Calculation of Geometrical Packing and Binding Energy of Self-Assembled Magnetic Tubular Structures

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Abstract—**This paper is dealing with tubular structures composed through the self-assembly of magnetic hard spheres, in a given geometric confinement. Since the structures are tubes, geometric confinement is a cylinder with a given radius (confinement radius). Interaction of interest is magnetic dipole-dipole interaction, therefore a detailed analysis of it is provided. Next step is formation of the structures. We are analyzing infinitely long tubes, therefore an efficient method (Lekner method) for summing the dipole-dipole interactions of 1D periodical systems (periodical along one direction, the z-axis) is implemented in MATLAB. One of the main goals is determination of energetically favoured configurations, so a comparison of the tubes' energy has been done.**

Key words-calculations; geometrical packing; binding energy; magnetic; tubes; MATLAB

I. INTRODUCTION

Self-assembly of magnetic particles is an interesting and relevant research topic which investigates the ways of forming regular structures composed of magnetic particles, in a fixed geometric confinement. Interaction between each two particles is magnetic dipole-dipole interaction [1]. What is a magnetic particle? It is a hard sphere which is a magnet (it has magnetic dipole moment). Why is this topic attractive? First of all, it is relevant from the theoretical point of view, since the dipole-dipole interaction is a long-ranged ($\sim 1/r^3$, r is the distance) and unisotropic interaction. Applications of magnetic structures are numerous, especially in nanoelectronics and biotechnology. For example, in nanotechnology, mixtures of self-assembled magnetic particles can lead to the formation of very strong magnets [2,3]. Interaction between magnetic planar layers can lead to 3D structures with a great potential for the microfabrication of electronic devices [4]. Ground states of microstructures in ferofluid monolayers, in which the interaction is magnetic dipole-dipole interaction, have been investigated [5]. In the paper [6] self-assembled magnetic structures with minimal energy (ground state) have been found. It has been shown that as the number of particles, N, increases, the dimensionality of the ground state structures increases as well. For a small number of particles ($N = \{2, 3\}$), a chain is the ground state. For ($3 < N < 14$), a chain closes into a ring. In the end, for a sufficiently big number of particles ($N > 13$) ground state is obtained via ring stacking. There is a clear transition with the increase of N, since a chain is 1D, a ring is 2D and stacked rings is a 3D structure. The subject of this paper is investigation of 3D structures (infinitely long tubes) formed via ring stacking into tubes. In the first part of this paper, a detailed analysis of the magnetic dipole-dipole interaction is performed, in order to better understand self-assembly of magnetic particles. There are two specific geometrical packings of the rings into tubes (square and triangular), leading to so called, AA and AB tubes. Our goal is to form a certain structure and calculate its binding energy, which is a result of the dipole-dipole interactions of each pair of particles that are building it. Once a structure is built geometrically, its dipole orientation (also called magnetization) should be defined. We have introduced three different magnetizations (ST/MT/ZZ magnetization) and compared their impact on the energy. Also, for a fixed magnetization, a scan over a wide range of confinement radii has been done, in order to understand how does the energy change when the confinement radius increases. When the confinement radius goes to infinity, then a convergence to corresponding lattice plane happens [6], which confirms the accuracy of the implemented summation method.

II. MAGNETIC DIPOLE-DIPOLE INTERACTION

Interaction for modelling the self-assembly of hard magnetic spheres is magnetic dipole-dipole interaction.
It occurs between two particles with magnetic moments $\mathbf{m_1}$ and $\mathbf{m_2}$. Potential energy of this interaction has the form:

$$U_{dd}(\vec{r}_{12}) = C\left[\frac{(\vec{m}_1 \cdot \vec{m}_2)}{r^3} - 3\frac{(\vec{m}_1 \cdot \vec{r}_{12})(\vec{m}_2 \cdot \vec{r}_{12})}{r^5}\right] \quad (1)$$

In the above equation, constant C is:

$$C = \frac{\mu_0}{4\pi} = 10^{-7}\left[\frac{H}{m}\right] \quad (2)$$

and the position vector connecting the two particles is $\mathbf{r_{12}} = \mathbf{r_1} - \mathbf{r_2}$. Distance between the particles is the moduo of this vector and we note it as r. Let us assume that magnetic moments belong to the same plane. In such a case, they have two components, one normal to the direction of $\mathbf{r_{12}}$, $\mathbf{m_n}$ and the other one parallel to it, $\mathbf{m_p}$. It leads to the expression for the potential energy:

$$U_{dd} = C\left[\frac{\left(m_{1n}m_{2n} + m_{1p}m_{2p}\right)}{r^3} - 3\frac{m_{1p}m_{2p}r^2}{r^5}\right] \quad (3)$$
$$\Rightarrow U_{dd} = C\frac{m_{1n}m_{2n} - 2m_{1p}m_{2p}}{r^3}$$

In the next figure, a sketch of the two dipoles that we are analyzing is shown.

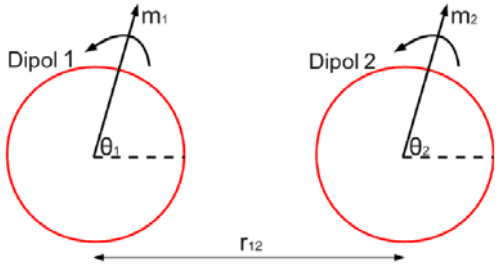

Figure 1. A sketch of two dipoles interacting via magnetic dipole-dipole interaction

Potential of their interaction has been derived. Let us normalize the values of the variables in it:

$$C = 1.\left|\vec{m}_1\right| = \left|\vec{m}_2\right| = 1, \vec{r}_1 = [000], \vec{r}_2 = [010] \quad (4)$$

Vectors $\mathbf{m_1}$ and $\mathbf{m_2}$ form the angles θ_1 and θ_2 with the direction of vector $\mathbf{r_{12}}$. Let us write:

$$m_p = m\cos\theta$$
$$m_n = m\sin\theta \quad (5)$$

There is a compact expression for the potential:

$$U_{dd} = C\frac{m_1m_2\sin\theta_1\sin\theta_2 - 2m_1m_2\cos\theta_1\cos\theta_2}{r^3} \quad (6)$$

Let us test how does the potential depend on the mutual orientation of the dipoles. We are scanning the angle θ_1 in 1000 points over the full range,, and angle θ_2 takes selected values. In Fig. 2 the potential depending on the mutual dipole orientation is shown. Potential has a minimum when the dipoles are parallel to vector $\mathbf{r_{12}}$ and they point to the same direction. It has a maximum when the dipoles have opposite directions, parallel to vector $\mathbf{r_{12}}$. The same stands if the dipoles are normal to vector $\mathbf{r_{12}}$, just the absolute values of the potential are smaller. Stars indicate the higher absolute value minimum and maximum, while triangles indicate lower absolute value minimum and maximum.

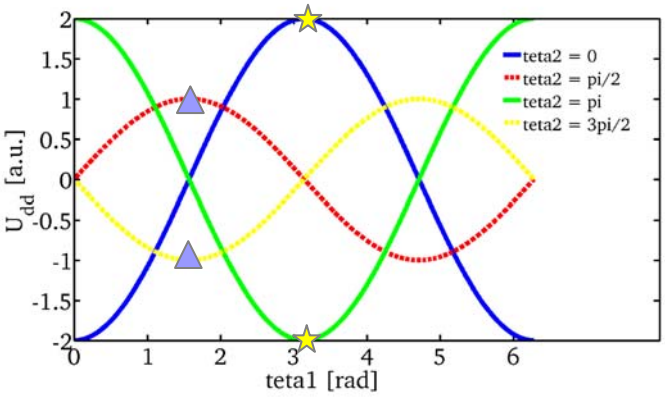

Figure 2. Potential of the dipole-dipole interaction depending on the dipole orientation

From the previous analysis, we have learned that two dipole orientations are of interest: parallel and normal to the vector $\mathbf{r_{12}}$. Distance was kept fixed and the dipole orientation was being changed. Now, we will keep the orientation fixed, but the distance will be changing.
In Fig. 3 a sketch of two dipoles parallel to the position vector $\mathbf{r_{12}}$ is shown. This system corresponds to the minimum marked with a star in Fig. 2.

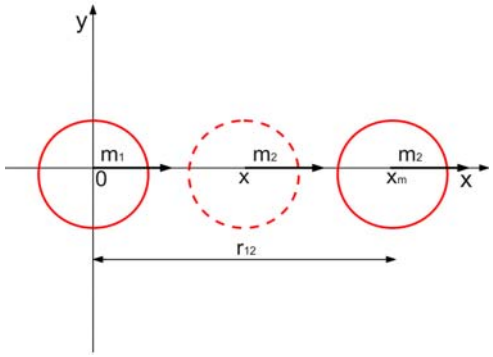

Figure 3. A sketch of two dipoles parallel to the position vector

In Fig. 4 dependence of potential on distance is shown. Obviously, absolute value of interaction potential decreases as the distance increases. This is an example of attraction between two dipoles. In Fig. 5 a sketch of two dipoles normal to the position vector $\mathbf{r_{12}}$ is shown. This system corresponds to the maximum marked with a triangle in Fig. 2.
In Fig. 6 dependence of potential on distance is shown. The same remark applies here, absolute value of interaction potential decreases as the distance increases. This is an example of repulsion between two dipoles.

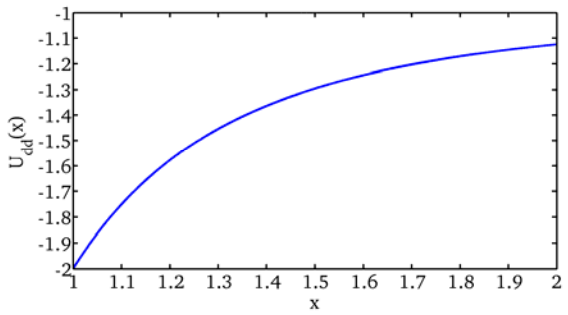

Figure 4. Dependence of the interacion potential on the position of dipole 2

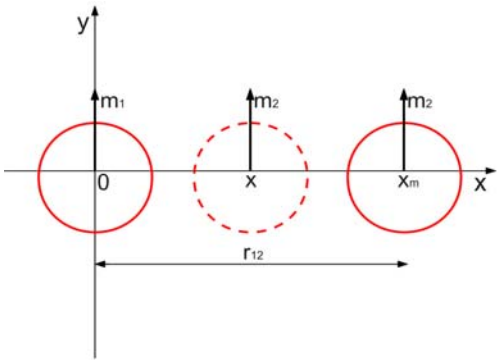

Figure 5. A sketch of two dipoles normal to the position vector

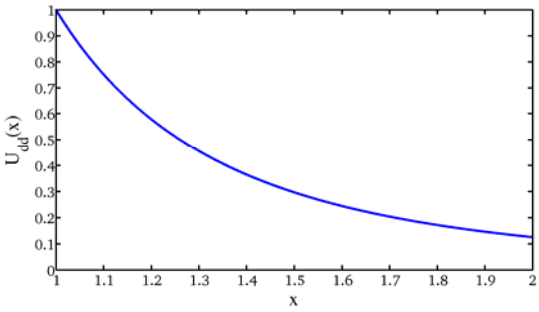

Figure 6. Dependence of the interaction potential on the position of dipole 2

This was the analysis of two systems of interest based on the general picture presented in Fig. 2. On the other side, from the Eq. 3, we can conclude that for a specific dipole orientation, interaction potential will be equal to zero [7]. We came up with a sketch shown in Fig. 7, in order to find out how does the system look like when this is the case. In Fig. 8 dependence of potential on distance is shown. When the angle is equal to the magic angle, potential is equal to zero. From the Eq. 3 we can derive what should be the angle α which causes the dipole-dipole interaction potential to be equal to zero.

$$\begin{aligned} & m_{1n}m_{2n} - 2m_{1p}m_{2p} = 0 \\ \Leftrightarrow\ & \sin^2\alpha - 2\cos^2\alpha = 0 \\ \Leftrightarrow\ & \alpha = \arccos\left(\frac{1}{\sqrt{3}}\right) = 54.74^\circ \end{aligned} \tag{7}$$

Angle α = 54.74° is the magic angle, interaction potential goes through the zero value at the x-coordinate (see Fig. 8) which corresponds to this angle. For this system, there is a switch of potential's sign, so there are both, attraction and repulsion between two dipoles.

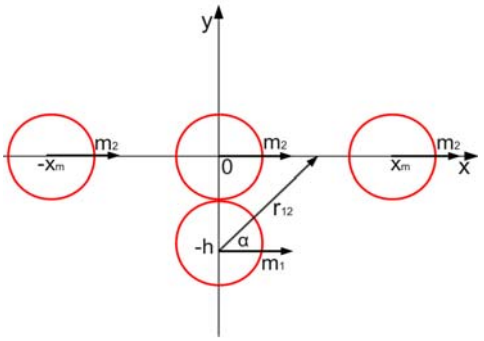

Figure 7. An illustration of the magic angle in the dipole-dipole interactions

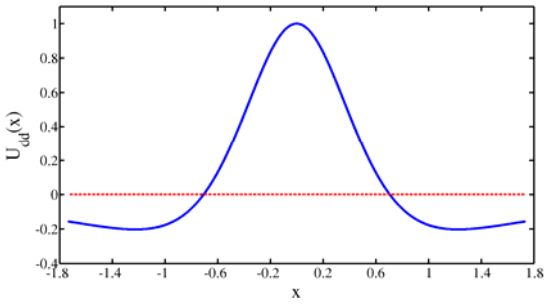

Figure 8. Dependence of the interaction potential on the position of dipole 2

III. CALCULATION OF THE BINDING ENERGY

In this chapter, a method for calculating the binding energy of a tubular structure is provided. Since we are analyzing infinitely long tubes, an efficient method for summing the dipole-dipole interactions of 1D periodical structures (periodical along one direction, the z-axis) had to be found. There are two well known and widely applied methods for this type of calculations, those are Ewald summs and Lekner method. Ewald sums are usually used for 2D periodical systems, while Lekner summation method converges faster in the 1D case, therefore we decided to implement Lekner method. The key feature of Lekner method is the choice of a periodic cell. It is a part of the infinite structure which is being replicated. Since we are dealing with tubes, one has to define its cell which is being replicated along the tube's axis (z – axis). Energy of an infinitely long tube is calculated as a sum of the self and cross energy. In next

expressions, we are dividing by N, since the energy is defined per particle, which allows a comparison of different structures with different number of particles in a cell.

Self energy represents the interaction energy of a selected particle in a cell, with all of its copies in the other cells. Total self energy is got as a sum over all particles in a cell, where number of particles in one cell is equal to N.

Self energy is given as [8]:

$$E_{self} = \frac{1}{L_z^3} \frac{\sum_{i=1}^{N} \left(1 - 3m_{z_i}^2\right) \zeta(3)}{N} \tag{8}$$

Cross energy represents the interaction energy of a selected particle in a cell, with all other particles of the same cell and with all their copies in the other cells. Total cross energy is got as a sum over all particles in a cell, i = {1, N}, j = {1, N} [8]:

$$E_{cross} = \frac{\sum_{i \neq j} U_{cross}\left(\vec{r}_i, \vec{r}_j, \vec{m}_i, \vec{m}_j, L_z\right)}{N} \tag{9}$$

In the above equation, the cross energy is got as a sum of cross potentials of pairs of particles (*i, j*). Cross potential is defined as a sum of four sums. In those sums a modified Bessel function of the second kind, zero and first order, K_0 and K_1 appears, respectively. In the following text, those sums are presented.

$$U_{cross}\left(\vec{r}_i, \vec{r}_j, \vec{m}_i, \vec{m}_j, L_z\right) = \sum_{i=1}^{4} S_i \tag{10}$$

Method for calculation of the binding energy of 1D infinitely long periodic structures is presented briefly. Goal of this paper is geometric formation and calculation of the binding energy of structures with minimal energy. Since the dipole orientation dictates the interaction potential, energy minimization means finding the optimal dipole orientation.

$$S_1 = \frac{-8\pi}{L_z^2}\left[\frac{2\left(\vec{m}_{\rho_i} \cdot \vec{\rho}\right)\left(\vec{m}_{\rho j} \cdot \vec{\rho}\right)}{\rho^3} - \frac{\vec{m}_{\rho_i} \cdot \vec{m}_{\rho j}}{\rho}\right] \times$$

$$\times \sum_{k=1}^{+\infty} k \cos\left(k\eta_z\right) K_1\left(k\eta_\rho\right)$$

$$S_2 = \frac{-16\pi^2}{L_z^3}\left[\frac{\left(\vec{m}_{\rho_i} \cdot \vec{\rho}\right)\left(\vec{m}_{\rho j} \cdot \vec{\rho}\right)}{\rho^2} - m_{z_i} m_{z_j}\right] \times$$

$$\times \sum_{k=1}^{+\infty} k^2 \cos\left(k\eta_z\right) K_0\left(k\eta_\rho\right)$$

$$S_3 = \frac{2}{L_z}\left[\frac{2\left(\vec{m}_{\rho_i} \cdot \vec{\rho}\right)\left(\vec{m}_{\rho j} \cdot \vec{\rho}\right)}{\rho^4} - \frac{\vec{m}_{\rho_i} \cdot \vec{m}_{\rho_j}}{\rho^2}\right]$$

$$S_4 = \frac{-16\pi^2}{L_z^3} \frac{\left(\vec{m}_{\rho_i} \cdot \vec{\rho}\right) m_{z_i} + \left(\vec{m}_{\rho j} \cdot \vec{\rho}\right) m_{z_j}}{\rho} \times$$

$$\times \sum_{k=1}^{k=+\infty} k^2 \sin\left(k\eta_z\right) K_1\left(k\eta_\rho\right) \tag{11}$$

IV. GEOMETRIC FORMATION OF THE STRUCTURES

In this paper we are analyzing tubes composed of magnetic particles. A specific configuration of a tube is defined by the geometry and the dipole orientation. There are two possible tube's geometries depending on the ring stacking. If the rings are stacked one on top of each other, those are AA tubes. Otherwise, if the rings are stacked in the way that there is one particle in the upper ring between two particles in the lower ring, those are AB tubes. There are only two ways of ring stacking, but there is a huge number of different dipole orientations. We took both stackings, and three well-defined dipole orientations. Those dipole orientations are called: single-thread (ST), multi-thread (MT) and ZZ dipole orientation. ST means that dipoles follow one thread that is tangential to the contour of the tube. MT means that dipoles follow multi threads of which the tube is composed, while ZZ means that all the dipoles are parallel to the z-axis. We have analyzed all three chosen dipole orientations for AA and AB tubes. When calculating binding energy of an infinite periodic structure using Lekner method, the key task is to define the periodic cell. In an AA tube, a cell is one ring. In an AB tube, a cell is composed of two rings. Normalization of the system includes dimension and energy scales. The diameter of every particle is d = 1. The distance between two particles is calculated from centre to centre, which means that the distance between two touching particles is equal to 1. On the other side, it is very convenient to introduce energy scale, so the energy is not defined in joules or electronvolts, but rather in arbitraty units [a. u.]. Energy scale is defined via repulsive potential of two touching dipoles standing side by side. The dipole moment is also normalized so that the length of dipole moment vector is equal to 1. Now we will explain geometric formation of the structures. For a tube, the basis is a ring composed of magnetic particles. In Fig. 9 the cross-section of a tube is presented.

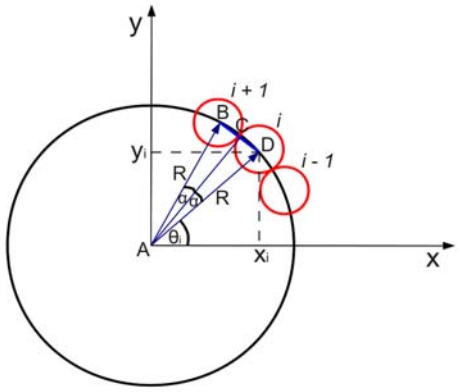

Figure 9. A sketch of the tube's cross-section

A ring is composed of N touching particles. Angular distance between two successive particles is $\Delta\theta = \frac{2\pi}{N}$ for an arbitraty chosen i-th particle, its angular position in respect to the positive x-semiaxis is $\theta_i = i\frac{2\pi}{N}$. Let us look at the triangle ABC in Fig. 9. Since the distance between touching particles is equal to 1, then BC = 1/2. There are relations:

$$\sin\alpha = \frac{1}{2R}$$
$$2\alpha = 2\frac{\pi}{N} \Rightarrow \alpha = \frac{\pi}{N} \tag{12}$$

Therefore, the relation between ring's radius and number of particles is:

$$R = \frac{1}{2\sin(\pi/N)} \tag{13}$$

A. Formation of AA tubes

In AA tubes, a periodic cell is one ring. Next array of equations defines coordinates of the particles, i = {1, N}.

$$x_i = \frac{1}{2\sin(\pi/N)}\cos\left(i\frac{2\pi}{N}\right)$$
$$y_i = \frac{1}{2\sin(\pi/N)}\sin\left(i\frac{2\pi}{N}\right) \tag{14}$$
$$z_i = 0$$

Dipole moments are defined in the next way, i = {1, N}.

$$\mu_{x_i} = \cos\left(i\frac{2\pi}{N} + \frac{\pi}{2}\right)$$
$$\mu_{y_i} = \sin\left(i\frac{2\pi}{N} + \frac{\pi}{2}\right) \tag{15}$$
$$\mu_{z_i} = 0$$

In the case of AA tubes, period along the z-axis is Lz = 1.

B. Formation of AB tubes

In AB tubes, periodic cell is a pair of rings. There are two arrays of equations, one for the lower ring, and another one for the upper ring. For the lower ring, coordinates of the particles are defined like in the case of AA tubes. There was a problem defining the z-coordinates of upper ring particles, which was solved using the definition of the distance between touching particles. Let us look at two arbitrary chosen particles in the lower ring (particles A and B) and one particle in the upper ring (particle C), which is placed between them. As it stands AC = BC = 1, from this condition we can derive how much are the upper ring particles displaced compared to the lower ring particles, along the z direction:

$$\Delta z = \sqrt{1-(x_A - x_C)^2 - (y_A - y_C)^2} \tag{16}$$

In the upper ring, coordinates of the particles are those:

$$x_i = \frac{1}{2\sin(\pi/N)}\cos\left(i\frac{2\pi}{N} + \frac{\pi}{N}\right)$$
$$y_i = \frac{1}{2\sin(\pi/N)}\sin\left(i\frac{2\pi}{N} + \frac{\pi}{N}\right) \tag{17}$$
$$z_i = \Delta z$$

In this case, period along the z-axis is Lz = 2 Δz.

V. Results of the Structure and Energy Calculations

In this chapter, results of the structure and energy calculations are presented. In Fig. 10, a geometry of one tube configuration is shown, obtained via MATLAB calculations. We are showing how does the tube (AA tube) look like in a side and in a top view.

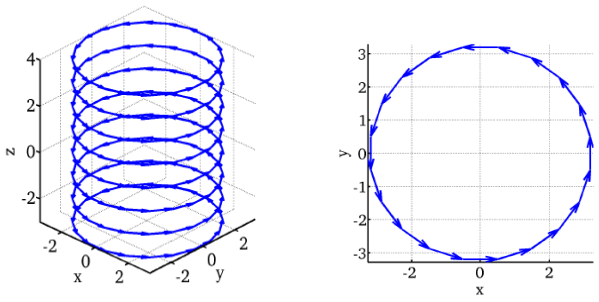

Figure 10. A side and a top view of an AA tube

In Fig. 11 and Fig. 12, dependence of binding energy on the confinement radius for AA and AB tubes is shown, including three different magnetizations.

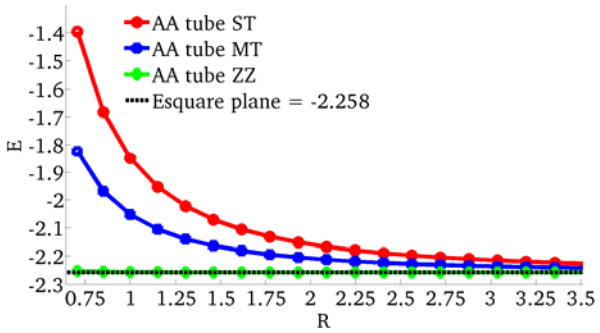

Figure 11. Energy in function of the confinement radius for different magnetizations (AA tube)

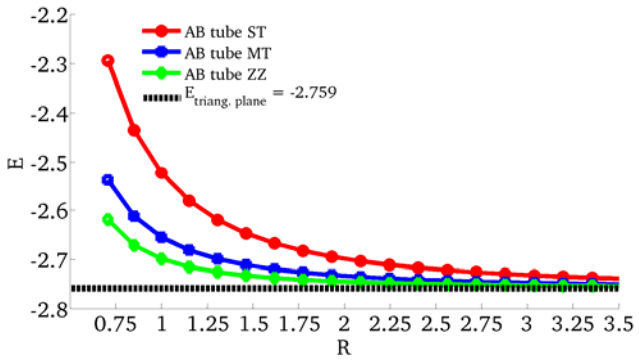

Figure 12. Energy in function of the confinement radius for different magnetizations (AB tube)

It is clear that for a fixed packing geometry (AA or AB), binding energy decreases as the magnetization changes from ST and MT into ZZ. Tubes with ZZ dipole orientation have minimal binding energy, and therefore they are the most stable tube configurations. When the confinement radius goes to the infinity, energy of all differently oriented tubes (ST/MT/ZZ) converges into the energy of an infinite plane. Energy of a square lattice plane is $E_{square} = -2.258$, all AA tubes converge into a square lattice plane. Energy of a triangular lattice plane is $E_{triangular} = -2.759$, all AB tubes converge into a triangular lattice plane.

VI. Conclusion

We have developed MATLAB simulations which form tubular structures composed of magnetic particles and calculate its binding energy. Both AA and AB ring stackings, including three different magnetizations, have been investigated.

From the results, we conclude that all those tube configurations are stable, since their binding energy is negative. For a fixed packing geometry (AA or AB), binding energy decreases as magnetization changes in the way:
ST - MT - ZZ. For a fixed magnetization, AB tubes have lower energy than AA tubes. Since AB tubes are more densely packed than AA tubes, we may say that bigger packing density implies lower binding energy and more stable structures.

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