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Dynamic Properties of Magnetic Colloidal Particles and Holes

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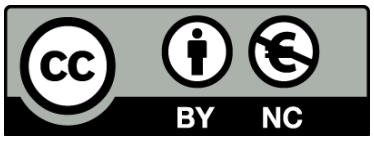

Universitat de Barcelona

Facultat de Física

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Dynamic properties of magnetic colloidal particles and holes

Certifico que la present tesi doctoral ha estat realitzada sota la meva direcció

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Propiedades dinámicas de partículas y huecos magnéticos coloidales

Introducción

Las partículas magnéticas de pequeño tamaño son de gran importancia en multitud de áreas de la ciencia y la tecnología. No obstante, hay escasos ejemplos de sistemas formados por estas partículas suspendidas en un medio líquido de manera que las interacciones magnéticas desempeñen un papel principal, tanto en su comportamiento dinámico como en la formación de estructuras. Entre estos pocos casos figuran los *ferrofluidos* y las partículas de látex dispersas en un ferrofluido (*huecos magnéticos*).

Un *fluido magnético* o *ferrofluido* es una suspensión coloidal estable de partículas monodominio de un material magnético en un líquido común, como agua u otro compuesto orgánico. Inicialmente fueron concebidos como la primera muestra de un líquido artificial en el que las propiedades magnéticas y reológicas se viesen incrementadas hasta ser comparables a las de un sólido ferromagnético, y se manufacturaron debido al hecho de que la existencia de

monofases ferromagnéticas líquidas reales era bastante improbable. Aunque la estabilidad de la suspensión está asegurada esencialmente por el movimiento browniano de las partículas, usualmente éstas se recubren de una capa de surfactante a fin de inhibir su coalescencia a distancias cortas.

Los ferrofluidos tienen muchas aplicaciones tecnológicas, incluyéndose entre ellas los precintos de exclusión para las disqueteras de ordenador, amortiguadores en altavoces, impresoras, instrumentos para tranferencia de masa y calor, lubricantes, etc. Por ejemplo, resulta complicado mantener un lubricante dentro de la zona de contacto de las parte móviles de un determinado mecanismo ya que las fuerzas centrífugas o la geometría tienden a expulsarlo. Sin embargo, un campo magnético puede ayudar a retener un lubricante magnético en la zona de fricción donde es más necesario. Más aún, la eficacia de un lubricante depende principalmente de su viscosidad y de su capacidad para formar una capa adsorbida. Los lubricantes magnéticos son más efectivos que los comunes incluso en ausencia de campos magnéticos porque las partículas magnéticas que lo componen se ven atraídas por las superficies de acero y aumentan

así tanto la viscosidad como el grosor de esta capa límite. Los ferrofluidos encuentran también aplicaciones en ecología y medicina. Por ejemplo, sirven para eliminar residuos oleosos de los vertidos industriales. Los fluidos magnéticos con un hidrocarburo como base se pueden disolver en los productos oleosos para formar un ferrofluido más diluido. Un flujo de agua que contiene esta suspensión circula a través de un separador magnético donde un campo magnético que varía fuertemente en el espacio separa los residuos magnéticos del agua. Pero son los múltiples y cualitativamente diversos efectos procedentes de la interacción entre ferrofluidos y campos magnéticos los que han abierto la posibilidad de nuevas y prometedoras aplicaciones tecnológicas. Además de sus propiedades magnéticas, ópticas y reológicas, que discutiremos a lo largo de esta monografía, los ferrofluidos exhiben otros fenómenos poco comunes de gran interés científico, como las inestabiliades superficiales y curiosas estructuras de no equilibrio.

Hace algunos años se descubrió que las esferas monodispersas de poliestireno, dispersas en un ferrofluido, constituyen un modelo conveniente para el estudio de varios tipos de fenómenos que muestran transiciones orden-desorden. La base de ello es que las esferas desplazan al ferrofluido y se comportan como *huecos magnéticos* con un momento magnético efectivo igual al momento total del ferrofluido desplazado. Las esferas (entre 1 y $100\mu m$) son mucho mayores que las partículas magnéticas del ferrofluido ($100\ \AA$) y, por tanto, se comportan como si se hallasen en un medio magnético uniforme.

En general, las microesferas monodispersas presentan una gran variedad de aplicaciones industriales, científicas y médicas, debido a la singularidad de sus muchas propiedades como el poseer una distribución de tamaños extremadamente uniforme, una forma esférica casi perfecta, con un diámetro determinado con gran precisión, la gran diversidad de tipos de partículas (sólidas, porosas, magnéticas, etc.) y la posibilidad de manufacturar sus propiedades superficiales. Las microesferas de poliestireno con inclusiones magnéticas se han empleado satisfactoriamente para separar diversos materiales orgánicos (células, virus, micelas, etc.) El principio de esta aplicación se basa en una interacción selectiva entre los antígenos de la membrana de las células y los anticuerpos situados sobre las esferas. Las esferas con las células adheridas pueden eliminarse posteriormente por medio de un campo magnético. Es posible limpiar así la médula espinal de pacientes afectados de neuroblastoma o de ciertas formas de leucemia, limitando los tratamientos con radioterapia y/o quimioterapia, que puede afectar perjudicialmente al resto de células sanas del organismo. Mediante esta técnica, es posible limpiar hasta una décima parte de la médula de los pacientes,

antes de recurrir a otras terapias más radicales. Las partículas magnéticas se pueden usar también como marcadores si se las recubre con ciertos componentes químcicos o con anticuerpos. Durante la migración de las partículas dispersas, éstas se adhieren a blancos específicos y facilitan su localización. Otra prometedora aplicación es su uso como portadores; se sitúan ciertos productos químicos sobre la superficie de las partículas y se transporta a éstas a los lugares donde las medicinas serán efectivas. Los bioquímicos están valorando actualmente las potencialidades de este método para tratar el cáncer.

Conclusiones

A lo largo de esta monografía nos hemos ocupado del estudio de sistemas fluidos, tanto con monodominios magnéticos como con dos tipos distintos de partículas, magnéticas y no magnéticas, en dispersión en un líquido newtoniano en situaciones fuera del equilibrio. El comportamiento de estos sistemas se ve influenciado en gran medida por la presencia de un campo magnético externo, lo que da lugar a nuevos fenómenos que han sido el fundamento de muchas aplicaciones prácticas. Sin embargo, esta influencia depende de los diferentes procesos de relajación que tienen lugar dentro las partículas, con respecto a su ejes cristalinos, así como fuera de ellas, con respecto al fluido portador. Hemos descrito cuáles son estos procesos y obtenido la dependencia con respecto de los parámetros que describen las partículas y el fluído, de algunos coeficienes que caracterizan las propiedades reológicas, magéticas y ópticas de la suspensión coloidal.

Para ser más precisos, en la primera parte del Capítulo I hemos analizado la dinámica de una esfera ferromagnética en la que el momento magnético se encuentra fijado rígidamente a su cuerpo, así como también las viscosidades de una suspensión diluida de este tipo de partículas. La base teórica fundamental es la ecuación de Navier-Stokes, en la que se ha incluído una fuerza inducida que representa las perturbaciones introducidas en la dinámica del fluido por el movimiento de la partícula, y una fuente de ruido tipo Langevin, procedente de las fluctuaciones de los campos hidrodinámicos. Esta ecuación da cuenta del acoplamiento de las dinámicas del fluido y la partícula. Una expansión multipolar de las cantidades que aparecen en la solución formal de la ecuación de Navier-Stokes nos permite calcular las expresiones para la fuerza y el momento de las fuerzas ejercidos sobre la partícula, los cuales contienen contribuciones aleatorias cuyas propiedades estadísticas están dictadas por la teoría de fluctuaciones hidrodinámicas. Hemos empleado dos métodos para obtener las viscosidades de cizalladura y rotacional. Uno de ellos es determinista, y se basa

en la fórmula de Kirkwood para el tensor de presiones viscosas, el cual a su vez está relacionado con el multipolo de segundo orden de la fuerza inducida. El otro método se basa en la teoría de respuesta lineal, que da los coeficientes de transporte en términos de funciones de correlación dependientes del tiempo. La presencia del campo magnético provoca la aparición de contribuciones antisimétricas al tensor de presiones y da lugar a la viscosidad rotacional que aparece como un nuevo coeficiente de transporte. Esta parte antisimétrica del tensor de presiones proviene del balance que se establece entre el momento de las fuerzas ejercidas por el campo magnético sobre un dipolo y el momento de las fuerzas hidrodinámicas. Como consecuencia, el momento angular de las partículas puede diferir del valor de la vorticidad del fluido en el punto que aquella ocupa. Este formalismo es bastante general y se emplea en la segunda parte del Capítulo para calcular la dependencia de la viscosidad rotacional con respecto de la energía magnética de anisotropía del material. Considerando otro límite específico, en el cual los momentos magnéticos ya han relajado y apuntan en la dirección del campo, obtenemos que la viscosidad aumenta al aumentar el parámetro de anisotropía, alcanzando un límite de saturación. Hemos comparado nuestros resultados con los de otros autores y con los datos experimentales disponibles para dipolos rígidos. Los resultados procedentes de otra solución aproximada de la ecuación estacionaria de Smoluchowski sobreestiman los nuestros, mientras que los basados en ecuaciones de relajación fenomenológicas propuestas para el momento angular interno de la suspensión son muy próximos a los que hemos obtenido nosotros, y reproducen bastante bien los datos experimentales.

Siguiendo un procedimiento análogo, en el Capítulo II hemos presentado un formalismo general para estudiar la dinámica de relajación de partículas ferromagnéticas, con el propósito principal de proporcionar expresiones explícitas tanto para la viscosidad como para algunos tiempos de relajación que caracterizan diferentes propiedades del material (birrefringencia, susceptibilidad magnética,...). Los resultados cubren todo el rango de situaciones experimentales posibles. Hemos obtenido la ecuación de Smoluchowski que describe la evolución de la distribución de probabilidad de los grados de libertad relevantes de las partículas y que nos permite obtener una jerarquía de ecuaciones dinámicas para las diferentes funciones de correlación. Esta jerarquía se puede cerrar utilizando las conocidas aproximaciones de desacoplo apropiadas. A partir de las ecuaciones dinámicas para las correlaciones, uno puede encontrar expresiones para los tiempos de relajación característicos y éstos constituyen el punto de partida para determinar los coeficientes de transporte por medio de las fórmulas de Green-Kubo. En particular, hemos visto que la viscosidad rotacional alcanza de nuevo

un límite de saturación, pero ahora depende los dos parámetros que comparan la energía magnética y la energía de anisotropía con la energía térmica. Para contrastar la validez de nuestro formalismo, hemos comparado nuestros resultados para el tiempo de relajación de las partículas con los experimentos de birrefringencia llevados a cabo con dos tipos de materiales ferromagnéticos. En ambos casos, nuestros resultados concuerdan muy bien con los datos experimentales. También hemos proporcionado una expresión general para la susceptibilidad magnética compleja del fluido magnético bajo la acción simultánea de un campo magnético polarizante y de un pequeño campo alterno, perpendiculares entre sí, lo que abre posibilidades para nuevas medidas experimentales.

En el Capítulo III hemos estudiado la dinámica de partículas no magnéticas, o huecos magnéticos, suspendidos en un ferrofluido en presencia de un campo magnético rotativo. Calculamos las fuerzas hidrodinámicas y el momento de las fuerzas ejercidas sobre el hueco, de donde podemos identificar los tensores de fricción traslacional y rotacional. Estas cantidades dependen de la fracción volúmica de partículas magnéticas y del campo magnético, el cual otorga al sistema un carácter anisótropo. El conocimiento de la fuerza y del momento de las fuerzas que actúan sobre el hueco nos permite estudiar las dinámicas de traslación y de rotación de las partículas cuando aplicamos un campo magnético rotativo. Nos hemos concentrado particularmente en el caso en que el ferrofluido está en reposo y el hueco puede girar bajo la influencia del campo magnético. Bajo estas condiciones, hemos probado que la velocidad angular del hueco es proporcional a la frecuencia del campo, pero que tiene una dirección opuesta. El coeficiente de proporcionalidad es lineal con la fracción volúmica de las partículas de ferrofluido, y depende de una función de la intensidad del campo magnético que muestra un comportamiento de saturación. Hemos comparado nuestros resultados con experimentos realizados con partículas de poliestireno dispersas en diferentes ferrofluidos. En el rango de frecuencias consideradas, hemos reproducido los resultados experimentales concernientes a la velocidad de rotación del hueco como función del campo magnético externo. También hemos realizado un estudio preliminar de las interacciones hidrodinámicas entre los huecos en el ferrofluido. Esencialmente, hemos obtenido expresiones para los tensores de Oseen y Rotne-Prager de un ferrofluido como el primer paso en el estudio del importante papel que las interacciones hidrodinámicas pueden desempeñar en las propiedades físicas de estos materiales a bajas concentraciones. Para mostrar la estructura de estos tensores y su influencia en la dinámica de los huecos magnéticos, hemos dado también expresiones para las valocidad de una pareja de partículas depositándose bajo la acción de la gravedad en

el seno de un ferrofluido. Como esperábamos, para diferentes configuraciones iniciales, la velocidad depende de los parámetros que caracterizan el ferrofluido. Resulta útil señalar que, aunque hemos realizado el estudio para un ferrofluido compuesto por dipolos rígidos, para el que la energía de anisotropía es mucho mayor que la energía asociada con la interacción de los momentos magnéticos con el campo externo, se puee hacer una análisis similar en una situación más general, en la que estas dos energías de las partículas magnéticas presenten valores arbitrarios.

El Capítulo IV se presenta como un estudio preliminar de los fenómenos de agregación que tienen lugar en sistemas de partículas magnéticas en suspensión, así como de las estructuras resultantes. Nuestro primer propósito ha sido elucidar la influencia de las interacciones hidrodinámicas en la cinética del proceso de agregación. Hemos extendido la teoría clásica de la coagulación de Smoluchowski para dar cuenta de la presencia de estas interacciones, importantes cuando se traspasa el régimen de concentraciones diluidas. Tales interacciones actúan antes de que las diferentes partículas lleguen a la esfera de influencia de una partícula dada. Hemos obtenido las ecuaciones cinéticas para el proceso de agregación y, a partir de ellas, hemos analizado la formación de agregados. Nuestra principal conclusión es que la presencia de interacciones hidrodinámicas ralentiza el proceso de agregación. Como un segundo problema, hemos estudiado la dinámica de una cadena de partículas magnéticas bajo la influencia de una flujo externo elongacional. En particular, hemos calculado las contribuciones de la cadena al tensor de presiones del sistema a partir de la ecuación reológica propuesta por Kramers. De esta cantidad hemos obtenido la corrección a la viscosidad debida a la presencia de interacciones dipolares. Estos resultados preliminares constituyen el objeto de futuros trabajos.

Diferentes líneas de investigación pueden surgir de los contenidos de esta tesis. Entre ellas, podemos citar la necesidad de incorporar en el análisis efectos inerciales y de la polidispersidad de las partículas. Como comentamos brevemente en la introducción de la tesis, los efectos inerciales darían lugar a un régimen oscilatorio adicional en los procesos de relajación para valores muy altos del campo magnético. Sin embargo, resultan ser esenciales para la descripción de la dinámica rotacional de las partículas a frecuencias muy altas. Con respecto a la polidispersidad, debido a que los diferentes procesos de relajación dependen de forma distinta del volumen de las partículas, sus contribuciones a las magnitudes calculadas no son las mismas en un medio polidisperso. Por ejemplo, el espectro de los tiempos de relajación puede ensancharse. Otra posible línea de investigación consistiría en ir más allá de la respuesta lineal del sistema en condiciones alejadas del equilibrio.

Las partículas ferromagnétics han probado su eficacia como particulas traza para medir la vicosidad de los fluidos portadores. Sería muy interesenta llevar a cabo un análisis teórico de los mismos fenómenos de relajación rotacional en un medio elástico o viscoelástico, para determinar módulos de elasticidad o para caracterizar la transición sol-gel en diferentes medios de este tipo. Descendiendo al régimen de bajas temperaturas, un monodominio ferromagnético suspendido en helio líquido serviría para comprobar la importancia de la conservación del momento angular en las transiciones magnéticas por efecto túnel.

A altas concentraciones, el estudio de la reología de agregados con formas irregulares constituye ya hoy en día una materia que ha atraído un gran interés. Además, todavía permanece abierta la problemática relacionada con el diagrama de fases de un fluido dipolar.

Hemos comenzado a trabajar en las denominadas fases ferroesmécticas, en las que un ferrofluido se inyecta en una fase lamelar polimérica. El estudio de la dinámica de las partículas en esta geometría confinada constituye otro tema de gran interés teórico, para el cual ya existen resultados experimentales.

Contents

INTRODUCTION

Fine magnetic particles are important in many areas of science and technology. There are, however, few examples of moving particles suspended in a medium where the magnetic interactions play an important role in both its dynamical behavior and the structure formation. These include *ferrofluids* and latex particles dispersed in ferrofluids (*magnetic holes*).

A *magnetic fluid* or *ferrofluid* is a stable colloidal suspension of monodomain particles of a ferromagnetic material in any ordinary liquid like water or other organic compounds [1, 2, 3]. They were envisaged as an artificial liquid in which both magnetic and rheological properties are enhanced to an extent comparable with those of ferromagnetic solids, and based on the fact that the existence of real monophase ferromagnetic liquids is rather questionable. The stability of the suspension is essentially ensured by the Brownian motion of the particles, although for inhibiting their coalescence at shorter distances the particles are usually coated with a layer of surfactant.

Ferrofluids have a wide range of technological applications [4] including exclusion seals for computer disc drives, dampers in loud speakers, printers, heat and mass transfer instruments, lubricants, etc. It is, for instance, difficult to keep a lubricant at the contact zone of the moving parts because it is ejected by centrifugal forces or because of the geometry. The magnetic field may retain the magnetic lubricant at the contact of the friction surfaces. What is more, the lubricant efficiency is mainly determined by its viscosity and capability of forming an adsorbed layer. Magnetic lubricants are more effective than the ordinary ones even in the absence of a magnetic field because the magnetic particles are attracted by steel surfaces thus increasing both the viscosity and the thickness of the boundary layer. They are used in ecology and medicine. The ferrofluid is able to remove oil products from industrial effluents like sewage waters. Hydrocarbon-based magnetic fluids can be dissolved in oil products in order to make them a more dilute ferrofluid. A flow of water containing the mag-

netic suspension passes through a magnetic separator where there is a high-gradient magnetic field separating oil products from water. But the multiple and qualitatively diverse effects coming from the interaction between them and an electromagnetic field provide the basis of new and promising technological applications. Moreover, apart from their magnetic, optical, and rheological properties that we will discuss along the monograph, they also exhibit other unusual phenomena of scientific interest such as surface instabilities and labyrinthine patterns.

Some years ago it was discovered that monodisperse polystyrene spheres dispersed in ferrofluid provided a convenient model system for the study of various order-disorder phenomena [5]. The basis for this is that the spheres displace ferrofluid and behave as *magnetic holes* with effective moments equal to the total moment of the displaced ferrofluid. The spheres are much larger ($1 - 100\mu m$) than the magnetic particles in a ferrofluid ($100\AA$) and therefore they move around in an approximately uniform magnetic background.

In general, monodisperse microspheres have a variety of important applications in industry, research and medicine. The basis for this is several unique properties such as an extremely uniform size distribution, almost perfect spherical shape with precisely measured diameter, a wide range of particle types (solid, porous, magnetic, etc.) and the possibility of manufacturing the surface properties. Polystyrene microspheres with a magnetic core have been used very successfully for separation of various organic materials (cells, viruses, micelles, etc.) [6]. The principle is based on a selective interaction between cell surface antigens and antibodies bound to the spheres. The spheres with the attached selected cells may then be removed from the suspension by the application of a magnetic field. Patients with either neuroblastoma or certain forms of leukemia have had their bone marrow cleaned by means of monodisperse magnetic particles and specific monoclonal antibodies. Treatment of malignant diseases by radiotherapy and/or chemotherapy is dose-limited because of the toxicity to normal cells in the body. In particular, bone marrow cells, producing all the red and white blood cells and the platelets, may be damaged. With this technique about one tenth of the patient's bone marrow is cleaned prior to high-dose therapy. The particles may also be used as markers in that they are coated with certain site-specific chemicals or antibodies, etc. During particle migration in dispersions they will stick to the target sites to be localized. Another promising application is the use of particles as carriers. Certain chemicals are bound to the particle surface and the particles are transported to sites where the chemical can be effective. In the biochemical field this technique is being evaluated for cell poison and used against cancer.

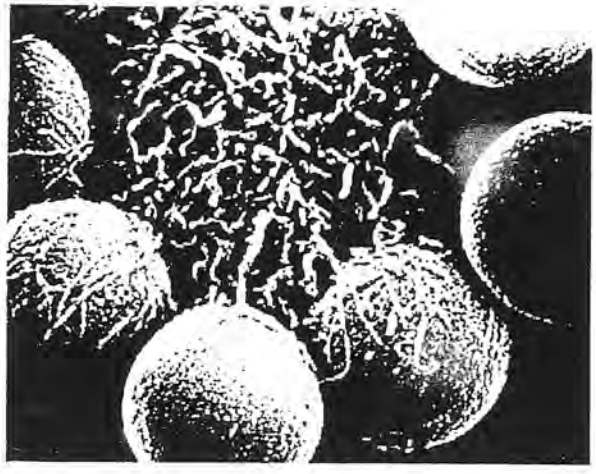

Figure .1: Scanning electron micrograph of magnetic microspheres with anti-H2 monoclonal antibodies attached to hepatocyte.

1 The ferromagnetic particles

We will disregard for the moment the liquid in which the particles are dispersed and concentrate in the description of the fine ferromagnetic particles.

Ferromagnetic particles in a ferrofluid are monodomain and possess almost constant magnetic moments. It is well known that ferromagnetic crystals consist of regions where the magnetization is oriented differently. This regions are called magnetic domains. The shape and size of these magnetic domains in thermodynamic equilibrium are determined by the condition that the total free energy of the material should be a minimum. Moreover, the magnetic domains are separated from each other by domain walls, i.e., a transition layer in which the distribution of the magnetization orientation is nonuniform but changes continuously. Frenkel and Dorfman [7] predicted that by reducing the size of a ferromagnetic sample, one would reach a point at which domain boundaries would no longer be energetically favorable so that the whole sample would become a single domain. On one hand, every domain wall means an additional amount of surface tension energy which limits the number of possible domains. On the other hand, the energy associated to the magnetic field surrounding the sample favors their formation. Based on this simple argument of competition one can estimate the critical size (d_c) below which the sample can be considered a magnetic monodomain. In the estimation one should distinguish between strong and weak magnetocrystalline anisotropy because it also hinders the creation of a domain wall

favoring the increase of the critical monodomain size. But, even for the less favored cases of weak magnetocrystalline anisotropy, the estimations give $d_c \sim 300\mathring{A}$ which is well above the mean size of the ferromagnetic particles used in ferrofluids whose typical diameter does not usually exceed $150\mathring{A}$. Thus, even allowing for a possible polydispersity, the colloidal dispersed particles are definitely *monodomain*.

Although we are interested in enhancing for instance the magnetic properties of the magnetic liquid, and these are clearly determined by the suspended particles, there is a restriction in their size to essentially *avoid aggregation phenomena* which are mainly due to dipolar magnetic energy. If we define a dimensionless parameter $\lambda = m^2/d^3 k_B T$ comparing dipolar magnetic and thermal energies, where m and d are the magnetic moment strength and the diameter of one particle, the stability condition imposes that $\lambda \leq 1$ which can only be achieved if the particle diameter is small enough (for a ferromagnetic material whose saturation magnetization $M_s \simeq 500G$ this condition holds if $d \leq 100\mathring{A}$).

An intermediate solution of the problem can be thought consisting in reducing the linear size of the particles but keeping the same volume fraction ($\phi = nV_m$), where n is the particle number density and V_m the volume of one monodomain. However, this strategy also manifests some problems. By pursuing this method one arrives at highly dispersed colloidal suspension but no longer magnetic. It is clear that the electron spins responsible for the magnetic ordering are affected by the presence of the boundary of the volume in which they are enclosed. The absence of partners for exchange interaction manifest itself on the formation of a thin demagnetized layer whose thickness can be comparable to that of the whole particle. This fact is verified by experiments [8, 9]. Moreover, there exists an alternative point of view which explains this demagnetized layers by chemical modification of the particles surfaces due, for instance, to oxidation or to the interaction with the surfactant which is usually added to stabilize colloidal suspensions. This question has been the subject of many studies [10, 11, 12] and it remains open. For our purposes in this thesis, this problem it is not crucial because we will always assume that $m = M_s V_m$ with V_m the volume of the magnetic core, which due to the above considerations can be less than the geometric volume.

When looking at the particles, another aspect that should be kept in mind is that even though it might seem that a monodomain magnetic particle behaves like a permanent magnet, this is not always the case. The orientation of the poles in a magnet is fixed by the magnetic anisotropy energy. At room temperature, the dimensionless parameter $\sigma = K_a V_m / k_B T$, comparing anisotropy and thermal energies

with K_a the effective anisotropy constant, for a monodomain particle is not large ($d \sim 100\mathring{A}$, $K_a \sim 10^4 - 10^5 J/m^3$). Consequently, the probability of thermal rotational fluctuations of the magnetic moment inside the particle becomes important. At $\sigma \leq 1$, the magnetic moment are not practically affected by the potential barrier and its motion is similar to the Brownian rotation of a colloidal particle in a viscous liquid. Néel was the first to indicate the possibility of fluctuational remagnetization of small particles, that is why this process is usually referred to as the *Néel relaxation*. The characteristic time of this spontaneous reorientation, τ_σ depends on the parameter σ. For time intervals shorter than τ the particle behaves like a permanent magnet, whereas for measuring times greater than τ the particle's magnetic moment can be considered zero. These differences can be corroborated, for instance, by means of Mössbauer spectroscopy. The alignment tends to be disrupted by thermal agitation, and of course, beyond the Curie temperature the domain possesses no magnetization any longer.

In the above discussion we have considered the relaxation of the magnetic moment in the absence of an *external magnetic field*. But, if a magnetic field is applied the energy of a magnetically uniaxial particle is the following

$$U = -\vec{m} \cdot \vec{H} - K_a V_m (\hat{n} \cdot \hat{R})^2, \tag{1.1}$$

where $\vec{m} = m\hat{R}$ is the magnetic moment of the particle, $\vec{H}$ is the external magnetic field, and $\hat{n}$ is the unit vector along the direction of the axis of easy magnetization, or the anisotropy axis. The effective constant K_a contains, in general, contributions coming from the crystalline anisotropy of the particle as well as the shape anisotropy. From this expression it will be easy to see that the dynamics of the two degrees of freedom for a particle in a liquid, $\hat{R}$ and $\hat{n}$, are coupled. It is also worth mentioning a this point that there will be essentially two relevant dimensionless parameters in the analysis. These parameters are the above introduced $\sigma = K_a V_m / k_B T$ and the parameter $\mu = mH/k_B T$, comparing the magnetic energy of interaction with the magnetic field and thermal energy. The derivative of this magnetic energy with respect to $\vec{m}$ determines the value and orientation of the effective magnetic field:

$$\vec{H}_{eff} = -\frac{\partial U}{\partial \vec{m}} = \vec{H} + \frac{2K_a V_m}{m} \hat{n}(\hat{n} \cdot \hat{R}), \tag{1.2}$$

which includes the external field $\vec{H}$ and the anisotropy field $\vec{H}_a$ directed along the anisotropy axis. In the absence of the external field, the magnetic moment is just under the action of the anisotropy field and there are two equivalent equilibrium

orientations $\hat{R} = \hat{n}$ and $\hat{R} = -\hat{n}$ between which the relaxation can take place. Now, the equilibrium condition is given by the absence of magnetic torques acting upon the particle, so that in the absence of thermal fluctuations the magnetic moment is parallel to $\vec{H}_{eff}$.

When this is the case there are two different orientational relaxation processes of the magnetic moment of the particle relative to its crystallographic axes. The *intrinsec motion* of the magnetic moment consist of a regular *precession* around the effective field and of *chaotic reorientations* due to thermal fluctuations. The regular motion relative to the crystalline axes of the particle is described by the classical Landau-Gilbert equation, which we introduce in Chapter II. This equation represents the precession of the magnetic moment with the Larmor frequency ω_L as well as the decay of this motion due to collisions, magnetoelastic interaction,... Associated to this decay there is a characteristic time $\tau_o = \alpha\omega_L$., where α is a dimensionless damping constant. Another characteristic time $\tau_D = (2D_m)^{-1}$ is connected with the rotational diffusion of the magnetic moment inside the particle $D_m = k_B T h$, where, as we will see in Chapter II, h plays the role of a rotational mobility of the magnetic moment.

2 Motion of the magnetic particle in the liquid

Besides the internal motion relative to the particle body, the magnetic moment also undergoes an external rotational diffusion as a consequence of the motion of the magnetic particles in the liquid they are suspended. The ferromagnetic particles suspended in a nonmagnetic fluid experience the action of the carrier liquid through viscous friction.

We will now consider the rotational Brownian motion of a colloidal particle. Its deterministic motion is described by the equation for the rotational dynamics of a solid body suspended in a viscous liquid

$$I\frac{d\vec{\Omega}}{dt} = -\xi_r(\vec{\Omega} - \vec{\omega}_o) + \vec{T}, \tag{2.1}$$

where I is the moment of inertia of the particle, $\vec{\Omega}$ its angular velocity, ξ_r the rotaional friction coefficient of the particle in a viscous liquid, and $\vec{T}$ the external torques acting on the particle.

In the absence of external torques, the rotational motion of the particle decays with the characteristic time $\tau_I = I/\xi_r$. For a spherical particle in the Stokes approximation $\xi_r = 8\pi\eta_o a^3$, where η_o is the viscosity of the liquid and a is the radius of the particle.

If we consider $\eta = 10^{-2} Ps$ and $d \sim 100\mathring{A}$, it follows that $\tau_I \sim 10^{-11} s$. This value is so small that in all cases of practical interest the inertial term in Eq. (2.1) may be neglected in comparison with the viscous one. Indeed, this term may be relevant only for characteristic frequencies of external excitation $\geq 100 GHz$. Compared to the characteristic times of hydrodynamic processes τ_I is almost zero.

Besides τ_I there exists a much larger characteristic time of the rotational motion of the particle. This time is determined by the rotational Brownian motion of the axis $\hat{n}$ representing the particle. This Brownian time is given by $\tau_B = (2D_r)^{-1}$, which taking into account the Stokes-Einstein relation it can be rewritten as $\tau_B = \xi_r / 2k_B T$. For the same values given above at room temperature, $\tau_B \sim 10^{-6}$. During this time, the particle under the influence of thermal fluctuations rotates by a finite angle. The higher the viscosity of the carrier liquid the slower the rotation. Conversely, the higher the viscosity the bigger the time τ_I. Nevertheless, τ_B and τ_I will be comparable just for $\eta_o \sim 10^{-4} Ps$, and such a viscosity would just correspond to aerosols or cryogenic liquids.

In real ferrofluids, depending on the particle volume and on the magnetic anisotropy constant the relation among the different characteristic times, and of the parameters μ and σ may be arbitrary. Thus the relaxation time of the magnetization will be in general a combination of the different times already introduced. The limiting case of an infinitely strong coupling for $\sigma \gg 1$, i.e. when the magnetic moment of the particle is rigidly coupled to the easy axis of magnetization, is known as the *rigid dipole model.* Despite its simplicity, this approximation is widely used in the theory of magnetic fluids, and allows one to explain a wide range of magnetic and hydrodynamic phenomena experimentally observed.

3 The rotational diffusion equation

As a single ferromagnetic particle experiences both a systematic damping and random thermal fluctuations of its magnetization and itself, the study of its dynamics can be performed by following two different methods: Langevin's approach to the theory of Brownian motion, and by Brown's intuitive method [9] which is an adaptation of the arguments developed by Einstein in 1905, or in other words, by Fokker-Planck or Smoluchowski diffusion equations for the probability density. In order to accomplish this, Brown followed the procedure of Wang and Uhlenbeck [14] together with the Stratonovich definition of the derivative of a stochastic variable [15]. He also proposed an alternative and simple approach to writing down the Fokker-Planck or

Smoluchowski equation using a continuity equation argument as Einstein did in his treatment about the translational Brownian movement. Although Brown's approach was developed for a ferromagnetic particle in a solid matrix, his formalism can be further developed to describe the dynamic behavior of suspensions of these particles in fluids. Shliomis and co-workers [10] first obtained this equation for a suspension of rigid dipoles, and then for the general case with arbitrary values of the ratio μ/σ, they also deduced the appropriate Smoluchowski equation from a model similar to the itinerant oscillator model, [12]-[14].

The normalized stationary solution of the Smoluchowski equation enables one to obtain any equilibrium orientational characteristics of an assembly of magnetic particles. Moreover, in most of the cases one has to deal with the moments of the distribution function. Particularly interesting among these moments is the first one, which determines the equilibrium magnetization.

To find out the solution of the kinetic equation of rotational diffusion different techniques have been proposed, especially for the rigid dipole model. For instance, for an assembly of rigid dipoles under constant external conditions any deviation of the distribution function from its equilibrium value may be expanded into a series of *normal modes*, each of which decays according to a simple exponential law. The relaxation time spectrum of the distribution function comes from the eigenvalues of the resulting equation. In fact, the lifetime of any departure from equilibrium is determined by the relaxation time of the most long-living modes. The *effective field method* and the *decoupling approximations* constitute other approachs to the problem.

From the diffusion equation one can easily obtain an infinite set of coupled equations for the moments of the distribution. In order to solve the set, one can truncate it somewhere. But, if one wants to study the field dependence of the relaxation process, the number of calculations and the difficulty in understanding the results obtained grows drastically with the external field. To avoid these inconveniences related to the numerical solution, it would help to have a nontrivial scheme of closure of the moment equations that is capable of giving a compact analytical description of the orientational processes in a ferrofluid. Such a closure prescription will be better the smaller the number of equations. Ideally, for a suspension of rigid dipoles one should have only one equation, since only the first moment has a direct physical meaning. In such a way one would be able to give a correct description of the averaged dynamics of the magnetic particles for a wide range of values of the field, anisotropy, temperature, etc. The first idea meeting all these requirements for a suspension of rigid dipoles is *the effective field method* [10], considered by Leontovitch in his book [21]. Thus, in

the nonequilibrium state one may consider any arbitrary value of the magnetization as an equilibrium one in a certain effective field. During the relaxation process, the effective field tends to the true field, so that the magnetization relaxes via a sequence of quasi-equilibrium states. Furthermore, one should represent the nonequilibrium distribution function in the same form as the stationary distribution with the effective field. This technique also yields an expression for the field dependence of the relaxation times of a suspension of rigid dipoles under nonstationary conditions but in a quiescent fluid.

In this monograph we propose another alternative and simple procedure to solve the set of infinite and coupled equations for the moments of the distribution function which appears to provide good results not only for the rigid dipole model but in any arbitrary situation including a moving suspension or the case of finite anisotropy energy. The method is based on the *decoupling approximation* of some of the quantities involved in the analysis, to be precise, of the quantities which vanish at equilibrium, when averaged, and those which are different from zero. This approximation may be justified from the fact that in equilibrium both quantities are not correlated, so, in non-equilibrium conditions but in a linear regime, for instance when there is small but non-vanishing value of the vorticity of the fluid flow, we will assume that these components remain uncorrelated. In addition, we ensure the main characteristics of the decoupled quantities such that after performing the decouplings they are still proportional to the vorticity, or the invariance under reflections of the easy axis of magnetization, $\vec{n}$, and so on. We really expect that the decouplings are more accurate for quite small and high values of the external field, because in the former case higher order moments will be negligible and in the latter the dynamics of the particles is mainly determined by the field rather than being influenced by Brownian motion. There are many possible ways of carrying out the decouplings. Such approximations are broadly used in the context of stochastic processes, and particularly, we will see throughout the thesis the most convenient decouplings to be performed in our system.

In this system the stability of the stationary distribution in a constant external field appears as a natural fact. Furthermore, from these approximations one usually obtain a single characteristic time of the relaxation process. In the absence of an external field the relaxation of the initial disordered distribution takes place by means of free orientational diffusion which is a monotonic process with just one characteristic time. In the strong field limit the dynamics of the magnetic moments is mainly deterministic, and they approach the field direction monotonically according to an exponential law with a characteristic time. Thus, although the external field

will reduce the relaxation time, it does not change the character of the decay process. In principle, the formal cause of this behavior is that we are neglecting the inertial term due to their smallness. Keeping this term would lead to an oscillatory regime of the relaxation process for enormous and almost unreachable values of the external field. However, inertial effects are essential if one considers the high-frequency behavior of rotating objects of molecular size. Here the treatment becomes much more complicated. A review of the problem and particular results is given by Coffey *et al.* [20].

4 Macroscopic hydrodynamic theory of magnetic fluids

Having characterized the different relaxation mechanism studied, we proceed to analyze their implications in the macroscopic behavior of the system.

Ferrofluids can be treated as a homogeneous one-component monophase fluids. This approximation implies that the processes that should be considered are such that their characteristic dimensions are much larger than the size of the constituent magnetic particles. Thus, the magnetization of the system is assumed to be distributed throughout any elementary fluid volume. Establishing the equations of motion and heat transfer in a ferrofluid constitute one of the most important problems to study in these systems. Moreover, their peculiar properties manifest themselves most evidently in their hydrodynamic behavior.

The set of hydrodynamic equations for an uncharged, magnetizable, and electrically nonpolarizable fluid is based on the balance equations of mass, linear and angular momentum, and heat transfer for a homogeneous monophase medium. As regards the momentum balance equation one should take into account the Maxwell tensor, which in this case is antisymmetric unless the magnetization density vector and the field strength are parallel (due to the finite value of the relaxation time of the transverse component of the magnetization, this condition does not hold under the influence of hydrodynamic torques acting upon the particles either in magnetic fields that change their direction or in a fluid having been set in motion). The asymmetry of the stress tensor demands a generalization of classical hydrodynamics in the sense that one should take into account the rotational degrees of freedom of the particles. Thus one ought to consider that the angular momentum density is made off two parts, the orbital associated with the translational motion of the suspended particles and

molecules of the solvent, and the spin momentum caused by the rotation of the particles. For simple fluids this spin is zero and the symmetry of the stress tensor is a necessary and sufficient condition for the conservation of the angular momentum. The situation is different if there exists internal rotation because the stress tensor should not be symmetric any longer. The different fluid elements move with different velocities relative to the angular velocity of the liquid suspending them giving rise to an internal friction. In the absence of external torques acting on the particles, the difference between the averaged angular velocity of the particles and the local value of the vorticity of the fluid flow disappears as fast as inertial effects do. On the other hand, this difference results in an irreversible process (with dissipation of kinetic energy) of transfer of angular momentum between solid and liquid phases of the suspension due to the viscosity of the solvent.

Related to the presence of *antisymmetric stresses* in a ferrofluid there appears a new transport coefficient: the *rotational viscosity*, that in general contributes to the effective viscosity of the suspension. This contribution tends to an asymptotic limit at high field strength, it is maximum when the magnetic field and the vorticity are perpendicular and is zero when both vectors are parallel since in this case, if we neglect inertial effects, the angular velocity of the particle is equal to the vorticity of the fluid at the point occupied by the particle and only the contribution due to symmetric stresses will remain. In other words, the ferrofluid motion modifies the value of its magnetization, so if we consider a magnetic fluid with nonzero vorticity uniform shear (Couette flow) in a constant magnetic field perpendicular to the plane of shear, the field tends to align the particle magnetic moments and, therefore, the particles themselves. Moreover, the vorticity flow simultaneously attempts to rotate the particles destroying the magnetization created by the field. By means of the Smoluchowski equation for the rotational motion of the particles and after considering all their possible mechanism of orientation, we will be able to provide a solution of the macroscopic equation for the magnetization in a moving fluid. This magnetization, in turn, enters the equations of hydrodynamic motion of a magnetic fluid and thus affects the state of motion of the fluid. The rotational viscosity comes quite easily from this analysis using a rheological equation of state for the antisymmetric part of the pressure tensor or by using the corresponding Green-Kubo formula.

To correct the hydrodynamics for fluctuations, one must add to the total fluid pressure tensor a thermal fluctuating pressure tensor whose average, but not square average, vanishes. This fluctuation reflects the fact that the first principles from which the complete macroscopic theories must follow, are time reversible. Also the

fluctuation are seen to be related to the dissipation through the fluctuation-dissipation relation, showing indeed that a dissipative theory is not complete until fluctuations are included.

In particular, if one consider the quiescent equilibrium states of a magnetic fluid in a nonuniform stationary magnetic field, one observes that such a field is not able to induce the ferrofluid motion, the magnetic pressure is balanced by the hydrostatic pressure. This fact provides the basis for numerous practical applications [2].

Once we have characterized the macroscopic behavior of a ferrofluid, giving expressions for the viscosities, as well as for the average of its magnetization, one can go further and analyze the dynamics of a nonmagnetic particle (magnetic hole) suspended in a ferrofluid. Recently, an increasing interest in the study of the dynamic properties of this magnetic holes has arisen [5, 3, 4]. Although the particles are not magnetic, when they are suspended in a carrier ferrofluid they *acquire* an induced magnetic moment equal to the magnetic moment of the ferrofluid volume they displace. The interaction of these induced magnetic moments of the holes causes a number of peculiar phenomena, such as the order-disorder transition in magnetic hole lattices and the non-linear phenomena observed in assemblies of holes [7]. Furthermore, knowledge of the dynamics of such particles may constitute a way of characterizing the transport properties of the ferrofluid. For example, the friction coefficient of the particle gives us information about the viscosity of the carrier fluid.

The rotational dynamics of the particle is strongly influenced by the presence of a rotating magnetic field. We have found that the hole rotates in the opposite direction to that of the field at low and moderate frequencies of the field rotation, and this result is corroborated by recent experiments, obtaining quite a good agreement in the frequency range we are considering. As we have commented previously, for high frequencies one ought to account for inertial effects, and for the ferromagnetic resonance of the ferrofluid, which is the Larmor precession of the magnetic moment inside the particle excited by an alternating magnetic field.

The system holes-ferrofluid can be modeled as a suspension of particles (holes) in a carrier fluid (ferrofluid) because different length scales exist for the ferrofluid and the holes. Consequently, the ferrofluid can be viewed as a continuous medium through which the holes may move. The dynamics of the ferrofluid is governed, at the continuum level, by the aforementioned *generalized* equations.

5 Stability of the suspension

As the size of the particles in a ferrofluid increases or at high concentration, the dipole-dipole interaction between them is enhanced. The Brownian motion is no longer able to avoid the particle aggregation to form chains or clusters. The structurization of the magnetic phase becomes relevant and results in non-Newtonian fluid properties which typically appear when considering suspensions with micrometric particles, as well as in hysteresis of the magnetization curve. The structures which appear at zero applied field are linear or ramified fractals of low dimensions. When an external field is applied, fiber type structures grow along the field direction and for high enough concentrations periodic columns form as observed by optical microscopy [25]. After the field is removed at a fixed temperature these structures stay on a macroscopic time scale. The remaining structure has remanent magnetization and both the structure and the remanent magnetization depend on temperature, field, geometry, and history.

Magnetorheological and electrorheological fluids have attached considerable attention in recent years because of potential applications in electrically controllable shock absorbers, clutches, and other systems as well as interest in unsolved scientific questions [26, 27, 9]. Studies on electrorheological fluids are hindered by many problems related to surface charge, electrode polarization, adsorbed water, field inhomogeneities, etc. But an analogous field-induced behavior is shown by magnetorheological fluids, e.g., in a suspension of magnetically susceptible micrometer particles in an oil [5], or in a suspension of nonmagnetizable spheres in a ferrofluid (magnetic holes) [30]. In a pure ferrofluid one observes similar phenomena but, due to fact that the particles are permanently magnetized, there are polarization forces even without an applied magnetic field. In all these cases, one has the advantage that they are not susceptible to the above mentioned problems. Thus, studying the kinetics of the formation of the aggregates and their rheology are topics of practical importance and have provided the bases of theoretical and experimental studies [6, 8] as well as numerical simulations [34]-[11]. In the absence of a magnetic field, the system behaves like a Newtonian fluid. Under applied magnetic field, the system becomes solid, and like a Bingham plastic reverts to the fluid state when applied stress exceeds the so-called yield stress.

Although it is beyond the scope of our analysis, it is worth illustrating at this point recent results concerning the structure and the possible coexistence of different phases in dipolar fluids under the action of an external field. Dipolar forces influence different types of fluids ranging from fluids of polar molecules where the dipolar interaction is electrostatic to ferrofluids where it is magnetostatic. The strength of dipolar coupling

also differs widely in different fluids. In many dipolar fluids, three dominant interactions determine the thermodynamics: short range repulsion, long range dipole-dipole interaction, and the dispersive van der Waals attraction. When the dipolar coupling is weak, it is treated as a perturbation to the dispersive attraction after an orientational averaging, with a van der Waals-like attraction (r^{-6}) as the leading term. But strongly coupled dipolar fluids such as ferrofluids exhibit those unusual phenomena commented before, such as particle chaining or field induced phase separation. Although simple dipolar fluids are a fundamental test system for doing theory and are used as model systems for ferrofluids, magnetorheological and electrorheological fluids [37, 38], their phase diagrams remain partially understood. The dipolar hard sphere model may display phase separation as suggested by its solution via the mean spherical approximation [39]. More likely it displays a magnetized liquid state as suggested by recent computer simulations [40]. It has also been shown that the presence of additional attractive interaction besides the dipolar interaction affects the fluid phase diagram. Using a soft sphere dipolar fluid (SSD) which consist in dipoles which have a soft sphere potential (r^{-12}) as the excluded volume interaction, in contrast to the theoretical predictions of phase coexistence for hard sphere dipoles in zero field conditions one does not find the phase coexistence in the absence of a van der Waals attraction. Instead, the SSD fluid forms chain reminiscent of living polymers [41]. In an applied field the system shows phase coexistence and both phases consist of chains. On the other hand, the Stockmayer fluid models a ferrofluid better (in the Stockmayer fluid the dipoles also interact via the Lennard-Jones potential) showing a liquid-gas coexistence in the absence or presence of an applied field [37]. Real polar molecules and ferrofluids with strong dipolar couplings do exhibit phase separation into dilute gas and dense liquid phases at appropriate temperatures and densities. On the other hand, the spontaneous magnetization has never been confirmed in the liquid state.

6 Scope of the thesis

Finally, in this section we summarize the main problems covered in the thesis. Our main goal is to study certain aspects of the dynamics of fluids with magnetic particles in suspension, based on their promising practical applications as new materials as well as on its fundamental scientific interest.

In the introduction we brief the reader on the most essential properties of the system. We have characterized the monodomain magnetic particles and the time scales inherent to magnetic fluids. Having introduced the rotational diffusion equation

as the most convenient tool to take into account the different mechanism influencing the dynamics of the particles, we have also proposed a fruitful approach for solving it in any general situation. We have also highlighted the macroscopic properties of the magnetic fluid treated now as a continuous medium and showed up the different phenomena associated with the lack of stability in the system.

In Chapter I we concentrate on two limit cases whose analysis is easier but very illustrative. The first part of the chapter is devoted to the study of a suspension of rigid dipoles, in which the magnetic moments are rigidly attached to the body of the particles themselves. In these conditions, if we apply an external magnetic field both the magnetic moment and the particle move together so that the magnetic torque acting upon it becomes zero. Thermal fluctuations tends to disrupt this order, and it turns out that, for instance, that the effective viscosity of the suspension depends on the dimensionless parameter comparing magnetic and thermal energies. In the second part we consider magnetic materials with finite anisotropy energy at high magnetic fields. For such monodomain particles the magnetic moments rapidly orient along the direction of the external field, and then as a second step the mechanical rotation of the particles takes place. In this case, the effective viscosity of the suspension is a function of the magnetic anisotropy constant of the material, of the volume of the particles as well as the thermal energy. Our results are compared to experimental measurements.

The second chapter is concerned with the determination of the viscosity and of some magnetic and optical properties of magnetic fluids in the whole range of possible experimental situations. The magnetic moments and the particles inside the liquid reorient separately but their dynamics are coupled thus giving rise to a more intricate relaxation process. We have compared part of our results with available experimental data for different ferrofluids showing quite a good agreement.

In Chapter III we joint to our discussion of magnetic fluids the presence of nonmagnetic particles of micrometer size and study their motion through the ferrofluid. The ferrofluid is considered now as a continuous medium with new transport coefficients already determined in the previous sections. Under the action of a rotating external magnetic field, we study the rotational motion of the nonmagnetic particles and compare our expressions to some measurements carried out in these composite systems. In this chapter we are also concerned with the characterization of the hydrodynamic interactions among these particles in a carrier ferrofluid.

Chapter IV is intended as a brief introduction to the multiple problems which arise when one handle the aggregation phenomena which may take place in these

systems. We study the kinetics of the formation of the aggregates by means of the Smoluchowski theory of coagulation in colloids. But we account for hydrodynamic interactions which are not usually considered when studying such process and that gives rise to some corrections for high concentrations of particles. In addition, the rheology of the chains that are usually observed in systems with dipolar interactions is given for a rather simplified situation in order to elucidate the effects of the dipolar magnetic interactions.

Finally, we sum up our main conclusions and indicate some of the perspectives stimulated by the contents of this monograph and in which we plan to pursue work in the near future.

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CHAPTER I

DYNAMICS OF FERROMAGNETIC PARTICLES IN SUSPENSION: LIMIT CASES

In this chapter we study the dynamics of a ferromagnetic particle and compute the transport coefficients of a dilute suspension constituted by these particles under the action of a constant magnetic field. We will develop a formalism which makes it possible to construct a general scheme to analyze the dynamics of the system. In particular, we carry out an explicit calculation of the viscosities for a dilute suspension of spherical particles. The viscosities are essentially computed by means of Green-Kubo formulas in the linear response theory framework. Moreover, the Smoluchowski equation for the orientational degrees of freedom of the particles enable us to obtain the averaged values and the correlation functions involved in the calculations. Depending on the ratio μ/σ, comparing both magnetic and anisotropy energies, two simple experimentally reachable regimes show up, and their analysis constitutes the scope of this chapter. The first part of it deals with the limit $\sigma \gg \mu$, that will be referred to as *suspension of rigid dipoles*. In the second part, we have analyzed the implications of the sphere's anisotropy energy on its dynamics at high magnetic field ($\mu \gg \sigma$). The rotational viscosity has also been calculated as a function of the anisotropy parameter. For a given geometry, this magnitude is responsible for the increase of the effective viscosity of the system due to the presence of an external magnetic field. Our results are compared with that obtained by other authors based on different approaches.

Part I

RIGID DIPOLES

1 Introduction

Transport phenomena in colloidal suspensions and polymer solutions have played a prominent role in the study of these systems due to their potential applications to different areas of physics, physico-chemistry and biophysics. In dealing with transport phenomena, one is mainly concerned with two levels of description. In the macroscopic level, one considers the system as a whole and establishes evolution equations for the relevant quantities in the framework of theories of continuum media and non-equilibrium thermodynamics. In the other level, one distinguishes the suspended objects from the carrier fluid and uses Langevin or Smoluchowski descriptions which should be complemented with the knowledge of the dynamics of the individual objects, i.e., we have to know the force and the torque exerted by the fluid on the particle moving through it.

Furthermore, one of the main problems about transport phenomena in different systems is the calculation of transport coefficients, which are characteristic of the response of the system to external forces. This task has been accomplished extensively for particles of different shape and there exist many well-founded results in the literature [1, 2].

In this part, we will deal with suspensions of dipolar particles composed of a carrier fluid and particles having dipolar moments rigidly attached. In particular we will discuss the case of ferromagnetic particles. Thus, one may consider that the magnetic moments are only oriented by the magnetic field, the rotational Brownian motion of the ferromagnetic particles and by the external flow. This last mechanism depends on the shape of the particles. As an example, when the particles are spheres they are oriented by the vorticity of the flow, whereas elongated particles are oriented by the elongational flow as well. The possibility of the orientation of the particles by the magnetic field is responsible for the peculiar behavior of the viscosities of ferrofluids. Particularly, it has been shown that in the case of a suspension of ferromagnetic particles, there appears a new transport coefficient: the rotational viscosity, related to the presence of antisymmetric stresses [3]. The rotational viscosity of the suspension was calculated by Shliomis [4] using a continuum medium approach in which the difference between the vorticity of the fluid and the averaged angular velocity of the particles (spin) leads to the introduction of an internal angular momentum of the fluid elements. For this reason, it becomes necessary to formulate a new balance equation for this quantity, which is coupled with the momentum balance equation.

Our purpose in this part of the thesis is to present a unified formalism able to

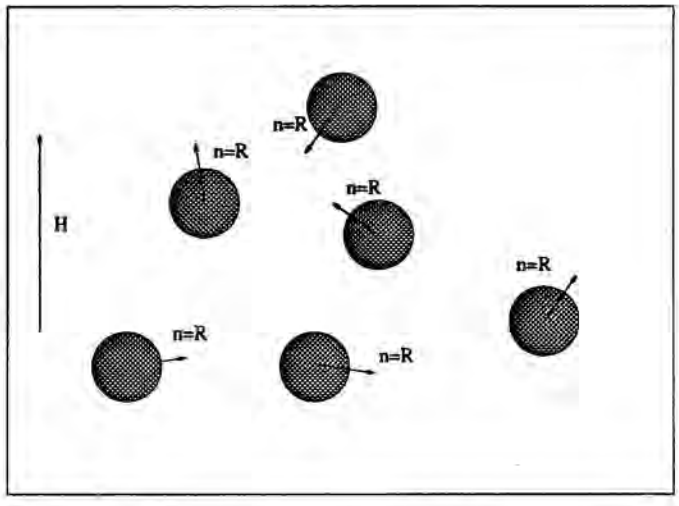

Figure I.1: In suspension of rigid dipoles the magnetic moments are rigidly coupled to the easy axis of magnetization of the particles and relax together.

describe the dynamics of the particles and to compute the transport coefficients. Here we present two versions: one where the viscosities are calculated from a rheological equation of state, giving the expression of the pressure tensor, and the other based on the linear response theory, which assumes the existence of fluctuations in the fluid and requires the knowledge of the fluctuating dynamics.

To this end, we have organized this part of the chapter in the following way. In Section 2, we analyze the dynamics of a ferromagnetic sphere by using an induced force in the Navier-Stokes equation, accounting for the perturbation caused by the sphere due to its motion. We find the expression for the force and torque exerted on the particle which split up into systematic and random contributions, and discuss the origin of antisymmetric stresses. Likewise, in Section 3 the expressions for the shear and rotational viscosities are obtained using a rheological equation of state for the contribution to the pressure tensor due to the presence of particles in suspension. We introduce the Smoluchowski equation and we get the expression for the average of the magnetic moment to obtain the rotational viscosity. Section 4 is devoted to the calculation of the viscosities by using Green-Kubo formulas. For this purpose, we need to know the fluctuation dynamics which follows from fluctuating hydrodynamics [5], and from the analysis of the corresponding Smoluchowski equation for the orientation of the particles [6]-[8]. Finally, in the last section we summarize our main results.

2 Dynamics of a ferromagnetic sphere

Let us consider a dilute suspension of ferromagnetic spherical particles of radius a immersed in a nonpolar incompressible solvent, under the influence of an external magnetic field. Our starting point for analyzing the stationary motion of the particle will be the linearized stationary Navier-Stokes equation

$$0 = -\nabla p + \eta_o \nabla^2 \vec{v} + \vec{F}^i - \nabla \cdot \boldsymbol{\Pi}^R \tag{2.1}$$

in which $p(\vec{r}, t)$ is the pressure field, η_o the viscosity of the solvent and $\vec{v}(\vec{r}, t)$ is the velocity field. Owing to the incompressible nature of the carrier fluid the velocity field also satisfies

$$\nabla \cdot \vec{v} = 0. \tag{2.2}$$

In Eq. (2.1) we have assumed that the perturbation caused by the motion of the particle may be taken into account by introducing an induced force field $\vec{F}^i(\vec{r}, t)$ [10, 11]. Furthermore, we have considered the possibility of fluctuations in the fluid by means of the Langevin-like fluctuating source $-\nabla \cdot \boldsymbol{\Pi}^R$, coming from the decomposition of the viscous pressure tensor in its systematic and random $\boldsymbol{\Pi}^R$ parts [5].

To be consistent, the induced force should be defined in such a way that stick boundary conditions at the surface of the particle,

$$\vec{v}(\vec{r}, t) = \vec{u}(t) + \vec{\Omega}(t) \times a\hat{n}, \quad \text{for } |\vec{r} - \vec{R}_{cm}(t)| = a, \tag{2.3}$$

are satisfied. In this equation $\vec{u}$ and $\vec{\Omega}$ are the translational and rotational velocities of the particle, respectively, $\vec{R}_{cm}(t)$ is the position of the center of mass of the sphere, and $\hat{n} \equiv (\vec{r} - \vec{R}_{cm}(t))/|\vec{r} - \vec{R}_{cm}(t)|$. Since inertial and memory effects relative to the motion of the particle are neglected in the stationary case, the induced force is a surface force and can be expressed as [10, 11]

$$\vec{F}^i(\vec{r}) = \vec{f}^i(\hat{n})\delta(|\vec{r} - \vec{R}_{cm}| - a), \tag{2.4}$$

where $\vec{f}^i(\hat{n})$ is an induced force density per unit area. The velocity field given by Eq. (2.1) is therefore valid in the whole space, even inside the spheres.

To compute the mobility tensor we need, first of all, to know the formal solution for the velocity field. This solution follows from (2.1) by Fourier transforming in $\vec{k}$. In fact, after elimination of the pressure, by applying the transversal projector $(\boldsymbol{I} - \hat{k}\hat{k})$, with $\hat{k} \equiv \frac{\vec{k}}{k}$, one obtains

$$\vec{v}(\vec{k}) = \vec{v}_o(\vec{k}) + \boldsymbol{T}(\vec{k}) \cdot [\vec{F}^i(\vec{k}) - i\vec{k} \cdot \boldsymbol{\Pi}^R(\vec{k})], \tag{2.5}$$

where we have used the incompressibility condition which, in Fourier space, reads $\vec{k} \cdot \vec{v} = 0$ and we have introduced the propagator

$$\boldsymbol{T}(\vec{k}) = \frac{1}{\eta_o k^2} \, (\boldsymbol{I} - \hat{k}\hat{k}), \tag{2.6}$$

with $\boldsymbol{I}$ as the unit matrix and $\vec{v}_o$ the unperturbed velocity field in the absence of the particle. The propagator $\boldsymbol{T}(\vec{k})$ is the Fourier transform of the Oseen tensor given by

$$\boldsymbol{T}(\vec{r}) = \frac{1}{8\pi\eta_o r}(\boldsymbol{I} + \hat{r}\hat{r}), \tag{2.7}$$

where $\hat{r} \equiv \frac{\vec{r}}{r}$. This formal solution can be rewritten in real space in the form

$$\vec{v}(\vec{r}) = \vec{v}_o(\vec{r}) + \int d\vec{r}\,' \boldsymbol{T}(\vec{r} - \vec{r}\,') \cdot \vec{F}^i(\vec{r}\,') + \vec{v}^R(\vec{r}), \tag{2.8}$$

where the random velocity field is given by the inverse Fourier transform of

$$\vec{v}^R(\vec{k}, t) = -\frac{i}{\eta_o} \, \frac{(\boldsymbol{I} - \hat{k}\hat{k})}{k^2} \cdot [\vec{k} \cdot \boldsymbol{\Pi}^R(\vec{k}, t)]. \tag{2.9}$$

The average and correlation of this quantity then follows from the stochastic properties of the random part of the viscous pressure tensor. According to fluctuating hydrodynamics, $\boldsymbol{\Pi}^R$ introduces a Gaussian white noise stochastic process of zero mean and fluctuation-dissipation theorem [5]

$$\langle \, \Pi^R_{ij}(\vec{k}, t)\Pi^R_{kl}(\vec{k}', t)\rangle = 2k_B T \, \eta_o \Delta_{ijkl} \, (2\pi)^3 \, \delta(\vec{k} + \vec{k}') \, \delta(t - t'), \tag{2.10}$$

where we have defined $\Delta_{ijkl} = \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \frac{2}{3}\delta_{ij}\delta_{kl}$.

The formal solution (2.8) gives the velocity field at any point. Therefore, for a given point at the surface of the sphere, in view of the stick boundary condition, one has

$$\vec{u} + \vec{\Omega} \times a\hat{n} = \vec{v}_o(\vec{R}_{cm} + a\hat{n}) + \int d\hat{n}\,' \, \boldsymbol{\mu}(\hat{n}, \hat{n}') \cdot \vec{f}^i(\hat{n}') + \vec{v}^R(\vec{R}_{cm} + a\hat{n}), \tag{2.11}$$

where we have introduced the response function $\boldsymbol{\mu}(\hat{n}, \hat{n}')$

$$\boldsymbol{\mu}(\hat{n}, \hat{n}') = \frac{a^2}{(2\pi)^3} \int d\vec{k} \; exp\,(ia\vec{k} \cdot (\hat{n} - \hat{n}')) \; \boldsymbol{T}(\vec{k}). \tag{2.12}$$

To proceed further, we will expand the velocities and the induced force of (2.11) in multipoles [10, 11]. For an unspecified quantity $\vec{\Psi}(a\hat{n})$ of that equation, one has

$$\vec{\Psi}(a\hat{n}) = \sum_{l=0}^{\infty} \frac{(2l+1)!!}{l!}\, \hat{\boldsymbol{n}}^l \odot \boldsymbol{\Psi}^{l+1}. \tag{2.13}$$

Here $\hat{\boldsymbol{n}}^l$ is an irreducible tensor of rank l, i.e. the tensor of rank l traceless and symmetric in any pair of its indexes, constructed with the vector $\hat{n}$. The symbol $\odot$ stands for full contraction and $\boldsymbol{\Psi}^{l+1}$ is the multipole of order $l+1$, which is a tensor of rank $l+1$. These quantities are given by

$$\boldsymbol{\Psi}^{l+1} = \frac{1}{4\pi} \int d\hat{n}\, \hat{\boldsymbol{n}}^l \vec{\Psi}(\hat{n}). \tag{2.14}$$

Inserting these expressions into the formal solution (2.11), one gets

$$\boldsymbol{v}^{(l+1)} = \sum_{l'=0}^{\infty} \frac{(2l'+1)!!}{l'!} \boldsymbol{\mu}^{(l+1,l'+1)} \odot \boldsymbol{\mathcal{F}}^{(l'+1)} + \boldsymbol{v}_o^{(l+1)} + \boldsymbol{v}_R^{(l+1)}, \tag{2.15}$$

which relates the multipoles of the velocity and of the induced force density. In this expression the matrix elements $\boldsymbol{\mu}^{(l+1,l'+1)}$ have been defined as

$$\boldsymbol{\mu}^{(l+1,l'+1)} = \frac{1}{(4\pi)} \int d\hat{n} \int d\hat{n}'\, \hat{\boldsymbol{n}}^l\, \boldsymbol{\mu}(\hat{n},\hat{n}')\, \hat{\boldsymbol{n}}'^{l'}. \tag{2.16}$$

The representation of the mobility kernel in terms of irreducible multipoles is diagonal in the indexes l and l' [10, 11]. As an example, we have

$$\boldsymbol{\mu}^{(1,1)} = \frac{2a}{3\eta_o} \boldsymbol{I}. \tag{2.17}$$

According to equation (2.15) for $l = 0$, we get

$$\boldsymbol{v}^{(1)} = \boldsymbol{\mu}^{(1,1)} \odot \boldsymbol{\mathcal{F}}^{(1)} + \boldsymbol{v}_o^{(1)} + \boldsymbol{v}_R^{(1)}. \tag{2.18}$$

The multipole $\boldsymbol{v}^{(1)}$ can be computed through its definition outlined in equation (2.14). One has

$$\boldsymbol{v}^{(1)} = \frac{1}{4\pi} \int d\hat{n}\, (\vec{u} + \vec{\Omega} \times a\hat{n}) = \vec{u}. \tag{2.19}$$

In the same way, by assuming that $\vec{v}_o(\vec{r}) = \boldsymbol{\beta} \cdot (\vec{R}_{cm} + a\hat{n})$ at the surface of the particle, we obtain

$$\boldsymbol{v}_o^{(1)} = \frac{1}{4\pi} \int d\hat{n}\, \boldsymbol{\beta} \cdot (\vec{R}_{cm} + a\hat{n}) = \boldsymbol{\beta} \cdot \vec{R}_{cm}. \tag{2.20}$$

Since $\vec{f}^1(\hat{n})$ is the force per unit area exerted by the particle on the fluid, the drag force exerted by the fluid on the particle is given by

$$\vec{F}^H = -\int dS\vec{f}^1(\hat{n}) = -a^2\int d\hat{n}\vec{f}^1(\hat{n}) = -4\pi a^2\,\mathcal{F}^{(1)}, \tag{2.21}$$

according to Eq. (2.14). Joining the results given through Eq. (2.19)-(2.21) and using Eq. (2.18) and the expression for the matrix element given in Eq. (2.17), we get the hydrodynamic force

$$\vec{F}^H = -6\pi\eta_o a(\vec{u} - \boldsymbol{\beta}\cdot\vec{R}_{cm} - \vec{v}_R^{(1)}), \tag{2.22}$$

from which one identifies the friction coefficient $6\pi\eta_o a$ corresponding to the inverse of the mobility, as well as the Brownian force $\vec{F}^B = -6\pi\eta_o a\vec{v}_R^{(1)}$.

We can also proceed by considering the case $l = 1$ in Eq. (2.12). One may show that this equation gives rise to

$$\boldsymbol{v}^{(2)} = 3\boldsymbol{\mu}^{(2,2)}\odot\boldsymbol{\mathcal{F}}^{(2)} + \boldsymbol{v}_o^{(2)} + \boldsymbol{v}_R^{(2)}, \tag{2.23}$$

where the mobility $\boldsymbol{\mu}^{(2,2)}$ follows from Eq. (2.12) and is given by

$$\boldsymbol{\mu}^{(2,2)} = \frac{a}{15\eta_o}\boldsymbol{S} + \frac{a}{9\eta_o}\boldsymbol{A}. \tag{2.24}$$

In this expression $\boldsymbol{S}$ and $\boldsymbol{A}$ have been defined as the isotropic tensors

$$S_{ijkl} = \frac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - \frac{1}{3}\delta_{ij}\delta_{kl} \tag{2.25}$$

and

$$A_{ijkl} = \frac{1}{2}(\delta_{il}\delta_{jk} - \delta_{ik}\delta_{jl}), \tag{2.26}$$

symmetric and antisymmetric in any pair of its indexes.

The mobility (2.24), together with the results

$$\boldsymbol{v}^{(2)} = \frac{1}{4\pi}\int d\hat{n}\;\hat{n}\;[\vec{u} + \vec{\Omega}\times a\hat{n}] = \frac{a}{3}\;\boldsymbol{\epsilon}\cdot\vec{\Omega} \tag{2.27}$$

and

$$\boldsymbol{v}_o^{(2)} = \frac{1}{4\pi}\int d\hat{n}\;\hat{n}\;[\boldsymbol{\beta}\cdot(\vec{R} + a\hat{n})] = \frac{a}{3}\;\boldsymbol{\beta}^{\,T}, \tag{2.28}$$

obtained by means of Eq. (2.14), with $\boldsymbol{\epsilon}$ being the Levi-Civita tensor and ^{T} standing for the transposed matrix, can be used in (2.23). One finally arrives at the expression

$$\frac{a}{3}(\boldsymbol{\epsilon}\cdot\vec{\Omega}-\boldsymbol{\beta}^{T})-\boldsymbol{v}_R^{(2)}=\frac{a}{\eta_o}(\frac{1}{5}\boldsymbol{S}+\frac{1}{3}\boldsymbol{A})\odot\boldsymbol{\mathcal{F}}^{(2)}. \tag{2.29}$$

The induced force multipole $\boldsymbol{\mathcal{F}}^{(2)}$ may be obtained from this equation. Multiplying both sides of Eq. (2.29) by $\boldsymbol{S}$, one has

$$\boldsymbol{\mathcal{F}}^{(2s)}=-(\frac{5\eta_o}{3}\boldsymbol{\beta}^{(s)}+\frac{5\eta_o}{a}\boldsymbol{v}_R^{(2s)}), \tag{2.30}$$

where, for an arbitrary tensor of second rank $\boldsymbol{\tau}$, $\boldsymbol{\tau}^{(s)}$ stands for its symmetric traceless part

$$\tau_{ij}^{(s)}\equiv\frac{1}{2}(\tau_{ij}+\tau_{ji}-\frac{2}{3}\tau_{kk}\delta_{ij}). \tag{2.31}$$

On the other hand, multiplying both sides of Eq. (2.29) by $\boldsymbol{A}$, one obtains

$$\boldsymbol{\mathcal{F}}^{(2a)}=\eta_o(\boldsymbol{\epsilon}\cdot\vec{\Omega}+\boldsymbol{\beta}^{(a)})-\frac{3\eta_o}{a}\boldsymbol{v}_R^{(2a)}, \tag{2.32}$$

where, again for an arbitrary tensor of second rank, $\boldsymbol{\tau}^{(a)}$ is defined as

$$\tau_{ij}^{(a)}\equiv\frac{1}{2}(\tau_{ij}-\tau_{ji}). \tag{2.33}$$

Moreover, from Eq. (2.29) we can obtain the equation for the hydrodynamic torque since, as in Eq. (2.21), we have

$$\vec{T}^H=-a^2\int d\hat{n}\;a\hat{n}\times\vec{f}^{\,i}(\hat{n})=a^3\boldsymbol{\epsilon}:\int d\hat{n}\;\hat{n}\;\vec{f}^{\,i}=4\pi a^3\boldsymbol{\epsilon}:\boldsymbol{\mathcal{F}}^{(2)}, \tag{2.34}$$

so that only the antisymmetric part of $\boldsymbol{\mathcal{F}}^{(2)}$ is involved. Making use of the fact that $\boldsymbol{\epsilon}:\boldsymbol{\epsilon}=-2\boldsymbol{I}$, in Eq. (2.29), we arrive at

$$\vec{T}^H=-8\pi\eta_o a^3(\vec{\Omega}-\vec{\omega}_o+\frac{3}{2a}\boldsymbol{\epsilon}:\boldsymbol{v}_R^{(2)}). \tag{2.35}$$

where we have defined the vorticity $\vec{\omega}_o\equiv\frac{1}{2}\boldsymbol{\epsilon}:\boldsymbol{\beta}^{(a)}$, and one can identify the Brownian torque $\vec{T}^B=-12\pi\eta_o a^2\boldsymbol{\epsilon}:\boldsymbol{v}_R^{(2)}$.

As follows from (2.22) and (2.35), the expressions for the force and torque split up into systematic and random contributions. The latter originates from the presence of fluctuations in the fluid and their statistical properties follow from fluctuating hydrodynamics according to Eq. (2.9) and (2.10).

Once we have obtained the hydrodynamic force and torque, we can proceed to obtain the equations for the translational and rotational motion of the particle. Since ferromagnetic particles are very small (radius about 100 Å) inertial effects can be

neglected and the equations of motion simply reflect the fact that both the sum of forces and torques acting on the particle are zero. Thus, the hydrodynamic torque, given in (2.35) is balanced out by the presence of a magnetic torque $\vec{m} \times \vec{H}$, where $\vec{m} = m\hat{R}$ is the magnetic moment of the sphere, with m being the magnetic moment strength and $\vec{H}$ the external field. Consequently, in the presence of a magnetic field, the angular velocity and the vorticity are different. This fact gives rise to the appearance of antisymmetric stresses and of the rotational viscosity. In the non-equilibrium thermodynamics framework, the antisymmetric pressure tensor is given by a linear law and is proportional to the difference between the spin (averaged angular velocity of the particles inside a volume element) and the vorticity [3].

3 Shear and rotational viscosities of the ferrofluid

Our main purpose in this section is to calculate the viscosities of the ferrofluid. To compute the shear and rotational viscosities, we will use the expression for the contribution to the pressure tensor of the suspension due to the presence of particles

$$\boldsymbol{\Pi}_p = \frac{a^3}{V} \int d\hat{n}\, \hat{n}\, \vec{f}^{\mathrm{I}}, \tag{3.1}$$

where $\vec{f}^{\mathrm{I}}$ is precisely the force per unit area exerted by the particle on the fluid and V is the volume of the system. Using Eq. (2.14), the pressure tensor can be expressed in terms of the second-order multipole of the induced force in the form

$$\boldsymbol{\Pi}_p = \frac{4\pi a^3}{V} \mathcal{F}^{(2)}. \tag{3.2}$$

The expression for the shear viscosity follows from (3.2). In fact, by taking the symmetric and traceless part of the corresponding tensors and neglecting the contribution due to the Brownian stress (we disregard fluctuating contributions because after averaging in order to obtain the rheological equation of state, they do not contribute), one has

$$\boldsymbol{\Pi}_p^{(s)} = \frac{4\pi a^3}{V} \mathcal{F}^{(2s)} = -5\eta_o \phi \boldsymbol{\beta}^{(s)}, \tag{3.3}$$

where we have employed Eq. (2.30) and we have already introduced the contribution of all the particles in the system through the volume fraction of particles ϕ. This equation can be compared with the linear law $\boldsymbol{\Pi}_p^{(s)} = -2\eta_p \boldsymbol{\beta}^{(s)}$ where η_p is the contribution to the viscosity of the system due to the presence of particles. Considering the expression

for the pressure tensor of the solvent $\boldsymbol{\Pi}_o^{(s)} = -2\eta_o\boldsymbol{\beta}^{(s)}$, we can define the effective viscosity of the system

$$\eta = \eta_o + \eta_p = \eta_o(1 + \frac{5}{2}\phi), \tag{3.4}$$

which can be identified with Einstein's formula.

The rotational viscosity can also be derived from the formalism introduced previously. Our starting point will be again Eq. (3.2). Taking the antisymmetric part of the terms of this equation and using Eq. (2.32) we get

$$\boldsymbol{\Pi}_p^{(a)} = \frac{4\pi a^3}{V}\boldsymbol{\mathcal{F}}^{(2a)} = 3\phi\eta_o(\boldsymbol{\epsilon}\cdot\vec{\Omega} + \boldsymbol{\beta}^{(a)}) = 3\phi\eta_o\boldsymbol{\epsilon}\cdot(\vec{\Omega} - \vec{\omega}_o), \tag{3.5}$$

where we have neglected the Brownian torque after averaging, and use has been made of the relation $\boldsymbol{\epsilon}\cdot\vec{\omega}_o = -\boldsymbol{\beta}^{(a)}$, which follows from the definition of the vorticity. It is clear from this equation that the appearance of antisymmetric stresses in the system originates from the difference between the angular velocity of the particles and the vorticity $\vec{\omega}_o$. Furthermore, the angular velocity will depend on the direction of the magnetic field which exerts a magnetic torque on the particle.

3.1 High magnetic field limit

In the case of high magnetic fields, the angular velocity is parallel to the field [12], and has the form

$$\vec{\Omega} = \vec{\omega}_o\cdot\hat{H}\hat{H}, \tag{3.1.1}$$

where $\hat{H}$ is the unit vector along the direction of the field. Equation (3.5) can be rewritten in terms of the corresponding axial vectors. One then obtains

$$\vec{\Pi}_p^{(a)} = 3\eta_o\phi(\vec{\Omega} - \vec{\omega}_o) = 2\eta_r(\vec{\Omega} - \vec{\omega}_o) = -2\eta_r(\boldsymbol{I} - \hat{H}\hat{H})\cdot\vec{\omega}_o, \tag{3.1.2}$$

where $\vec{\Pi}^{(a)}$ is the axial vector related to the antisymmetric part of the pressure tensor defined in the following way:

$$\vec{\Pi}_p^{(a)} = -\frac{1}{2}\boldsymbol{\epsilon} : \boldsymbol{\Pi}_p^{(a)}. \tag{3.1.3}$$

In fact, we have

$$\boldsymbol{\Pi}_p^{(a)} = -2\eta_r\boldsymbol{\epsilon}\cdot(\boldsymbol{I} - \hat{H}\hat{H})\cdot\vec{\omega}_o = 2\eta_r\{\boldsymbol{A} + \frac{1}{2}(\boldsymbol{\epsilon}\cdot\hat{H})(\boldsymbol{\epsilon}\cdot\hat{H})\} : \boldsymbol{\beta}^{(a)}, \tag{3.1.4}$$

and consequently, the rotational viscosity tensor is given by

$$\eta_r = \eta_r\{\boldsymbol{A} + \frac{1}{2}(\epsilon \cdot \hat{H})(\epsilon \cdot \hat{H})\} \equiv \eta_r \beta_\perp^{(a)}, \tag{3.1.5}$$

where we have defined the antisymmetric tensor $\beta_\perp^{(a)} \equiv \boldsymbol{A} + \frac{1}{2}(\epsilon \cdot \hat{H})(\epsilon \cdot \hat{H})$, and where η_r is the rotational viscosity. For high values of the magnetic field, it has the value

$$\eta_r = \frac{3}{2}\eta_o\phi \tag{3.1.6}$$

according to refs. [3, 4].

Once we have obtained the rotational viscosity, one may calculate its contribution to the effective viscosity of the suspension. In Ref. [4] it was shown that for a Couette flow the effective viscosity is given by

$$\eta_{ef} = \eta_o(1 + \frac{5}{2}\phi + \frac{3}{2}\phi \sin^2\alpha), \tag{3.1.7}$$

with α being the angle between $\hat{H}$ and $\vec{\omega}_o$. This coefficient has the maximum value $\eta_o(1 + 4\phi)$, occurring when the magnetic field and the vorticity are perpendicular, and has its minimum value $\eta_o(1 + \frac{5}{2}\phi)$ when both vectors are parallel since in this case, the angular velocity of the particle is equal to the vorticity of the fluid at the point occupied by the particle and only the contribution due to symmetric stresses will remain. The result (3.1.7) was obtained in [4] by considering the suspension as a fluid with internal angular momentum. Experimental corroboration of this formula in the case of a Poiseuille flow was carried out by Mc Tague [17].

3.2 The Smoluchowski equation

To obtain the rotational viscosity in the general case (for any value of the external field), we have to solve the corresponding Smoluchowski equation in order to compute the involved averages. This equation introduces the distribution function giving the probability density of the location of each particle and the orientation of its magnetic moment. If the suspension is dilute enough, interactions between particles (dipolar, van der Waals, hydrodynamic) are negligible and we can assume that the system is homogeneous. Consequently, the only relevant quantity will be the orientation of the magnetic moments, $\hat{R}$, whose probability density, $\psi(\hat{R}, t)$, satisfies the Smoluchowski equation for the rotational motion of the particles

$$\frac{\partial \psi}{\partial t} = -\vec{\mathcal{R}} \cdot (D_r \mu \hat{R} \times \hat{H} + \vec{\omega}_o)\psi + D_r \vec{\mathcal{R}} \cdot \vec{\mathcal{R}}\psi, \tag{3.2.1}$$

where $\vec{\mathcal{R}} \equiv \hat{R} \times \frac{\partial}{\partial \hat{R}}$ is the rotational operator, $D_r = \frac{k_B T}{\xi_r}$ is the rotational diffusion coefficient with k_B the Boltzmann constant, T the temperature and ξ_r the rotational friction coefficient. Furthermore, $\hat{H}$ is the unit vector parallel to the external magnetic field, $\vec{H}$, μ is the Langevin parameter $\frac{m_o H}{k_B T}$, comparing magnetic and thermal energies, where m is the magnetic moment strength of a particle and $\vec{\omega}_o = \frac{1}{2} rot \vec{v}$ is the vorticity of the flow. Note that the right-hand side of Eq.(3.2.1) introduces the three possible mechanisms responsible for the variation of the magnetic moments, namely, magnetic torque, vorticity and Brownian diffusion.

From the Smoluchowski equation we can obtain the equations for the moments of order n of the orientation $\hat{R}$, which follow from (3.2.1) after multiplying this equation by the tensor $\hat{R}^n$ and integrating over all the possible orientations. For the first moment, one obtains

$$\frac{d\langle \hat{R} \rangle}{dt} = -2D_r \langle \hat{R} \rangle + D_r \mu \hat{H} + \langle \vec{\omega}_o \times \hat{R} \rangle - D_r \mu \langle \hat{R}\hat{R} \rangle \cdot \hat{H}, \qquad (3.2.2)$$

from which we can identify the contributions related to the three different mechanisms accounting for the orientation of the magnetic moment. To arrive at this equation, use has been made of the property of the rotational operator $\vec{\mathcal{R}}^2 \hat{R} = -2\hat{R}$.

It is clear from Eq.(3.2.2) that to find the value for the first moment we need the expression for the second one. This last quantity can also be obtained from the Smoluchowski equation by following the procedure indicated above and is found to depend on the third moment. One then concludes that (3.2.2) constitutes the first equation of a hierarchy relating moments of different orders.

To get a solution for the stationary orientation, we break the hierarchy by performing a decoupling approximation

$$\langle \hat{R}\hat{R} \rangle \cdot \hat{H} = \langle \hat{R}\hat{R}_z \rangle \simeq \langle \hat{R}_x \rangle \langle \hat{R}_z \rangle \hat{e}_x + \langle \hat{R}_y \rangle \langle \hat{R}_z \rangle \hat{e}_y + \langle \hat{R}_z \hat{R}_z \rangle \hat{e}_z, \qquad (3.2.3)$$

where $\hat{e}_x$, $\hat{e}_y$ and $\hat{e}_z$ are unit vectors forming an orthonormal basis considering the magnetic field parallel to $\hat{e}_z$. Note that this approximation assumes the independence of the perpendicular components of the orientation vector, or in more general words, of the quantities which vanish at equilibrium, when averaged, and those which are different from zero. This approximation may be justified from the fact that in equilibrium both quantities are not correlated, $\langle R_x R_z \rangle_{eq} = \langle R_y R_z \rangle_{eq} = 0$; on the other hand, $\langle R_z \rangle_{eq} \neq 0$, whereas $\langle R_x \rangle_{eq} = \langle R_y \rangle_{eq} = 0$. In non-equilibrium conditions, i.e., when $\vec{\omega}_o$ is a small but non-vanishing quantity, we will assume that these components remain uncorrelated. In addition, we ensure that after performing the decouplings,

both terms are still proportional to the vorticity. In the following subsection, we will see that this simple approximation gives rise to pretty good results for a suspension of rigid dipoles, and, what is more, it will allow us to obtain a good agreement with the experiments when studying more intricate magnetic materials.

Quite recently, in Ref. [16] the authors followed a similar procedure to calculate the frequency-dependent viscosity of a ferrofluid. They first attempted to solve the hierarchy of equations by carrying out a different approximation consisting of a progressive truncation of the hierarchy of equations. They showed that by means of this procedure it is not possible to recover the stationary rotational viscosity that we will compute in the following subsection and that has been experimentally corroborated, except for small values of the parameter μ. Then, they also tried a specific decoupling approximation, which reduces to the one discussed before when applied to the second moment, for higher order moments. Thus, by decoupling the second moment one converts the problem to the case studied in this section, which seems to meet all the physical information required to explain the behavior of the suspension, and introducing the decoupling in the equation for higher order moments may give rise to some unexpected behavior for finite values of μ. In view of all these results, it is worth mentioning that we really expect that the decouplings are more accurate for quite small and high values of μ, because in the former case higher order moments will be negligible and in the latter the dynamics of the particles is mainly determined by the external field rather than being influenced by Brownian motion. On top of that, we must add that there are many possible ways of carrying out the decouplings. Such approximations are broadly used in the context of stochastic processes, and particularly, for moments of order higher than two, it is convenient to smooth out the truncation and, correspondingly, its unexpected consequences, by introducing a term in the denominator. We will see an example in part II and in the following chapter.

Our next step will be to formulate an expression for the stationary orientation consistent with the behaviour of this quantity at low and high magnetic fields. With the method introduced in Ref. [14] it is possible to show that for $\mu \ll 1$, the stationary orientation behaves as

$$\langle \hat{R} \rangle = \mathcal{L}(\mu)\hat{H} + \frac{3}{4} D_r^{-1} [\mathcal{L}(\mu) - \frac{\mu}{9}](\vec{\omega}_o \times \hat{H}), \tag{3.2.4}$$

whereas for $\mu \gg 1$, one has

$$\langle \hat{R} \rangle = \mathcal{L}(\mu)\hat{H} + D_r^{-1} \frac{\mathcal{L}(\mu)}{\mu}(\vec{\omega}_o \times \hat{H}). \tag{3.2.5}$$

Here $\mathcal{L}(\mu) = \coth\mu - \frac{1}{\mu}$ is the Langevin function. We then conclude that in both limits the orientation has two contributions, one parallel to the field similar to the one found for a paramagnetic gas and the other perpendicular to the field, along the direction of the vector $\vec{\omega}_o \times \hat{H}$. In view of eqs. (3.2.4) and (3.2.5), we then propose for any value of μ

$$\langle \hat{R} \rangle = \mathcal{L}(\mu)\hat{H} + D_r^{-1} F(\mu)(\vec{\omega}_o \times \hat{H}), \tag{3.2.6}$$

where $F(\mu)$ is an unspecified function of the field that should reproduce the behaviour of $\langle \hat{R} \rangle$ in both limits dicussed previously.

To determine the form of $F(\mu)$, in Eq. (3.2.3) we will use the expression for the averages of the components of $\hat{R}$ obtained from (3.2.6). Furthermore, the second moment $\langle \hat{R}_x \hat{R}_z \rangle$ can be computed exactly since it does not depend on $F(\mu)$. One then obtains

$$\mu \langle \hat{R}\hat{R} \rangle \cdot \hat{H} \simeq [\mu - 2\mathcal{L}(\mu)]\hat{H} + D_r^{-1} \mu F(\mu)\mathcal{L}(\mu)(\vec{\omega}_o \times \hat{H}). \tag{3.2.7}$$

The result (3.2.7) can be employed in the stationary version of Eq.(3.2.2). Neglecting a term of second order in the vorticity, we arrive at

$$F(\mu) = \frac{\mathcal{L}(\mu)}{2 + \mu\mathcal{L}(\mu)}. \tag{3.2.8}$$

From Eq.(3.2.6) along with (3.2.8), we can derive the expression for the average of the magnetization $\vec{M} = n\vec{m}$, where n is the number density of dipoles and $\vec{m}$ the magnetic moment of one particle, provided that $\vec{m} = m_o \hat{R}$, obtaining

$$\langle \vec{M} \rangle = n m_o \mathcal{L}(\mu)\hat{H} + n m_o D_r^{-1} F(\mu)(\vec{\omega}_o \times \hat{H}). \tag{3.2.9}$$

In view of (3.2.9), we see that this quantity consists of the magnetization for a paramagnetic gas, given by the Langevin theory, and of a term perpendicular to the field whose origin is the presence of vorticity in the carrier fluid.

This result can be compared with others obtained previously. In Ref. [4], a phenomenological theory, founded on the postulation of a relaxation equation for the magnetization, was proposed. This theory gives exactly the same value. In Ref. [6], the authors carried out the same task using a particular mean field approximation based on the definition of an effective field. However, as shown in Fig. I.2, their result was in disagreement with the one obtained from the phenomenological theory and with ours.

3.3 Rotational viscosity and the external magnetic field

The quantity between brakets in Eq. (3.5) can be transformed by using the equation for the rotational motion of a ferromagnetic particle, which follows from the total angular momentum equation

$$I\frac{d\vec{\Omega}}{dt}+\gamma_o^{-1}\frac{d\vec{m}}{dt}=-\xi_r(\vec{\Omega}-\vec{\omega}_o)+\vec{m}\times\vec{H} \tag{3.3.1}$$

where I is its moment of inertia, and γ_o the electron gyromagnetic factor. We will neglect the term coming from the angular momentum of the electrons determining the magnetic moment of the particles. Moreover, if the particle is small enough, as occurs for ferrofluids, inertial effects can also be neglected. Therefore the hydrodynamical and magnetic torques balance each other out and Eq. (3.5) transforms into

$$\boldsymbol{\Pi}_p^{(a)}=3\phi\eta_o D_r\mu\epsilon\cdot(\hat{R}\times\hat{H}). \tag{3.3.2}$$

In view of (3.3.2), we conclude that the antisymmetric part of the pressure tensor depends on the relative orientation of the magnetic moment and the field. To compute the corresponding transport coefficient namely, the rotational viscosity, η_r, we have to average this part over all possible orientations of $\hat{R}$. We then obtain

$$\langle\boldsymbol{\Pi}_p^{(a)}\rangle=3\eta_o\phi D_r\mu\epsilon\cdot(\langle\hat{R}\rangle\times\hat{H}), \tag{3.3.3}$$

where the average on the right-hand side follows from the expression for the first moment of $\hat{R}$ computed by the Smoluchowski equation and given by (3.2.6) along with (3.2.8). We finally obtain

$$\langle\boldsymbol{\Pi}_p^{(a)}\rangle=3\eta_o\phi\mu F(\mu)\beta_\perp^{(a)}. \tag{3.3.4}$$

This equation yields the rotational viscosity

$$\eta_r=\frac{3}{2}\eta_o\phi\,\frac{\mu-\tanh\mu}{\mu+\tanh\mu}. \tag{3.3.5}$$

This last quantity behaves for $\mu\ll 1$ as

$$\eta_r\simeq\frac{1}{4}\eta_o\phi\mu^2 \tag{3.3.6}$$

and is then quadratic in the field. For $\mu\gg 1$, one has

$$\eta_r\simeq\frac{3}{2}\eta_o\phi(1-\frac{1}{\mu}). \tag{3.3.7}$$

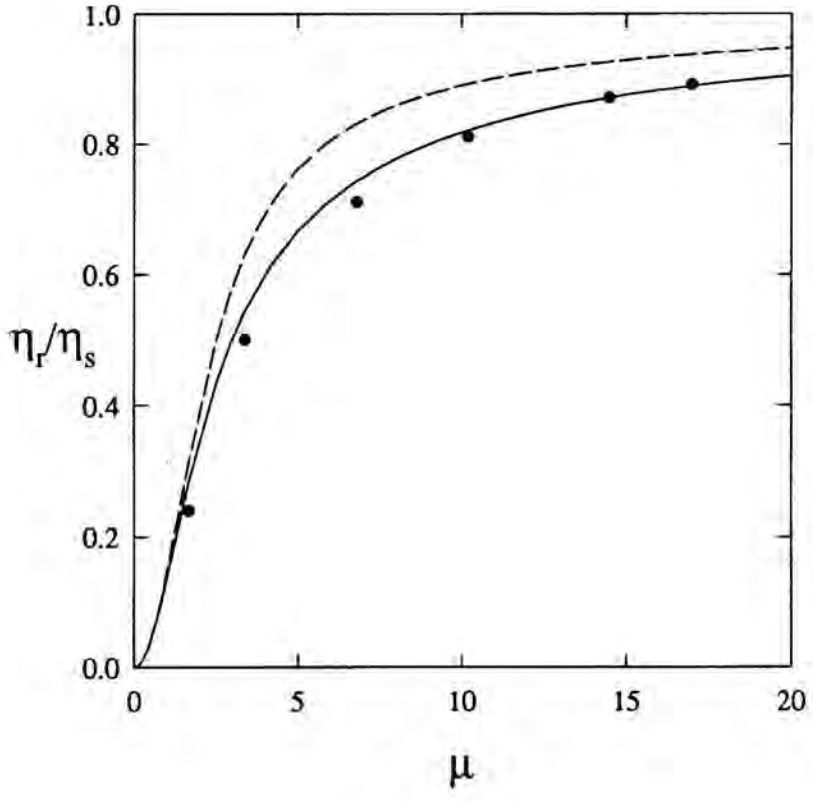

Figure I.2: The quantity η_r/η_s versus the parameter μ. The solid line corresponds to our result given in Eq. (3.3.5) and with the result coming from a phenomenological theory proposed in Ref.[4], whereas the dashed line is obtained from the solution of the Smoluchowski equation given in Ref.[6]. The dots represent experimental data from Ref. [13].

Consequently, the rotational viscosity tends towards the asymptotic limit $\frac{3}{2}\eta_o\phi$. In Fig. I.2 we have plotted the reduced rotational viscosity η_r/η_s, with $\eta_s \equiv \frac{3}{2}\eta_o\phi$, as a function of the parameter μ. The presence of the rotational viscosity leads to the introduction of an effective viscosity of the ferrofluid. For the case of a planar Couette flow where the applied magnetic field is choosen perpendicular to the vorticity, this quantity gives the increase of the viscosity of the suspension due to the action of the external field. These results agree with the ones obtained in Ref. [4] by means of a phenomenological theory and with the experiments performed by Mc Tague [17].

In our former calculation of the first moment of $\hat{R}$, we have neglected a term of second order in the vorticity. This approximation can be removed by computing the distribution function up to second order in this quantity at low magnetic field. The resulting averages can be given, for example, when the vorticity is parallel to $\hat{e}_x$. For the average of the y-component, one has

$$\langle \hat{R}_y \rangle = -\frac{\omega_o \mu}{6D_r[1+(\omega_o^2/4D_r^2)]}, \tag{3.3.8}$$

which is in good agreement with the corresponding result obtained in Ref. [15] by means of Brownian dynamics. Note, however, that since the ferromagnetic particles are very small, second order corrections in the vorticity are only important at very high shear rates.

4 Calculation of the viscosities using Green-Kubo formulas

Our purpose in this section is to present an alternative derivation of the shear and rotational viscosities. These quantities will be computed from the corresponding Green-Kubo formulas arising from linear response theory, which have been widely used to calculate transport coefficients. The contribution of the particles to the shear viscosity, introduced in Eq. (3.4), is then given by

$$\eta_p = \frac{1}{Vk_BT}\int_0^\infty dt \langle \Pi^{(s)}_{p,xz}(t)\Pi^{(s)}_{p,xz}(0)\rangle. \tag{4.1}$$

In order to compute the correlation of the symmetric part of the pressure tensor, we will use the relationship between the pressure tensor and the second order multipole of the induced force, given through eqs. (3.2) and (2.30). Provided that our reference state should be in equilibrium conditions ($\beta = 0$), this relationship is the following

$$\Pi^{(s)}_{p,xz}(t) = -20\pi a^2 \eta_o v^{(2s)}_{R,xz}(t), \tag{4.2}$$

which used in (4.1), yields

$$\eta_p = \frac{1}{V k_B T}(20\pi a^2 \eta_o)^2 \int_0^\infty dt \langle v^{(2s)}_{R,xz}(t) v^{(2s)}_{R,xz}(0)\rangle. \tag{4.3}$$

The correlation in this expression can be computed from fluctuating hydrodynamics. In fact, from (2.9) and (2.10) we get

$$\langle \vec{v}^R(\vec{k},t)\vec{v}^R(\vec{k}\,',t')\rangle = 2k_B T(2\pi)^3 \frac{(\boldsymbol{I} - \hat{k}\hat{k})}{\eta_o k^2}\, \delta(\vec{k}+\vec{k}\,')\, \delta(t-t'). \tag{4.4}$$

In real space this expression is given by

$$\langle \vec{v}^R(\vec{r},t)\vec{v}^R(\vec{r}\,',t')\rangle = 2k_B T\, \boldsymbol{T}(\vec{r}-\vec{r}\,')\delta(t-t'). \tag{4.5}$$

Using now the multipole expansion, for points at the surface of the particle, we can obtain the corresponding correlation of the second multipole of the random velocity. One arrives at

$$\langle v^{(2)}_R(t) v^{(2)}_R(t')\rangle = \frac{k_B T}{2\pi a^2}\mu^{(2,2)}\delta(t-t'), \tag{4.6}$$

where the matrix element $\mu^{(2,2)}$ has been given in (2.24). For the symmetric part of this correlation, one has

$$\langle v^{(2s)}_R(t) v^{(2s)}_R(t')\rangle = \frac{k_B T}{30\pi\eta_o a}\boldsymbol{S}\delta(t-t'). \tag{4.7}$$

Employing this expression in (3.3) and performing the integral, we then come to the result

$$\eta_p = \frac{5}{2}\eta_o \phi, \tag{4.8}$$

which corresponds to the contribution to the viscosity of the suspension owing to the presence of particles.

The rotational viscosity can be computed by means of the same procedure. The Green-Kubo formula is now

$$\eta_r = \frac{1}{V k_B T}\int_0^\infty dt \langle \Pi^{(a)}_{p,xz}(t)\Pi^{(a)}_{p,xz}(0)\rangle \tag{4.9}$$

or in terms of the corresponding axial vectors

$$\eta_r = \frac{1}{V k_B T} \int_0^\infty dt \langle \Pi_{p,y}^{(a)}(t) \Pi_{p,y}^{(a)}(0) \rangle. \tag{4.10}$$

Making use of equations (3.2) and (2.32) and the definition (3.1.3), we get

$$\Pi_{p,y}^{(a)}(t) = (4\pi a^3)\eta_o [\Omega_y(t) + \frac{3}{2a}(\epsilon : \boldsymbol{v}_R^{(2a)}(t))_y], \tag{4.11}$$

where we have employed again the requirement $\beta = 0$, for the reference state.

The correlation in Eq. (4.10) then follows from this last expression. One has

$$\langle \Pi_{p,y}^{(a)}(t) \Pi_{p,y}^{(a)}(0) \rangle = (4\pi a^3)^2 \eta_o^2 \langle [\Omega_y(t) + \frac{3}{2a}(\epsilon : \boldsymbol{v}_R^{(2a)}(t))_y] \, [\Omega_y(0) + \frac{3}{2a}(\epsilon : \boldsymbol{v}_R^{(2a)}(0))_y] \rangle \tag{4.12}$$

or alternatively

$$\langle \Pi_{p,y}^{(a)}(t) \Pi_{p,y}^{(a)}(0) \rangle = (4\pi a^3)^2 \frac{\eta_o^2}{\xi_r^2} \langle (\vec{m} \times \vec{H})_y(t) (\vec{m} \times \vec{H})_y(0) \rangle, \tag{4.13}$$

with $\xi_r = 8\pi a^3 \eta_o$ being the rotation friction coefficient. To obtain this equality we have used the equation of rotational motion of the particle

$$0 = \vec{T}^H + \vec{T}^M, \tag{4.14}$$

where the expression for the hydrodynamic torque is given in (2.35) and $\vec{T}^M$ is the magnetic torque. In (4.14) we have neglected inertial and gyromagnetic effects, thus the torques balance each other out. This fact provides the equation to derive (4.13) from (4.12).

The rotational viscosity can be finally expressed as

$$\eta_r = \frac{3}{2} \phi \eta_o D_r \mu^2 \int_0^\infty dt \langle \hat{R}_x(t) \hat{R}_x(0) \rangle, \tag{4.15}$$

where μ is the Langevin parameter $\frac{m_s H}{k_B T}$, comparing magnetic and thermal energies, and we have taken the magnetic field pointing towards the z-direction.

To perform the integral in (4.15) we have to know the correlation function for the x-component of the vector $\hat{R}$. The evolution equation for this correlation comes from the Smoluchowski equation

$$\frac{\partial \psi}{\partial t} = -\vec{\mathcal{R}} \cdot (D_r \mu \dot{\hat{R}} \times \dot{\hat{H}} \psi) + D_r \vec{\mathcal{R}} \cdot \vec{\mathcal{R}} \psi, \tag{4.16}$$

valid in the absence of vorticity. In fact, starting from (4.16) one may derive the evolution equation for the correlation

$$\frac{d\langle\hat{R}(t)\hat{R}(0)\rangle}{dt} = D_r\{-2\langle\hat{R}(t)\hat{R}(0)\rangle + \mu\hat{H}\langle\hat{R}(0)\rangle - \mu\langle\hat{R}(t)\hat{R}(0)\hat{R}(t)\rangle\cdot\hat{H}\}, \quad (4.17)$$

which for the perpendicular component yields

$$\frac{d\langle\hat{R}_\perp(t)\hat{R}_\perp(0)\rangle}{dt} = -D_r\{2\langle\hat{R}_\perp(t)\hat{R}_\perp(0)\rangle + \mu\langle\hat{R}_\perp(t)\hat{R}_\perp(0)\hat{R}_\parallel(t)\rangle\}. \quad (4.18)$$

To solve this equation we will introduce a decoupling approximation as in the previous section. This approximation consists of decoupling the perpendicular and parallel components of the vector $\hat{R}$, due to the different nature of the dynamics of both components, as we already pointed out, and can be formulated in the following way:

$$\langle\hat{R}_\perp(t)\hat{R}_\perp(0)\hat{R}_\parallel(t)\rangle \simeq \langle\hat{R}_\perp(t)\hat{R}_\perp(0)\rangle\langle\hat{R}_\parallel(t)\rangle. \quad (4.19)$$

In addition, in the linear regime, we may approximate in (4.19) $\langle\hat{R}_\parallel(t)\rangle$ by its equilibrium value $\langle\hat{R}_\parallel(0)\rangle_{eq} = \mathcal{L}(\mu)$. This equilibrium average is computed with the equilibrium distribution function

$$\psi_{eq} = \frac{\mu}{4\pi\sinh\mu}\exp(\mu\hat{R}\cdot\hat{H}). \quad (4.20)$$

Consequently, Eq.(4.18) transforms into the relaxation equation

$$\frac{d\langle\hat{R}_\perp(t)\hat{R}_\perp(0)\rangle}{dt} = -D_r(2+\mu\mathcal{L}(\mu))\langle\hat{R}_\perp(t)\hat{R}_\perp(0)\rangle, \quad (4.21)$$

from which we may identify the relaxation time $\tau_\perp$

$$\tau_\perp = D_r^{-1}\mathcal{L}^{-1}(\mu)F(\mu). \quad (4.22)$$

Thus we expect that the correlation decays exponentially according to

$$\langle\hat{R}_x(t)\hat{R}_x(0)\rangle = e^{-t/\tau_\perp}\langle\hat{R}_x(0)^2\rangle. \quad (4.23)$$

The rotational viscosity then follows from the Green-Kubo formula (4.15) together with (4.23). Performing the integral, one arrives at

$$\eta_r = \frac{3}{2}\phi\eta_o\mu^2\frac{\langle\hat{R}_x(0)^2\rangle_{eq}}{(2+\mu\mathcal{L}(\mu))}. \quad (4.24)$$

In view of the result $\langle\hat{R}_x(0)^2\rangle_{eq} = \frac{\mathcal{L}(\mu)}{\mu}$, which can also be obtained by computing the equilibrium average with the equilibrium distribution function (4.20), one obtains

$$\eta_r = \frac{3}{2}\eta_o\phi\,\frac{\mu - \tanh\mu}{\mu + \tanh\mu}, \tag{4.25}$$

which, as we expected, also coincides with the corresponding expression obtained by Shliomis using a continuum theory [4] and with the result of [7].

5 Conclusions

In this part we have analyzed the dynamics of a ferromagnetic spherical particle, as well as the viscosities of a dilute suspension constituted by these particles. Our theoretical framework is based on the Navier-Stokes equation in which an induced force, resulting from the perturbation introduced in the dynamics of the fluid by the particle, and a stochastic Langevin source, coming from the fluctuations of the hydrodynamical fields, have been included. This equation accounts for the coupled dynamics of the fluid and the particle. A multipolar expansion of the quantities appearing in the formal solution of the Navier-Stokes-Langevin equation leads to the expressions for the force and torque exerted on the particle which contain random contributions whose statistical properties are dictated by fluctuating hydrodynamics [5].

We use two methods to obtain the shear and rotational viscosities. One is deterministic and is based on the Kirkwood formula for the viscous pressure tensor which is shown to be related to the second order multipole of the induced force. The other is based on the linear response theory giving the transport coefficients in terms of time-dependent correlation functions. The presence of the field is responsible for the appearance of an antisymmetric contribution to the pressure tensor and introduces the rotational viscosity as a new transport coefficient. The existence of antisymmetric stresses comes from the fact that the torque exerted by the magnetic field on a dipole and the hydrodynamic torque balance each other out. Consequently, the angular velocity of the particle may differ from the value of the vorticity of the fluid at the point it occupies.

We have studied here a simple case in which the transport coefficients have already been calculated by other authors by means of different methods. Our main purpose has been to develop a rather general formalism that can be useful in the study of transport phenomena in ferrofluids in different and more intricate situations, which constitute the subject of some of the following parts of the monograph. Furthermore, the methods developed here can also be applied to study the dependence of the viscosity on frequency [16], or for higher concentrations, in which case dipolar interactions

play an essential role. Work is being done in the last case in order to find further theoretical results.

Part II

SOFT MAGNETIC MATERIALS IN HIGH MAGNETIC FIELDS

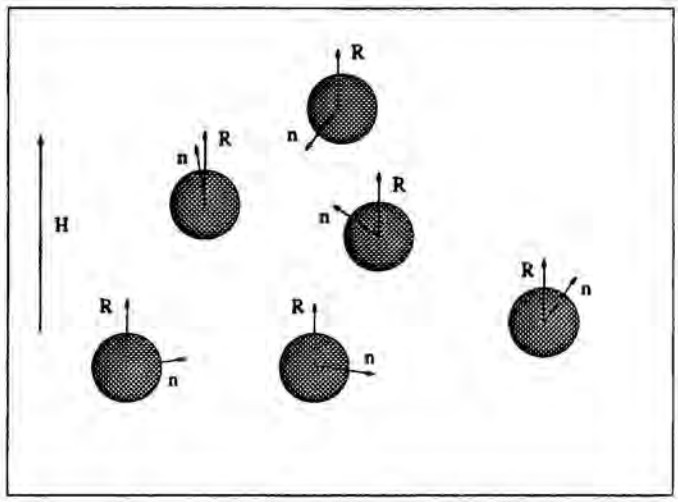

Figure I.3: For soft magnetic materials in sufficiently high magnetic fields the magnetic moments orient themselves in the direction of the field very quickly. Then it takes place the mechanical rotation of the particles to the stationary orientation.

6 Introduction

In this part of the chapter we apply the formalism developed in the previous part to the case in which after perturbing the system, the relaxation towards the magnetic field takes place in two steps: first a quick relaxation of the magnetic moment, then a mechanical rotation of the particle towards the equilibrium orientation, with the magnetic moment also parallel to the easy axis of magnetization [19]. This situation occurs for high magnetic fields and the energy of the magnetic particles reduces to the energy of anisotropy. Experimentally, it is found that the magnetization tends to lie along certain crystallographic axes; this effect is known as crystalline anisotropy. It is additional to the directional effects that occur when the samples' shape lacks spherical or cubic symmetry. The existence of crystalline anisotropy may be demonstrated by the magnetization curves. It is clear that much smaller fields are required to magnetize the crystals to saturation along certain directions than along others. The crystallographic axes along which the magnetization tends to lie are called easy directions; the axes along which it is most difficult to produce saturation are called hard directions.

With this goal in mind, this part has been distributed as follows. Section 7 is intended as a short review of the rotational dynamics which was previously analyzed.

Section 8, in which we give our main results, is devoted to the calculation of the rotational viscosity, from just the corresponding Green-Kubo formula, when the particles are affected by the above mentioned relaxation mechanism. Finally, in the last section, we point out our main conclusions.

7 Contribution of the energy of anisotropy to the rotational dynamics

We consider a dilute suspension of spherical single-domain ferromagnetic particles under the action of an external magnetic field. The energy of each particle is given by

$$U = -\vec{m} \cdot \vec{H} - K_a V_m (\hat{n} \cdot \hat{R})^2, \tag{7.1}$$

where $\vec{m} = m\hat{R}$ is the magnetic moment of the particles, $\vec{H}$ is the external magnetic field, K_a is the first anisotropy constant, assumed positive, V_m is the magnetic volume of one of these spheres, and $\hat{n}$ is the unit vector along the direction of the axis of easy magnetization for uniaxial magnetic crystals.

If the external magnetic field is strong enough, the magnetic moments will be all pointing towards the field direction. Then, apart from a constant, which does not produce any torque, the energy of the particles is given by

$$U = -K_a V_m (\hat{n} \cdot \hat{H})^2, \tag{7.2}$$

where we have assumed that the magnetic moment strength m is constant.

Neglecting inertial effects and the angular momentum of the electrons determining the magnetic moment of the particles, its rotational dynamics is now governed by the equation of motion

$$0 = \vec{T}^H + \vec{T}^A. \tag{7.3}$$

Here $\vec{T}^H$ is the hydrodynamic torque and $\vec{T}^A$ the torque related to the energy of anisotropy.

The second contribution to the total torque, $\vec{T}^A$, is given by

$$\vec{T}^A = -\vec{\mathcal{R}} U, \tag{7.4}$$

where $\vec{\mathcal{R}} \equiv \hat{n} \times \frac{\partial}{\partial \hat{n}}$ is the rotational operator.

Consequently, the torques balance each other out, and using the expression of the hydrodynamic torque (2.35), we obtain the relation

$$(\vec{\Omega} - \vec{\omega}_o + \frac{3}{2a}\epsilon : \boldsymbol{v}_R^{(2)}) = -\frac{1}{\xi_r}\vec{\mathcal{R}}U = \frac{2K_a V_m}{\xi_r}(\hat{n}\cdot\hat{H})(\hat{n}\times\hat{H}), \tag{7.5}$$

where $\xi_r = 8\pi\eta_o a^3$ is the rotational friction coefficient. This expression indicates that the presence of a magnetic field may give rise to differences between the angular velocity of the particle and the vorticity field at the point occupied by the particle. The magnetic field, through the energy of anisotropy of the particles, is then the origin of antisymmetric stresses in the suspension, and of the rotational viscosity.

8 Green-Kubo formula for the rotational viscosity

The rotational viscosity follows from a Green-Kubo formula giving this coefficient in terms of an integral of the correlation of the corresponding current. The Green-Kubo formula for the rotational viscosity,

$$\eta_r = \frac{1}{V k_B T}\int_0^\infty dt \langle \Pi^{(a)}_{p,xz}(t)\Pi^{(a)}_{p,xz}(0)\rangle, \tag{8.1}$$

where $^{(a)}$ means antisymmetric part, or alternatively

$$\eta_r = \frac{1}{V k_B T}\int_0^\infty dt \langle \Pi^{(a)}_{p,y}(t)\Pi^{(a)}_{p,y}(0)\rangle. \tag{8.2}$$

with $\vec{\Pi}^{(a)}_p$ the axial vector related to $\boldsymbol{\Pi}^{(a)}_p$.

We are now interested in computing the rotational viscosity when the only relaxation mechanism is the one for which the vector $\hat{n}$ relaxes towards the direction of the magnetic moment. As we already indicated in the previous part, in order to calculate the correlation of the corresponding current we start from the expression

$$\boldsymbol{\Pi}_p = \frac{a^3}{V}\int d\hat{r}\ \hat{r}\ \vec{f}^1, \tag{8.3}$$

where $\hat{r}$ is the unit vector along the direction of $\vec{r} - \vec{R}_{cm}$, with $\vec{R}_{cm}$ being the position vector of the center of mass of the particle, and $\vec{f}^1$ is the force per unit area exerted by the particle on the fluid. The contribution of the particles to the pressure tensor can be expressed in terms of the second order multipole of the induced force $\mathcal{F}^{(2)}$ as

$$\boldsymbol{\Pi}_p = \frac{4\pi a^3}{V}\mathcal{F}^{(2)}. \tag{8.4}$$

Because we are only interested in the correlation of the antisymmetric part of $\boldsymbol{\Pi}_p$, we have to know the expression for the antisymmetric part of $\mathcal{F}^{(2)}$ denoted by $\mathcal{F}^{(2a)}$. This quantity was computed in the first part of the chapter. We obtained

$$\mathcal{F}^{(2a)} = \eta_o(\boldsymbol{\epsilon}\cdot\vec{\Omega} + \boldsymbol{\beta}^{(a)}) - \frac{3\eta_o}{a}\boldsymbol{v}_R^{(2a)}. \tag{8.5}$$

Making use of equations (8.3), (8.4), (8.5), we get

$$\Pi_{p,y}^{(a)}(t) = (4\pi a^3)\eta_o[\Omega_y(t) + \frac{3}{2a}(\boldsymbol{\epsilon} : \boldsymbol{v}_R^{(2a)}(t))_y], \tag{8.6}$$

where we have employed the requirement $\boldsymbol{\beta} = 0$ for the reference state, which should be in equilibrium conditions.

The correlation in Eq. (8.2) then follows from this last expression. One arrives at

$$\langle \Pi_{p,y}^{(a)}(t)\Pi_{p,y}^{(a)}(0)\rangle = (4\pi a^3)^2\eta_o^2\langle[\Omega_y(t) + \frac{3}{2a}(\boldsymbol{\epsilon} : \boldsymbol{v}_R^{(2a)}(t))_y]\,[\Omega_y(0) + \frac{3}{2a}(\boldsymbol{\epsilon} : \boldsymbol{v}_R^{(2a)}(0))_y]\rangle \tag{8.7}$$

or alternatively,

$$\langle \Pi_{p,y}^{(a)}(t)\Pi_{p,y}^{(a)}(0)\rangle = (4\pi a^3)^2\frac{\eta_o^2}{\xi_r^2}(2K_aV_m)^2\langle((\hat{n}\times\hat{H})_y(\hat{n}\cdot\hat{H}))(t)((\hat{n}\times\hat{H})_y(\hat{n}\cdot\hat{H}))(0)\rangle, \tag{8.8}$$

where use has been made of Eq. (7.5), with $\vec{\omega}_o = 0$.

The rotational viscosity can be finally expressed as

$$\eta_r = \frac{3}{2}\phi\eta_o D_r 4\sigma^2\int_0^\infty dt\langle(\hat{n}_x\hat{n}_z)(t)(\hat{n}_x\hat{n}_z)(0)\rangle, \tag{8.9}$$

where $\sigma = \frac{K_aV_m}{k_BT}$ is the anisotropy parameter comparing anisotropy and thermal energies, and we have taken the magnetic field pointing towards the z-direction.

In order to perform the integral in (8.9) we have to know the correlation function. For this reason, our starting point will be the Smoluchowski equation, which in the absence of vorticity is given by

$$\frac{\partial\psi}{\partial t} = -\vec{\mathcal{R}}\cdot[2D_r\sigma(\hat{n}\times\hat{H})(\hat{n}\cdot\hat{H})\psi] + D_r\vec{\mathcal{R}}\cdot\vec{\mathcal{R}}\psi, \tag{8.10}$$

where $D_r = \frac{k_BT}{\xi_r}$ is the rotational diffusion coefficient. From this equation, we can derive the evolution equations for the moments. In fact, these equations result from (8.10) after multiplying it by the corresponding tensor and integrating over all possible orientations. As an example, for the second-order moment we obtain

$$\frac{\partial\langle\hat{n}\hat{n}\rangle}{\partial t} = 2D_r[\mathcal{I} - 3\langle\hat{n}\hat{n}\rangle + \sigma\hat{H}\hat{H}\cdot\langle\hat{n}\hat{n}\rangle + \sigma\langle\hat{n}\hat{n}\rangle\cdot\hat{H}\hat{H} - 2\sigma\hat{H}\cdot\langle\hat{n}\hat{n}\hat{n}\hat{n}\rangle\cdot\hat{H}]. \quad (8.11)$$

Note that from (8.10) one obtains a hierarchy of equations for the moments. In particular, Eq. (8.11) clearly shows that the equation for the second moment involves the fourth-order moment. To arrive at an explicit solution we have to introduce decoupling approximations.

In the same way, we can formulate the evolution equation for the correlation $\langle(\hat{n}_x\hat{n}_z)(t)(\hat{n}_x\hat{n}_z)(0)\rangle$ appearing in the expression for the rotational viscosity,

$$\frac{\partial\langle(\hat{n}_x\hat{n}_z)(t)(\hat{n}_x\hat{n}_z)(0)\rangle}{\partial t} = 2D_r[-3\langle(\hat{n}_x\hat{n}_z)(t)(\hat{n}_x\hat{n}_z)(0)\rangle + \sigma\langle(\hat{n}_x\hat{n}_z)(t)(\hat{n}_x\hat{n}_z)(0)\rangle - 2\sigma\langle(\hat{n}_z^2\hat{n}_x\hat{n}_z)(t)(\hat{n}_x\hat{n}_z)(0)\rangle]. \quad (8.12)$$

The right hand side of this expression contains a correlation of higher order. In order to render it solvable, we will introduce the following decoupling approximation

$$\langle(\hat{n}_z^3\hat{n}_x)(t)(\hat{n}_x\hat{n}_z)(0)\rangle \simeq \frac{\langle\hat{n}_z^4(t)\rangle}{\langle\hat{n}_z^2(t)\rangle}\langle(\hat{n}_x\hat{n}_z)(t)(\hat{n}_x\hat{n}_z)(0)\rangle, \quad (8.13)$$

which may be justified since the magnetic field is taken high enough to decouple the fluctuation dynamics of $\hat{n}_z$ from the remaining components. As we indicated in the previous part, we decouple the quantities which vanish at equilibrium, when averaged, and those which are different from zero. Moreover, when performing the decouplings we have to keep in mind the invariance under reflections of the easy axis of magnetization, $\hat{n}$, so that we cannot truncate $\langle\hat{n}\ldots\hat{n}\rangle$ into odd powers of $\hat{n}$. There are different ways of proceeding, but the most convenient in this case is that of Eq. (8.13), because $\langle(\hat{n}_z^3\hat{n}_x)\rangle_{eq} = 0$, and $\langle\hat{n}_z^4\rangle_{eq} \neq 0$, $\langle\hat{n}_z^2\rangle_{eq} \neq 0$, whereas $\langle(\hat{n}_z\hat{n}_x)\rangle_{eq} = 0$. After perturbing the system, we will assume that these quantities remain uncorrelated. With the factor $\langle\hat{n}_z^4\rangle/\langle\hat{n}_z^2\rangle$ we smooth any unexpected behavior due to the approximation. Furthermore, in the linear regime, we approximate $\langle\hat{n}_z^4(t)\rangle/\langle\hat{n}_z^2(t)\rangle$ by $\langle\hat{n}_z^4(0)\rangle/\langle\hat{n}_z^2(0)\rangle$ that can be computed by means of the equilibrium function

$$\psi_{eq} = \frac{1}{2\pi\sqrt{\frac{\pi}{\sigma}}Erfi(\sqrt{\sigma})}\exp(\sigma(\hat{n}\cdot\hat{H})^2). \quad (8.14)$$

since we have assumed that the system is initially at equilibrium. In Eq.(8.14), we have introduced the imaginary error function $Erfi(\sqrt{\sigma})$

$$Erfi(\sqrt{\sigma}) = 2\sqrt{\frac{\sigma}{\pi}}\int_0^1 dx\exp(\sigma x^2). \quad (8.15)$$

Using this approximation we then arrive at

$$\frac{\partial\langle(\hat{n}_x\hat{n}_z)(t)(\hat{n}_x\hat{n}_z)(0)\rangle}{\partial t} = -2D_r[3 + 2\sigma\frac{\langle\hat{n}_x^4(0)\rangle}{\langle\hat{n}_x^2(0)\rangle} - \sigma]\langle(\hat{n}_x\hat{n}_z)(t)(\hat{n}_x\hat{n}_z)(0)\rangle, \quad (8.16)$$

whose solution is

$$\langle(\hat{n}_x\hat{n}_z)(t)(\hat{n}_x\hat{n}_z)(0)\rangle = \langle(\hat{n}_x\hat{n}_z)(0)(\hat{n}_x\hat{n}_z)(0)\rangle \exp(-\frac{t}{\tau}). \quad (8.17)$$

Here we have introduced the relaxation time τ,

$$\tau \equiv (2D_r)^{-1}\left(\sigma + \frac{1}{Q(\sigma)}\right)^{-1}, \quad (8.18)$$

with the function $Q(\sigma)$ defined as follows

$$Q(\sigma) \equiv \langle\hat{n}_z^2(0)\rangle = \frac{1}{2\sigma}[\frac{2e^{\sigma}}{\sqrt{\frac{\pi}{\sigma}}Erfi(\sqrt{\sigma})} - 1]. \quad (8.19)$$

which has been computed using the equilibrium probability distribution (8.14).

The rotational viscosity then follows from the Green-Kubo formula (8.9). Performing the integral, one arrives at

$$\eta_r = 6\phi\eta_o\sigma^2 D_r\tau\langle(\hat{n}_x\hat{n}_z)(0)(\hat{n}_x\hat{n}_z)(0)\rangle, \quad (8.20)$$

with

$$\langle(\hat{n}_x\hat{n}_z)(0)(\hat{n}_x\hat{n}_z)(0)\rangle = \frac{[3Q(\sigma) - 1]}{4\sigma}. \quad (8.21)$$

The combination of (8.20) and (8.21) then leads to

$$\eta_r = \frac{3}{2}\phi\eta_o\frac{\sigma}{2}\frac{(3Q(\sigma) - 1)}{\left(\sigma + \frac{1}{Q(\sigma)}\right)} \equiv \frac{3}{2}\phi\eta_o F(\sigma). \quad (8.22)$$

In Fig. I.4 we have plotted the reduced rotational viscosity η_r/η_s, with $\eta_s = \frac{3}{2}\eta_o\phi$, as a function of the parameter σ. For the case of a planar Couette flow, where the applied magnetic field is chosen perpendicular to the vorticity, the rotational viscosity and the effective viscosity, η_{eff}, are related through the expression

$$\eta_{eff} = \eta + \eta_r. \quad (8.23)$$

Consequently, this quantity gives the increase of the viscosity of the suspension due to the action of the external field. Our results are similar to the ones obtained in

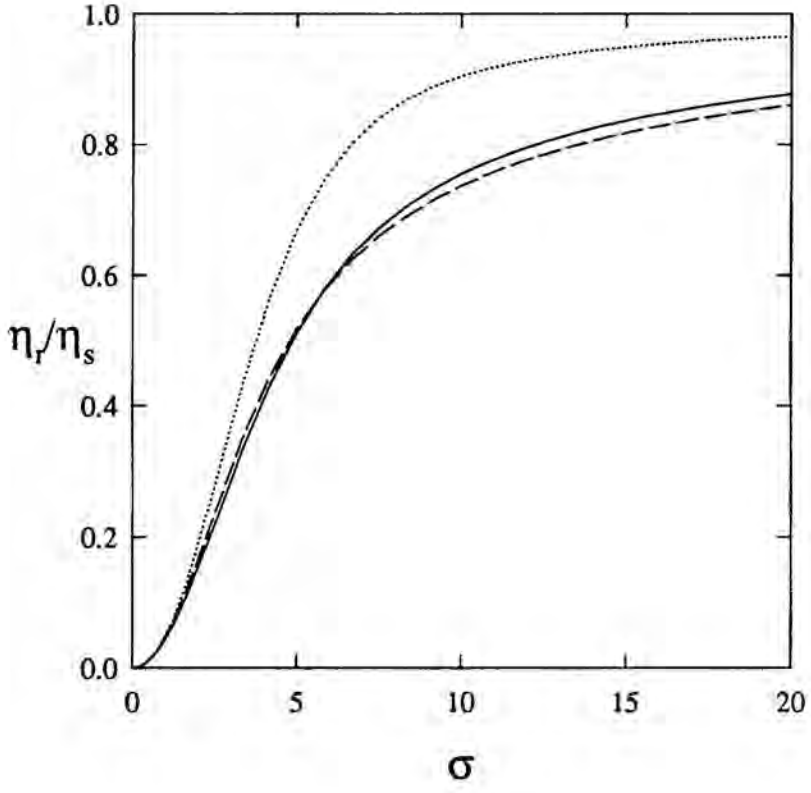

Figure I.4: The quantity η_r/η_s versus the anisotropy parameter σ. The solid line corresponds to our result given in Eq. (8.22), the dashed line comes from the phenomenological theory proposed in Ref. [18], whereas the dotted line is obtained from the solution of the Smoluchowski equation given in the same reference.

Ref. [18] using a phenomenological approach, based on the formulation of a relaxation equation for the internal angular momentum of the system in a continuum description. However, we have observed again some discrepancies in our results with respect to the ones obtained by those authors from an approximated solution of the Smoluchowski equation [18], especially for intermediate values of the anisotropy parameter.

9 Conclusions

By means of the formalism developed in the previous part, we have presented in this part a calculation of the rotational viscosity based on the Green-Kubo formula for this transport coefficient. Our results show that the viscosity increases when increasing the anisotropy parameter and reaches a saturation limit. We have compared our curve with the ones obtained in Ref.[18]. Their result coming from a solution of the stationary Smoluchowski equation overestimates ours, whereas the one based on a phenomenological relaxation equation they propose for the internal angular momentum of the suspension, is closer to ours. It would be interesting to gather experimental data in order to decide which of the three approaches is the most convincing.

We have also computed the rotational viscosity by means of the rheological equation of state proposed by Kirkwood, giving the pressure tensor in terms of the hydrodynamic force exerted by the fluid on the magnetic particle. The average of the pressure tensor has been calculated from the stationary solution of the Smoluchowski equation

$$\frac{\partial \psi}{\partial t} = -\vec{\mathcal{R}} \cdot [2D_r \sigma(\hat{n} \times \hat{H})(\hat{n} \cdot \hat{H})\psi + \vec{\omega}_o \psi] + D_r \vec{\mathcal{R}} \cdot \vec{\mathcal{R}} \psi, \tag{9.1}$$

which now contains a contribution due to the vorticity of the flow. Following the steps indicated in [7] we get the same result (8.22).

In the same way, we could solve the more general case in which both, the relaxation of the magnetic moment towards the field and towards the easy axis of magnetization, take place. Some related theoretical results have been obtained in [1] and it will be the subject of the following chapter.

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CHAPTER II

GENERAL DYNAMICS

In the previous chapter we have analyzed the dynamics of a ferromagnetic particle and the transport coefficients of a dilute suspension constituted by them in two limiting cases, namely, a suspension of rigid dipoles and a suspension of a soft magnetic material under the influence of a high magnetic field.

The main goal of this chapter is to provide a general theory covering the whole range of experimental situations. Indeed, different measurements carried out for magnetic liquids show that there is finite coupling between the orientation of the magnetic moment of a ferromagnetic monodomain and the orientation of the particle itself (characterized by the orientation of its crystalline axes). Because of this coupling, the relaxation of the magnetic moments takes place in two different ways that proceed simultaneously: rotation within the particle and together with the particle with respect to the carrier liquid. Both processes are of rotational diffusion type. Thus, for all practical purposes, the Smoluchowski equation, describing the evolution of the probability density for the directions of both the magnetic moment and the axis of easy magnetization of the particles, has been used. In particular, we compute the rotational viscosity from a Green-Kubo formula and give an expression for different relaxation times. These characteristic times come from the dynamic equations for the correlation functions which, in the linear response theory framework, are involved in the calculation of some of the material's physical properties we are interested in (optical, magnetic, ...). Our results agree quite well with experiments performed with different samples of ferromagnetic particles, which permit to distinguish the different relaxation regimes occurring when the size and the nature of the magnetic material of the grains are freely modified.

1 Introduction

Systems of single-domain ferromagnetic particles immersed in a solid or liquid phase exhibit a number of interesting relaxation phenomena which have been the subject matter of many experimental and theoretical analyses [1]-[4]. These phenomena are essential in the study of the dynamics of these particles, and, particularly, have a clear influence when determining the effective viscosity, the dynamic birefringence, and the magnetic susceptibility. One of the main peculiarities of these systems is that their properties are greatly influenced by the presence of an external magnetic field. It is precisely this fact which has been the basis of many practical applications [1].

The rotational dynamics of a ferromagnetic particle embedded in a liquid phase is the result of the competition of three orientational mechanisms related to the external field, the axis of easy magnetization, and rotational Brownian motion. That is, whereas the magnetic moment of the ferromagnetic particle relaxes towards the direction of the magnetic field, the axis of easy magnetization tends to be aligned with the magnetic moment, thus giving rise to different coupled relaxation phenomena. Until recently, the most frequent case that has been studied in the literature deals with rigid-dipoles [4]-[6], for which the anisotropy energy is dominant due to the large value of the anisotropy constant, and because the radius of the particle usually exceeds a critical value. What is more, when looking to the relaxation phenomena described by a rigid dipole, one disregards the precessional motion of the magnetic moment, and, consequently, the associated dissipation. Under these conditions, we cannot talk about the relaxation of the axis of easy magnetization towards the magnetic moment any longer, instead both vectors relax together. However, there are materials for which the anisotropy energy may be comparable to the energy associated with the interaction with the magnetic field, or even smaller. Therefore, a general theory encompassing such a wide variety of situations and accounting for experimental results should be developed. The presence of different relaxation mechanisms has implications in the form of the effective viscosity of the system, which exhibits significant corrections when compared to the viscosity of a suspension of non-magnetic particles of the same shape. Another point of interest is the appearance of relaxation times which are usually involved in the characterization of certain physical properties, and which are suitable for being measured by means of different experimental techniques.

The purpose of this chapter is to present a theory capable of giving expressions for the relevant transport coefficients of the system and of the corresponding characteristic relaxation times determining for instance, the effective viscosity, the dynamic

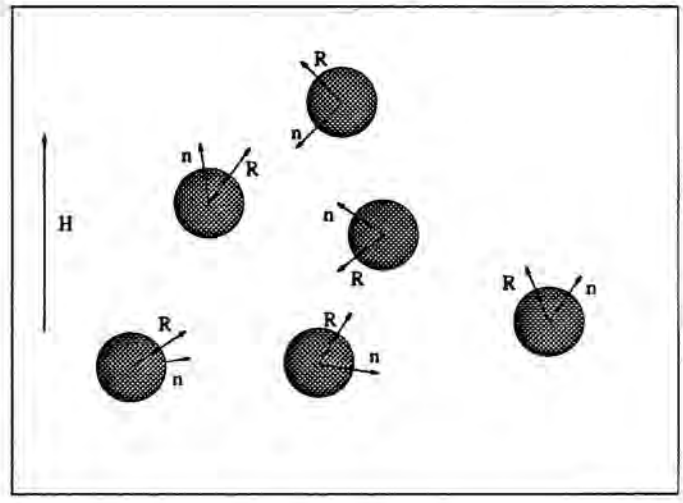

Figure II.1: The magnetic moments are oriented along an intermediate direction between that of the magnetic field and the easy axis of magnetization when both the anisotropy energy and the magnetic energy of interaction with the field are comparable. The relaxation of these two degrees of freedom is coupled.

birefringence, and the magnetic susceptibility of the suspension. We will focus on the general situation in which the magnetic and anisotropy energies of the particles may have arbitrary values. The formalism we have developed is based on the linear response theory where the correlation dynamics comes from a Smoluchowski equation. As we will show in one of the sections, our result for the relaxation time of the rotation of the particle is compared to experimental data and agrees quite well with birefringence experiments.

We have distributed the chapter in the following way: in Section 2, we establish basic equations describing the dynamics of the degrees of freedom. Of particular interest is the Smoluchowski equation for the probability density which is given in a general case for unspecified values of the magnetic and anisotropy energies. There are different ways of deriving such equation. Although we will not go through this question, the equation we propose can be compared to another one obtained previously from a different theoretical method. In Section 3, we deal with the calculation of the rotational viscosity using a Green-Kubo equation proposed from the linear response theory. This method leads to an expression for this transport coefficient which is studied in particular situations of interest. Section 4 is devoted to the calculation of the relaxation times of the particles and the transversal component of the magnetization

when considering the different orientational mechanisms. We have compared our results to experiments done for two samples of very common ferromagnetic particles for which the size and the nature of the magnetic material clearly establish different values of the magnetic energy and the energy of anisotropy, obtaining a good agreement in both situations. Finally, in the last section we summarize our main results.

2 Coupled dynamics of the degrees of freedom

The energy of a spherical single-domain ferromagnetic particle under the action of an external magnetic field is the sum of two contributions. These contributions originate from the externally imposed magnetic field and the presence of an axis of easy magnetization (for uniaxial crystals). Its expression is given by

$$U = -\vec{m} \cdot \vec{H} - K_a V_m (\hat{n} \cdot \hat{R})^2, \tag{2.1}$$

where $\vec{m} = m\hat{R}$ is the magnetic moment of the particles, $\vec{H}$ is the external magnetic field, K_a is the first anisotropy constant (assumed positive), V_m is the magnetic volume of one of these spheres, and $\hat{n}$ is the unit vector along the direction of the axis of easy magnetization for uniaxial magnetic crystals. It is clear from Eq. (2.1) that in the general case where both contributions may take arbitrary values, the relaxation mechanisms of the degrees of freedom, $\hat{R}$ and $\hat{n}$, of the ferromagnetic spheres in suspension are coupled.

The deterministic dynamics of $\hat{R}$ is governed by the Landau-Gilbert equation [7], proposed to study the relaxation of the magnetic moments of magnetic particles embedded in a solid matrix

$$\frac{d\hat{R}}{dt} = -\frac{\gamma_o}{m}\frac{\partial U}{\partial \hat{R}} \times \hat{R} - \alpha \frac{d\hat{R}}{dt} \times \hat{R}. \tag{2.2}$$

From this equation, one may identify the two mechanisms responsible for the variation of $\hat{R}$: the effective field $\vec{H}_{eff} \propto -\frac{\partial U}{\partial \hat{R}}$, which causes a Larmor precessional motion of $\hat{R}$, and the mean field, $\vec{H}_d \propto -\frac{d\hat{R}}{dt}$, which introduces a damping due to the collisions of the electrons determining the magnetic moment of the domain in a metal, or in a semiconductor, due to magnetoelastic interactions. In Eq. (2.2), γ_o is the gyromagnetic ratio for an electron, and the quantity α plays the role of a damping coefficient.

The Landau-Gilbert equation can be rewritten such that

$$\frac{d\hat{R}}{dt} = -h\hat{R} \times \frac{\partial U}{\partial \hat{R}} \times \hat{R} + \vec{\omega}_L \times \hat{R}, \tag{2.3}$$

with $\vec{\omega}_L = g\vec{H}_{eff}$ as the Larmor frequency of the precessional motion, and where $g \equiv \gamma_o(1+\alpha^2)^{-1}$ and $h \equiv \frac{\alpha\gamma_o}{m_o}(1+\alpha^2)^{-1}$ [2]. This equation is valid in a stationary frame of reference. If the ferromagnetic particle is rotating itself with the angular velocity $\vec{\Omega}$, we must modify Eq.(2.3) by adding on its right hand side the corresponding contribution coming from the rotation. One then has

$$\frac{d\hat{R}}{dt} = -h\left(\hat{R} \times \frac{\partial U}{\partial \hat{R}}\right) \times \hat{R} + (\vec{\omega}_L + \vec{\Omega}) \times \hat{R}. \tag{2.4}$$

Furthermore, the dynamics of $\hat{n}$ follows from the kinematic relation

$$\frac{d\hat{n}}{dt} = \vec{\Omega} \times \hat{n}. \tag{2.5}$$

This expression can be rewritten as

$$\frac{d\hat{n}}{dt} = [\vec{\omega}_o + \frac{1}{\xi_r}\vec{m} \times \vec{H}] \times \hat{n}, \tag{2.6}$$

with $\xi_r = 8\pi\eta_o a^3$ being the rotational friction coefficient of the particles; η_o is the viscosity of the carrier fluid, a is the hydrodynamic radius of the particles, and $\vec{\omega}_o$ the vorticity of the carrier fluid. One arrives at this expression after using the deterministic part of the balance equation for the total angular momentum

$$I\frac{d\vec{\Omega}}{dt} + \gamma_o^{-1}\frac{d\vec{m}}{dt} = -\xi_r(\vec{\Omega} - \vec{\omega}_o) + \vec{m} \times \vec{H} + \vec{T}^B, \tag{2.7}$$

provided that we neglect the term accounting for the inertial effects and the term coming from the angular momentum of the electrons determining the magnetic moment of the particles. Here $\vec{T}^B$ is the Brownian torque acting on the particle [8].

The evolution of the probability density, $\psi(\gamma, t)$, with $\gamma \equiv (\hat{R}, \hat{n})$, is governed by the Smoluchowski equation. When $\vec{\Omega} = 0$, which corresponds to the case of particles embedded in a solid matrix, the Smoluchowski equation was deduced by Brown [9] from the Landau-Gilbert equation. In these last conditions, and in order to preserve the total angular momentum conservation, the small magnetic particle should be embedded in a large rigid solid matrix. Otherwise, there will appear an elastic twist in the matrix, and one should take into account the corresponding elastic torque in the equation for the total angular momentum of the particle. The manner in which Brown expressed his intuitive method of deriving the Smoluchowski equation was to consider

the effect of thermal fluctuations on the probability density. Brown suggested that thermal agitation causes ψ to become more uniform so that, in an equation describing its time evolution, thermal agitation gives rise to a diffusion term in ψ. Shliomis and co-workers [10] obtained this equation for a suspension of rigid dipoles. If we define the dimensionless parameters $\mu = \frac{mH}{k_BT}$ and $\sigma = \frac{K_a V_m}{k_BT}$, comparing magnetic and anisotropy energies to thermal energy, respectively, this last situation corresponds to the limit $\sigma \gg \mu$. Rhaiker and Shliomis [11] also proposed the Smoluchowski equation for the opposite limit $\sigma \ll \mu$, in which the dipoles are rapidly oriented towards the field direction. As regards the general case for arbitrary values of the ratio μ/σ, Shliomis and co-workers also deduced the appropriate Smoluchowski equation from a model similar to the itinerant oscillator model, [12]-[14]. In such a general situation, the Smoluchowski equation can also be obtained from the continuity equation in the space spanned by the degrees of freedom $\gamma \equiv (\hat{R}, \hat{n})$

$$\frac{\partial \psi(\gamma, t)}{\partial t} = -\frac{\partial}{\partial \gamma} \cdot (\boldsymbol{J}(\gamma, t) + \psi(\gamma, t)\dot{\gamma}), \tag{2.8}$$

where $\dot{\gamma} \equiv d\gamma/dt$ and the current $\boldsymbol{J}(\gamma, t)$ is given by the Fick's law

$$J(\gamma, t) = -\boldsymbol{D} \cdot \frac{\partial \psi(\gamma, t)}{\partial \gamma}, \tag{2.9}$$

with $\boldsymbol{D}$ being a diffusion matrix.

Combining (2.8) and (2.9) we then arrive at

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial \gamma} \cdot (\boldsymbol{D} \cdot \frac{\partial}{\partial \gamma}\psi - \psi\dot{\gamma}). \tag{2.10}$$

The diffusion matrix is related to the mobility matrix $\boldsymbol{b}$ through the Einstein relation, $\boldsymbol{D} = k_BT\boldsymbol{b}$. After inserting eqs. (2.4) and (2.6) into (2.10), we can rewrite Eq. (2.10) in the form

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial \gamma} \cdot (\boldsymbol{D} \cdot \frac{\partial}{\partial \gamma}\psi - \psi\boldsymbol{b} \cdot \frac{\partial U}{\partial \gamma} - \psi\dot{\gamma}_{non-pot}), \tag{2.11}$$

where we have a contribution coming from a non-potential current $\dot{\gamma}_{non-pot}$, and the mobilities $\boldsymbol{b}$ are found to be (for more details see Appendix A)

$$\begin{aligned} \boldsymbol{b}_{nn} &\equiv \frac{1}{\xi_r}(\boldsymbol{I} - \hat{n}\hat{n}), \\ \boldsymbol{b}_{RR} &\equiv (h + \frac{1}{\xi_r})(\boldsymbol{I} - \hat{R}\hat{R}), \\ \boldsymbol{b}_{nR} &= \boldsymbol{b}_{Rn}^T \equiv \frac{1}{\xi_r}[(\hat{n} \cdot \hat{R})\boldsymbol{I} - \hat{n}\hat{R}]. \end{aligned} \tag{2.12}$$

Here the symbol ^{T} stands for transposition. These expressions can be employed in Eq.(2.11). After some mathematical transformations (see detailed calculations in Appendix A), one then arrives at the Smoluchowski equation

$$\begin{aligned}\frac{\partial \psi}{\partial t} &= D_r(\vec{\mathcal{R}}_{\hat{R}} + \vec{\mathcal{R}}_{\hat{n}}) \cdot [\psi(\vec{\mathcal{R}}_{\hat{R}} + \vec{\mathcal{R}}_{\hat{n}})\frac{U}{k_B T} + (\vec{\mathcal{R}}_{\hat{R}} + \vec{\mathcal{R}}_{\hat{n}})\psi] \\ &+ D_m \vec{\mathcal{R}}_{\hat{R}} \cdot \{\psi \vec{\mathcal{R}}_{\hat{R}} \frac{U}{k_B T} + \vec{\mathcal{R}}_{\hat{R}}\psi\} - \vec{\mathcal{R}}_{\hat{R}} \cdot (\vec{\omega}_L \psi) \\ &- (\vec{\mathcal{R}}_{\hat{R}} + \vec{\mathcal{R}}_{\hat{n}}) \cdot (\vec{\omega}_o \psi), \end{aligned} \tag{2.13}$$

where $\vec{\mathcal{R}}_{\hat{n}} \equiv \hat{n} \times \frac{\partial}{\partial \hat{n}}$ and $\vec{\mathcal{R}}_{\hat{R}} \equiv \hat{R} \times \frac{\partial}{\partial \hat{R}}$ are rotational operators, $D_r \equiv \frac{k_B T}{\xi_r}$ is the Brownian rotational diffusion coefficient, and $D_m \equiv k_B T h$ can be interpreted as the diffusion coefficient of the magnetic moment inside the particles. These diffusion coefficients are related to two relaxation times involved in the Smoluchowski equation, namely $\tau_D = (2D_m)^{-1}$ related to the chaotic reorientations of $\vec{m}$ inside the particle due to thermal fluctuations, and the Brownian time $\tau_B = (2D_r)^{-1}$. The Smoluchowski equation (2.13) agrees with the corresponding one obtained in Ref. [12] by using a model similar to the itinerant oscillator model and will be used in our subsequent analysis.

3 Green-Kubo formula for the rotational viscosity

In this section, we we will focus on the determination of the rotational viscosity from the corresponding Green-Kubo formula. This formula gives this transport coefficient in terms of the correlation function of the axial vector, $\vec{\Pi}_p^{(a)}$, related to the antisymmetric part of the contribution of the particles to the pressure tensor [8],

$$\eta_r = \frac{1}{V k_B T} \int_0^\infty dt \langle \Pi_{p,y}^{(a)}(t) \Pi_{p,y}^{(a)}(0) \rangle \tag{3.1}$$

where V is the volume of the system.

In Ref. [8], we obtained a relationship between the particle contribution to the pressure tensor, $\bar{\bar{\Pi}}_p$, and the external torque experienced by the particle during its motion. As a result, if we consider the magnetic field pointing towards the z-direction, it is found that the rotational viscosity can be finally rewritten as

$$\eta_r = \frac{3}{2}\phi \eta_o D_r \mu^2 \int_0^\infty dt \langle R_x(t) R_x(0) \rangle, \tag{3.2}$$

with $\phi = \frac{4/3\pi a^3}{V}$ being the volume fraction of particles.

To proceed further, we need to know the expression for the correlation function appearing in Eq. (3.2). This correlation function follows from the general prescription

$$\langle R_x(t)R_x(0)\rangle = \int d\hat{R}d\hat{R}'d\hat{n}d\hat{n}' R_x R_x' \psi(\hat{R},\hat{n},t;\hat{R}',\hat{n}',0), \tag{3.3}$$

with $\psi(\hat{R},\hat{n},t;\hat{R}',\hat{n}',0)$ being the joint probability, which, in the most general case, is a function of both the magnetic moment orientation, $\hat{R}$, and the particle orientation, $\hat{n}$. For a Markov process, this probability satisfies the same Smoluchowski equation as the one governing the evolution of the conditional probability. From the Smoluchowski equation (2.13) we then obtain the evolution equation for the correlation $\langle R_x(t)R_x(0)\rangle$,

$$\begin{aligned}\frac{1}{D_r}\frac{d}{dt}\langle R_x(t)R_x(0)\rangle &= (1+\frac{D_m}{D_r})\{-2\langle R_x(t)R_x(0)\rangle - \mu\langle (R_xR_z)(t)R_x(0)\rangle\} \\ &+\frac{D_m}{D_r}2\sigma\{\langle (n_x(\hat{n}\cdot\hat{R}))(t)R_x(0)\rangle - \langle (R_x(\hat{n}\cdot\hat{R})^2)(t)R_x(0)\rangle\}.\end{aligned} \tag{3.4}$$

where for the sake of simplicity, we have used the shorthand notation $(...)(t)$ to indicate that each component of the unitary vectors $\hat{R}$ and $\hat{n}$ inside the brackets is a function of time. At this point, it is interesting to realize that the right hand side of Eq. (3.4) involves other unknown correlation functions, whose evolution equations also come from the Smoluchowski equation (2.13). Instead of a closed equation, we then obtain a hierarchy of differential equations for the correlation functions. To arrive at an explicit solution, we must introduce decoupling approximations, as is usually done when dealing with the dynamics of complex systems [27] or with stochastic processes [14]. In our problem, the underlying idea to carry out the different decouplings comes from the approximation of statistical independency of the fluctuation dynamics of the quantities which vanish at equilibrium, when averaged, and those which are different from zero. Another aspect that should be kept in mind when performing such decouplings, is the invariance under reflections of the easy axis of magnetization, $\hat{n}$, from which we cannot separate $\langle \hat{n}\ldots\hat{n}\rangle$ into odd powers of $\hat{n}$. As an example, the correlation $\langle (R_xR_z)(t)R_x(0)\rangle$ may be approximated by

$$\langle (R_xR_z)(t)R_x(0)\rangle \sim \langle R_x(t)R_x(0)\rangle\langle R_z\rangle_{eq}. \tag{3.5}$$

This approximation may be justified from the fact that in equilibrium both quantities are not correlated, $\langle (R_xR_z)\rangle_{eq} = 0$; moreover, $\langle R_z\rangle_{eq} \neq 0$, whereas $\langle R_x\rangle_{eq} = 0$. After perturbing the system we will assume that these quantities remain uncorrelated. Furthermore, linearization in time has been taken into account and consequently

$\langle R_z(t)\rangle \sim \langle R_z\rangle_{eq}$ is approximated to its equilibrium value for small perturbations. In Appendix B, we indicate all of these decouplings, as well as the appropriate linearizations.

The quantity $\langle (n_x(\hat{n}\cdot\hat{R}))(t)R_x(0)\rangle$, appearing in Eq.(3.4), cannot be directly decoupled and, therefore, must be studied separately. Its corresponding evolution equation can also be obtained from the Smoluchowski equation (2.13). One has

$$\begin{aligned}\frac{1}{D_r}\frac{d}{dt}\langle (n_x(\hat{n}\cdot\hat{R}))(t)R_x(0)\rangle &= -\mu\langle (R_x(n_z(\hat{n}\cdot\hat{R})))(t)R_x(0)\rangle - 2\langle (n_x(\hat{n}\cdot\hat{R}))(t)R_x(0)\rangle \\ &+\frac{D_m}{D_r}\{\mu\langle (n_xn_z)(t)R_x(0)\rangle - \mu\langle (n_x(R_z(\hat{n}\cdot\hat{R})))(t)R_x(0)\rangle \\ &-2\langle (n_x(\hat{n}\cdot\hat{R}))(t)R_x(0)\rangle + 2\sigma\langle (n_x(\hat{n}\cdot\hat{R})(1-(\hat{n}\cdot\hat{R})^2))(t)R_x(0)\rangle\}. \qquad (3.6)\end{aligned}$$

Following the same line of reasoning, we decouple some of the quantities appearing in this equation. However, the correlation $\langle (n_xn_z)(t)R_x(0)\rangle$ cannot be approximated in the same way as we have done with the other quantities. Thus, we must also consider its dynamic equation

$$\begin{aligned}\frac{1}{D_r}\frac{d}{dt}\langle (n_xn_z)(t)R_x(0)\rangle &= \mu\langle (n_x(\hat{n}\cdot\hat{R}))(t)R_x(0)\rangle - \mu\langle (n_z^2R_x)(t)R_x(0)\rangle \\ &-\mu\langle (n_xn_zR_z)(t)R_x(0)\rangle - 6\langle (n_xn_z)(t)R_x(0)\rangle, \qquad (3.7)\end{aligned}$$

whose correlations can be decoupled as indicated in Appendix B.

The procedure that has been followed enables us to write a closed system of just three differential equations for the correlation functions $\langle R_x(t)R_x(0)\rangle$, $\langle (n_x(\hat{n}\cdot\hat{R}))(t)R_x(0)\rangle$, and $\langle (n_xn_z)(t)R_x(0)\rangle$. These are the only independent quantities in our approximation to the problem. After Laplace transforming, we can write the set of differential equations (3.4), (3.6) and (3.7) in the following way:

$$\mathcal{A}\cdot\vec{\mathcal{R}} = D_r^{-1}\vec{\mathcal{R}}^o \qquad (3.8)$$

where the components of the vector $\vec{\mathcal{R}} = (\mathcal{R}_1, \mathcal{R}_2, \mathcal{R}_3)$ are the three Laplace transforms of $\langle R_x(t)R_x(0)\rangle$, $\langle (n_x(\hat{n}\cdot\hat{R}))(t)R_x(0)\rangle$, and $\langle (n_xn_z)(t)R_x(0)\rangle$, respectively. $\vec{\mathcal{R}}^o = (\mathcal{R}_1^o, \mathcal{R}_2^o, \mathcal{R}_3^o)$ is a vector whose components are the initial values of these correlation functions

$$\mathcal{R}_1^o \equiv \langle R_x^2(0)\rangle = \frac{\mathcal{L}(\mu)}{\mu}, \qquad (3.9)$$

$$\mathcal{R}_2^o \equiv \langle (n_x R_x(\hat{n}\cdot\hat{R}))(0)\rangle = \frac{\mathcal{L}(\mu)}{\mu} Q(\sigma), \tag{3.10}$$

$$\mathcal{R}_3^o \equiv \langle (n_x R_x n_z)(0)\rangle = \frac{1}{2\mu}(1 - 3\frac{\mathcal{L}(\mu)}{\mu})(3Q(\sigma) - 1), \tag{3.11}$$

where $\mathcal{L}(\mu) = \coth\mu - \frac{1}{\mu}$ is the Langevin function and $Q(\sigma) = \frac{1}{2\sigma}(\frac{2e^{\sigma}}{\sqrt{\frac{\pi}{\sigma}}Erfi(\sqrt{\sigma})} - 1)$. These initial values are determined after averaging with the equilibrium distribution function

$$\Psi_{eq} = \frac{1}{8\pi^{5/2}\frac{\sinh\mu}{\mu}\frac{Erfi(\sqrt{\sigma})}{\sqrt{\sigma}}} \exp[\mu(\hat{R}\cdot\hat{H}) + \sigma(\hat{n}\cdot\hat{R})^2]. \tag{3.12}$$

The matrix $\mathcal{A} \equiv (A_{ij})$, $(i,j = 1,2,3)$, is found to be

$$\begin{pmatrix} \frac{s}{D_r} + 2 + \mu\mathcal{L}(\mu) + & -2\frac{D_m}{D_r}\sigma & 0 \\ +\frac{D_m}{D_r}[2 + \mu\mathcal{L}(\mu) + 2\sigma Q(\sigma)] & & \\ \mu\mathcal{L}(\mu)Q(\sigma) & \frac{s}{D_r} + 2 + & -\frac{D_m}{D_r}\mu \\ & +\frac{D_m}{D_r}(\mu\mathcal{L}(\mu) + \frac{1}{Q(\sigma)} - 1) & \\ \mathcal{L}(\mu)(1 - 3Q(\sigma)) + \mu Q(\sigma) & -\mu & \frac{s}{D_r} + 6 + \mu\mathcal{L}(\mu) \end{pmatrix} \tag{3.13}$$

whose diagonal elements characterize the decay of each correlation function in the absence of coupled dynamics, and whose nondiagonal elements describe the coupling between the relaxation dynamics of such correlations.

The Laplace transform $\mathcal{R}_1(s)$ of the correlation $\langle R_x(t)R_x(0)\rangle$ is defined as

$$\mathcal{R}_1(s) = \int_0^{\infty} dt e^{-st}\langle R_x(t)R_x(0)\rangle. \tag{3.14}$$

From Eq. (3.2), we then conclude that

$$\eta_r = \frac{3}{2}\phi\eta_o D_r\mu^2 \lim_{s\to 0}\mathcal{R}_1(s). \tag{3.15}$$

Consequently, after using Cramer's rule in Eq. (3.8) the rotational viscosity of the suspension is given by

$$\frac{\eta_r}{\eta_{sat}} = \mu^2 \lim_{s\to 0}\frac{(A_{22}A_{33} - A_{23}A_{32})\mathcal{R}_1^o - A_{12}A_{33}\mathcal{R}_2^o + A_{12}A_{23}\mathcal{R}_3^o}{|(A_{ij})|} \tag{3.16}$$

with $\eta_{sat} = 3/2\eta_o\phi$ as the saturation value of the rotational viscosity and $|(A_{ij})|$ the determinant of the matrix.

We have obtained an analytic expression for the rotational viscosity of a magnetic fluid in the general case where μ/σ may take arbitrary values and the orientation of the vectors $\hat{R}$ and $\hat{n}$ is random. The different terms in Eq. (3.16) are the matrix elements (A_{ij}) characterizing the coupled relaxation dynamics of the three independent correlation functions $\langle R_x(t)R_x(0)\rangle$, $\langle (n_x(\hat{n}\cdot\hat{R}))(t)R_x(0)\rangle$, and $\langle (n_x n_z)(t)R_x(0)\rangle$. Thus, the rotational viscosity depends on these three correlation functions due to their coupled dynamics and, as we expected, it is not only a function of the parameters μ and σ, but also of the ratio D_m/D_r. This last dependence comes from the fact that any departure of the magnetic moment of the particle from the equilibrium orientation is accompanied by a precession of the vector $\hat{R}$ with the corresponding dissipation of energy, as well as the dissipation due to the rotation of the particle in the viscous fluid. Previously, we have indicated that the parameter $D_m = k_B T h$ could be interpreted as a diffusion coefficient of the magnetic moment inside each particle. Thus, for a given value of the Brownian rotational diffusion coefficient D_r, the smaller the value of D_m the greater is the dissipation of energy and consequently the rotational viscosity increases. This is exactly what we observe in figures II.2 and II.3.

Moreover, from Eq. (3.16) we can rederive the rotational viscosity of a magnetic fluid consisting of what is commonly named rigid dipoles [6, 8, 10, 15], for which $\mu \ll \sigma$ and $D_m = 0$. It turns out to be

$$\frac{\eta_r}{\eta_{sat}} = \frac{\mu - \tanh\mu}{\mu + \tanh\mu} \tag{3.17}$$

In Ref. [8], we obtained this same result after performing one decoupling, following the same criteria, in a much simpler equation. But, exactly the same result was derived phenomenologically by Shliomis [15]. He compared this result to an experiment measuring the viscosity of the magnetic fluid [17]. The result reproduced these experimental data, and consequently this formula has been extensively used in the literature. Later on, Martsenyuk et al. [10] tried to solve this simple rigid-dipole case using the Smoluchowski equation formalism. They closed the infinite system of coupled equations with an effective-field approximation, and, although the result they obtained was close to Eq. (3.17), the phenomenological approach reproduced better the experiments. Based on this satisfactory result, we have solved this general situation with two degrees of freedom whose dynamics is coupled, following the same type of arguments. To our knowledge, there are no other theories providing an analytic expression for the viscosity, covering the whole range of values of the parameters μ

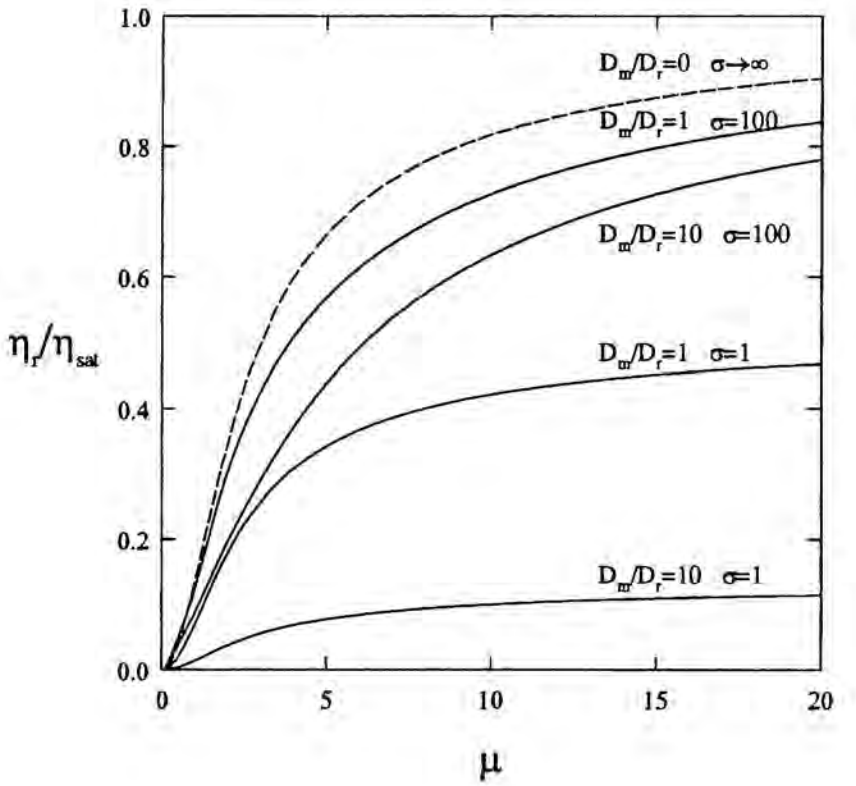

Figure II.2: Reduced rotational viscosity versus the parameter μ for different values of the ratio D_m/D_r and of the anisotropy parameter, as indicated in the plot. The dashed line corresponds to the rigid dipole limit.

and σ.

In figure II.2, we represent the rotational viscosity versus the parameter μ for the rigid dipole limit, and for different values of the parameters σ and D_m/D_r. At this point, it is interesting to discuss some limiting cases of Eq. (3.16) which have also been considered in the literature, specifically in Ref.[12]. For $\mu \ll 1$, Eq. (3.16) reduces to

$$\frac{\eta_r}{\eta_{sat}} = \frac{\mu^2}{6} F(\sigma), \tag{3.18}$$

where the function $F(\sigma)$ has been defined as follows

$$F(\sigma) \equiv \frac{1 + \frac{D_m}{2D_r}[(\frac{1}{Q(\sigma)} - 1) + 2\sigma Q(\sigma)]}{[1 + \frac{D_m}{D_r}(1 + \sigma Q(\sigma))][1 + \frac{D_m}{2D_r}(\frac{1}{Q(\sigma)} - 1)]}. \tag{3.19}$$

From expression (3.18), we conclude that for any value of the parameter σ, the rotational viscosity tends to zero as a second order power of the magnetic field strength. In particular, we can restrict ourselves to the cases where $\sigma \to 0$ and $\sigma \to \infty$. In these limits, we obtain

$$\frac{\eta_r}{\eta_{sat}} = \frac{\mu^2}{6} \frac{1}{(1 + \frac{D_m}{D_r})} \tag{3.20}$$

and

$$\frac{\eta_r}{\eta_{sat}} = \frac{\mu^2}{6}, \tag{3.21}$$

respectively. These values agree quite well with the corresponding expressions given in Ref.[12], and with the results collected in Refs.[8, 10], for the rigid dipole conditions ($\sigma \to \infty$).

In addition, from Fig. II.2, we observe that the initial slope of these curves depends on the ratio D_m/D_r, in such a way that the greater the ratio D_m/D_r the greater the value of μ until reaching the saturation limit corresponding to a given value of σ.

Regarding the limit $\mu \gg 1$, Eq. (3.16) can also be studied when $\sigma \to 0$ and $\sigma \to \infty$. We obtain

$$\frac{\eta_r}{\eta_{sat}} = \frac{1}{(1 + \frac{D_m}{D_r})} \tag{3.22}$$

and

$$\frac{\eta_r}{\eta_{sat}} = 1, \tag{3.23}$$

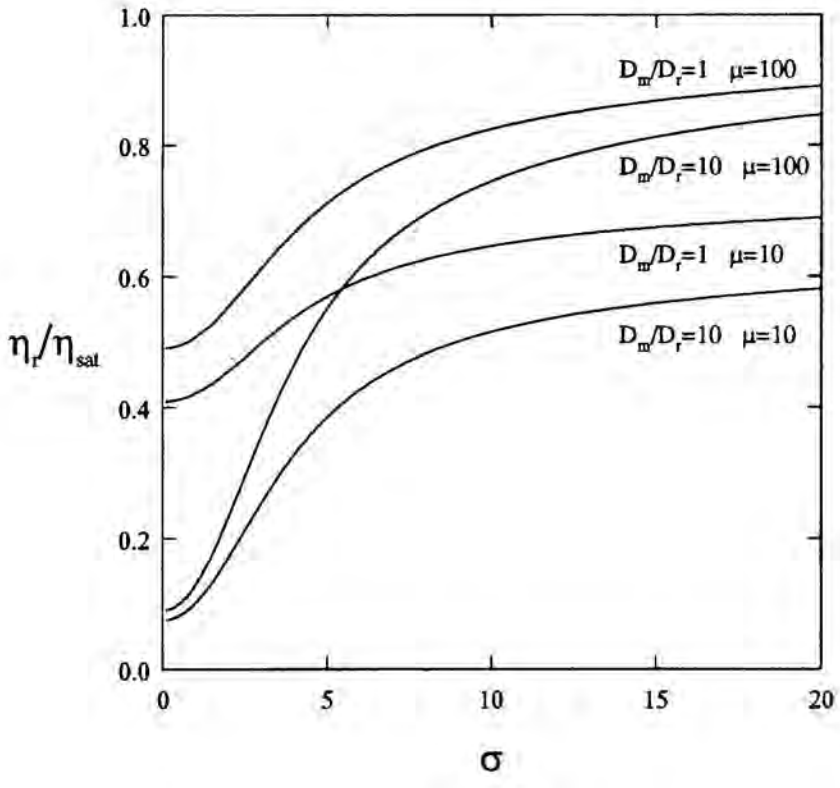

Figure II.3: Rotational viscosity versus the parameter σ for different values of the ratio D_m/D_r and of the parameter μ.

respectively, which also coincide with the results given in Ref.[12]. Even in this case, with $\mu \gg 1$, if σ takes moderate or small values, the rotational viscosity does not reach its saturation value any longer. In particular, if $\sigma \to 0$, this saturation value depends on the ratio D_m/D_r as we have pointed out in Eq. (3.22). That is, the dissipation not only depends on the solvent viscosity, but also on the damping constant α and the gyromagnetic factor γ_o. Additionally, the rotational viscosity increases with σ until it reaches its saturation value when $\sigma \to \infty$.

The behavior of η_r/η_s as a function of σ, and for different values of μ is depicted in Fig. II.3, from which we can corroborate the main features of our previous analysis. The ratio D_m/D_r has been obtained after considering the following values of the involved quantities: $\alpha \sim 10^{-2}$, $\gamma_o \sim 10^7 G^{-1}\, s^{-1}$, $M_s \sim 10^3 G$, $\eta_o \sim 10^{-2} \frac{g}{cm\ s}$ and the fact that the magnetic volume is almost the same as the hydrodynamic volume of the particles, with $a = 10^{-6} cm$.

An alternative procedure used to calculate the viscosity involves a rheological equation of state for the pressure tensor. In this way, it is also possible to obtain exactly the same expression for the rotational viscosity (3.16), but now in the presence of a linear vorticity field in stationary conditions.

4 Relaxation times. Comparison with experiments

4.1 Transient birefringence in crossed fields

The relaxation of the optical birefringence induced by magnetic grains dispersed in the analyzed medium, is among the simplest experimental tools available for rheological studies of viscoelastic solutions. A viscosimeter based on the determination of the relaxation of small magnetic particles in suspension in the studied medium turns the viscosity determination into an optical birefringence measurement with many advantages: *i*) it is a nondestructive method, *ii*) we just need to add a very small amount of particles ($\phi \sim 10^{-4}$), *iii*) it does not need any mechanical system, *iv*) the use of a laser beam for the birefringence measurement enables us the determination of the viscosity in the volume of a few mm^3. In addition, as the size of the magnetic probe is of the order of $100\mathring{A}$, the measured viscosity is a local quantity. The main limitation of the usual transient birefringence devices is the polydispersity of the magnetic particles. Usually, a log-normal distribution of spherical grain diameters, d, as the one given through the expression

$$P(d) = \frac{1}{\sqrt{2\pi}\sigma d} \exp\left(-\frac{1}{2\sigma^2} \ln^2\left(\frac{d}{d_o}\right)\right), \tag{4.1.1}$$

where d_o and σ are the mean diameter and the variance of the distribution, respectively, is suitable to describe the samples. Thus, in order to get an exponential relaxation with only one characteristic time a sample whose value of σ is about 0.3 or less must be used.

Each particle is first characterized through a static birefringence measurement as a function of the magnetic field. This is due to the anisotropy of the electric susceptibility tensor relating the polarizability of the system to the incident electric field. The main causes of the anisotropy are the internal optical anisotropy of the magnetic material (crystalline anisotropy) and the shape anisotropy of the particles.

Concerning the dynamic behavior of the birefringence, different experiments can be carried out:

In a liquid, if the magnetic field is switched off abruptly, particles thermally relax towards random directions. Thus looking at the birefringence relaxation is comparing viscous to thermal energies. If a square pulse of magnetic field H is applied to the ferrofluid solution, magnetic particles first tend to align along the field leading to birefringence $\delta n(t)$, and, as the field is switched off, they thermally relax to random directions. Birefringence decreases exponentially according to Perrin's law [18]

$$\delta n(t) = \delta n(d, H) \exp^{-t/\tau(d)} \tag{4.1.2}$$

where the characteristic time is $\tau(d) = (6D_r)^{-1}$, with D_r the rotational diffusion coefficient. In the quantity $\delta n(t)$, the polydispersity of the samples modifies both $\delta n(d, H)$ and $\tau(d)$. Owing to this fact, $\Delta n(t)$ is not a simple exponential function of time. But, in order to characterize $\Delta n(t)$, one can use the shortest time deduced from the initial slope of the function $\ln(\Delta n(t))$ versus t.

In a viscoelastic medium, looking at the birefringence response to an alternating magnetic field allows to reach the viscosity and the elastic modulus of the medium at high frequencies.

If a large magnetic field is superimposed, there is a magnetic restoring force and viscous energy is compared to that. Instead of relaxing at random, magnetic moments relax towards the direction of the superimposed field. In this case, the relaxation time associated with the orientation mechanism of the particles, τ_R, has been measured recently by Bacri et al. [19, 20]. This quantity comes from the relaxation time of the light intensity collected in a photocell after crossing the sample in the presence

of an external magnetic field, and when applying additional pulses of magnetic field to perturb the sample. These experiments permit us to distinguish the different relaxation regimes occurring when the size and the nature of the magnetic material of the particles are modified. These regimes are determined by the parameters μ and σ, comparing magnetic and anisotropy energies with thermal energy, respectively.

In the experiments, it was observed that ferrofluid particles, prevented from moving by being quenched in a tight gel network, do not exhibit birefringence although they still show magnetization. Consequently, the birefringence of the solution is closely related to a mechanical alignment of the particles along the equilibrium orientation.

In Refs. [8, 15, 21], two opposite limits were considered, one where $\sigma \gg \mu$ (rigid dipole approximation) and another for which $\sigma \ll \mu$. For the former limit, the relaxation time for the perpendicular component of the magnetization is found to be [8, 15]

$$\tau = D_r^{-1}(2 + \mu\mathcal{L}(\mu))^{-1}, \tag{4.1.3}$$

which, in the case when $\mu \to \infty$, tends to $\frac{1}{D_r\mu} = \frac{2\tau_B}{\mu}$. In the latter case, relaxation occurs in two steps, first a quick relaxation of $\hat{R}$ towards $\hat{H}$, then a mechanical rotation of the particle to the equilibrium orientation with the easy axis of magnetization parallel to $\hat{R}$ and $\hat{H}$. Under these conditions, the characteristic relaxation time could be obtained from the equation of motion of whatever component of the correlation function $\langle(\hat{n}_\perp n_z)(t)(\hat{n}_\perp n_z)(0)\rangle$ [21]. Performing the corresponding decouplings in its evolution equation, we obtain the relaxation time

$$\tau = (2D_r)^{-1}(\sigma + \frac{1}{Q(\sigma)})^{-1} = \tau_B(\sigma + \frac{1}{Q(\sigma)})^{-1}, \tag{4.1.4}$$

which for $\sigma \to \infty$, tends to $\frac{1}{2D_r\sigma} = \frac{\tau_B}{\sigma}$.

In the present analysis, we consider the less stringent case for which the ratio μ/σ may take arbitrary values. Consequently, both parameters μ and σ, are expected to determine the relaxation time associated with the rotational relaxation of the particles.

As for the limit $\sigma \ll \mu$ discussed previously, the appropriate quantity for describing this mechanical relaxational motion is again a component of the correlation function $\langle(\hat{n}_\perp n_z)(t)(\hat{n}_\perp n_z)(0)\rangle$. From the Smoluchowski equation, we obtain its dynamic equation

$$\begin{aligned}\frac{1}{D_r}\frac{d\langle(n_x n_z)(t)(n_x n_z)(0)\rangle}{dt} &= \mu\langle(n_x(\hat{n}\cdot\hat{R}))(t)(n_x n_z)(0)\rangle - \mu\langle(n_z^2 R_x)(t)(n_x n_z)(0)\rangle \\ &-\mu\langle(n_x n_z R_z)(t)(n_x n_z)(0)\rangle - 6\langle(n_x n_z)(t)(n_x n_z)(0)\rangle,\end{aligned} \tag{4.1.5}$$

Proceeding along the same lines as in the previous section, we arrive at a closed set of three differential equations for the correlation functions $\langle R_x(t)(n_x n_z)(0)\rangle$, $\langle (n_x(\hat{n}\cdot\hat{R}))(t)(n_x n_z)(0)\rangle$, and $\langle (n_x n_z)(t)(n_x n_z)(0)\rangle$. It is worthwhile pointing out that the quantities at time t appearing in the three independent correlation functions are the same as in the previous section. For the sake of simplicity, we will introduce the vector $\vec{\mathcal{Q}} = (\mathcal{Q}_1, \mathcal{Q}_2, \mathcal{Q}_3)$, whose components are the Laplace transforms of $\langle R_x(t)(n_x n_z)(0)\rangle$, $\langle (n_x(\hat{n}\cdot\hat{R}))(t)(n_x n_z)(0)\rangle$, and $\langle (n_x n_z)(t)(n_x n_z)(0)\rangle$, respectively; and the vector $\vec{\mathcal{Q}}^o = (\mathcal{Q}_1^o, \mathcal{Q}_2^o, \mathcal{Q}_3^o)$ representing the initial values of these correlation functions. These initial values can be calculated with the equilibrium probability density at $t = 0$. The system of differential equations can be written in matrix notation as

$$\mathcal{A}\cdot\vec{\mathcal{Q}} = D_r^{-1}\vec{\mathcal{Q}}^o \tag{4.1.6}$$

with $\mathcal{A}$ the coefficients matrix (3.13). We are particularly interested in the relaxation dynamics of $\langle (n_x n_z)(t)(n_x n_z)(0)\rangle$. From Eq. (4.1.6), we obtain its Laplace transform

$$\mathcal{Q}_3(s) = D_r^{-1}\frac{(A_{21}A_{23} - A_{31}A_{22})\mathcal{Q}_1^o + (A_{12}A_{31} - A_{11}A_{23})\mathcal{Q}_2^o + (A_{11}A_{22} - A_{21}A_{12})\mathcal{Q}_3^o}{|(A_{ij})|}, \tag{4.1.7}$$

from which we can identify the relaxation time we are interested in

$$\tau_R = D_r^{-1}\lim_{s\to 0}\frac{\mathcal{Q}_3(s)}{\mathcal{Q}_3^o} \tag{4.1.8}$$

In figure II.4, we have represented the relaxation time τ_R versus μ for different ferromagnetic samples, but, in order to compare with experimental data from Ref. [19], we have also represented the relaxation time τ_R versus H^{-1} in figure II.5. The data correspond to two samples of magnetic particles of the same mean size but made of different magnetic materials, namely $CoFe_2O_4$ and $\gamma - Fe_2O_3$. The Co-ferrite sample has an anisotropy constant $K = 2\cdot 10^5\frac{J}{m^3}$, and the saturation value of the magnetization is $M_s \simeq 250\frac{KA}{m}$. For the maghemite, the anisotropy constant is $K = 4\cdot 10^3\frac{J}{m^3}$ and $M_s \simeq 270\frac{KA}{m}$. With these values, the Co-ferrite sample can be considered as a rigid dipole ($\sigma \gg \mu$). On the other hand, the maghemite particles are such that $\mu \geq \sigma$. Regarding the values of the anisotropy constant, σ, and the ratio $m/k_BT = \mu_o M_s V_m/k_BT$, we have taken $\sigma \sim 15$, $m/k_BT \sim 2.8\cdot 10^{-4}\frac{m}{A}$ for the maghemite and $\sigma \sim 565$, $m/k_BT \sim 1.8\cdot 10^{-4}\frac{m}{A}$ for the Co-ferrite. For both samples, the values of the remaining quantities are : $\tau_B \sim 4.5ms$ and $D_m/D_r \sim 1$.

As it was observed in the experiments for the Co-ferrite sample, τ_R tends to zero when $H \to \infty$. Both $\hat{R}$ and $\hat{n}$, quickly relax towards the field direction due to the

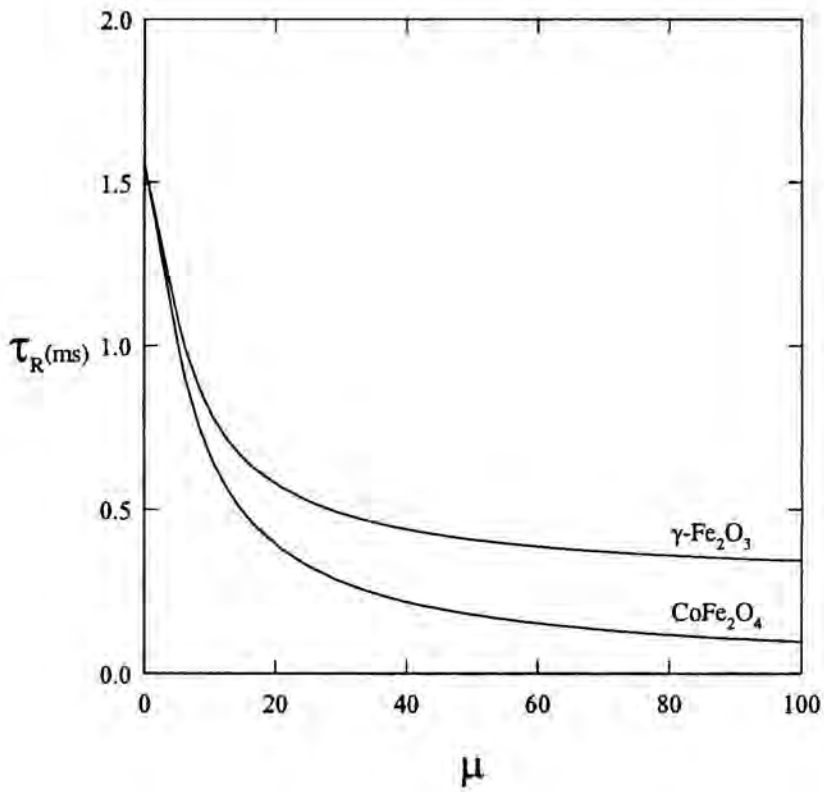

Figure II.4: Relaxation time of the particles as a function of μ for the Co-ferrite and maghemite samples.

rigidity of the dipoles. For the maghemite sample τ_R tends to a fixed, non-vanishing value (~ 0.3), which can also be obtained from Eq. (4.1.4). Under these particular conditions, the magnetic moments rapidly relax towards the field direction, but due to the moderate value of σ, the relaxation of the easy axis of magnetization, $\hat{n}$, or in other words, the mechanical relaxation of the particles, takes place in a finite period of time.

Concerning the behavior of τ_R when $H \to 0$, we observe that $\tau_R \to \frac{1}{6D_r} = \frac{\tau_B}{3}$ independently of the value of the parameter σ. This time corresponds to the well-known characteristic relaxation time of the correlations of the components of the second order tensor $(\hat{n}\hat{n} - \frac{\boldsymbol{I}}{3})$ for a purely diffusive process [27].

In figure II.5, we have also represented the extrapolation of the relaxation time coming from rather simple considerations made in Ref. [22] for the rigid dipole limit under the action of a very large external magnetic field. Our results agree with the asymptotic behavior in its validity range, but at the same time, they show the deviations at intermediate and low magnetic field. These simple arguments can also be proposed for the opposite case $\mu \gg \sigma$ reproducing the asymptotic value $\tau_R \sim 0.3ms$ for the maghemite sample, but they are not able to explain the μ-dependence of the relaxation time for this material.

4.2 Transverse complex susceptibility

In this section, we are interested in the linear response of the dispersion to an *ac* magnetic field of small amplitude. From an experimental point of view, it is much easier to observe different effects such as the saturation of the magnetization or the frequency dependence of its relaxation for a ferrofluid than for a polar dielectric fluid, because both the field strength and the frequencies required are much lower. Moreover, as we will see below, in a magnetic fluid the variation of the complex susceptibility with frequency depends on the relaxation time of the magnetic moment.

In the absence of an external *dc* field, Raikher and Shliomis [23] derived expressions for the complex *ac* susceptibility, $\chi(w) = \chi'(w) - i\chi''(w)$, of a single domain uniaxial particle. They calculated both the parallel and perpendicular susceptibilities with respect to the easy axis of magnetization. For that particular situation, they showed that the frequency dependence of the susceptibility was at the same time a function of the parameter σ, comparing anisotropy energy to the thermal energy. The applied *ac* field orientates both the magnetic moments and the particle axes, but in a linear approximation, i.e. for small values of the applied *ac* field, they neglected

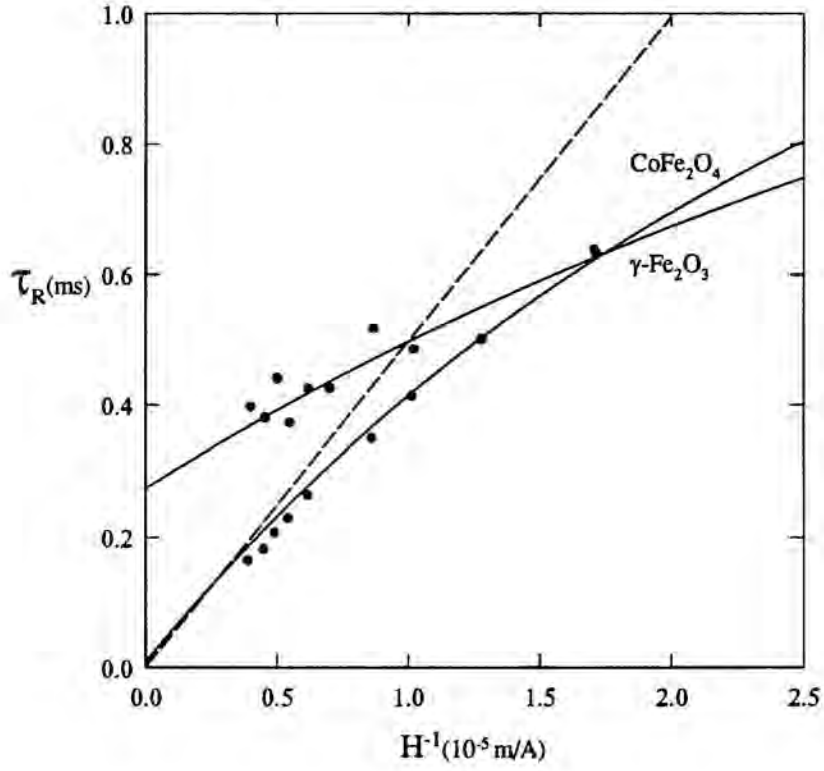

Figure II.5: Relaxation time of the particles as a function of H^{-1} for the Co-ferrite and maghemite samples. Experimental data of Ref. [19] correspond to the dots. The dashed line corresponds to the limit $\mu \gg 1$ for the Co-ferrite, Ref.[22].

the field-induced particle orientation. Thus, for a weak measuring field, the particle anisotropy axes were just oriented in a random fashion due to Brownian motion. Moreover, in Ref. [4] the authors obtained the expressions for the longitudinal and transverse components of the complex dielectric susceptibility tensor for a system of noninteracting polar molecules under the simultaneous action of a constant external electric field and a small *ac* electric field. This situation would be equivalent to the previously mentioned rigid dipole approximation. In this case, the susceptibilities depend on the bias field. For experimental measures in a liquid, it is much simpler to determine the parallel and perpendicular susceptibilities with respect to a fixed direction like that of the *dc* field than with respect to the axis of easy magnetization of the particles. Thus, in this subsection, we obtain the expression for the perpendicular susceptibility with respect to the bias field $\vec{H}$, i.e. the perturbing external field $\vec{H}' \perp \vec{H}$, when not only the magnetic moments but also the particles themselves are oriented by the external field, such as we have described throughout the chapter. We obtain that the susceptibility depends on the bias field through the parameter μ.

From linear response theory, the decay of the magnetization perpendicular component under the influence of a constant field $\vec{H}$, another small constant external field $\vec{H}'$ ($\vec{H}' \perp \vec{H}$ and such that $mH'/k_BT \ll 1$) having been switched off at time $t = 0$, is

$$\langle M_\perp(t)\rangle - \langle M_\perp(0)\rangle = \chi_\perp^s H' C_\perp(t), \tag{4.2.1}$$

where

$$\langle M_\perp\rangle = nm\langle R_\perp\rangle \tag{4.2.2}$$

is the perpendicular component of the magnetization,

$$\chi_\perp^s = \frac{nm^2}{k_BT}\left(\langle R_\perp^2(0)\rangle - \langle R_\perp(0)\rangle^2\right) \tag{4.2.3}$$

is the perpendicular component of the static magnetic susceptibility, and

$$C_\perp(t) = \frac{\langle R_\perp(t)R_\perp(0)\rangle - \langle R_\perp(0)\rangle^2}{\langle R_\perp^2(0)\rangle - \langle R_\perp(0)\rangle^2} \tag{4.2.4}$$

is the autocorrelation function of any perpendicular component of the magnetization.

The corresponding complex magnetic susceptibility $\chi_\perp(w)$ is

$$\chi_\perp(w) = -\chi_\perp^s \int_0^\infty e^{-iwt}\frac{dC_\perp(t)}{dt}dt = \chi_\perp^s\left(1 - iw\int_0^\infty e^{-iwt}C_\perp(t)dt\right). \tag{4.2.5}$$

In the limit of low frequencies, Eq. (4.2.5) may be written as

$$\chi_\perp(w) \simeq \chi'_\perp(1 - iw\tau_\perp), \tag{4.2.6}$$

where

$$\tau_\perp = \int_0^\infty C_\perp(t)dt = \lim_{s\to 0} C_\perp(s) \tag{4.2.7}$$

is the relaxation time. Moreover, $C_\perp(s)$ is the Laplace transform of the autocorrelation function. Eq. (4.2.6) can be written down, up to the same order of accuracy, in the form of the Debye equation

$$\chi_\perp(w) \simeq \frac{\chi'_\perp}{(1 + iw\tau_\perp)}. \tag{4.2.8}$$

This is the rotational diffusion limit where the behavior of $C_\perp(t)$ and, consequently, of $\langle M_\perp(t)\rangle - \langle M_\perp(0)\rangle$ may be approximated by the exponential

$$C_\perp(t) = exp\left(-\frac{t}{\tau_\perp}\right) \tag{4.2.9}$$

The relaxation time follows from (4.2.7) together with (4.2.4), and (3.8-3.14). In fact, when the perturbing external field is pointing towards the $\hat{e}_x$ axis, $\vec{H}' = H'\hat{e}_x$, and the constant polarizing magnetic field coincides with the $\hat{e}_z$ axis, $\vec{H} = H\hat{e}_z$, our autocorrelation function reduces to

$$C_x(t) = \frac{\langle R_x(t)R_x(0)\rangle}{\langle R_x^2(0)\rangle} \tag{4.2.10}$$

Consequently,

$$\tau_\perp = D_r^{-1} \lim_{s\to 0} \frac{\mathcal{R}_1(s)}{\mathcal{R}_1^o}. \tag{4.2.11}$$

In Fig. II.6, we have represented $\tau_\perp$ versus μ for the different values of the parameter σ corresponding to different available materials. The Debye spectra (single relaxation time approximation) is given by

$$\chi_\perp(w) \simeq \frac{\chi'_\perp}{(1 + iw\tau_\perp)} = 3\chi_o \frac{\mathcal{R}_1^o}{(1 + iw\tau_\perp)}, \tag{4.2.12}$$

where we have defined $\chi_o = nm^2/3k_BT$ as the static value of the susceptibility in the absence of the constant field.

In Figs. II.7 and II.8 we plot the real $\chi'_\perp(w)$ and imaginary $\chi''_\perp(w)$ parts of the transverse component of the normalized complex susceptibility for different values of

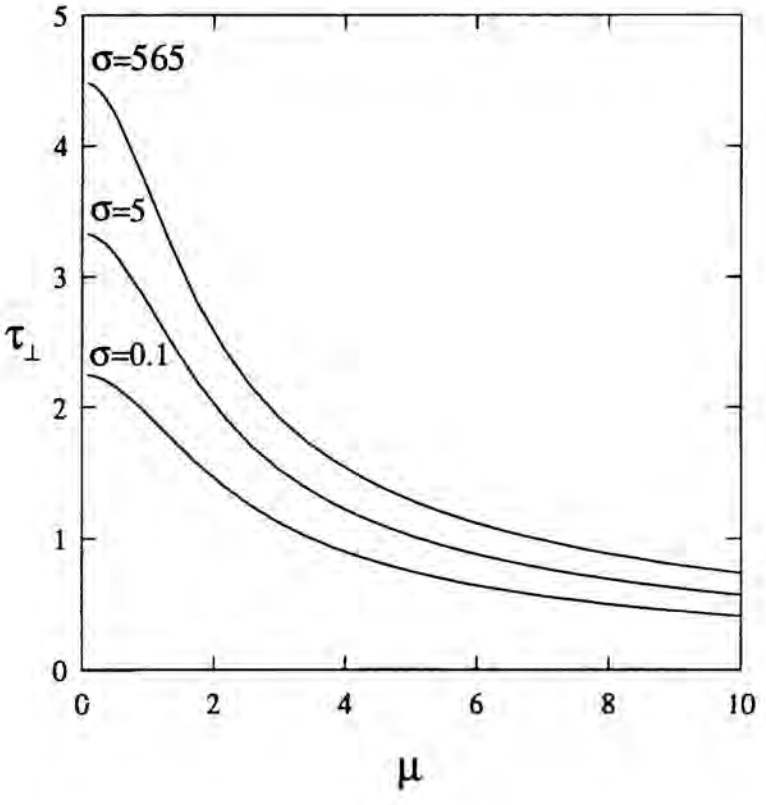

Figure II.6: Relaxation time of the perpendicular component of the magnetization versus the parameter μ for different values of σ.

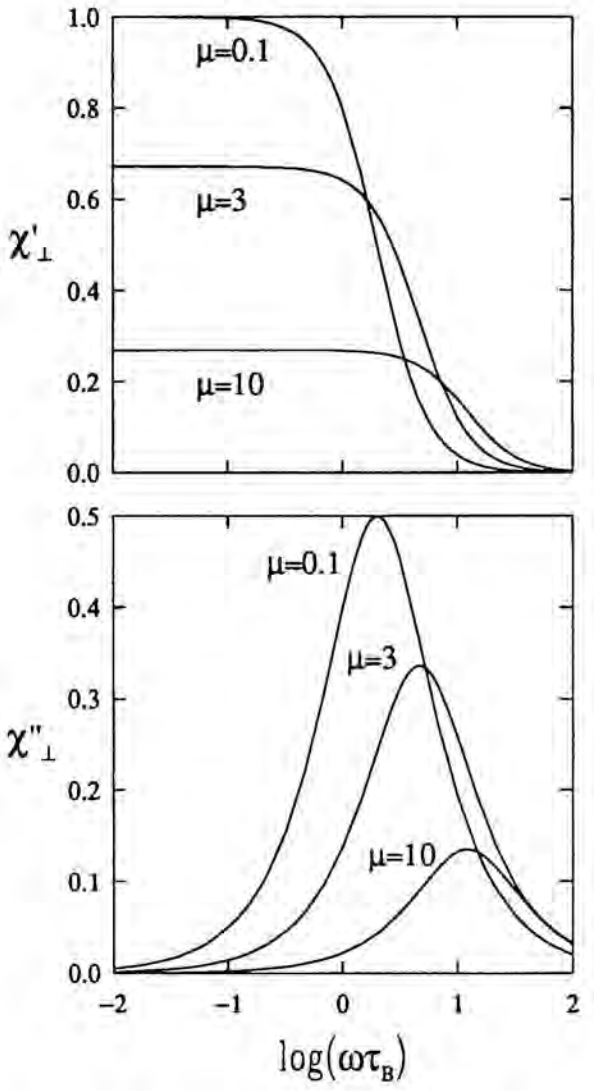

Figure II.7: Real $\chi'_{\perp}(w)$ and imaginary $\chi''_{\perp}(w)$ parts of the normalized transversal complex susceptibility as a function of $Log(w/D_r)$ for different values of the parameter μ as indicated in the plot. The parameter σ is set equal to 565 which may represent the rigid dipole limit.

μ and σ. To be precise, Fig. II.7 represents the effect of different constant external field strength, whereas Fig. II.8 shows the the influence of the anisotropy energy for two given values of the parameter μ.

From the formula it is easy to see that for the real part of the susceptibility, $\chi'_{\perp}(w)$, there exists a plateau for $\omega\tau_{\perp} \ll 1$ and that it goes to zero for $\omega\tau_{\perp} \gg 1$. The decrease takes place in a narrow interval of frequencies near a characteristic one

$$\omega^* = \frac{1}{\tau_{\perp}}. \tag{4.2.13}$$

Moreover, at this frequency, the imaginary component of the susceptibility $\chi''_{\perp}(w)$ has a pronounced maximum.

In view of the figures, for a given value of the parameter μ, the bigger the parameter σ, comparing anisotropy and thermal energies, the bigger the relaxation time $\tau_{\perp}$, so that the characteristic frequency ω^* decreases and the dispersion curves are shifted to the left. On the other hand, for a given value of σ, the bigger the parameter μ, comparing magnetic and thermal energies, the lower the relaxation time $\tau_{\perp}$. That is why the characteristic frequency increases with μ and the dispersion curves are shifted to the right.

We are using the Debye formula beyond its order of accuracy, however it is shown to be a good approximation up to the Larmor frequency of the precession of vector $\vec{R}$ around the equilibrium orientation [4, 25]. Above this frequency it is possible to observe a resonance behavior in the relaxation curves, characterized by the real part of the susceptibility going negative [23]-[25].

Our results generalize that of Raikher and Shliomis [23] as we include the simultaneous action of an external *dc* field of any strength, as well as the *ac* field on magnetic samples with different anisotropy energies, and open the possibility for new experimental measurements.

5 Conclusions

In this chapter, we have presented a general formalism to study the relaxation dynamics of ferromagnetic particles with the main purpose of providing explicit expressions for the viscosity and relaxation times, which can be applied to different situations ranging from the rigid-dipole limit to the limit where the anisotropy energy is dominant. Additionally, the appropriate relaxation times enable us to characterize different properties of the material, such as the birefringence and the complex magnetic susceptibility.

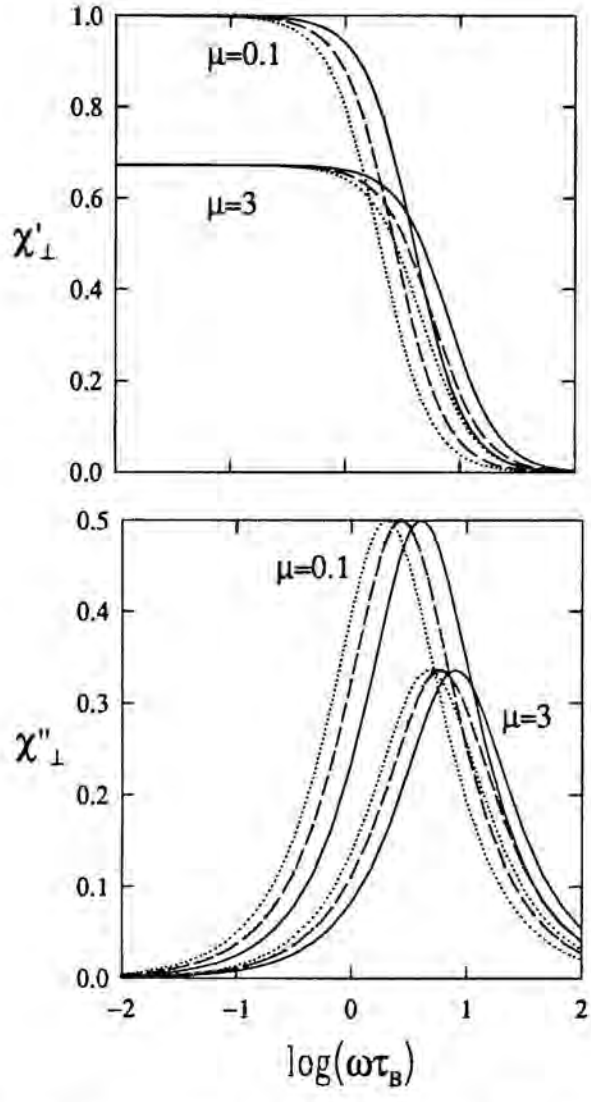

Figure II.8: Real $\chi'_\perp(w)$ and imaginary $\chi''_\perp(w)$ parts of the normalized transversal complex susceptibility as a function of $Log(w/D_r)$ for different values of the parameters μ and σ. The solid line corresponds to $\sigma = 0.1$, the dashed line to $\sigma = 5$, and the dotted line to $\sigma = 565$.

We have obtained the Smoluchowski equation describing the evolution of the probability density of the relevant degrees of freedom of the particles. This equation allows us to obtain a hierarchy of dynamic equations for the different correlation functions that can be closed using appropriate decoupling approximations. The correlation dynamics provides expressions for the characteristic relaxation times and they constitute the starting point to determine the transport coefficients using the Green-Kubo formulas. In particular, we have seen that the rotational viscosity reaches a saturation limit and depends on both parameters μ and σ. It is interesting to emphasize that the theory we have developed encompasses a wide number of situations characterized by the values of the magnetic and anisotropy energies of the ferromagnetic particles.

To check the validity of our formalism, we have compared our results for the relaxation time of the particles to birefringence experiments carried out with two types of ferromagnetic material, for which the dimensionless parameters μ and σ satisfy: $\sigma \gg \mu$ and $\mu \geq \sigma$, respectively. The first case corresponds to a rigid dipole, whereas in the second, the magnetic moment relaxes towards the field independently of the particle axis, which also relaxes towards the magnetic moment in a larger time scale. In both cases, our results are largely in agreement with the experiments.

We also provide a general expression for the complex magnetic susceptibility of the magnetic fluid under the simultaneous action of a constant polarizing magnetic field and a small *ac* field, perpendicular to each other. This quantity also depends on the parameters μ and σ. In this way, the analytic expression we have found covers the whole range of possible experimental conditions.

Appendix A

Explicit derivation of the Smoluchowski equation (2.13)

In this appendix, we explicitly derive the expressions for the mobility matrix $\boldsymbol{b}$ given through Eq. (2.12) and the Smoluchowski equation (2.13). Our starting point in the derivation is the diffusion-convection equation (2.11). After inserting eqs. (2.4) and (2.6), we have

$$\begin{aligned}\frac{\partial\psi}{\partial t} &= \frac{\partial}{\partial\hat{R}}\cdot\left(\boldsymbol{D}_{RR}\cdot\frac{\partial\psi}{\partial\hat{R}}+\boldsymbol{D}_{Rn}\cdot\frac{\partial\psi}{\partial\hat{n}}-\psi g\hat{R}\times\frac{\partial U}{\partial\hat{R}}\right.\\ &+ \left.\psi h\left(\hat{R}\times\frac{\partial U}{\partial\hat{R}}\right)\times\hat{R}-\psi\vec{\omega}_o\times\hat{R}-\psi\frac{mH}{\xi_r}(\hat{R}\times\hat{H})\times\hat{R}\right)\\ &+ \frac{\partial}{\partial\hat{n}}\cdot\left(\boldsymbol{D}_{nR}\cdot\frac{\partial\psi}{\partial\hat{R}}+\boldsymbol{D}_{nn}\cdot\frac{\partial\psi}{\partial\hat{n}}-\psi\vec{\omega}_o\times\hat{n}-\psi\frac{mH}{\xi_r}(\hat{R}\times\hat{H})\times\hat{n}\right). \quad \text{(A1)}\end{aligned}$$

Our next step will be to rewrite the non-diffusive contributions appearing in Eq. (A1) in terms of the rotational operators $\vec{\mathcal{R}}_{\hat{n}}\equiv\hat{n}\times\frac{\partial}{\partial\hat{n}}$ and $\vec{\mathcal{R}}_{\hat{R}}\equiv\hat{R}\times\frac{\partial}{\partial\hat{R}}$:

$$g\frac{\partial}{\partial\hat{R}}\cdot\left(\psi\hat{R}\times\frac{\partial U}{\partial\hat{R}}\right)=-g\vec{\mathcal{R}}_{\hat{R}}\cdot\left(\psi\frac{\partial U}{\partial\hat{R}}\right)\equiv\vec{\mathcal{R}}_{\hat{R}}\cdot(\vec{\omega}_L\psi), \quad \text{(A2)}$$

$$h\frac{\partial}{\partial\hat{R}}\cdot\left(\psi\left(\hat{R}\times\frac{\partial U}{\partial\hat{R}}\right)\times\hat{R}\right)=h\vec{\mathcal{R}}_{\hat{R}}\cdot(\psi\vec{\mathcal{R}}_{\hat{R}}U), \quad \text{(A3)}$$

$$\frac{\partial}{\partial\hat{R}}\cdot(\psi\vec{\omega}_o\times\hat{R})=\vec{\omega}_o\cdot\vec{\mathcal{R}}_{\hat{R}}\psi. \quad \text{(A4)}$$

Using the fact that

$$(\vec{\mathcal{R}}_{\hat{R}}+\vec{\mathcal{R}}_{\hat{n}})U=-\vec{m}\times\vec{H} \quad \text{(A5)}$$

we can write

$$\frac{1}{\xi_r}\frac{\partial}{\partial\hat{R}}\cdot\left(\psi(\vec{\mathcal{R}}_{\hat{R}}+\vec{\mathcal{R}}_{\hat{n}})U\times\hat{R}\right)=\frac{1}{\xi_r}\vec{\mathcal{R}}_{\hat{R}}\cdot\left(\psi(\vec{\mathcal{R}}_{\hat{R}}+\vec{\mathcal{R}}_{\hat{n}})U\right), \quad \text{(A6)}$$

$$\frac{\partial}{\partial\hat{R}}\cdot(\psi\vec{\omega}_o\times\hat{n})=\vec{\omega}_o\cdot\vec{\mathcal{R}}_{\hat{n}}\psi, \quad \text{(A7)}$$

$$\frac{1}{\xi_r}\frac{\partial}{\partial\hat{n}}\cdot\left(\psi(\vec{\mathcal{R}}_{\hat{R}}+\vec{\mathcal{R}}_{\hat{n}})U\times\hat{n}\right)=\frac{1}{\xi_r}\vec{\mathcal{R}}_{\hat{n}}\cdot\left(\psi(\vec{\mathcal{R}}_{\hat{R}}+\vec{\mathcal{R}}_{\hat{n}})U\right). \quad \text{(A8)}$$

Analogously, the potential terms (A3), (A6), and (A8) can be written in the form

$$h\frac{\partial}{\partial\hat{R}}\cdot\left(\psi\left(\hat{R}\times\frac{\partial U}{\partial\hat{R}}\right)\times\hat{R}\right)=\frac{\partial}{\partial\hat{R}}\left(\psi\underline{h(\boldsymbol{I}-\hat{R}\hat{R})}\cdot\frac{\partial U}{\partial\hat{R}}\right), \tag{A9}$$

$$\frac{1}{\xi_r}\frac{\partial}{\partial\hat{R}}\cdot\left(\psi(\vec{\mathcal{R}}_{\hat{R}}+\vec{\mathcal{R}}_{\hat{n}})U\times\hat{R}\right)=\frac{\partial}{\partial\hat{R}}\cdot\left(\psi\underline{\frac{1}{\xi_r}(\boldsymbol{I}-\hat{R}\hat{R})}\cdot\frac{\partial U}{\partial\hat{R}}+\psi\underline{\frac{1}{\xi_r}\{(\hat{R}\cdot\hat{n})\boldsymbol{I}-\hat{R}\hat{n}\}}\cdot\frac{\partial U}{\partial\hat{n}}\right), \tag{A10}$$

$$\frac{1}{\xi_r}\frac{\partial}{\partial\hat{n}}\cdot\left(\psi(\vec{\mathcal{R}}_{\hat{R}}+\vec{\mathcal{R}}_{\hat{n}})U\times\hat{n}\right)=\frac{\partial}{\partial\hat{n}}\cdot\left(\psi\underline{\frac{1}{\xi_r}(\boldsymbol{I}-\hat{n}\hat{n})}\cdot\frac{\partial U}{\partial\hat{n}}+\psi\underline{\frac{1}{\xi_r}\{(\hat{R}\cdot\hat{n})\boldsymbol{I}-\hat{n}\hat{R}\}}\cdot\frac{\partial U}{\partial\hat{R}}\right), \tag{A11}$$

where the underlined factors may be identified to the mobility matrices defined in Eq. (2.12). Moreover, the diffusion matrix is given by $\boldsymbol{D}=k_BT\boldsymbol{b}$, so that we can also rewrite the diffusive factors in terms of the rotational operators

$$\frac{\partial}{\partial\hat{R}}\cdot\left(\boldsymbol{D}_{RR}\cdot\frac{\partial\psi}{\partial\hat{R}}\right)=(D_m+D_r)\frac{\partial}{\partial\hat{R}}\cdot(\boldsymbol{I}-\hat{R}\hat{R})\cdot\frac{\partial}{\partial\hat{R}}\psi=(D_m+D_r)\vec{\mathcal{R}}^2_{\hat{R}}\psi, \tag{A12}$$

$$\frac{\partial}{\partial\hat{n}}\cdot\left(\boldsymbol{D}_{nn}\cdot\frac{\partial\psi}{\partial\hat{n}}\right)=D_r\vec{\mathcal{R}}^2_{\hat{n}}\psi, \tag{A13}$$

$$\frac{\partial}{\partial\hat{R}}\cdot\left(\boldsymbol{D}_{Rn}\cdot\frac{\partial\psi}{\partial\hat{n}}\right)=D_r\frac{\partial}{\partial\hat{R}}\cdot\{(\hat{R}\cdot\hat{n})\boldsymbol{I}-\hat{R}\hat{n}\}\cdot\frac{\partial\psi}{\partial\hat{n}}=D_r\vec{\mathcal{R}}_{\hat{R}}\cdot\vec{\mathcal{R}}_{\hat{n}}\psi, \tag{A14}$$

$$\frac{\partial}{\partial\hat{n}}\cdot\left(\boldsymbol{D}_{nR}\cdot\frac{\partial\psi}{\partial\hat{R}}\right)=D_r\vec{\mathcal{R}}_{\hat{n}}\cdot\vec{\mathcal{R}}_{\hat{R}}\psi. \tag{A15}$$

Finally, substituting eqs. (A2)-(A8) and (A12)-(A15) in Eq. (A1), we arrive at equation (2.13).

Appendix B

Decoupling approximations

In Section 3, we have introduced decouplings of some correlation functions appearing in the evolution equations for the correlations. The purpose of this appendix is to give more details about the procedure followed to carry out such decouplings. In Eq. (3.4), the approximated quantities are

$$\langle (R_x R_z)(t) R_x(0) \rangle \sim \langle R_x(t) R_x(0) \rangle \langle R_z \rangle_{eq} = \mathcal{L}(\mu) \langle R_x(t) R_x(0) \rangle, \qquad \text{(B1)}$$

and

$$\langle (R_x(\hat{n} \cdot \hat{R})^2)(t) R_x(0) \rangle \sim \langle R_x(t) R_x(0) \rangle \langle (\hat{n} \cdot \hat{R})^2 \rangle_{eq} = Q(\sigma) \langle R_x(t) R_x(0) \rangle, \qquad \text{(B2)}$$

where linearizations in time have been performed. The approximation (B1) was already discussed in the text (see Eq. (3.5) and comments below). For the correlation (B2), we decouple the quantities R_x and $(\hat{n} \cdot \hat{R})^2$ because they are not coupled in equilibrium conditions, $\langle R_x(\hat{n} \cdot \hat{R})^2 \rangle_{eq} = 0$, $\langle R_x \rangle_{eq} = 0$, and $\langle (\hat{n} \cdot \hat{R})^2 \rangle_{eq} \neq 0$. Thus, in a situation not far from equilibrium, we will assume that both quantities remain also decoupled.

By similar arguments, in Eq. (3.6) we have also performed the following approximations

$$\langle (R_x(n_z(\hat{n} \cdot \hat{R})))(t) R_x(0) \rangle \sim \langle R_x(t) R_x(0) \rangle \langle (n_z(\hat{n} \cdot \hat{R})) \rangle_{eq} = \mathcal{L}(\mu) Q(\sigma) \langle R_x(t) R_x(0) \rangle, \qquad \text{(B3)}$$

$$\langle (n_x(R_z(\hat{n} \cdot \hat{R})))(t) R_x(0) \rangle \sim \langle (n_x(\hat{n} \cdot \hat{R}))(t) R_x(0) \rangle \langle R_z \rangle_{eq} = \mathcal{L}(\mu) \langle (n_x(\hat{n} \cdot \hat{R}))(t) R_x(0) \rangle, \qquad \text{(B4)}$$

and

$$\langle (n_x(\hat{n} \cdot \hat{R})(1 - (\hat{n} \cdot \hat{R})^2))(t) R_x(0) \rangle \sim \langle (n_x(\hat{n} \cdot \hat{R}))(t) R_x(0) \rangle (1 - \frac{\langle (\hat{n} \cdot \hat{R})^4 \rangle_{eq}}{\langle (\hat{n} \cdot \hat{R})^2 \rangle_{eq}}). \qquad \text{(B5)}$$

In Eq. (3.7), we have used

$$\langle (n_z^2 R_x)(t) R_x(0) \rangle \sim \langle R_x(t) R_x(0) \rangle \langle n_z^2 \rangle_{eq} = (\frac{\mathcal{L}(\mu)}{\mu}(1 - 3Q(\sigma)) + Q(\sigma)) \langle R_x(t) R_x(0) \rangle, \tag{B6}$$

$$\langle (n_x n_z R_z)(t) R_x(0) \rangle \sim \langle (n_x n_z)(t) R_x(0) \rangle \langle R_z \rangle_{eq} = \mathcal{L}(\mu) \langle (n_x n_z)(t) R_x(0) \rangle. \tag{B7}$$

Notice that the decoupling in the correlation $\langle (n_x(\hat{n} \cdot \hat{R})^3)(t) R_x(0) \rangle$ of Eq. (B5) is $\langle (n_x(\hat{n} \cdot \hat{R}))(t) R_x(0) \rangle \frac{\langle (\hat{n} \cdot \hat{R})^4 \rangle_{eq}}{\langle (\hat{n} \cdot \hat{R})^2 \rangle_{eq}}$ and not $\langle (n_x(\hat{n} \cdot \hat{R}))(t) R_x(0) \rangle \langle (\hat{n} \cdot \hat{R})^2 \rangle_{eq}$, which leads to divergencies of the rotational viscosity at small values of μ. As regards this fact, it is worthwhile to emphasize that these approximations are more accurate for moderate and higher values of parameters μ and σ. This type of truncation was already proposed by Stratonovich in the context of stochastic processes.

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CHAPTER III

DYNAMICS OF MAGNETIC HOLES DISPERSED IN A FERROFLUID

Once we have characterized the macroscopic behavior of a ferrofluid, giving expressions for the viscosities and, correspondingly, for both the symmetric and antisymmetric parts of the pressure tensor, as well as for the average of its magnetization, in this chapter we analyze the dynamics of a nonmagnetic particle (magnetic hole) suspended in a ferrofluid. The rotational dynamics of the particle is strongly influenced by the presence of a rotating magnetic field. As a result, we have found that the hole rotates in the opposite direction to that of the field. Our analysis is valid at low and moderate frequencies of the field rotation and may be compared to recent experiments obtaining quite a good agreement in the frequency range we are considering, in which a linear relationship between both the rotation frequency of the field and the angular velocity of the particle is found. In addition, the dependence of the frequency of the particle on the magnetic field strength is also compared to the experiments. For a slightly greater concentration of holes, we also determine the Rotne-Prager and Oseen equivalent tensors, as the first steps in the characterization of hydrodynamic interactions between the nonmagnetic particles in the ferrofluid.

1 Introduction

Recently, an increasing interest in the study of the dynamic properties of the so-called magnetic holes, which are colloidal nonmagnetic particles dispersed in a carrier magnetic fluid, has arisen [1]-[4]. Although the particles are not magnetic, when they are suspended in a carrier ferrofluid they *acquire* an induced magnetic moment equal to the magnetic moment of the ferrofluid volume they displace. The interaction of these induced magnetic moments of the holes causes a number of peculiar phenomena, such as the order-disorder transition in magnetic hole lattices [5, 6] and the non-linear phenomena observed in assemblies of holes [7]. Furthermore, knowledge of the dynamics of such particles may constitute a way of characterizing the transport properties of the ferrofluid. For example, the friction coefficient of the particle gives us information about the viscosity of the carrier fluid.

The system holes-ferrofluid can be modeled as a suspension of particles (holes) in a carrier fluid (ferrofluid). This simplification can be accomplished when different length scales exist for the ferrofluid and the holes. Consequently, the ferrofluid can be viewed as a continuous medium through which the holes may move. The dynamics of the ferrofluid is governed, at the continuum level, by a *generalized* Navier-Stokes equation. The rotations of the ferromagnetic particles lead to the presence of an antisymmetric part of the pressure tensor giving rise to the appearance of a new transport coefficient: the rotational viscosity [8, 9]. This coefficient enters the expression of the effective viscosity of the suspension [10].

The purpose of this chapter is to analyze the translational and rotational dynamics of a magnetic hole immersed in a ferrofluid under the influence of a rotating magnetic field. In particular, we are interested in explaining the phenomenon of the rotation of the hole in the opposite direction to that of the rotating field, as has been observed in recent experiments. As we will see, the expression for the angular velocity of the hole comes from its corresponding rotational equation of motion involving the hydrodynamic torque exerted by the fluid on the particle, which is calculated in a nonstationary situation.

Furthermore, we intend to characterize the hydrodynamic interactions between the non-magnetic particles in a ferrofluid by giving expressions for the corresponding Oseen and Rotne-Prager equivalent tensors. In particular, the Oseen tensor for a simple fluid is well known for being the simplest approximation when computing hydrodynamic interactions, i.e. when the suspension is dilute enough that the particles are located at a relative large distance from each other. This means that the

suspension of non-magnetic particles under consideration is dilute enough to avoid aggregation phenomena among the holes, but at the same time, there is a sufficient number of particles that makes it necessary to take into account hydrodynamic interactions between pairs of spheres. As an example to understand the influence of hydrodynamic interactions on the dynamics of the magnetic holes, we will also study their sedimentation in the presence of an external magnetic field.

With this goal in mind, we have distributed the chapter in the following way. In Section 2, we formulate the basic equations for the whole system in the continuum approximation. Under this approximation, the magnetic hole may be viewed as a macroscopic particle moving through a continuum medium with internal degrees of freedom. In Section 3, we analyze the motion of the hole until obtaining explicit expressions for the force and torque exerted on the particle. From these equations, we then derive the translational and rotational friction tensors. Moreover, from the analysis of the rotational motion, we infer a linear law relating the angular velocity of the hole and the rotation frequency of the field. These results are compared to experiments in Section 4. In Section 5 we study the hydrodynamic interactions between pairs of magnetic holes. We derive the expressions of the Oseen and Rotne-Prager equivalent tensors and we study the sedimentation of two holes in the presence of an external magnetic field for different configurations in order to show the influence of such interaction. Finally, in the last section, we summarize our main results.

2 Basic equations in the continuum approximation

Let us consider a dilute suspension of spherical magnetic holes of radius a in a ferrofluid under the influence of an external magnetic field, which rotates with the constant frequency ω_o. In the continuum approach, the ferrofluid (understood as a suspension of small magnetic particles in a non-polar solvent) is assumed to be a continuum medium with a new hydrodynamic field: the spin or mean angular velocity of the volume elements of the continuum [8]. This approximation is justified under the mild requirement that the size of the holes (tipically about $10^{-3} - 10^{-4} cm$) be much larger than that of the ferromagnetic particles ($10^{-6} cm$).

The magnetic field rotation frequencies are taken low enough to consider the quasistationary limit in which the derivatives of the hydrodynamic fields, although time dependent, may be neglected. Under this approximation, the equations of motion are

$$0 = -\nabla p + \eta \nabla^2 \vec{v} - \nabla \times \vec{\Pi}^{(a)} + \vec{F}^{i}, \tag{2.1}$$

$$0 = 2\vec{\Pi}^a + \vec{M} \times \vec{H} + \vec{\tau}^i, \tag{2.2}$$

where $p(\vec{r},t)$, $\vec{v}(\vec{r},t)$, and $\vec{\Pi}^{(a)}(\vec{r},t) \equiv -1/2\epsilon : \boldsymbol{\Pi}^{(a)}(\vec{r},t)$ are the pressure, velocity, and the axial vector related to the antisymmetric part of the pressure tensor, $\boldsymbol{\Pi}^{(a)}$, respectively. Moreover, ϵ is the Levi-Civita tensor, $\vec{M}(\vec{r},t)$ is the average magnetization density, and $\vec{H} = H\hat{H}$ is the external magnetic field. The appearance of antisymmetric stresses in the ferrofluid comes from the difference between the mean angular velocity and the vorticity of the flow, $1/2\nabla \times \vec{v}$. In addition, we have introduced the induced force and torque densities, $\vec{F}^i(\vec{r},t)$ and $\vec{\tau}^i(\vec{r},t)$, which originate from the perturbation caused by the motion of the hole. The shear viscosity η, according to Einstein's law is

$$\eta = \eta_o(1 + \frac{5}{2}\phi). \tag{2.3}$$

This expression holds up to linear order in the volume fraction of magnetic particles $\phi = 4\pi b^3/V$, where b is the radius of one ferromagnetic monodomain, and V is the volume occupied by the system. We have also defined η_o as the viscosity of the carrier fluid. Furthermore, these equations are complemented with the incompressibility condition $\nabla \cdot \vec{v} = 0$.

The induced force and torque density fields, $\vec{F}^i(\vec{r},t)$ and $\vec{\tau}^i(\vec{r},t)$ are introduced so that the equations of motion of the fluid, given by eqs. (2.1) and (2.2), are also valid for the points inside the sphere [11, 12]. This consideration imposes the requirement

$$\vec{F}^i(\vec{r},t) = \vec{\tau}^i(\vec{r},t) = 0, \quad \text{for } |\vec{r} - \vec{R}_{cm}(t)| > a. \tag{2.4}$$

Additionally, they must be chosen in such a way for the velocity and the pressure fields to satisfy

$$\vec{v}(\vec{r},t) = \vec{u}(t) + \vec{\Omega}(t) \times a\hat{n}, \quad \text{for } |\vec{r} - \vec{R}_{cm}(t)| = a, \tag{2.5}$$

$$p(\vec{r},t) = 0, \quad \text{for } |\vec{r} - \vec{R}_{cm}(t)| < a, \tag{2.6}$$

and the magnetization of the hole

$$\vec{M}(\vec{r},t) = 0, \quad \text{for } |\vec{r} - \vec{R}_{cm}(t)| \leq a. \tag{2.7}$$

In these equations, we have introduced $\vec{u}$ and $\vec{\Omega}$ as the translational and rotational velocities of the particle, respectively; $\vec{R}_{cm}(t)$ as the position of the center of mass of the sphere, and $\hat{n} \equiv (\vec{r} - \vec{R}_{cm}(t))/|\vec{r} - \vec{R}_{cm}(t)|$.

After considering the conditions (2.4) - (2.7), and for the quasistationary case, $\frac{d}{dt}(\vec{u}(t) + \vec{\Omega}(t) \times a\hat{n}) \simeq 0$, we have

$$\vec{F}^i(\vec{r},t) = \vec{f}^i(\hat{n},t)\delta(|\vec{r} - \vec{R}_{cm}(t)| - a), \tag{2.8}$$

and

$$\vec{\tau}^i(\vec{r},t) = \vec{\tau}^i(t)\Theta(a - |\vec{r} - \vec{R}_{cm}(t)|), \tag{2.9}$$

where Θ is the Heaviside step function.

We will now proceed to derive a formal solution in terms of the induced force and torque densities with the purpose of obtaining expressions for the hydrodynamic force and torque on the nonmagnetic particle as a function of its velocity and the velocity fields in the absence of the sphere. The procedure we use does not require explicit knowledge of either $\vec{F}^i(\vec{r},t)$, $\vec{\tau}^i(\vec{r},t)$ or the real velocity field $\vec{v}(\vec{r},t)$.

Equations (2.1) and (2.2) can be combined to eliminate the term proportional to the antisymmetric axial vector, $\vec{\Pi}^a$, in Eq. (2.1). We then obtain

$$0 = -\nabla p + \eta\nabla^2\vec{v} + \frac{1}{2}\nabla \times (\vec{M} \times \vec{H}) + \vec{\mathcal{F}}^i, \tag{2.10}$$

where we have defined $\vec{\mathcal{F}}^i$ as the combination of the induced force and torque fields

$$\vec{\mathcal{F}}^i(\vec{r},t) \equiv \vec{F}^i(\vec{r},t) + \frac{1}{2}\nabla \times \vec{\tau}^i(\vec{r},t). \tag{2.11}$$

To solve for the velocity field from Eq. (2.10) , we need to know the expression for the magnetization density. The procedure used to obtain this quantity was introduced in Ref. [13] for the case of a constant magnetic field, and was based upon the solution of the corresponding Smoluchowski equation. In appendix A, we present an extension of the method for rotating magnetic fields. Our solution is

$$\vec{M} = nm\langle\hat{R}\rangle = nm\{\mathcal{L}(\mu)\hat{H} + \frac{F(\mu)}{D_r}[(\frac{1}{2}\nabla \times \vec{v}) \times \hat{H} - \frac{d\hat{H}}{dt}]\}, \tag{2.12}$$

where n is the number density of dipoles, $\langle\hat{R}\rangle$ is the averaged orientation vector of each magnetic moment, $\mu = mH/k_BT$ is the Langevin parameter, comparing magnetic and thermal energies, with m the magnetic moment strength, assumed constant, k_B the Boltzmann's constant, and $D_r = \frac{k_BT}{\xi_r}$ is the rotational diffusion coefficient; with $\xi_r = 8\pi\eta_o b^3$ the rotational friction coefficient of a ferromagnetic particle. Additionally, $\mathcal{L}(\mu) = \coth\mu - 1/\mu$, is the Langevin function and $F(\mu) \equiv \frac{\mathcal{L}(\mu)}{2+\mu\mathcal{L}(\mu)}$ is introduced and obtained in appendix A.

Now, using this last result in Eq. (2.10), it can be written in the form

$$0 = -\nabla p + (\eta + \eta_r)\nabla^2 \vec{v} + \eta_r \nabla \times \hat{H}(\hat{H} \cdot \nabla \times \vec{v}) + \vec{\mathcal{F}}^i, \tag{2.13}$$

where η_r is the rotational viscosity, characteristic of a continuum medium with an internal degree of freedom [8], which is given by

$$\eta_r = \frac{3}{2}\eta_o \phi \frac{\mu - \tanh \mu}{\mu + \tanh \mu}, \tag{2.14}$$

and which is also valid up to the linear order in the volume fraction ϕ. After Fourier transforming in $\vec{k}$ this equation and applying the transversal projector $(\boldsymbol{I} - \hat{k}\hat{k})$, with $\hat{k} \equiv \vec{k}/k$, one arrives at the formal solution

$$\vec{v}(\vec{k}, t) = \boldsymbol{T}(\vec{k}, t) \cdot \vec{\mathcal{F}}^i(\vec{k}, t), \tag{2.15}$$

where we have introduced the propagator

$$\boldsymbol{T}(\vec{k}, t) \equiv \frac{1}{k^2}\boldsymbol{h}^{-1}(\vec{k}, t) \cdot (\boldsymbol{I} - \hat{k}\hat{k}). \tag{2.16}$$

In order to accomplish Eq. (2.16) we have also employed the incompressibility condition which, in Fourier space, reads $\vec{k} \cdot \vec{v} = 0$.

In the expression of the propagator we have introduced the quantity

$$\boldsymbol{h}^{-1}(\vec{k}, t) = \frac{1}{\eta + \eta_r}[\boldsymbol{I} - (\hat{k} \times \hat{H})(\hat{k} \times \hat{H})] + \frac{1}{\eta}(\hat{k} \times \hat{H})(\hat{k} \times \hat{H}), \tag{2.17}$$

with $\boldsymbol{I}$ being the unit matrix. The tensor $\boldsymbol{h}$ can be interpreted as a viscosity tensor due to the analogy of Eq. (2.16) with the expression of the Oseen tensor, which is the propagator of velocity perturbations in a simple liquid.

The formal solution can be rewritten in real space as

$$\vec{v}(\vec{r}, t) = \vec{v}_o(\vec{r}, t) + \int d\vec{r}\,' \boldsymbol{T}(\vec{r} - \vec{r}\,') \cdot \vec{\mathcal{F}}^i(\vec{r}\,', t), \tag{2.18}$$

where $\vec{v}_o$ is the unperturbed velocity field in the absence of the hole. This relationship will be used in the next section to obtain the hydrodynamic force and torque on the particle.

3 Motion of the hole

Having obtained the formal solution for the velocity field, we will now focus on the explicit calculation of the force and torque exerted by the ferrofluid on the hole. This

task may be accomplished using multipole expansions of the velocity and the induced force and torque fields [11, 12, 14].

Equation (2.18) gives the velocity field at any point. Therefore, for a given point at the surface of the sphere, in view of the stick boundary condition (2.5), one has

$$\vec{u}(t) + \vec{\Omega}(t) \times a\hat{n} = \vec{v}_o(a\hat{n}, t) + \int d\hat{n}\,' \boldsymbol{\mu}(\hat{n}, \hat{n}\,', t) \cdot [\vec{f}(\hat{n}\,', t) - \frac{\hat{n}\,' \times \vec{\tau}(t)}{2}], \quad (3.1)$$

where we have introduced the response function

$$\boldsymbol{\mu}(\hat{n}, \hat{n}\,', t) = \frac{a^2}{(2\pi)^3} \int d\vec{k}\; exp\,(ia\vec{k} \cdot (\hat{n} - \hat{n}')) \; \boldsymbol{T}(\vec{k}, t), \quad (3.2)$$

and use has been made of the relations (2.8), (2.9) and (2.11).

Following the same line of reasoning as in Ref. [14], we will now expand the velocities and the induced force on the surface of the particle in multipoles. For an unspecified quantity of Eq. (3.1), $\boldsymbol{\Psi}$, the multipole of order $l+1$, which is a tensor of rank $l+1$, is defined as

$$\boldsymbol{\Psi}^{(l+1)} = \frac{1}{4\pi} \int d\hat{n} \hat{\boldsymbol{n}}^l \boldsymbol{\Psi}(\hat{n}). \quad (3.3)$$

The general relationship between the $(l+1)$ order multipoles of the quantities defined over the surface of the sphere is found to be,

$$\mathbf{v}^{(l+1)} = \sum_{l'=0}^{\infty} \frac{(2l'+1)!!}{l'!} \boldsymbol{\mu}^{(l+1,l'+1)} \odot \boldsymbol{\mathcal{F}}^{(l'+1)} + \mathbf{v}_o^{(l+1)}, \quad (3.4)$$

which involves the matrix elements

$$\boldsymbol{\mu}^{(l+1,l'+1)} = \frac{1}{(4\pi)} \int d\hat{n} \int d\hat{n}' \; \hat{\boldsymbol{n}}^l \; \boldsymbol{\mu}(\hat{n}, \hat{n}') \; \hat{\boldsymbol{n}}'^{l'}. \quad (3.5)$$

Here $\hat{\boldsymbol{n}}^l$ is an irreducible tensor of rank l, i.e. the tensor of rank l traceless and symmetric in any pair of its indexes, constructed with the vector $\hat{n}$. The symbol $\odot$ stands for full contraction.

3.1 Translational motion

The first-order irreducible multipole will allow us to determine the translational friction coefficient. For this purpose, our starting point will be the relationship between velocity and force multipoles which comes from Eq. (3.4) for $l = 0$

$$\mathbf{v}^{(1)} = \mathbf{v}_o^{(1)} + \boldsymbol{\mu}^{(1,1)} \odot \boldsymbol{\mathcal{F}}^{(1)}, \tag{3.1.1}$$

where the multipole $\mathbf{v}^{(1)}$ is

$$\mathbf{v}^{(1)} = \frac{1}{4\pi} \int d\hat{n}\ (\vec{u} + \vec{\Omega} \times a\hat{n}) = \vec{u}. \tag{3.1.2}$$

In the same way, by assuming that $\vec{v}_o(\vec{r}) = \boldsymbol{\beta} \cdot (\vec{R}_{cm} + a\hat{n})$ at the surface of the particle, we obtain

$$\mathbf{v}_o^{(1)} = \frac{1}{4\pi} \int d\hat{n}\ \boldsymbol{\beta} \cdot (\vec{R}_{cm} + a\hat{n}) = \boldsymbol{\beta} \cdot \vec{R}_{cm}, \tag{3.1.3}$$

where $\boldsymbol{\beta}$ is a constant traceless tensor with elongational and rotational contributions. The representation of the mobility kernel in terms of irreducible multipoles is

$$\boldsymbol{\mu}^{(1,1)} = \frac{2a}{3\eta_o} \{[1 - \frac{5}{2}\phi - \frac{3}{2}\phi\mu F(\mu)]\boldsymbol{I} + \frac{3}{4}\phi\mu F(\mu)(\boldsymbol{I} - \hat{H}\hat{H})\}. \tag{3.1.4}$$

Now, using the fact that the drag force exerted by the fluid on the particle (written in terms of the induced force) is [14]

$$\vec{F}^H = -\int dS \vec{f}^{\,i}(\hat{n}), \tag{3.1.5}$$

it follows that

$$\boldsymbol{\mathcal{F}}^{(1)} = \frac{1}{4\pi} \int d\hat{n} (\vec{f}^{\,i} - \frac{\hat{n} \times \vec{\tau}}{2}) = -\frac{\vec{F}^H}{4\pi a^2}. \tag{3.1.6}$$

Combining the results given through eqs. (3.1.1)-(3.1.6), we get the hydrodynamic force

$$\begin{aligned} \vec{F}^H(t) &= -6\pi\eta_o a\{[1 + \frac{5}{2}\phi + \frac{3}{4}\phi\mu F(\mu)](\boldsymbol{I} - \hat{H}(t)\hat{H}(t)) \\ &+ [1 + \frac{5}{2}\phi + \frac{3}{2}\phi\mu F(\mu)]\hat{H}(t)\hat{H}(t)\} \cdot (\vec{u}(t) - \boldsymbol{\beta} \cdot \vec{R}_{cm}), \end{aligned} \tag{3.1.7}$$

from which one can identify the translational friction tensor, valid up to the first order in the volume fraction of magnetic particles, ϕ, and for any value of the Langevin parameter μ, as

$$\begin{aligned} \boldsymbol{\xi}_t(t) &\equiv 6\pi\eta_o a\{[1 + \frac{5}{2}\phi + \frac{3}{4}\phi\mu F(\mu)](\boldsymbol{I} - \hat{H}(t)\hat{H}(t)) \\ &+ [1 + \frac{5}{2}\phi + \frac{3}{2}\phi\mu F(\mu)]\hat{H}(t)\hat{H}(t)\}. \end{aligned} \tag{3.1.8}$$

This tensor has two different components, one for the direction of the applied field and the other for the transversal directions, which are given by

$$\xi_t^{\parallel} \equiv 6\pi\eta_o a[1 + \frac{5}{2}\phi + \frac{3}{2}\phi\mu F(\mu)] \tag{3.1.9}$$

$$\xi_t^{\perp} \equiv 6\pi\eta_o a[1 + \frac{5}{2}\phi + \frac{3}{4}\phi\mu F(\mu)], \tag{3.1.10}$$

respectively.

For the saturation limit, $\mu \gg 1$, one has $\mu F(\mu) \rightarrow 1$. Consequently we obtain

$$\xi_t(t) \equiv 6\pi\eta_o a\{(1 + \frac{13}{4}\phi)(\boldsymbol{I} - \hat{H}(t)\hat{H}(t)) + (1 + 4\phi)\hat{H}(t)\hat{H}(t)\}. \tag{3.1.11}$$

This result coincides with the one given by Sellers and Brenner [1] for a suspension of gravitational dipoles in the saturation case.

Furthermore, from Eq. (3.1.7) , we can observe that the time dependence of the magnetic field does not introduce additional terms in the hydrodynamic force for this quasistationary situation. As we will demonstrate later, the hydrodynamic torque contains a new term involving the time derivative of the field.

As an illustration of the friction tensor structure, we consider the situation in which the hole is sedimenting under the action of gravity. If the magnetic fluid is initially at rest, and if the magnetic field is rotating in a plane perpendicular to the gravity direction, the sedimenting velocity decreases by a factor of $[1 - 5/2\phi - 3/4\phi\mu F(\mu)]$ compared to the one corresponding to a Newtonian fluid case. For a constant magnetic field, ($w_o = 0$), pointing towards direction $\hat{e}_z$, the terminal velocity is now reduced by a factor of $(1 - 4\phi)$. In addition, even if we consider a magnetic field rotating in a plane containing the gravity vector, the motion of the hole is slightly dependent on the field rotation frequency.

3.2 Rotational motion

In order to study the rotational motion of the nonmagnetic particle, we will consider the relationship between the second order irreducible multipoles

$$\mathbf{v}^{(2)} = 3\boldsymbol{\mu}^{(2,2)} \odot \boldsymbol{\mathcal{F}}^{(2)} + \mathbf{v}_o^{(2)}, \tag{3.2.1}$$

which comes from the general expression (3.4) for $l = 1$. The different multipoles are given by

$$\mathbf{v}^{(2)} = \frac{1}{4\pi}\int d\hat{n}\,\hat{n}\,[\vec{u} + \vec{\Omega}\times a\hat{n}] = \frac{a}{3}\,\epsilon\cdot\vec{\Omega}, \tag{3.2.2}$$

$$\mathbf{v}_o^{(2)} = \frac{1}{4\pi}\int d\hat{n}\,\hat{n}\,[\boldsymbol{\beta}\cdot(\vec{R} + a\hat{n})] = \frac{a}{3}\,\boldsymbol{\beta}^{\,T}, \tag{3.2.3}$$

and the corresponding matrix element by

$$\begin{aligned}\boldsymbol{\mu}^{(2,2)} &= \frac{a}{3\eta_o}\{[1 - \frac{5}{2}\phi - \frac{3}{2}\phi\mu F(\mu)](\frac{\mathbf{S}}{5} + \frac{\mathbf{A}}{3}) \\ &+ \frac{\phi}{10}\mu F(\mu)\mathcal{H}\},\end{aligned} \tag{3.2.4}$$

where we have defined the isotropic tensors $\mathbf{S}$ and $\mathbf{A}$, symmetric and antisymmetric in any pair of its indexes, respectively

$$S_{ijkl} = \frac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - \frac{1}{3}\delta_{ij}\delta_{kl}, \tag{3.2.5}$$

$$A_{ijkl} = \frac{1}{2}(\delta_{il}\delta_{jk} - \delta_{ik}\delta_{jl}), \tag{3.2.6}$$

and the tensor

$$\mathcal{H}_{ijkl} = \epsilon_{jim}\hat{H}_m\epsilon_{kln}\hat{H}_n + \epsilon_{jlm}\hat{H}_m\epsilon_{kin}\hat{H}_n + (\delta_{il}\delta_{jk} - \delta_{ik}\hat{H}_k\hat{H}_j). \tag{3.2.7}$$

The second-order multipole for the induced force is given by

$$\mathcal{F}^{(2)} = \frac{1}{4\pi}\int d\hat{n}\hat{n}(\vec{f}^{\,i} - \frac{\hat{n}\times\vec{\tau}^{\,i}}{2}). \tag{3.2.8}$$

After full contraction of Eq. (3.2.8) with the Levi-Civita tensor we obtain

$$\epsilon : \mathcal{F}^{(2)} = \frac{1}{4\pi a^3}[\vec{T}^H + \int_{r\le a} d\vec{r}(\vec{M}\times\vec{H})]. \tag{3.2.9}$$

To arrive at this expression, Eq. (2.2) has been used. The definition of the hydrodynamic torque rewritten in terms of the induced force and $\vec{\Pi}^a$ has been employed as well,

$$\vec{T}^H = -a^3\int d\hat{n}\hat{n}\times\vec{f}^{\,i} + 2\int d\vec{r}\vec{\Pi}^a. \tag{3.2.10}$$

Making use of Eq. (3.2.10) we can obtain an expression for the hydrodynamic torque acting on the magnetic hole. Actually, after multiplying Eq. (3.2.1) by ϵ on the left hand side and combining eqs. (3.2.1) - (3.2.9) we have

$$\begin{aligned}\vec{T}^H(t) &= -8\pi\eta_o a^3\{[1+\frac{5}{2}\phi+\frac{27}{20}\phi\mu F(\mu)](\boldsymbol{I}-\hat{H}(t)\hat{H}(t)) \\ &+ [1+\frac{5}{2}\phi+\frac{3}{10}\phi\mu F(\mu)]\hat{H}(t)\hat{H}(t)\}\cdot(\vec{\Omega}(t)-\vec{\Omega}_o) \\ &- \int_{r\leq a} d\vec{r}(\vec{M}\times\vec{H}),\end{aligned} \tag{3.2.11}$$

where we have defined the vorticity field $\vec{\Omega}_o \equiv \frac{1}{2}\boldsymbol{\epsilon} : \boldsymbol{\beta}$. In particular, if the particle is rotating with the same angular velocity as that of the magnetic fluid in the absence of the hole, $\vec{\Omega}_o$, it turns out that the hydrodynamic torque exerted on such a hole is equal to the external torque acting upon the volume of the magnetic fluid displaced by the particle, but with the opposite sign. One then obtains

$$\vec{T}^H(t) = -\int_{r\leq a} d\vec{r}(\vec{M}\times\vec{H}). \tag{3.2.12}$$

From this expression, we conclude that under these conditions the magnetic hole bears an induced magnetic moment equal to that which corresponds to the volume of ferrofluid displaced by the hole. This result was also achieved in Ref. [1] for gravitational dipoles.

However, in a more general case where $\vec{\Omega} \neq \vec{\Omega}_o$, using Eq. (2.12) we obtain

$$\int_{r\leq a} d\vec{r}(\vec{M}\times\vec{H}) = -8\pi\eta_o a^3\phi\mu F(\mu)[(\boldsymbol{I}-\hat{H}(t)\hat{H}(t))\cdot\vec{\Omega}+\frac{d\hat{H}}{dt}\times\hat{H}], \tag{3.2.13}$$

which replaced in Eq. (3.2.11) yields

$$\begin{aligned}\vec{T}^H(t) &= -8\pi\eta_o a^3\{[1+\frac{5}{2}\phi+\frac{7}{20}\phi\mu F(\mu)](\boldsymbol{I}-\hat{H}(t)\hat{H}(t)) \\ &+ [1+\frac{5}{2}\phi+\frac{3}{10}\phi\mu F(\mu)]\hat{H}(t)\hat{H}(t)\}\cdot(\vec{\Omega}(t)-\vec{\Omega}_o) \\ &+ 8\pi\eta_o a^3\phi\mu F(\mu)[(\boldsymbol{I}-\hat{H}(t)\hat{H}(t))\cdot\vec{\Omega}_o+\frac{d\hat{H}}{dt}\times\hat{H}].\end{aligned} \tag{3.2.14}$$

For a constant field and under saturation conditions, the last expression reads

$$\begin{aligned}\vec{T}^H &= -8\pi\eta_o a^3\{[1+\frac{57}{20}\phi](\boldsymbol{I}-\hat{H}\hat{H})+[1+\frac{14}{5}\phi]\hat{H}\hat{H}\}\cdot(\vec{\Omega}-\vec{\Omega}_o) \\ &+ 8\pi\eta_o a^3\phi(\boldsymbol{I}-\hat{H}\hat{H})\cdot\vec{\Omega}_o.\end{aligned} \tag{3.2.15}$$

This expression is also similar to the corresponding one obtained by Sellers and Brenner for gravitational dipoles.

It is worth mentioning that, for the rotational motion, the time dependence of the magnetic field gives rise to an extra term in the hydrodynamic torque proportional to $\frac{d\hat{H}}{dt} \times \hat{H}$ for the quasistationary analysis. As we will see, for the field rotation frequencies under consideration, this term is responsible for the counter-rotation of the hole in respect to the field rotation, as observed by Helgesen and Skjeltorp [2] and by Popplewell *et al.* [15].

The magnetic hole rotational equation of motion is given by

$$I\frac{d\vec{\Omega}}{dt} = \vec{T}^H, \tag{3.2.16}$$

where I is the moment of inertia of the particle. Again, since the inertial term is negligible, the result is that $\vec{T}^H = 0$. For a ferrofluid initially at rest, where $\vec{\Omega}_o = 0$, and up to the first order in the volume fraction, ϕ, from Eq. (3.2.14) we obtain

$$\vec{\Omega}(t) = \phi\mu F(\mu)(\frac{d\hat{H}}{dt} \times \hat{H}). \tag{3.2.17}$$

In particular, if we consider an external magnetic field rotating in the XY plane with angular frequency ω_o, $\hat{H}(t) = \cos w_o t\hat{e}_x + \sin w_o t\hat{e}_y$, the magnetic hole angular velocity reduces to

$$\vec{\Omega} = -\phi\mu F(\mu)\omega_o\hat{e}_z. \tag{3.2.18}$$

From this expression, we then conclude that the direction of the rotation of the spheres is opposite the field rotation. Additionally, we obtain a linear relationship between the field frequency and the rotation frequency of the spheres for the range of field frequencies we are considering in our analysis, that is, for frequencies which enable us to perform a quasistationary treatment. Moreover, under these conditions, $\vec{\Omega}$ is independent of the size of the spheres, it only depends on the volume fraction of magnetic particles and on the Langevin parameter.

4 Comparison with experiments

The rotation of magnetic holes induced by a rotating magnetic field has been observed in recent experiments [2, 15]. The experimental setup consists of a thin layer of ferrofluid, confined between two glass plates, in which spherical particles of polystyrene are dispersed. When applying a magnetic field rotating in the plane of the plates,

it was observed that the particles rotate in the opposite direction. The experiments were performed for kerosene-based [2] and water-based ferrofluids [2, 15]. The rotation frequency of the hole, $\vec{\Omega}$, for the kerosene-based ferrofluid, which showed good signs of homogeneity, was measured for different samples containing polystyrene spheres of various sizes. They saw that $\vec{\Omega}$ was independent of the size of the spheres, for the size range they took into consideration. Furthermore, in the intermediate frequency range, they observed a linear relationship between the angular velocity of the sphere and the angular velocity of the magnetic field.

In the case of a water-based ferrofluid, it has been clarified that it shows a weak tendency of sedimentation and aggregation phenomena under the action of the field [2]. In the same reference, the different response of the magnetic hole when suspended in both types of ferrofluids was also emphasized. At this point, it should be noted that there is not total agreement between the results of [2] and [15] concerning such a ferrofluid. In particular, Popplewell and coworkers conclude that particles of about $2a \simeq 70\mu m$ rotate opposite the direction of the field, for any value of ω_o, whereas smaller particles, $2a \simeq 20\mu m$, rotate in the field direction at field frequencies below $70Hz$ and in the opposite direction at higher frequencies. However, Helgesen and Skjeltorp were not able to reproduce these results. Additionally, in both papers there are also experimental data relating the holes rotation frequency and the external field strength at intermediate values of ω_o.

In regards to the coupling between translational and rotational motion, the experimental observations corroborate our results. This can easily be concluded after inspection of the equations for the force and torque given by eqs. (3.1.7) and (3.2.14) . Moreover, our result given through Eq. (3.2.18) is in complete agreement with the observations carried out for the kerosene-based ferrofluid in the range of intermediate field frequencies, which, as we have stated before, enables us to perform a quasistationary study of the system. This can be seen in Fig. III.1 for a ferrofluid with the same characteristic as that considered in Ref. [2], that is, for volume fraction of magnetic particles $\phi \simeq 0.1$ and saturation magnetization of $200G$. On the other hand, as far as the theory is concerned, we can also indicate that we have obtained a rotation frequency which does not depend on the viscosity of the solvent (3.2.18) .

Despite the possibility of the inhomogeneities in water-based ferrofluids, mentioned in Ref. [2], the dependence of Ω on the field strength seems to be represented by a saturation curve as the one corresponding to the quantity

$$\mu F(\mu) = \frac{\mu - \tanh \mu}{\mu + \tanh \mu} \tag{4.1}$$

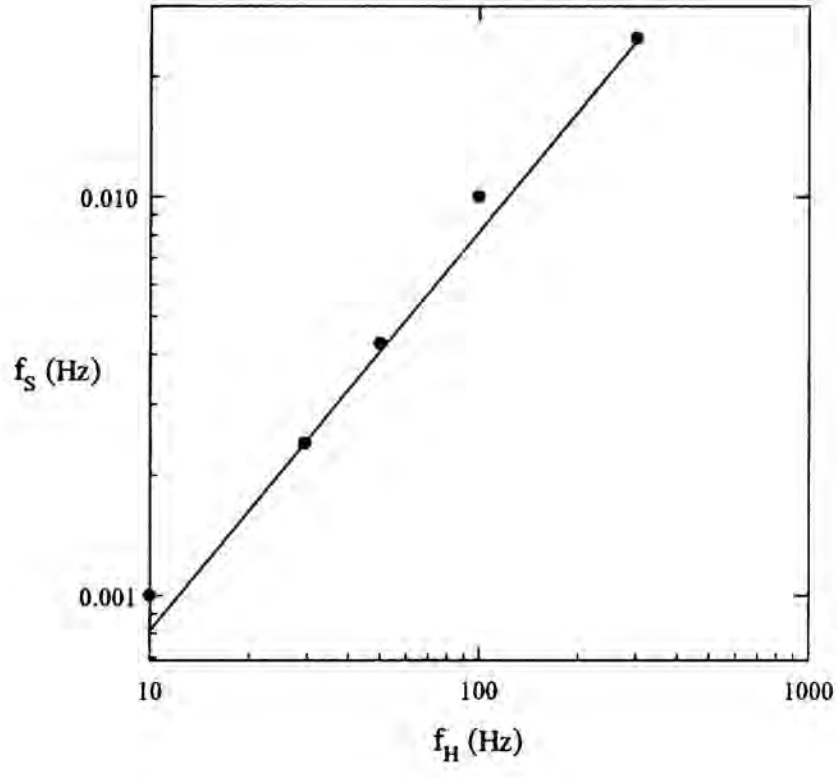

Figure III.1: Rotation frequency of a magnetic hole in a kerosene-based ferrofluid layer versus the frequency f_H of the rotating magnetic field for $H = 14Oe$. The direction of rotation of the spheres is opposite to that of the field.

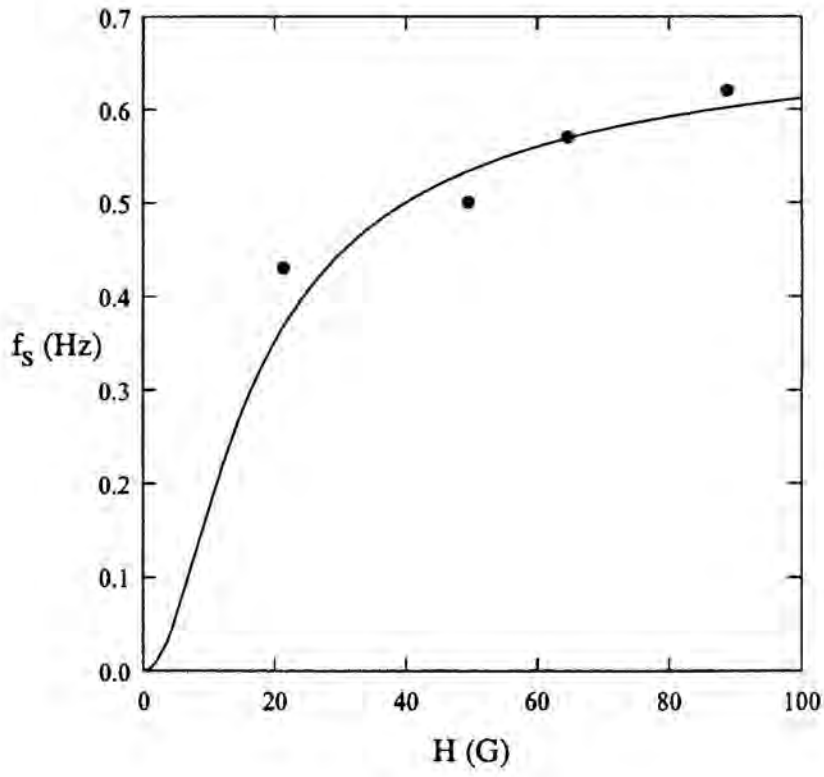

Figure III.2: Variation of particle rotation with the field strength. Rotation counter to the field rotation. ($a = 35\mu m, f_H = 60Hz$)

involved in our Eq. (3.2.18) . In Fig. III.2, we have represented the frequency as a function of the imposed field for a ferrofluid with the same magnetization as that considered by Popplewell and coworkers. Finally, it is worth mentioning that in accordance with Ref. [2], we cannot reproduce the dependence of the frequency on the size of the particles as observed in Ref. [15].

5 Hydrodynamic interactions between pairs of magnetic holes

Hydrodynamic interactions among different objects moving in a viscous fluid have been extensively studied because of their effects on the dynamics and consequently on certain properties of the whole dispersion [17, 18]. The first studies of these interactions were undertaken by Smoluchowski using the so-called methods of reflection. But, due to their complexity, they have only been applied to the case of a pair of particles. On the other hand, the method of induced forces, first introduced by Mazur [19] and generalized in Ref. [12] for a system of N spheres moving in a simple liquid, permits to calculate the mobility tensors to any desired order of approximation as an expansion in the inverse distance between the particles. In this section, we first develop the latter technique to study the hydrodynamic interactions between pairs of spherical nonmagnetic particles moving in an anisotropic magnetic liquid.

5.1 Oseen and Rotne-Prager tensors for the ferrofluid

We will now consider a suspension of N spherical magnetic holes of radii a_i, $(i = 1, ..., N)$, in an unbounded incompressible ferrofluid under the influence of an external magnetic field, which may rotate with constant angular velocity w_o. The suspension under consideration is dilute enough to avoid aggregation due to the interaction of the induced magnetic moments of the holes. On the other hand, it contains a sufficient number of particles so that hydrodynamic interactions between pairs of spheres must be considered. As in the previous sections, the ferrofluid is assumed to be a continuum medium based on the fact that the size of the holes is much larger than that of the ferromagnetic particles constituting such a ferrofluid.

Our starting point for analyzing the quasistationary motion of the particles will be the linearized equations of conservation of the linear and angular momenta, which now read

$$0 = -\nabla p + \eta \nabla^2 \vec{v} - \nabla \times \vec{\Pi}^{(a)} + \sum_{j=1}^{N} \vec{F}_j^{ind}, \tag{5.1.1}$$

$$0 = 2\vec{\Pi}^a + \vec{M} \times \vec{H} + \sum_{j=1}^{N} \vec{\tau}_j^{ind}, \tag{5.1.2}$$

together with

$$0 = \nabla \cdot \vec{v}, \tag{5.1.3}$$

where we have introduced a set of induced forces and torques densities, $\vec{F}_j^{ind}(\vec{r},t)$ and $\vec{\tau}_j^{ind}(\vec{r},t)$, $(j = 1,...,N)$ which originate from the perturbation caused by the motion of the holes. As we have explained before, the extension of the fluid velocity field inside the particles imposes the requirement $\vec{F}_j^{ind}(\vec{r},t) = \vec{\tau}_j^{ind}(\vec{r},t) = 0$, for $|\vec{r} - \vec{R}_j(t)| > a_j$ and $(j = 1,...,N)$. $\vec{R}_j(t)$ gives the position of the sphere center at time t. Furthermore, the set of equations including induced forces and torques must be completely equivalent with the original boundary value problem

$$\vec{v}(\vec{r},t) = \vec{u_j}(t) + \vec{\Omega_j}(t) \times (\vec{r} - \vec{R}_j(t)), \quad \text{for } |\vec{r} - \vec{R}_j(t)| \leq a_j, \tag{5.1.4}$$

i.e., stick boundary conditions at the surfaces of the spheres. Similarly, for the hydrostatic pressure we impose the condition

$$p(\vec{r},t) = 0, \quad \text{for } |\vec{r} - \vec{R}_j(t)| < a_j, \tag{5.1.5}$$

and for the magnetization

$$\vec{M}(\vec{r},t) = 0, \quad \text{for } |\vec{r} - \vec{R}_j(t)| \leq a_j, \tag{5.1.6}$$

where we have introduced $\vec{u}_j$ and $\vec{\Omega}_j$ as the translational and rotational velocities of the particle j, respectively. Consequently, considering these conditions and for the quasistationary case, all the induced force and torque densities must be of the same form as in Section 2. If we want to consider a rotating magnetic field, its angular frequency should be low enough to consider the quasistationary limit in which the derivatives of the hydrodynamic fields, although time dependent, may be neglected.

In appendix A we obtain the expression for the magnetization density. Substituting this result in Eq. (5.1.2), and combining eqs. (5.1.1) and (5.1.2) we can write the following equation

$$0 = -\nabla p + (\eta + \eta_r)\nabla^2 \vec{v} + \eta_r \nabla \times \hat{H}(\hat{H} \cdot \nabla \times \vec{v}) + \sum_{j=1}^{N} \vec{\mathcal{F}}_j^{ind}, \tag{5.1.7}$$

where η_r is the rotational viscosity, and where we have defined $\vec{\mathcal{F}}_j^{ind}$ as the combination of the induced force and torque field densities

$$\vec{\mathcal{F}}_j^{ind}(\vec{r}, t) \equiv \vec{F}_j^{ind}(\vec{r}, t) + \frac{1}{2}\nabla \times \vec{\tau}_j^{ind}(\vec{r}, t). \tag{5.1.8}$$

In order to solve formally the equation of motion of the fluid (5.1.7), we introduce Fourier transforms of the velocity field $\vec{v}$. From now on, we will omit the explicit dependence on time of the different fields. We also define the Fourier transform of the induced force density $\vec{\mathcal{F}}_j^{ind}$ in a reference frame in which sphere j is at rest at the origin

$$\vec{\mathcal{F}}_j^{ind}(\vec{k}) = \int d\vec{r} exp[-i\vec{k} \cdot (\vec{r} - \vec{R}_j)]\vec{\mathcal{F}}_j^{ind}(\vec{r}). \tag{5.1.9}$$

After Fourier transforming this equation and applying the transversal projector $(\boldsymbol{I} - \hat{k}\hat{k})$, with $\hat{k} \equiv \vec{k}/k$, one arrives at the formal solution for the transversal component of the velocity field

$$\vec{v}(\vec{k}) = \boldsymbol{T}(\vec{k}, t) \cdot \sum_{j=1}^{N} exp(-i\vec{k} \cdot \vec{R}_j)\vec{\mathcal{F}}_j^{ind}(\vec{k}), \tag{5.1.10}$$

where, as in Section 2, we have introduced the propagator (2.16).

As we have indicated before, the spheres are allowed to move with arbitrary velocity through the fluid, which may itself be in arbitrary stationary non-uniform unperturbed flow. For the sake of simplicity, we will consider that the unperturbed fluid is at rest, and we will study the hydrodynamic interactions which are set up between the spheres when they move. In particular our main goal is to calculate the translational mobility up to a given order of approximation in a series expansion in powers of inverse distances between the spheres, when only hydrodynamic interactions between two spheres contribute.

The formal solution can be rewritten in real space

$$\vec{v}(\vec{r}, t) = \sum_{j=1}^{N} \int d\vec{r}\,' \boldsymbol{T}(\vec{r} - \vec{r}\,') \cdot \vec{\mathcal{F}}_j^{ind}(\vec{r}\,'). \tag{5.1.11}$$

In particular, for those points on the surface of the sphere i, and after taking into consideration the properties of the generalized induced force, we have

$$\vec{v}(\vec{R}_i + a_i\hat{n}_i) = \sum_{j=1}^{N} \int d\hat{n}_j \mu(\hat{n}_i, \hat{n}_j) \cdot [\vec{f}_j^{ind}(\hat{n}_j) - \frac{\hat{n}_j \times \vec{\tau}_j^{ind}}{2}], \tag{5.1.12}$$

where we have introduced the response function

$$\mu(\hat{n}_i, \hat{n}_j) = \frac{a_j^2}{(2\pi)^3} \int d\vec{k}\ exp(i\vec{k} \cdot (\vec{R}_{ij} + a_i\hat{n}_i - a_j\hat{n}_j))\ \boldsymbol{T}(\vec{k}) \tag{5.1.13}$$

with the definition $\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$. For the purpose of evaluating hydrodynamic interactions, it is convenient to introduce irreducible induced force multipoles, defined in terms of the surface induced forces according to

$$\mathcal{F}_i^{(l+1)} = \frac{1}{4\pi} \int d\hat{n}_i\ \hat{n}_i^l [\vec{f}_i^{ind}(\hat{n}_i) - \frac{\hat{n}_i \times \vec{\tau}_i^{ind}}{2}], \tag{5.1.14}$$

where $\hat{n}_i^l$ is an irreducible tensor of rank l, traceless and symmetric in any pair of its indices. The expansion in terms of irreducible force multipoles, which is written in a coordinate free way, is equivalent to an expansion in spherical harmonics, to which it can be reduced if polar coordinates are used.

We also introduce irreducible surface moments of the fluid velocity field, and we obtain a relationship between the induced force multipoles and the surface moments of the fluid velocity field through a hierarchy of equations. It is this hierarchy which will then enable us to obtain expressions for the mobility tensors which relate the forces and torques on the spheres to their lineal and angular velocities.

The general relationship between the $(l+1)$ order multipoles of the quantities defined over the surface of the sphere is found to be,

$$\mathbf{v}_i^{(l+1)} = \sum_{j=1}^{N} \sum_{l'=0}^{\infty} \frac{(2l'+1)!!}{l'!} \boldsymbol{\mu}_{ij}^{(l+1,l'+1)} \odot \mathcal{F}_j^{(l'+1)}, \tag{5.1.15}$$

which involves the tensors

$$\boldsymbol{\mu}_{ij}^{(l+1,l'+1)} = \frac{1}{(4\pi)} \int d\hat{n}_i \int d\hat{n}_j \hat{n}_i^l\ \mu(\hat{n}_i, \hat{n}_j) \hat{n}_j^{l'}. \tag{5.1.16}$$

As we already pointed out in Section 3, the first order irreducible multipole will allow us to determine the translational mobility. Thus, our starting point will be the relationship between velocity and force multipoles which comes from Eq. (5.1.15) for $l = 0$

$$\mathbf{v}_i^{(1)} = \sum_{j=1}^{N} \sum_{l'=0}^{\infty} \frac{(2l'+1)!!}{l'!} \boldsymbol{\mu}_{ij}^{(1,l'+1)} \odot \mathcal{F}_j^{(l'+1)}, \tag{5.1.17}$$

where the multipole $\mathbf{v}_i^{(1)}$ is

$$\mathbf{v}_i^{(1)} = \frac{1}{4\pi}\int d\hat{n}_i\ (\vec{u}_i + \vec{\Omega}_i \times a_i\hat{n}_i) = \vec{u}_i. \tag{5.1.18}$$

Moreover, using the fact that the drag force exerted by the fluid on the particle j (written in terms of the induced force) is

$$\vec{F}_j^H = -\int dS_j \vec{f}_j^{ind}(\hat{n}_j), \tag{5.1.19}$$

it follows that

$$\mathcal{F}_j^{(1)} = \frac{1}{4\pi}\int d\hat{n}_j(\vec{f}_j^{ind} - \frac{\hat{n}_j \times \vec{\tau}_j}{2}) = -\frac{\vec{F}_j^H}{4\pi a_j^2}. \tag{5.1.20}$$

In Section 3, we already gave the exact form of this relationship for the case $i = j$. We obtained,

$$\begin{aligned}\vec{F}_i^H &= -6\pi\eta_o a_i\{[1+\frac{5}{2}\phi+\frac{3}{4}\phi\mu F(\mu)](\boldsymbol{I}-\hat{H}\hat{H}) \\ &+ [1+\frac{5}{2}\phi+\frac{3}{2}\phi\mu F(\mu)]\hat{H}\hat{H}\}\cdot\vec{u}_i,\end{aligned} \tag{5.1.21}$$

Now, we will look at the case $i \neq j$. In this case, the tensors $\mu_{ij}^{(l+1,l'+1)}$ are no longer diagonal in their upper indices, so that there is a coupling between different multipoles. But, if we set $l = 0$, we will restrict ourselves to the lowest value of l' ($l' = 0$), because beyond that, we will obtain contributions proportional to $(a/R)^p$ with $p \geq 4$ [12], negligible for the concentration of holes we are considering. The corresponding matrix is

$$\mu_{ij}^{(1,1)} = \frac{a_j^2}{(2\pi^2)}\int d\vec{k}\int dk\ exp(i\vec{k}\cdot\vec{R}_{ij})\ \boldsymbol{h}^{-1}(\hat{k})\cdot(\boldsymbol{I}-\hat{k}\hat{k})j_o(ka_i)j_o(ka_j). \tag{5.1.22}$$

where $j_o(x)$ is the spherical Bessel function of zero order. In appendix C we obtain that

$$\begin{aligned}\mu_{ij}^{(1,1)} &= \frac{a_j^2}{2\eta_o R_{ij}}\{[1-\frac{5}{2}\phi-\frac{3}{2}\phi\mu F(\mu)](\boldsymbol{I}+\hat{R}_{ij}\hat{R}_{ij}) \\ &+ \frac{3}{2}\phi\mu F(\mu)[\boldsymbol{I}-\hat{H}\hat{H}-(\hat{R}_{ij}\times\hat{H})(\hat{R}_{ij}\times\hat{H})]\} \\ &+ \frac{a_j^2(a_i^2+a_j^2)}{2\eta_o R_{ij}^3}\{[1-\frac{5}{2}\phi-\frac{3}{2}\phi\mu F(\mu)](\frac{1}{3}\boldsymbol{I}-\hat{R}_{ij}\hat{R}_{ij}) \\ &- \frac{3}{2}\phi\mu F(\mu)[\frac{1}{3}(\boldsymbol{I}-\hat{H}\hat{H})-(\hat{R}_{ij}\times\hat{H})(\hat{R}_{ij}\times\hat{H})]\},\end{aligned} \tag{5.1.23}$$

from which the translational mobility tensor comes up straightforwardly, after taking into account eqs. (5.1.17) - (5.1.20)

$$\begin{aligned}
\boldsymbol{\mu}_{ij}^{RP} &= \frac{1}{8\pi\eta_o R_{ij}}\{[1-\frac{5}{2}\phi-\frac{3}{2}\phi\mu F(\mu)](\boldsymbol{I}+\hat{R}_{ij}\hat{R}_{ij}) \\
&+ \frac{3}{2}\phi\mu F(\mu)[\boldsymbol{I}-\hat{H}\hat{H}-(\hat{R}_{ij}\times\hat{H})(\hat{R}_{ij}\times\hat{H})]\} \\
&+ \frac{(a_i^2+a_j^2)}{8\pi\eta_o R_{ij}^3}\{[1-\frac{5}{2}\phi-\frac{3}{2}\phi\mu F(\mu)](\frac{1}{3}\boldsymbol{I}-\hat{R}_{ij}\hat{R}_{ij}) \\
&- \frac{3}{2}\phi\mu F(\mu)[\frac{1}{3}(\boldsymbol{I}-\hat{H}\hat{H})-(\hat{R}_{ij}\times\hat{H})(\hat{R}_{ij}\times\hat{H})]\}, \qquad (5.1.24)
\end{aligned}$$

This mobility tensor represents the velocity of a sphere i with respect to the fluid velocity due to the motion of the particle j, and per unit of force exerted on sphere j. It is valid up to the first order in the volume fraction of magnetic particles, ϕ, and up to third order in the ratio (a/R_{ij}), for any value of the Langevin parameter μ.

From this expression, we can also obtain the corresponding Oseen tensor for the ferrofluid. The Oseen tensor is the first approximation when computing hydrodynamic effects. Nevertheless, it is a valid approximation when the particles are far apart enough, and we can assume that particle j generates the same perturbation as would be produced by a point force situated at its center. Thus, the Oseen tensor is obtained after neglecting the third power of (a/R_{ij}),

$$\begin{aligned}
\boldsymbol{\mu}_{ij}^{O} &= \frac{1}{8\pi\eta_o R_{ij}}\{[1-\frac{5}{2}\phi-\frac{3}{2}\phi\mu F(\mu)](\boldsymbol{I}+\hat{R}_{ij}\hat{R}_{ij}) \\
&+ \frac{3}{2}\phi\mu F(\mu)[\boldsymbol{I}-\hat{H}\hat{H}-(\hat{R}_{ij}\times\hat{H})(\hat{R}_{ij}\times\hat{H})]\}, \qquad (5.1.25)
\end{aligned}$$

Obviously, if we set the volume fraction of magnetic particles equal to zero, $\phi = 0$, this Oseen tensor reduces to the well-known expression

$$\boldsymbol{\mu}_{ij}^{O} = \frac{1}{8\pi\eta_o R_{ij}}(\boldsymbol{I}+\hat{R}_{ij}\hat{R}_{ij}), \qquad (5.1.26)$$

which is the propagator of the perturbations in a simple fluid.

5.2 Sedimentation of two magnetic holes in a ferrofluid

To illustrate the influence of hydrodynamic interactions on the suspension of magnetic holes, we will study the sedimentation in the presence of an external magnetic field.

For the sake of simplicity, we will consider two equal-sized non-rotating ($\vec{\Omega}_i = 0$) magnetic holes of radii a and mass m falling down under the influence of gravity. In accordance with the definition of the mobilities we can establish the following relations

$$\vec{u}_1 = -\boldsymbol{\mu}_{11} \cdot \vec{F}_1 - \boldsymbol{\mu}_{12} \cdot \vec{F}_2, \tag{5.2.1}$$

$$\vec{u}_2 = -\boldsymbol{\mu}_{21} \cdot \vec{F}_1 - \boldsymbol{\mu}_{22} \cdot \vec{F}_2, \tag{5.2.2}$$

where $\boldsymbol{\mu}_{ij}$, $(i,j = 1,2)$ are translational mobility tensors. We also assume that both particles are located at a relatively large distance from each other, and that we may compute the translational effect of particle 1 by considering the Rotne-Prager or the Oseen tensor obtained in the previous subsection.

Alternatively, we can write

$$\vec{F}_1 = -\boldsymbol{\mu}_{11}^{-1} \cdot [\boldsymbol{I} - \boldsymbol{\mu}_{12} \cdot \boldsymbol{\mu}_{22}^{-1} \cdot \boldsymbol{\mu}_{21} \cdot \boldsymbol{\mu}_{11}^{-1}]^{-1} \cdot [\vec{u}_1 - \boldsymbol{\mu}_{12} \cdot \boldsymbol{\mu}_{22}^{-1} \cdot \vec{u}_2], \tag{5.2.3}$$

and a similar expression for $\vec{F}_2$ by changing the index 1 by 2. However, for two equal-sized spheres the force acting on each particle is the same, and their velocities are also equal. If we introduce $\vec{u}_\infty$ as the sedimentation velocity of the spheres falling alone in an infinite viscous fluid

$$\vec{F}_1 = -\boldsymbol{\mu}_{11}^{-1} \cdot \vec{u}_\infty, \tag{5.2.4}$$

we have that

$$\vec{u}_\infty = [\boldsymbol{I} - \boldsymbol{\mu}_{12} \cdot \boldsymbol{\mu}_{22}^{-1} \cdot \boldsymbol{\mu}_{21} \cdot \boldsymbol{\mu}_{11}^{-1}]^{-1} \cdot [\boldsymbol{I} - \boldsymbol{\mu}_{12} \cdot \boldsymbol{\mu}_{22}^{-1}] \cdot \vec{u}. \tag{5.2.5}$$

But we can also write

$$\vec{u} = [\boldsymbol{I} + \boldsymbol{\mu}_{12} \cdot \boldsymbol{\mu}_{22}^{-1} + O(a/R)^3] \cdot \vec{u}_\infty, \tag{5.2.6}$$

where

$$\begin{aligned} \boldsymbol{\mu}_{12} \cdot \boldsymbol{\mu}_{22}^{-1} &= \frac{3a}{4R}\{[1 + \frac{3}{4}\phi\mu F(\mu)](\boldsymbol{I} - \hat{H}\hat{H}) + \hat{H}\hat{H} + [1 - \frac{3}{4}\phi\mu F(\mu)]\hat{R}\hat{R} \\ &+ \frac{3}{4}\phi\mu F(\mu)(\hat{R} \cdot \hat{H})\hat{R}\hat{H} - \frac{3}{2}\phi\mu F(\mu)(\hat{R} \times \hat{H})(\hat{R} \times \hat{H})\}. \end{aligned} \tag{5.2.7}$$

Starting from Eq. (5.2.6), let us consider two particular cases:

a) The orientation of the vector $\vec{R} = R\hat{R}$ giving the relative position of the couple of particles is contained in the YZ-plane and forms an angle θ with the $\hat{e}_y$ axis, $\hat{R} = \cos\theta\hat{e}_y + \sin\theta\hat{e}_z$, the magnetic field is pointing towards the $\hat{e}_z$ axis $\hat{H} = \hat{e}_z$, gravity is directed opposite to the magnetic field $\vec{g} = -g\hat{e}_z$, and consequently, $\vec{u}_\infty = -u_\infty\hat{e}_z$. For this configuration, we have

$$u_z = [1 + \frac{3a}{4R}(1 + \sin^2\theta)]u_\infty, \tag{5.2.8}$$

$$u_y = \frac{9a}{16R}\phi\mu F(\mu)\sin\theta\cos\theta u_\infty. \tag{5.2.9}$$

Thus, for $\theta = 0$, i.e. for two spheres falling perpendicular to their line of centers

$$u_z = (1 + \frac{3a}{4R})u_\infty, \tag{5.2.10}$$

$$u_y = 0. \tag{5.2.11}$$

And for $\theta = \pi/2$, i.e. two spheres falling parallel to their line of centers

$$u_z = (1 + \frac{3a}{2R})u_\infty, \tag{5.2.12}$$

$$u_y = 0. \tag{5.2.13}$$

So, up to first order in (a/R), we obtain exactly the same ratio u/u_∞ as in the case of two spheres falling in a simple fluid [18].

b) The orientation of the relative position vector is pointing towards the $\hat{e}_y$ axis, $\hat{R} = \hat{e}_y$, the magnetic field is in the YZ-plane forming an angle α with the $\hat{e}_y$ axis, $\hat{H} = \cos\alpha\hat{e}_y + \sin\alpha\hat{e}_z$, $\vec{g} = -g\hat{e}_z$, and, consequently, $\vec{u}_\infty = u_{\infty,y}\hat{e}_y - u_{\infty,z}\hat{e}_z$.

In this case, the velocity of the particles is given by

$$u_z = u_{\infty,z} + \frac{3a}{4R}\left((1 + \frac{3}{4}\phi\mu F(\mu)\cos^2\alpha)u_{\infty,z} - \frac{3}{4}\phi\mu F(\mu)\sin\alpha\cos\alpha u_{\infty,y}\right), \tag{5.2.14}$$

$$u_y = (1 + \frac{3a}{2R})u_{\infty,y}, \tag{5.2.15}$$

where the components of the free particle velocity $\vec{u}_\infty$ are

$$u_{\infty,z} = -\frac{mg}{6\pi\eta_o a}\left((1 - \frac{5}{2}\phi) - \frac{3}{4}\phi\mu F(\mu)(1 + \sin^2\alpha)\right), \tag{5.2.16}$$

$$u_{\infty,y} = \frac{mg}{8\pi\eta_o a}\phi\mu F(\mu)\sin\alpha\cos\alpha. \qquad (5.2.17)$$

In contrast with the previous result, for this configuration the ratio $u_z/u_{\infty,z}$ depends not only on the orientation of the magnetic field in the YZ-plane but also on the parameters characterizing the ferrofluid, the Langevin parameter μ and the volume fraction of magnetic particles ϕ. But, we can also conclude that the very components of the sedimentation velocity are different from that of a simple fluid for both configurations. The origin of such a difference is simply the velocity of a free magnetic hole in a ferrofluid, $\vec{u}_\infty$.

6 Conclusions

We have studied the dynamics of a nonmagnetic particle or magnetic hole suspended in a ferrofluid in the presence of a rotating magnetic field. Our analysis leads to expressions for the hydrodynamic force and torque exerted on the hole from which we can identify the translational and rotational friction tensors. These quantities depend on the volume fraction of magnetic particles and of the magnetic field, which gives an anisotropic character to the system. The knowledge of the force and torque acting on the hole enables us to study both the translational and rotational dynamics of the particles when applying a rotating magnetic field.

In particular, we have focused on the case when the ferrofluid is at rest and the hole may rotate influenced by the magnetic field. Under these conditions, we have shown that the angular velocity of the hole is proportional to the frequency of the field, but has an opposite direction. The proportionality coefficient is linear in the volume fraction of ferromagnetic particles and depends on a function of the parameter μ, which tends to one in the saturation limit. Our theory is valid for frequencies of the field up to $10^3 Hz$ approximately.

We have compared our results to experiments done with particles of polystyrene dispersed in different ferrofluids. In the frequency range we are considering, our linear law agrees with the experiments. Additionally, we have also reproduced experimental results giving the rotational velocity of the hole as a function of the external magnetic field.

A preliminary study of the hydrodynamic interactions in the carrier ferrofluid has also been carried out. Essentially, we have obtained the expressions for the Rotne-Prager and the Oseen equivalent tensors as the simplest approximation for the propagator of the perturbations in a ferrofluid. Despite of its simplicity, they constitute the

first steps in the study of the important role that hydrodynamic interactions can play in the physical properties of these composite materials at low concentrations. Two show up the structure of these tensors and their influence on the dynamics of the magnetic holes, we have also given the velocities of a couple of particles falling under the action of gravity in a ferrofluid. As we expected, for the different initial configurations, the velocity does depend on the parameters characterizing the ferrofluid.

Finally, it is worth pointing out that although we have performed the study for a ferrofluid constituted by rigid dipoles, for which the energy of anisotropy is much greater than the energy associated with the interaction of the magnetic moments and the external field, the same analysis could be carried out for a general situation in which these two energies of the magnetic particles in the ferrofluid may take arbitrary values.

Appendix A

The Smoluchowski equation for a rotating magnetic field

The Smoluchowski equation giving the probability density $\psi(\hat{R},t)$ for the orientation of the magnetic moment vector, $\hat{R}$, is

$$\frac{\partial\psi}{\partial t} = -\vec{\mathcal{R}}\cdot(D_r\mu\hat{R}\times\hat{H}(t)+\vec{\Omega}_o)\psi + D_r\vec{\mathcal{R}}\cdot\vec{\mathcal{R}}\psi, \tag{A1}$$

where $\vec{\mathcal{R}}\equiv\hat{R}\times\frac{\partial}{\partial\hat{R}}$ is the rotational operator. This equation was first introduced by Martsenyuk it et al. [16] for a constant magnetic field without the vorticity field.

In Section 3.2 of the first chapter and in Ref. [13] we indicated how to calculate the first moment of $\hat{R}$ from the Smoluchowski equation. For the case in which the magnetic field is time-dependent, one obtains

$$\frac{d\langle\hat{R}\rangle}{dt} = D_r\{-2\langle\hat{R}\rangle+\mu\hat{H}-\mu\langle\hat{R}\hat{R}\rangle\cdot\hat{H}+\frac{\vec{\Omega}_o}{D_r}\times\langle\hat{R}\rangle\}. \tag{A2}$$

As a solution for this equation we propose,

$$\langle\hat{R}\rangle = \mathcal{L}(\mu)\hat{H}(t)+D_r^{-1}[F(\mu)(\vec{\Omega}_o\times\hat{H}(t))+G(\mu)\frac{d\hat{H}}{dt}], \tag{A3}$$

which is valid up to first order in Ω_o/D_r. Note that the underlying idea for such a proposition is that both the vorticity of the flow and the rotation of the field are the only mechanisms responsible for the deviation of the averaged orientation vector from the direction of the applied magnetic field.

In expression (A3) the functions F and G are simply undetermined quantities. To know their explicit form, we have to substitute such a solution in Eq. (A2) . In addition, and as a previous step, we must know the value of the second moment of $\hat{R}$ appearing in the same equation. To this end, we will introduce the decoupling approximation

$$\begin{aligned}\mu\langle\hat{R}\hat{R}\rangle\cdot\hat{H} &= \mu[\langle\hat{\mathbf{R}}_\perp\hat{R}_\parallel\rangle+\langle\hat{\mathbf{R}}_\parallel\hat{R}_\parallel\rangle] \simeq \mu\langle\hat{\mathbf{R}}_\perp\rangle\langle\hat{R}_\parallel\rangle+\mu\langle\hat{\mathbf{R}}_\parallel\hat{R}_\parallel\rangle \\ &= D_r^{-1}\mu\mathcal{L}(\mu)[F(\mu)(\vec{\Omega}_o\times\hat{H})+G(\mu)\frac{d\hat{H}}{dt}]+[\mu-2\mathcal{L}(\mu)]\hat{H}, \end{aligned}\tag{A4}$$

which was first used in Ref. [13] (see the physical justification of such an approximation in Section 3.2 of the first chapter) to compute the viscosity of the ferrofluid.

A combination of eqs. (A2) - (A4) then leads to

$$\mathcal{L}(\mu)\frac{d\hat{H}}{dt} = \{-2F(\mu)(\vec{\Omega}_o \times \hat{H}) - 2G(\mu)\frac{d\hat{H}}{dt} - \mu\mathcal{L}(\mu)[F(\mu)(\vec{\Omega}_o \times \hat{H}) + G(\mu)\frac{d\hat{H}}{dt}] + \mathcal{L}(\mu)(\vec{\Omega}_o \times \hat{H})\}, \quad \text{(A5)}$$

where we have taken into account that for low frequency fields $\omega_o^2/D_r^2 \simeq 0$ as well as $\omega_o\Omega_o/D_r^2 \simeq 0$, for the vorticity flows under consideration.

Now, identifying terms from both members of Eq. (A5) we obtain the explicit form of the functions F and G:

$$F(\mu) = -G(\mu) \equiv \frac{\mathcal{L}(\mu)}{2 + \mu\mathcal{L}(\mu)}, \quad \text{(A6)}$$

and consequently,

$$\langle\hat{R}\rangle(t) = \mathcal{L}(\mu)\hat{H}(t) + \frac{F(\mu)}{D_r}[(\vec{\Omega}_o \times \hat{H}(t)) - \frac{d\hat{H}}{dt}]. \quad \text{(A7)}$$

This expression then justifies the equation for the magnetization density (2.12) .

Appendix B

Explicit derivation of Eq. (5.1.24)

Starting from Eq. (5.1.22)

$$\boldsymbol{\mu}_{ij}^{(1,1)} = \frac{a_j^2}{(2\pi^2)} \int d\hat{k} \int dk \; exp(i\vec{k}\cdot\vec{R}_{ij})\; \boldsymbol{h}^{-1}(\hat{k})\cdot(\boldsymbol{I}-\hat{k}\hat{k}) j_o(ka_i) j_o(ka_j), \qquad \text{(B1)}$$

we can make an expansion such that

$$\boldsymbol{\mu}_{ij}^{(1,1)} = \frac{a_j^2}{(2\pi^2)} \int d\hat{k} \int dk \; exp(i\vec{k}\cdot\vec{R}_{ij})\; \boldsymbol{h}^{-1}(\hat{k})\cdot(\boldsymbol{I}-\hat{k}\hat{k}) \left(1 - \frac{(a_i^2+a_j^2)}{6}k^2 + O(k^4)\right). \qquad \text{(B2)}$$

In a reference frame in which the $\hat{e}_z$-axis is parallel to the unitary vector $\hat{R}_{ij}$ ($\vec{R} = R_{ij}\hat{R}_{ij}$), we may write $d\hat{k} = d\xi_{ij}d\phi_{ij}$, where $\xi_{ij} = \hat{R}_{ij}\cdot\hat{k}$ is the cosine of the polar angle between $\hat{R}_{ij}$ and $\hat{k}$, and ϕ_{ij} is the azimutal angle.

$$\begin{aligned}\boldsymbol{\mu}_{ij}^{(1,1)} &= \frac{a_j^2}{(2\pi^2)} \int_{-1}^{1} d\xi_{ij} \int_0^{2\pi} d\phi_{ij} \int_0^{\infty} dk \; exp(ikR_{ij}\xi_{ij})\; \boldsymbol{h}^{-1}(\hat{k})\cdot(\boldsymbol{I}-\hat{k}\hat{k}) \\ &\left(1 - \frac{(a_i^2+a_j^2)}{6}k^2 + O(k^4)\right). \qquad \text{(B3)}\end{aligned}$$

Making use of the identity

$$\frac{1}{2\pi}\int_{-1}^{1} dx x^p \int_{-\infty}^{\infty} dy y^q e^{ixy} = i^q \int_{-1}^{1} dx x^p \frac{d^q}{dx^q}\delta(x) = \delta_{pq} p!(-1)^p, \qquad \text{(B4)}$$

it then follows that the terms of order k^4 and higher of the expansion in the integrand of Eq. (B3) give vanishing contributions upon integration, since any element of the tensor $\boldsymbol{h}^{-1}(\hat{k})\cdot(\boldsymbol{I}-\hat{k}\hat{k})$ will be, after integration over ϕ_{ij}, a polynomial in ξ_{ij} whose highest order is proportional to ξ_{ij}^2 [12],

$$\boldsymbol{h}^{-1}(\hat{k})\cdot(\boldsymbol{I}-\hat{k}\hat{k}) = C_1(\boldsymbol{I}-\hat{k}\hat{k}) + C_2(\hat{k}\times\hat{H})(\hat{k}\times\hat{H}) \qquad \text{(B5)}$$

where

$$C_1 = \frac{1}{\eta+\eta_r} \sim \frac{1}{\eta_o}\left(1 - \frac{5}{2}\phi - \frac{3}{2}\phi\mu F(\mu)\right), \qquad \text{(B6)}$$

and

$$C_2 = \frac{\eta_r}{\eta(\eta+\eta_r)} \sim \frac{1}{\eta_o}\frac{3}{2}\phi\mu F(\mu). \tag{B7}$$

Thus, we can rewrite Eq. (B3) in the following form

$$\boldsymbol{\mu}_{ij}^{(1,1)} = \frac{a_j^2}{(2\pi)R_{ij}}\int_{-1}^{1} d\xi_{ij}\int_0^{2\pi} d\phi_{ij}\, \boldsymbol{h}^{-1}(\hat{\boldsymbol{k}})\cdot(\boldsymbol{I}-\hat{\boldsymbol{k}}\hat{\boldsymbol{k}})\left(\delta(\xi_{ij}) + \frac{(a_i^2+a_j^2)}{6R_{ij}^2}\frac{\partial^2}{\partial^2\xi_{ij}}\delta(\xi_{ij})\right). \tag{B8}$$

For the sake of simplicity, we define

$$\boldsymbol{\mu}_{ij}^{(1,1)} = \boldsymbol{G}_{ij}^{(1,1)}R_{ij}^{-1} + \boldsymbol{H}_{ij}^{(1,1)}R_{ij}^{-3}, \tag{B9}$$

with

$$\boldsymbol{G}_{ij}^{(1,1)} = \frac{a_j^2}{(2\pi)}\int_{-1}^{1} d\xi_{ij}\int_0^{2\pi} d\phi_{ij}\left(C_1(\boldsymbol{I}-\hat{\boldsymbol{k}}\hat{\boldsymbol{k}}) + C_2(\hat{\boldsymbol{k}}\times\hat{H})(\hat{\boldsymbol{k}}\times\hat{H})\right)\delta(\xi_{ij}), \tag{B10}$$

and

$$\boldsymbol{H}_{ij}^{(1,1)} = \frac{a_j^2(a_i^2+a_j^2)}{(12\pi)}\int_{-1}^{1} d\xi_{ij}\int_0^{2\pi} d\phi_{ij}\left(C_1(\boldsymbol{I}-\hat{\boldsymbol{k}}\hat{\boldsymbol{k}}) + C_2(\hat{\boldsymbol{k}}\times\hat{H})(\hat{\boldsymbol{k}}\times\hat{H})\right)\frac{\partial^2}{\partial^2\xi_{ij}}\delta(\xi_{ij}). \tag{B11}$$

After performing the integrals appearing in eqs. (B10) and (B11), they reduce to

$$\boldsymbol{G}_{ij}^{(1,1)} = \frac{a_j^2}{2}\left(C_1(\boldsymbol{I}+\hat{R}_{ij}\hat{R}_{ij}) + C_2[\boldsymbol{I}-\hat{H}\hat{H}-(\hat{R}_{ij}\times\hat{H})(\hat{R}_{ij}\times\hat{H})]\right), \tag{B12}$$

$$\boldsymbol{H}_{ij}^{(1,1)} = \frac{a_j^2(a_i^2+a_j^2)}{2}\left(C_1(\frac{\boldsymbol{I}}{3}-\hat{R}_{ij}\hat{R}_{ij}) - C_2[\frac{(\boldsymbol{I}-\hat{H}\hat{H})}{3} - (\hat{R}_{ij}\times\hat{H})(\hat{R}_{ij}\times\hat{H})]\right). \tag{B13}$$

The way of solving the integral in Eq. (B10) is the following

$$\boldsymbol{G}_{ij}^{(1,1)} = C_1(g_1\boldsymbol{I} + g_2\hat{R}_{ij}\hat{R}_{ij}) + C_2[g_3(\boldsymbol{I}-\hat{H}\hat{H}) + g_4(\hat{R}_{ij}\times\hat{H})(\hat{R}_{ij}\times\hat{H})] \tag{B14}$$

where we have introduced the constants $(g_1,\ldots,g_4)$ which can be found by contracting the tensors in both sides of the equation, firstly with the identity matrix, $\boldsymbol{I}$, and secondly with the tensor $\hat{R}_{ij}\hat{R}_{ij}$. In doing so, and after calculating the simple scalar integrals resulting from these contractions, we arrive at a determined system of equations for the above introduced constants. The solutions are $g_1 = g_2 = g_3 = -g_4 = a_j^2/2$.

The integral in Eq. (B11) can be carried out following exactly the same procedure.

Finally, once we have substituted the constants C_1 and C_2 given through eqs. (B6) and (B7), Eq. (B9) turns out to be Eq. (5.1.23).

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CHAPTER IV

AGGREGATION PHENOMENA

This chapter is intended to be an introductory analysis of the aggregation phenomena that arise for instance, as the size of the particles in a ferrofluid increases or at higher concentrations. In such conditions the dipole-dipole iteraction between the particles is enhanced and Brownian motion is no longer able to stabilize the suspension. Moreover, in the presence of a high magnetic field the particles show up a tendency to form chains. We study the kinetics of the formation of the aggregates by means of the Smoluchowski theory of coagulation in colloids accounting for hydrodynamic interactions. These interactions become relevant for the concentration of particles which give rise to these phenomena and slow down the aggregation process. In addition, the rheology of the chains that are usually observed in systems with dipolar interactions is studied for a rather simplified situation in order to elucidate the effects of the dipolar magnetic interactions in the contribution of the chains to the pressure tensor of the suspension.

1 Introduction

Colloidal dispersions play an important role in many natural phenomena as well as in various industrial processes. The stability of the suspension against aggregation of the particles is of essential importance for its behavior [1]. As long as one can neglect interparticle interactions, one does not observe aggregation phenomena and then the main problem is to understand how the physical properties of the fluid, for example its viscosity, are modified due to the presence of the particles. But when interactions between particles start to be important, the preceding problem becomes much more complicated. In this case, the aggregation mechanism in a colloidal solution is quite complex because the fluid does keep into an active role. The nature of inter-particle interactions depends on the properties of the fluid, and, concerning its driving motion, hydrodynamic effects cannot be neglected.

The concepts of hard and soft particles are commonly used in the literature [2]. A hard particle is a rigid sphere on which only hydrodynamic forces are acting, they do not undergo other interaction forces except for an infinitely strong repulsion on contact to prevent interpenetration. In contrast, a soft particle is a sphere subject to interactions, other than hydrodynamic ones, felt at finite distances. In the last case, one can think of such spheres as having a surface boundary layer (*sphere of influence*) whose thickness is determined by a characteristic interaction length. Thus, for electrostatically stabilized dispersions this thickness can be identified with the double-layer thickness, for van der Waals interactions with the thickness where the interaction energy becomes comparable to the thermal energy, and for sterically stabilized colloids with the length of the polymer tails adsorbed on the surface of the suspended particles. This idea was in a certain way exploited by von Smoluchowski [3], who first analized the problem of coagulation in the absence of any repulsive barrier (rapid coagulation). A sphere with a surface boundary layer can be considered soft because this layer can be deformed and penetrated during the approach of two particles. Moreover, in the literature the term *coagulation* is applied to aggregation that is induced by the van der Waals attraction between the colloidal particles. On the other hand, the term *flocculation* is reserved for polymer-induced aggregation. Coagulation usually gives rise to compact aggregates whereas flocculation frequently produces more open structures.

Particularly, the monodomain magnetic particles are usually sufficiently small that Brownian forces, along with short-range steric repulsion due to either natural or synthetic polymers, dominate in the zero-field limit to guarantee the stability of the particles. However, when a non very dilute suspension of these particles is under

the action of an applied magnetic field, particle aggregation occurs when the magnetic attraction between the permanent moments is strong enough to outweigh the stabilizing forces. Thus the thickness of the boundary layer can be identified with the thickness for which the magnetic interaction energy is comparable to the thermal energy rather than with the length of the polymer, due to the long range character of such interaction.

In the late 1930's, Winslow [4] observed interesting phenomena when dielectric particles suspended in oil were subject to an electric field. He saw the induced formation of chains of particles aligned with the electric field and, even of more practical importance, that the effective viscosity of the suspension could be varied by orders of magnitude by modifying the applied electric field. However, studies on electrorheological fluids are hindered by many problems related to surface charge, electrode polarization, adsorbed water, field inhomogeneities, etc. An analogous field-induced behavior is shown by magnetorheological fluids, e.g., in a suspension of magnetizable paramagnetic particles in a nonmagnetic fluid [5] or in a suspension of nonmagnetizable spheres in a ferrofluid (magnetic holes, see previous chapter). In a pure ferrofluid one observes similar phenomena but, due to fact that the particles are permanently magnetized, there are polarization forces even without an applied magnetic field. In all these cases, one has the advantage that they are not susceptible to the above mentioned problems. Thus, studying the kinetics of the formation of the aggregates and their rheology are topics of practical importance and has provided the bases of theoretical and experimental studies [6]-[8] as well as numerical simulations [9]-[11].

Having all these in mind, the structure of this chapter is as follows. In Section 2 we discuss the influence of hydrodynamic interaction in the kinetics of aggregates formation by using the Smoluchowski's theory of coagulation. We write the corresponding kinetic differential equations giving the time evolution of the dynamic cluster size distribution function and solve them for a rather simplified case. In this section we also discuss the scaling behavior of the cluster size distribution. Section 3 is intended to be an introductory analysis of the rheology of the chains which commonly appear when the aggregation process occurs under the action of an external field. (falta)

The conclusions are summed up in the last section.

2 Hydrodynamic interactions in the Smoluchowski theory of coagulation

The investigation of aggregation processes by means of computer simulations have been enhanced during the last 10 years after the pioneering work of Witten and Sander where they proposed their diffusion-limited aggregation model referred to as DLA [12]. This work stimulated the development of the diffusion-limited cluster-cluster aggregation model by Meakin [13] and Kolb *et al.* [14], which, particularly, provides a better understanding of structural and kinetic aspects of colloid aggregation. The coagulation process can also be discussed in terms of the Smoluchowski's theory which, as we will see below, due to the nature of the approximation inherent in its derivation is a mean-field theory. Nevertheless, this theory is expected to hold for dimensions greater than the upper critical dimension above which fluctuations become irrelevant and that for this coagulation processes is 2.

Smoluchowski first found out a very interesting application of the theory of Brownian motion in the coagulation exhibited by colloidal particles when an electrolyte is added to the solution. His theory is based on the suggestion of Zsigmondy that coagulation is a consequence of the existence of a *sphere of influence* of a certain radius R surrounding each colloidal particle such that its Brownian motion remains unaffected unless another particle enters within its sphere of influence. When this happens they stick to one another to form a single unit. For this particular problem, the spheres of influence are supposed to originate in the formation of electric double layers around each particle. The double particle continues moving randomly so long as it does not come within the spheres of influence of a single or another double particle. Then we will have the formation of a triple or a quadrupole particle, and so on. This process will eventually lead to the total coagulation of all the colloidal particles into one cluster.

Recent real-time experiments performed with suspensions of superparamagnetic latex particles [15] corroborate Smoluchowski's hypotheses. In this case, the magnetic field induces chain formation, and one observes two aggregation time scales. When particles are far enough away from each other that their dipolar interaction is weak relative to k_BT, Brownian motion dominates. When this random motion happens to bring two particles close enough that their dipolar interaction is of the same order as k_BT, a rapid transition between random and ballistic motion occurs and the particles aggregate immediately. Moreover, numerical simulations incorporating induced-dipolar interaction forces and Brownian motion also corroborate that there is

a citrical value of the interparticle separation within which particle motion ceases to be random. Thus, each particle can be thought of as having a capture volume defined by equating dipolar interaction energy to thermal energy. If one particle enters this volume, the two particles undergo ballistic aggregation. On the other hand, the applicability of the Smoluchowski equation is limited to low cluster concentrations because it assumes that there are only binary collisions.

We are interested in determining the concentrations $n_1, n_2, \ldots$, of single, double, triple, quadrupole, etc., particles at time t given that at time $t = 0$ there are n_o single particles. Moreover, once we know these concentrations we can write the scaling laws which show how these quantities behave for long times or for large radius of the spheres of influence. But, in this section we will introduce a modification to the simple theory proposed by Smoluchowski by considering hydrodynamic effects. For distances greater or of the same order of magnitude as the interparticle separation threshold ($\sim 2a - 7a$, with a the radius of one particle), hydrodynamic interactions should be taken into account when studying the diffusive motion of the particles. There are previous attemps to incorporate this effects in the final stages of the approach of two non-magnetic particles (i.e. when just short range interactions between the particles are considered) when, because it is difficult for the remaining film of liquid to escape, the process is clearly slowed down. Honig *et al.* [16] for instance examined the problem deriving an approximate relation for a modified diffusion coefficient:

$$\frac{D(h)}{D(h \to \infty)} = \frac{1 + 2a/3h}{1 + 13a/6a + a^2/3h^2} \tag{2.1}$$

where $h = r - 2a$ is the distance of closest approach. This effect was also tested experimentally by Lichtenbelt *et al.* [17] who found that the rate of coagulation was reduced to less than half of the Smoluchowski value for those colloidal suspensions. However, when dealing with long range interactions, we believe that it would be enough to introduce hydrodynamic interactions represented by the Oseen and Rotne-Prager tensors discussed in the previous chapter. This will enable us to find analytic expressions not only for the rate of coagulation but also for the different concentrations of clusters $n_1, n_2, \ldots$

2.1 Kinetic equation of irreversible aggregation

For the time intervals we are interested in the motion of the particles is diffusive, i.e., local fluctuations in the concentration due to Brownian motion determine a global diffusion from the higher to the lower concentrated regions. We will start considering

the following elementary situation:

Initially, we will assume that a particle is fixed in the origin of our frame of reference and in an infinite medium. A number of similar Brownian particles are distributed uniformly at time $t = 0$, and such that they just can aggregate with the particle located at the origin but not between themselves. According with the definition of the sphere of influence, we can replace the surface $\mid r \mid = R$ by a perfect absorber. We have therefore to look for a solution of the diffusion equation

$$\frac{\partial n}{\partial t} = \nabla \cdot (\boldsymbol{D} \cdot \nabla n) \tag{2.1.1}$$

which satisfies the boundary conditions

$$\begin{aligned} n(r) = n_o \text{ at } t = 0, \text{ for } \mid r \mid > R, \\ n(R) = 0 \text{ and } n(\infty) = n_o \text{ for } t > 0, \end{aligned} \tag{2.1.2}$$

where n_o is the average concentration of particles at time $t = 0$, $\boldsymbol{D}$ is the relative diffusion tensor which is introduced to take also into account the Brownian motion of the particle at the origin, and that has the following form

$$\boldsymbol{D} = k_B T \boldsymbol{\mu}_{rel}. \tag{2.1.3}$$

Under the present circumstances, we have clearly to deal with the relative displacements of the two particles which coalesce. In the original theory of Smoluchowski, these two particles are supposed to describe Brownian motions independently of each other. Correspondingly, the relative diffusion tensor is just the sum of their respective diffusion coefficients $D = D_1 + D_2$ with $D_{1,2} = k_B T / 6\pi\eta a_{1,2}$ the Stokes-Einstein diffusion coefficient of a single free sphere. But, in general, there exists a coupling between the Brownian motion of the two spheres due to hydrodynamic interactions. The relative motion can be split into two components, one along the line of centers and another perpendicular to it. The translational relative motion is the most important one because it determines the rate at which particles coagulate in a dispersion. If we choose one particular direction, x, the relative mean square displacement of two particles is

$$\langle (x_{(1)} - x_{(2)})^2 \rangle = \langle x_{(1)}^2 - 2x_{(1)}x_{(2)} + x_{(2)}^2 \rangle \tag{2.1.4}$$

where the coupling term $\langle x_{(1)}x_{(2)} \rangle$ is non-zero. Consequently, the relative mobility along the line of centers is given by

$$\mu_{rel}^{\parallel} = \mu_{11}^{\parallel} + \mu_{22}^{\parallel} - 2\mu_{12}^{\parallel}, \tag{2.1.5}$$

where the symbol $\parallel$ means parallel components of the tensors $\boldsymbol{\mu}_{11} = \boldsymbol{\mu}_{22} = \frac{\boldsymbol{I}}{6\pi\eta a_{1,2}}$, which are the Stokes mobilities of a free particle of radius $a_{1,2}$, respectively, in a liquid of shear viscosity η, and $\boldsymbol{\mu}_{12} = (\boldsymbol{I} - \hat{r}\hat{r})/8\pi\eta r$ is the Oseen tensor characterizing the hydrodynamic coupling between the relative motion of two particles which are at sufficiently large distance in this simple liquid. The relative diffusion parallel to the line of centers is thus

$$D^{\parallel} = \frac{k_B T}{6\pi\eta}\left(\frac{1}{a_1} + \frac{1}{a_2} - \frac{3}{r}\right), \tag{2.1.6}$$

for two particle with different radius $a_{1,2}$. As this diffusion coefficient only depends on the the interparticle distance, the distribution of particles is radially symmetric. In such case Eq. (2.1.1) reduces to

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial r}\left(r^2 D^{\parallel}\frac{\partial n}{\partial r}\right). \tag{2.1.7}$$

At long times the distribution of particles around a reference sphere located at the origin approaches a steady state, given by

$$\frac{\partial}{\partial r}\left(r^2 D^{\parallel}\frac{\partial n}{\partial r}\right) = 0, \tag{2.1.8}$$

whose solution, satisfying the boundary conditions $n(\infty) = n_o$ and $n(R) = 0$, is:

$$n(r') = n_o\left(1 - \frac{\ln(1 - \frac{k}{r'})}{\ln(1 - \frac{k}{R'})}\right), \tag{2.1.9}$$

where we have defined the following dimensionless quantities

$$\begin{aligned} r' &\equiv \frac{2r}{a_1 + a_2} \\ R' &\equiv \frac{2R}{a_1 + a_2} \\ k &\equiv \frac{6a_1 a_2}{(a_1 + a_2)^2}. \end{aligned} \tag{2.1.10}$$

n gives the concentration of particles of radius a_2 around a reference sphere of radius a_1 or *vice versa*. At this point it is worth mentioning that, although we are not considering explicitly the interaction between the particles, it usually takes a long time

for the steady-state distribution to be reached when there are long range attractive forces between the particles.

Now we are interested in determining the rate at which particles aggregate, i.e., the number of particles that are captured by the reference sphere per unit time. The first step in the coagulation process is the formation of doublets. The frequency of doublet formation can be found by computing the flux of particles crossing the sphere of radius R_{12}, for two particles approaching each other, and with spheres of influence of radius R_1 and R_2, respectively. This means that each particle whose sphere of influence is R_2, will be captured when its centre enters this sphere of radius R_{12}. According to Fick's law, the flux of particles crossing this surface is given by

$$J = 4\pi R_{12}^2 (D_1 + D_2 - D_{12}^{\parallel}) \frac{\partial n}{\partial r} \mid_{r=R_{12}} \equiv 4\pi n_o (D_1 + D_2) R_{12}^{ef}, \tag{2.1.11}$$

where D_1 and D_2 are the diffusion constants of isolated hard spheres, and where we have introduced the following definition of the effective radius R_{12}^{ef} for the mutual capture volume which takes into account hydrodynamic effects

$$R_{12}^{ef} \equiv -\frac{3a_1 a_2}{(a_1 + a_2)\ln(1 - \frac{k}{R_{12}^{l}})}. \tag{2.1.12}$$

The following step, will be to generalize this result for any pair of clusters containing a given number of spheres, i, k, with diffusion coefficients denoted by D_i, D_k, respectively, and whose concentrations are n_i, n_k. Furthermore, let R_{ik}^{ef} denote the effective distance to which two *particles* (one of each sort) must approach in order that they may coalesce to form a multiple particle. Then, the rate of formation of these multiple particles, $i + k$, is given by

$$J_{i+k} = 4\pi n_i n_k (D_i + D_k) R_{ik}^{ef} \equiv 4\pi n_i n_k D_{ik} R_{ik}^{ef} \tag{2.1.13}$$

where

$$R_{ik}^{ef} \equiv -\frac{3a_i a_k}{(a_i + a_k)\ln(1 - \frac{k}{R_{ik}^{l}})}. \tag{2.1.14}$$

and R_{ik} is the distance for which the *particles* aggregate irreversibly.

Now, once we know this rate, we can write down the kinetic differential equations giving the variations of the cluster size distribution functions $n_1, n_2, \ldots$ with time:

$$\frac{dn_k}{dt} = 4\pi(\frac{1}{2}\sum_{i+j=k} n_i n_j D_{ij} R_{ij}^{ef} - n_k \sum_{j=1}^{\infty} n_j D_{kj} R_{kj}^{ef}) \qquad k = 1, 2, \ldots \tag{2.1.15}$$

The first summation on the right-hand side of this equation represents the increase of the concentration n_k due to the formation of clusters of k particles by the aggregation of a cluster of i particles and a cluster of j particles ($i + j = k$), whereas the second summation represents the decrease of n_k due to the formation of a cluster of $k + j$ particles in which one of the coalescing clusters has k particles. Let us remind that the applicability of this equation is restricted to low concentrations of clusters because of the assumption of binary collisions.

2.2 Dynamic cluster size distribution functions

A general solution of the above system of equations (2.1.15) valid under all practical circumstances does not seem feasible. In this subsection we will obtain an illustrative simple solution by introducing some assumptions similar to that previously proposed by Smoluchowski.

Let us suppose that $D_i = \frac{k_B T}{6\pi\eta a_i}$, that is, independently of the cluster structure we will consider that it diffuses like a hard sphere of effective radius a_i. Thus we have

$$(D_i + D_k)R_{ik}^{ef} = -\frac{3k_B T}{6\pi\eta \ln(1 - \frac{k}{R_{ik}'})}. \tag{2.2.1}$$

Moreover, concerning R_{ik}, the assumption is made that:

$$R_{ik} = \frac{1}{2}(R_i + R_k) \tag{2.2.2}$$

where R_i and R_j are the radii of the spheres of influence of the clusters with i and j particles, respectively. As the diffusion coefficient is inversely proportional to the effective radius of the particle and, based on experimental evidences, it appears that the radii of the spheres of influence of the clusters are proportional to their effective radii, we make the additional assumptions that for all i

$$D_i R_i = DR \tag{2.2.3}$$

where D and R denote the diffusion coefficient and the radius of the sphere of influence of the single particles, and

$$(D_i + D_k)R_{ik} = 2DR. \tag{2.2.4}$$

In this way, we also have that

$$(D_i + D_k)R_{ik}^{ef} = -\frac{k_B T}{2\pi\eta \ln(1 - \frac{3a}{2R})} \tag{2.2.5}$$

and, equation (2.1.15) can be expressed as follows

$$\frac{dn_k}{dt} = L\left(\sum_{i+j=k} n_i n_j - 2n_k \sum_{j=1}^{\infty} n_j\right) \qquad k = 1, 2, \ldots \tag{2.2.6}$$

where we have defined

$$L \equiv -\frac{k_B T}{\eta \ln(1 - \frac{3a}{2R})}. \tag{2.2.7}$$

If we now sum over all possible values of k

$$\frac{d}{dt}\sum_{k=1}^{\infty} n_k = L\sum_{k=1}^{\infty}\Big(\sum_{i+j=k} n_i n_j - 2n_k \sum_{j=1}^{\infty} n_j\Big)$$

$$= L\Big(\sum_{i=1}^{\infty} n_i \sum_{j=1}^{\infty} n_j - 2\sum_{k=1}^{\infty} n_k \sum_{j=1}^{\infty} n_j\Big) = -L\Big(\sum_{j=1}^{\infty} n_j\Big)^2. \tag{2.2.8}$$

we have that for the total number of clusters $\sum_{j=1}^{\infty} n_j$, independently of their constituting number of particles, that

$$\sum_{j=1}^{\infty} n_j = \frac{n_o}{1 + n_o L t}, \tag{2.2.9}$$

because for $t = 0$ we have the initial condition

$$\sum_{j=1}^{\infty} n_j|_{t=0} = n_1 = n_o. \tag{2.2.10}$$

From equation (2.2.8) we can obtain the evolution in time of the different clusters. For instance, we have

$$\frac{dn_1}{dt} = -2Ln_1 \sum_{j=1}^{\infty} n_j = -\frac{2Ln_1 n_o}{1 + n_o L t} \tag{2.2.11}$$

and, consequently

$$n_1 = \frac{n_o}{(1 + n_o L t)^2}. \tag{2.2.12}$$

Equally, we have that the concentration of doublets

$$\frac{dn_2}{dt} = L\left(n_1^2 - 2n_2 \sum_{j=1}^{\infty} n_j\right) = L\left(\frac{n_o^2}{(1 + n_o L t)^4} - \frac{2n_2 n_o}{(1 + n_o L t)}\right) \tag{2.2.13}$$

whose solution is the following

$$n_2 = n_o \frac{n_o L t}{(1 + n_o L t)^3} \tag{2.2.14}$$

In view of all these results, for any value of k we come up to the expression

$$n_k = n_o \frac{(n_o L t)^{k-1}}{(1 + n_o L t)^{k+1}}. \tag{2.2.15}$$

which shows the evolution of all the quantities $n_1, n_2, \ldots$ with time. These dynamic cluster size distribution functions n_k which give the number of clusters per unit volume consisting of k particles at time t determine many properties of a polydispersed system. They were the subject of some experimental investigation which seemed to indicate that the cluster size distribution has a scaling behavior in both k and t. In Fig. 1 we plot the variations of these quantities with time and compare them with Smoluchowski's first results. We can conclude that when we introduce the hydrodynamic interactions in a simple way through the Oseen tensor, the quantity $L = k_B T/\eta \ln(1 - 3a/2R)$ plays the role of the radius of the sphere of influence R. As we expected, the different concentrations behave qualitatively the same as in the initial model and we just obtain quantitative differences. Moreover, for large values of R we approach the same result obtained in the simplified theory. There exists an interval of values of R, $(R < 3a/2)$, for which we obtain meaningless results. This interval is also expected, because it is fully included in the range of short distances, and consequently the Oseen tensor is by no means representing the hydrodynamic corrections for such distances. In any case, we can sum up this subsection by saying that hydrodynamic interactions clearly slow down the process of aggregation.

2.3 Scaling behavior of the cluster size distribution

The formation of large aggregates from small particles and their growth started being a subject of considerable interest in the early eighties [12, 13, 14]. Some of these studies of the aggregation and growth phenomena showed that the clusters formed showed a scale-invariant, fractal structure. From that time on, the fractal properties of aggregates has been a subject of intensive investigations. More recently, magnetic systems (ferrofluids, magnetic aerosols, and magnetic holes) have stimulated further studies about the influence of long-range dipolar forces on the different fractal and scaling properties [18, 19, 20]. In this subsection we will just consider certain limiting cases which will give rise to the characteristic scaling laws and the corresponding characteristic exponents in the framework of this mean field theory

- For large values of R, i.e., for a long range interaction, and provided that $3a/2R < 1$ L will be also large so that we can rewrite Eq. (2.2.15) as follows

$$n_k = \frac{n_o}{(n_o L t)^2}\left(1+\frac{1}{n_o L t}\right)^{-(k+1)} \simeq \frac{n_o}{k^2}\left(\frac{k}{n_o t L}\right)^2 e^{-\frac{k}{n_o L t}}, \tag{2.3.1}$$

or, equivalently

$$n_k \propto k^{-\tau} f\left(\frac{k}{L^\gamma}\right), \tag{2.3.2}$$

where we found out the characteristic exponents $\tau = 2$ and $\gamma = 1$.

- On the other hand, for sufficiently large times

$$n_k = \frac{n_o}{(n_o L t)^2}\left(1+\frac{1}{n_o L t}\right)^{-(k+1)} \simeq \frac{n_o}{k^2}\left(\frac{k}{n_o L t}\right)^2 e^{-\frac{k}{n_o L t}}, \tag{2.3.3}$$

from which it is possible to write the size distribution function under the following scaling form

$$n_k \propto k^{-\tau} f(\frac{k}{t^z}) \tag{2.3.4}$$

whose characteristic exponents are $\tau = 2$ and $z = 1$.

Vicsek and Family [21] and independently Kolb [22] introduced a dynamic scaling description for the cluster size distribution in the cluster-cluster aggregation model. Monte Carlo simulations showed that a dynamic scaling of the above introduced form

$$n_k(t) \propto k^{-2} f(\frac{k}{t^z}) \tag{2.3.5}$$

represented well the behavior of $n_k(t)$. Here $f(x)$ is a scaling function which depends on the dimension and on the cluster mobility. The exponent z has been measured both experimentally and by Monte Carlo simulations of diffusion-limited cluster-cluster aggregation. The experimental result are generally in agreement with the simulations and, at the same time, the Mote Carlo results agree with the Smoluchowski approach in $d = 2, 3$, but disagree in one dimension. That was consistent with the observation that Smoluchowski's theory, without the incorporation of spatial fluctuations, fails below a critical dimension $d_c = 2$.

As an application of the scaling laws, let us look at the case of magnetic particles with dipolar interactions, when we neglect hydrodynamic effects, i.e. for large values of R. In this case, as we already pointed out in the introduction, we can estimate the value of R in the following way

$$\frac{m^2}{R^3} \sim k_B T \tag{2.3.6}$$

which follows by equating both magnetic and thermal energies. Consequently,

$$R \sim m^{2/3} \tag{2.3.7}$$

so that the concentration of clusters of k particles scales with the particle's magnetic moment

$$n_k \propto k^{-2} f(\frac{k}{m^{2/3}}) \tag{2.3.8}$$

with characteristic exponents $\tau = 2$ y $\gamma = 2/3$. Janssen *et al.* [11] used a numerical approach to solve the basic equation for flocculation, considering a cylindrically symmetric interaction in order to model the dipolar interaction in paramagnetic particles. In particular they investigated the rate of initial flocculation $J = 8\pi D n_o R/W$, where in their notation W stands for the stability factor which indicates how the interactions modify the total flux in comparison with the case of rapid aggregation, in which no repulsive forces are present to slow down the process. They obtained that this stability factor depends on the dimensionless parameter characterizing the dipolar interaction, or in other words on the magnetic moment of the particles, $W \propto m^{-2/3}$, with the same characteristic exponent. This result was also verified experimentally at high magnetic fields.

Moreover, recent experimental investigations on the magnetic-field-induced chain formation of superparamagnetic latex particles [15] show a power-law dependence on time as can also be obtained by the Smoluchowski equation and three-dimensional simulations of dipolar particles. But they also found that the value of the exponent z have a weak inverse dependence on the particle volume fraction and in the dimensionless constant characterizing the dipolar interaction strength. We plan to pursue work on this experimental observations in the near future.

3 Chains of magnetic particles in an elongational flow

Colloidal particles may give rise to either fixed or free structure aggregates depending on the nature of the aggregation processes and the type of interparticle bonds established [25]. We will consider the case in which the spheres are in close contact but are

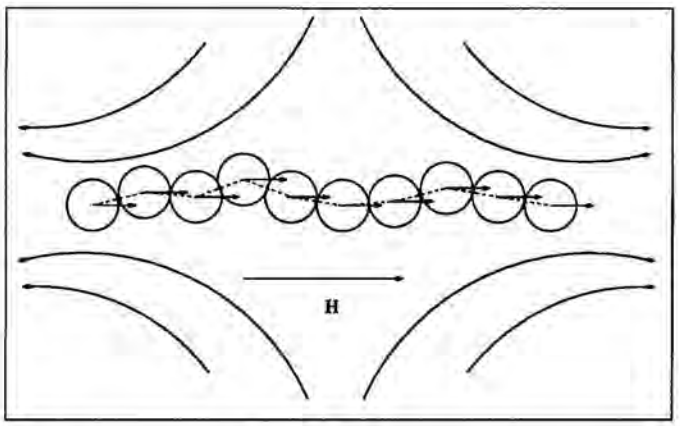

Figure IV.1: Chain of magnetic particles in an elongational flow. All the magnetic moments towards the direction of the high external field applied.

still able to translate relative to one another under the action of an elongational flow. If the particles are non-magnetic, this internal motion is resisted by hydrodynamic lubrication forces and, although the relative motion is very small, it has seen to have a big effect on the stress transmission. Now, the particles interact with each other because of the dipolar magnetic interaction and we want to know the effect of this interaction on the internal motion and the viscosity of such a system.

We define the following dimensionless parameters $\lambda \equiv m^2/(d^3 k_B T)$ and $\mu = mH/k_B T$, where m and d are the magnetic moment and the diameter of each sphere, H is the external magnetic field strength, k_B is the Boltzmann constant, and T the absolute temperature. When $\mu \to \infty$, all the magnetic dipoles align parallel to the external magnetic field. Under this condition, the energetically favourable arrengement of N grains is a linear chain. As we will see below, the analytic study of these particular aggregates requires considerable approximations, even in the limit case $\lambda \gg 1$ and $\mu \to \infty$. On the other hand, entropy considerations will suggest that other more complex structures may arise when the particle density is too large or λ is too small [26]. But for low density and large λ, the most favourable phase is a linear chain.

Direct calculations [26] show that despite there are long-range contributions to the energy of a chain containing N particles, the amplitude of the vibrations and oscillations of the spheres are almost entirely taken into account by just considering the effects due to first and second nearest-neighbour interactions. The long range effects still exist, but they are dominated by short range attractive contributions. As a matter of fact, the important regions correspond to relative distances among the

particles $r \sim d$ and relative deviations $\theta \sim 0$ or π. In addition, for our magnetic colloids the interactions of one grain are essentially saturated when it has come into close contact with two others.

Moreover, in the high field limit, the state of a sphere will be entirely described by the position of its centre. This will simplify considerably the equation of continuity that describes the conservation of system points in the configuration space. Finally, we will disregard London-Van der Waals forces as well as steric effects.

3.1 Contribution of the chains to the pressure tensor of the system

Apart from the contribution of the solvent to the total pressure tensor of a supension, there is another contribution coming from the direct interaction of the suspended particles [27, 28]. Thus, following Kramers' theory, the contribution of a chain to the pressure tensor of the whole system is

$$\boldsymbol{\Pi}_p = -\frac{1}{V}\sum_{k=1}^{N-1}\left\langle \vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k}\right\rangle + \frac{N-1}{V}k_B T \boldsymbol{I}, \tag{3.1.1}$$

where V is the volume of the system, $\vec{q}_k$ are the relative position vectors, V_{mag} is the dipole-dipole magnetic potential, N is the number of particles of the chain, and $\boldsymbol{I}$ is the unitary matrix.

In order to do the averages appearing on the right hand side of Eq. (3.1.1), we need to solve the corresponding diffusion equation in the configurational space:

$$\frac{\partial \psi}{\partial t} = \sum_i \left\{ \frac{\partial}{\partial \vec{R}_i} \cdot \sum_j \boldsymbol{\mu}_{ij}^{TT} \cdot \left(k_B T \frac{\partial \psi}{\partial \vec{R}_j} + \frac{\partial V_{mag}}{\partial \vec{R}_j}\psi \right) - \frac{\partial}{\partial \vec{R}_i} \cdot (\boldsymbol{\beta} \cdot \vec{R}_i)\psi \right\} \tag{3.1.2}$$

where $\vec{R}_i$ is the postion vector of the i-sphere, $\boldsymbol{\mu}_{ij}^{TT}$ is the relative translational mobility, and $\boldsymbol{\beta}$ is the elongational rate ($\boldsymbol{\beta} = \boldsymbol{\beta}^T$) corresponding to the stationary homogeneous external flow, $\vec{v}_o = \boldsymbol{\beta} \cdot \vec{r}$. We are also assuming that the spheres move through the solvent without disturbing the velocity field (*free draining*), so that

$$\boldsymbol{\mu}_{ij}^{TT} = \frac{1}{6\pi\eta a}\boldsymbol{I}\delta_{ij}. \tag{3.1.3}$$

where we consider that all the spheres in the chain have exactly the same radius a. Moreover, we will disregard the rotational contribution to the diffusion equation

because in the high field limit the state of a particle is fully represented by the position of its centre. Substituting Eq. (3.1.3) into Eq. (3.1.2), we arrive at

$$\frac{\partial \psi}{\partial t} = \frac{k_B T}{6\pi\eta a} \sum_i \left\{ \frac{\partial^2 \psi}{\partial \vec{R}_i^2} + \frac{\partial}{\partial \vec{R}_i} \cdot \left(\frac{\partial V_{mag}/k_B T}{\partial \vec{R}_i} \psi \right) - \frac{\partial}{\partial \vec{R}_i} \cdot (\beta \cdot \vec{R}_i)\psi \right\}. \quad (3.1.4)$$

In addition, as we are considering the limit $\lambda \gg 1$, $\mu \to \infty$, we will assume that the potential can be expressed as a sum of the nearest neighbours interaction

$$\frac{V_{mag}}{k_B T} = \sum_{i=1}^{N-1} \Phi_{i,i+1} \quad (3.1.5)$$

As we have previously indicated, the amplitude of the vibrations and oscillations of the spheres are well represented by such interactions. After taking into account that the most important contributions come from relative distances $r \sim d$ and relative deviations $\theta \sim 0$, each term in the sum of Eq. (3.1.5) can be written as follows

$$\Phi_{i,i+1} \sim -\lambda(2 - 3\theta_i^2 - 6\xi_i) \quad (3.1.6)$$

where we have introduced the relative position vector $\vec{q}_i = \vec{R}_{i+1} - \vec{R}_i$ whose components in spherical coordinates are $\vec{q}_i \equiv (q_i, \theta_i, \varphi)$. Moreover, we have carried out a development around the maximum contribution

$$\begin{aligned} q_i &= d(1 + \xi_i) \text{ with } \xi_i \sim 0 \\ \theta_i &\sim 0. \end{aligned} \quad (3.1.7)$$

Now, we will write the diffusion equation in terms of the relative position vectors, $\vec{q}_i$. But before that, we introduce the transformation

$$\vec{q}_i = \sum_k B_{ik} \vec{R}_k \text{ with } B_{ik} = \delta_{i+1,k} - \delta_{i,k}, \quad (3.1.8)$$

from which one infers the relation

$$\frac{\partial}{\partial \vec{R}_i} = \sum_k B_{ki} \frac{\partial}{\partial \vec{q}_k} \quad (3.1.9)$$

with

$$\sum_k B_{ik} B_{jk} \equiv A_{ij} = \begin{cases} 2 & \text{if } i = j \\ -1 & \text{if } i = j \pm 1 \\ 0 & \text{otherwise} \end{cases} \quad (3.1.10)$$

Taking into account Eqs. (3.1.8)-(3.1.10), the diffusion equation reads

$$\frac{\partial \psi}{\partial t} = \frac{k_B T}{6\pi\eta a} \sum_j \frac{\partial}{\partial \vec{q}_j} \cdot \sum_k A_{jk} \left(\frac{\partial \psi}{\partial \vec{q}_k} + \frac{\partial V_{mag}/k_B T}{\partial \vec{q}_k} \psi \right) - \sum_j \frac{\partial}{\partial \vec{q}_j} \cdot (\boldsymbol{\beta} \cdot \vec{q}_j)\psi. \quad (3.1.11)$$

The stationary solution for this homogeneous potential flow field is

$$\psi_{st}(\vec{q}_1, \ldots, \vec{q}_{N-1}) = C exp \left\{ \frac{-V_{mag}}{k_B T} + \frac{3\pi\eta a}{k_B T} (\boldsymbol{\beta} : \sum_i \sum_j C_{ij}\ \vec{q}_i\ \vec{q}_j) \right\}, \quad (3.1.12)$$

where C is a normalization constant and C_{ij} is the Kramers' matrix defined in the following way:

$$C_{ij} = \begin{cases} i(N-j)/N & \text{if } i \leq j \\ j(N-i)/N & \text{if } j \leq i \end{cases} \quad (3.1.13)$$

Once we know the stationary solution of the diffusion equation, we will compute the contribution of the chain to the pressure tensor, i.e., the average appearing on the right hand side of equation (3.1.1)

$$\left\langle \vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k} \right\rangle = \int \prod_{l=1}^{N-1} d\vec{q}_l \left(\vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k} \right) \psi_{st}(\vec{q}_1, \ldots, \vec{q}_{N-1}). \quad (3.1.14)$$

As we are interested in finding the Newtonian viscosity tensor, we can expand the exponential factor $(3\pi\eta a)/(k_B T)(\boldsymbol{\beta} : \sum_i \sum_j C_{ij} \vec{q}_i \vec{q}_j)$ in Eq. (3.1.12) up to first order in $\boldsymbol{\beta}$. If we were also interested in the first non-Newtonian contribution we would include the second order, ... At first we will use

$$\psi_{st}(\vec{q}_1, \ldots, \vec{q}_{N-1}) = C' exp \left(\frac{-V_{mag}}{k_B T} \right) \left\{ 1 + \frac{3\pi\eta a}{k_B T} (\boldsymbol{\beta} : \sum_i \sum_j C_{ij}\ \vec{q}_i\ \vec{q}_j) \right\}, \quad (3.1.15)$$

or if we introduce the translational diffusion coefficient for a single particle $D = k_B T/(6\pi\eta a)$ and Eq. (3.1.5)

$$\psi_{st}(\vec{q}_1, \ldots, \vec{q}_{N-1}) = C' \prod_{k=1}^{N-1} exp(-\Phi_{k,k+1}) \left\{ 1 + \frac{1}{2D} (\boldsymbol{\beta} : \sum_i \sum_j C_{ij}\ \vec{q}_i\ \vec{q}_j) \right\}, \quad (3.1.16)$$

where C' is the new normalization constant that we compute in Appendix A

$$\frac{1}{C'} = \left(\frac{\pi d^3 \exp^{2\lambda}}{18\lambda^2}\right)^{N-1}\left(1+\frac{5}{18\lambda}\right)^{N-1}\left\{1+\frac{d^2}{24D}N(N^2-1)\beta_{zz} + \frac{d^2}{72\lambda D}\left(1+\frac{5}{18\lambda}\right)^{-1}(N^2-1)\boldsymbol{\beta}:(\boldsymbol{I}-\hat{e}_z\hat{e}_z)\right\}. \quad (3.1.17)$$

Consequently, Eq. (3.1.14) reduces to

$$\left\langle \vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k} \right\rangle = C' \int \left(\prod_{l=1}^{N-1} d\vec{q}_l \; exp(-\Phi_{l,l+1})\right)\left(\vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k}\right) \left\{1+\frac{1}{2D}(\boldsymbol{\beta}:\sum_i\sum_j C_{ij}\vec{q}_i\vec{q}_j)\right\}. \quad (3.1.18)$$

In order to evaluate this average, we will decompose it into different parts (detailed calculations have been collected in Appendix B). Up to first in $\boldsymbol{\beta}$ we have

$$\left\langle \vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k} \right\rangle = k_B T\left\{\boldsymbol{I}+\frac{d^2}{D}\sum_i C_{ik}\boldsymbol{\beta}\cdot\hat{e}_z\hat{e}_z + \frac{d^2}{6D\lambda}\left(1-\frac{5}{18\lambda}\right)C_{kk}\boldsymbol{\beta}\cdot(\boldsymbol{I}-\hat{e}_z\hat{e}_z)\right\} \quad (3.1.19)$$

Once we have been able to compute this average, the contribution of one chain to the pressure tensor (3.1.1)

$$\boldsymbol{\Pi}_p = -\frac{1}{V}\sum_{k=1}^{N-1}\left\langle \vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k}\right\rangle + \frac{N-1}{V}k_B T\boldsymbol{I} = -\frac{\pi\eta_o d^3}{4V}(N^2-1) \left\{N\boldsymbol{\beta}\cdot\hat{e}_z\hat{e}_z + \frac{1}{3\lambda}\left(1-\frac{5}{18\lambda}\right)\boldsymbol{\beta}\cdot(\boldsymbol{I}-\hat{e}_z\hat{e}_z)\right\}. \quad (3.1.20)$$

In view of Eq. (3.1.20), we can conclude that we obtain an expansion in powers of the inverse of the parameter λ, comparing dipolar and thermal energies, starting from the assymptotic value which corresponds to the rigid chain limit and increasing or decreasing when λ decreases, i.e. when the chain becomes more flexible, depending upon the structure of the flow rate. It worths pointing out that, as we are not taking into account the hydrodynamic interaction between the particles, the rigid chain limit pressure tensor grows simply as the third power of the chain length. This interactions are the responsible for the logarithmic term that should also appear when dealing with a long straight line of spheres [27], but which is less important for shorter chains.

Moreover, from this expression we can also obtain the contribution of the chain to the viscosity tensor, η_p

$$\Pi_p = -2\eta_p : \beta \tag{3.1.21}$$

and

$$\eta_p = \frac{\pi\eta_o d^3}{8V}(N^2-1)\left\{N\hat{e}_z I\hat{e}_z + \frac{1}{3\lambda}\left(1-\frac{5}{18\lambda}\right)(S-\hat{e}_z I\hat{e}_z)\right\}. \tag{3.1.22}$$

Here S is a symmetric tensor such that $S_{ijkl} = 1/2(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})$.

As the external magnetic field that we are applying is such that $\mu \to \infty$, the chain will be always oriented in the direction of the field and smoothly vibrates and oscillates around this orientation. In this case, the symmetries of the fluid flow essentially determine the characteristics of both the pressure and the viscosity tensor. Thus, as the chain is oriented along the z-axis, if the flow field rate β is diagonal, the pressure tensor will also be diagonal, i.e. it will be a symmetric tensor. On the other hand, we will have, in general, both a symmetric and an antisymmetric contribution for a non-diagonal flow rate. Let us consider some particular cases:

i) Flow through a pore oriented along the same direction as the chain. In this case the flow rate β has the following form:

$$\beta = \beta\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \tag{3.1.23}$$

where β is the flow rate strength, and the system has a rotational symmetry around the z-axis. The chain in these conditions is stretched by the elongational flow giving rise to the so-called *elogational viscosity* defined as follows

$$-\frac{\Pi_{zz}-\Pi_{xx}}{2\beta} = \frac{\pi\eta_o d^3}{8V}(N^2-1)\left\{2N+\frac{1}{3\lambda}\left(1-\frac{5}{18\lambda}\right)\right\}. \tag{3.1.24}$$

For a fluid flow with rotational symmetry around the x (or y) axis, we will have two different contributions coming from the differences

$$-\frac{\Pi_{xx}-\Pi_{zz}}{2\beta} = \frac{\pi\eta_o d^3}{8V}(N^2-1)\left\{N+\frac{2}{3\lambda}\left(1-\frac{5}{18\lambda}\right)\right\}, \tag{3.1.25}$$

$$-\frac{\Pi_{xx}-\Pi_{yy}}{2\beta}=\frac{\pi\eta_o d^3}{8V}(N^2-1)\left\{\frac{1}{3\lambda}\left(1-\frac{5}{18\lambda}\right)\right\}. \tag{3.1.26}$$

Moreover, in both cases we have a contribution coming from the trace of the pressure tensor, which for the flow rate given by Eq. (3.1.23) reads

$$-\frac{Tr\Pi}{6\beta}=\frac{\pi\eta_o d^3}{8V}(N^2-1)\left\{2N-\frac{2}{3\lambda}\left(1-\frac{5}{18\lambda}\right)\right\}, \tag{3.1.27}$$

and for the flow with rotational symmetry around the x axis is

$$\frac{Tr\Pi}{6\beta}=\frac{\pi\eta_o d^3}{8V}(N^2-1)\left\{N-\frac{1}{3\lambda}\left(1-\frac{5}{18\lambda}\right)\right\}. \tag{3.1.28}$$

ii) Planar elongational flow. This flow can be generated by four rotating infinite cylinders. If we locate the cylinders such that the flow rate is again a diagonal matrix, the pressure tensor will be diagonal and symmetric in view of Eq. (3.1.20), i.e. for

$$\boldsymbol{\beta}=\beta\begin{pmatrix}1&0&0\\0&0&0\\0&0&-1\end{pmatrix} \tag{3.1.29}$$

we will find a similar behavior of the system as the one described above. On the other hand if we rotate the four cylinders 45°, i.e. for

$$\boldsymbol{\beta}=\beta\begin{pmatrix}1&0&1\\0&0&0\\1&0&-1\end{pmatrix} \tag{3.1.30}$$

the pressure tensor has both a symmetric and an antisymmetric part. Related to these parts, we will find not only elongational viscosities but also a shear viscosity and a rotational viscosity given by

$$\Pi^{(s)}_{xz}=-2\eta\beta=-2\frac{\pi\eta_o d^3}{16V}(N^2-1)\left\{N+\frac{1}{3\lambda}\left(1-\frac{5}{18\lambda}\right)\right\}\beta, \tag{3.1.31}$$

$$\Pi^{(a)}_{xz}=-2\eta_r\beta=-2\frac{\pi\eta_o d^3}{16V}(N^2-1)\left\{N-\frac{1}{3\lambda}\left(1-\frac{5}{18\lambda}\right)\right\}\beta, \tag{3.1.32}$$

where we identify the shear and rotational viscosities

$$\eta = \frac{\pi\eta_o d^3}{16V}(N^2-1)\left\{N + \frac{1}{3\lambda}\left(1 - \frac{5}{18\lambda}\right)\right\}, \tag{3.1.33}$$

$$\eta_r = \frac{\pi\eta_o d^3}{16V}(N^2-1)\left\{N - \frac{1}{3\lambda}\left(1 - \frac{5}{18\lambda}\right)\right\}. \tag{3.1.34}$$

4 Conclusions

This chapter is intended as a preliminary study of the aggregation phenomena taking place in systems of magnetic particles in suspension and of the resulting structures.

Our first point has been to elucidate the influence of the hydrodynamic interactions (HI) in the kinetics of the aggregation process. We have extended the classic Smoluchowski theory of coagulation to account for the presence of HI ocurring when one goes beyond the dilute regime. Such interactions act before the different particles arrive at the sphere of influence of a given particle. We have obtained the kinetic equations for the aggregation process and from them we have analyzed the cluster formation. Our main conclusion is that the presence of HI slows down the aggregation process.

As a second problem we have studied the dynamics of a chain of magnetic particles under the influence of an external elongational flow. In particular, we have computed the contribution of the chain to the pressure tensor of the system from the rheological equation of state proposed by Kramers. From this quantity we have obtained the correction to the viscosities due to the presence of dipolar interactions.

These preliminary results will constitute the subject of future work.

Appendix A

Computation of the normalization constant C'

In this appendix we compute the normalization constant C' given in Eq. (3.1.17) of the Section 3. Its definition is the following

$$\frac{1}{C'} = \int (\prod_{l=1}^{N-1} d\vec{q}_l) \prod_{k=1}^{N-1} exp(-\Phi_{k,k+1}) \left\{ 1 + \frac{1}{2D} (\beta : \sum_i \sum_j C_{ij}\ \vec{q}_i\ \vec{q}_j) \right\}. \qquad \text{(A1)}$$

Using the fact that

a)

$$\begin{aligned}
&\int (\prod_{l=1}^{N-1} d\vec{q}_l) \prod_{k=1}^{N-1} exp(-\Phi_{k,k+1}) = \left(\int d\vec{q}_k exp(-\Phi_{k,k+1}) \right)^{N-1} \\
\simeq\ & \left(2\pi \int_0^\infty q_k^2 dq_k \int_0^\pi \sin\theta_k d\theta_k e^{\lambda(2-3\theta_k^2-6\xi_k)} \right)^{N-1} \\
\simeq\ & \left(2\pi d^3 e^{2\lambda} \int_0^\infty (1+2\xi_k) d\xi_k e^{-6\lambda\xi_k} \int_0^\infty \left(\theta_k - \frac{\theta_k^3}{3!} \right) d\theta_k e^{-3\lambda\theta_k^2} \right)^{N-1} \\
\simeq\ & \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2} \right)^{N-1} \left(1 + \frac{5}{18\lambda} \right)^{N-1}, \qquad \text{(A2)}
\end{aligned}$$

b)

$$\begin{aligned}
&\frac{\beta}{2D} : \sum_i \sum_{j(i\neq j)} C_{ij} \int (\prod_{l=1}^{N-1} d\vec{q}_l) \prod_{k=1}^{N-1} exp(-\Phi_{k,k+1})\ \vec{q}_i\ \vec{q}_j \\
\simeq\ & \frac{\beta}{2D} : \sum_i \sum_{j(i\neq j)} C_{ij} \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2} \right)^{N-3} \left(1 + \frac{5}{18\lambda} \right)^{N-3} \left(\int d\vec{q}_i exp(-\Phi_{i,i+1})\ \vec{q}_i \right)^2 \\
\simeq\ & \frac{\beta}{2D} : \sum_i \sum_{j(i\neq j)} C_{ij} \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2} \right)^{N-1} \left(1 + \frac{5}{18\lambda} \right)^{N-1} d^2\ \hat{e}_z \hat{e}_z \\
\simeq\ & \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2} \right)^{N-1} \left(1 + \frac{5}{18\lambda} \right)^{N-1} \frac{d^2 \beta_{zz}}{2D} \sum_i \sum_{j(i\neq j)} C_{ij}, \qquad \text{(A3)}
\end{aligned}$$

c)

$$\frac{\beta}{2D} : \sum_i C_{ii} \int (\prod_{l=1}^{N-1} d\vec{q}_l) \prod_{k=1}^{N-1} exp(-\Phi_{k,k+1})\ \vec{q}_i\ \vec{q}_i$$

$$\simeq \frac{\beta}{2D} : \sum_i C_{ii} \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-2} \left(1+\frac{5}{18\lambda}\right)^{N-2} \left(\int d\vec{q}_i exp(-\Phi_{i,i+1})\ \vec{q}_i\ \vec{q}_i\right)$$

$$\simeq \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-1} \left(1+\frac{5}{18\lambda}\right)^{N-2} \frac{d^2\beta}{2D} : \left\{\frac{1}{6\lambda}(\boldsymbol{I}-\hat{e}_z\hat{e}_z)+\right.$$

$$+ \left.\left(1+\frac{5}{18\lambda}\right)\hat{e}_z\hat{e}_z\right\} \sum_i C_{ii} \qquad \text{(A4)}$$

and the relations

$$\sum_{i=1}^{N-1}\sum_{j=1}^{N-1} C_{ij} = \frac{N(N^2-1)}{12}$$

$$\sum_{i=1}^{N-1} C_{ii} = \frac{N^2-1}{6} \qquad \text{(A5)}$$

we finally arrive at the expression (3.1.17)

$$\frac{1}{C'} = \left(\frac{\pi d^3 \exp^{2\lambda}}{18\lambda^2}\right)^{N-1} \left(1+\frac{5}{18\lambda}\right)^{N-1} \left\{1+\frac{d^2}{24D}N(N^2-1)\beta_{zz}+\right.$$

$$+ \left.\frac{d^2}{72\lambda D}\left(1+\frac{5}{18\lambda}\right)^{-1}(N^2-1)\boldsymbol{\beta} : (\boldsymbol{I}-\hat{e}_z\hat{e}_z)\right\}. \qquad \text{(A6)}$$

Appendix B

Explicit derivation of Eq. (3.1.19)

To solve Eq. (3.1.18), we first separate the integral into different parts

a)

$$\begin{aligned}
&\int (\prod_{l=1}^{N-1} d\vec{q}_l \; exp(-\Phi_{l,l+1})) \left(\vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k}\right) \\
\simeq \; & \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-2} \left(1+\frac{5}{18\lambda}\right)^{N-2} \left(\int d\vec{q}_k \; \vec{q}_k \frac{\partial \Phi_{k,k+1}}{\partial \vec{q}_k} exp(-\Phi_{k,k+1})\right) \\
\simeq \; & \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-1} \left(1+\frac{5}{18\lambda}\right)^{N-1} k_B T \boldsymbol{I} \qquad \text{(B1)}
\end{aligned}$$

b)

$$\begin{aligned}
&\frac{\beta}{2D} : \sum_{i(i\neq k)} \sum_{j(j\neq i,k)} C_{ij} \int (\prod_{l=1}^{N-1} d\vec{q}_l \; exp(-\Phi_{l,l+1})) \vec{q}_i \; \vec{q}_j \left(\vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k}\right) \\
\simeq \; & \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-2} \left(1+\frac{5}{18\lambda}\right)^{N-2} \frac{d^2 \beta_{zz}}{2D} \sum_{i(i\neq k)} \sum_{j(j\neq i,k)} C_{ij} \\
& \left(\int d\vec{q}_k \; \vec{q}_k \frac{\partial \Phi_{k,k+1}}{\partial \vec{q}_k} exp(-\Phi_{k,k+1})\right) \\
\simeq \; & \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-1} \left(1+\frac{5}{18\lambda}\right)^{N-1} \frac{k_B T d^2 \beta_{zz}}{2D} \sum_{i(i\neq k)} \sum_{j(j\neq i,k)} C_{ij} \boldsymbol{I} \qquad \text{(B2)}
\end{aligned}$$

c)

$$\begin{aligned}
&\frac{\beta}{2D} : \sum_{i(i\neq k)} C_{ii} \int (\prod_{l=1}^{N-1} d\vec{q}_l \; exp(-\Phi_{l,l+1})) \vec{q}_i \; \vec{q}_i \; \left(\vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k}\right) \\
\simeq \; & \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-2} \left(1+\frac{5}{18\lambda}\right)^{N-3} \frac{d^2}{2D} \boldsymbol{\beta} : \left\{\frac{1}{6\lambda}(\boldsymbol{I} - \hat{e}_z \hat{e}_z) + \right. \\
+ \; & \left. \left(1+\frac{5}{18\lambda}\right) \hat{e}_z \hat{e}_z \right\} \sum_{i(i\neq k)} C_{ii} \left(\int d\vec{q}_k \; \vec{q}_k \frac{\partial \Phi_{k,k+1}}{\partial \vec{q}_k} exp(-\Phi_{k,k+1})\right) \\
\simeq \; & \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-1} \left(1+\frac{5}{18\lambda}\right)^{N-2} \frac{k_B T d^2}{2D} \boldsymbol{\beta} : \left\{\frac{1}{6\lambda}(\boldsymbol{I} - \hat{e}_z \hat{e}_z) + \right. \\
+ \; & \left. \left(1+\frac{5}{18\lambda}\right) \hat{e}_z \hat{e}_z \right\} \sum_{i(i\neq k)} C_{ii} \boldsymbol{I} \qquad \text{(B3)}
\end{aligned}$$

d)

$$\begin{aligned}
&\frac{\boldsymbol{\beta}}{2D} : \sum_{i(i\neq k)} C_{ik} \int \Big(\prod_{l=1}^{N-1} d\vec{q}_l \; exp(-\Phi_{l,l+1})\Big) \vec{q}_i \; \vec{q}_k \left(\vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k}\right) \\
\simeq \; & \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-2} \left(1+\frac{5}{18\lambda}\right)^{N-2} \frac{d}{2D} \sum_{i(i\neq k)} C_{ik} \\
& \boldsymbol{\beta} : \hat{e}_z \left(\int d\vec{q}_k \; \vec{q}_k \; \vec{q}_k \frac{\partial \Phi_{k,k+1}}{\partial \vec{q}_k} exp(-\Phi_{k,k+1})\right) \\
\simeq \; & \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-1} \left(1+\frac{5}{18\lambda}\right)^{N-1} \frac{k_B T d^2}{2D} \sum_{i(i\neq k)} C_{ik} \\
& \boldsymbol{\beta} : \hat{e}_z (\boldsymbol{I}\hat{e}_z + \hat{e}_z \boldsymbol{I})
\end{aligned} \tag{B4}$$

e)

$$\begin{aligned}
&\frac{\boldsymbol{\beta}}{2D} : C_{kk} \int \Big(\prod_{l=1}^{N-1} d\vec{q}_l \; exp(-\Phi_{l,l+1})\Big) \vec{q}_k \; \vec{q}_k \left(\vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k}\right) \\
\simeq \; & \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-2} \left(1+\frac{5}{18\lambda}\right)^{N-2} C_{kk} \\
& \frac{\boldsymbol{\beta}}{2D} : \left(\int d\vec{q}_k \; \vec{q}_k \; \vec{q}_k \; \vec{q}_k \frac{\partial \Phi_{k,k+1}}{\partial \vec{q}_k} exp(-\Phi_{k,k+1})\right) \\
\simeq \; & \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-1} \left(1+\frac{5}{18\lambda}\right)^{N-2} \frac{k_B T d^2}{2D} C_{kk} \\
& \left(2\boldsymbol{I}\cdot\boldsymbol{\beta}\cdot\left\{\frac{1}{6\lambda}(\boldsymbol{I}-\hat{e}_z\hat{e}_z) + \left(1+\frac{5}{18\lambda}\right)\hat{e}_z\hat{e}_z\right\} + \right. \\
+ \; & \left. \boldsymbol{I}\boldsymbol{\beta} : \left\{\frac{1}{6\lambda}(\boldsymbol{I}-\hat{e}_z\hat{e}_z) + \left(1+\frac{5}{18\lambda}\right)\hat{e}_z\hat{e}_z\right\}\right) .
\end{aligned} \tag{B5}$$

where we have used some of the integrals that we have computed in Appendix A. Once we have evaluated these different contributions, Eq. (3.1.18) reads

$$\begin{aligned}
\left\langle \vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k} \right\rangle \; = \; & C' \left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-1} \left(1+\frac{5}{18\lambda}\right)^{N-1} k_B T \\
& \left\{1 + \frac{d^2 \beta_{zz}}{2D} \sum_{i(i\neq k)} \sum_{j(j\neq i,k)} C_{ij} \boldsymbol{I} + \frac{d^2}{2D}\left(1+\frac{5}{18\lambda}\right)^{-1}\right. \\
& \boldsymbol{\beta} : \left\{\frac{1}{6\lambda}(\boldsymbol{I}-\hat{e}_z\hat{e}_z) + \left(1+\frac{5}{18\lambda}\right)\hat{e}_z\hat{e}_z\right\} \sum_{i(i\neq k)} C_{ii} \boldsymbol{I} +
\end{aligned}$$

$$
\begin{aligned}
&+ \frac{d^2}{2D}\left(\sum_{i(i\neq k)} C_{ik} + \sum_{j(j\neq k)} C_{jk}\right)\boldsymbol{\beta} : \hat{e}_z(\boldsymbol{I}\hat{e}_z + \hat{e}_z\boldsymbol{I}) + \\
&+ \frac{d^2}{2D}\left(1+\frac{5}{18\lambda}\right)^{-1} C_{kk}\left(2\boldsymbol{I}\cdot\boldsymbol{\beta}\cdot\left\{\frac{1}{6\lambda}(\boldsymbol{I}-\hat{e}_z\hat{e}_z)+\right.\right. \\
&+ \left.\left(1+\frac{5}{18\lambda}\right)\hat{e}_z\hat{e}_z\right\} + \boldsymbol{I}\boldsymbol{\beta} : \left\{\frac{1}{6\lambda}(\boldsymbol{I}-\hat{e}_z\hat{e}_z)+\right. \\
&+ \left.\left.\left(1+\frac{5}{18\lambda}\right)\hat{e}_z\hat{e}_z\right\}\right)\Bigg\} = C'\left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-1}\left(1+\frac{5}{18\lambda}\right)^{N-1} k_B T \\
&\left\{\left(1+\frac{d^2\beta_{zz}}{2D}\sum_{i,j} C_{ij}\right)\boldsymbol{I} + \frac{d^2}{12D\lambda}\left(1+\frac{5}{18\lambda}\right)^{-1}\sum_i C_{ii}\right. \\
&\boldsymbol{\beta} : (\boldsymbol{I}-\hat{e}_z\hat{e}_z)\boldsymbol{I} + \frac{d^2}{2D}\left(2\sum_i C_{ik}\boldsymbol{\beta}\cdot\hat{e}_z\hat{e}_z\right) + \\
&+ \left.\frac{d^2}{6D\lambda}\left(1+\frac{5}{18\lambda}\right)^{-1} C_{kk}\boldsymbol{\beta}\cdot(\boldsymbol{I}-\hat{e}_z\hat{e}_z)\right\}. \qquad \text{(B6)}
\end{aligned}
$$

And considering again the relations (A5), we arrive at

$$
\begin{aligned}
\left\langle \vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k} \right\rangle &= C'\left(\frac{\pi d^3 e^{2\lambda}}{18\lambda^2}\right)^{N-1}\left(1+\frac{5}{18\lambda}\right)^{N-1} k_B T \\
&\left\{\boldsymbol{I} + \frac{d^2\beta_{zz}}{24D}N(N^2-1)\boldsymbol{I} + \frac{d^2}{D}\sum_i C_{ik}\,\boldsymbol{\beta}\cdot\hat{e}_z\hat{e}_z + \right. \\
&+ \frac{d^2}{12D\lambda}\left(1+\frac{5}{18\lambda}\right)^{-1}\left(\boldsymbol{\beta} : (\boldsymbol{I}-\hat{e}_z\hat{e}_z)\frac{N^2-1}{6}\boldsymbol{I} + \right. \\
&+ \left.\left. 2C_{kk}\boldsymbol{\beta}\cdot(\boldsymbol{I}-\hat{e}_z\hat{e}_z)\right)\right\}. \qquad \text{(B7)}
\end{aligned}
$$

Finally, if we introduce the normalization constant (3.1.17), up to first order in $\boldsymbol{\beta}$ we obtain

$$
\begin{aligned}
\left\langle \vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k} \right\rangle &= k_B T\left\{\boldsymbol{I} + \frac{d^2\beta_{zz}}{24D}N(N^2-1)\boldsymbol{I}\right. \\
&+ \frac{d^2}{D}\sum_i C_{ik}\,\boldsymbol{\beta}\cdot\hat{e}_z\hat{e}_z + \frac{d^2}{12D\lambda}\left(1+\frac{5}{18\lambda}\right)^{-1}(\boldsymbol{\beta} : (\boldsymbol{I}-\hat{e}_z\hat{e}_z) \\
&\left.\frac{N^2-1}{6}\boldsymbol{I} + 2C_{kk}\boldsymbol{\beta}\cdot(\boldsymbol{I}-\hat{e}_z\hat{e}_z)\right)\Big\} \\
&\left\{1 - \frac{d^2\beta_{zz}}{24D}N(N^2-1) - \frac{d^2}{72D\lambda}\left(1+\frac{5}{18\lambda}\right)^{-1}(N^2-1)\,\boldsymbol{\beta} : \right. \\
&\left.(\boldsymbol{I}-\hat{e}_z\hat{e}_z)\right\}, \qquad \text{(B8)}
\end{aligned}
$$

which after simplifying reduces to Eq. (3.1.19), valid up to linear order in the flow rate $\boldsymbol{\beta}$

$$\left\langle \vec{q}_k \frac{\partial V_{mag}}{\partial \vec{q}_k} \right\rangle = k_B T \left\{ \boldsymbol{I} + \frac{d^2}{D} \sum_i C_{ik} \boldsymbol{\beta} \cdot \hat{e}_z \hat{e}_z + \frac{d^2}{6D\lambda} \left(1 - \frac{5}{18\lambda} \right) C_{kk} \boldsymbol{\beta} \cdot (\boldsymbol{I} - \hat{e}_z \hat{e}_z) \right\}. \tag{B9}$$

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CONCLUSIONS AND PERSPECTIVES

Along the lines of this monograph we have been mainly concerned with the study of fluid systems either with magnetic monodomains or with two types of particles magnetic and non-magnetic dispersed in a Newtonian fluid in non-equilibrium conditions. The behavior of these systems is greatly influenced by the presence of an external magnetic field giving rise to new phenomena which have provided the basis of many practical applications. Nevertheless, this influence depends upon the different relaxation process which take place inside the particles with respect to their crystalline axis, as well as outside them with respect to the the carrier fluid. We have described which are these processes and obtained the dependence of some coefficients characterizing the rheological, magnetic, and optical properties of the colloidal suspension, on the magnetic field and on the parameters describing the particles and the liquid.

To be precise, in the first part of Chapter I we have analyzed the dynamics of a ferromagnetic spherical particle in which the magnetic moment is rigidly attached to the particle body, as well as the viscosities of a dilute suspension constituted by these type of probes. The starting theoretical framework is mainly based on the Navier-Stokes equation in which an induced force, resulting from the perturbation introduced in the dynamics of the fluid by the particle, and a stochastic Langevin source, coming from the fluctuations of the hydrodynamical fields, have been included. This equation accounts for the coupled dynamics of the fluid and the particle. A multipolar expansion of the quantities appearing in the formal solution of the Navier-Stokes-Langevin equation leads to the expressions for the force and torque exerted on the particle which contain random contributions whose statistical properties are dictated by fluctuating hydrodynamics. We use two methods to obtain the shear and rotational viscosities. One is deterministic and is based on the Kirkwood formula for the viscous pressure tensor which is shown to be related to the second order multipole

of the induced force. The other is based on the linear response theory giving the transport coefficients in terms of time-dependent correlation functions. The presence of the field is responsible for the appearance of an antisymmetric contribution to the pressure tensor and introduces the rotational viscosity as a new transport coefficient. In addition, the antisymmetric stresses come from the fact that the torque exerted by the magnetic field on a dipole and the hydrodynamic torque balance each other out. Consequently, the angular velocity of the particle may differ from the value of the vorticity of the fluid at the point it occupies. This rather general formalism is used in the second part to calculate the dependence of the rotational viscosity on the magnetic anisotropy energy of the material. By considering another specific limit in which the magnetic moments have already relaxed towards the field direction, we obtain that the viscosity increases when increasing the anisotropy parameter and reaches a saturation limit. We have compared our results to that given by other authors and to available experimental data for rigid dipoles. The result coming from another approximate solution of the stationary Smoluchowski equation overestimates ours, whereas the one based on a phenomenological relaxation equation they propose for the internal angular momentum of the suspension, is closer to ours and reproducing quite well the experiments.

Following a similar procedure, in Chapter II we have presented a general formalism to study the relaxation dynamics of ferromagnetic particles with the main purpose of providing explicit expressions not only for the viscosity but for some relaxation times characterizing different properties of the material (birefringence, magnetic susceptibility,...). The results cover the whole range of possible experimental situations. We have obtained the Smoluchowski equation describing the evolution of the probability density of the relevant degrees of freedom of the particles. This equation allows us to obtain a hierarchy of dynamic equations for the different correlation functions that can be closed using appropriate decoupling approximations. The correlation dynamics provides expressions for the characteristic relaxation times and they constitute the starting point to determine the transport coefficients using the Green-Kubo formulas. In particular, we have seen that the rotational viscosity reaches again a saturation limit but now depends on both of the parameters comparing magnetic and anisotropy energy to thermal energy. To check the validity of our formalism, we have compared our results for the relaxation time of the particles to birefringence experiments carried out with two types of ferromagnetic material. In both cases, our results are largely in agreement with the experiments. We also provide a general expression for the complex magnetic susceptibility of the magnetic fluid under the simultaneous action of a

constant polarizing magnetic field and a small *ac* field, perpendicular to each other, openning the possibility for new experimental measurements.

In Chapter III we have studied the dynamics of a nonmagnetic particle or magnetic hole suspended in a ferrofluid in the presence of a rotating magnetic field. We compute the hydrodynamic force and torque exerted on the hole from which we can identify the translational and rotational friction tensors. These quantities depend on the volume fraction of magnetic particles and of the magnetic field, which gives an anisotropic character to the system. The knowledge of the force and torque acting on the hole enables us to study both the translational and rotational dynamics of the particles when applying a rotating magnetic field. We have particularly focused on the case when the ferrofluid is at rest and the hole may rotate influenced by the magnetic field. Under these conditions, we have shown that the angular velocity of the hole is proportional to the frequency of the field, but has an opposite direction. The proportionality coefficient is linear in the volume fraction of ferromagnetic particles and depends on a function of the the magnetic field strength which shows up a saturation behaviour. We have compared our results to experiments done with particles of polystyrene dispersed in different ferrofluids. In the frequency range we are considering, our linear law agrees with the experiments. Additionally, we have also reproduced experimental results giving the rotational velocity of the hole as a function of the external magnetic field. A preliminary study of the hydrodynamic interactions among the holes in the ferrofluid has also been carried out. Essentially, we have obtained the expressions for the Oseen and Rotne-Prager equivalent tensors as the first steps in the study of the important role that hydrodynamic interactions can play in the physical properties of these composite materials at low concentrations. Two show up the structure of these tensors and their influence on the dynamics of the magnetic holes, we have also given the velocities of a couple of particles falling under the action of gravity in a ferrofluid. As we expected, for the different initial configurations, the velocity does depend on the parameters characterizing the ferrofluid. It is worth pointing out that although we have performed the study for a ferrofluid constituted by rigid dipoles, for which the energy of anisotropy is much greater than the energy associated with the interaction of the magnetic moments and the external field, a similar analysis can be carried out for a general situation in which these two energies of the magnetic particles in the ferrofluid may take arbitrary values.

Chapter IV is intended as a preliminary study of the aggregation phenomena taking place in systems of magnetic particles in suspension and of the resulting structures. Our first point has been to elucidate the influence of the hydrodynamic interactions in

the kinetics of the aggregation process. We have extended the classic Smoluchowski theory of coagulation to account for the presence of these interactions ocurring when one goes beyond the dilute regime. Such interactions act before the different particles arrive at the sphere of influence of a given particle. We have obtained the kinetic equations for the aggregation process and from them we have analyzed the cluster formation. Our main conclusion is that the presence of hydrodynamic interactions slows down the aggregation process. As a second problem we have studied the dynamics of a chain of magnetic particles under the influence of an external elongational flow. In particular, we have computed the contribution of the chain to the pressure tensor of the system from the rheological equation of state proposed by Kramers. From this quantity we have obtained the correction to the viscosities due to the presence of dipolar interactions. These preliminary results will constitute the subject of future work.

There are different lines of research whose starting point will be the contents of this thesis. Among them, we can mention that it will worth taking into account inertia and polydispersity effects in the whole analysis. As we have briefly commented in the introduction, inertial effects would determine an additional oscillatory regime of the relaxation process for really high magnetic fields, but it becomes essential for describing the high-frequency behavior of rotating particles. With regards to polydispersity, as the different relaxation processes depend in a different way on the volume of the particles, their contributions to the computed magnitudes is not the same for a real polydisperse colloidal suspension. For instance, the spectrum of the relaxation times might be rather wide. Another line of possible research would go beyond the linear response of the system in non-equilibrium conditions.

Ferromagnetic probes have shown to be a successful way of measuring viscosities of the carrier liquids. It will be very interesting to provide a theoretical analysis of the same rotational relaxation phenomena in a viscoelastic or elastic media to determine the elastic modulus, or to characterize the sol-gel transition in different viscoelastic media. Going to the low temperatures regime, a ferromagnetic monodomain suspended in liquid helium can check the relavance of the conservation of the angular momentum in magnetic quantum tunneling transitions.

At higher concentrations, the rheology of irregular-shaped aggregates will be another problem in which a great deal of attention is being concentrated nowadays. In addition, it is still open the question of the phase diagram of a dipolar fluid.

We have started pursuing work on the so-called ferrosmectiques phases, in which a polymeric lamellar phase is swollen with a ferrofluid. The study of the particle's

dynamics in such a confined geometry constitutes another interesting subject of theoretical research for which experimental measurements are available.

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