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Dispersion Stability, Microstructure and Phase Transition of Anisotropic Nanodiscs

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Dispersion Stability, Microstructure and Phase Transition of Anisotropic Nanodiscs

Doctoral Thesis accepted by
Jawaharlal Nehru University, New Delhi, India

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This thesis is dedicated to my parents
for their endless love, support
and encouragement…

Supervisor's Foreword

Some of the most remarkable recent advances in colloid science have exploited the specific pairing of clay platelets to create dynamic three-dimensional structures that precisely self-assemble from individual clay particles. Pioneering work in this area has been reported by various research groups in the recent past. Colloidal self-assembly often leads to gel or glass-like organization of internal structure.

Colloidal gels can be thought of as a space filling or percolating network of particles and particulate suspensions, which can form when the system is destabilized. Under appropriate thermodynamic conditions, sufficient particle concentration and provided that the attraction between the particles is strong enough to induce aggregation, a space filling macroscopic structure is formed that effectively traps the solvent molecules. Although not in a thermodynamic equilibrium state, the network can undergo a remarkable kinetic slowdown and the resulting gel attains age-dependent viscoelastic attributes. The important parameter that affects this kinetic slowdown is the range of the attractive potential and its relation to the particle size and density. It is also important whether the contact of two particles results in a permanent bond, or if the particles have the additional freedom of rotating on top of each other. In the first case, the formation of the network is dominated by the diffusion while in the second case there is a slow kinetic evolution driven by the phase separation occurring in the system.

On the other hand, colloidal glasses are concentrated suspensions of microscopic particles in a liquid in which the particles' movements are constrained; they hold some freedom for local Brownian motions, but are unable to diffuse over large lengths. Due to this localization, colloidal glasses at rest are amorphous solids. Nevertheless, they are typically soft solids, deforming elastically under small applied stresses, but yielding and flowing when stressed more strongly.

The objective of this thesis was to develop a general understanding of self-assembly of anisotropically charged platelets through coarse grained model that is simple enough to be experimentally verifiable, but complex enough to capture the structural, thermodynamic, and mechanical properties of the material. By focusing on the basic physics of single platelets, their finite clusters, and the transitions to gel or glass phases, Dr. Ravi Kumar Pujala was able to quantitatively describe many of the underlying physical processes that can be exploited to generate smart functional nanostructures from clay particles. At the same time, detailed analysis of the experimental data helped constrain and improve the theoretical models considerably.

Dr. Ravi Kumar was able to provide detailed information about the pathways explored during a full cycle of colloidal dispersion, gelation, glass formation, and their aging dynamics. These new observations are a step-change improvement over previous attempts to quantify aging dynamics of colloidal self-assembly. The results and conclusions contained in this thesis are thought-provoking and will guide future researchers for a long time to come.

New Delhi, April 2014 Prof. Himadri B. Bohidar

Abstract

This thesis explores the dispersion stability, microstructure and phase transitions involved in the nanoclay system. It describes the recently discovered formation of colloidal gels via two routes: the first is through phase separation and second is by equilibrium gelation and includes the first reported experimental observation of a system with high aspect ratio nanodiscs. The phase behaviour of anisotropic nanodiscs of different aspect ratio in their individual and mixed states in aqueous and hydrophobic media is investigated. Distinct phase separation, equilibrium fluid and equilibrium gel phases are observed in nanoclay dispersions with extensive aging. The work then explores solution behavior, gelation kinetics, aging dynamics and temperature-induced ordering in the individual and mixed states of these discotic colloids. Anisotropic ordering dynamics induced by a water-air interface, waiting time and temperature in these dispersions were studied in great detail along with aggregation behavior of nanoplatelets in hydrophobic environment of alcohol solutions.

Acknowledgments

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Thank you Lord, for always being there for me.

Dr. Ravi Kumar Pujala

Contents

Chapter 1
Introduction

Abstract This chapter introduces the basic elements of the soft matter and colloids, gives the motivation, formulates the importance of present work and finally presents the outline of the thesis.

1.1 Soft Matter

Undoubtedly, soft matter science is rapidly growing and this interdisciplinary field of research has equally attracted attention from diverse group of scientists ranging from chemists, physicists to engineers. What is "Soft Matter"? In the words of Noble Laureate, P.G. de Gennes "*What do we mean by soft matter? Americans prefer to call it "complex fluids". This is a rather ugly name, which tends to discourage the young students. But it does indeed bring in two of the major features:* (1) *complexity and* (2) *flexibility*" [3]. In the most general terms, soft condensed matter is a matter that is "*soft*" at room temperature. The term "*soft*" is referred to substances whose molecules can be moved to significant distances by the application of relatively weak forces. Moreover, soft matter is easily deformed by electromagnetic fields, thermal fluctuations and external stresses. The field of soft matter science consists of polymers, colloids, liquid crystals and biological materials. One picture is worth a thousand words, so the entire field of soft matter science is summarized in Fig. 1.1.

Typically the interactions involved in soft matter science can be divided into two main categories: simple and structural. Simple interactions: dipole–dipole interactions, ionic interactions, steric interactions and hydrogen bonding. Structural interaction: excluded volume interaction which is responsible for local order and space filling. Nevertheless, the crossover from simple to structural interactions has to do with the connection between microscopic and mesoscopic scales [10]. My research focuses on colloids, which exhibit numerous interesting and complex features.

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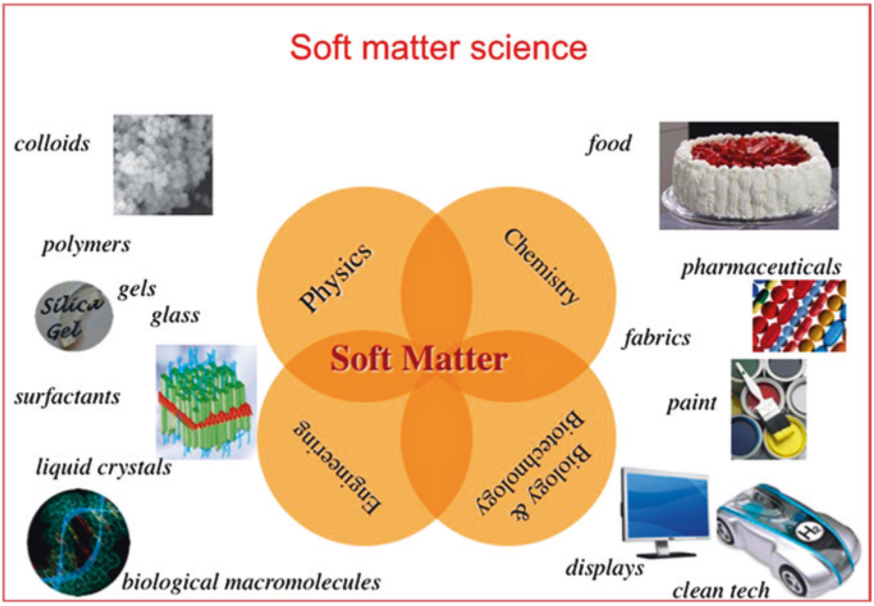

Fig. 1.1 Display of significance of soft matter in various fields of science and technology. (From the lecture "Soft Matter Physics HT08" by Aleksandar Matic)

1.2 Colloids

Colloidal systems of gold particles were already known many centuries ago, and their nature, being "extremely finely divided gold in fluid", was realized as early as 1774 by Juncher and Macquer. Thomas Graham coined the term "colloid" (which means "glue" in Greek) in 1861 to describe Selmi's "pseudosolutions" [6]. This term punctuates their lack of crystallinity and low rate of diffusion. He derived that the low rate of diffusion implied that the particles were fairly large enough than the solvent molecules—in modern terms it is at least 1 nm in size. But then, the absence of particle sedimentation implied an upper size limit of 1 μm. Till date Graham's definition of the range of particle sizes that characterize the colloidal domain is still widely employed. Thus the colloidal systems are solutions of "*large molecules*". The large molecules are *Brownian* or *colloidal particles*. These particle sizes should be large compared to the solvent molecules, but still small enough to exhibit thermal motion in a fluid background solvent. Colloidal solutions are most commonly referred to as *dispersions* or *suspensions* or since here materials is "dispersed" or "suspended" in a liquid phase.

Nowadays colloid science is examining the systems involving particle sizes defined earlier of wide range of systems of scientific and technological importance. Some examples: paints, ceramics, soils, agricultural sprays, cosmetics, biological cells, detergents and many food formulations. Nearly almost all experimental techniques and theoretical procedures of modern physics and modern