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Particle size distribution in ferrofluid macro-clusters

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ABSTRACT

Under an applied magnetic field, many commercial and concentrated ferrofluids agglomerate and form large micron-sized structures. Although large diameter particles have been implicated in the formation of these macro-clusters, the question of whether the particle size distribution of the macro-clusters are the same as the original fluid remains open. Some studies suggest that these macro-clusters consist of larger particles, while others have shown that there is no difference in the particle size distribution between the macro-clusters and the original fluid. In this study, we use X-ray imaging to aid in a sample (diluted EFH-1 from Ferrotec) separation process and conclusively show that the average particle size in the macro-clusters is significantly larger than those in the original sample. The average particle size in the macro-clusters is 19.6 nm while the average particle size of the original fluid is 11.6 nm.

1. Introduction

Ferrofluids are colloids with nano-sized (~10 nm diameter) magnetic particles dispersed in a carrier fluid. In order to avoid agglomeration, the particles are typically coated with a ~2 nm surfactant layer for steric repulsion. Nonetheless, in most ferrofluids, agglomeration remains an issue. This is an important problem because it is well known that the microstructure of ferrofluids affects its macroscopic properties. For example, one of the most studied features of ferrofluids is that of magneto-viscosity, i.e.; the change in viscosity under an applied magnetic field. While magneto-viscosity in dilute ferrofluids can be explained [1] by the additional energy required to rotate a single-particle dipole moment in an applied magnetic field when the vorticity is not parallel to the dipole moment, the magneto-viscosity effects in commercial ferrofluids and more concentrated ferrofluids are much higher than those predicted by single-particle theory. It has been suspected that this is due to particle agglomeration [2].

It should be pointed out that in the ferrofluid research literature, the term agglomeration, or clustering is broadly used to describe all agglomeration phenomena, ranging from a few particles (< 10) forming single-particle-wide chains, to billions of particles forming complicated 1–10 μm-thick three-dimensional structures such as columns, labyrinths and sheets [3]. A few studies have suggested that the micron-sized structures are formed by the agglomeration of the short few-particle chains [4–6]. The focus of this study is on the micron-sized agglomerates; and to avoid confusion, we will refer to these as macro-clusters. In particular, the goal is to determine if there is any difference in particle size distribution between the particles in the macro-clusters and the particles in the surrounding fluid. There are two primary reasons why this question is relevant. First, as will be discussed below, there are differing conclusions based on previous experimental, computational and theoretical studies regarding this particular question. Secondly, this is an important issue for understanding the stability parameter space for ferrofluids, which is a crucial consideration for all ferrofluid applications. The formation of aggregates or clusters in ferrofluids has been the subject of many studies as evidenced by several reviews [3,7,8] in this particular topic.

There have been a number of theoretical studies regarding agglomeration of the magnetic particles in ferrofluids under an applied field. Early investigations were microscopic in nature, and describe formation of short (< 10 particles) chains by dipole–dipole attraction [9,10]. This is parameterized by the ratio of the dipole–dipole interaction energy with thermal energy (SI units) [9]:

$$\lambda = \frac{4\pi\mu_0 M_s^2 a^6}{9d^3 kT}$$

where μ_0 is the vacuum permeability, M_s is the saturation magnetization of the bulk material, a is the magnetic core radius, k is the Boltzmann's constant, T is the temperature and d is the distance of closest approach between two particles. One would expect that the ferrofluids would be stable against aggregation if $\lambda < 1$. For 10 nm diameter magnetite particles ($a = 5$ nm) with

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2 nm surfactant layers, $d=14$ nm and $\lambda\sim0.56$. Thus, based on this simple consideration, 10 nm particles should not aggregate. On the other hand, if the magnetic core radius $a=8$ nm, then $\lambda=3.2$, which suggests that the particles would be prone to agglomeration.

Although the interaction parameter is useful for estimating short chain formation, it does not explain the formation of large macro-clusters [11]. Later studies [12–19] focus more on the macroscopic properties and are generally more easily compared with experiments. Most of these studies view the formation of macro-clusters as a phase transition from a homogeneous system to one with high- and low-density phases. Most of the theoretical studies are based on mono-dispersed particle sizes, but several have been able to incorporate bi-disperse (small and large) distributions [17,20]. These studies suggest that the macro-clusters (high-density phase) are formed by the larger sized particles, with negligible numbers of the smaller particles; while the low-density phase (the rest of the sample) consists of smaller particles with negligible numbers of large particles. A recent study suggests that the formation of macro-clusters is preceded by the formation of linear chains, which provides a link between the microscopic and the macroscopic scales [4]. In this paper, following the convention, we use the terms 'macro-cluster' and 'high-density phase' synonymously; while the term 'low-density phase' will refer to the rest of fluid that are not the macro-clusters.

The theoretical challenges in studying the complexity of ferrofluids have led to studies using computer simulations, either, Monte Carlo type simulations [21–25] or molecular dynamics [26,27]. They have been performed in both 2D and 3D and are generally limited to about 1000 particles. Thus, they do not truly describe the macro-clusters, which typically have $>10^6$ particles. Nonetheless, 2D Monte Carlo simulations [24] with polydispersed particles show that clusters (few chains wide) are formed by larger particles. On the other hand, 3D Monte Carlo simulations [25] using polydispersed particles show that while the probability of agglomeration increases with average particle size, the average particle size within the clusters is no different than the average particle size of the sample. The molecular dynamics studies thus far only look at the formation of linear chains and does not extend to the formation of macro-clusters. Nonetheless, they show that in a bi-dispersed distribution of small and large particles, the linear chains are formed only by the large particles [27]. An interesting result from molecular dynamics studies is that the presence of small particles can hinder is the formation of chains. A large concentration of small particles can inhibit the formation of the agglomerates because they change the magnetic permeability of the background as felt by the larger particles and they increase the chances that chains are broken due to collision [27].

In general, both theoretical and computer simulations suggest that large particles play a significant role in the formation of macro-clusters. The results suggest that micron-sized macro-clusters are formed by the coalescence of small chains [4,22]. The predictions are that these small chains are formed mainly by larger sized particles where the dipole–dipole energy is larger than the thermal energy ($\lambda>1$). The chains grow and become nucleation sites for the gas–liquid phase transition. However, there are different predictions regarding the particle size distribution differences between the macro-clusters (high-density phase) and the surrounding fluid (low-density phase) or the original fluid.

Experimentally, there have been several different approaches to study ferrofluid agglomeration. Peterson and Krueger [28] used a Colpitts oscillator to measure the spatio-temporal variations in the magnetization of ferrofluid columns under different applied magnetic fields. They interpret the changes in electrical inductance as changes in sample concentration and they found that upon exposure to a vertical uniform applied magnetic field, the bottom of the vertical sample column has a higher concentration than the top. They hypothesized that upon exposure to an applied field, the magnetic particles agglomerate to form very large and dense clusters that fall to the bottom of the sample. By extracting samples from the top (no agglomeration) and bottom (agglomerated) of the sample column, they concluded, from electron micrographs, that particles of all sizes participate in the agglomeration process; that is, there was no particle size difference between the top and bottom samples. O'Grady [29], using a high gradient magnetic filtration system to separate out the agglomerates, and then measuring particle sizes using transmission electron microscopy, also concluded that there were no particle size differences between the filtered (no agglomerates) and unfiltered (contains agglomerates) samples. Odenbach [30–32] utilized a similar separation process as Peterson and Krueger, but measured magneto-viscosity and magnetization instead of electrical inductance. Their measurements show that a higher fraction of larger particles leads to a large increase in magneto-viscosity. However, while his measurements showed that there were concentration differences between the ferrofluid taken from the top and bottom of the separation set-up, both magneto-viscosity and magnetization measurements did NOT show any particle size distribution differences between the top and bottom portion. Odenbach concludes that the measurements are consistent with the theoretical work of Zubarev [33]: the large magneto-viscosity effects are due to chaining of large particles. That the effect depends on shear rate is explained by suggesting that the chains are broken by shear. However, it should be noted that his measurements are only compared with Zubarev's work where the chains are only a few particles long (<10). Thus, while Odenbach's measurements suggests that chain formation is linked to larger particles, there is no evidence that these small chains are what forms the large macro-clusters we are studying; nor does his measurements say anything about the actual particle size distribution of the chains versus the surrounding non-chained fluid. X-ray and neutron scattering measurements are also inconsistent. Small-angle neutron scattering measurements suggest that the particle sizes within the agglomerates are larger than the average particle sizes [34]; but small angle X-ray scattering studies [35]show that the mean particle radius of the clusters is the same as the mean particle radius of the original ferrofluid. With regards to the macro-cluster formation process, there is experimental evidence supporting the view that it is a two-stage process: first, simple chains are formed, and then, the chains aggregate to form the macro-clusters [5,6]. One challenge of the experimental efforts thus far has been the inability to directly link the existence of the macro-clusters to the observed phenomena, be it magneto-viscosity or concentration changes. Thus, while the results of Odenbach clearly links large magneto-viscosity effects to higher volume fraction of larger particles, it does not provide direct information on whether the large particles form macro-clusters. In fact, the measurements are only explained in terms of independent particle chains; chain-chain interactions are not taken into account. The viscosity measurements only indicate some sort of agglomeration, but do not provide quantitative information regarding whether the agglomerates are simple chains or micron-sized structures.

In summary, theoretical, computational and experimental studies are generally consistent in implicating larger particles with chain formation. All the studies support the idea that the macro-clusters are formed by the agglomeration of chains. However, with regards to whether the particle size distribution within the macro-clusters is the same as the surrounding fluid, the results remain inconclusive.