manner. As the free energy density increases, the probability of finding such configuration is lesser. However, for large sets it becomes increasingly difficult to sample and differentiate between equilibrated configurations due to the large number of possible combinations, as evidenced for the case with $N = 10$.

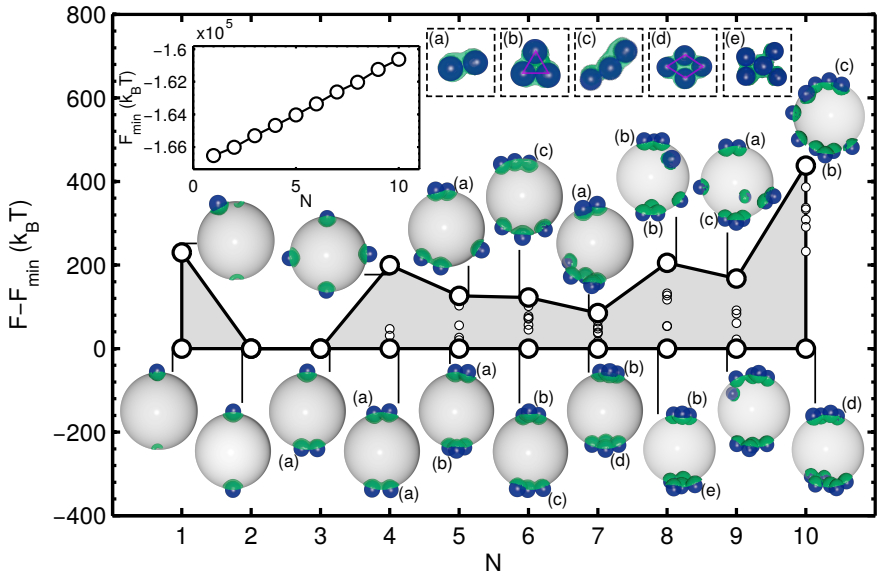

Figure 5.5. Free energy difference for planar particles with anchoring strength $W = 1 \times 10^{-4}$ J/m^2, taking the minimum free energy for each N as reference and shown in the insert. Small round markers indicate metastable configurations (not shown), while big markers represent configurations with the maximum and minimum free energy density. Labels (a)-(e) are assigned to the most characteristic assembly of nanoparticles pictured in the inserts.

5.2.3 Segregation of particles

Taking the criterion of minimum free energy lead us towards the most stable configuration. However, other arrays are also found even though its energy can be considerably higher. This is caused by entropic frustration, where the large number of possible combinations makes it impossible to always reach the same state. However, the mechanism through which particles group stems from free energy minimization. This is more explicit in figure 5.6.

Different scenarios were considered to understand why particles of the same type of anchoring repel each other and tend to locate on specific regions of the droplet. One scenario consists on

one particle being fixed at the boojum and the other particle traveling on the surface by changing its position with respect to the first particle by an angle θ. The distance between particles is also measured with the arc length between the particles, $d = \theta\pi R/180$. This is done for a pair of particles and each type of anchoring, until the two particles are diametrically opposed. Another scenario fixes a planar particle on the equator of the droplet as the second particle is displaced until the angle between them is $\theta = 180$. Ginzubrg-Landau simulations were carried out for each scenario on high resolution regular meshes.

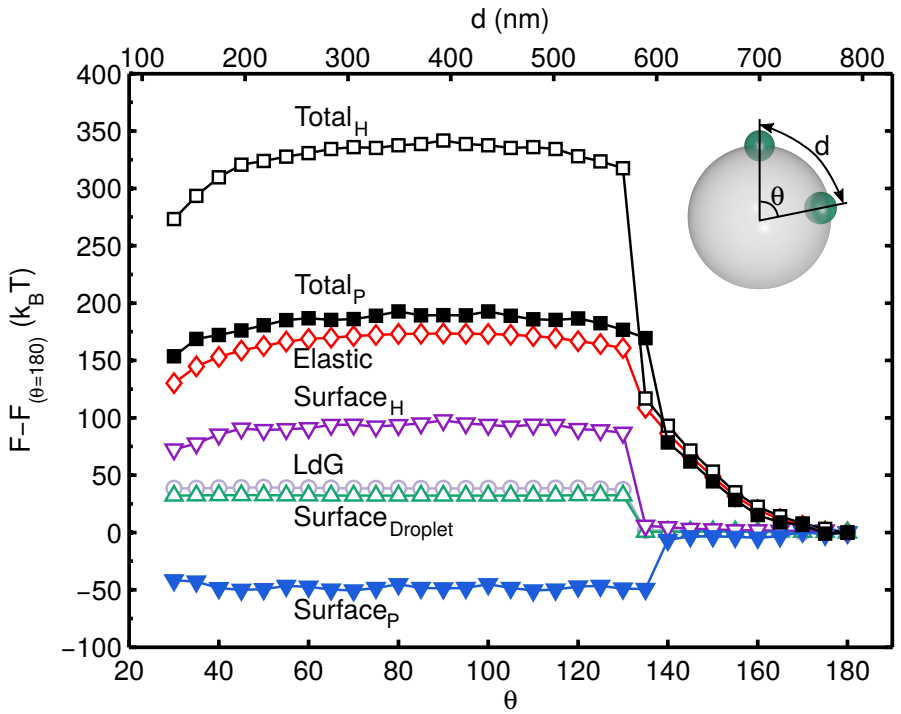

Figure 5.6. Free energy difference as a function of the angle between two nanoparticles on the surface of a bipolar droplet. Void and filled markers correspond to the case of homeotropic and planar particles respectively.

For a pair of homeotropic nanoparticles, white markers in figure 5.6, there is an energetic barrier of nearly 300 k_BT to group both nanoparticles in one boojum. As stated previously, a boojum vanishes when in contact with a homeotropic nanoparticle because the director field within the droplet does not suffer additional distortions. This makes for the boojum to disappear and the LC naturally adapts a perpendicular orientation. This phenomenon is reflected on the reduction of the Landau-de Gennes and surface contributions since there are no defects present, a smooth decay of

the elastic free energy because of the annihilation of high splay regions, as well as a decrease of the surface contribution from the particle. Accordingly, a homeotropic particle located at the equator is surrounded by a half saturn ring and a boojum survives opposite to the fixed nanoparticle.

For a pair of planar particles, the effect of a particle travelling from one pole to the other causes the same additional energetic gain in the Landau-de Gennes, elastic, and droplet surface contributions of the previous study case, with an increase of 200 k_BT. However, we observe that a planar particle at the equator fits the bipolar structure of the droplet and so represents a lower surface penalty than when the particle is near the boojum where the defect structure resembles a half spherical shell.