Supplementary Information

Magnetically Controlled Cluster formation/dissociation in High-Moment Nanoparticle-based Ferrofluids

*M. Vasilakaki, D. Fiorani, D. Peddis, K.N. Trohidou**

M. Vasilakaki and K. N. Trohidou
Institute of Nanoscience and Nanotechnology, NCSR 'Demokritos', Aghia Paraskevi, Attiki, 153 10, Greece
E-mail: k.trohidou@inn.demokritos.gr
D. Fiorani
Istituto di Struttura della Materia, CNR, Monterotondo Scalo 00015, Rome, Italy
D. Peddis
Department of Chemistry and Industrial Chemistry (DCIC), University of Genova, Genova 16126, Italy; Istituto di Struttura della Materia, CNR, Monterotondo Scalo 00015, Rome, Italy

S1. Time evolution of the initially randomly dispersed Co ferrite multicore particles in the fluid in the absence of a magnetic field.

In Figure S1 below, we show the time evolution of a part of the Co ferrite multicore particles initially randomly dispersed in the fluid without the application of magnetic field at t = 0 MCS, t = 200 MCS and t =1000 MCS. As it can be seen, the particles are well separated and this continues even at longer times. As we discuss in the main text, because of the low particle density, there is very small probability very few of the particles to create dimers or trimers. The same holds for the FeCo alloy nanoparticles based FFs. In the case of the uncoated nanoparticles where Van der Walls interactions are included in the simulations, we get the same picture at the times of figure S1.

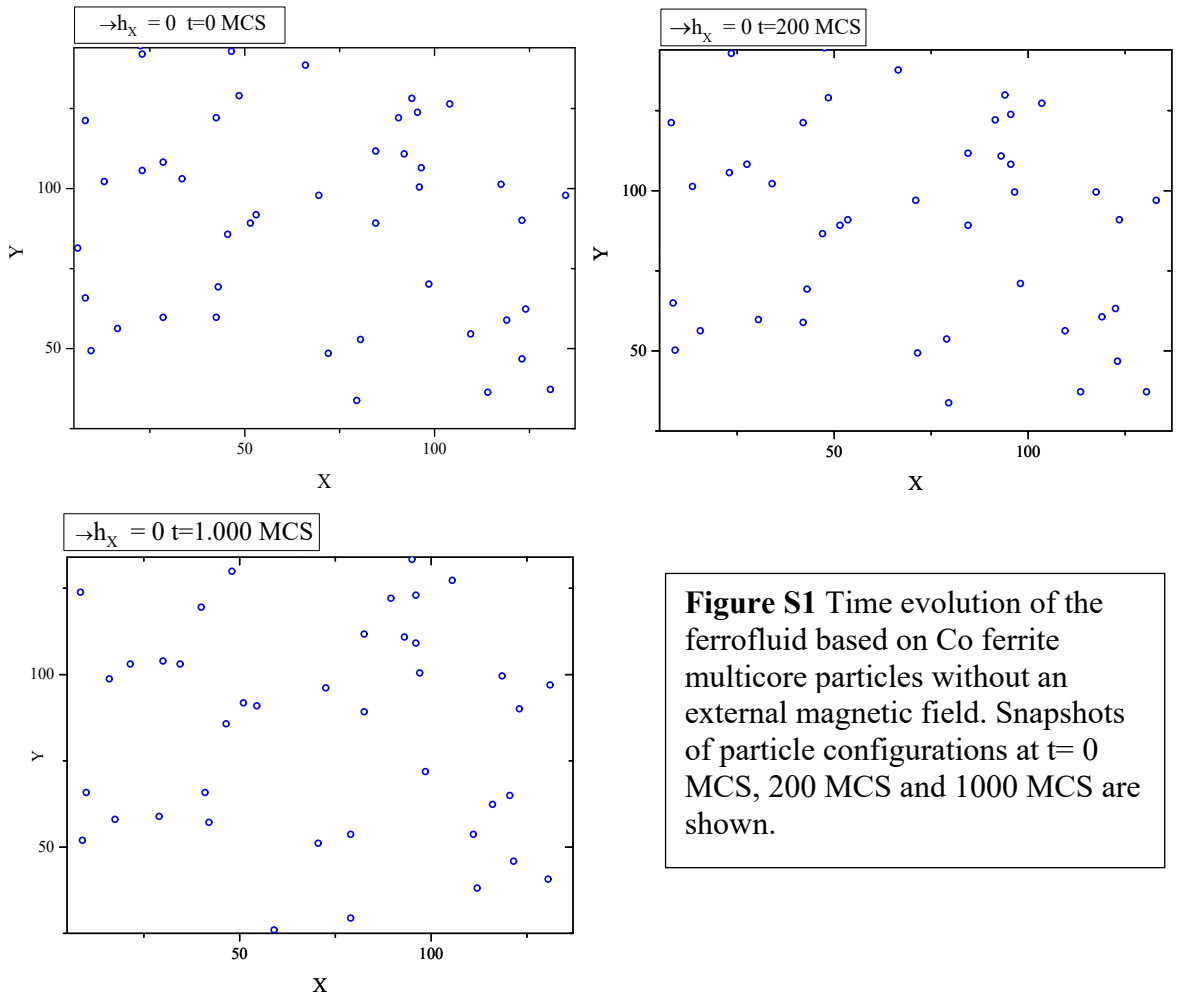

Figure S1 Time evolution of the ferrofluid based on Co ferrite multicore particles without an external magnetic field. Snapshots of particle configurations at t= 0 MCS, 200 MCS and 1000 MCS are shown.

S2. Cluster formation/dissociation of the Co ferrite multicore based FF under the applied magnetic field at longer times.

In Figure S2, the snapshots of the clusters time evolution under the applied magnetic field are given from 10^6 to 2×10^7 MCS (Figs S2(a), (c) and (e)). Despite the fact that we have increased the MC time significantly (more than one order of magnitude) the morphology of the clusters is not significantly changed. Furthermore, at these longer times after removing the field, as we can see from Fig S2((b), (d) and (f)), the clusters are dissociated.

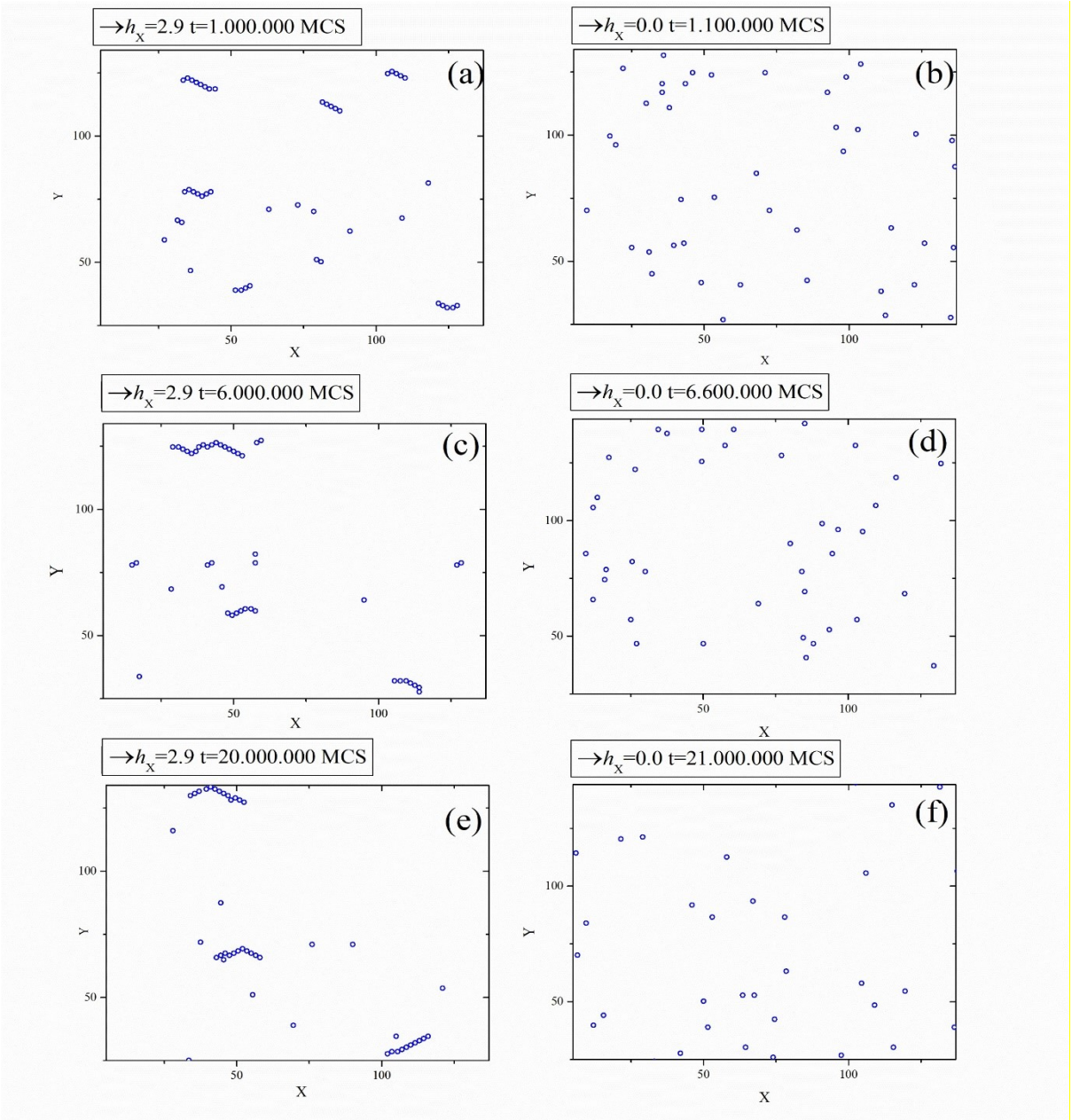

Figure S2. Snapshots of the ferrofluid with Co ferrite multicore particles under in-plane magnetic field h_x at times t= 10^6 (a), 6×10^6 (c), 2×10^7 MCS (e) and when the field is switched off at t =1.1×10^6 (b), 6.6×10^6 MCS (d), 21×10^6 MCS (f) respectively.

S3. Effect of cluster formation / dissociation process by applying the magnetic field out-of-plane for the FF based on the Co ferrite multicore particles.

In Figure S3 snapshots of the particle configurations are shown when the magnetic field is applied out-of-plane (Fig. S3(b)) and consequently switched off (Fig. S3 (c)-(d)) starting from a randomly dispersed particle configuration in zero field (Fig. S3 (a)). We see in Fig. S3(b) that cluster formation is not observed by applying an out of plane field. As it is discussed in the main text, this is attributed to the competition between the dipolar interaction that tends to align the spins in plane and the magnetic field interaction that tends to align the spins out of plane.

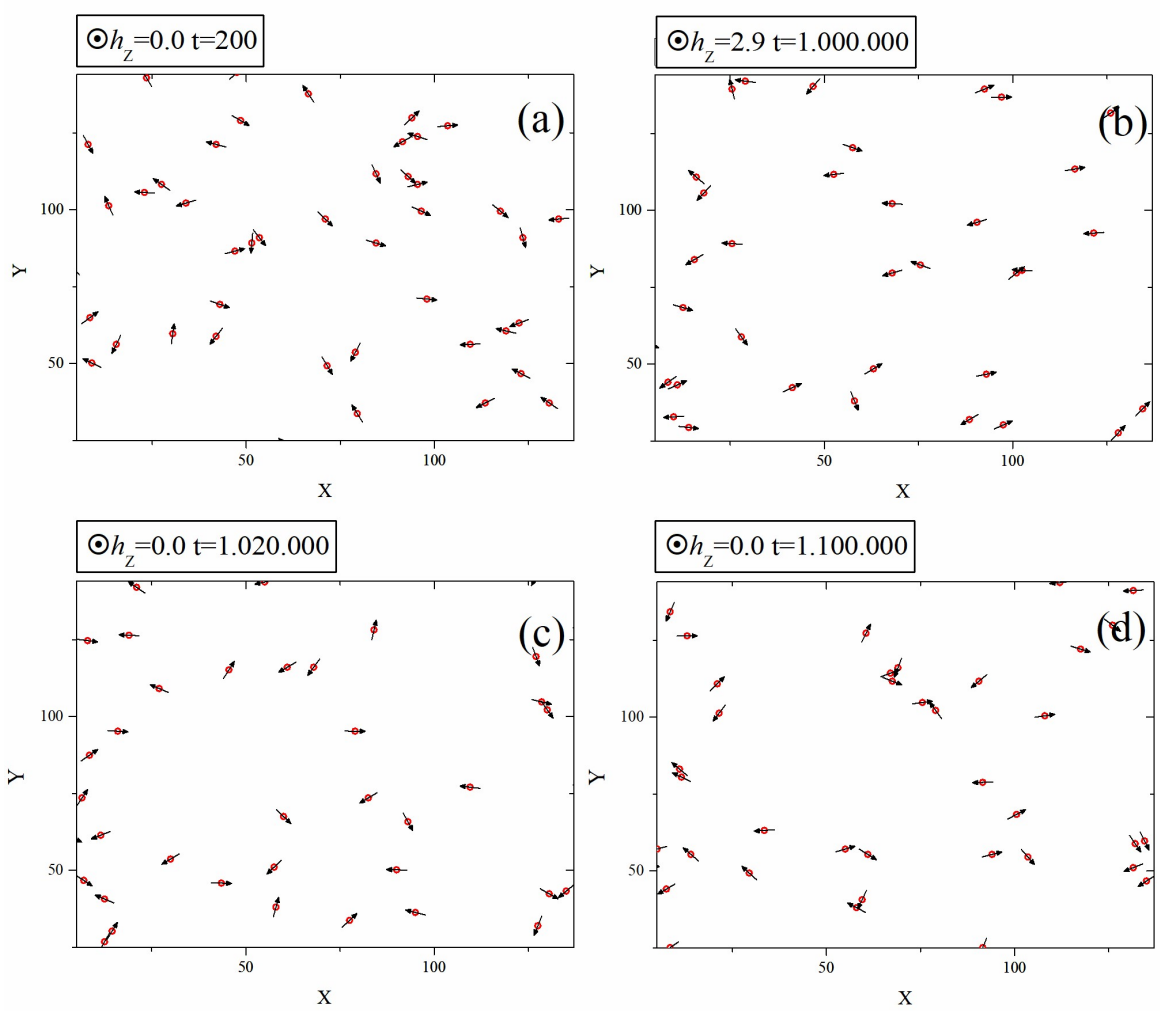

Figure S3. Snapshots of the coated Co ferrite multicore particle configurations (spin direction is given by black arrows): 1) at the beginning of the process when the particles are randomly placed inside the liquid (a), 2) by applying an out-of-plane magnetic field $h_Z = 2.9$ (b), 3) the removal of the $h_Z = 0.0$ (c), (d). The X and Y axes are calculated in units of particle size $d = 60$ nm and the time in MCS.

The same behaviour is observed in the FF2 based on the FeCo alloy nanoparticles when an out-of-plane field is applied.

S4. Role of the magnetic particle anisotropy in the cluster formation / dissociation process for the Co ferrite multicore particle based FF.

In Figure S4, snapshots of the Co ferrite multicore particle configuration are shown for higher magnetic anisotropy $k = 5$ at the initial state in zero field (a), when the magnetic field is applied in-plane (Fig. S4(b)) and consequently switched off (Fig. S4 (c)-(d)) or applied out-of-plane (Fig. S4 (e-f)). We see that the number and the size of the clusters is smaller than that of the case of $k = 2.53$ anisotropy (Figure 3(b) in the main text). This is attributed in the fact that the higher random anisotropy disorients the magnetic moments and consequently weakens the

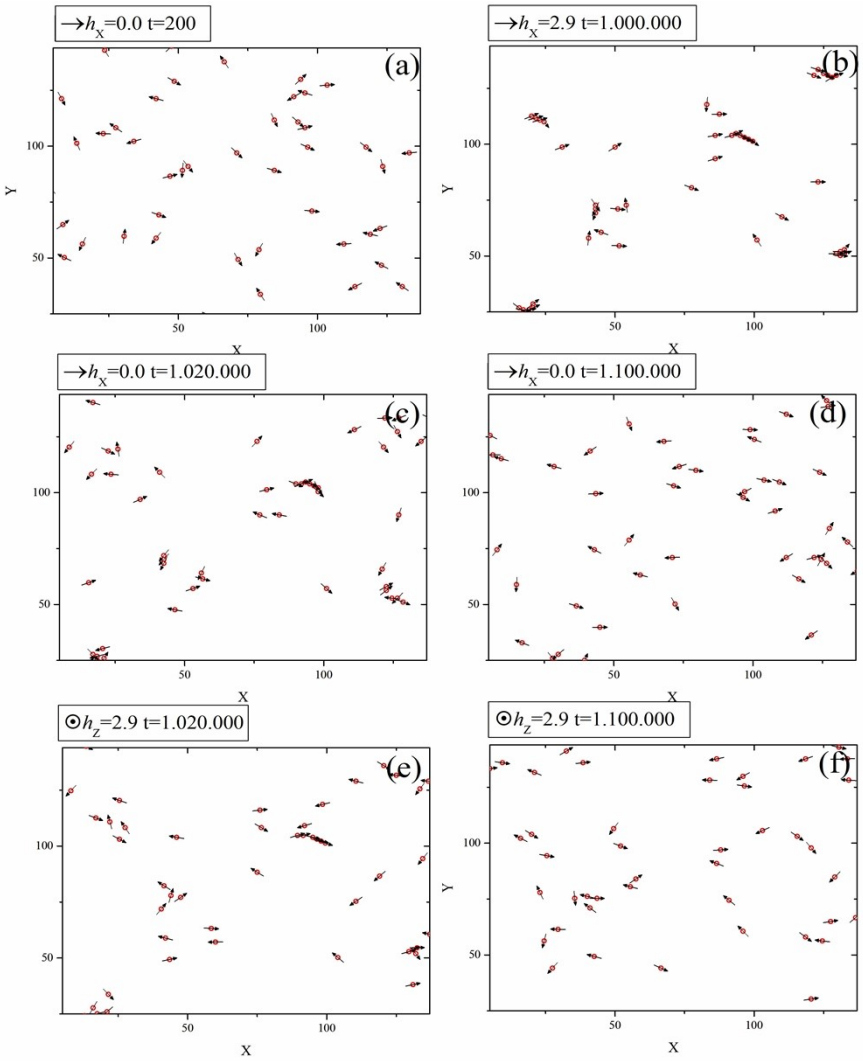

Figure S4. Snapshots of the coated Co ferrite multicore particle configurations (spin direction is given by black arrows) with magnetic anisotropy $k = 5$: 1) at the beginning of the process (a) 2) by applying an in-plane magnetic field $h_X = 2.9$ (b), 3) removing the field $h_X = 0$ (c)-(d) or 4) by applying the field out -of-plane $h_Z = 2.9$.

dipolar interactions delaying the cluster formation process and favouring the cluster dissociation when the field is switched off or applied vertically to the plane.

S5. Role of the surfactant layer in the cluster formation / dissociation process for Co ferrite multicore particles and FeCo alloy nanoparticles in the fluid

Interestingly, the importance of role of the steric interactions to the reversibility of the cluster formation/dissociation process becomes evident, when the energy term of steric interactions (E_s = 0) is switched off in the calculations. In this case, as we discussed in the main text, we add in the energy of the system (Eq. 6) the Van der Walls interaction originated from the spontaneous attractive interaction between electric dipoles generated by charge density fluctuations in the electron clouds, [1] since they can contribute to the aggregation process in the absence of the surfactant coating.

The Van der Waals interactions between all particles is described by the energy term:

$$E_{VdW} = -\sum_{i \neq j}^{N} \frac{A}{12}\left[\frac{d^2}{r_{ij}^2 - d^2} + \frac{d^2}{r_{ij}^2} + 2ln\frac{r_{ij}^2 - d^2}{r_{ij}^2}\right] \qquad (S1)$$

In Eq. S1, the strength of the Van der Waals interactions is $\frac{A}{12}$, where A is the Hamaker constant, which can be described in terms of macroscopic characteristics of the nanoparticles and the solvent. [2] We take $A = 2.5 \times 10^{-19}$J an average value found in ref. [3] for elemental polycrystalline metal combinations embedded in water. An energy cutoff at a distance r = $1.011\times d$ very close to the surface is considered.

Figure S5 shows the MC simulations results for the cluster formation/dissociation process of uncoated FeCo alloy nanoparticles starting from a state of randomly dispersed particles without applying a magnetic field (Figure S5(a)). It is observed that large aggregates of irregular shape are formed (Figure S5(b)) within the same time of observation comparing to the coated particles (see Figure 4 of the main text) in the presence of the in-plane field h_X = 2.9. In Figure S5 (c)-(d), we give the snapshots when the field is removed. In Figure S5 (e)-(f) we show snapshots for the case that instead of switching off the field we apply an out-of-plane field. We observe that the clusters do not dissociate instead, they are getting larger, when the field is applied out-of-plane as in the case of CFO multicore particles (Figure 7 in the main text) and they continue to grow even at larger times. As it has been explained in the main text this is attributed to the fact that in the clusters of irregular shape, the number of the nearest neighbours is more than two particles, thus the intra-cluster dipolar interactions are very strong inhibiting the cluster dissociation.

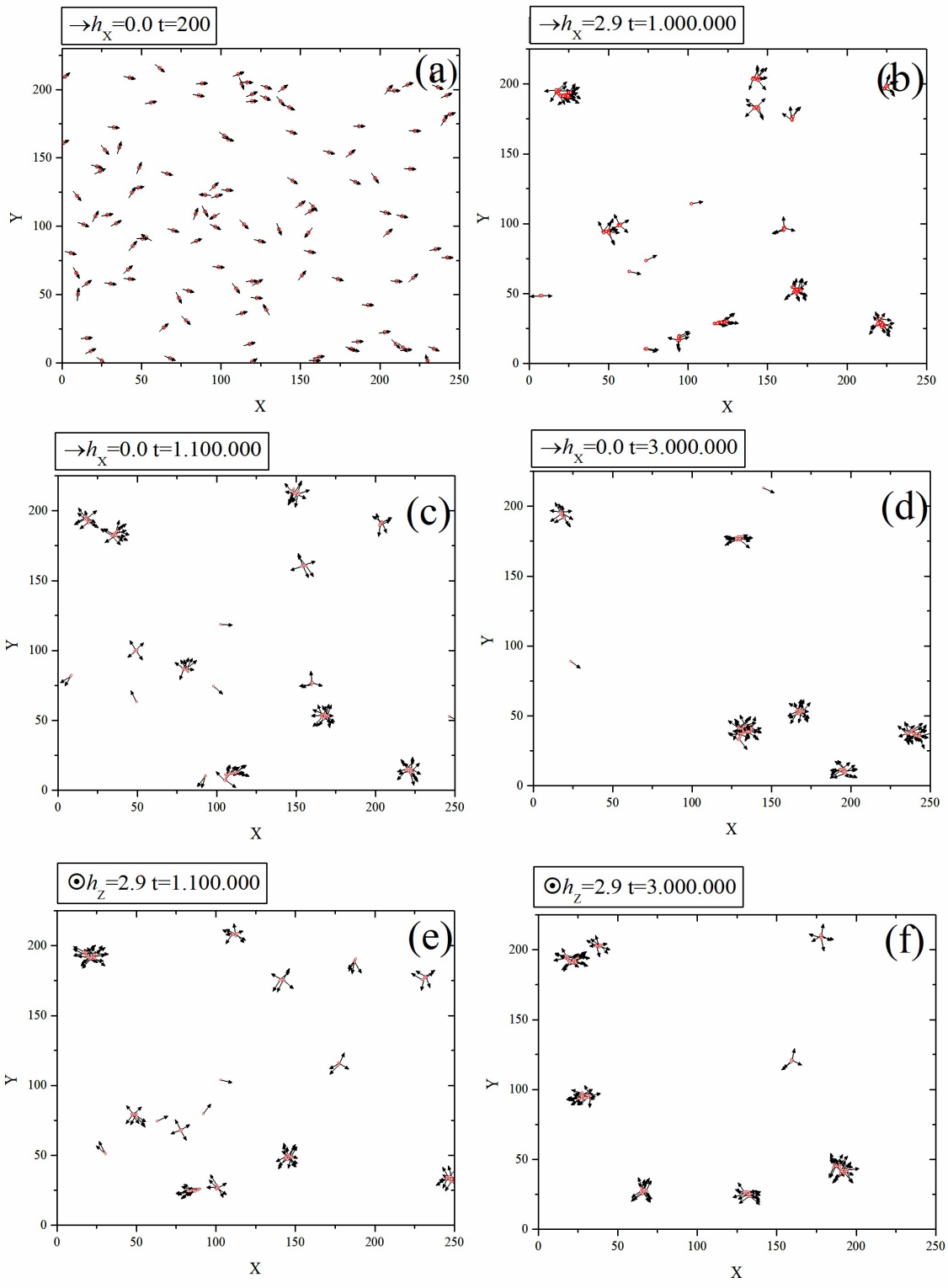

Figure S5. Snapshots of the uncoated FeCo alloy nanoparticle configurations (spin direction is given with black arrows) : 1) at the beginning of the process (a) 2) by applying an in-plane magnetic field h_X = 2.9 (b), 3) removing the field h_X = 0 (c)-(d) or 4) by applying the field out -of-plane h_Z = 2.9.

REFERENCES

1. Durhuus, F.L., Wandall, L.H., Boisen, M.H., Kure, M., Beleggia, M., Frandsen, C.: Simulated clustering dynamics of colloidal magnetic nanoparticles. Nanoscale. 13, 1970–1981 (2021). https://doi.org/10.1039/d0nr08561h.
2. Bakuzis, A.F., Branquinho, L.C., Luiz E Castro, L., De Amaral E Eloi, M.T., Miotto, R.: Chain formation and aging process in biocompatible polydisperse ferrofluids: Experimental investigation and Monte Carlo simulations. Adv. Colloid Interface Sci. 191–192, 1–21 (2013). https://doi.org/10.1016/j.cis.2012.12.003.
3. Tolias, P.: Non-retarded room temperature Hamaker constants between elemental metals. Surf. Sci. 700, 121652 (2020). https://doi.org/10.1016/j.susc.2020.121652.