colloids provide a nice model system in which to study them because colloid suspensions are comparatively simple. Thus progress in studying and understanding the new phenomena is achieved most easily.

We anticipate that the high standards set by the authors of these initial two volumes will inspire a similar level in those participating in subsequent ones. For our part, we will strive to ensure that the contents of future volumes will be as stimulating as these initial ones.

November 2005   Gerhard Gompper and Michael Schick

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1
Phase Behavior of Rod-Like Viruses and Virus–Sphere Mixtures

Zvonimir Dogic and Seth Fraden

Abstract

An overview is given of the experimental work on the liquid crystalline phase behavior of semi-flexible viruses in an aqueous solution. We start by briefly summarizing the theoretical work of Onsager which describes the isotropic-nematic phase transitions of perfectly rigid rods. Extensions of the Onsager theory to the case of semi-flexible and charged rods are presented. In the first part of the review we focus on the phase behavior of a pure solution of semi-flexible virus *fd*. With increasing concentration *fd* form isotropic, cholesteric and smectic phase. In the limit of high ionic strength the agreement between the Onsager theory and experiments on the isotropic-nematic phase of *fd* virus is quantitative. The discrepancies at low ionic strength strongly hint at a need to rigorously incorporate electrostatic interactions into phase behavior of rigid rods. In the second part of the review we focus on the phase behavior of mixtures of rods with either hard spheres or flexible polymers. Amongst others we described a number of novel phases observed in these mixtures such as a lamellar phase, columnar phase, colloidal membranes and surface induced smectic phase. These structures are still very poorly understood and there is a clear need for the theoretical work explaining their stability.

1.1
Introduction

The reasons physicists give for studying colloids are varied. Our initial motivation was that colloids can serve as model experimental systems to study simple fluids because, with careful preparation, colloids approximate hard particles. Numerous studies have investigated the phase behavior, structure,

and macroscopic viscoelastic properties of suspensions of spherical colloids (Poon and Pusey 1995). Far less studied have been colloids of anisotropic shape, in spite of their long-recognized similarity to liquid crystals. Counterintuitively, hard-rod fluids are theoretically simpler systems to understand than hard spheres (Forsyth et al. 1978). This surprising fact was first recognized by Onsager (1949), who realized that the isotropic–nematic (I–N) transition in the rod-like colloid tobacco mosaic virus (TMV) occurred at such low concentrations that only two-body interactions were necessary in order to quantitatively explain the I–N phase transition. In fact, in the limit of long thin rods, Onsager's theory becomes exact. This is in contrast to the theory of phase transitions of hard spheres, for which no exact results exist (in three dimensions).

For some years, the Complex Fluids Group at Brandeis has studied the liquid-crystalline behavior of suspensions of TMV (Fraden et al. 1985; Hurd et al. 1985; Wen and Meyer 1987; Oldenbourg et al. 1988; Fraden et al. 1989; Meyer 1990; Fraden et al. 1993; Wang et al. 1994; Fraden 1995; Adams and Fraden 1998) and filamentous phage *fd* (Tang and Fraden 1993; Tang and Fraden 1995; Fraden 1995; Tang and Fraden 1996; Dogic and Fraden 1997; Adams et al. 1998; Dogic et al. 2000; Dogic and Fraden 2001; Grelet and Fraden 2003; Dogic 2003; Purdy et al. 2003; Purdy and Fraden 2004a; Purdy and Fraden 2004b; Purdy et al. 2005). TMV is a beautiful colloidal rod (Kreibig and Wetter 1980; Wetter 1985). It is completely rigid and forms isotropic, nematic, smectic and colloidal crystalline phases. However, TMV is difficult to work with. One must cultivate tobacco plants, infect them with virus, harvest the crop, extract the virus – which takes months – and, in addition, all this must be done with care to preserve the monodispersity of the virus. Physics graduate students rebel at the thought of producing enough virus for a PhD thesis! Without an abundant source of TMV, studies of its phase behavior are impracticable.

So our laboratory switched from TMV to the semi-flexible bacteriophage *fd*, which also forms several liquid-crystalline phases: isotropic, cholesteric, and smectic, but not colloidal crystals. Because *fd* infects bacteria, growing *fd* is relatively quick and easy. Furthermore, genetic engineering of *fd* is well established, and we have produced mutants of varying length and charge.

This chapter describes the phase behavior of *fd* virus suspensions. First, we present our results on *fd* alone. The results obtained up to 1995 are summarized in another review article (Fraden 1995). While theory and experiment are in agreement for the isotropic–cholesteric phase transition for suspensions with high salt concentrations used to screen long-range electrostatic repulsion, theoretical explanations of all other phases fail. We see a quantitative discrepancy between theory and experiment for the nematic phase at low ionic strength, and multiple quantitative and qualitative breakdowns of the

theory of the smectic phase. Also, we have not even a clue of why a cholesteric phase is observed in *fd*, but a nematic in a closely related species, *pf1*, which has a nearly identical atomic structure (Grelet and Fraden 2003). Second, we present results on mixtures of the viral rods with spherical colloids or spherical polymers. Some of the phase behavior, such as depletion-induced phase separation, was as anticipated. But an astounding array of unexpected results was also observed. A laundry list includes microphase separation of rods and spheres into columnar, cubic, and lamellar structure; isolated colloidal membranes consisting of a sheet of rods and stabilized via protrusion forces; and a quasi-two-dimensional smectic phase that exists on the isotropic–nematic interface that plays a key role in phase separation kinetics. While originally we were motivated to study virus suspensions because they are model systems of simple fluids, now we are motivated by a spirit of exploration driven by the expectation that more unexpected results will follow the ones described below.

1.2
Entropy-Driven Ordering Within the Second Virial Approximation

In the first part of this chapter we briefly review the theoretical work describing liquid-crystalline phase transitions in colloidal rods. This is not meant to be exhaustive. For more detailed theoretical accounts, the reader is referred to recent review articles (Stephen and Straley 1974; Odijk 1986; Vroege and Lekkerkerker 1992) and the original article by Onsager (1949).

The majority of studies of the ordering transitions in hard-particle fluids belong to a class of theories called density-functional theories (DFTs) (Hansen and McDonald 1986). The simplest version of DFT takes into account the interactions between particles at the level of second virial approximation. The free energy of a hard-particle fluid is then

$$\frac{F}{k_{\mathrm{B}}T} = \int_V \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r}) \ln[\rho(\boldsymbol{r})] - \frac{1}{2} \int_V \mathrm{d}\boldsymbol{r}_1 \int_V \mathrm{d}\boldsymbol{r}_2\, \rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)\beta(\boldsymbol{r}_1, \boldsymbol{r}_2) \qquad (1.1)$$

where k_{B} is the Boltzmann constant, T is the absolute temperature, $\rho(\boldsymbol{r})$ denotes the density of particles, $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are vectors denoting the position and/or orientation of two particular particles, and $\beta(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the Meyer–Meyer overlap function. Its value equals -1 if there is any overlap between two hard particles located at $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$; otherwise its value is equal to zero. This expression has been used for a variety of cases to study entropy-induced ordering in hard-particle fluids. Onsager (1949) was the first to show that Eq. (1.1) is essentially exact for isotropic spherocylinders when $L/D_{\mathrm{sc}} \to \infty$, where L is the length and D_{sc} is the diameter of the spherocylinder. As

the aspect ratio of spherocylinders is increased, the third and higher virial coefficients become negligible.

The second virial theory also predicts a stable smectic phase in a solution of perfectly aligned spherocylinders as well as for spherocylinders with both positional and orientational degrees of freedom (Hosino et al. 1979; Mulder 1987; van Roij et al. 1995; van der Schoot 1996). However, to describe the suspensions quantitatively at the densities of the nematic–smectic (N–S) phase transition, it is necessary to include higher virial coefficients in the free-energy expression. For perfectly aligned spherocylinders, inclusion of the third and fourth virial coefficients into the free energy results in theoretical predictions for the N–S transitions that are in quantitative agreement with simulation results. The calculations that consider ordering transitions using only second virial coefficients are uncontrolled approximations, unless it can be shown that higher virial coefficients are negligible, as is the case of the Onsager treatment of the I–N phase transition.

In any hard-particle fluid, due to the simplicity of the interaction potential, the energy of any allowed configuration is simply proportional to $n k_B T$, with n being the number density of particles. Due to this simple fact, the minimum of the free energy of a hard-particle fluid $F = E - ST = T(\alpha - S)$ (α is a constant) is equivalent to the maximum of the entropy. Furthermore, the resulting phase diagram is temperature-independent (athermal) because both α and S are independent of temperature. Ordering transitions in hard-particle fluids are still possible because the expression for entropy, or equivalently free energy, splits into two parts. The first integral in Eq. (1.1) is the ideal part of the free energy and always attains a minimum value for the uniform probability distribution $\rho(\boldsymbol{r}) = $ constant. Therefore, this contribution to the total free energy always suppresses an ordering transition. The second integral in Eq. (1.1) represents the second virial approximation for the interaction free energy, which is proportional to the excluded volume, and under certain circumstances is lower for an ordered state. Therefore, the interaction part of the free energy drives the system toward ordering. The actual location of the ordering transition is determined from the competition between the ideal and interaction contributions to the total free energy. In this section, we briefly review the theoretical description of phase transitions that can be described using Eq. (1.1) for pure hard rods.

1.2.1
Isotropic–Nematic Phase Transition Within the Second Virial Approximation

The density functional of the sort shown in Eq. (1.1) was first used in a seminal paper by Onsager (1949). He was seeking to explain the formation of the nematic phase in solutions of rod-like tobacco mosaic virus (TMV), inorganic