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Anisometric and anisotropic magnetic colloids: How to tune the response

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ABSTRACT

We present a comparative study of the anisometric and anisotropic magnetic colloids at low temperatures. As examples we choose the ellipsoidal and cubic magnetic colloids to illustrate the influence of the shape (particle anisometry) on the ground state structures. To scrutinise the influence of the internal particle anisotropy we address particles with dipoles shifted out from the centre of mass. Of the latter, we distinguish between two types: the first type has a dipole moment pointing radially outwards; the other has a dipole pointing perpendicular to the radius along which it is shifted.

1. Introduction

Nowadays, materials whose properties can be fine-tuned by external fields of moderate and low strengths are widely studied. “Green” environmentally friendly systems and biologically compatible materials are of particular interest, especially for medical applications. In order to obtain a system with desired properties, for example, with a controllable response to electric/magnetic fields, one needs to design this system on the level of its microstructure. When it comes to dipolar systems, the characteristic sizes of this microstructure can vary from several Ångström to tens of microns. Experimental studies of these new dipolar “smart materials” often involve rather expensive equipment and compounds, and can turn out to be very time consuming. Thus, the first step would be to predict theoretically (analytically and/or in computer simulations) the relationship between a certain microstructure and the macroscopical behaviour of the system.

The self-assembly of nano and micron sized particles play a crucial part in the microstructure formation. Understanding and predicting the processes by which these particles assemble is allowing taylor-made materials to be built from the bottom up. Usual model to study self-assembly in dipolar soft matter employs the system of dipolar hard spheres (DHS)—monodisperse hard spheres of diameter d, possessing a point dipole moment $\mathbf{m}$ in their centres [1–10]. The main conclusion of the latter works is that DHS at room temperatures form a gas phase, then, on cooling, the chain formation starts, which at low temperatures are replaced by that of rings or branched structures depending on the particle concentration. There are two possible ways to make the DHS model more complex. The first one is to change the properties of the carrier, and to introduce a certain magneto-elastic coupling into the system, like, for example, in magnetic gels [11] or magnetoelastomers [12].

Another avenue often exploited in self-assembling systems is to keep the carrier matrix simple, but to modify the particles themselves [15–20]. This can come in a number of forms: the shape of the particle can be anisotropic e.g. spheroids, rods and spherocylinders [21,22], or you can manipulate the positioning of the dipole within the spherical particle, like with sd-particles or magnetic Janus ones [23].

In the present manuscript we decided to study one pair of anisometric magnetic colloids, namely magnetic ellipsoids [24] and magnetic cubes; and one pair of anisotropic particles, namely sd-partcles [14,25–27] and magnetic Janus particles. We focus here on the ground states of these systems, i.e. we investigate the mostly energetically advantageous configurations of particles at 0 K. This way, one can deeper understand the influence of various parameters on the energy landscapes for various anisotropic and anisometric systems.

The manuscript is organised as follows. The first section is dedicated to shape anisotropy. In the first part of Section 1.1 we present the comparative analysis of the two-particle ground states for ellipsoids and cubes with various orientations of the dipole moment. In the second part of this section we discuss the topology

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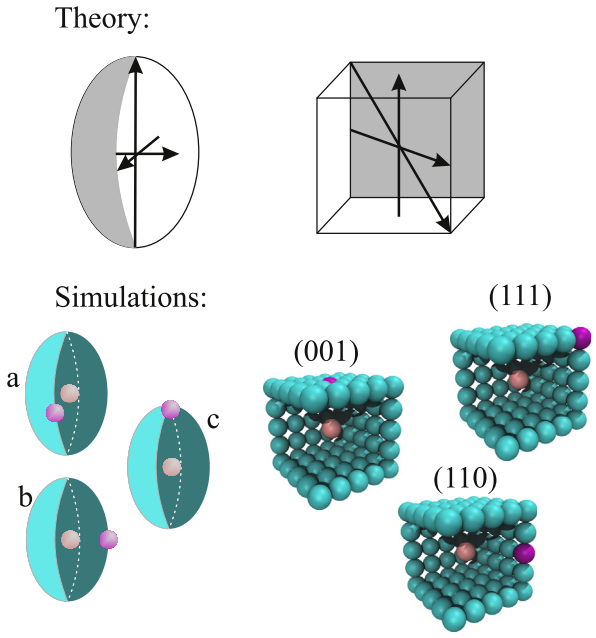

Fig. 1. Sketch of the dipole orientations in theory and simulations for anisometric particles. Cubes in simulations are made of spheres, whereas the ellipsoids are modified Gay–Berne gaussians [13]. In simulations the dipole moment is in the virtual-site particle [14]; the violet particle is just to show the orientation of the dipole. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

of small clusters and study the dependence of the clusters' total dipole moment on the cluster size. Section 2 contains the study of the spherical particles with internal anisotropy, namely, we compare a model for so-called sd-particles to a model for magnetic Janus particles. Here, we mainly focus on the two-particle ground states, and then discuss shortly the larger clusters. The manuscript ends with a brief summary and outlook.

1.1. Ellipsoids versus cubes

Let us first consider an ellipsoidal and a cubic particle. For an ellipsoid we choose three possible orientations of the dipole moment (along each of the axis), see Fig. 1. As one can see, for a cube, one can also choose three different directions of a dipole (crystallographic axes (001), (110) and (111)). In the present manuscript in order to make a comparison easier, for ellipsoids the shortest axes (a) is 1, the next one (b) is $\sqrt{2}$, and the longest axes (c) is $\sqrt{3}$.

We employ computer simulations and analytical calculations to find the ground states of the systems. The details of the method could be found in [7,28]. Computer simulations are performed in ESPResSo [29].

1.2. Two particles

Let us consider two-particle interaction as the one between two hard bodies with point dipoles in their centres of mass. In this case the interaction potentials have the following form:

$$U_d(ij) = -\frac{\mu_0}{4\pi}\left[3\frac{(\mathbf{m}_i\cdot\mathbf{r}_{ij})(\mathbf{m}_j\cdot\mathbf{r}_{ij})}{r_{ij}^5} - \frac{(\mathbf{m}_i\cdot\mathbf{m}_j)}{r_{ij}^3}\right], \quad (1)$$

$$r_{ij} = |\mathbf{r}_{ij}| = |\mathbf{r}_i - \mathbf{r}_j|,$$

where $\mathbf{r}_{ij}$ is the displacement vector of the two particles and μ_0 is the vacuum permeability. The steric potential in a general form can be written

$$U_s = \begin{cases} \infty & \text{if ovelap;} \\ 0 & \text{otherwise.} \end{cases} \quad (2)$$

Thus, for two ellipsoids only two ground states are possible. If the dipole is aligned along the shorter axes, the head-to-tail configuration is the most energetically advantageous, whereas if the dipole is aligned along the long axes, and the minimal semiaxis ratio is smaller than a critical one ($2^{1/3}$), the antiparallel pair becomes the state with the lowest energy. For cubes we obtain the head-to-tail or zig-zag structures to provide the ground states. It is important to underline that already at this stage we see an important difference between the cubes and the ellipsoids: two ellipsoids do have the ground state with a zero total dipole moment, whereas two cubes do not.

1.3. Small clusters

In this subsection we investigate small systems of ellipsoids and cubes in quasi two dimensions (q2D) with the total number of particles N less than 16. From earlier studies we know that for ellipsoids with the dipole moment along the short axis, both for two and three dimensions, that a chain or a daisy (a ring of ellipsoids) are the ground state topologies. The number of particles

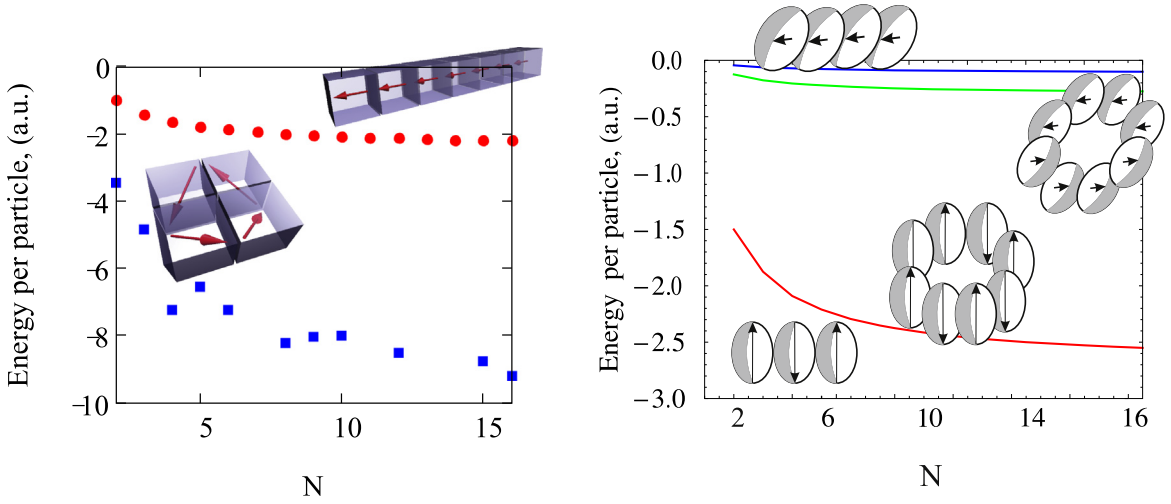

Fig. 2. The energy per particle as a function of N: (left) cubes, two different orientations are used as shown in the inset; (right) ellipsoids and three different orientations of the dipole. Note that all chain-forming ellipsoids will exhibit a closing chain-ring transition, whereas the cubes never do, and the chain remains.