Chapter

Introductory Chapter: An Example in Superparamagnetic Colloids

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1. Magnetic beads aggregation

Magnetic colloids is an increasingly growth field that includes all the physical phenomena related to magnetic interactions in a colloidal suspension. Research on magnetic suspensions is extensive and of high importance in the physics community. The involved areas range from theoretical statistical mechanics and experimental physics to numerical methods such as Monte Carlo, Langevin dynamics and the Lattice-Boltzmann method. A good review of the main components of the theory of ferromagnets can be found in [1], which is used as a standard textbook in any solid-state physics course. The aim of this introduction is to straightforward lead to a concrete example in ferrofluids. I will provide a brief description as a demonstrative instance of how the research topics in this field become rapidly complex and rich in contents (more than three areas of physics combined). In the present case, the involved research areas are statistical mechanics, electromagnetism, thermodynamics of mixing and solid-state physics.

In thermodynamic equilibrium, superparamagnetic monomers at the micron scale gather forming chains [2] parallel to the magnetic field direction. In turn, chains aggregate building one-layered structures (ribbons or bundles) due to the screening effect inherited by the magnetic potential of a dipole [3] and the effective potential between chains or between a chain and a bundle. The latter was experimentally found in a quasi-two-dimensional vessel under a uniform magnetic field. A detailed study of the interaction between a magnetic particle and a chain and between two chains is given in [4]. In the latter reference, the formation process is addressed including compact packing and noncompact cases (referred as barely touching chains).

2. Cohesion energy of the aggregates

The study of formed (after aggregation) compact regular and quasi-rectangular bundles of number of particles n, width d and length s (these distances are measured in number of grains) has been performed in [5]. In addition to these cases here, a description of non-rectangular (irregular) bundles is included. Rectangular aggregates contain a number of particles $n = ds$, quasi-regular aggregates hold $n = ds + n\%d$ and non-rectangular bundles have irregular forms due to the aggregation process in thermodynamic equilibrium (see **Figure 1**). $n\%d$ is equal to the rest of the integer division n/d. Regular and quasi-rectangular aggregates of the same width cannot have the same amount of particles since the rest $n\%d$ is zero only in regular cases. Nevertheless, rectangular and quasi-regular bundles of different width can contain the same number of grains. Irregular ribbons can coincide in n with a rectangular or a quasi-regular bundle (see **Figure 1b,c**). The energies of the

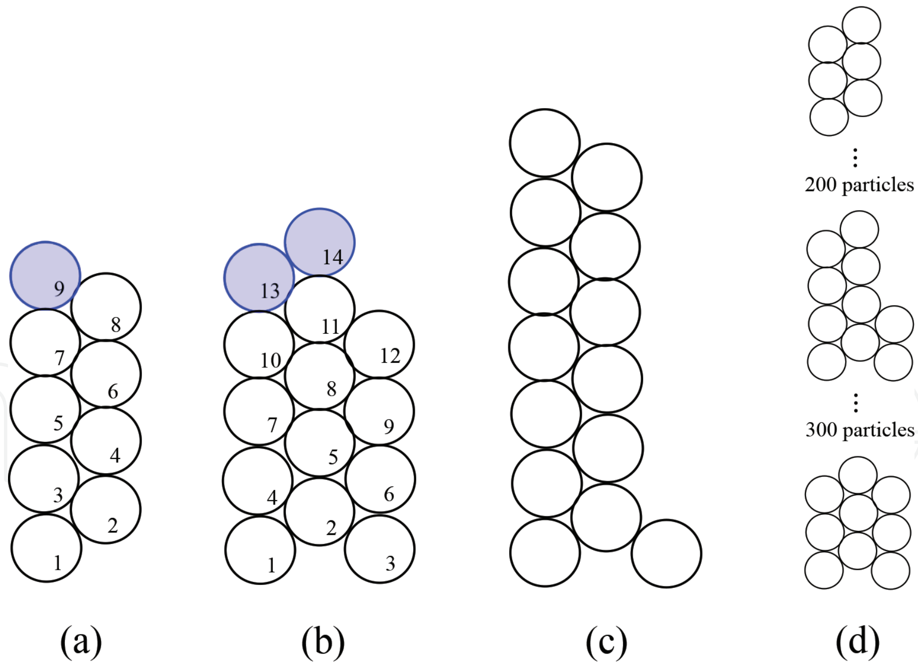

Figure 1.
Indexed compact (quasi-)rectangular bundles in the cases (a) (d, s) = (2, 4) and (b) (d, s) = (3, 4) with a total number of particles n = ds + n%d and rest particles (blue) filled. (c) Not indexed compact irregular aggregate at n = 14. (d) Non-rectangular aggregate of size n = 500 with upper width $d_1 = 2$ and lower width $d_2 = 3$.

latter cases are different. The amount of magnetic interactions in a ribbon is separated in the number of negative interactions $n_m^{(i)}$ and the number of positive bonds $n_p^{(i)}$ (relative to attractive and repulsive forces, respectively) at each order i, which is employed to compute the energy of a chain or regular bundle up to order i_{max}:

$$U^{(i_{max})}(d,n) = \sum_{i=1}^{i_{max}} n_m^{(i)} e_m^{(i)} + n_p^{(i)} e_p^{(i)} \tag{1}$$

Here $e_m^{(i)}$ and $e_p^{(i)}$ are the magnitude of negative and positive bonds at each order, respectively. The order of positive and negative interactions is relative to the distance between two grains in a ribbon [1]. Eq. (1) (see **Figure 2**) yields the explicit dependence of the aggregate energy on d and s; at higher orders the results converge to the exact curves obtained in [5] with a different method (indexing grains). Thus, the exact curves serve as a reference of the rectangular or quasi-regular ribbon magnetic energy dependency on the number of particles, although this dependence is different if irregular cases are considered. Eq. (1) is also useful to fit the exact results and to compute the energy of irregular bundles.

Quasi-regular bundles can be approximated to rectangular cases; this is called coarse-grained approximation since it does not take into account details (local groups of points) [5]. Irregular ribbons can have the same energy and number of grains of the reference (exact) curves (d = 1, 2, 3, 4), although their energy is in general located around these curves. Some cases are similar to rectangular or quasi-regular aggregates as shown in **Figure 1c**, where a non-rectangular ribbon is similar to a bundle of width d = 2; in this case its energy is equal to the energy of the regular aggregate plus all the interactions relative to the extra particle. Irregular aggregates occur also at higher n (see **Figure 1d**); the energy of a bundle at n = 500 is equal to the rectangular case n = 600 minus all the interactions relative to the 100 particles lacking at the third column. An intersection point in **Figure 2** occurs when two bundles of different width have the same number of particles and energy; the reference curves indicate that wider aggregates are more stable at increasing the number of particles, which is a plausible explanation for the experimental observation of

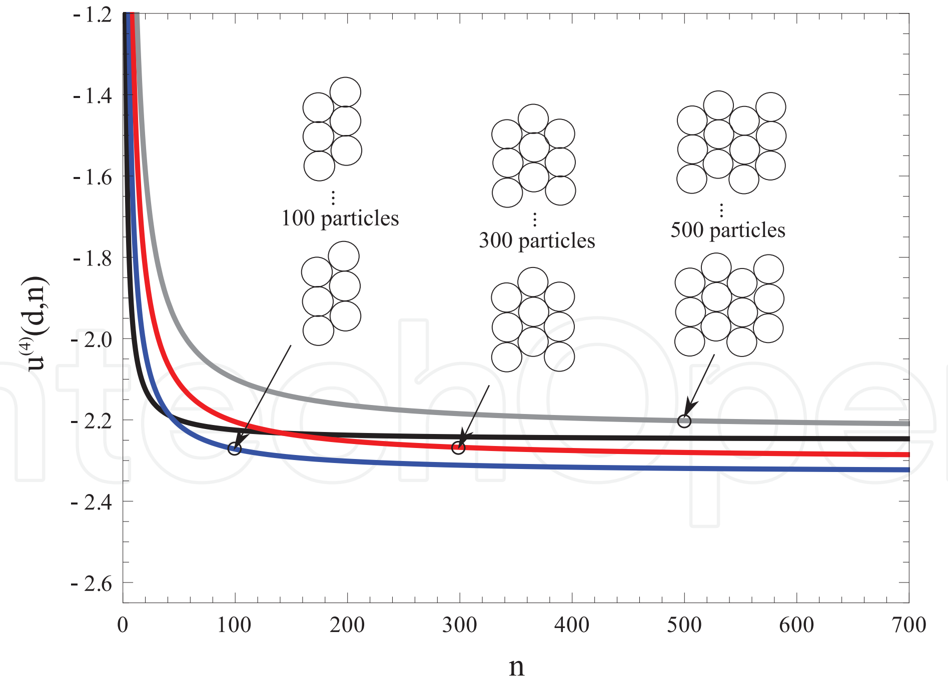

Figure 2.
Normalised magnetic energy of regular bundles at the fourth order, d = 1 (black), d = 2 (blue), d = 3 (red) and d = 4 (grey) curves. First intersection at about n = 40. Schemes of regular aggregates at (d, n) = (2, 100), (3, 300) and (4, 500) marked in circles. Convergence to the exact curves and intersections at n = 30, 113, 263 are obtained at higher orders.

ribbons in the suspension. The exact curves can be employed in statistical tools such as the standard part of the chemical potential and the equilibrium constant in order to obtain the mean length of the aggregates, which present multistability at increasing the magnitude of the imposed magnetic field.

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