Current Opinion in Colloid & Interface Science 21 (2016) 76–85

Contents lists available at ScienceDirect

Current Opinion in Colloid & Interface Science

journal homepage: www.elsevier.com/locate/cocis

Collective dynamics of dipolar and multipolar colloids: From passive to active systems

Sabine H.L. Klapp

Institut für Theoretische Physik, Sekr. EW 7–1, Technische Universität Berlin, Hardenbergstrasse 36, D-10623 Berlin, Germany

ARTICLE INFO

Article history:
Received 4 October 2015
Received in revised form 25 January 2016
Accepted 26 January 2016
Available online 11 February 2016

Keywords:
Dipolar colloids
Computer simulations
Dynamical structures
Colloidal networks
Synchronization
Laning transition

ABSTRACT

This article reviews recent research on the collective dynamical behavior of colloids with dipolar or multipolar interactions. Indeed, whereas equilibrium structures and static self-assembly of such systems are now rather well understood, the past years have seen an explosion of interest in understanding dynamicals aspects, from the relaxation dynamics of strongly correlated dipolar networks over systems driven by time-dependent, electric, or magnetic fields, to pattern formation and dynamical control of active, self-propelled systems. Unraveling the underlying mechanisms is crucial for a deeper understanding of self-assembly in and out of equilibrium and the use of such particles as functional devices. At the same time, the complex dynamics of dipolar colloids poses challenging physical questions and puts forward their role as model systems for nonlinear behavior in condensed matter physics. Here we attempt to give an overview of these developments, with an emphasis on theoretical and simulation studies.

1. Introduction and scope of this article

Colloids with anisotropic, directional interactions play nowadays a major role in the field of self-assembly of colloidal matter, in microfluidics, the design of functional devices such as robots and sensors, but also as theoretically and experimentally accessible model systems in condensed matter physics. A paradigm example is dipolar colloids whose interactions are governed by permanent or field-induced, magnetic or electric dipole moments, as well as particles with more complex multipolar interactions.

While earlier research has rather focused on understanding the (often unusual) equilibrium phase behavior and static self-assembly of such systems, the last years have seen substantial progress in understanding dynamical properties [1], from the single-particle response over the collective dynamics of strongly correlated, driven systems [2,3] toward the dynamics of active dipolar systems [4,5]. The purposes of the present review are to give an overview of recent developments in this emerging field from a theoretical point of view and to outline perspectives for future research. The focus lies on systems composed of *spherical* particles with dipolar or multipolar interactions since these have been studied in most detail so far. However, a trend toward shape-anisotropic dipolar systems is already foreseeable [6•,7•].

We start by discussing dynamical properties close to equilibrium, such as the relaxation dynamics and gelation of self-assembled structures. These properties are highly relevant, e.g., for the resulting materials' elastic response and conductivity [8]. A second topic is the *non-equilibrium* behavior of dipolar systems generated by a time-dependent, rotating external field. Indeed, time-dependent fields have recently shown to induce not only unusual (quasi-static) structures but also complex nonlinear dynamics such as synchronization (and related structural) transitions [2]. Third, we discuss the collective (translational) transport properties of dipolar systems in alternating fields [9] and in "active" systems where the particles are driven by an internal energy source [5]. Indeed, active dipoles are an exemplary topic where current research on active-particle systems and that on passive complex systems meet, and where a stimulating interplay can be foreseen. In fact, there are many research themes which are "hot topics" in both areas, such as the interplay of clustering/aggregation and equilibrium phase separation [10, 11], as well as the control of (single-particle and collective) motion by external, magnetic or electric fields [4]. Thus, a comprehensive discussion highlighting the interface of these fields of research is timely.

There are a number of topics which are related to the overall theme of this article but are not covered or touched only briefly here. Examples are the equilibrium structures of dipolar colloids in the ground state and at finite temperatures (see, e.g. [12]), the behavior of electro- and magnetorheological systems in static fields [13], the dynamics under

E-mail address: klapp@physik.tu-berlin.de.

http://dx.doi.org/10.1016/j.cocis.2016.01.004
1359-0294/

shear flow [14], the behavior of magnetic elastomers [15, 16], and the dynamics and growth of the closely related patchy particle systems [17,18].

2. Models

This section gives an overview of models typically discussed in the context of dipolar colloidal systems. We focus here on monodisperse systems of *spherical* particles. The directional interaction between particles i and j, $U^{\text{aniso}}(ij)$, results either from permanent magnetic (ferromagnetic) moments or charge distributions, respectively, or it is induced by an external field. In addition, the spheres interact via a short-range potential $U^{\text{sr}}(ij)$, such as the purely repulsive hard-sphere and soft-sphere potentials, or the Lennard–Jones potential which includes attractive (van der Waals) interactions. Some important representatives of such particles are shown in Fig. 1. The "paradigm" model for ferromagnetic particles (permanent moment) are hard spheres with embedded point dipoles $\boldsymbol{\mu}_i$ and $\boldsymbol{\mu}_j$ (the so-called "dipolar hard sphere" (DHS) model) in their center, Fig. 1(a), where the anisotropic part of the interaction is given by the usual dipole–dipole potential,

$$U^{\text{D}}\left(\boldsymbol{r}_{ij},\boldsymbol{\mu}_i,\boldsymbol{\mu}_j\right)=\frac{\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j}{r_{ij}^3}-\frac{3\left(\boldsymbol{r}_{ij}\cdot\boldsymbol{\mu}_i\right)\left(\boldsymbol{r}_{ij}\cdot\boldsymbol{\mu}_j\right)}{r_{ij}^5}, \tag{1}$$

with $\boldsymbol{r}_{ij}$ being the connecting vector and $r_{ij}=|\boldsymbol{r}_{ij}|$. Fig. 1(b) shows a variant characterized by an *off-centered*, laterally shifted permanent point dipole; this (and related off-centered) model(s) has been recently introduced [19-22] to describe the behavior of chemically heterogeneous spherical particles such as magnetic Janus spheres composed of two different magnetic materials (see, e.g., [23,24]). In some cases, the point dipole approximation has found to be inappropriate or computationally inefficient, thus, models with spatially separated charges (see Fig. 1(c)) interacting either with true Coulombic interactions [8,25,26] or exponentially screened, Yukawa-like potentials [27] are used as well.

The bottom row of Fig. 1 shows models of particles with "multipolar" interactions, involving either more than one (point) dipole moment, or more than two spatially separated charges. The models in Fig. 1(d and e) have been inspired by metallodielectric Janus spheres such as polystyrene colloids with gold patches. Experimentally, such particles have been extensively investigated [28-30] in a quasi-2D set-up (realized by two confining glass plates), where they are dissolved in water and exposed to an in-plane AC electric field. The latter creates an induced dipole moment in both parts of the metallodielectric particles. Interestingly, not only the magnitude of these dipoles but also their direction (and thus, the character of the resulting interaction) depends on the frequency (f) of the AC field, the physical reason being the frequency dependence of the polarizability of the two particle domains. In particular, while the gold patch is strongly polarized along the field at any f, the polarizability of the dielectric part (together with its counterionic atmosphere) switches its sign from positive, Fig. 1(e), to negative, Fig. 1(d), at a critical frequency f_c. Corresponding models have been suggested in [31,32]. The resulting anisotropic interaction between two spheres is then the sum of the dipole–dipole interactions, Eq. (1), between each moment (polarization effects have so far not been investigated). Finally, Fig. 1(f) sketches a particle with crossed, extended dipoles induced by a combination of two external fields [6,33]. Even more complex charge distributions have been suggested in the context of "inverse patchy colloids" [34,35].

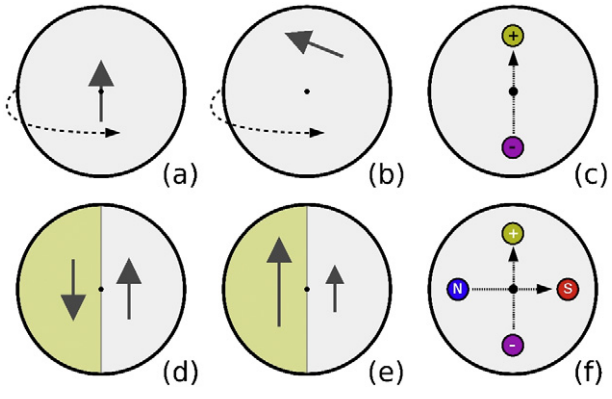

Fig. 1. Sketches of model colloids with dipolar (a–c) or multipolar (d–e) character. Specifically: (a) Dipolar hard or soft sphere with permanent point dipole moment in its center; (b) sphere with off-centered point dipole shifted laterally (dipole moment is perpendicular to the radius vector); (c) sphere with two charges representing an extended (permanent or induced) dipole; (d) Janus-like sphere with two induced, off-centered point dipoles oriented in opposite direction; (e) Janus-like sphere with two induced, parallel dipoles; (d) sphere with two crossed, electric and magnetic, dipoles induced by bi-directional fields.

2.1. Common theoretical and computational methods

Many of the theoretical studies on passive dipolar systems involve particle-resolved computer simulations such as molecular dynamics (MD), that is, solution of the coupled Newtonian equations of motion; Langevin dynamics (LD), which is based on underdamped stochastic differential equations with friction and white noise, and Brownian dynamics (BD) based on overdamped Langevin equations. Combinations of MD and the Navier–Stokes equation to incorporate hydrodynamic flows have been used as well [36]. Besides particle-resolved computations, the dynamics of dipole-coupled colloids has been investigated by a variety of effective single-particle theories (to which we will refer in the text) and field methods such as (dynamical) density functional theory. The latter is based on a generalized diffusion equation, where particle interactions are incorporated adiabatically via a free energy density functional derived from equilibrium (static) density functional theory (see, e.g., [37]). Similar to the passice case, current theoretical studies of active particle systems heavily involve particle-based simulations such as BD, but also methods incorporating hydrodynamics at low Reynolds numbers where the Navier–Stokes equation reduces to the Stokes equation. Common representatives are multi-particle collision dynamics (see, e.g., [38,39]) and Stokesian dynamics [40]. At the same time, these systems are studied on the basis of kinetic (Fokker–Planck–type) equations [41], by dynamical density functional theory [42] as well as via continuum approaches [43•].

3. Aggregation and relaxation dynamics

In this section, we summarize recent theoretical work on the dynamics of dipolar and multipolar colloids close to thermodynamic equilbrium, that is, in the absence of a driving field or an intrinsic propulsion mechanism. In particular, we discuss aspects of kinetic aggregation and dynamical slowing-down.

3.1. Simple dipolar systems: Self-diffusion and gelation

Dipolar particles are prototypes of self-assembling systems: even for the simplest systems, that is, spheres with centered point dipoles (see Fig. 1(a)), the resulting interaction given in Eq. (1) is characterized by strong anisotropy favoring head-to-tail ordering. Equilibrium aspects of the resulting cluster- and chain formation in model systems with dipolar (or multipolar) interactions have been studied extensively by computer simulations, ground state calculations, and association theories (see, e.g., [12,44,45] and references therein) and are nowadays quite well understood. This concerns both systems in external fields and zero-field systems involving permanent dipoles. We note, however, that establishing the precise relation between clustering and the equilibrium *phase diagram*, particularly the existence of a first-order