Dynamics of magnetic nanoparticle suspensions

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Abstract

We study the dynamical response of suspensions of single-domain magnetic nanoparticles. The effect of sample parameters on Néel and Brownian relaxation times which characterize the response is studied. Their effect on the ac susceptibility is also investigated. As the relaxation times are strongly size dependent we study the effect of polydispersity on the response functions next. A procedure to extract particle-size distribution in polydisperse samples from Cole–Cole plots is provided. Further, the presence of attractive and repulsive interactions amongst MNP yields a distribution of clusters of varying sizes. We propose a model incorporating the phenomena of aggregation and fragmentation to understand the formation of clusters and their distributions. Finally, we compare our numerical results with the experimental data. These comparisons are satisfactory.

1. Introduction

Single-domain magnetic nanoparticles (MNPs) and their colloidal suspensions have attracted a lot of attention in recent years [1–4]. The growing interest is due to a variety of technological applications associated with them. These range from mechanical and thermal applications involving their usage as sealants, lubricants and coolants to challenging applications in medicine for the purpose of magnetic resonance imaging, targeted drug delivery and biomarkers and biosensors to name a few. The main reason behind their wide applicability is the ease with which they can be detected and manipulated by the application of an external magnetic field. Their response times are strongly size dependent, thus introducing the possibility of synthesizing particles to yield application tailored response times.

Most practical applications require surfactant coatings to prevent agglomeration and sedimentation of MNPs. Many biological and medical applications require nanoparticles with biologically relevant coatings in order to use them as probes and carriers [4–6]. The Néel and Brownian relaxation times which characterize the dynamics of the suspension depend not only upon the constituting material but also upon the magnetic volume and the enhanced volume due to surfactant coating. In this paper, we systematically analyse the effect of the above parameters on the relaxation times. We also study their effect on the ac susceptibility $\chi(\omega)$, which is the most commonly studied response function in the laboratory. As the Néel and Brownian relaxation times have a strong dependence on particle size, we find that polydispersity (inherent in experimental samples) results in significant changes in the response function. We have also worked out a procedure to obtain particle-size distributions from the susceptibility data via Cole–Cole plots when they are unavailable.

The above approach assumes the single-particle model [7] applicable to dilute suspensions in which magnetic interactions amongst particles may be ignored. When present in sufficient concentration, clustering and chaining of MNP are rather common as observed by electron microscopy or dynamic light scattering studies [8–10]. This behaviour is undesirable in many applications using magnetic fluids as sealants, coolants, lubricants, printing inks, etc. where invariance of the magnetic and fluid properties are paramount [1]. On the other hand, magnetic domain detection, optical shutters, tagging of surfaces and other entities benefit from clustering of MNP [1, 11]. It is hence useful to understand clustering and its dependence on sample parameters to introduce the possibility of application tailored suspensions. In this spirit, we introduce a model incorporating the competing mechanisms of aggregation and fragmentation. We obtain steady-state cluster-size distributions and mean-cluster sizes for different ratios characterizing the relative strengths of the aggregation and
fragmentation processes. Both these functions exhibit scaling. We have then compared our results with sets of experimental data to lend credence to the aggregation–fragmentation model.

The paper is organized as follows. Section 2 deals with relaxation mechanisms and response functions of dilute MNP suspensions. In section 2.1, we introduce the Néel and Brownian relaxation times and identify regimes where either or both relaxation times contribute. Polydispersity and its characterization is introduced in section 2.2. The calculation of the ac susceptibility $\chi(\omega)$ for monodisperse and polydisperse samples in the different regimes described above is presented in section 2.3. In section 2.4, we provide a procedure to obtain particle-size distributions (for polydisperse samples) using Cole–Cole plots. Section 3 deals with aspects of clustering occurring in samples which are no longer governed by the single-particle approximation. Interactions responsible for clustering are introduced in section 3.1. We introduce the aggregation–fragmentation model in section 3.2. The numerical results are presented in section 3.3. Their comparisons with corresponding measurements in a variety of experimental systems are presented in section 3.4. Finally, we conclude this paper with a summary of results in section 4.

2. Relaxation mechanisms and response functions of dilute MNP suspensions

We now study the relaxation properties and the response functions in dilute MNP suspensions where inter-particle interactions can be ignored. In this regime the particles essentially behave as independent, single-domain, super paramagnetic entities.

2.1. Néel and Brownian relaxation times

If we assume that the anisotropy responsible for single-domain MNP is uniaxial (in the $z$-direction say), the magnetic energy is given by [12]

$$E = VK \sin^2 \theta,$$

where $V = 4\pi r^3/3$ is the magnetic volume of a particle with radius $r$, usually referred to as the core radius, $K$ is the effective magnetic anisotropy constant and $\theta$ is the angle between the $z$-axis and $\hat{h}$. Minimum energy occurs at $\theta = 0$ and $\pi$ defining two equilibrium orientations corresponding to magnetizations $+ VM_o$ and $- VM_o$. If thermal fluctuations are strong enough, magnetic moment reversal takes place within the particle by overcoming the energy barrier (of height $VK$). As a result the time-averaged magnetization is zero and the particle is paramagnetic. The reversal or switching time is called the Néel relaxation time and is given by

$$\tau_N = \tau_0 e^{VK/k_B T},$$

where $\tau_0$ is related to the inverse of the attempt frequency of magnetic reversal.

There is another mechanism by which the magnetic moment of a super paramagnetic particle suspended in a fluid can relax. This mechanism of relaxation can be due to the physical rotation of the particle within the fluid. It is referred to as Brownian rotational motion as it occurs due to the thermal fluctuations in the suspended medium. The Brownian relaxation time is given by [3, 13]

$$\tau_B = \frac{4\pi \eta r^3}{k_B T},$$

where $\eta$ is the dynamic viscosity of carrier liquid and $r^3$ is the magnetic volume of a particle with radius $r$, usually referred to as the core radius, $K$ the anisotropy constant and $\theta$ is the angle between the $z$-axis and $\hat{h}$. Minimum energy occurs at $\theta = 0$ and $\pi$ defining two equilibrium orientations corresponding to magnetizations $+ VM_o$ and $- VM_o$. If thermal fluctuations are strong enough, magnetic moment reversal takes place within the particle by overcoming the energy barrier (of height $VK$). As a result the time-averaged magnetization is zero and the particle is paramagnetic. The reversal or switching time is called the Néel relaxation time and is given by

$$\tau_N = \tau_0 e^{VK/k_B T},$$

where $\tau_0$ is related to the inverse of the attempt frequency of magnetic reversal.

Thus, it is possible to tailor time scales by an appropriate choice of parameters, particularly $K$, $r_c$, and $r_o$. With this in mind, we have systematically studied the effect of $r_c$ and $r_o$ on $\tau_N$ and $\tau_B$ and consequently $\tau_e$ for maghemite (Fe$_2$O$_3$) particles used most commonly in making magnetic fluids.

In table 1, we summarize our evaluations of $\tau_N$, $\tau_B$, and $\tau_e$ for particles with varying magnetic core radius $r_c$, the thickness of the surfactant coating $\delta$, and the particle size. For critical particle sizes, $\tau_e \approx \tau_N$. The relaxation then takes place by rotation of the magnetic moment inside the particle. For large particles, on the other hand, $\tau_B \ll \tau_N$. Consequently, $\tau_e \approx \tau_B$ and the relaxation is due to a physical rotation of the particle in the suspension. Thus, the choice of the relaxation mode is primarily governed by the particle size. For critical particle sizes, often called the cross-over radius $r^* (~8$ nm in table 1), it is found that both mechanisms contribute to the relaxation of the suspended particle.

We have studied the effect of temperature $T$, the surfactant coating $\delta$ and the anisotropy constant $K$ on the cross-over radius $r^*$. Most applications require an operating temperature in the range 270–320 K. We find that $r^*$ does not change perceptibly in this range. Further, as seen from table 1 the variation of $\delta$ does not significantly alter $r^*$. The anisotropy constant $K$, on the other hand, leads to a substantial change in the corresponding value of the cross-over radius. For instance, our evaluations show that spherical MNP of Co having an anisotropy constant $K = 4 \times 10^6$ J m$^{-3}$ has $r^* \sim 2.5$ nm while spherical MNP of Fe having an anisotropy constant $K = 4 \times 10^5$ J m$^{-3}$ has $r^* \sim 5$ nm. Thus, amongst the three parameters of relevance, the anisotropy constant $K$ affects the cross-over radius $r^*$ the most.

2.2. Polydispersity

Monodisperse samples are an idealization. All experimental samples have a distribution of particle sizes and are referred
to as polydisperse. Transmission electron microscopy (TEM) studies of several samples have revealed a log-normal distribution for the variation of particle sizes [1, 14, 15]. Thus, the probability density \( P(r_c) \) of having particles within radius \( r_c \) and \( r_c + dr_c \) can be written as

\[
P(r_c) \, dr_c = \frac{1}{\sqrt{2\pi} \sigma} \exp \left[ -\frac{1}{2} \left( \frac{r_c - \bar{r}_c}{\sigma} \right)^2 \right] \, dr_c, \quad (5)
\]

where \( \bar{r}_c \) and \( \sigma \) are the mean and variance of the distribution. Due to the strong dependence of both Néel and Brownian relaxation times on particle size, it is evident that a distribution of relaxation times will be obtained if the suspended particles have a distribution of sizes. The presence of polydispersity leads to a significant change in the behaviour of the response function of the sample as we shall see in the following subsection.

2.3. Ac susceptibility measurements

The complex susceptibility \( \chi(\omega) \) of a suspension of monodisperse MNP in the linear response regime has the Debye form given by [12]

\[
\chi(\omega) = \frac{\chi_0}{1 - i\omega\tau_c}, \quad (6)
\]

where \( \chi_0 = \chi(\omega = 0) = NV^2M_0^2/k_BT \) is the static susceptibility of the sample comprising \( N \) monodisperse particles of volume \( V \) with a saturation magnetization \( M_0 \). The effective relaxation time \( \tau_c \) is defined by equation (4).

The susceptibility response gets substantially altered in the presence of polydispersity. For polydisperse samples \( \chi(\omega) \) needs to be averaged over the particle-size distribution \( P(r_c) \). Thus,

\[
\chi'(\omega) = \chi_0 \int \, dr_c \, P(r_c) \, \frac{1}{1 + \omega^2 \tau_c^2(r_c)} \quad (7)
\]

and

\[
\chi''(\omega) = \chi_0 \int \, dr_c \, P(r_c) \, \frac{\omega \tau_c(r_c)}{1 + \omega^2 \tau_c^2(r_c)}. \quad (8)
\]

In the case of monodisperse samples, \( \chi''(\omega) \) versus \( \omega \) exhibits a symmetric Debye peak around \( \omega = \tau_c^{-1} \).

In figure 1, we plot \( \chi''(\omega) \) for monodisperse samples (open circles) corresponding to three different values of \( r_c = 4, 8 \) and 12 nm. The chosen values correspond to (a) \( r_c < r^* \), (b) \( r_c \approx r^* \) and (c) \( r_c > r^* \), respectively, for maghemite particles used to generate data of table 1. All cases exhibit the characteristic Debye form. To understand the effect of polydispersity, we also plot equation (8) (filled circles) in the same figure. The distribution \( P(r_c) \) versus \( r_c \) used for the evaluations were obtained from a TEM analysis of maghemite samples used in [14]. These distributions had a log-normal form with a variance \( \sigma \approx 0.35 \). The mean value \( \bar{r}_c \) is the particle size of the corresponding monodisperse evaluation.

As seen in figure 1, a broadening of the response function is observed in all cases after the inclusion of polydispersity. The response no longer has the symmetric Debye form. In figure 1(a), the peak frequency provides information about the mean core radius \( \bar{r}_c \). The width of the log-normal distribution often gives rise to a small Brownian peak although \( \bar{r}_c < r^* \) and the particles predominantly exhibit Néel relaxation. A pronounced two-peak response is obtained in figure 1(b) since \( \bar{r}_c \approx r^* \). Both Néel and Brownian relaxations contribute in this regime, the latter being the dominant mode. The larger (Brownian) peak is an indication that a larger number of particles are primarily undergoing Brownian relaxation. The frequencies of the peak values yield information about the average values of core and the hydrodynamic radii \( \bar{r}_c \) and \( \bar{r}_B \) of the particles. Finally, when \( \bar{r}_c > r^* \), the Brownian

| \( r_c \) (nm) | \( \tau_N \) (s) | \( \delta_1 = 2 \text{ nm} \) | \( \delta_2 = 4 \text{ nm} \) | \( \delta_3 = 6 \text{ nm} \) | \( \tau_B \) (s) |
|----------------|----------------|----------------|----------------|----------------|----------------|
| 4              | \( 10^{-9} \)  | \( 10^{-7} \)  | \( 10^{-6} \)  | \( 10^{-6} \)  | \( 10^{-6} \)  |
| 6              | \( 10^{-7} \)  | \( 10^{-6} \)  | \( 10^{-5} \)  | \( 10^{-5} \)  | \( 10^{-5} \)  |
| 8              | \( 10^{-5} \)  | \( 10^{-6} \)  | \( 10^{-5} \)  | \( 10^{-5} \)  | \( 10^{-5} \)  |
| 10             | \( 10^{-1} \)  | \( 10^{-6} \)  | \( 10^{-5} \)  | \( 10^{-5} \)  | \( 10^{-5} \)  |
| 15             | \( 10^{-2} \)  | \( 10^{-5} \)  | \( 10^{-5} \)  | \( 10^{-5} \)  | \( 10^{-5} \)  |
| 20             | \( 10^{6} \)   | \( 10^{-5} \)  | \( 10^{-5} \)  | \( 10^{-5} \)  | \( 10^{-5} \)  |

Table 1. Variation of the Néel (\( \tau_N \)) and effective (\( \tau_B \)) relaxation times as a function of the core radius \( r_c \) of the MNPs. \( \tau_B \) has also been evaluated for three values of the surfactant coating \( \delta \). The corresponding \( \tau_e \) for these values is also evaluated.

![Figure 1](image-url)
relaxation dominates and the frequency corresponding to the peak provides information regarding the hydrodynamic radius \( r_0 \) of the particle. Comparing figures 1(a) and (c), it is clear that polydispersity affects Néel relaxation more significantly than Brownian relaxation as expected (cf. equations (2) and (3)).

2.4. Particle size distributions from Cole–Cole plots

The information on distribution of relaxation times can be obtained from susceptibility measurements by empirical models. The most frequently used models for this purpose are the Cole–Cole and the Cole–Davidson models. The Cole–Cole model is suitable for systems exhibiting a symmetrical form of \( \chi''(\omega) \) about a vertical axis passing through its peak value \([16, 17]\). The Cole–Davidson model, on the other hand, is employed for asymmetrical forms of \( \chi''(\omega) \).

As observed in figure 1, the response functions of typical MNP suspensions are indeed asymmetrical. Therefore, these can be conveniently represented by the Cole–Davidson expression for the ac susceptibility \([18]\):

\[
\chi(\omega) = \frac{\chi_c}{(1 + i\omega\tau_c)^\beta},
\]

(9)

where \( \tau_c \) is the central relaxation time about which all the other relaxation times are distributed and \( \beta \) is a fitting parameter with limits \( 0 \leq \beta \leq 1 \). When \( \beta = 1 \), the above equation reduces to the Debye form of equation (6) characterized by a single relaxation time. Separating the real and imaginary parts of equation (9) results in

\[
\chi'(\omega) = \chi_c \cos \beta \phi \cos \beta \phi
\]

(10)

and

\[
\chi''(\omega) = \chi_c \cos \beta \phi \sin \beta \phi,
\]

(11)

where \( \phi = \arctan \omega \tau_c \).

Cole and Cole proposed a method of graphically representing the effects of multiple relaxation times \([16, 17]\). The method consists of plotting \( \chi''(\omega) \) for a certain frequency against \( \chi'(\omega) \) at the same frequency. When \( \beta = 1 \), the Cole–Cole plot is semicircular. The plot is symmetrical about the vertical line passing through the point \( \chi'(\omega) = \chi_c/2 \) when \( \chi''(\omega) \) is maximum at a frequency \( \omega = \tau_c^{-1} \). Other values of \( \beta \) yield a ‘skewed arc’ in the Cole–Cole plots which characterizes the presence of multiple relaxation times. The parameter \( \beta \) can be determined from the Cole–Cole plot by a graphical construction. It may also be determined by the best fits of equations (10) and (11) to the experimental data.

In figure 2 we show the Cole–Cole plots for the same polydisperse samples that were used to obtain data of figure 1. Cases (a), (b) and (c) correspond to \( \bar{r}_c < r^* \), \( \bar{r}_c \approx r^* \) and \( \bar{r}_c > r^* \), respectively. The skewed arcs observed in all the cases are a consequence of multiple relaxation times introduced due to polydispersity in the samples. Further, the asymmetry in the particle-size distributions is reflected in the asymmetry of the arcs. The Cole–Cole plots are distinct in each of the regimes. In particular, the cross-over regime is characterized by a two-humped form signifying a contribution of both Néel and Brownian relaxations to the response function. Thus, significant information regarding the experimental sample can be inferred from the Cole–Cole plots.

We now provide a simple procedure for evaluating the particle-size distribution \( P(r_c) \) versus \( r_c \) in the experimental sample when the response function exhibits multiple relaxation times. Assuming a log-normal form, \( P(r_c) \) versus \( r_c \) is characterized by its mean \( \bar{r}_c \) and variance \( \sigma \) signifying the spread in the particle-size distributions. While the evaluation of \( \bar{r}_c \) is straightforward, the variance \( \sigma \) needs to be estimated. Recalling that multiple relaxation times are a consequence of polydispersity, it is imperative to connect \( \beta \) with \( \sigma \). In order to find this relationship, we have gone through the following sequence of steps. Firstly, \( \chi'(\omega) \) and \( \chi''(\omega) \) were evaluated using equations (7) and (8) for a chosen value of \( \bar{r}_c \) and \( \sigma \). The corresponding values of \( \tau_c \) and \( \beta \) were then obtained by fitting the above susceptibility data with equations (10) and (11) of the Cole–Davidson model. This procedure was then repeated for a number of \( \sigma \) values in the range 0.1–0.5, keeping \( \bar{r}_c \) constant. Larger values of \( \sigma \) were not considered as they resulted in extremely broad log-normal distributions which are not of relevance in experiments. The above evaluation was then performed for three different values of \( K \). The results obtained are plotted in figure 3 on a semi-logarithmic scale. The solid lines follow the equation

\[
\sigma = A(K)e^{-B\beta}.
\]

(12)

The parameters \( A(K) \) and \( B \) in each case are obtained from the best fits of the above equation to the evaluated data. We find that \( B = 2.45 \pm 0.05 \) and is independent of \( K \). We also find that equation (12) and the parameter \( B \) are unaffected by \( \bar{r}_c \), which was varied from 4 to 12 nm.
3. Clustering in MNP suspensions

The properties of the magnetic fluid are considerably affected by the aggregation of particles (in spite of surfactant coating) due to the presence of attractive and repulsive interactions. It is hence instructive to consider the different interaction energies in MNP suspensions and understand their interplay which leads to the formation of aggregates or clusters of different sizes.

3.1. Interactions in MNP suspensions

The primary interaction energies in these systems are enumerated below [1]:

1. Dipolar interaction. The dipolar interaction energy between two MNPs, each having a magnetic moment $\mu$ is given by

$$E_d(s) = -\frac{\mu_0}{4\pi} \left( \frac{3\mu \cdot (\mu \cdot \hat{s})\hat{s}}{s^5} - \frac{\mu^2}{s^7} \right),$$

where $s$ is the center-to-center separation between the two nanoparticles and the permeability of free space $\mu_0 = 4\pi \times 10^{-7}$ H m$^{-1}$.

2. van der Waal interaction. This arises spontaneously between neutral particles because of the fluctuating electric dipolar forces and is attractive in nature. Hamaker calculated this interaction for identical spheres separated by a surface-to-surface distance $l$ to be [19]

$$E_v = \frac{A}{6} \left( \frac{2}{l^2 + 4l} + \frac{2}{(l + 2)^2} + \ln \left( \frac{l^2 + 4l}{l^2 + 4l + 4} \right) \right).$$

In the above equation, the Hamaker constant $A = 10^{-19}$ N m.

3. Steric interaction. The steric energy comes into play due to the presence of long chained surfactant molecules coating the particles. This mechanism prevents the particles from approaching very close to one another. This repulsive energy for spherical particles has been calculated by Papell and is given by [20]

$$E_s = \frac{E}{1.325} \left( 2\delta - \frac{s}{2} \right)^{\frac{3}{2}} (r_c + \delta)^{\frac{1}{2}}.$$

In the above form, $E$ is the Young’s modulus which is usually of the order of 10$^8$ Pa for polymeric matrices and biological membranes.

Apart from the above interaction energies, the thermal energy responsible for the Brownian motion of the suspended particles also plays an important role in the aggregation dynamics. We expect the thermal degrees of freedom, in conjunction with steric repulsion, to not only hamper the aggregation process but also remove particles from the parent cluster leading to its fragmentation. At this juncture we define a parameter $\Omega$ as the ratio of energies leading to aggregation to those which lead to fragmentation as follows:

$$\Omega = \frac{E_d + E_v}{E_s + k_B T}.$$  

It is expected that the distribution of cluster sizes and the mean-cluster size will be governed by the ratio $\Omega$. In the following subsection, we present a model which incorporates the competing mechanisms of aggregation and fragmentation.
3.2. The aggregation–fragmentation model

The formulation introduced by Smoluchowski is especially useful to model a suspension of MNPs [21, 22]. To begin with, we assume that the suspension contains identical, single particles executing Brownian motion. The latter leads to the aggregation of two particles if they come within an appropriate range of one another and the net interaction between them is attractive. The resulting cluster of size two also executes Brownian motion, but with a reduced diffusion rate till it encounters a particle or a cluster of particles. The process goes on and eventually a single large cluster comprising all the particles is formed. Such a cluster is usually referred to as an infinite aggregate. In most useful suspensions, however, there is a distribution of clusters of varying sizes. As discussed in the preceding subsection, the combined effects of thermal energy and inter-particle repulsion can introduce fragmentation in the cluster dynamics thereby preventing the formation of large aggregates. We thus include this additional mechanism in the rate equations which describe the evolution of clusters.

Let \( P(k, t) \) denote the probability of having a cluster containing \( k \) particles at time \( t \). The time evolution of \( P(k, t) \) is governed by the following rate equations:

\[
\frac{\partial P(k, t)}{\partial t} = \sum_{i+j=k} K_{ij} P(i, t) P(j, t) - P(k, t) \sum_{j=1}^{\infty} K_{kj} P(j, t) + \omega P(k+1, t) - \omega P(k, t), \quad k > 1, \tag{17}
\]

\[
\frac{\partial P(1, t)}{\partial t} = -P(1, t) \sum_{j=1}^{\infty} K_{j1} P(j, t) + \omega \sum_{j=2}^{\infty} P(j, t), \quad k = 1. \tag{18}
\]

In equations (17) and (18), \( K_{ij} \) is the aggregation kernel which describes the coalescence of a cluster containing \( i \) particles with another containing \( j \) particles to yield a larger aggregate comprising \( k = i + j \) particles. It is assumed to have a mass-dependent form defined by \( K_{ij} = D(i^{-\mu} + j^{-\mu}) \) to take into account the reduced mobility of large clusters. A value of \( \mu = 0 \) implies a mass-independent mobility, i.e., clusters of all sizes diffuse with the same ease. Non-zero values of \( \mu \) result in a slower mobility of larger clusters and consequently a slower growth rate of clusters. In the limit of \( \mu = \infty \), only monomers are mobile. The choice of \( \mu \) is dictated by the experimental parameters as we shall see in a short while. The parameter \( \omega \), on the other hand, describes the loss or fragmentation of a particle from a parent cluster. The parameters \( D \) and \( \omega \) define the relative strength of the aggregation and fragmentation processes.

The first and the third terms in equation (17) are referred to as the gain terms which result in the formation of clusters of size \( k \). The former describes the aggregation of two clusters to yield a cluster containing \( k \) particles while the latter describes the generation of a cluster comprising \( k \) particles due to fragmentation of a particle from a cluster of size \( k + 1 \). The second and the fourth terms on the other hand, are referred to as the loss terms which describe processes leading to the loss of clusters of size \( k \). This could be due to aggregation of a cluster of size \( k \) with another or its fragmentation. The terms of equation (18) can be interpreted similarly. It is easy to check that the following sum rule is satisfied:

\[
\frac{\partial}{\partial t} \left( \sum_{k=1}^{\infty} P(k, t) \right) = 0 \quad \text{or} \quad \sum_{k=1}^{\infty} P(k, t) = 1, \tag{19}
\]

as required by conservation conditions.

The condition \( \partial P(k, t)/\partial t = 0 \) describes the steady state which is of interest to us. In the absence of the fragmentation term, equation (17) reduces to the Smoluchowski equation describing coagulation phenomena [22]. There have been a few studies of this model, both analytical and numerical, to predict scaling forms associated with cluster growth and cluster-size distributions [23–29]. The growth of clusters with time is a power governed by the relation \( \langle k(t) \rangle \sim t^\gamma \). Choosing \( \mu = 1 \), the value of \( \gamma \) was estimated to be \( \approx 0.5 \). The steady state in this model was found to be an infinite (single) aggregate comprising all the \( N \) particles. Note that in the absence of fragmentation, the constant \( D \) can be absorbed by redefining \( t \) as \( D t \) in equation (17), making the latter independent of the aggregation rate.

To mimic those physical situations which do not have an infinite aggregate as a steady state but rather have a distribution of clusters of varying sizes, it is essential to include fragmentation as a competing mechanism to aggregation. Of relevance in the context of this study is the model incorporating mass-independent aggregation and mass-dependent evaporation processes reported in [27]. The competition between aggregation and evaporation leads to several asymptotic outcomes of the steady-state solution of this model. For instance, if evaporation dominates over aggregation, the steady-state cluster-size distribution \( P(k) \) versus \( k \) decays exponentially. On the other hand, for a critical evaporation rate, the distribution decays as \( k^{-5/2} \).

3.3. Numerical results

We now solve the set of equations defined by equations (17) and (18) numerically to obtain the steady-state cluster-size distribution \( P(k) \) versus \( k \). It is useful to define the ratio \( R \) characterizing the relative strengths of the aggregation and fragmentation mechanisms:

\[
R = \frac{D}{\omega}. \tag{20}
\]

Identifying the physical origin of \( D \) in the attractive interactions between clusters and that of \( \omega \) in the disordered agents (such as repulsive interactions and temperature), we can expect \( R \) to have the same qualitative effect as the ratio \( \Omega \) defined in equation (16) on steady-state cluster-size distributions. We use this correspondence to bring contact between numerical results and experimental observations on cluster formation in MNP suspensions.

In figure 5(a), we look at the variation of the mean-cluster size \( \langle k(R, t) \rangle \) as a function of \( t \) for different values of \( R \) on a double logarithmic scale. The parameter \( \mu \) was chosen to be 2.0. After an initial growth period obeying a power law, the cluster size attains a steady-state value of \( \langle k(R) \rangle \) due to
The initial growth of clusters obeys a power law characterized by the exponent \( z \). For these data, the growth exponent \( z \) depends upon the value of \( \mu \). We find that \( z = 0.78 \) for \( \mu = 1 \) and \( \mu = 2 \) for different values of the ratio \( R \). Similar data corresponding to \( \mu = 1 \) are also indicated in the inset. For these data, the growth exponent \( z = 0.78 \pm 0.02 \) as indicated.

As expected, \( \langle k(R) \rangle \) increases with increasing values of \( R \). In fact, we find that \( \langle k(R) \rangle \sim R^\alpha \) with \( \alpha = 0.85 \pm 0.02 \) as can be seen in the inset. Further, in the diffusion-dominated regime \( (R \gtrsim 0.5) \) the data in figure 5(a) can be scaled by reploting \( \langle k(R, t) \rangle / \langle k(R) \rangle \) versus \( t/t_s \) where \( t_s \) is the time taken to attain the steady state. The initial cluster growth is of the form \( \langle k(t) \rangle \sim t^z \). We find that the growth exponent \( z = 0.38 \pm 0.02 \). The scaled data are shown in figure 5(b) on a double logarithmic scale. The best-fit line with a slope of 0.38 is also indicated. The value of the growth exponent also depends upon the value of \( \mu \). For \( \mu = 1 \), our simulations yield \( z = 0.78 \pm 0.02 \). The corresponding scaled data and the power law fit are also shown in the inset of figure 5(b). The faster growth of clusters is a consequence of increased mobility due to a lower value of \( \mu \).

Next in figure 6(a) we plot the steady-state distribution \( P(k) \) versus \( k \) for \( \mu = 2 \) for the same set of \( R \) values considered above. We find that the tails of the distributions fit well to a power law in \( k \). In figure 6(b), we plot \( \langle k(R) \rangle P(k) \) versus \( k/\langle k(R) \rangle \) where \( \langle k(R) \rangle \) is the steady-state average cluster size for the corresponding value of \( R \). These plots indicate that the distribution functions \( P(k) \) corresponding to different values of \( R \) obey scaling in the diffusion-dominated regime. The scaling relation can be summarized in the following equation:

\[
P(k) = \frac{1}{\langle k(R) \rangle} f \left( \frac{k}{\langle k(R) \rangle} \right), \quad \langle k(R) \rangle \sim R^\alpha.
\]

### 3.4. Comparisons with experimental data

We now compare our simulation results with the experimental data on average cluster sizes in a variety of MNP suspensions. Eberbeck et al studied the aggregation of various MNPs in a variety of media such as water, phosphate buffered saline, calf serum, bovine serum and human serum [30, 31]. The experimental measurements were performed at room temperature. In all cases, formation of dimers and trimers were reported by the authors. To make comparisons with the simulation results of our model, we first calculate the ratio \( \Omega \)
droplets were small Fe$_3$O$_4$ grains in kerosene coated with a emulsions of ferrofluid droplets in water. The ferrofluid authors have studied aggregation dynamics in very dilute fragmentation model are reported in [8]. In this paper, the especially relevant in the context of the aggregation–fragmentation model with $\mu = 1$ obtained with $\mu = 1$ and $\mu = 1$ (refer the inset of figure 5(a) and corresponding text).

defined in equation (16) for each of the samples. These along with the sample specifications are tabulated in table 2. As can be seen in column 4, $\Omega$ is in the range 0.35–0.70. Referring to the plot of $\langle k(R) \rangle$ versus $R$ for $\mu = 2$ in the inset of figure 5(a), a value of $R$ in the above range yields dimers and trimers in the steady state.

A set of experimental measurements which we find especially relevant in the context of the aggregation–fragmentation model are reported in [8]. In this paper, the authors have studied aggregation dynamics in very dilute emulsions of ferrofluid droplets in water. The ferrofluid droplets were small Fe$_3$O$_4$ grains in kerosene coated with a surfactant to prevent agglomeration. The data on average chain lengths as a function of time for different volume fractions replotted on scaled axes as shown in the figure. The solid line corresponds to a slope of 0.78 obtained from a numerical solution of the aggregation–fragmentation model with $\mu = 1$ (refer the inset of figure 5(b) and corresponding text).

Table 2. Calculated value of the ratio $\Omega$ and the corresponding estimated value of the cluster size for a variety of MNP used in experiments by Eberbeck et al [30, 31]. The experimental parameters associated with each sample are also specified.

| MNP sample | Core | Shell          | $\Omega$ | $\langle k \rangle$ |
|------------|------|----------------|----------|--------------------|
| DDN128     | Fe$_3$O$_4$ | carboxydextran | 0.5364   | 2.3                |
| FluidMagD5 | Fe$_3$O$_4$ | starch         | 0.36     | 2.0                |
| MagBSA     | Fe$_3$O$_4$ | BSA            | 0.676    | 2.5                |
| Resovist   | Fe$_3$O$_4$ | Carboxydextran | 0.51     | 2.4                |

Figure 7. Data from [8] on average chain length as a function of time for different volume fractions replotted on scaled axes as shown in the figure. The solid line corresponds to a slope of 0.78 obtained from a numerical solution of the aggregation–fragmentation model with $\mu = 1$ (refer the inset of figure 5(b) and corresponding text).

On the quantitative side, we find that the experimental data are well represented by a growth exponent $z = 0.78 \pm 0.02$ obtained with $\mu = 1$ in our simulations. The corresponding line is depicted in figure 7. It is pertinent to recall here that the dipolar interaction becomes dominant in the presence of the applied magnetic field thereby increasing the diffusivity of the clusters. In the aggregation–fragmentation model, the latter can be achieved by an increase in the value $D$ as well as a decrease in the value of $\mu$. Consequently, we find that our data on $\langle k(R, t) \rangle$ versus $t$ for a value of $\mu = 1$ rather than $\mu = 2$ results in accurate comparisons with the experimental data. We note here that theoretical studies on systems of this kind were so far based on Smoluchowski kinetic equations for irreversible aggregation [23, 24]. However, the observed growth exponent does not conform with the predicted value of $z = 0.5$ (also obtained with $\mu = 1$) of this model.

A similar set of experimental results were obtained in [9] where the power law prediction for cluster growth was checked by performing a large number of experiments on aqueous solutions of super paramagnetic polystyrene beads having a uniform distribution of Fe$_3$O$_4$ particles. The data were obtained for five values of the volume fraction in the presence of low field strengths and higher field strength using optical microscopy. The exponent $z$ describing the cluster growth in these studies was found to be much larger than the predicted value of 0.5 especially for small volume fractions and low field strengths. These observations further reiterate the appropriateness of introducing fragmentation along with aggregation especially in the above limits where the thermal energy plays a significant role in the dynamics.

4. Summary

We conclude this paper with a summary of results presented here. Our main interest was to understand the factors governing the dynamical response of suspensions of single-domain MNPs. Such an understanding introduces the possibility of synthesizing particles with application tailored response times. The effect of sample parameters on the Néel and Brownian relaxation times which characterize the response was studied. Amongst all the parameters of relevance, the anisotropy of the constituting material and the particle size affect the relaxation time most significantly. In fact, the dominant relaxation time is also decided primarily by the particle size. We also studied how these parameters affect the ac susceptibility $\chi(\omega)$ which is the most commonly studied response function in the laboratory. This understanding proves to be useful in estimating relaxation times as well as sample parameters from the measurement of $\chi(\omega)$ in the laboratory.

We have then studied the effect of polydispersity, an inherent feature of all samples on the response characteristics. These exhibit significant changes due to the strong dependence of relaxation times on particle sizes. The primary effect is the broadening of response functions and in some cases the latter exhibits a two peaked structure. We have also worked
out a procedure to obtain the particle-size distribution from $\chi(\omega)$ using Cole–Cole plots and the analysis of Cole and Davidson. This provides an alternative procedure to TEM analysis which is usually employed to obtain particle-size distributions.

The above studies assumed a single-particle model applicable to dilute suspensions. However, in many cases the inter-particle interactions cannot be ignored. Clustering of particles is inevitable in such suspensions. While the formation of clusters is undesirable in some applications, it is beneficial in many others. Hence, we have tried to understand the mechanisms responsible for clustering and the experimental parameters which govern the properties of cluster-size distribution and the average cluster size. This knowledge is useful for the synthesis of application tailored suspensions.

A model incorporating the phenomena of aggregation and fragmentation was used to understand aspects of clustering. The steady-state cluster-size distributions of the model were obtained by numerically solving the rate equations describing the evolution of clusters. We have obtained scaling forms for the cluster-size distributions and the average cluster size. Our results agree well with experiments where clustering or chain formation has been observed.

An interesting extension of this work is to small ferromagnetic particles with an antiferromagnetic coating which have recently generated considerable research interest [32–34]. The resulting ferromagnetic–antiferromagnetic interfaces, under suitable experimental conditions, yield an anisotropy referred to as exchange bias. The latter results in locking of the magnetic moment of the superparamagnetic particle. As a result, we can expect the relaxation behaviour of these particles to be quite different from that of superparamagnetic particles considered in this paper. At present, we are attempting to develop a theoretical framework to understand the response behaviour of a suspension MNPs with exchange bias. We believe that it will be possible to formulate the necessary arguments.

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