THE EFFECTIVE FIELD METHOD IN THE ORIENTATIONAL KINETICS OF MAGNETIC FLUIDS

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**Introduction**

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<thead>
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<th>Description</th>
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<tbody>
<tr>
<td>$\lambda$</td>
<td>dimensionless parameter of the magnetic dipole-dipole interparticle interaction</td>
</tr>
<tr>
<td>$\mu$</td>
<td>magnetic moment of a single-domain ferroparticle</td>
</tr>
<tr>
<td>$r$</td>
<td>interparticle distance</td>
</tr>
<tr>
<td>$k_BT$</td>
<td>thermal motion energy</td>
</tr>
<tr>
<td>$I$</td>
<td>saturation magnetization of a ferromagnetic material</td>
</tr>
<tr>
<td>$d$</td>
<td>mean diameter of a single-domain particle</td>
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**Chapters 1–3**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\sigma_w$</td>
<td>surface tension coefficient of a magnetic domain wall</td>
</tr>
<tr>
<td>$d_c$</td>
<td>reference value of a particle diameter below which the particle retains the single-domain state</td>
</tr>
<tr>
<td>$U_n$</td>
<td>density of the non-uniform exchange interaction</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>non-uniform exchange constant</td>
</tr>
<tr>
<td>$K$</td>
<td>density of the magnetic anisotropy energy of a single-domain ferroparticle</td>
</tr>
<tr>
<td>$A$</td>
<td>exchange integral of a ferromagnetic material</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Curie temperature of a ferromagnetic material</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>uncertainty of energy of an electron</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>uncertainty of momentum of an electron</td>
</tr>
<tr>
<td>$m$</td>
<td>mass of an electron</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck constant</td>
</tr>
<tr>
<td>$e$</td>
<td>unit vector in the direction of the magnetic moment of a particle</td>
</tr>
<tr>
<td>$U_a$</td>
<td>magnetic anisotropy energy of a particle</td>
</tr>
<tr>
<td>$V_m$</td>
<td>magnetic volume of a particle</td>
</tr>
<tr>
<td>$\eta_m$</td>
<td>effective magnetic viscosity of a particle</td>
</tr>
<tr>
<td>$\tau_D$</td>
<td>reference time of orientational diffusion of the magnetic moment inside a particle</td>
</tr>
<tr>
<td>$\tau_N$</td>
<td>Néel relaxation time</td>
</tr>
<tr>
<td>$\mu_B$</td>
<td>Bohr magneton</td>
</tr>
<tr>
<td>$H$</td>
<td>external magnetic field</td>
</tr>
<tr>
<td>$n$</td>
<td>unit vector of the particle anisotropy axis</td>
</tr>
<tr>
<td>$N_{ik}$</td>
<td>tensor of demagnetization factors</td>
</tr>
<tr>
<td>$U$</td>
<td>orientation-dependent part of the internal magnetic energy of a particle</td>
</tr>
<tr>
<td>$H_s$</td>
<td>net magnetic field experienced by the particle magnetic moment</td>
</tr>
<tr>
<td>$H_a$</td>
<td>magnetic anisotropy field</td>
</tr>
</tbody>
</table>
α  Landau-Lifshitz dissipation constant
γ  gyromagnetic ratio
D  orientational diffusion coefficient
σ  dimensionless ratio of the anisotropy energy of the particle to its thermal energy
τ₀  decay time the Larmor precession of the magnetic moment
J  moment of inertia of a particle
ωₚ  angular velocity of a particle
\mathcal{M}  external torque
ζ  rotary friction coefficient of a particle
η  viscosity coefficient of the liquid matrix of a suspension
τₛ  relaxation time of the mechanical rotation of the particle
τₐ  reference time of orientational diffusion of the particle in a viscous fluid
ξ  dimensionless ratio of the particle energy in the external field to its thermal energy (the Langevin argument)
τₙ  characteristic time of the particle mechanical rotation under the influence of the anisotropy-energy torque
W  orientation distribution function of the particle magnetic moment
h  unit vector in the direction of the external magnetic field
\hat{\mathcal{J}}  infinitesimal rotation operator
W₀  equilibrium orientation distribution function of the particle magnetic moment
Z₀  equilibrium partition integral
\dot{\theta}, \phi  polar coordinates of the magnetic moment
L  Langevin function
I_{n+1/2}  modified Bessel function of the half-integer index
λₙm  decrements of the normal modes of the orientational distribution function
fₙm  eigenfunctions (coordinate parts) of the normal modes of the orientational distribution function
τₙm  relaxation times of the normal modes
Mₗl, Mₜₜ  components of magnetization of magnetic fluid in the parallel and perpendicular to the external field directions, respectively
ω  frequency of oscillations of the external field
χ₀  initial magnetic susceptibility of a magnetic fluid
Yu. L. Raikher and M. I. Shliomis. The effective-field method...

\( \tau_\parallel, \tau_\perp \) relaxation times of the components of magnetization of magnetic fluid in the parallel and perpendicular to the external field directions, respectively

\( \mathbf{\xi}_e \) dimensionless vector of the effective-field

\( \chi_\parallel, \chi_\perp \) diagonal components of the magnetic susceptibility tensor of a magnetic fluid

\( \chi', \chi'' \) real and imaginary parts of a component of the dynamic susceptibility tensor

\( n_o, n_e \) refraction indices for ordinary and extraordinary light rays in a birefringent medium

\( n_\parallel, n_\perp \) refraction indices of the magnetic fluid in the directions parallel and perpendicular to the external field, respectively

\( \delta \) optical phase lag

\( Q, Q_0 \) intensities of the transmitted and incident light, respectively

\( S_{ik} \) orientation tensor of a magnetic fluid

\( \varepsilon_{ik} \) dielectric permeability tensor of a magnetic fluid

\( \kappa \) effective dielectric permeability constant of a particle

\( \phi \) volume density of solid phase in a suspension

**Chapters 4–7**

\( \omega_H \) frequency of the Larmor precession of the particle magnetic moment

\( X_{ik,...} \) tensors of equilibrium statistical moments of the products of components of the vector \( \mathbf{e} \)

\( R \) polar-angle part of the partition integral of a magnetic particle with a uniaxial anisotropy

\( P^m_n \) associated Legendre functions

\( \chi_\parallel, \chi_\perp \) diagonal components of the magnetic susceptibility tensor of a magnetic particle

\( \alpha_e \) effective constant of the Larmor precession damping

\( H_{res} \) resonance field of FMR in a magnetic particle

\( \Delta H \) FMR absorption line width in a magnetic particle

\( Y_{ik}(\varepsilon, \varphi) \) spherical harmonics

\( K_u \) uniaxial anisotropy constant

\( K_c \) cubic anisotropy constant

\( \chi_+ \) dynamic susceptibility of a magnetic particle with respect to a circularly polarized external field

\( \overline{\chi}_+ \) dynamic susceptibility of a random assembly of magnetic particles

\( U \) partially equilibrium energy function of a magnetic particle

\( P(n, t) \) orientational distribution function of a particle in a state of partial equilibrium

\( J_n \) Bessel function

\( Q_c, Q_0^{(2\omega)} \) zero and second Fourier harmonics of the intensity of light transmitted through a magnetic fluid specimen
Introduction

Anticipating the reader’s reaction to the title of this paper, we admit that it combines certain terms whose standings in the conventional physical thesaurus are rather distant. Indeed, the notion of an effective field is used widely and frequently to refer to any auxiliary field (real or artificial) introduced into a theoretical model (and usually namely by this transforming a rigorous theory into an approximate model) in order to build up a simplified way to take into account the effect of some complicated factors, like interparticle interactions, which either are too difficult for exact evaluation or even are not yet sufficiently clear in detail. The classic example of such a usage of the “effective field” term is the Weiss model for the spin–spin exchange interactions in the theory of ferromagnetism, see the title and content of the book [1].

Since the term under discussion is to the highest extent general, every author imparts to it one’s own precise meaning, and apparently should make his point as clear as possible before involving an innocent reader into the particularities of calculation and interpretation of the results obtained. Here, in the introductory remarks, we restrict our dealing with this question to a declaration that we are aware of the necessity of being careful with the terms used, and in below would try to prevent any misleading terminological similarities.

From now on and everywhere throughout this paper the references to the “effective field” or the “effective-field method” mean that we use the concept of an auxiliary external (one- or multi-component) field that is constructed just for consideration of the non-equilibrium processes. Namely, the addition of the corresponding (proportional to this field) term to the Hamiltonian of the system makes the state of the latter an equilibrium one in any given instant of time. In result, the kinetic equation describing the evolution of a non-equilibrium system is reduced to a much more simple equation for the corresponding effective field. This very idea, that we had once invented to handle one particular case [2], has proved itself to be a plausible method to treat a number of problems of the theory of the rotational Brownian motion. The discussion of the physical basis of the effective-field concept, as we see and understand it, is given in Sec.3, which is principal and essential for all the considerations following it.

Conversely, the term “magnetic fluid” is much younger and has not yet become a common place in the physical lexicon. As far as we know, it is for the first time that it appears as a title word in the Advances in Chemical Physics. If even not so, the main object of our studies deserves to be clarified from the very beginning.

According to the now well-adopted terminology (which as always in such cases cannot be considered entirely adequate), we call a magnetic fluid or ferrofluid a stable colloidal suspension of ultra-fine particles of a ferromagnet or ferrite in any ordinary liquid (e.g. water, a liquid hydrocarbon, ester etc.). Since the existence of real monophase liquid ferromagnets is to the highest extent questionable, the magnetic fluids were created as artificial media in a pursue of an idea to enhance the magnetic properties (susceptibility, saturation magnetization) of a liquid substance to degrees comparable with those of solid ferromagnets by embedding a sufficient number of small ferromagnetic particles into a usual dia- or paramagnetic liquid.

The media, thus obtained, are highly stable colloidal solutions (only microscopically heterogeneous) of single-domain ferroparticles which do not coagulate with ageing or under
the influence of an external magnetic field. The methods and applications of the colloidal
chemistry invented and used to achieve this goal, undoubtedly, might have comprise a
content of a separate ample review or book. Not to the least being able to deal here with
the questions of the synthesis of the wide variety of magnetic fluids already existing, we can
only address an interested reader to the monograph [3], book [4], references therein and
ample bibliographic directories [5] published regularly by the International Conferences
on Magnetic Fluids.

The particular area of the magnetic fluid science, which we have been working at for
a number of years and intend to highlight in this paper, is the statistical physics and
physical kinetics of non-aggregated magnetic fluids.

The theoretical basis capable to provide both correct qualitative understanding and
reliable quantitative predictions upon this class of ferrofluids may be considered to be
well developed now. This progress has been achieved due to the effort of numerous
researches, who were and still are attracted by interesting and, often, challenging physical
problems arisen basically by the mere fact of existence of magnetic fluids. Since it is
impossible to pack into one paper all the knowledge acquired by the world-wide magnetic
fluid scientific community [5], we have written this our review as a modern revision and
updated continuation of our previous ones [6, 7].

The assumption about a magnetic fluid, being not aggregated, means a lot for the
physical essence of the problems under consideration. One of the main features of a mag-
netic fluid, as a colloidal system, is its enhanced tendency towards coagulation. Indeed,
besides usual van der Waals forces and electrochemical potentials, in ferrocolloids we
have the powerful magnetic dipole-dipole interparticle interaction. The latter is capable
to produce aggregation and, hence, sedimentation of clamps of single-domain particles,
thus entirely destroying the magnetic fluid. The problem of the aggregation stability of
ferrofluids is a very difficult one to treat and up to now has not got a satisfactory solu-
tion. But to understand the general line, one does not need to be acquainted with the
details of complicated contemporary theories [8–10]. The major criterion responsible for
the particle aggregation in a magnetic fluid may be obtained directly from a comparison of
the reference energy $\mu^2/r^3$ of the dipole-dipole attraction of two identical single-domain
magnetic particles separated by a distance $r$ and having magnetic moments $\mu$ to the
thermal agitation energy $k_B T$. Thus constructed dimensionless ratio

$$\lambda = \frac{\mu^2}{r^3 k_B T}$$  \hspace{1cm} (0.1)

measures the tendency to coagulation for a particular ferrocolloid and points out to the
main factors influencing it. Apparently, in order to be granted the absence or low rate of
magnetic coagulation, the parameter $\lambda$ should be sufficiently small.

The most tough situation for the stability of a colloid occurs when in the process of
the Brownian motion two single-domain particles run into one another. In case of such
a collision the denominator in formula (0.1) assumes minimum, because the interparticle
distance $r$ becomes equal to the particle diameter $d$. Being single-domain, means that for
a given size the particle possesses the highest possible magnetic moment $\mu = (\pi/6) I d^3$,
where $I$ is the magnetization of the particle substance. Therefore, the maximum value of
the interaction constant is

$$\lambda = (\pi/6) I^2 d^3 / k_B T.$$  \hspace{1cm} (0.2)
According to the conclusions of modern theory of coagulation stability of ferrocolloids [11], the latter retain their stability in the range \( \lambda \leq 4.5 \), with \( \lambda \) defined by Eq.(0.2). Setting \( I \approx 500 \text{ G} \), as for magnetite (the most popular ferrite material to prepare magnetic fluids), one finds that the last inequality holds for the colloids with the particle diameter \( d \leq 15 \text{ nm} \).

Adopting the absence of coagulation as a basic assumption, one arrives at a theoretical model of a ferrocolloid as an assembly of independent non-interacting magnetic grains suspended in a liquid matrix and subjected to the rotational Brownian motion \(^1\). This, in turn, pre-defines the natural mathematical framework of the paper—it is the theory of orientational diffusion, which we specify and apply to a number of important physical problems.

We begin Chapter 1 with briefing the reader on some necessary to know of properties of single-domain magnetic particles and consider the reference time-scales inherent to magnetic fluids. Then, after having made an acquaintance with the rotary diffusion equation for the simplest—rigid dipole—model of magnetic fluid, where the magnetic anisotropy of the particles is assumed infinitely large, we put forward and explain the concept of the effective field. The last three sections illustrate the procedure of solution of several magnetic and optical problems important to the physics of magnetic fluids and discuss the results obtained.

The most part of Chapter 4 is devoted to consideration of the kinetics of magnetization processes taking place inside a single-domain ferromagnetic particle: Néel superparamagnetism and the effect of thermal fluctuations on the Larmor precession, i.e., ferromagnetic resonance. The study of these phenomena is based on a modified rotary diffusion equation, where a finiteness of the particle magnetic anisotropy energy is taken into account. In the last section of the Chapter we show how the intraparticle superparamagnetism manifests itself in the low-frequency dynamic birefringence of a magnetic fluid.

\(^1\)Further on we consider only the situations where the external magnetic fields are supposed to be uniform, so that the spatial degrees of freedom of the particles, and, hence, their translational Brownian motion, does not need to be taken into account.
1 Magnetic properties of fine ferroparticles

1.1 Single-domain magnetic particles and superparamagnetism

It is clear that the magnetic properties of a ferrocolloid are determined by the magnetic properties of its disperse phase. Thus, it is necessary to have a brief acquaintance with the essential facts concerning magnetic properties of fine ferromagnetic particles.

A massive ferromagnetic crystal in the absence of an external field is known to consist of magnetic domains. Inside each domain magnetization is uniform but the magnetization directions of different domains point different directions thus reducing the stray fields around the sample. Particular shapes and sizes of ferromagnetic domains formed in the thermodynamic equilibrium are determined by the condition that the total free energy of the sample must be minimum. In a simplest case the free energy density of a ferromagnet writes

\[ E = q \left( \frac{\partial I}{\partial r} \right)^2 - \frac{K}{I_S^2} (I \cdot n)^2 - \frac{1}{2} (I \cdot H_{dm}) - (I \cdot H). \]  

(1.1)

Here the first term in the right-hand side is known as the non-uniform exchange contribution. As it follows from the phenomenology of ferromagnetism, the inter-spin exchange interaction sets all the spins parallel to each other thus establishing a long-range orientational order in the spin subsystem of the crystal or, in other words, creates a spontaneous magnetization. If, due to some cause, a non-collinearity of spins occurs, the energy density increment is rendered by this term. At room temperature the exchange interaction is very strong and normally cannot be counteracted by any other interaction at the length scale of several lattice periods. This means that locally the crystal is always magnetized to saturation. Thence, the magnetization vector may be written as

\[ I = I_S e, \]  

(1.2)

with \( e \) being a unit vector. Carrying on this consideration one comes to a conclusion that under spin collinearity established by the exchange interaction the changes of \( I \) are exhausted by slow spatial variations of the vector \( e \). Rearranging the corresponding contribution in Eq. (1.1) one gets

\[ E_{\text{non-uniform}} = q I_S^2 \frac{\partial e}{\partial x_i} \frac{\partial e}{\partial x_i} = q I_S^2 (\nabla e)^2, \]  

(1.3)

where we indicate explicitly summation of the components.

The second term in the right-hand side of Eq. (1.1) presents the simples phenomenological form of the inter-crystal spin-orbit interaction that in phenomenology is called magnetic anisotropy. As this term describes the interaction of the magnetization with the crystal field, one understands that the direction of the unit vector \( n \) is determined by the lattice structure of a given sample. The parameter \( K \) has the meaning of the magnetic anisotropy energy density of the crystal. With allowance for the constant length of the magnetization vector the anisotropy term writes

\[ E_{\text{anisotropy}} = -K (e \cdot n)^2. \]  

(1.4)

To be specific, we assume \( K \) to be positive and thus arrive at the case that is well-known in ferromagnetism as the easy-axis anisotropy. Indeed, as formula (1.4) shows, parallelism
of \( e \) to the axis \( n \) is energetically the most favorable magnetization orientation in the crystal.

The third term in Eq. (1.1) results from interaction of the sample magnetization with the field created by the magnetic poles which necessarily exist at the boundaries of a ferromagnetic body. Equivalent names for it are the magnetostatic term or the demagnetizing term. As the demagnetizing field of the poles is due to the magnetization of the same body, one has

\[
E_{\text{demagn}} = -\frac{1}{2} I_S (e \cdot H_{\text{dm}}) \sim I_S^2.
\]  

The last term in Eq. (1.1) rewrites as

\[
E_{\text{Zeeman}} = -I_S (e \cdot H),
\]  

and is easily recognizable as the Zeeman energy of magnetization interaction with the external magnetic field \( H \).

As already mentioned, the most developed domain pattern is inherent to the case of zero external field. Thence the sample splits to a maximum number of domains. The boundary between them—the domain wall—is a transition layer inside which the direction of magnetization changes. Such a structure apparently augments the non-uniform exchange and the anisotropy terms in the energy expression at the expense of reducing the magnetostatic energy of the sample as a whole. In a macroscopic sample the width of domain walls is far smaller than the equilibrium size of a domain. Note that only under this condition it is possible to speak about some domains structure and not of a smoothly distorted uniform distribution. Thus it becomes possible [12] to introduce the surface energy density \( \sigma_w \) of the wall.

![Figure 1.1: Schematic representation of a magnetic domain wall. This type of the wall is known as the Bloch wall](image)

To get an idea of the structure of a domain wall and to estimate its tension, let us imagine a long horizontal bar of a ferromagnet whose anisotropy axis is directed vertically; the external field is absent. The bar is divided in two parts, domains, whose magnetizations look opposing directions. The domains are separated by a vertical transition zone (wall), inside which the magnetization vector, if to move from left to right, turns by 180°.
Schematically, this magnetization distribution is shown in Fig. (1.1). On its consideration it becomes clear that the domain wall with necessity is a non-uniform structure. Because of the non-parallelism of vector $e$ with the easy axis and the dependence of $e$ on the horizontal coordinate the magnetic free energy inside the wall is enhanced due to all the three contributions described by formula (1.1) at $H = 0$.

Estimating the spatial derivative as $1/l$, where $l$ is the reference wall width, one gets for the non-uniform exchange energy increment (per unit area of the wall)

$$\delta E_{\text{non-uniform}} \sim \frac{qI_2^2}{l}. \quad (1.7)$$

As it follows from Eq. (1.1), both the anisotropy and the magnetostatic energies are proportional to the sample volume, so that for the energy per unit area one finds.

$$\delta E_{\text{anisotropy}} \sim Kl, \quad \delta E_{\text{demagn}} \sim I_2^2 l. \quad (1.8)$$

To simplify the situation, with respect to the latter contributions we shall consider only the limiting cases. They are quite customary in magnetism: a magnetically hard material where $K \gg I_2^2 S$ and a magnetically soft substance with $I_2^2 S \gg K$.

In the magnetically hard case it is possible to neglect magnetostatics, and the main part of the energy increment due to occurrence of the wall is

$$\delta E \sim \frac{qI_2^2}{l} + Kl. \quad (1.9)$$

This expression explicitly shows that in equilibrium the wall cannot be neither too narrow nor too thick. In both cases the increment will be too large. Obviously, the sought for estimate for the wall thickness follows from minimization of $\delta E$ with respect to $l$. This gives

$$l^{(\text{mh})} \sim I_2 S \sqrt{\frac{q}{K}}, \quad (1.10)$$

where the subscript reminds that we are dealing with a magnetically hard material. Substituting this in either of the terms of Eq. (1.9), we get for the energy per unit area of the wall

$$\sigma_{w}^{(\text{mh})} \sim I_2 S \sqrt{qK}. \quad (1.11)$$

Equivalently, one may call this the surface tension of a domain wall.

Repeating the above calculations for a magnetically soft particle that requires merely to change $K$ for $I_2^2 S$ in Eq. (1.9), one finds

$$l^{(\text{ms})} \sim \sqrt{q}, \quad \sigma_{w}^{(\text{ms})} \sim I_2^2 S \sqrt{q}. \quad (1.12)$$

The criterion for a magnetic particle of any kind to transit into a single-domain state can be formulated as follows. We compare the energy of a particle (let it be a sphere) being in a two-domain state, $E_{2d} \sim \sigma_w d^2$, where $d$ is its diameter, and the energy of the same particle in a single-domain state, $E_{1d} \sim I_2^2 d^3$, which in fact is the energy of stray fields around the particle. Thus one sees that as the particle becomes smaller, the stray-field energy decreases proportional to the cube of the particle size whilst the energy produced by internal domain walls is only quadratic in the particle size. Consequently,
as the particle size becomes small enough, the energy of a particle with a domain wall inside exceeds that of the same particle but magnetized uniformly. Requiring that the single-domain configuration becomes favorable, with the aid of Eq. (1.9) we arrive at the quantitative estimates

\[ d_{c}^{(mh)} \sim \sqrt{qK/I}S, \quad d_{c}^{(ms)} \sim \sqrt{q}, \]  

where \( d_{c} \) is called the critical size of single-domainness.

The greatest contribution to the non-uniformity energy originates from the exchange interaction. Owing to that, for the non-uniform exchange intensity in Eq. (1.3) one may set \( qI_{S}^{2} \sim A/a_{0} \), where \( A \) is the uniform exchange energy (the exchange integral of the ferromagnet), and \( a_{0} \) is the period of the crystal lattice. Now, expressing \( q \) in the second of Eqs. (1.13) through the exchange parameter, we recover a relation similar to the formula given by Kondorsky, see Ref. [16], for magnetically soft materials,

\[ d_{c}^{(ms)} \sim I^{-1}S^{-1}\sqrt{A/a_{0}}. \]  

The reference exchange energy \( A \) is of the order of magnitude of \( k_{B}T_{c} \), where \( T_{c} \) is the Curie temperature (the point where ferromagnetism vanishes). For typical ferromagnets \( T_{c} \sim 10^{3} \) K, \( I \sim 10^{3} \) G and \( a_{0} \sim 0.1 \) nm. Using these values, from Eq. (1.14) one gets the estimate \( d_{c} \sim 30 \) nm. This is in fair agreement with the more accurate calculations which yield from 12 nm [14] to 20 nm [16] for iron and about 60 nm for nickel [14,16].

Magnetic anisotropy impedes occurrence of a domain wall, i.e., favors the increase of \( d_{c} \). Comparing the respective expressions in Eqs. (1.13), one sees that the critical diameter at which a magnetically rigid particle becomes single-domain is \( \sqrt{K/I}S \) times greater than that of a magnetically soft one. For example, for a highly anisotropic ferromagnet SmCo\(_{5}\) (the first anisotropy constant \( K \sim 10^{8} \) erg/cm\(^3\) and \( I \approx 700 \) G) the coefficient \( \sqrt{K/I}S \) equals 14, that yields \( d_{c}^{(mh)} \geq 400 \) nm.

We recall that the mean size of ferroparticles used in magnetic fluids does not exceed 15 nm. Comparison of this value with the above-obtained estimates for \( d_{c} \) shows that the disperse particles of a colloidal ferromagnet are definitely subdomain (\( d < d_{c} \)) even allowing for their possible polydispersity. What does then prevent one from enhancing the magnetic properties of a ferrofluid by simply employing larger particles: setting \( d \) closer to \( d_{c} \)? The major restriction is imposed by the requirement of coagulation stability with respect to the magnetic dipole-dipole interparticle attraction. Indeed, for example, for magnetite particles where \( I \approx 480 \) G at \( d \approx 30 \) nm the interaction parameter rendered by Eq. (1.3) ranges \( \lambda \approx 35 \), that is obviously far too large. For any reasonable thickness of the protective coating it is impossible to reduce this value down to unity without reducing the particle size. Thus we once again recover the conclusion that in a magnetite ferrocolloid the stability condition (\( \lambda \leq 1 \)) can be achieved only at \( d \leq 10 \) nm.

The dependence \( \lambda \propto d^{3} \) suggests the idea to improve the quality of a magnetic fluid (i.e., to enhance stability without reducing magnetization)) by diminishing the mean linear size of the particles. If, upon doing so, one would be able to maintain constant the solid-phase volume fraction \( \phi = nV \) (here \( n \) is the particle number density) of the colloid, then the saturation magnetization achieved in a strong field would not reduce. However, choosing this strategy one would soon finish with a highly dispersed but non-magnetic colloid. The fact of the matter is that ferromagnetism, being a cooperative phenomenon, does really exist only in sufficiently multi-atomic clusters. Because of that, with reduction
of the particle size in the subdomain range, the particle magnetization \( I_S(d) \) begins to fall down drastically at \( d < 2\text{-}3 \text{ nm} \). The explanation is simple: such clusters merely do not contain the sufficient number of atoms!

The idea how could one estimate the minimum size \( d^* \) up to which a particle retains noticeable magnetization, belongs to Vonsovsky, see [16]. According to the Heisenberg uncertainty relation, the momentum \( p \) of an electron localized in a cell with the volume \( \sim d^3 \), acquires the uncertainty \( \Delta p \sim \hbar d \). This \( \Delta p \) value, in turn, produces the uncertainty in the kinetic energy as large as

\[
\Delta E = \frac{(\Delta p)^2}{2m} \sim \frac{\hbar^2}{md^2},
\]

where \( m \) is the electron mass and \( \hbar \) is the Planck constant. It is clear that magnetic ordering could exist only if the exchange energy \( A \approx k_B T_c \) is greater than the electron kinetic energy \( \Delta E \). From this condition one finds \( d^* \geq 1 \text{ nm} \). Indeed, in the particles with \( d \leq d^* \) almost all the atoms lie on the particle surface. With such a dearth of neighbors, the “full-scale” exchange interaction, yielding the customary ferromagnetism, is impossible.

Without doubt, even at \( d > d^* \) the electron spins “feel” the presence of the boundary of the volume inside which they are enclosed. The absence of partners for exchange interaction at the opposite side of the boundary manifests itself in a formation of a thin—with thickness \( \sim d^* \)—layer on the particle surfaces. At first, when some evidence indicating that this layer is not magnetized in the absence of an external field had been obtained [18,19], this layer was considered as completely magnetically “dead”. For example, in Ref. [18] creation of such a dead layer was attributed to chemical modification of the particle surfaces, viz. formation of paramagnetic iron oleate on the surface of magnetite particles. Moreover, a very good agreement between theoretical and experimental magnetization curves was achieved when the thickness of the dead layer was set equal to the period \( a_0 = 0.84 \text{ nm} \) of the magnetite crystal lattice. Later on, a thorough investigation done on a variety of magnetic nanoparticles revealed the fact that at the particle surface one deals with a specific state of the spin system known as the \textit{spin-glass} arrangement. In customary terms, a spin glass may be described as a ferromagnet where the distribution of the magnetic anisotropy is random both in direction and in strength.

However a simple model which we are going to develop here does not take into account the spin-glass properties of the particles, and takes the particle surface to be both non-magnetic and non-magnetizable. Then the magnetic moment \( \mu \) may be presented in the form

\[
\mu = \mu e, \quad \mu = I_S V_m, \quad (1.15)
\]

where \( e \) is the unit vector in the direction of the magnetic moment introduced in Eq. (1.2), \( I_S \) is the saturation magnetization of the ferromagnetic material the particle is made of, and \( V_m \) is the volume of the “magnetic core” of the particle which, due to the above-presented considerations, is always less than its geometric volume \( V \).

At the first sight, a subdomain ferromagnetic particle magnetized up to saturation might, by its magnetic properties be regarded as a sort of a permanent magnet similar to a compass needle. One end of such a magnet is always the “North pole” while the other—the “South” one. But let us consider the situation in some more detail. Location of the poles in a magnet is fixed by the magnetic anisotropy energy \( U_a \sim KV_m \). For an
iron compass needle the magnetic anisotropy is determined by its shape (a needle), so that \( K \sim 2\pi I_s^2 \). For \( V \sim 0.1 \, \text{cm}^3 \) the value of \( U_a \) is about \( 4 \times 10^6 \, \text{erg} \) and thus corresponds to the temperature \( U_a/k_B \sim KV_m/k_B \sim 10^{22} \, \text{K} \). The probability of a spontaneous re-magnetization of the particle, i.e., its magnetic moment flipping over the potential barrier \( U_a \) due to thermal fluctuations, is proportional to \( \exp(-KV_m/k_BT) \). This factor enters the relation \( \nu = \nu_0 \exp(-KV_m/k_BT) \) which renders the frequency of spontaneous change of polarity of the magnet. At room temperature by the order of magnitude the ratio \( KV_m/k_BT \) ranges \( 10^{22}/300 \sim 10^{20} \). This means that on a magnetic needle the poles are fixed once and forever. Indeed, the factor \( \exp(-10^{20}) \) is so small that after multiplying by any scaling coefficient \( \nu_0 \) reduces the transition frequency \( \nu \) to an absolutely negligible value.

The situation for a subdomain particle with linear dimensions \( \sim 10 \, \text{nm} \) is entirely different. For the magnetic anisotropy constant \( K \sim 10^5 / 10^6 \, \text{erg/cm}^3 \) (it includes contributions from both the crystalline and magnetostatic anisotropies) the dimensionless ratio \( \sigma = KV_m/k_BT \) at room temperature is not large. Thus, the probability of thermofluctuational rotations of the magnetic moment becomes substantial. The quantity \( \tau(\sigma) = \nu^{-1} \), i.e., the inverse transition frequency, determines the reference time interval during which the tiny magnet—the ferroparticle—may be considered as a permanent one. At \( \sigma \leq 1 \) the vector \( \mu \) is “hardly aware” of the existence of the potential barrier, and its motion very closely resembles the Brownian rotation of a solid particle inside a viscous liquid. The reference time of the rotary diffusion \( \tau_D \equiv \tau(\sigma < 1) \) that is the period of rotation of the particle by a significant angle can be written as

\[
\tau_D = 3\eta_m V_m/k_BT, \tag{1.16}
\]

where \( \eta_m \) is the “intrinsic magnetic viscosity” depending on the nature of the actual ferromagnet (see the details in below). For usual ferromagnets \( \eta_m \) lies in the range \( 10^{-5} \sim -10^{-3} \, \text{g/cm} \cdot \text{sec} \), so that for particles with the reference size \( \simeq 10 \, \text{nm} \) at \( T \sim 3 \cdot 10^2 \, \text{K} \) we arrive at the estimate \( \tau_D \sim 10^{-9} \sim 10^{-7} \, \text{sec} \).

In particles with a pronounced anisotropy \( (\sigma \geq 10) \) the magnetic moment motion acquires the features of the thermally-activated diffusion, since the re-magnetization time \( \tau_N \equiv \tau(\sigma \geq 2) \) grows exponentially with \( \sigma \):

\[
\tau_N = \sqrt{\frac{\pi}{4\sigma^3}} e^\sigma \tau_D. \tag{1.17}
\]

The asymptotic formula (1.17) was obtained by Brown [20]; however, we intentionally use here the subscript \( N \) in honor of Néel who in 1949 was the first to point (see, for example, Ref. [21]) to the possibility of fluctuational re-magnetization of fine particles.

The time of spontaneous re-magnetization \( \tau(\sigma) \), the limiting values of which are rendered by formulas (1.17) and (1.18), determines the period of self-averaging of the particle magnetic moment. For the time intervals shorter than \( \tau \), the particle behaves as a permanent magnet with the magnetization \( I_S \). If, conversely, the duration of the magnetization measurement, for example, the period \( t_0 \) of the probing field, is greater than \( \tau \), then the measurement would yield zero because the particle magnetic moment would be averaged down to an infinitesimal value. In other words, for \( t_0 \gg \tau \) the subdomain particles and their assemblies do not display any remanence magnetization.
Direct confirmation of radically different magnetic behavior of fine particles under 
\( t_0 \geq \tau(\sigma) \) is obtained with the aid of Mössbauer (nuclear gamma resonance) spectroscopy. Of numerous examples for particles of various ferro- and ferrimagnetic materials we point out to magnetite [22], amorphous Fe-C alloy [23] and maghemite [24]. In Fig. 1.2 a set of experimental data from Ref. [24] is shown presenting the spectra of highly dispersed (mean particle diameter about 7 nm) maghemite that is \( \gamma\text{-Fe}_2\text{O}_3 \). At low temperatures, see curves for 80 K and 150 K, a characteristic sextet of the hyper-fine structure lines pertinent to ferromagnets is observed. As the temperature increases, the hyper-fine splitting gradually vanishes (curve 200 K), and at \( T \geq 250 \) K the spectrum degenerates into a doublet inherent to paramagnets. The mechanism of this transformation is as follows. In the Mössbauer experiments the measurement time \( t_0 \sim 10^{-8} \) s is determined by the period of the Larmor precession which the spin of nuclei \( ^{57}\text{Fe} \) undergoes in the hyper-fine field \( H_{hf} \). The direction of \( H_{hf} \) fluctuates together with the particle magnetic moment with the time rate \( 1/\tau(\sigma) \). The existence of the ferromagnetic sextet at \( T \ll 100 \) K means that at low temperatures the condition \( \tau(\sigma) < t_0 \) holds, i.e., \( \sigma = KV_m/k_BT > 1 \).

With the temperature growth the frequency of the hyper-fine field \( H_{hf} \) fluctuations increases, and the sextet of lines weakens due to self-averaging. A complete collapse of the ferromagnetic-type spectrum takes place at \( \tau(\sigma) < t_0 \), that is in the temperature range where \( \sigma < 1 \).

The absence of remanent magnetization for fine particle assemblies at \( \tau < t_0 \) manifest itself in the fact that in an external field such systems magnetize without hysteresis, i.e., similar to paramagnetic gases. This explains why a special term superparamagnetism was introduced [25,26] for their description. Classical examples of superparamagnets are cobalt precipitates with \( d \sim 5 \) nm produced while fission of Cu–Co solid solutions and iron precipitates in \( \beta \)-brass. Unlike usual paramagnets, the role of elementary carriers of magnetism in superparamagnets is played not by single molecules with \( \mu \sim \mu_B \) (Bohr magneton) but by multi-atomic particles with \( \mu \sim 10^4–10^5 \mu_B \). Another difference between those systems is of the qualitative kind: in a gas under the influence of thermal fluctuations (collisions) these are the molecules themselves which change their orientation whereas in solid superparamagnets the particles are motionless and only their magnetic moment orientations change.

Apparently, in magnetic fluids, where the fine ferromagnetic particles possess the full set of mechanical rotational degrees of freedom, both mechanisms of orientational relaxation of magnetic moments are possible: rotations of \( \mu \) inside the particle as well as rotations together with it. This specific feature makes ferrocolloids “double superparamagnetic” and enables one to distinguish them amongst various magnetic media as a special class: fluid superparamagnets.

1.2 Reference times of the particle magnetodynamics

In an external field \( H \) the energy of a particle with uniaxial magnetic anisotropy is

\[
U = -\mu (e \cdot H) - KV_m (e \cdot n)^2 , \tag{1.18}
\]

The constant \( K \) is regarded as some effective value incorporating contributions from both the crystallographic anisotropy of the particle and its shape anisotropy. These terms are comparable for magnetically rigid ferromagnets (cobalt, barium ferrite, etc.).
For particles made of magnetically soft materials (iron, nickel, magnetite, maghemite, etc.) the magnetostatic anisotropy is predominant. In such grains the anisotropy energy density $K$ is determined by the demagnetization tensor $N_{ik}$ [12] and the ferromagnet magnetization $I_S$. For ellipsoids of revolution $a = b \neq c$ the matrix $N_{ik}$ as referred to its principal axes takes the form

$$
N_{ik} = \begin{pmatrix}
N_{\perp} & 0 & 0 \\
0 & N_{\perp} & 0 \\
0 & 0 & N_{\parallel}
\end{pmatrix}
$$
or, in the index notation,

$$
N_{ik} = N_{\perp} \delta_{ik} + (N_{\parallel} - N_{\perp}) n_i n_k,
$$

where we assume that the anisotropy axis $\mathbf{n}$ coincides with the symmetry axis of the ellipsoid and

$$
K = -\frac{1}{2} (N_{\parallel} - N_{\perp}) I_S^2.
$$ (1.19)
The difference \((N_\parallel - N_\perp)\) is positive for oblate ellipsoids \((c < a = b)\) and negative for prolate ones \((c > a = b)\).

Substituting \(K\) from Eq. (1.19) into expression (1.18), one finds that in the absence of an external field the minimum of magnetic energy \(U\) for a prolate ellipsoid is achieved at \(\mu || n\), i.e., in equilibrium the magnetic moment of the particle is directed along the long axis of the ellipsoid. As mentioned above, the case of positive \(K\) is usually referred to as the easy-axis anisotropy. In an oblate ellipsoid, \(U\) is minimal at \(\mu \perp n\) that means that the equilibrium magnetic moment is confined in the plane perpendicular to \(n\), where its direction is degenerate. Such a case is called the easy-plane anisotropy. However, for colloidal ferroparticles the latter type of anisotropy is hardly of any importance \(^2\). Further on we will assume that the particles possess the easy-axis anisotropy with \(K > 0\).

The derivative of the magnetic energy (1.19) with respect to \(\mu = \mu e\) determines the value and direction of the summary (total) magnetic field

\[ H_s = -\frac{\partial U}{\partial \mu} = H + \frac{2K}{I_S} (en) n, \]  

(1.20)

acting on the particle magnetic moment. This field combines the external field \(H\) and the anisotropy field \(H_a\) directed along the singled-out axis \(n\) of the ellipsoid. The equilibrium orientation of the particle magnetic moment is determined by the absence of magnetic torques acting upon it:

\[ (\mu \times H_a) = 0, \]  

(1.21)

whence it follows that in a constant field and without thermal fluctuations the magnetic moment points along \(H_s\).

An essential property of a magnetic fluid that distinguishes it from all the other kinds of disperse ferromagnets is that for the magnetic moment \(\mu e\) of a ferroparticle two kinds of orientational motion are possible. Namely, that with the particle relative to the liquid matrix and that inside the particle relative to its crystallographic axes. Let us consider first the intrinsic motion of the magnetic moment. It consists of a combination of regular precession in the field \(H_s\) and chaotic re-orientations of vector \(\mu\) under the action of thermal fluctuations. The fluctuation-field \(H_f\) amplitude has the order of magnitude \(\sim k_B T/\mu\). Since the magnetic moment of the particle is proportional to its volume (see Eq. (1.15)), then for subdomain particles with \(d \sim 10\) nm one gets \(\mu \sim 10^{-16}\) erg/Oe. This means that at room temperature \(H_f \sim 100\) Oe and thus is comparable with \(H\) and \(H_a\).

The regular motion of the magnetic moment relative to the crystallographic axes of the particle is described by the Landau-Lifshitz equation \([12, 27]\) that we write in the form

\[ \frac{de}{dt} = -\gamma (e \times H_s) - \alpha \gamma (e \times (e \times H_s)), \]  

(1.22)

where \(\gamma\) is the gyromagnetic ratio and \(\alpha\) denotes a phenomenological parameter known as the spin-lattice relaxational constant. In a constant field the first term in the right-hand side of Eq. (1.22) represents the free precession of the magnetic moment around

\(^2\) Even an infinitesimal deviation of the particle shape from that of an ellipsoid of revolution breaks down the degeneracy of the magnetic moment orientation inside the easy plane. But as soon as any preferred or singled-out direction in this plane appears we return to the easy-axis case.
the direction of $H_s$ with the Larmor frequency $\omega_L = \gamma H_s$, while the second term—the decay of this precession with the time $\tau_0 = (\alpha \omega_L)^{-1}$. If at the instant $t = 0$ the vector $e$ deviates from its equilibrium direction by an angle $\vartheta_0$, then, according to Eq. (1.22), the angle between $e$ and $H_s$ vanishes as

$$\vartheta(t) = \vartheta_0 \exp(-t/\tau_0).$$

For the majority of ferromagnets $\alpha \sim 10^{-1} \div 10^{-2}$. Using this, one finds $\omega_L \tau_0 \sim 10^1 \div 10^2$, which means that during the relaxation time the magnetic moment makes about at least a dozen of turns.

Another characteristic time is related to the rotary diffusion of the magnetic moment inside the particle. The factor $b = \alpha \gamma / \mu$ before the relaxational term in Eq. (1.22) has the meaning of the rotary mobility of the magnetic moment. Therefore, for the rotary diffusion coefficient of vector $\mu$, according the Einstein formula $D = b k_B T$, one gets

$$D = \alpha \gamma k_B T / \mu.$$ 

Defining, as usual [28], the diffusion time by the relation $\tau_D = (2D)^{-1}$, one finds

$$\tau_D = I_S V_m / 2 \alpha \gamma k_B T.$$ 

On comparison of Eqs. (1.16) and (1.23), the explicit expression for the above-introduced magnetic viscosity $\eta_m$ via the parameters of the ferromagnet is retrieved,

$$\eta_m = I_S / 6 \alpha \gamma.$$ 

Let us compare the magnetic moment relaxation times $\tau_0$ and $\tau_D$. To accomplish this, it is convenient to set the external field to zero, so that the field $H_s$ reduces to the anisotropy field with the amplitude $H_a = 2K/I_S$. Then the Larmor precession frequency is $\omega_L = 2 \gamma K / I_S$ and $\tau_0 = \alpha I_S / 2 \gamma K$. With allowance for the last relation, from Eq. (1.23), we obtain

$$\tau_D = \sigma \tau_0, \quad \sigma = KV_m / k_B T.$$ 

It is noteworthy that this simple formula connects both limiting values of the relaxation time of the magnetic moment precession. As a more rigorous analysis shows, see Ref. [29], these limiting values are $\tau_0$ for $\sigma \gg 1$ and $\tau_D$ at $\sigma \ll 1$. Indeed, for a ferromagnetic crystal of a macroscopic size and/or at low temperatures ($\sigma \to \infty$) thermal fluctuations are negligible and the precession damps with the reference time $\tau_0$. As it ought to be in the low temperature limit, $\tau_0$ does not depend explicitly upon temperature. Conversely, in small particles and/or at high temperatures, when $\sigma \to 0$, the influence of thermal fluctuations on the magnetic moment re-orientation is the most strong one. Due to that the relaxation time almost exactly coincides with the rotary diffusion time $\tau_D$. In other words, in the asymptotic cases $\sigma \gg \ll 1$ the role of the relaxation time is played by the shorter of the two times entering formula (1.25).

In the above discussion we have considered the relaxation of the magnetic moment precession, i.e., the decay of the component of the vector $e$ perpendicular to $H_s$. However, in the absence of the external field, when the magnetic moment is subjected to the field of a quadrupole symmetry, $H_s = (2K/I_S)(e \cdot n) n$, there exist two equivalent equilibrium positions, those with $e = n$ and $e = -n$. This requires us to consider one more
relaxation process: the relaxation of the component of $e$ parallel to $H_a$. The process under discussion is the one by which the populations of the potential wells separated by the barrier of the height $KV_m$, become equal. For macroscopic particles this barrier is practically impenetrable: the time of “dwelling” in either of the wells tends to infinity, see Sec. 1.1 above. At moderate values of $\sigma = KV_m/k_BT$ the time of longitudinal relaxation turns out to be finite and may be described by Eq. (1.17) for $\tau_N$, that is valid for $\sigma \geq 2$. For $\sigma < 1$, when the magnetic moment is virtually unaffected by the barrier, the difference between the notions of transverse and longitudinal relaxations disappears. In this limit, the rotation of the magnetic moment through a finite angle in any plane takes the same time $\tau_D$.

Besides the “internal” diffusion relative to the particle body, the magnetic moment may also take part in the “external” rotary diffusion, i.e., together with the particle relative to the liquid matrix of a suspension. Proceeding to the study of the rotary motion of a colloidal particle we remark that its regular component is described by the rotational dynamics equation for a solid body suspended in a viscous liquid

\[ \mathcal{J} \frac{d\omega_p}{dt} + \zeta \omega_p = \mathcal{M}, \]  

where $\mathcal{J}$ is the moment of inertia of a spherical particle, $\omega_p$ its angular velocity, $\zeta$ the rotary friction coefficient, and $\mathcal{M}$ is the external torque. For a particles with the orientation-dependent potential $U$ the torque is given by a standard formula

\[ \mathcal{M} = -(n \times \partial U/\partial n). \]  

The free (at $\mathcal{M} = 0$) particle rotation decays with the characteristic time

\[ \tau_s = \mathcal{J}/\zeta. \]  

By its meaning, this time equals a period which it takes for a particle to equalize its angular velocity with that of the liquid environment. In the Stokes approximation the friction coefficient is $\zeta = 6\eta V$, where $\eta$ is viscosity of the liquid and $V$ is the total volume of a particle. Substituting this expression and $\mathcal{J} = \rho_p V d^2/10$, where $\rho_p$ is the density of the particle substance, into the formula for $\tau_s$, we find

\[ \tau_s = \rho_p d^2/60\eta. \]  

For $\eta \sim 10^{-2}$ Ps and $d \approx 10$ nm from this formula it follows that $\tau_s \sim 10^{-11}$ s. As the value obtained is rather small. Consequently, in all practically relevant cases the first (inertial) term in Eq. (1.26) may be neglected in comparison with the second (viscous) one. Indeed, these terms may be comparable only under external excitations within the frequency range $\geq 100$ GHz. But last value is many orders of magnitude greater than any conceivable frequency of a hydrodynamic or a Brownian kinetic process.

Besides $\tau_s$ there exists a much larger time scale, characterizing the rotary motion of the particle. It is determined by orientational fluctuations of the singled-out axis $n$, i.e., by the usual Brownian rotary diffusion. Once more using the Einstein relation $D = b k_B T$ but this time substituting therein the mobility coefficient $b = 1/\zeta$, one gets the well-known Debye expression

\[ \tau_B = 1/2D = 3V\eta/k_B T. \]
For the above cited values of the parameters and room temperature the relaxation time $\tau_B$ has the order of magnitude about $10^{-6}$ s. This means that normally the rotary diffusion time exceeds the dynamical one by about five decades: $\tau_B/\tau_s = 10^5$.

During the Brownian time $\tau_B$ the particle under the influence of thermal fluctuations rotates by a finite angle. The higher is the viscosity of the liquid matrix, the slower is the rotation. Conversely, the dynamical time $\tau_s$ diminishes with increase of the viscosity: the free rotation of the particle relative to the liquid ceases the more rapidly the greater is the viscosity. Taking into account the opposing character of the dependencies of $\tau_B$ and $\tau_s$ upon $\eta$ one concludes that these time scales get closer as the viscosity decreases; for colloidal particles they become comparable at $\eta \sim 10^{-4}$ Ps. However, such a viscosity is inherent only to gases at normal pressure, and so condition $\tau_s \approx \tau_B$ might hold only in aerosols or suspensions based on cryogenic liquids.

Thus we see that in the absence of an external field the only cause of orientational changes of the magnetic moment is thermal excitation. It drives the “internal” diffusion with the reference time $\tau_N$ (for $\sigma \geq 2$) as well as the “external” one with the reference time $\tau_B$. Being involved into this combined diffusion, the magnetic moment rotates chaotically, and its mean-square angular displacement during the time interval $t$ obeys the random-walk law

$$\langle \theta^2 \rangle = 2t \left( \tau_N^{-1} + \tau_B^{-1} \right),$$  \hspace{1cm} (1.31)

where the angular brackets denote averaging over the statistical ensemble. If one magnetizes a ferrocolloid by subjecting it to the external field $H$ and at the instant $t = 0$ turn the field off, then according to formula (1.31) the magnetization $M(0)$ would decay to zero with the reduced time

$$\tau = \tau_N \tau_B / (\tau_N + \tau_B).$$  \hspace{1cm} (1.32)

Here it is apparent that the dominant contribution to the rate of relaxation is yielded by the diffusion processes that has the shortest reference time. Indeed, for $\tau_N \ll \tau_B$ the decay of the colloid magnetization occurs owing to transitions of the particle magnetic moments over the internal potential barriers $\sim KV_m$ separating the equivalent directions of easy magnetization. After the time interval $\sim \tau_N$, approximately half the number of magnetic moments will rotate by an angle $\sim \pi$ relative to the direction of $M(0)$, and magnetization will decay to zero much faster than one would expect owing to the particle mechanical rotation. We would like to emphasize that this relaxational mechanism is the only one that exist in solid superparamagnets, for example, frozen magnetic fluids. Conversely, for $\tau_N \gg \tau_B$ demagnetization of the colloid is caused only by the Brownian rotary diffusion of the particles together with their magnetic moments, since the Néel mechanism is “frozen up”.

It is quite clear that the magnetization relaxation as well retains its diffusive nature in the presence of an external field, providing that its orienting energy $\sim \mu H$ is small in comparison with the energy $k_B T$ of thermal fluctuations. In the opposite case, i.e., when the ratio

$$\xi = \mu H/k_B T$$  \hspace{1cm} (1.33)

is large, the rate of settling of the equilibrium orientation of the particle magnetic moments is determined predominantly by the action of regular forces. This brings more relaxation times to the fore, the influence of which needs to be assessed.
Omitting in Eq. (1.26) the inertia term and substituting there the external torque from Eqs. (1.27) and (1.17), we arrive at the equality expressing the balance of magnetic and viscous torques:

\[ 6\eta V \omega_p = -2KV_m (e \cdot n)(e \times n). \]  

(1.34)

Since in the coordinate framework attached to the particle (it rotates with the angular velocity \( \omega_p \)), \( n \) is a constant vector, its change relative to the stationary framework is given by the kinematic relationship \( d\mathbf{n}/dt = (\omega_p \times \mathbf{n}) \). Multiplying Eq. (1.34) vectorially by \( n \), we get

\[ \frac{dn}{dt} = -\frac{KV_m}{3\eta V} (n \times (n \times e)). \]

(1.35)

However, this neat equation is not closed since it contains two dynamical variables, \( n \) and \( e \). Neither does it include the external field—the only source of the magnetic torque. To obtain the closed set, it is necessary to accompany Eq. (1.35) with the one for \( d\mathbf{e}/dt \) that follows from the Landau-Lifshitz equation (1.22):

\[ \frac{d\mathbf{e}}{dt} = -\gamma (\mathbf{e} \times \mathbf{H}_s) - \alpha \gamma (\mathbf{e} \times (\mathbf{e} \times \mathbf{H}_s)), \]

(1.36)

with \( \mathbf{H}_s \) determined by Eq. (1.20). In a constant field \( \mathbf{H} = H\mathbf{h} \) equations (1.35) and (1.36) describe the process of establishment of the equilibrium orientational state; in the entire equilibrium \( \mathbf{e} = \mathbf{n} = \mathbf{h} \).

In a strong magnetic field—when \( \xi \gg 1 \)—the relaxation times of magnetic and rotary mechanical degrees of freedom differ greatly. As we will show soon, \( \tau_0 \) (the time of relaxation of the magnetic moment to the direction of \( \mathbf{H}_s \)) is always much smaller than the relaxation time \( \tau_n \) of the particle orientation. In other words, the settling of equilibrium occurs in two steps. First, during a short time \( \tau_0 \), the magnetic moment settles parallel to \( \mathbf{H}_s \). The second step is the slow (with the reference time \( \tau_n \)) rotation of the particle axis \( \mathbf{n} \) to the direction of \( \mathbf{H} \). We remark that the change of \( \mathbf{n} \) causes the change of \( \mathbf{H}_s \), see Eq. (1.20) which, in turn, deviates vector \( \mathbf{e} \) from its equilibrium. However, due to the adiabatic condition \( \tau_0 \ll \tau_n \) these perturbations of \( \mathbf{e} \) decay rapidly, so that in the process of the orientational relaxation of a ferroparticle its magnetic moment undergoes a sequence of quasi-equilibrium states determined by equation (1.20).

In a constant or slowly changing magnetic field (i.e., when its frequency satisfies the adiabatic condition \( \omega \tau_0 \ll 1 \)), instead of the Landau-Lifshitz equation, it is sufficient to use the equilibrium solution (1.21) of that equation, namely,

\[ \mu H(e \times h) = -2KV_m(e \cdot n)(e \times n). \]

(1.37)

Note that the right-hand sides of Eqs. (1.34) and (1.37) coincide. With allowance for this, equation (1.35) may be rearranged as

\[ \frac{dn}{dt} = -I_S HV_m (n \times (e \times h)). \]

(1.38)
approximate solution of Eq. (1.37) is \( e \approx n \). Substitution into Eq. (1.28) yields the closed equation

\[
\frac{dn}{dt} = -\frac{1}{\tau_n} (n \times (n \times h)), \quad (1.39)
\]

\[
\tau_n = \frac{6\eta V}{I_S H V_m}, \quad (H \ll H_a). \quad (1.40)
\]

One also obtains the same equation (but with a different relaxation time) in the opposite limiting case when \( H \gg H_a \). Here [from Eq. (1.37)] it follows that \( e \approx h \), and so Eq. (1.35) again takes the form (1.39) where now

\[
\tau_n = \frac{3\eta V}{K V_m}, \quad (H \gg H_a). \quad (1.41)
\]

Let us prove that the relaxation time \( \tau_0 \) remains much smaller than the orientation relaxation time \( \tau_n \) regardless of the actual relationship between \( H \) and \( H_a \). At \( H \ll H_a \) we have \( H_s \approx H_a \) and from the definition \( \tau_0 = (\alpha \gamma H_a)^{-1} \) there readily follows the estimate \( \tau_0 = (\alpha \gamma H_a)^{-1} \). Thus, for the ratio of the magnetic and mechanical times we get

\[
\tau_0/\tau_n = \frac{\eta_m V_m H}{\eta V H_a}, \quad (H \ll H_a), \quad (1.42)
\]

where \( \eta_m \sim 10^{-4} - 10^{-3} \) Ps is the magnetic viscosity, defined by formula (1.16). For \( H \gg H_a \) we have \( H_s \approx H \) and \( \tau_0 = (\alpha \gamma H)^{-1} \). In this limit, we find for the time ratio

\[
\tau_0/\tau_n = \frac{\eta_m V_m H_a}{\eta V H}, \quad (H \gg H_a). \quad (1.43)
\]

If we note that by definition \( V_m / V \leq 1 \) and recall that the quotient \( \eta_m / \eta \) for low-viscous liquids is less than \( 10^{-1} \), then from Eqs. (1.42) and (1.43) it follows that the inequality \( \tau_0 \ll \tau_n \) holds for an arbitrary relation between the field strengths \( H \) and \( H_a \).

The consideration given in this chapter may be summarized as follows. In a weak external field (\( \xi \ll 1 \)) the rate of magnetization relaxation is determined by the joint action of two diffusion mechanisms, “internal” and “external”, reflected by formula (1.32) for the reduced time. The relaxation time of the particle orientation is, apparently, determined only by the “external” diffusion process, and its reference scale is always \( \tau_B \). In strong fields (\( \xi \gg 1 \)) the coupling between the magnetic and mechanical degrees of freedom of the particle breaks down, so that the magnetization relaxes to the direction of \( H \) almost immediately—during a very short time \( \tau_0 \). Meanwhile, the time necessary to settle the equilibrium orientation of the particle is much longer and depends upon the ratio \( H / H_a \) as

\[
\tau_n = \begin{cases} 
2\tau_B / \xi & \text{for } H \ll H_a, \\
\tau_B / \sigma & \text{for } H \gg H_a.
\end{cases} \quad (1.44)
\]
2 Rigid dipole model

2.1 Rotary diffusion equation for the magnetic moment

Now that we are acquainted with the time scales characterizing relaxational processes in magnetic fluids, let us proceed to constructing a quantitative theory. The most adequate mathematical framework for this is provided by the theory of rotary Brownian motion.

As already explained, the magnetic moment of a colloidal particle is involved into two types of motion: rotation inside the particle (with the reference time $\tau_N$) and rotation along with the particle (with the reference time $\tau_B$). Thus the relaxation time of magnetization $\tau$ (1.32) is a combination of the two time constants, namely

$$\tau^{-1} = \tau_N^{-1} + \tau_B^{-1}. \quad (2.1)$$

In real ferrocolloids, owing to a strong—exponential—dependence of $\tau_N$ upon the particle volume, the relation between $\tau_N$ and $\tau_B$ may be arbitrary. This means that at certain $\sigma = \sigma_*$ the equality $\tau_N = \tau_B$ should be satisfied. Using expressions for the relaxation times given by formulas (1.17) and (1.29), one arrives at the estimate $\sigma_* \simeq 5 \div 7$. This numerical quantity determines the reference magnetic volume $V_* = \sigma_* k_B T/K$ and the corresponding particle diameter $d_*$; the latter turns out to be $5 \div 20$ nm depending on magnetic anisotropy constant of the particles.

The condition $\tau_N \ll \tau_B$ holds for $V_m < V_*$, i.e., the magnetization of a ferrocolloid relaxes owing to the internal diffusion of the particle magnetic moments. If, conversely, $V_m \gg V_*$, then $\tau_B \ll \tau_N$ (the Néel process is frozen), and the magnetization relaxation occurs via Brownian rotary diffusion of the particles in the liquid matrix. The higher the value of the parameter $\sigma$ the better the condition of “freezing up” of the particle magnetic moment holds. At $\sigma \gg 1$ the vector $\mathbf{e}$ is rigidly coupled to the easy-magnetization axis ($\mathbf{e} = \mathbf{n}$); thus relaxation of magnetization and that of the particle orientation become one and the same process with the reference timescale $\tau_B$.

The limiting case of infinitely strong coupling is known as the rigid dipole model. This approximation is widely used in the theory of magnetic fluids. Despite its simplicity, it allows one to explain a wide range of magnetic and hydrodynamic phenomena that one observes in them. We now derive the basic kinetic equation for a suspension of rigid dipoles.

The statistical properties of an assembly of rigid dipoles are conventionally described by a distribution function $W$, which yields the manner of partition of the particles with respect to the orientation of their magnetic moments. Since the function $W(\mathbf{e}, t)$ is a probability density, it must satisfy the corresponding continuity equation

$$\frac{\partial W}{\partial t} + \text{Div} \left( W \frac{d\mathbf{e}}{dt} \right) = 0, \quad (2.2)$$

(law of conservation of the probability) and the normalizing condition

$$\int W(\mathbf{e}, t) \, d\mathbf{e} = 1.$$
The regular part of the velocity $\frac{de}{dt}$ of motion of the tip of this vector on the surface of the unit sphere is given by equation (1.39):

$$\frac{de}{dt} = -\frac{\mu H}{6\eta V} (e \times (e \times h)); \quad (2.3)$$

for the convenience of further treatment, while writing down Eq. (2.3) we have replaced $n$ by $e$, making use of the rigid coupling relation $e = n$. Under this condition magnetic energy of the particle (1.9) reduces to

$$U = -\mu H (e \times h),$$

so that Eq. (2.3) acquires the form

$$\frac{de}{dt} = \frac{1}{6\eta V} (e \times \hat{J} U), \quad (2.4)$$

where

$$\hat{J} = \left( e \times \frac{\partial}{\partial e} \right), \quad (2.5)$$

is the infinitesimal rotation operator. Now, in order to pass from the dynamic equation Eq. (2.4) to the corresponding Langevin equation, we must include in the equation for $\frac{de}{dt}$ a random force term. To shorten our treatment, we shall do that modifying $U$ in equation (2.4) by adding a statistical contribution:

$$U \Rightarrow U + k_B T \ln W, \quad (2.6)$$

which yields

$$\frac{de}{dt} = \frac{1}{2\tau_B} \left( e \times \hat{J} \right) \left( \frac{U}{k_B T} + \ln W \right). \quad (2.7)$$

In equilibrium, when the probability flux density tends to zero, from Eq. (2.7) it follows that $W$ has the Gibbs distribution

$$W_0(e) = Z_0^{-1} \exp(-U/k_B T), \quad Z_0 = \int \exp(-U/k_B T) \, de. \quad (2.8)$$

This result provides an heuristic justification for the transformation (2.6), that incorporates the random force by adding to the the energy $U$ a term which depends upon the distribution function.

Substituting Eq. (2.7) for $\dot{e}$ into the flux term of the continuity equation (2.2), we carry out a series of identical transformations:

$$\text{Div} \left( W \frac{de}{dt} \right) = \frac{\partial}{\partial e} \left( W \frac{de}{dt} \right) = \frac{1}{2\tau_B} \frac{\partial}{\partial e} \left[ \left( e \times W \hat{J} \right) \left( \frac{U}{k_B T} + \ln W \right) \right]$$

$$= \frac{1}{2\tau_B} \left( \frac{\partial}{\partial e} \times e \right) W \hat{J} \left( \frac{U}{k_B T} + \ln W \right); \quad (2.9)$$

here we have made use of the permutability of the mixed vector product:

$$\frac{\partial}{\partial e} \left( e \times A \right) = \left( \frac{\partial}{\partial e} \times e \right) A.$$

Taking into account that one of the vectors involved is a differential operator, we get

$$\left( \frac{\partial}{\partial e} \times e \right) A = A \left( \frac{\partial}{\partial e} \times e \right) - \left( e \times \frac{\partial}{\partial e} \right) A.$$
The first term of the right-hand side identically equals zero (since it is the rotor of a unit vector), whereas the second term—in view of the definition (2.5) may be written as $-\hat{J}A$.

Returning to formulas (2.9), we rearrange the flux term as

$$\text{Div} \left( W \frac{de}{dt} \right) = - \frac{1}{2\tau_B} \hat{J} W \hat{J} \left( \frac{U}{k_B T} + \ln W \right).$$

Thus the probability conservation law finally transforms into the kinetic equation of rotary diffusion

$$2\tau_B \frac{\partial W}{\partial t} = \hat{J} W \hat{J} \left[ \ln W - \xi (e \times h) \right].$$

Substituting there the rigid dipole magnetic energy $U = -\mu H (eh)$, we get

$$2\tau_B \frac{\partial W}{\partial t} = \hat{J} W \hat{J} \left[ \ln W - \frac{\xi}{4\pi} \exp(\xi x), \quad x = (e \cdot h) = \cos \vartheta. \right. \tag{2.13}$$

The normalized stationary solution of equation (2.10) or the equivalent one (2.11) is

$$W_0 = \frac{\xi}{4\pi \sinh \xi} \exp(\xi x), \quad x = (e \cdot h) = \cos \vartheta. \tag{2.14}$$

The function $W_0$ enables one to obtain any equilibrium orientational characteristics of a rigid dipole assembly. In a vast majority of cases one has to deal with the moments of the distribution function which we will denote as

$$\langle x^k \rangle_0 \equiv 2\pi \int_{-1}^{1} x^k W_0 \, dx. \tag{2.15}$$

The most important among these is the first moment, which determines the equilibrium magnetization $M_0 = n\mu \langle x \rangle_0$, where $n$ is the number density of the particles. Substituting Eq. (2.13) into (2.14) at $k = 1$, we get

$$\langle x \rangle_0 = \coth \xi - 1/\xi = L(\xi),$$

where $L$ is the Langevin function well known from the classic theory of paramagnetic gases. The expression $M_0 = n\mu L(\xi)$ fairly well describes the magnetization curves of ferrocolloids. In the limiting cases of strong and weak fields the asymptotics of the Langevin function yield the expressions

$$\begin{cases} M_0 = \chi_0 H, \quad \chi_0 = n\mu^2 / 3k_B T, & \text{for } \xi \ll 1, \\ M_0 = n\mu (1 - 1/\xi) & \text{for } \xi \gg 1. \end{cases} \tag{2.15}$$

Actually, because of the polydispersity of real ferrocolloids (in the description of the experimental magnetization curves) a superposition of the Langevin functions is taken, viz., $M_0(H) = \sum n_i \mu_i L(\mu_i H/k_B T)$. 

which determine the initial magnetic susceptibility $\chi_0$ and of $M_0$ approach to saturation.

At the end of this section we would like to present, following Ref. [30] some useful for further considerations formulas determining the equilibrium averages of the tensors composed of the components of vector $\mathbf{e}$:

$$\langle e_i \rangle_0 = L_1 h_i,$$
$$\langle e_i e_k \rangle_0 = (L_1/\xi) \delta_{ik} + L_2 h_i h_k,$$  \hspace{1cm} (2.16)

$$\langle e_i e_k e_l \rangle_0 = (L_2/\xi^2) (\delta_{ik} \delta_{lm} + \delta_{il} \delta_{km} + \delta_{lm} \delta_{kl})$$
$$+ (L_3/\xi) (h_i h_k \delta_{lm} + h_l h_m \delta_{ik} + h_i h_m \delta_{lk} + h_k h_m \delta_{il} + h_k h_l \delta_{im} + h_l h_m \delta_{ki})$$
$$+ L_4 h_i h_k h_l h_m.$$ \hspace{1cm} (2.17)

Here the functions $L_n(\xi)$ may be expressed in terms of the modified Bessel functions of of the first kind of imaginary argument as

$$L_n(\xi) = I_{n+1/2}(\xi)/I_{1/2}(\xi).$$

The latter formula is based on the expansion [31] of the Langevin exponent, entering $W_0$, in a series of Legendre polynomials,

$$e^{\xi x} = \sqrt{\pi/2\xi} \sum_{n=0}^{\infty} (2n+1) I_{n+1/2}(\xi) P_n(x).$$

The functions $L_n$ are connected with each other by the recursion relation

$$L_{n-1} - L_{n+1} = \frac{2n+1}{\xi} L_n,$$

wherein $L_0 = 1$ and $L_1 = L$, so that the last one coincides with the conventional definition of the Langevin function.

We shall show how to obtain formulas of the type of Eqs. (2.16)–(2.18) taking the second moment as an example. In a system of rigid dipoles the only singled-out direction is that of the external field, i.e., the vector $\mathbf{h}$. So it is clear that the sought second-rank tensor must have the structure

$$\langle e_i e_k \rangle_0 = C_1 \delta_{ik} + C_2 h_i h_k.$$ \hspace{1cm} (2.19)

The set of linear algebraic equations for the coefficients $C_\alpha(\xi)$ is obtained by contracting the tensor expansion (2.18)—once with $\delta_{ik}$ and the second time with $h_i h_k$. Thus we get

$$3C_1 + C_2 = 1,$$
$$C_1 + C_2 = \langle x^2 \rangle_0.$$ \hspace{1cm} (2.20)

Evaluating the coefficients $C_\alpha(\xi)$ from Eq. (2.19) and substituting them into equation (2.18), we recover the second of the formulas (2.16).
2.2 Spectrum of decrements in the external field

A fundamental property of the kinetic equation of rotary diffusion (from now abbreviated as KERD) is its linearity; thus, the superposition principle is taken for granted in what follows. Under constant external conditions any deviation of the distribution function \( W(t) \) from its equilibrium value \( W_0 \) may be expanded into a series of normal modes, each of which decays according to a simple exponential law. It is convenient to present the solution of Eq. (2.11) as

\[
W = W_0 \left[ 1 + \sum_{n=1}^{\infty} \sum_{m=-n}^{m=n} A_{nm} f_{nm}(x) e^{im\varphi} e^{-\lambda_{nm} t/2\tau_B} \right],
\tag{2.21}
\]

where the coefficients \( A_{nm} \) are determined by the initial conditions—the orientational configuration of the dipole system at the time moment \( t = 0 \). Substitution of Eq. (2.21) into KERD (2.12) yields the equation

\[
-\lambda f = (1 - x^2)f'' - [2x - \xi(1 - x^2)]f' - \frac{m^2}{1 - x^2} f, \tag{2.22}
\]

the eigenfunctions \( f_{nm}(x) \) and eigenvalues \( \lambda_{nm}(\xi) \) of which determine, respectively, the structure of normal modes and the relaxation time spectrum of the distribution function. Note that normal modes must be bounded in the interval \(-1 \leq x \leq 1\).

Let us show that all the eigenvalues of Eq. (2.22) are real and positive. In order to do that, we multiply both parts of this equation by \( f_{nm} \exp(\xi x) \) and integrate over \( x \). The first term in the right-hand side with the aid of integration by parts takes the form

\[
\int_{-1}^{1} (1 - x^2) f f'' e^{\xi x} \, dx = -\int_{-1}^{1} (1 - x^2) f'^2 e^{\xi x} \, dx + \int_{-1}^{1} [2x - \xi(1 - x^2)] f f' e^{\xi x} \, dx,
\]

which results in the following expression for any decrement \( \lambda \):

\[
\lambda \int_{-1}^{1} f'^2 e^{\xi x} \, dx = \int_{-1}^{1} \left[ (1 - x^2) f'^2 + \frac{m^2 f^2}{1 - x^2} \right] e^{\xi x} \, dx.
\]

All the integrals entering it are real and nonnegative, which proves the above-made conclusion. The positiveness of all the eigenvalues means that the stationary distribution \( W_0 \) is stable: any its perturbation decays as \( \exp(-t/\tau) \). This decay proceeds monotonically, since the decrements are real; \( \text{Im} \lambda \neq 0 \) means an oscillatory regime of relaxation.

Whereas the stability of equilibrium in a constant external field appears natural, the conclusion that the approach to equilibrium at arbitrary strengths of the applied field is monotonic, appears much less obvious. So it may be useful to give an additional comment on this particular problem. In the absence of the field (\( \xi = 0 \)) relaxation of the initial anisotropic distribution \( W(t = 0) \) to the equilibrium isotropic distribution, \( W_0 = 1/4\pi \), takes place by means of free orientational diffusion. It is apparent that this process is monotonic and has the characteristic time \( \tau_B \): if the field is zero, there is no force that might induce oscillations. But why are they absent in a strong external field,
where the restoring force is large? In order to answer this question, let us first note that at $\xi \gg 1$ orientational diffusion of the particles might be neglected. Indeed, since $\xi$ is proportional to the ratio $H/T$, strong fields are equivalent to low temperatures. But in the low-temperature limit the solution of KERD should coincide with that of a much more simple—dynamic—equation (1.40). The latter has been studied in Section 1.2 and the result is as follows. The magnetic moment of the particle approaches the direction of the external field monotonically according to the exponential law with the characteristic time $2\tau_B/\xi$, see Eq. (1.44).

So we see that the external field, although reducing the relaxation time, does not change the character of the decay process: it remains monotonic. The formal cause of this is, apparently, our neglect of the inertial term in equation (1.26) for the particle rotary motion. The physical reasons of the non-inertial approximation was discussed in detail in Sec. 1.2, the main reason being the smallness of the inertial time $\tau_s = J/\zeta$. Now it is worthwhile to add one more item to the estimates given there. If one retains the inertial term in Eq. (1.26), then there appears the fundamental frequency of oscillations $\omega_0 = \sqrt{\mu H/J}$. Thus, the roots of the characteristic equation, corresponding to Eq. (1.26), become complex for $\mu H > \zeta^2/4J$, i.e., if $2\omega_0\tau_s > 1$. This means that the oscillatory regime of relaxation is possible only for $H > \zeta^2/J\mu$. Estimation, carried out according to this formula, for magnetic particles of the diameter $\sim 10$ nm suspended in liquids with the viscosity $\sim 10^{-2}$ Ps yields $H \sim 10^7$ Oe. Thus, in any field really available the decay remains aperiodic. However, the inclusion of inertial effects is essential if one considers the high-frequency behavior of rotating objects of molecules size. Here the KERD becomes much more complicated, and requires special treatment. A detailed review of the corresponding methods of molecular dynamics, their development and particular results obtained for various kinds of systems is given by Coffey et al. [32]. Examples of systems where retention of the inertial term is essential for the correct description of the oscillatory behavior are given in Refs. [33–36].

Now we proceed to solution of the eigenvalue problem (2.20). There our main interest is focused on the field-dependence of the decrements $\lambda(\xi)$. As it may be seen from Eq. (2.19), the relaxation times of the distribution function are related to these decrements as $\tau = 2\tau_B/\lambda$. At $\xi = 0$ equation (2.20) transforms into that for the associated Legendre functions $P_n^m(x)$, its normalized solution being

\[
f_{nm}(x,0) = \left[ \frac{2n+1}{2} \frac{(n-|m|)!}{(n+|m|)!} \right]^{1/2} P_n^m(x), \quad \lambda_{nm}(0) = n(n+1),
\]

where $n \geq 1$. Therefore, in the absence of an external field the relaxation time spectrum is rendered by a simple expression

\[
\tau_{nm} = 2\tau_B/n(n+1),
\]

where the subscript $n$ is the order of the corresponding Legendre polynomial. According to Eq. (2.24) the small-scaled modes, those with $n \gg 1$, decay rapidly. Thus, the lifetime of any departure from equilibrium is determined, in fact, by the relaxation time of the most large-scaled (long-living) modes. In the absence of the field, whereupon there is no preferential direction, the spectrum $\{\tau_{nm}\}$ is degenerate with respect to $m$, see Eq. (2.24). Due to that, to the maximal relaxation time $\tau_1$ (it equals $\tau_B$) there simultaneously correspond three modes: with $m = 0, \pm 1$. 

The magnetic field to a certain extent reduces this degeneracy: each \((2n + 1)\)-fold degenerate level splits into \((n + 1)\) levels, differing in their \(|m|\) values. In a weak field \((\xi < 1)\) one might use perturbation theory. In the linear approximation in \(\xi\) only the eigenfunctions change whilst the decrements do not acquire any corrections since the decay rate cannot depend upon the direction of the field. To the second order in \(\xi\) we get

\[
\lambda_{nm}(\xi) = n(n + 1) + \frac{1}{2(2n + 1)} \left\{ \frac{n(n + 2)[(n + 1)^2 - m^2]}{(n + 1)(2n + 3)} \right. - \frac{(n^2 - 1)(n^2 - m^2)}{n(2n - 1)} \left. \right\} \xi^2. \tag{2.25}
\]

The subject of our main interest, as has already been emphasized, are the minimal eigenvalues (maximal \(\tau_{nm}\)). For the longest relaxation times from Eq. (2.25) we find

\[
\tau_{1,0} = \left( 1 - \frac{1}{10} \xi^2 \right) \tau_B, \quad \tau_{1,\pm 1} = \left( 1 - \frac{3}{30} \xi^2 \right), \tag{2.26}
\]

whereas the corresponding eigenfunctions

\[
f_{1,0} = \sqrt{3/2} \cos \vartheta, \quad f_{1,\pm 1} = \sqrt{3/2} \sin \vartheta,
\]

coincide (to within the normalizing factors) with the projections of the particle magnetic moment on the coordinate axes. So it becomes clear that \(\tau_{1,0}\) determines the relaxation time of the parallel and \(\tau_{1,\pm 1}\) the transverse, i.e., the perpendicular to the field, components of the macroscopic magnetization \(M\) of a ferrocolloid. Indeed, evaluating averages of the corresponding projections of this vector \(M_\parallel = n\mu \cos \vartheta\) and \(M_\perp = n\mu \sin \vartheta\)) with the function (2.21), in the first order in \(\xi\) we get

\[
M_\parallel(t) - M_\parallel(0) = [M_\parallel(0) - \chi_0 H] \exp(-t/\tau_\parallel), \quad M_\perp(t) = M_\perp(0) \exp(-t/\tau_\perp),
\]

with relaxation times \(\tau_\parallel = \tau_{1,0}\) and \(\tau_\perp = \tau_{1,\pm 1}\). Thus, as follows from Eq. (2.26), in the presence of the field the rate of orientational relaxation increases. Moreover, the longitudinal perturbations of magnetization (deviations of \(M_\parallel\) from its equilibrium value that equals to \(M_0\)) decay slightly more rapidly than the transverse ones.

We employed the Galerkin method for the calculation of the eigenfunctions and eigenvalues of Eq. (2.22) at finite \(\xi\). The function \(f_{nm}(x)\) with a fixed value of \(m\) was approximated by a linear combination of the first \(N\) Legendre functions

\[
f_{nm}(x) = \sum_{l=1}^{N} B_{lm}^n P_l^m(x).
\]

Substituting this expansion into Eq. (2.22) and successively multiplying the latter by \(P_l^m(x)\) with \(n = 1, N\), we obtain after integrating a set of \(N\) linear algebraic equations for the coefficients \(B\):

\[
\xi \frac{(l - 1)(l - m)}{2l - 1} B_{l-1,m}^n + [l(l + 1) - \lambda] B_{lm}^n - \xi \frac{(l + m + 1)(l + 2)}{2l + 3} B_{l+1,m}^n = 0. \tag{2.27}
\]

We have made use of the recursion relations for the associated Legendre functions in deriving this formula. The matrix corresponding to the set (2.27) has a three-diagonal
form; its diagonalization at every step in parameter $\xi$ had been accomplished numerically. The maximum dimension of the functional basis used was $N = 20$. The eigenvalues so found are exactly the decrements $\lambda_{nm}(\xi)$. The results of the calculation show that for a fixed basis dimension the chosen numerical procedure is able to evaluate the lowest levels of the spectrum with accuracy not worse than 1% in the range $\xi \leq N$. The obtained

Figure 2.1: Magnetic moment relaxation time for a rigid dipole. Fig. a gives the longitudinal time: curve 1 corresponds to the numerically evaluated $\tau_{10}$ and curve 2 renders $\tau_\parallel$ described by the first of Eqs. (4.15). Fig. b gives the transverse time: curve 1 corresponds to the numerically evaluated $\tau_{11}$ and curve 2 renders $\tau_\perp$ described by the second of Eqs. (4.15)

spectrum $\lambda_{nm}(\xi)$ does not contain intersections, that means that for any $\xi$ the principal relaxation times are $\tau_{1,0} = \tau_\parallel$ and $\tau_{1,\pm 1} = \tau_\perp$. Their dependencies upon $\xi$ are presented in Fig. 2.1; at $\xi \gg 1$ those curves perfectly comply with the low-temperature asymptotics

$$\tau_\parallel = \tau_B/\xi, \quad \tau_\perp = 2\tau_B/\xi,$$

prescribed by the dynamic equation (2.3). Let us show from where the last two expression originate. Making use of the vector identity

$$\mathbf{(h \times (e \times h)) = e - h (e \cdot h)},$$

we present the vector $e$ as a sum of components, respectively, parallel and perpendicular to the external field direction:

$$e_\parallel = h (e \cdot h), \quad e_\perp = (h \times (e \times h)).$$
in equilibrium $e_\parallel = h$ and $e_\perp = 0$. One finds from Eq. (2.3) that, when the orientational deviations $e_\perp$ and $e_\parallel - h$ are small,

$$
\frac{d}{dt} (e_\parallel - h) = -\frac{\xi}{\tau_B} (e_\parallel - h), \quad \frac{d}{dt} e_\perp = -\frac{\xi}{2\tau_B} e_\perp.
$$

So we see that in the low-temperature limit $\tau_\parallel$ and $\tau_\perp$ indeed differ by the factor of two.
3 The effective-field method in magnetodynamics of magnetic fluids

3.1 Equation of motion of magnetization in the effective-field model

There corresponds to the infinite set of equations (2.27) an infinite chain of equations for the moments \( \langle e_ie_k \ldots \rangle \) of the distribution function \( W \). This chain is produced by multiplying KERD (2.11) from the left by \( e_ie_k \ldots \) and integrating it over the angle variables of vector \( e \). Making use of the fact that operator \( \hat{J} \) is anti-Hermitian it is easy to remove the function \( W \) from its action:

\[
\int e \ldots (\hat{J} W \hat{A}) \, de = - \int W (\hat{A} \hat{J}) e \ldots de \equiv \langle (\hat{A} \hat{J}) e \ldots \rangle. \tag{3.1}
\]

We shall now show how to derive the equation for the first moment of the distribution function. Multiplying KERD (2.11) by \( e \) and integrating the result, we find for the left-hand part

\[
2\tau_B \int e \partial W / \partial t \, de = 2\tau_B \frac{d}{dt} \langle e \rangle,
\]

(here we have reversed the order of taking the time derivative and angle integration). The second term in the right-hand side of Eq. (2.11) is transformed with the aid of scheme (3.1) setting \( \hat{A} = -\xi (e \times h) \):

\[
-\xi \int e (\hat{J} W (e \times h)) \, de = \xi \int W (e \times h) \hat{J} \, e \, de
\]

\[
= -\xi \langle (e \times (e \times h)) \rangle.
\]

The first term of the right-hand side needs the application of Eq. (3.1) twice, since \( \hat{A} = \hat{J} \) is the differential operator:

\[
\int e \hat{J}^2 W \, de = - \int (\hat{J} W \hat{J}) \, e \, de = \int W \hat{J}^2 e \, de.
\]

Operator \( \hat{J}^2 = (e \times \partial / \partial e)^2 \) coincides with the angular part of the Laplace operator; the components of the unit vector \( e = (P^1_1(\vartheta) \cos \varphi, \quad P^1_1(\vartheta) \sin \varphi, \quad P^1_1(\vartheta)) \) being its eigenfunctions for \( n = 1 \). Thus \( \hat{J}^2 e = -2e \) and

\[
\int W \hat{J}^2 e \, de = -2 \langle e \rangle.
\]

Thus we finally arrive at equation for the first moment in the form

\[
2\tau_B \frac{d}{dt} \langle e \rangle = -2 \langle e \rangle - \langle e \times (e \times \xi) \rangle, \tag{3.2}
\]

where we have introduces a vector \( \xi = \xi h \) directed along the external field.
Let us now write the equations for the first and second moments in tensor notation:

\[
2\tau_B \frac{d}{dt} \langle e_i \rangle = -2\langle e_i \rangle + \xi_i - \langle e_i e_k \xi_k \rangle, \tag{3.3}
\]

\[
2\tau_B \frac{d}{dt} \langle e_i e_k \rangle = 2\delta_{ik} - 6\langle e_i e_k \rangle + \xi_i \langle e_k \rangle + \xi_k \langle e_i \rangle - 2\xi_l \langle e_i e_k e_l \rangle. \tag{3.4}
\]

Continuation of this chain, results in an endless set of cross-linked equations: the equation for the first moment contains the second moment \( \langle e_i e_k \rangle \), the equation for the second moment, the third \( \langle e_i e_k e_l \rangle \) and so on. In order to solve the set, one should stop somewhere, i.e., to truncate the infinite chain or, as it is called, close it. A primitive way of closure we have already used in Section 2.2, where we have solved the matrix set (2.19) by the Galerkin method. There we have replaced the infinite chain of equations for coefficients of \( P_m^n \) by a finite one, setting to zero all the coefficients of the Legendre polynomials with \( n > N \). It turns out that the amount of calculations grows drastically with \( \xi \): in order to monitor the field-dependence of the lowest spectrum levels (as already mentioned, these characteristics are of primary physical interest) we had to take a rather large basis, namely, to set \( N \geq \xi \). The necessity of solving a massive set of equations not only implies a very large number of calculations but to a great extent impedes the understanding and analysis of the obtained results.

To avoid the inconveniences owing to the numerical solution, it would help to have a non-trivial scheme of closure of the moment-equation set that is capable of giving a compact analytical description of the orientational processes in a magnetic fluid. Ideally, one should have only one equation, since only the first moment \( \langle e \rangle \)—magnetization—has a direct physical meaning. If properly constructed, such an equation would deliver a correct description of the magnetodynamics of a ferrocolloid in a wide range of the external field frequencies and amplitudes.

A fruitful physical idea, capable of meeting the above-stated demands is the effective-field method. Having proposed it for solution of the problems of the orientational kinetics of ferrocolloids, we have really re-introduced into the statistical physics a beautiful idea first put forward in thermodynamics by M.A. Leontovitch. Consider how in his book *Introduction to Thermodynamics* [28] first published in 1944, he introduces the idea (the following is the translation from Russian, as rendered by us):

“Let us begin with a simple example. Consider a gas in a vessel in the absence of external fields. In the equilibrium state the density of the substance will be everywhere the same and the center of mass will be situated in the geometric center of the vessel. Any state of the gas with a non-uniform density distribution, when the center of mass does not coincide with the geometric center of the vessel, will be a non equilibrium one. However, in the presence of an appropriate gravity field the cited state with nonuniform density will be the real equilibrium one.”

And in due course there follows a generalization:

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4This set is generated by the same KERD that yields the set of moment equations and is completely equivalent to the latter: any product of the form \( e_i e_k \ldots e_l \) may be expanded into a series of spherical functions \( P_m^n (\vartheta) \exp(\imath m \varphi) \).
"For an arbitrary nonequilibrium state of any thermally uniform system, that is characterized by definite values of internal parameters . . . the transition into the [equilibrium] state with the same values of those internal parameters might be performed by introducing an additional force field. By definition, the entropy of this non equilibrium state is equal to the entropy of the equilibrium (being that due to the presence of the additional force field) state characterized by the same values of the considered internal parameters."

In the magnetic systems that we study here, the role of this internal parameter is played by the magnetization $M$. Only in the true equilibrium state is it the function of the field given by

$$M_0 = n\mu L(\xi) \xi / \xi.$$  \hspace{1cm} (3.5)

Out of equilibrium there is no connection between $M$ and $H$; and arbitrary magnetization may be created “manually” despite the absence of the field. However, following Leontovitch, we may consider any arbitrary $M$ as an equilibrium one in a certain—specially prepared—field. This effective field $H_e$ and the corresponding dimensionless field $\xi_e$ are related to the instantaneous (nonequilibrium) magnetization by the equilibrium formula

$$M = n\mu L(\xi_e) \xi_e / \xi_e.$$  \hspace{1cm} (3.6)

During the equilibrium settling process the effective field $\xi_e$ tends to the true field $\xi$ so that the magnetization $M$ relaxes to its equilibrium value $M_0$ via a sequence of quasi-equilibrium states according to Eq. (3.6).

There is only one step left in order to translate Leontovitch’s concept into statistical physics language. Note that the magnetization is always determined by the expression $M = n\mu \langle e \rangle$, where $\langle e \rangle$ is the result of averaging of the vector $e$ with the distribution function $W(e, t)$. Averaging with function $W_0$ from Eq. (2.21) yields expression (3.5) for the equilibrium magnetization. Comparing Eqs. (3.5) and (3.6), we see that the latter is obtained by averaging $e$ with the distribution function

$$W_e = \frac{\xi_e}{4\pi \sinh \xi_e} \exp(\xi_e e),$$  \hspace{1cm} (3.7)

which retains the form of the Gibbs distribution (2.21) but differs from it by replacement of the true field $\xi$ by the effective one $\xi_e(t)$.

We remark that representation of the non-equilibrium distribution function in the form (3.7) does not yet, per se, imply any approximation: we simply replace one unknown function, ($W_e$), by another, ($\xi_e$). The effective-field approximation is really adopted when we assume that $\xi_e$ is independent of the angles: $\xi_e = \text{const} \langle e \rangle$. Moreover, it is clear that not at all any arbitrary nonequilibrium $M$ can be transformed into an equilibrium one by adding to the true field $\xi$ some uniform field $\nu = \xi_e - \xi$. For instance, from Eq. (3.7) it is apparent that the direction of $\xi_e$ is the symmetry axis for $W_e$ whereas an arbitrary distribution might not have any symmetry at all.

Carrying out the averaging in Eq. (3.2) with the distribution function (3.7), we arrive at the following equation [2]

$$2\tau_B \frac{d}{dt} \left[ \frac{L(\xi_e) \xi_e}{\xi_e} \right] = -2 \frac{L(\xi_e)}{\xi_e} (\xi_e - \xi) - \frac{\xi_e - 3 L(\xi_e)}{\xi_e^3} (\xi_e \times (\xi_e \times \xi)),$$  \hspace{1cm} (3.8)

which determines the dependence of the effective field $\xi_e$ on the true field $\xi$ and time; the distribution function and magnetization are evaluated then via Eqs. (3.7) and (3.6).
3.2 The linearized equation of magnetization motion: Relaxation times

The closed set of transcendental (and nonlinear with respect to $\xi_e$) relations (3.7) and (3.9) describes the dynamics of a suspension of rigid dipoles. Note that, at least in principle, one can use Eq. (3.7) to eliminate the quantities $\xi_e$ and $L(\xi_e)$ from Eq. (3.9), i.e., transform it into an equation for $dM/dt$. However, it would have required the introduction of very inconvenient notations alike $\xi_e = L^{-1}(M/n\mu)$, where $L^{-1}(x)$ is the function inverse to the Langevin function. There are no such problems in the case of a small deviations from equilibrium, where the effective field may be presented as a sum of the true field and some small correction $\nu$, viz. $\xi_e = \xi + \nu(t)$. For the non equilibrium part of magnetization

$$m = M - M_0 = n\mu \left[ L(\xi_e) \frac{\xi_e}{\xi_e} - L(\xi) \frac{\xi}{\xi} \right],$$

(3.9)
in the linear in $\nu$ approximation we get

$$\xi_e = \xi + \frac{\nu \cdot \xi}{\xi}, \quad \frac{\xi_e}{\xi_e} = \frac{\xi}{\xi} + \frac{(\xi \times (\nu \times \xi))}{\xi^3}, \quad L(\xi_e) = L(\xi) + \frac{(\nu \cdot \xi) \frac{dL}{d\xi}}{\xi}.$$  

(3.10)

Substituting this into Eq. (3.10) and splitting the non equilibrium part of magnetization as $m = m_\parallel + m_\perp$, i.e., into the components, which are, respectively, parallel and perpendicular to the external field, we have

$$m_\parallel = n\mu L(\xi) \frac{d}{d\ln\xi} \frac{\xi(\nu \cdot \xi)}{\xi^2}, \quad m_\perp = n\mu L(\xi) \frac{(\xi \times (\nu \times \xi))}{\xi^3}.$$  

(3.11)

Noting the expression $M_0 = n\mu L(\xi) \xi_e/\xi_e$ that represents the equilibrium part of the magnetization vector, Eqs. (3.12) might be as well rewritten in the form

$$m_\parallel = M_0 \frac{(\nu \cdot \xi)}{\xi^2} \frac{d}{d\ln\xi} \frac{L}{\xi}, \quad m_\perp = M_0 \times \frac{(\nu \times \xi)}{\xi^2}.$$  

Linearization of the right-hand side of equation (3.8) yields

$$-2L(\xi) \frac{\xi(\nu \cdot \xi)}{\xi^3} - [\xi - L(\xi)] \frac{(\xi \times (\nu \times \xi))}{\xi^3},$$

which after multiplying by $n\mu$ in the notations of Eq. (3.11) gives

$$-2m_\parallel \frac{d}{d\ln\xi} \frac{\xi}{\xi} - m_\perp \frac{\xi - L}{L}. $$

(3.12)

Making use of expressions (3.10)–(3.12), we can now write the linearized equation Eq. (3.8) as

$$\frac{d}{dt} (m_\parallel + m_\perp) = -\frac{d}{d\ln L} \frac{m_\parallel}{\tau_B} - \frac{\xi - L}{2L} \frac{m_\perp}{\tau_B},$$

(3.13)
or else, in terms of the full magnetization $M = M_0 + m$, as

$$\frac{d}{dt} M = -\frac{1}{\tau_\parallel H^2} H [(M - M_0) H] - \frac{1}{\tau_\perp H^2} (H \times (M \times H)).$$

(3.14)
Here we have introduced the relaxation times
\[ \tau_\parallel = \frac{d \ln L}{d \ln \xi} \tau_B, \quad \tau_\perp = \frac{2L}{\xi - L} \tau_B, \] (3.15)
for the components of magnetization parallel and perpendicular to the external field, respectively; the expressions in Eqs. (3.15) follow directly from comparison of Eqs. (3.13) and (3.14). Comparison between the approximate relaxation times rendered by Eq. (3.15) and the corresponding numerical results is presented in Fig. 2.1 in page 30. Both curves obey the Ritz rule according to which in a positive spectrum the approximate eigenvalues are always larger than the exact ones. Here, as we plot the relaxation times, i.e. inverses of the decrements, this is reflected by the fact that the curves plotted according to Eqs. (3.15) lie below the exact ones.

Thus we see that the relaxation rates of the longitudinal and transverse components of magnetization are different. Of course, in weak fields this difference is small—
\[ \tau_\parallel = \left(1 - \frac{2}{15} \xi^2\right) \tau_B, \quad \tau_\perp = \left(1 - \frac{1}{10} \xi^2\right) \tau_B \quad (\xi \ll 1), \] (3.16)
—and it vanishes in the absence of a field, when the notions of longitudinal and transverse directions become meaningless. In the opposite limit—at \( \xi \to \infty \)—Eq. (3.15) yields the asymptotics
\[ \tau_\parallel = \tau_B/\xi, \quad \tau_\perp = 2\tau_B/\xi, \quad (\xi \gg 1), \] (3.17)
i.e., the relaxation times of the magnetic moment components differ by the factor of 2.

Let us consider the origin of the last relationship. Note that in Eq. (3.17) we deal with the dynamical limit, i.e., the case where the Brownian motion of the particles is negligible. Indeed, substituting to Eq. (3.17) expressions \( \tau_B = 3nV/k_B T \) and \( \xi = \mu H/k_B T \), we find out that the relaxation times do not contain the temperature:
\[ \tau_\parallel = 3nV/\mu H, \quad \tau_\perp = 6nV/\mu H. \]

In such a completely magnetized suspension the magnetization vector has a constant length \( |M| = n\mu \), and thus the relaxation process reduces to a simple rotation of \( M \) towards the direction of \( H \). Denoting the angle between these two vectors is \( \theta \), one finds that the component \( M_\perp \) tends to its zero equilibrium value as
\[ M_\perp(t)/M_0 = \sin \theta(t) = \theta_0 \exp(-t/\tau_\perp). \] (3.18)

Since in the considered limit the motion of the vector \( M \) is pure rotation, the longitudinal component \( M_\parallel \) tends to the equilibrium value \( M_0 = n\mu \) as
\[ M_\parallel/M_0 = \cos \theta(t) \simeq 1 - \frac{1}{2} \theta^2(t). \] (3.19)

Noting that at small angles \( \sin \theta \approx \theta \), and using Eq. (3.18) one can rewrite Eq. (3.19) in the form
\[ (M_0 - M_\parallel)/M_0 = \frac{1}{2} \theta^2 \exp(-2t/\tau_\perp) \] (3.20)
Thus we see that the longitudinal magnetization relaxes according to the exponential law with the time \( \tau_\parallel = \tau_\perp/2 \).
We have shown that the effective-field method yields not only a macroscopic equation of motion for the ferrocolloid magnetization but may be used as well to obtain expressions for the field dependence of the relaxation times of the vector $M$. We remind the reader that the same dependencies were evaluated in Section 2.2 directly from the rotary diffusion equation, but the latter requires a cumbersome numerical procedure. A substantial argument in favor of the effective-field method is based on the fact that the calculated (with high precision) curves $\tau_{1,0}(\xi)$ and $\tau_{1,\pm 1}(\xi)$ in Fig. 2.1 are approximated by the simple expressions (3.15) with accuracy $\leq 15\%$ (in the longitudinal case) and $\leq 7\%$ (in the transverse case) in the entire range of the parameter $\xi$ considered.

The presented results are easily generalized for suspensions of nonspherical particles. As real suspensions usually comprise particles of various shapes, just due to that in zero approximation they may be considered as spherical on the average. There exist, however, areas of magnetic fluid physics, orientational magneto-optics for instance, where the effects observed are caused only by the departure of the particles from spherical shape. Indeed, the macroscopic anisotropy of the dielectric permeability tensor of a suspension is proportional to the difference between the principal depolarizing factors of individual particles. In the simplest approximation the particles may considered as ellipsoids of revolution with the semi-axes $a \neq b = c$. For them the orientational diffusion time differs from that given by expression (1.30) in two ways. First, for the particle volume one should substitute $V = 4\pi ab^2/3$ and, second, the formula should be multiplied by a certain function $\Phi(\varepsilon)$, where $\varepsilon = b/a$. We would rather not cite here the cumbersome equations evaluating $\Phi(\varepsilon)$ separately for oblate ($\varepsilon < 1$) and prolate ($\varepsilon > 1$) ellipsoids; they can be found, for example, in Refs. [37, 38]. We would only emphasize that the value $\Phi(1) = 1$ is a minimum. Hence, any nonsphericity of the particles leads to an increase of the magnetization relaxation times.

It is useful to get acquainted with yet another way of deriving of the magnetization motion equation. We remind the reader that the nonlinear equation (3.8) is the equation for the first moment of distribution function (3.7); in this step the nonequilibirity $\nu = \xi - \xi$ is not yet supposed to be small. The linear equation (3.14) is obtained by linearization of Eq. (3.8) providing $|\nu| \ll 1$. If one is concerned only with linearized equations of motion (and, hence, with corresponding relaxation times) then it is convenient to perform the aforementioned operations in inverse order: first to linearize the distribution function with respect to $\nu$, and only after that average the moment equations. Let us demonstrate this route taking as an example the equation for the first moment. Linearizing the function (3.7), we get

$$W_e = W_0 \left[ 1 + \nu_i(e_i - \langle e_i \rangle_0) \right],$$  

(3.21)

where $W_0$ is the equilibrium distribution function (2.12) and the angular brackets with the subscript 0 denote its moments, see Eq. (2.17). The function (3.21) satisfies the normalizing condition $\langle 1 \rangle = 1$ with linear in $\nu$ accuracy. Evaluating the two first moments with the linearized function $W_e$, we obtain

$$\langle e_i \rangle = \int e_i W_e \, de = \int W_0 \left[ e_i + e_i e_k \nu_k - e_i \langle e_k \rangle_0 \nu_k \right] \, de$$

$$= \langle e_i \rangle_0 + [\langle e_i e_k \rangle_0 - \langle e_i \rangle_0 \langle e_k \rangle_0] \nu_k,$$  

(3.22)
\[
\langle e_i e_k \rangle = \int e_i e_k W_e d\mathbf{e} = \int W_0 \left[ e_i e_k + e_i e_k e_l \nu_l - e_i e_k \langle e_l \rangle_0 \nu_l \right] d\mathbf{e} = \langle e_i e_k \rangle_0 + \left[ \langle e_i e_k e_l \rangle_0 - \langle e_i e_k \rangle_0 \langle e_l \rangle_0 \right] \nu_k. \tag{3.23}
\]
Substituting these expressions into Eq. (3.5) we rearrange it in the form
\[
2\tau_B \left[ \langle e_i e_k \rangle_0 - \langle e_i \rangle_0 \langle e_k \rangle_0 \right] \frac{d\nu_k}{dt} = - \left[ \langle e_i e_k \rangle_0 - \langle e_i \rangle_0 \langle e_k \rangle_0 \right] \nu_k - \frac{1}{2} \xi_k \left[ \langle e_i e_k e_l \rangle_0 - \langle e_i e_k \rangle_0 \langle e_l \rangle_0 \right] \nu_k. \tag{3.24}
\]
The next step is to replace the nonequilibrium part of the effective field \( \mathbf{v} \) by the nonequilibrium part of magnetization \( \mathbf{m} \) making use of relation
\[
\nu_i = \eta \mu \left[ \langle e_i e_k \rangle_0 - \langle e_i \rangle_0 \langle e_k \rangle_0 \right] \nu_k, \tag{3.25}
\]
which follows from Eq. (3.22). Expressing the equilibrium moments in terms of the Langevin functions according to Eqs. (2.16)–(2.18) and inverting relation (3.25) with the aid of the formula
\[
\left[ \langle e_i e_k \rangle_0 - \langle e_i \rangle_0 \langle e_k \rangle_0 \right]^{-1} = \frac{\xi}{L} \left( \delta_{ik} - \frac{\xi - 3L}{\xi - L} h_i h_k \right),
\]
we arrive again at equation (3.14) with the relaxation times (3.15).

As a matter of fact, the scheme considered is capable of yielding more general expressions for the relaxation times of magnetization. In order to show that, let us transform equation (3.24) using the relations between the equilibrium moments of different order. The relations sought follow from Eqs. (3.5) and (3.6) in the stationary case. Setting \( d/dt = 0 \) there, we have
\[
\xi_k \langle e_i e_k \rangle_0 = \xi_i - 2 \langle e_i \rangle_0,
\]
\[
\xi_l \langle e_i e_k e_l \rangle_0 = \frac{1}{2} \left( \xi_i \langle e_k \rangle_0 + \xi_k \langle e_i \rangle_0 - 3 \langle e_i e_k \rangle_0 + \delta_{ik} \right).
\]
Employing these relations to reduce the order of the moments in Eq. (3.24), we bring the latter to the form
\[
\tau_B \frac{d}{dt} m_i = - \frac{1}{4} \left( 2 \delta_{il} - 2 \langle e_i e_k \rangle_0 + \xi_i \langle e_k \rangle_0 + \xi_k \langle e_i \rangle_0 \right) \left( \langle e_i e_k \rangle_0 - \langle e_i \rangle_0 \langle e_k \rangle_0 \right)^{-1} m_k,
\]
whence we have the equations for the magnetization projections \( m_\parallel \) and \( m_\perp \), namely,
\[
\frac{d}{dt} m_\parallel = - \frac{1}{\tau_\parallel} m_\parallel, \quad \frac{d}{dt} m_\perp = - \frac{1}{\tau_\perp} m_\perp,
\]
with the relaxation times
\[
\tau_\parallel = 2 \tau_B \frac{\langle \cos^2 \vartheta \rangle_0 - \langle \cos \vartheta \rangle_0^2}{1 - \langle \cos^2 \vartheta \rangle_0}, \quad \tau_\perp = 2 \tau_B \frac{1 - \langle \cos^2 \vartheta \rangle_0}{1 + \langle \cos^2 \vartheta \rangle_0}, \tag{3.26}
\]
where \( \cos \vartheta = (e \cdot h) \).

For the dipolar potential \( U = -\mu H (e \cdot h) \) these formulas reduce to those of Eqs. (3.15). However, the range of validity of expressions (3.26) is wider: in the framework of the effective-field approximation they retain their form for an arbitrary uniaxial potential. In particular, they yield correct relaxation times for a magnetic moment subjected to a quadrupole field.
3.3 Dynamic magnetic susceptibility

The dynamic magnetic susceptibility is a fundamental characteristic of a ferrocolloid. In the rigid dipole model considered in this Chapter, it takes the most simple form. In order to find it, we present the external field as a sum of a constant part of arbitrary in strength and a small alternating one, \( H = H_0 + H_1 e^{-i\omega t} \), and study the linear response of magnetization to the alternating field.

For calculation of the dynamic susceptibility

\[
\chi_{ik}(H_0, \omega) = \frac{\partial M_i}{\partial H_{1k}}, \tag{3.27}
\]

we will use equation (3.14). However concerning the latter and important remark should be made. Up to the present, since we assumed that the ferrocolloid was subjected to a constant field \( H_0 \), the quantity \( M_0 \) there was taken to be the equilibrium magnetization. From now on, as the applied field contains an alternating component, there is no equilibrium in the system. So the notion of the equilibrium magnetization loses its direct meaning. In this situation one should treat \( M_0 \) as the instantaneous value of magnetization proportional to \( L(\mu H(t)/k_B T) \), which would have been the stationary solution of Eq. (3.14) at zero relaxation times. Introducing dimensionless amplitudes of the magnetic fields

\[
\xi_0 = \mu H_0/k_B T, \quad \xi_1 = \mu H_1/k_B T,
\]

and assuming that \( \xi_1 \ll 1 \), we may expand \( M_0 \) from Eq. (3.14) as a sum of constant and alternating terms as

\[
m_0 = n\mu L(\xi_0) \frac{\xi_0}{\xi_0} + n\mu L(\xi_0) e^{-i\omega t} \times \left[ \frac{d\ln L(\xi_0)}{d\ln \xi_0} \frac{\xi_0 (\xi_1 \cdot \xi_0)}{\xi_0^3} + \frac{(\xi_0 \times (\xi_1 \times \xi_0))}{\xi_0^3} \right]. \tag{3.28}
\]

We shall seek the solution of Eq. (3.14) in the form

\[
M = m + n\mu L(\xi_0) \frac{\xi_0}{\xi_0}, \tag{3.29}
\]

supposing that the alternating magnetization \( m \) has the same order of magnitude as the field \( H_1 \) inducing it—compare with Eqs. (3.21) and (3.22). Substituting these expressions into Eq. (3.14), we arrive at the equation for the linear response:

\[
\frac{d m}{d t} = -\frac{1}{\tau_{\|}} \left[ m - n\mu L(\xi_0) e^{-i\omega t} \frac{d\ln L(\xi_0)}{d\ln \xi_0} \frac{\xi_0 (\xi_1 \cdot \xi_0)}{\xi_0^3} \right] - \frac{1}{\tau_{\perp}} \left[ (\xi_0 \times (m \times \xi_0)) \frac{\xi_0^3}{\xi_0^3} - n\mu L(\xi_0) e^{-i\omega t} (\xi_0 \times (\xi_1 \times \xi_0)) \right]. \tag{3.30}
\]

Setting \( m \propto e^{-i\omega t} \) and directing the \( z \)-axis of the coordinate framework along the constant field, we find the dynamic susceptibility tensor \( \chi_{ik}(\xi_0, \omega) \). In the chosen framework it takes the diagonal form with its components being \( \chi_{xx} = \chi_{yy} = \chi_{\perp} \), \( \chi_{zz} = \chi_{\|} \), where [2]

\[
\chi_{\perp} = 3\chi_0 \frac{L(\xi_0)}{\xi_0} \cdot \frac{1}{1 - i\omega \tau_{\perp}}, \quad \chi_{\|} = 3\chi_0 \frac{dL(\xi_0)}{d\xi_0} \cdot \frac{1}{1 - i\omega \tau_{\|}}. \tag{3.31}
\]
In the absence of a constant field ($\xi_0 = 0$) from Eq. (3.31) we have

$$\chi_\perp = \chi_\parallel = \frac{\chi_0}{1 - i\omega\tau_B},$$

for the initial susceptibility, where $\chi_0 = n\mu^2/3k_B T$ is its static value—compare with Eq. (2.14). In a strong field $\xi_0 \gg 1$ from Eq. (3.31) we get the asymptotic dependencies

$$\chi_\perp = \frac{n\mu}{H_0} \left(1 - i\frac{6\eta V\omega}{\mu H_0}\right)^{-1}, \quad \chi_\parallel = \frac{n k_B T}{H_0^2} \left(1 - i\frac{3\eta V\omega}{\mu H_0}\right)^{-1}. \quad (3.32)$$

Note that in the dynamic limit ($T \to 0$) the transverse susceptibility remains finite whereas the longitudinal one tends to zero.

Equations (3.31) and (3.32) show that frequency dependence of the susceptibility in an assembly of rigid dipoles has a simple relaxational (the, so-called, Debye) form: its real part $\chi' = \Re \chi \propto (1 + \omega^2\tau^2)^{-1}$ is always positive and decays monotonically with frequency, whereas the imaginary part $\chi'' = \Im \chi \propto \omega\tau (1 + \omega^2\tau^2)^{-1}$ has a smooth low maximum at $\omega = \tau^{-1}$. Formally, these dependencies would hold at infinitely large frequencies. However, it is well-known that in a ferromagnet at high frequencies ($\sim 10^8 \div 10^{10}$ Hz) there occurs a magnetic resonance. The latter yields a change of sign of $\chi'(\omega)$ and a sharp peak of $\chi''(\omega)$ (the, so-called, Lorentzian absorption line). But it is incorrect to expect the rigid dipole model to describe ferromagnetic resonance. In fact, its applicability range is constrained by the condition $\omega \ll \omega_L$, where $\omega_L$ is the Larmor precession frequency of the magnetic moment in the net field $\mathbf{H}$ of Eq. (1.11). Indeed, the magnetic moment precession means its motion relative to the crystallographic axes of the particle whereas the very notion of a rigid dipole implies its “freezing” into the particle body, see in this connection the remark following Eq. (1.26).

It is useful to make one more comment on the lack of resonance properties in a system of rigid dipoles. The rotary diffusion equation (2.10) contains only one quantity with the dimension of frequency: relaxational “frequency” $\tau_B^{-1}$ which essentially determines the Debye character of $\chi(\omega)$ dispersion. However, one encounters the fundamental frequency

$$\omega_0 = \sqrt{\mu H/J}, \quad (3.33)$$

only if the inertial term in the equation of motion of the magnetic particle (1.17) is retained. Allowing for inertia, there are possible two regimes of settling the equilibrium orientation $\mu \parallel \mathbf{H}$ of magnetic moment in a constant external field $\mathbf{H}$: aperiodic motion at $\omega\tau_s < 1$, or damped oscillations at $\omega\tau_s > 1$; here $\tau_s$ is the viscous time defined by Eq. (1.29). Equation $\omega_0(H)\tau_s$ renders the lower bound $H_s$ of the field range inside which the oscillatory relaxation—the rotary oscillations of the particle in a plane passing through the vectors $\mathbf{e}$ and $\mathbf{H}$—takes place. Substituting into this equation $\tau_s$ from Eq. (1.29) and $\omega_0(H)$ from Eq. (3.33), we have

$$H_s = 45\eta^2/2\rho_p I_S d^2. \quad (3.34)$$

Setting here $\rho_p \simeq 5 \text{ g/cm}^3$, $I_S \simeq 10^3 \text{ G}$, and $d \simeq 10^{-6} \text{ cm}$, we find that even for low-viscosity liquids with $\eta \simeq 10^{-2} \text{ P}$ the value of $H_s$ is of the order of $10^7 \text{ Oe}$ (!). This estimate shows that fields $H > H_s$, above which the oscillatory motion of colloidal particles with the frequency $\omega_0$ may be possible, cannot be produced under terrestrial conditions.
Figure 3.1: Field dependencies of the dynamic susceptibilities given by Eqs. (4.31). (a) Longitudinal susceptibility, $T$; (b) transverse susceptibility; solid lines $\text{Im} \chi$, dashed lines $\text{Re} \chi$; curves 1, $\omega \tau_B = 2$; curves 2, $\omega \tau_B = 4$.
Whereas the frequency dependence of the dynamic susceptibility of the rigid dipole model is described by simple Debye-type expressions (3.31) and (3.32), the field dependence, $\chi(\xi_0)$, is sufficiently complicated. It accounts for the fact that the coefficients preceding the Debye factors as well as the relaxation times entering the latter are nonlinear functions of $\xi_0$, see Eqs. (3.15). The reference field-dependencies of real and imaginary parts of the susceptibility are shown in Fig.3.1. Note the non-monotonic character of the $\chi'(\xi_0)$ curves.

3.4 Static field-induced birefringence

In a magnetic field, owing to the presence of nonspherical particles, a ferrosuspension becomes optically anisotropic. As already been mentioned in Sec. 3.2, in first approximation nonspherical particles may be treated as uniaxial ellipsoids (ellipsoids of revolution). The ultimate cause of the optical anisotropy of the colloid is that the external field $H$, orienting the particle magnetic moments, via them makes the particles to align their long axes. Apparently, the higher the field strength, the higher is the macroscopic anisotropy and the stronger is the correlation between the directions of the particle magnetic moments $e$ and long axes $n$. In accordance with the rigid dipole model considered here, we will assume that the frozen magnetic moment is directed along the long axis of the particle: $e = n$, thus providing the perfect parallelism of the both.

A ferrocolloid comprising elongated particles under an external magnetic field becomes optically uniaxial. The field-induced magneto-optical effects—dichroism, birefringence, anisotropic light scattering—have a giant magnitude (5–7 orders higher that those in molecular fluids) that opens wide prospects of their practical use. In below we consider the most simple of these effects—magnetic birefringence in constant and alternating fields (the Cotton–Mouton effect).

A linearly polarized light beam, passing through a plane-parallel layer of magnetized suspension (the field $H$ lies in the plane of the layer) transforms into elliptically polarized light beam. The acquired ellipticity rate is determined by the difference between the refractive indices of ordinary ($n_o = n_{\perp}$) and extraordinary ($n_e = n_{\parallel}$) rays. The latter are the components of the light wave with the electric vectors oriented, respectively, perpendicular and parallel to the optical axis which coincides with the direction of magnetization $M$. There exist classic experimental methods providing a direct measurement of the phase lag between the components:

$$\delta = 2 \pi \frac{l}{\lambda} (n_{\parallel} - n_{\perp}),$$  \hspace{1cm} (3.35)

where $l/\lambda$ is the ratio of the layer thickness to the wavelength of the light. If the polaroids (polarizer and analyzer) are crossed, then the intensity of the light having passed through analyzer is (see [39], for example):

$$Q = Q_0 \sin^2 2\beta \sin^2(\delta/2),$$ \hspace{1cm} (3.36)

where $Q_0$ is the intensity of the incident light and $\beta$ the angle between directions of the incident light polarization and the vector $M$. At $\beta = 45^\circ$ and small $\delta$ equation (3.36) reduces to $Q/Q_0 = \delta^2/4$. Let us evaluate the dependence of phase lag $\delta(H)$ in a dilute suspension of rigid dipoles.
The field-induced orientational anisotropy of the long axes $n$ of the particles is conveniently described by a symmetrical traceless tensor

$$S_{ik} = \frac{3}{2} \left( \langle n_in_k \rangle - \frac{1}{3} \delta_{ik} \right),$$

widely used in the theory of liquid crystals. Its normalization is adjusted in such a way that for ideal ordering of the particle long axes (all $n$ parallel to $H = (0, 0, H)$) the component $S_{zz}$ equals to unity, and $S_{xx} = S_{yy} = -1/2$. In the absence of the field, when vectors $n$ are distributed randomly, from definition (3.37) there follows $S_{xx} = S_{yy} = S_{zz} = 0$. The dielectric permeability tensor of such a suspension may be presented as a linear combination of the isotropic and orientation tensors:

$$\varepsilon_{ik} = \varepsilon_0 \left( \delta_{ik} + \varkappa \phi S_{ik} \right);$$

here $\varepsilon_0$ is the dielectric permeability of the system in the absence of the field; $\phi$, the volume fraction of the solid phase of the colloid; and $\varkappa$, a coefficient depending upon the relative dielectric permeability of the particle substance and carrier liquid (at low nonsphericity of the particles $\varkappa$ is proportional to the squared eccentricity of the equivalent ellipsoid). At optical frequencies the magnetic permeability of any suspension should be set to unity [12]; then for the refractive indices of the ordinary and extraordinary rays one gets from Eq. (3.38):

$$n_\parallel = \sqrt{\varepsilon_{zz}} = n_0 \sqrt{1 + \varkappa \phi S_{zz}}, \quad n_\perp = \sqrt{\varepsilon_{xx}} = n_0 \sqrt{1 + \varkappa \phi S_{xx}},$$

where $n_0 = \sqrt{\varepsilon_0}$ is the refractive index at $H = 0$. In the linear approximation in $\phi$ we have

$$n_\parallel - n_\perp = \frac{3}{4} \varkappa n_0 \varepsilon_0 S_{zz}.$$

Thus Eq. (3.35) yields for the phase lag

$$\delta = \frac{3\pi l}{2\lambda} \varkappa \phi n_0 S_{zz}.$$

Making use of our expression (2.15) for the equilibrium second moment, in a constant field $H = H\mathbf{h}$ we have

$$S_{ik} = \frac{3}{2} \left( 1 - \frac{3L}{\xi} \right) \left( h_i h_k - \frac{1}{3} \delta_{ik} \right).$$

Taking the projection along the direction of the field, we see that

$$S_{zz} = 1 - 3L(\xi)/\xi$$

is the function that determines the field-strength and temperature dependencies of the phase lag $\delta$ (3.40). The asymptotics of this function following from Eq. (3.42) are

$$\delta = \frac{3\pi l}{2\lambda} \varkappa \phi n_0 \begin{cases} \xi^2/15 & \text{for } \xi \ll 1, \\
1 - 3/\xi & \text{for } \xi \gg 1. \end{cases}$$

Equations (3.40) and (3.42) are capable of providing a fairly good agreement with the results of static measurements of $\delta(H, T)$ [40]. The plots from the latter paper showing it are presented in Figs. 3.2 and 3.3.
Figure 3.2: Normalized field dependence of the birefringence phase lag: solid line, plot of function $\delta(H)$ according to Eqs. (3.39)–(3.41) with $\xi = 8.4 \cdot 10^{-3} H$; open circles, experimental data by Ref. [40]; solid circles, measurements of Ref. [41]

Figure 3.3: Temperature dependence of the birefringence phase lag $\delta$. Solid line is plotted according to Eqs. (3.39)–(3.41) normalized with the aid of two experimental points, namely, $T = 323$ and $348$ K; circles, measurement data by Ref. [40]
Note that we have treated refractive coefficients above as real quantities, i.e., we have ignored the absorption of light by a suspension. The generalization of the expressions obtained to complex refractive indices $n_{∥,⊥} = n_{∥,⊥}' - i n_{∥,⊥}''$ in linear in $\phi$ approximation does not encounter any difficulties. In particular, one can derive for the magnetic dichroism, i.e., anisotropy of absorption of ordinary and extraordinary rays, an analog of Eq. (3.39): $n_{∥}'' - n_{⊥}'' \propto S_{zz}$. Comparison of this dependence with Eq. (3.39) shows that under appropriate scaling the functions

$$\Delta n'(\xi) = n_{∥}' - n_{⊥}' \quad \text{and} \quad \Delta n''(\xi) = n_{∥}'' - n_{⊥}'',$$

should exactly reproduce one another. The results of testing of this conclusion employing experimental data from Ref. [41] are presented in Fig.3.4. It is apparent that the relation $\Delta n''/\Delta n' = \text{const}(\xi)$ holds with reasonable accuracy.

![Figure 3.4: Comparison of the field dependencies of birefringence and dichroism in magnetic fluids: solid line, evaluation by Eqs. 3.39)–(3.41); circles, the data from Ref. [41]: $n'$ (empty circles), $n''$ (solid circles)](image)

Before finishing our consideration of magnetic fluid birefringence in constant fields, we would like to emphasize that such optical experiments yield, in principle, the equal amount of information about a magnetic suspension (mean particle size, concentration, granulometric content of the dispersed phase) as magnetization curves $M(H)$ measurements. The only difference is that instead of the odd in the field-strength Langevin function $L(\xi)$ describing magnetization, the birefringence is rendered by the even dependence

$$L_2(\xi) = 1 - 3L(\xi)/\xi.$$

This difference in parity is because magnetization is proportional to the mean particle dipolar moment whereas birefringence is proportional to the average value of the tensor $n_in_k$ characterizing orientation of the particle axes. The bilinearity of the latter combination reflects the double-directedness of the ellipsoid rotation axis: the orientation tensor $S_{ik}$ does not change upon replacement of $\mathbf{n}$ by $-\mathbf{n}$. 
3.5 Dynamic field-induced birefringence

Let us now study the optical anisotropy of a suspension of rigid dipoles under non-stationary conditions. Since the orientation tensor is expressed by the second moment of the distribution function [which follows from its definition (3.37)] then in order to describe the dynamic birefringence we ought to use at least two equations for the distribution function moments. These equations have been given in Sec. 3.1 denoted there as Eqs. (3.5) and (3.6). Here we present them once again replacing $e$ by $n$:

$$2\tau_B \frac{d}{dt} \langle n_i \rangle = -2\langle n_i \rangle + \xi_i - \langle n_i n_k \xi_k \rangle, \quad (3.43)$$

$$2\tau_B \frac{d}{dt} \langle n_i n_k \rangle = 2\delta_{ik} - 6 \langle n_i n_k \rangle + \xi_i \langle n_k \rangle + \xi_k \langle n_i \rangle - 2\xi_l \langle n_i n_k n_l \rangle. \quad (3.44)$$

This form is more convenient here, because the magneto-optical response that we seek is determined by the orientation tensor composed of the components of vector $n$.

In order to close the set of equations even in the case of a small deviation from equilibrium, we cannot restrict ourselves to the linear variant of the effective-field method, where the distribution function is taken as

$$W_e = W_0 \left[ 1 + a_i (n_i - \langle n_i \rangle_0) \right]. \quad (3.45)$$

Indeed, calculation of the moments entering equations (3.43)–(3.44) with the aid of function (3.45) would lead to an overdetermined set, namely: six equations for three components of vector $a$. Apparently, the number of “effective fields” of different tensor dimensionality in the approximate representation of the distribution function should coincide with the number of moment equations solved. Therefore, for closure of the set (3.43)–(3.44) one has to use the function

$$W_e = W_0 \left[ 1 + a_i (n_i - \langle n_i \rangle_0) + b_{ik} (n_i n_k - \langle n_i n_k \rangle_0) \right]. \quad (3.46)$$

As well as function (3.45) in the magnetization relaxation problem, the last one is pertinent to the case of small deviations from equilibrium.

Let us acquaint ourselves with some properties of tensor $b_{ik}$, which we have introduced to the expansion (3.46) of function $W_e$. Firstly, it is easy to prove that a replacement $b_{ik} \rightarrow b_{ik} + C$, where $C$ is an arbitrary scalar quantity, does not change the distribution function. Noting that the vector $n$ has unit length and function $W_0$ has unit norm, we get

$$C \delta_{ik} (n_i n_k - \langle n_i n_k \rangle) = 0. \quad$$

Hence, while dealing with a second-order (quadrupole) effective field, it is feasible to use a convenient zero-gauge condition: $b_{ii} = 0$. Now consider a situation, where the true static field changes its strength by an increment $\Delta H = H - H_0$ such that $\Delta \xi = \xi - \xi_0 \ll 1$. Then the equilibrium distribution function, expanded up to the second order of accuracy with respect to $\Delta \xi$, takes the form

$$W_e = W_0(\xi_0) \left[ 1 + \Delta \xi h_i (n_i - \langle n_i \rangle_0) + \frac{1}{2} (\Delta \xi)^2 (h_i h_k - \frac{1}{3} \delta_{ik}) (n_i n_k - \langle n_i n_k \rangle_0) \right], \quad (3.47)$$
where symbol $\langle \ldots \rangle_0$ denotes averaging with the distribution function $W_0(\xi_0)$. It is easy to see that Eq. (3.47), which determines the result of variation of the external field-strength, is a particular case of Eq. (3.46) as $t \to \infty$. As may be seen from Eq. (3.47), the coefficient preceding the vector $(n_i - \langle n_i \rangle_0)$ is linear and that preceding the tensor $(n_i n_k - \langle n_i n_k \rangle)$ is squared with respect to the perturbation amplitude: $a_i \sim \Delta \xi$ and $b_{ik} \sim (\Delta \xi)^2$. Extending this conclusion to the non equilibrium situations, we will later assume that $b_{ik} \sim (a_i)^2$ when treating relaxation problems and $b_{ik} \sim \xi^2$ when dealing with oscillations induced by a weak alternating field $\xi_1(t)$.

Let us now study in detail the problem of birefringence relaxation in a suspension of rigid dipoles. Note that in the approximation adopted, i.e., when using the distribution function (3.46), we have

$$\langle n_in_k \rangle_c = \langle n_in_k \rangle_0 + a_l \left[ (\langle n_in_k n_l \rangle_0 - \langle n_in_k \rangle_0 \langle n_l \rangle_0) + b_{lm} \left[ \langle n_in_k n_l n_m \rangle_0 - \langle n_in_k \rangle_0 \langle n_l n_m \rangle_0 \right] \right].$$

We find noting the explicit moment tensors (2.15), the $zz$–component of the last expression in the form

$$\langle n_i^2 \rangle_c = \left( 1 - 2\frac{L}{\xi} \right) \frac{2}{\xi} \left( L^2 - L_2 \right) a_z(t) + \frac{6}{\xi^2} \left( 2L_2 - L^2 \right) b_{zz}(t); \quad (3.48)$$

here the constant external field $H$, as before, is directed along the positive direction of the $z$–axis. It follows from Eq. (3.48) that for a description of the dynamic birefringence one needs only the $z$–components of the effective fields. Substitution of the distribution function $W_c$ from Eq.(3.46) into Eqs.(3.43) and (3.44) shows that the $z$–components of $a_i$ and $b_{ik}$ form a closed set

$$\tau_B \frac{d}{dt} \left( \xi L'a_l + \xi L_2 b_l \right) = -La - 3L_2 b, \quad (3.49)$$

$$\tau_B \frac{d}{dt} \left[ \left( L^2 - L_2 \right) a + \frac{3}{\xi} \left( 2L_2 - L^2 \right) b \right] = -L_2 a - 3 \left( L - \frac{4}{\xi} L_2 \right), \quad (3.50)$$

where the prime denotes differentiation with respect to $\xi$ and we have omitted indices such as $a_z$ and $b_{zz}$.

A choice of solution in the form $a = a_0 e^{-\lambda t}$ and $b = b_0 e^{-\lambda t}$ provides a set of linear algebraic equations. Setting the determinant of this set equal to zero, one gets the equation

$$\begin{vmatrix} L - \lambda \tau_B \xi L' & 3L_2 - \lambda \tau_B \xi L_2' \\ L_2 - \lambda \tau_B (L^2 - L_2) & 3 \left( (L - 4L_2/\xi) + \lambda \tau_B (2L_2 - L^2)/\xi \right) \end{vmatrix} = 0, \quad (3.51)$$

the roots of which are the decrements $\lambda$, i.e., the inverse relaxation times of orientational perturbations.

We obtain solutions of Eq. (3.51) in the limiting cases of weak and strong fields. At $\xi \ll 1$ expansion of Eq. (3.51) with $\xi^2$ accuracy yields

$$(\lambda \tau_B)^2 - 4\lambda \tau_B (1 + 9\xi^2/140) + 3(1 + 16\xi^2/105) = 0,$$

whence

$$\lambda_1 \tau_B = (1 + \xi^2/10), \quad \lambda_2 \tau_B = (3 + 11\xi^2/70),$$
or, for the relaxation times,

\[ \tau_1 = \tau_B \left( 1 - \frac{11}{210} \xi^2 \right), \quad \tau_2 = \frac{\tau_B}{3} \left( 1 - \frac{1}{10} \xi^2 \right). \]  

(3.52)

At \( \xi \gg 1 \) an expansion up to \( 1/\xi^3 \) transforms Eq. (3.50) into

\[ \frac{1}{\xi^2} \left( \lambda \tau_B \right)^2 - \frac{1}{\xi} \left( 3 - \frac{5}{\xi} \right) \lambda \tau_B + \left( 2 - \frac{6}{\xi} + \frac{3}{\xi^2} \right) = 0, \]

whence

\[ \lambda_1 \tau_B = \xi \left( 1 - \frac{1}{\xi} - \frac{1}{\xi^2} \right), \quad \lambda_2 \tau_B = 2\xi \left( 1 - \frac{2}{\xi} + \frac{1}{2\xi^2} \right), \]

and

\[ \tau_1 = \frac{\tau_B}{\xi} \left( 1 + \frac{2}{\xi} + \frac{7}{2\xi^2} \right), \quad \tau_2 = \frac{\tau_B}{2\xi} \left( 1 + \frac{1}{\xi} + \frac{2}{\xi^2} \right). \]  

(3.53)

The quantities \( \tau_1 \) and \( \tau_2 \), so obtained, are the relaxation times of the fundamental modes of the set of equations (3.49) and (3.50). The time \( \tau_1 \), as it is clear from these equations, is connected with the dipolar mode: at \( \xi = 0 \) this time governs the decay of vector \( \langle n_i \rangle \), and the time \( \tau_2 \) is connected with the quadrupole mode since at \( \xi = 0 \) it controls the decay of perturbations of the tensor \( \langle n_i n_k \rangle \). The existence of the set of fundamental modes means that relaxation of the orientation tensor—and hence that of the birefringence—depends on the actual configuration of the initial perturbation, i.e., the numerical values of the coefficients of expansion of the initial state into fundamental modes. However, for strong fields it is possible to make some general predictions.

Let us find the fundamental modes of the set constituted by Eqs. (3.49) and (3.50) for \( \xi \gg 1 \). In this limit from Eqs. (3.37) and (3.50), for the component of the orientation tensor that we are interested in, we get

\[ S_{zz} = 1 - \frac{3}{\xi} + \frac{3}{\xi^2} [a(t) + 3b(t)]. \]  

(3.54)

The general solution of the set formed by Eqs. (3.49) and (3.50)

\[ a(t) = a_1 e^{-\lambda_1 t} + a_2 e^{-\lambda_2 t}, \quad b(t) = b_1 e^{-\lambda_1 t} + b_2 e^{-\lambda_2 t}, \]  

(3.55)

contains four constants coupled by the initial conditions

\[ a_1 + a_2 = a_0, \quad b_1 + b_2 = b_0, \]  

(3.56)

and by Eqs. (3.49) and (3.50). Substituting \( \lambda_1 \) and \( \lambda_2 \) in turn in either of the latter, we get two more relations imposed on the sought for coefficients, namely,

\[ a_1 + 6b_1 = 0, \quad a_2 + 3b_2 = 0. \]  

(3.57)

Solving the linear equations (3.55) and (3.57), we have

\[ a(t) + 3b(t) = (a_0 + 3b_0) e^{-\lambda_1 t}. \]

Whence in view of Eq. (3.52) it follows that in strong fields birefringence relaxation obeys a simple exponential law with a single dipolar time \( \tau_1 = \tau_B/\xi \) which coincides with the
relaxation time of the longitudinal component of the magnetic moment (3.17). Note that while solving Eqs. (3.49) and (3.50) we did not need to compare the orders of magnitude of the coefficients $a_i$ and $b_{ik}$, in this aspect the carried out calculation is exact.

Therefore, the two-moment effective-field approximation Eq. (3.47) leads to the following conclusions concerning birefringence relaxation in a system of rigid dipoles. In weak external fields the process of settling of the equilibrium optical anisotropy cannot be characterized by a single relaxation time. Both fundamental modes—dipolar and quadrupolar ones—render comparable contributions to the orientation tensor $S_{zz}(t)$; the involved relaxation times differ from one another only by the factor of three, see formulas (3.51). As the field grows, the relative weight of the quadrupole mode diminishes and for $\xi \gg 1$ the relaxation of birefringence with good accuracy is described by a single-mode formula with $\tau_1 = \tau_B/\xi$.

Now we consider birefringence in the regime of stationary oscillations of the external field $H_0 \exp(-i\omega t)$. We assume that its dimensionless amplitude is small: $\xi = \mu H_0/k_B T \ll 1$ and owing to that in Eq. (3.46) set $a_i \sim \xi$ and $b_{ik} \sim \xi^2$. Taking into account that in the absence of the external field the equilibrium distribution function is isotropic ($W_0 = 1/4\pi$), it is easy to evaluate the moments taken with the nonequilibrium distribution (3.46):

\[
\langle n_i \rangle = \frac{1}{3} a_i , \quad \langle n_i n_k \rangle = \frac{1}{3} \delta_{ik} + \frac{2}{15} b_{ik} , \\
\langle n_i n_k n_l \rangle = \frac{1}{15} (a_i \delta_{kl} + a_k \delta_{il} + a_l \delta_{ik}) .
\]

Substituting these into equations (3.43) and (3.44), we obtain the set of equations for the effective fields:

\[
\left( \tau_B \frac{d}{dt} + 1 \right) a_i = \xi_i e^{-i\omega t} , \\
\left( \frac{\tau_B}{3} \frac{d}{dt} + 1 \right) b_{ik} = \frac{1}{4} \left( \xi_i a_k + \xi_k a_i - \frac{2}{3} \xi_i a_l \delta_{ik} \right) e^{-i\omega t} .
\]

Then vector $a_i$ is readily eliminated from the second equation, yielding a closed equation for $b_{ik}$:

\[
\left( \frac{\tau_B}{3} \frac{d}{dt} + 1 \right) b_{ik} = \frac{1}{2(1 - i\omega \tau_B)} \left( \xi_i \xi_k - \frac{1}{3} \xi^2 \delta_{ik} \right) e^{-i\omega t} .
\] (3.58)

This shows that $b_{ik}$ oscillates with the frequency twice as large as that of the applied field, which one would expect since birefringence is an even effect. Directing the $z$–axis along $\mathbf{H}$, from Eq. (3.58) we get

\[
b_{zz} = \frac{\xi^2 e^{-2i\omega t}}{3(1 - i\omega \tau_B) (1 - \frac{2}{3} i\omega \tau_B)} .
\]

Separating here the real and imaginary parts, for the lag-angle tangent we have

\[
\tan \delta = \frac{\text{Im} \ b_{zz}}{\text{Re} \ b_{zz}} = \frac{5\omega \tau_B}{3(1 - \frac{2}{3} \omega^2 \tau_B^2)} .
\]
The complete solution in the form of a lagged oscillation comprises a constant and alternating parts reads:

$$b_{zz}(t) = \frac{1}{6} \xi^2 \left[ \frac{\cos(2\omega t - \psi)}{\sqrt{(1 + \omega^2 \tau_B^2)(1 + 4\omega^2 \tau_B^2/9)}} + \frac{1}{1 + \omega^2 \tau_B^2} \right]. \quad (3.59)$$

Note that at $\omega \to 0$ expression (3.59) transforms into the static relation $b_{zz} = \xi^2 / 3$ whereas at $\omega \to \infty$ the parameter $b_{zz}$ vanishes as $\omega^{-2}$. Apparently, when the field oscillations are too fast, the particles suspended in a viscous liquid are unable to react, and the orientational response of the suspension tends to zero.

Some remarks are worthwhile here. According to the concept stated above, the effective-field method may be used as well in the cases where the constant component of the external field is nonzero. However, the alternating part of the field causing deviations from equilibrium should always be small, i.e., $\xi \ll 1$. From general considerations it follows that turning on the magnetizing (constant) field that creates a substantial frequency-independent birefringence, will simultaneously reduce the alternating part of the optical response of the system: a constant field “freezes” the orientation of the particles. For large ($\xi > 1$) amplitudes of the alternating field ($\xi > 1$) the effective-field method in its linearized form (3.47) becomes inappropriate. Indeed, in this situation one can no longer use small-parameter expansions like Eq. (3.47). Then one has intense frequency multiplication in the system, and an adequate treatment requires one to take into account a great number of oscillatory modes. The exact solution of this problem, carried out numerically, yields a number of novel results on birefringence in dipolar suspensions, see Refs. [42,43].
4 Magnetodynamics of particles with finite anisotropy. Intrinsic magnetic resonance

4.1 Magnetic moment motion inside the particle.

Orientational diffusion equation

In this chapter we discuss application of the effective-field method to the resonance phenomena in dispersed ferromagnets—magnetic fluids and solid systems. As it has been explained in the above, the only resonance, existing in colloidal magnetic particles, is the ferromagnetic resonance (FMR)—the Larmor precession of magnetic moment inside the particle excited by alternating external field. According to the already given estimates, the frequency range, within which FMR may be observed, is located around $10^8 - 10^{10}$ Hz. It is apparent, that relatively to these much faster processes the mechanical degrees of freedom of the particles—rotations with the reference time $\sim \tau_B$—are “frozen up”. Therefore, upon the time-scale of the exciting field period, the orientation of particles might be considered as constant. Note, that in a certain sense the approximation now adopted is opposite to the used in Chapter 1 model of rigid dipoles: here we are going to deal only with those motions of vector $\mu$, which occur when it is torn off from the particle anisotropy axis.

General qualitative impression about the particularities of FMR in an assembly of single-domain particles one can get from consideration of the resonance condition for an individual particle. Neglecting dissipation, it may be written down as

$$\omega_L = \gamma |H_s + H_f|, \quad H_s = H + (2KV_m/\mu)(e \cdot n)n.$$ (4.1)

Here $H_s$ is a sum of the external magnetic field $H$ and the anisotropy field [see also formula (1.12)], $H_f$ is the fluctuational field. Dependence of $H_s$ upon the particle axis orientation $n$ means that for differently oriented particles the resonance condition (4.1) would be fulfilled at different $H$. In other words, the observed FMR line would comprise a great number of single-particle lines the centers of which are shifted relative to each other. The result of this spread of the resonance frequencies is that the enveloping line (the net FMR signal) would experience the so-called inhomogeneous broadening [45].

An important and, sometimes, dominating effect in fine-particle assemblies is caused by the action of thermal fluctuations on the magnetic moment precession. Indeed, when we deal with the particles whose volume is $V_m \sim 10^{-18}$ cm$^3$, even at room temperature the amplitude $H_f$ of the equivalent fluctuational magnetic field by the order of magnitude reaches hundreds of Oersteds and thus becomes comparable with the magnetic anisotropy field $H_a = 2KV_m/\mu$. In such situations the stochastic motion of the magnetic moment (superparamagnetism), induced by $H_f$, strongly affects both the frequency and damping coefficient of the Larmor precession. Under appropriate conditions superparamagnetism might almost entirely wipe off the regular precession of the magnetic moment.

The effective-field method was applied for the first time to the problems of FMR in magnetic suspensions in papers [46, 47]. Therein two characteristic marginal cases of formula (4.1) were addressed: magnetic resonance in the absence of the external field—the so-called, intrinsic FMR [46], see Sections 4.2 and 4.3 and magnetic resonance in isotropic ferroparticles [47], i.e., at $K = 0$, see Section 5. Each one of those approximations has
its own validity range depending upon how large or small is the parameter $KV_m/\mu H$ for real particles.

To take into account the orientational diffusion of the particle magnetic moment (the Néel superparamagnetism), is possible, apparently, only in the framework of the statistical description of the vector $\mathbf{u} = \mu \mathbf{e}$ motion. It means that we have to construct a corresponding kinetic equation for the distribution function $W(\mathbf{e}, t)$. Note that since hereby we are considering the high-frequency processes, function $W$, according to the above-made remark, might depend on vector $\mathbf{n}$ only as on the parameter. The Langevin equation of the problem under solution is provided by the Landau-Lifshitz equation (2.14) modified by incorporating the fluctuational field:

$$
\frac{d\mathbf{e}}{dt} = -\gamma (\mathbf{e} \times [H_s + H_f]) - \alpha \gamma (\mathbf{e} \times (\mathbf{e} \times [H_s + H_f])).
$$

(4.2)

The general expression for the summary magnetic field inside a single-domain particle reads

$$
H_s = -(1/\mu) \frac{\partial U}{\partial \mathbf{e}},
$$

(4.3)

where $U(\mathbf{e})$ is the orientation-dependent part of the particle energy. In the case of uniaxial anisotropy, formula (4.3) transforms into (1.12) or (4.1). For the fluctuational field, as in Sec. 3, we shall use the compact representation

$$
H_f = -(k_BT/\mu) \frac{\partial \ln W}{\partial \mathbf{e}}.
$$

(4.4)

Substitution of the magnetic moment velocity $d\mathbf{e}/dt$ from Eq. (4.2) into the continuity equation for the probability density

$$
\frac{\partial W}{\partial t} + \text{Div} (W \frac{d\mathbf{e}}{dt}) = 0,
$$

—cf. Eq. (1.37)—with allowance for relations (4.3) and (4.4) enables to write the kinetic equation in the form

$$
2\tau_D \frac{\partial W}{\partial t} = \hat{J} W \left( \hat{J} + \frac{1}{\alpha} \frac{\partial}{\partial \mathbf{e}} \right) \left( \frac{U}{k_BT} + \ln W \right).
$$

(4.5)

We remark that here $\hat{J} = (\mathbf{e} \times \partial/\partial \mathbf{e})$ is the operator of infinitesimal rotation and $\tau_D = \mu/2\alpha \gamma k_BT$ is the reference time of the orientational diffusion of the particle magnetic moment introduced by formula (1.15).

In the case of uniaxial anisotropy which we shall study in below, the particle magnetic energy acquires the form

$$
U = -\mu H(\mathbf{e} \cdot \mathbf{h}) - KV_m(\mathbf{e} \cdot \mathbf{n})^2,
$$

(4.6)

see Eq. (1.10) and, hence, KERD (4.5) might be specified as

$$
2\tau_D \frac{\partial W}{\partial t} = -\hat{J} W \left( \hat{J} + \frac{1}{\alpha} \frac{\partial}{\partial \mathbf{e}} \right) \left[ \xi (\mathbf{e} \cdot \mathbf{h}) + \sigma (\mathbf{e} \cdot \mathbf{n})^2 - \ln W \right],
$$

(4.7)

where $\xi = \mu H/k_BT$ is the dimensionless (scaled with respect to thermal energy) energy of the magnetic moment in the external field $\mathbf{H} = H \mathbf{h}$, and $\sigma = KV_m/k_BT$ is the
The effective-field method. The same-way scaled magnetic anisotropy energy. The parameters $\xi$ and $\sigma$ may be regarded as the measures of the influence of the regular magnetic fields—external and internal, respectively—on the motion of the particle magnetic moment $e$. Apparently, at $\xi, \sigma \ll 1$ the orientational diffusion is almost free while at $\xi, \sigma \to \infty$ we return to the case of entirely deterministic motion, i.e., the conventional Landau-Lifshitz equation (1.14). Note that the correctness of the used here simplified scheme of KERD derivation is confirmed by comparison of Eqs. (4.5) and (4.7) with the corresponding equations from [20], where these particular KERD had been derived by a rigorous calculation.

In a constant external field the general normalized stationary solution of equation (4.5) is the Gibbs distribution

$$ W_0 = Z_0^{-1} \exp(-U/k_BT), \quad Z_0 = \int \exp(-U/k_BT) \, de, \quad (4.8) $$

which in the case of uniaxial anisotropy takes the form

$$ W_0 = Z_0^{-1} \exp \left[ \xi(e \cdot h) + \sigma(e \cdot n)^2 \right], \quad Z_0 = \int \exp \left[ \xi(e \cdot h) + \sigma(e \cdot n)^2 \right] \, de. \quad (4.9) $$

Since we assume that the angular positions of particle anisotropy axes are fixed, we take $W_0$ from Eqs. (4.8) and (4.9) as the equilibrium distribution function. Rigorously speaking, such a function pertains to the case of so-called “partial” thermodynamic equilibrium, that is established only with respect to one of the dynamic variables of the system. In our case—to the magnetic moment orientation. However, we consciously go in for such a splitting of the configurational space in the partition integral, because it provides us with certain advantages. Firstly, while studying FMR in magnetic suspensions, due to the great difference between “internal” ($\tau_D$ and $(\alpha\omega_L)^{-1}$) and “external” ($\tau_B$ and $\tau$) time scales, the averaging over $n$ always might be either delayed for “afterwards” or carried out using the symmetry considerations. Secondly, the results obtained with the aid of function $W_0$ from Eqs. (4.8) and (4.9) are directly applicable to the particles which constitute the solidified magnetic fluids or, which one encounters more often, dispersed ferromagnets formed on the basis of solid matrices (rocks, zeolites etc.). For the latter systems the anisotropy axes distribution $f(n)$ should not necessarily be a consequence of any particular equilibrium settling process. It might, for example, be a result of the pre-history of the specimen: quenching of dispersed magnets, freezing of the magnetic fluid, etc.

4.2 Spectrum of decrements. Complex eigenvalues

For the intrinsic ferromagnetic resonance the character of the magnetic moment motion is determined by the internal anisotropy field of the particle. In order to understand how does this motion undergo and what part do play there the fluctuational effects, we shall consider the eigenmodes of the rotary oscillations of vector $\mu$ using KERD (4.7) and setting there $H = 0$. In the coordinate system with the $z$–axis directed along the easy magnetization axis of the particle, the desired equation reads

$$ 2\tau_D \frac{\partial W}{\partial t} = \frac{\partial^2 W}{\partial \vartheta^2} + \cotan \vartheta \frac{\partial W}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 W}{\partial \varphi^2} $$

$$ -2\frac{\sigma}{\alpha} \cos \vartheta \frac{\partial W}{\partial \varphi} + 2\sigma \sin \vartheta \cos \vartheta \frac{\partial W}{\partial \theta} + 2\sigma (3\cos^2 \vartheta - 1) W, \quad (4.10) $$
and its equilibrium solution, according to Eq. (4.9), may be written down as

\[ W_0 = \frac{1}{4\pi R} e^{\sigma x^2}, \quad R(\sigma) = \int_0^1 e^{\sigma x^2} \, dx, \quad x = (e \cdot n). \] (4.11)

Note that here the configurational integral \( R(\sigma) \), which unlike the rigid dipole model cannot be expressed in terms of elementary functions, is closely related to a sufficiently well-known quantity, namely, the Dawson integral \([31]\).

Being in possession of this solution, we would have been able, using the effective-field method, to construct the approximate non-equilibrium distribution function, to close with its aid the set of the moment equations and begin the analysis of the latter. However, before producing any particular approximate results, it is very useful for the understanding of the problem to establish some general relations. The latter are pertinent to the physical essence of the considered problem and as such are independent of any concrete form of the approximation or method of solution. Let us, following paper \([46]\), show how this can be done.

We expand an arbitrary deviation of the non-equilibrium distribution function \( W(e, t) \) from the equilibrium one \( W_0 \) determined by formulas (4.11) into the normal modes:

\[ W = \sum_{l,m} C_{lm} W_{lm}(x, \varphi, t), \quad W_{lm} = \Psi_{lm}(x) \exp(\sigma x^2 + im\varphi - \Lambda_{lm}t); \] (4.12)

where \( C_{lm} \) are constant coefficients determined by the form of the initial condition, \( \varphi \) is the azimuth angle of vector \( e \) in the coordinate system of Eq. (4.10). Substituting Eq. (4.12) into Eq. (4.10), one gets for the amplitudes of the normal modes \( \Psi_{lm} \) and dimensionless decrements \( \lambda_{lm} = 2\Lambda_{lm}\tau_D \) the equation

\[ -\lambda\Psi = \hat{A}\Psi, \] (4.13)

\[ \hat{A} \equiv \frac{d}{dx} \left[ (1 - x^2) \frac{d}{dx} \right] - \frac{m^2}{1 - x^2} + 2\sigma x(1 - x^2) \frac{d}{dx} - 2im \frac{\sigma}{\alpha}. \]

Solutions \( \Psi(x) \) of Eq. (4.13) are orthogonal to the solutions of the conjugate equation

\[ -\lambda^*\Phi = \hat{A}^+\Phi, \] (4.14)

where \( \hat{A}^+ \) is the Hermitian conjugate to \( \hat{A} \). Operator \( \hat{A}^+ \) looks especially simple if we introduce the orthogonality with weight:

\[ \int_{-1}^1 \Psi_{km}(x) \Phi_{ln}^*(x) e^{\sigma x^2} \, dx = N \delta_{kl}; \] (4.15)

here \( N \) stands for the normalizing integral. To get the conjugate equation, we multiply the complex conjugate of Eq. (4.13) by \( \Phi(x) \exp(\sigma x^2) \) and integrate over \( x \):

\[ \int_{-1}^1 \Phi e^{\sigma x^2} (\hat{A}^*\Psi^* + \lambda^*\Psi^*) \, dx = 0. \]
Making use of Eq. (4.13) it is easy to rearrange this to

$$\int_{-1}^{1} \Psi^* \sigma^2 (\hat{A}^* \Phi + \lambda \Phi) \, dx = 0,$$

where from for $\Psi(x)$ there follows the equation

$$-\lambda \Phi = \hat{A}^* \Phi.$$

Comparing it with Eq. (4.14), we conclude that $\hat{A}^+ = \hat{A}^*$, i.e., the operator $\hat{A}^+$ differs from $\hat{A}$ only by the sign of the last term in Eq. (4.13). This circumstance provides a simple relation between eigenfunctions: $\Phi^* = \Psi$, due to which the orthogonality condition (4.15) takes the form

$$\int_{-1}^{1} \Psi_{km}(x) \Psi_{lm}(x) e^{\sigma x^2} \, dx = N \delta_{kl}. \quad (4.16)$$

The lack of self-conjugation of the operator $\hat{A}$ indicates that its eigenvalues might be complex.

It is natural to begin the study of the spectrum $\lambda(\sigma)$ with the case of small $\sigma$. At $\sigma = 0$ equation (4.13) is satisfied by the associated Legendre functions

$$\Psi_{lm}^{(0)}(x) = i^l \left[ \frac{2l + 1}{2} \frac{(l-m)!}{(l+m)!} \right]^{\frac{1}{2}} P^m_l(x), \quad \lambda_{lm}(0) = l(l+1); \quad (4.17)$$

here we have chosen the normalizing coefficients so, that they give $N = 1$ for even and $N = -1$ for odd $l$’s.

At non-zero but sufficiently small $\sigma$ the solution of Eq. (4.13) may be constructed of the power series in $\sigma$. We would not present these simple calculations, but would like to note, that decrements $\lambda$ in any order of the perturbation theory remain real. Eigenfunctions $\Psi$ at $\sigma \neq 0$ loose their parity and may be rearranged into two-term sums of real even (subscript $g$) and imaginary odd (subscript $u$) parts:

$$\Psi = \Psi_g + i \Psi_u; \quad (4.18)$$

for example, an expansion, originating from the even level, at small $\sigma$ contains a small imaginary part odd in $x$. As a matter of fact, one may even at $\sigma \neq 0$ still distinguish “even” and “odd” solutions depending upon what level of spectrum do they reduce to at $\sigma \to 0$. Note that the normalizing integrals in Eq. (4.16)

$$N = \int_{-1}^{1} \Psi^2 e^{\sigma x^2} \, dx = \int_{-1}^{1} (\Psi_g^2 - \Psi_u^2) e^{\sigma x^2} \, dx$$

are positive for even functions (since at $\sigma \to 0$ the odd part $\Psi_u$ vanishes) and are negative for the odd ones.

Evidently, as long as the power series in $\sigma$ converge, the described by them perturbations (4.11) of the distribution function change monotonically in time. This may be as
well shown explicitly. If we multiply equation (4.13) by $\Psi^\ast \exp(\sigma x^2)$, integrate it over $x$ and, finally, subtract from the expression obtained its complex conjugate, we get

$$\text{Im} \lambda = 2m \sigma \frac{\int x |\Psi|^2 \exp(\sigma x^2) \, dx}{\int |\Psi|^2 \exp(\sigma x^2) \, dx}.$$  

The integral in the numerator of this formula after substitution $\Psi$ from Eq. (4.18) identically turns into zero due to the evenness of its $\Psi$-dependent part. Apparently, $\text{Im} \lambda = 0$ indicates the absence of oscillating perturbations.

Thus, the oscillating perturbations might appear only at finite values of $\sigma$ greater than certain $\sigma_*$. The latter is just that very value of the parameter that determines the upper bound of the radius of convergence for the above-presented expansions. Multiplying equation (4.13) by $\Psi \exp(\sigma x^2)$ and then acting exactly as in derivation of the former relation, with allowance for Eq. (4.18) we get

$$(\lambda^* - \lambda) \int (\Psi_g^2 - \Psi_u^2) e^{\sigma x^2} \, dx = 0.$$  

From here we see that the appearance of oscillating ($\lambda^* \neq \lambda$) perturbations at $\sigma > \sigma_*$ is preceded by tending to zero the normalizing integral $N$ at the point $\sigma_*$. Such singularities in the spectra of non-self-conjugate operators are known [48] to appear as a result of intersection of a pair of levels, which in the range of reality $\sigma < \sigma_*$ have the normalizing integrals of opposing signs [49].

For the study of intersections in the decrement spectrum, it is convenient to employ the method used by Landau and Lifshitz [50] in the theory of electron terms of molecules. Let at certain $\sigma = \sigma_0$ two neighboring decrements, $\lambda_1$ and $\lambda_2$, be real and close in magnitude (“quasi-degeneration”). Due to alternation of even and odd levels the normalizing integrals of amplitudes $\Psi_1$ and $\Psi_2$ have opposing signs (say, $N_1 = +1$ and $N_2 = -1$). The value of the amplitude in some close point $\sigma_0 + \varepsilon$ one might present as

$$\Psi = c_1 \Psi_1 + c_2 \Psi_2.$$  

To evaluate the expansion coefficients $c_1$ and $c_2$, from Eq. (4.13) we derive by usual means an algebraic set of two uniform linear equations. Setting its determinant equal to zero, one finds the decrements in the vicinity of the point $\sigma_0$:

$$\lambda_{\pm} = \frac{1}{2} [\lambda_1 + \lambda_2 - (B_{11} - B_{22}) \varepsilon] \pm \left\{ \frac{1}{4} [\lambda_1 - \lambda_2 - (B_{11} - B_{22}) \varepsilon]^2 - B_{12} B_{21} \varepsilon^2 \right\}^{1/2},$$  

where we have introduced the notation

$$B_{ik} = \int_{-1}^1 \Psi_i \frac{\partial \hat{A}}{\partial \sigma} \Psi_k \exp(\sigma x^2) \, dx.$$  

In order to analyze formula (4.19), first of all, let us note that in the range of reality of decrements, where functions $\Psi_i$ might be presented in the form (4.18), all the matrix elements $B_{ik}$ are real. The decrements $\lambda_1$ and $\lambda_2$ intersect (coincide) at the point $\sigma_0 = \sigma_0 + \varepsilon$, where $\varepsilon$ is to be found from the condition of vanishing of the subradical expression in
Eq. (4.19). This condition can be satisfied only when $B_{12}B_{21} \geq 0$, because at $B_{12}B_{21} < 0$ the subradical expression is essentially positive for all $\varepsilon$. At $B_{12}B_{21} > 0$ at the point $\sigma_*$ two real terms “fuse”: the subradical expression changes its sign, and at $\sigma > \sigma_*$ decrements $\lambda_+$ and $\lambda_-$ form a complex-conjugate pair. Note that a “simple” intersection, at which the decrements would have remained real on both sides of the point $\sigma_*$, is impossible since it demands that the product $B_{12}B_{21}$ would vanish identically with respect to $\sigma_0$, which is manifestly untrue.

Therefore, the neighboring decrements either fuse at a certain point $\sigma_*$, or else do not intersect at all. The decrement spectrum of the eigenvalue problem under consideration has been evaluated numerically by the Galerkin method. As a set of basic functions we have taken $\Psi_{lm}^{(0)}$ from Eq. (4.17) which are the solutions of equation (4.13) at $\sigma = 0$. To obtain the dependence $\lambda(\sigma)$ in a sufficiently wide range of values of the parameter $\sigma$, it turned out to be necessary to take rather a large number of the basis functions. In the studied interval $0 < \sigma < 20$ we used an approximation

$$\Psi = \sum_{l=1}^{n} c_{lm} \Psi_{lm}^{(0)}$$

with $n = 20$ and carried out control calculations with $n = 30$.

In Fig.4.1 we present the low levels of the spectrum for $m = 1$ and $\alpha = 0.1$. Their form fairly well corresponds to the predicted qualitative picture of the structure of the eigenvalue spectrum of equation (4.13). One can see the fusion of real terms $\lambda_{11}$ and $\lambda_{21}$ that gives rise to the oscillating modes. The dashed line shows the real part of the complex-conjugate decrements beyond the fusion point. The imaginary part is also presented there, the fusion-point coordinate being $\sigma_* \simeq 0.24$.

At $\sigma \geq 15$ (low-temperature limit) all the decrements approach the asymptote

$$\text{Re} \lambda = 2\sigma, \quad \text{Im} \lambda = \pm 2\sigma/\alpha.$$  (4.21)

From here for the dimensional decrements $\Lambda = \lambda/2 \tau_D$ with allowance for relation (1.17) connecting relaxation times $\tau_0$ and $\tau_D$, there follow the standard expressions [12]

$$\text{Re} \Lambda = \alpha \omega_L, \quad \text{Im} \Lambda = \omega_L,$$  (4.22)

where $\omega_L = 2K\gamma/I$ is the frequency of the uniform Larmor precession in a massive ferromagnetic crystal with uniaxial positive (“easy-axis”) anisotropy in the absence of external field, see [51], for example.

Our analysis shows that in the system under consideration the parameter $\sigma_*$ determines the critical volume of a ferromagnetic particle $V_* = \sigma_* k_B T/K$ below which the fundamental frequency of precession of a particle magnetic moment does not any longer exist, even in principle. For the critical diameter $d_*$ of a spherical particle at room temperature and reference range of the magnetic anisotropy $K \simeq 10^5 - 10^6$ erg/cm$^3$ one obtains $d_* \simeq 6 - 12$ nm. The last estimate coincides with the characteristic size of the particles constituting magnetic fluids ($d \sim 10$ nm). Such coincidence means that in colloidal particles the regime of the magnetic moment motion may either take the form of precessional rotation or resemble that of over-damped (relaxational) oscillations. Taking into account the proportionality between the parameter $\sigma$ and the ratio $V_m/T$, we arrive
at conclusion that real (i.e., polydisperse) magnetic suspensions must be the mixtures of particles with different magneto-dynamic behavior. In every such mixture one may tentatively distinguish the particles of a “resonator” and “relaxator” types. Moreover, even in a given suspension the relative concentration of the particles of each kind is not an once and forever predetermined quantity, since it depends upon temperature. Apparently, the number density of resonators/relaxators would grow upon decrease/increase of temperature. The existence of such a strong size- and temperature-sensitive effect, caused, of course, by superparamagnetism, makes FMR a powerful and informative tool for the study of dispersed ferromagnets.

4.3 Magnetic resonance in the uniaxial anisotropy field

Having studied the spectral properties of the operator of equation (4.7) and thus being aware of the dependence of character of the relaxation upon the dimensionless height $\sigma$ of the potential barrier of magnetic anisotropy, we now proceed to the description of stationary magnetic moment oscillations induced in a uniaxial single-domain particle by a weak external field. Let us transform Eq. (4.7) into a set of equations for the moments of the non-equilibrium distribution function. Using the rules already described in Chapter 1,
for the first two moments we get

$$\begin{align}
\tau_D \frac{d}{dt} \langle e_i \rangle &= -\langle e_i \rangle + \sigma n_n k \langle e_i \rangle - \sigma n_k n_l \langle e_i e_k e_l \rangle \\
&\quad - \frac{\sigma}{\alpha} e_{klm} n_m \langle e_k e_m \rangle + \frac{\xi}{2} \left( h_i + \frac{1}{\alpha} e_{kl} h_k \langle e_i \rangle - h_k \langle e_i e_k \rangle \right),
\end{align}$$

(4.23)

$$\tau_D \frac{d}{dt} \langle e_i e_k \rangle = \delta_{ik} - 3 \langle e_i e_k \rangle + \sigma \left( n_i n_l \langle e_i e_l \rangle + n_k n_l \langle e_i e_l \rangle \right)$$

$$\quad - 2 \sigma n_m n_l \langle e_i e_k e_l e_m \rangle + \frac{\sigma}{\alpha} n_k n_l \left( e_{klm} \langle e_i e_m e_n \rangle + e_{ilm} \langle e_k e_m e_n \rangle \right)$$

$$\quad + \frac{\xi}{2} \left[ h_i \langle e_k \rangle + h_k \langle e_i \rangle - 2 h_l \langle e_i e_k e_l \rangle \right] + \frac{\xi}{2\alpha} h_l \left( e_{klm} \langle e_i e_m \rangle + e_{ilm} \langle e_k e_m \rangle \right).$$

(4.24)

Note that while deriving this set we have not employed any relations between $\xi$ and $\sigma$, so it is exact and, in principle, capable to provide the description of FMR at arbitrary amplitudes of the external and anisotropy fields. Simultaneously, due to its exactness, the obtained set is unclosed: the written down equations for the first two moments contain the third and forth ones, thus starting the infinite set.

However, equations (4.23)–(4.24) form the minimal set required to study the intrinsic FMR in a superparamagnetic particle. To make it clear, let us have a look at the structure of Eq. (4.23). As it follows from Eqs. (4.2), (4.5) and (4.7), the gyromagnetic effect—the only source of the precession motion—in Eq. (4.23) is represented by those terms which are proportional to $\alpha^{-1}$. Being after dynamic susceptibility, i.e., adopting linear approximation, we consider the external field $\xi$ to be small. The same are the perturbations of the magnetic moment direction $\mathbf{e}$. Taking into account these circumstances, we see immediately that the external field by itself does not yield any precession frequency: the terms $\propto \xi/\alpha$ drop out, since they are non-zero only in the second order of magnitude in perturbations. This fact is natural, since we are studying the intrinsic FMR and should expect that the fundamental frequency is formed by the anisotropy field. The gyromagnetic contribution of the latter is represented in Eq. (4.23) by the term $\propto (\sigma/\alpha) \langle e_k e_m \rangle$. At the first sight, it survives linearization undertaken with the effective-field distribution function of the type (3.24) or (3.45). But running a more thorough check, one finds that for the case of the intrinsic FMR it is not so. Indeed, expanding the cited term with the aid of distribution functions (3.24) or (3.45), we split it into two parts, proportional, respectively, to $\langle e_k e_m \rangle_0$ and $\langle e_k e_m e_j \rangle_0$. The bilinear combination, that expresses to the zero-order approximation, is obviously symmetrical and due to that vanishes identically after contraction with the Levi-Civita tensor. Trying the first-order correction, one finds that it also is an identical zero, though due to less obvious reasons. The latter follow from the symmetry of the equilibrium state of the particle magnetic moment. In the considered situation the stationary state corresponds to the absence of the external field; setting in Eq. (4.9) $\xi = 0$, we come to the equilibrium distribution function

$$W_0 = Z_0^{-1} \exp \left[ \sigma (\mathbf{e} \cdot \mathbf{n})^2 \right], \quad Z_0 = \int \exp \left[ \sigma (\mathbf{e} \cdot \mathbf{n})^2 \right] d\mathbf{e}.$$  

(4.25)

These expressions are even with respect to the components of vector $\mathbf{e}$ and, hence, all the odd-order equilibrium moments of distribution Eq. (4.25) are identical zeroes. Less formal but exactly equivalent qualitative formulation of this result is well-known: “There
are no permanent magnets in statistical thermodynamics, true ergodicity forbids their existence”.

So, we have demonstrated that the quadrupole symmetry of the uniaxial anisotropy energy demands that at least two effective fields should be used in order to study the intrinsic FMR in a magnetic particle. This conclusion agrees with the one obtained in the preceding section: to get the oscillatory relaxation one should consider at least two eigenmodes with different parity.

According to this, we choose the approximate (effective-field) distribution function in the form

\[ W_e = W_0 \left[ 1 + a_i (n_i - \langle n_i \rangle_0) + b_{ik} (n_i n_k - \langle n_i n_k \rangle_0) \right], \tag{4.26} \]

that exactly resembles Eq. (3.45) in its form but, in fact, is qualitatively different. It is so because, firstly, now both \( a_i \) and \( b_{ik} \) are supposed to be of equal order of magnitude and, secondly, the equilibrium distribution function \( W_0 \) in (4.26) is given by Eq. (4.25) or in even more convenient form—by Eq. (4.11).

Assuming that the dimensionless amplitude of the external magnetic field \( \xi(t) = \xi \exp(-i\omega t) \) is small comparing to unity, imposing the already discussed conditions \( a_i \sim b_{ik} \sim \xi \) on the perturbations of the distribution function of Eq. (4.25) and using the latter to close the set of equations (4.23)–(4.24), we finally transform it into

\[
2\tau_D X_{ik} \frac{d}{dt} a_k = -a_i + X_{ik} a_k + \xi e^{-i\omega t} (h_i - X_{ik} h_k) - \frac{2}{\alpha} e_{ikl} \langle e_i e_m \rangle b_{km}, \tag{4.27}
\]

\[
2\tau_D (X_{iklm} - X_{ik} X_{lm}) \frac{d}{dt} b_{lm} = -2X_{il} b_{kl} - 2X_{kl} b_{il} + 4X_{iklm} b_{lm} \tag{4.28}
\]

+ \frac{1}{\alpha} (e_{ilm} X_{kl} + e_{klm} X_{il}) a_m - \frac{\xi}{\alpha} e^{-i\omega t} (e_{ilm} X_{kl} + e_{klm} X_{il}) h_m,

where for the sake of brevity we have introduced the notations

\[ X_{ik...p} \equiv \langle e_i e_k \ldots e_p \rangle_0 = (4\pi R)^{-1} \int e_i e_k \ldots e_p \exp[\sigma(e \cdot n)^2] \, de, \]

for the moments of the equilibrium distribution function \( W_0 \). These quantities are expressed via the derivatives of function \( R(\sigma) \) with respect to its argument and their tensor structure—via the Kronecker δ’s and even-number products of the components of vector \( n \). For example, the second and the forth tensor moments entering the set (4.27)–(4.28) are

\[ X_{ik} = \frac{1}{2} \left( 1 - \frac{R'}{R} \right) \delta_{ik} + \frac{3}{2} \left( \frac{R'}{R} - \frac{1}{3} \right) n_i n_k, \tag{4.29} \]

\[ X_{iklm} = \frac{1}{8} \left( 1 - 2\frac{R'}{R} + \frac{R''}{R} \right) (\delta_{ik} \delta_{lm} + \delta_{il} \delta_{km} - \delta_{im} \delta_{kl}) - \frac{1}{8} \left( 1 - 6\frac{R'}{R} + 5\frac{R''}{R} \right) (n_i n_k \delta_{lm} + n_l n_m \delta_{ik} + n_i n_l \delta_{km} + n_k n_l \delta_{im} + \right. \]

\[ + n_i n_m \delta_{kl} + n_k n_m \delta_{il}) + \frac{1}{8} \left( 3 - 30\frac{R'}{R} + 35\frac{R''}{R} \right) n_i n_k n_l n_m. \tag{4.30} \]

Noteworthy that due to the uniaxial symmetry of the equilibrium state, the expression relating the first moment of the non-equilibrium distribution function Eq. (4.26), i.e., dimensionless non-equilibrium magnetization, to the effective-field amplitude, is very simple

\[ \langle e_i \rangle = X_{ik} a_k. \tag{4.31} \]
Let us firstly determine the longitudinal susceptibility $\chi_\parallel$, assuming that the external field is parallel to the anisotropy axis: $h = n = (0, 0, 1)$. In this case the equation for $a_z$ following from Eq. (4.27) does not involve the gyration term and due to this is closed:

$$
\tau_D X_{zz} \frac{d}{dt} a_z = - (1 - X_{zz}) \left( a_z - \frac{1}{2} \xi e^{-i\omega t} \right).
$$

Substituting here $X_{zz} = R'/R$ and using Eq. (4.31), we rearrange the latter equation as

$$
\frac{d}{dt} \langle e_z \rangle = - \frac{1}{\tau_\parallel} \langle e_z \rangle + \frac{\xi}{2\tau_D} e^{-i\omega t} \left( 1 - \frac{R'}{R} \right),
$$

(4.32)

where

$$
\tau_\parallel = 2\tau_D \frac{R'}{R - R'}.
$$

In the absence of the external field Eq. (4.32) describes the relaxation of the projection of the magnetic moment $\mu$ on the direction of the external field. Thermal fluctuations induce flops between the states with $\mu = \pm \mu n$. The probability of the flop depends upon the ratio of the potential barrier height $KV_m$ to the thermal energy $k_B T$, i.e., on the parameter $\sigma$. If at the initial moment the particle had been magnetized along the $z$-axis, then the projection of the magnetic moment onto this axis would diminish with time as $\exp(-t/\tau_\parallel)$ thus displaying the superparamagnetic behavior.

The dependence $\tau_\parallel(\sigma)/\tau_D$ is shown in Fig. 4.2 by the dashed line. Solid line corresponds to the exact solution $2\lambda_{1,0}(\sigma)$ evaluated from Eq. (4.13) by the Galerkin method—see Section 4.2—with approximation Eq. (4.20) at $m = 0$ and $n = 20$. For $\sigma \geq 2$ the solid curve with good accuracy obeys the Brown’s asymptotic formula (2.9) whereas the dashed one approaches the line $\tau_\parallel/\tau_D = 2\sigma$. Using formulas from Appendix and Eq. (1.17), we get from (4.32):

$$
\tau_\parallel = \begin{cases} 
\sigma & \text{for } \sigma \ll 1, \\
2\sigma^2 & \text{for } \sigma \gg 1.
\end{cases}
$$

(4.33)

The discrepancy in asymptotic behavior of the exact and approximate results is a rare example of incurable failure of the effective-field method. It is important to understand the cause of that in order to know the boundaries of our, usually successful, approximation. The detailed answer demands a thorough analysis of spectra of different KERD operators, Eqs. (2.22) and (4.13) among them, but the essential idea is simple. If the dependencies of all the eigenvalues upon the amplitude of the orientational potential are qualitatively similar (e.g. all of them grow), then the reduced description that replaces the whole set of levels by one or two decrements, works fairly well—see Section 3.2 and the continuation of the present one. If, conversely, the spectrum comprises the eigenvalues with qualitatively different parametric behavior, a simple reduction provided by the effective-field description cannot handle the situation. Just such a case we have run into while studying the longitudinal relaxation in a uniaxial particle. Indeed, the spectrum of the $z$-projection decrements $\{\lambda_{n,0}\}$ of operator (4.13), as it has been shown in Ref. [52], is somewhat peculiar: all the eigenvalues with $n \geq 2$ grow with $\sigma$ whereas $\lambda_{1,0}$ falls down becoming at $\sigma > 2$ exponentially small. It is not surprising that in such a spectrum the effective-field description has poor chances to be valid. However, it “does its best” at moderate $\sigma$—see Fig. 4.2, and even having been left far behind at larger values still points out the correct direction of the change of the relaxation time.
Figure 4.2: Comparison of longitudinal relaxation times of the magnetic moment in a uniaxial anisotropy field; solid line: the effective-field calculation, dashed line: $1/\lambda_{10}$ obtained by the numerical procedure

Equation (4.32) leads to a simple Debye-type expression for the longitudinal susceptibility. Evaluating it for the unit volume of the particle substance, one finds

$$
\chi_{\|} = \frac{\chi_{\|}^{(0)}}{1 - i\omega\tau_{\|}}, \quad \chi_{\|}^{(0)} = \frac{2I}{H_{a}} \frac{\sigma R'}{R}.
$$

(4.34)

The frequency dependence of $\chi_{\|}$ is inherent to the relaxational systems: as $\omega$ grows, $\chi_{\|}'$ falls down monotonically while $\chi_{\|}''$ has a shallow maximum at $\omega = \tau_{\|}$. In the limit of small $\sigma$ the “resonant” frequency $\omega_r = \omega_0 \alpha/\sigma$ tends to infinity and the static susceptibility with the accuracy up to the second order is

$$
\chi_{\|}^{(0)} = \frac{I}{H_{a}} \frac{2}{3} \frac{\sigma}{3} \left( 1 + \frac{4}{15} \sigma \right) = \frac{\mu I}{3k_B T} \left( 1 + \frac{4K V_m}{15k_B T} \right).
$$

(4.35)

Therefore, the leading term in the static magnetic susceptibility of ultra-fine ferroparticle ($\sigma \ll 1$) is given by the Langevin formula (2.15) originally obtained for paramagnetic gases. The real and imaginary parts of $\chi_{\|}$ at $\sigma \leq 0.3$ are presented in Fig. 4.3.

At $\sigma \gg 1$ the fluctuational mechanism of the magnetic moment re-orientation “freezes up” (according to Eq. (4.33) $\tau_{\|}$ grows as $\sigma^2$). Under these conditions a weak external field $\xi \ll \sigma$, $\omega\tau_{\|} \ll 1$ cannot provide any noticeable probability of flopping between the states $\mu = \pm\mu_n$, and at $\sigma \to \infty$ the effective-field approximation predicts the longitudinal susceptibility (4.34) tending to zero as $\chi_{\|}' \propto \sigma^{-3}$, $\chi_{\|}'' \propto \sigma^{-1}$.

Let us now consider the point of our main interest—the gyromagnetic effect in a uniaxial superparamagnetic particle, i.e., evaluate its response to the transversal external field. We assume the latter to be directed along the $x$-axis retaining the $z$-axis parallel to the anisotropy field. For this case from Eqs. (4.27)–(4.30) we get the following set of
Figure 4.3: Frequency dependence of the longitudinal dynamic susceptibility of a uniaxial superparamagnetic particle at $\alpha = 0.1$; solid lines: $\text{Im} \chi_\parallel$, dashed lines: $\text{Re} \chi_\parallel$. The set of lines 1 corresponds to $\sigma = 0.1$ and the set 2 to $\sigma = 0.3$

equations for the components $a = a_x$ and $b = b_yz$ (remember that, as it has been shown in Section 3.4, tensor $b_{ik}$ is symmetrical):

$$
2\tau_D \frac{d}{dt} a = -\lambda_a a - \frac{2}{\alpha} \frac{3R' - R}{R - R'} b + \frac{R + R'}{R - R'} \xi e^{-i\omega t},
$$

$$
2\tau_D \frac{d}{dt} b = -\lambda_b b - \frac{\sigma}{\alpha} a - \frac{\sigma}{\alpha} \xi e^{-i\omega t}.
$$

Here we have introduced the notations

$$
\lambda_a = \frac{R + R'}{R - R'}, \quad \lambda_b = \frac{R - 3R' + 4R''}{R' - R''}.
$$

A uniform set corresponding to Eqs. (4.36) at $\xi = 0$ has the decaying solutions

$$
a = a_0 e^{-\lambda/2\tau_D}, \quad b = b_0 e^{-\lambda/2\tau_D},
$$

where the decrements are determined by the compatibility condition

$$
(\lambda - \lambda_a)(\lambda - \lambda_b) + \left(\frac{2\sigma}{\alpha^2}\right) \frac{(3R' - R)(R - R'')}{(R - R')} = 0.
$$

The roots of this square equation display a fairly good agreement with the curves of Fig. 4.1. At $\sigma = 0$ one has $\lambda_1 = \lambda_a(0) = 2$ and $\lambda_2 = \lambda_b(0) = 6$ which coincide with the first eigenvalues (4.17) of KERD. Now let us take into account that for all usual ferromagnets $\alpha \ll 1$. With allowance for that fact, at small $\sigma$ it is sufficient to retain this parameter in Eq. (4.38) only in a combination $\sigma/\alpha$. In this approximation the discriminant of equation (4.38) reverses its sign at the point $\sigma_* = \alpha \sqrt{5}$. For $\alpha = 0.1$ it
gives, therefore, \( \sigma_\ast \approx 0.22 \) that is close to the value \( \sigma_\ast \approx 0.24 \) obtained in Section 4.2. Finally, at \( \sigma \gg 1 \) equation (4.38) has the roots (cf. Eq. (4.21)):

\[
\lambda_{1,2} = 2\sigma(1 \pm i\alpha^{-1})
\]

(4.39)

and the dimensional decrements corresponding to the values (4.39) coincide with the eigenvalues (4.22) of the Landau-Lifshitz equation (2.14).

Let us evaluate the dynamic susceptibility \( \chi_\perp \) in the periodic external field. Setting in Eq. (4.36)

\[
(a, b) = (a_0, b_0) e^{-i\omega t}
\]

and solving the algebraic linear set for the amplitudes \( a_0 \) and \( b_0 \), we find

\[
a_0 = \frac{\Delta_a}{\Delta}, \quad \Delta = (\lambda_1 - 2i\omega \tau_D)(\lambda_2 - 2i\omega \tau_D),
\]

\[
\Delta_a = \xi(R - R')^{-1}[(R + R')(\lambda_b - 2i\omega \tau_D) + (2\sigma/\alpha^2)(3R' - R)];
\]

here in the determinant \( \Delta \) the quantities \( \lambda_1 \) and \( \lambda_2 \) denote the roots of equation (4.38).

For the transverse dynamic susceptibility of the particle with allowance for Eq. (4.31) we get

\[
\chi_\perp = \frac{\mu I}{\xi k_B T} \frac{R - R'}{2R} \frac{\Delta_a}{\Delta}.
\]

After a number of simple algebraic transformations making use of formulas (4.37) and (4.38) and those from Appendix, the last expression may be rearranged to the form

\[
\chi_\perp = \frac{I}{H_n} \frac{\omega_L}{\omega^2} \left( \omega_L F_3 - i\omega F_4 \right).
\]

(4.40)

Coefficients \( F_i \) here are functions of \( \sigma \):

\[
F_1 = \frac{1}{2\sigma} \frac{3R' - R}{R - R'} + \frac{\alpha^2}{4\sigma^2} \frac{R + R' - 3R' + 4R''}{R' - R''},
\]

(4.41)

\[
F_2 = \frac{\alpha}{4\sigma} \frac{R + R'}{R - R'} \left( \frac{R - 3R' + 4R''}{R' - R''} \right),
\]

\[
F_3 = \frac{3R' - R}{2R} + \frac{\alpha^2}{4\sigma} \frac{R + R' - 3R' + 4R''}{R' - R''},
\]

\[
F_4 = \frac{\alpha}{2} \frac{R + R'}{2R}.
\]

With the aid of the formulas, presented in Appendix, for small \( \sigma \) one finds

\[
F_1 = 3 \left( \frac{\alpha}{\sigma} \right)^2 \left( 1 + \frac{16}{105} \frac{\sigma}{\alpha} \right), \quad F_2 = 2\frac{\alpha}{\sigma} \left( 1 + \frac{1}{70} \frac{\sigma}{\alpha} \right),
\]

\[
F_3 = 2\frac{\alpha^2}{\sigma} \left( 1 + \frac{2}{105} \frac{\sigma}{\alpha} \right), \quad F_4 = \frac{2}{3} \alpha \left( 1 + \frac{1}{15} \frac{\sigma}{\alpha} \right),
\]

(4.42)

and the asymptotic values at \( \sigma \to \infty \):

\[
F_1 = F_3 = 1 + \alpha^2, \quad F_2 = F_4 = \alpha.
\]

(4.43)
In the latter case, as it must be at \( KV_m \gg k_B T \), from Eqs. (4.40) and (4.43) there follows the Landau-Lifshitz [12] result:

\[
\chi_\perp = \gamma I \frac{(1 + \alpha^2) \omega_L - i\alpha \omega}{(1 + \alpha^2) \omega_L^2 - \omega^2 - 2i\alpha \omega \omega_L},
\]

whereas at \( KV_m \ll k_B T \) substitution of Eqs. (4.42) into (4.40) yields

\[
\chi_\perp = \frac{\chi_\perp^{(0)}}{1 - i\omega \tau_D}, \quad \chi_\perp^{(0)} = \frac{\mu I}{3k_B T} \left( 1 - \frac{2K V_m}{15k_B T} \right).
\]

At \( \sigma \to 0 \) the longitudinal and transverse static susceptibilities coincide—see Eqs. (4.35) and Eq. (4.45). The same holds for the dynamic ones, since in this limit the difference between the parallel and perpendicular relaxation times vanishes. For example, at \( \sigma = 0.1 \) the frequency dependences of \( \chi_\perp \) evaluated according to formulas (4.40) and (4.41) are practically indistinguishable from those of \( \chi_{||} \) shown in Fig. 4.2. The lines \( \chi_\perp(\omega) \) presented in Fig. 4.4 are intermediate between the relaxational curves of Fig. 4.3 and the resonance ones of Fig. 4.5.

![Figure 4.4: Transverse dynamic susceptibility of a uniaxial superparamagnetic particle at the precession damping parameter \( \alpha = 0.1 \). Solid lines: \( \text{Im} \chi_\perp \), dashed lines: \( \text{Re} \chi_\perp \). The set of lines 1 corresponds to \( \sigma = 0.5 \) and the set 2 to \( \sigma = 1.0 \).](image)

For \( \sigma = 0.5 \) the frequency behavior of \( \chi_\perp \) is still not so far from the relaxational type, though at the curve \( \chi_\perp' \) there already appears a node pertinent to resonance lines. However, already at \( \sigma = 1 \) the susceptibility curves undoubtedly belongs to the resonance (Lorentzian) type of dispersion.

The “global view” on the results of treating the intrinsic FMR in a superparamagnet on the basis of the effective-field method render the plots of the conventional FMR characteristics. In Figs. 4.6 and 4.7 by solid lines there are plotted, against the parameter \( \sigma \), the resonance frequency \( \omega_r \) determined as the position of the maximum on the
Figure 4.5: Transverse dynamic susceptibility of a uniaxial superparamagnetic particle at for the precession damping parameter \( \alpha = 0.1 \). Solid lines: \( \text{Im} \chi_\perp \), dashed lines: \( \text{Re} \chi_\perp \). The sets of lines correspond to \( \sigma = 5.0 \) (1), \( \sigma = 10.0 \) (2), \( \sigma = \infty \) (3); the latter is the Landau-Lifshitz susceptibility given by Eq. (4.44).

curve \( \chi''_\perp(\omega) \) and the half-height width \( \Delta \omega \) of this line. Function \( \omega_r(\sigma) \) has a minimum at \( \sigma_0 \approx 0.73 \). This value might be regarded as a conditional boundary separating the ranges of resonance \( (\sigma > \sigma_0) \) and relaxational \( (\sigma < \sigma_0) \) dispersion of the magnetic susceptibility. This estimate imparts some quantitative meaning to the verbal description of “resonator” and “relaxator” types of the particles given in Section 4.2. When \( \sigma \) exceeds \( \sigma_0 \), there occurs the increase of the resonance frequency and the narrowing of the resonance line; at \( \sigma \to \infty \) the limiting values \( \omega_r \approx \omega_L \) and \( \Delta \omega \approx 2\alpha \omega_L \) are approached, these relations holding the more accurately the smaller is \( \alpha \).

Note that the numerical value of \( \sigma_0 \) is approximately three times larger than the critical value \( \sigma_* \) at which the first oscillatory decrement appears in the spectrum of the KERD for the magnetic moment. To understand this, one should bear in mind that in the interval \( \sigma_* < \sigma < \sigma_0 \) the eigenfrequency, though being already nonzero, is yet too small. So, because of the strong damping of the precession motion, in this interval the character of magnetic moment dispersion is hardly distinguishable from the pure relaxational one that exists at \( \sigma < \sigma_* \). However, even in the relaxational range, i.e., at \( \sigma < \sigma_0 \), at the absorption curves \( \chi''_\perp \) there is observed a maximum—“resonance”—see Fig. 4.3 for \( \chi_\perp = \chi_\parallel \). As \( \sigma \) decreases, this maximum becomes smoother and shifts towards larger frequencies. In the case \( \sigma \ll 1 \), when formula (4.45) is valid, this “resonance” frequency is equal to \( \tau_0^{-1} = \alpha \omega_L / \sigma \) that makes both \( \omega_r \) and \( \Delta \omega \) tend to infinity at \( \sigma \to 0 \).

In light of possible shortcomings of the effective-field method, it is important to make an independent check of the above-presented results. An example of such a verification for the rigid dipole model has been given in Section 3. Similar question for the considered here case of intrinsic FMR had been solved numerically in paper [53] on a slightly different basis. Apparently, it is entirely equivalent, whether to compare the computed eigenvalues with
Figure 4.6: The frequency of the intrinsic FMR determined as the position of the maximum of $\chi''(\omega)$ curves; $\alpha = 0.1$. Solid line: the two-moment effective-field approximation given by Eq. (4.40), short-dashed line: the result of the numerical calculation [53], long-dashed horizontal line: the asymptotic value at $\sigma = \infty$.

Figure 4.7: The linewidth of the intrinsic FMR determined at the half-height of the $\chi''(\omega)$ curves for the precession damping parameter $\alpha = 0.1$. Solid line: two-moment effective-field approximation Eq. (4.40), short-dashed line: the result of numerical calculation [53], long-dashed horizontal line: the asymptotic value at $\sigma = \infty$. 
their analogs yielded by the approximate procedure, or use for comparison the dynamic susceptibilities evaluated for one and the same set of parameters by the effective-field and numerical methods. Moreover, the last way looks even more logical, since the susceptibility curve, determined numerically, i.e., exactly, is the sum of contributions from all levels of the KERD-operator spectrum, whereas comparing the first decrements one is totally ignorant of the weights they have in the expansion of some particular observable quantity. In [53] a direct method of matrix algebra had been used to solve a set of sufficiently large number of moment equations (we have taken 24 functions) and get the real and imaginary parts of the transverse dynamic susceptibility $\chi_\perp(\omega)$. The results were compared with those obtained via formulas (4.40) and (4.41). In the whole range $0 < \sigma < 15$ studied the deviations of the exact solution from the effective-field one did not exceed 15%. The global characteristics of the exact susceptibility lines are shown in Figs. 4.6 and 4.7 by dashed curves. Though moderately differing quantitatively, the tested dependencies display entire qualitative agreement thus confirming fair reliability of the effective-field method for the FMR case under consideration.

Finishing the study of the intrinsic FMR, we would like to make almost obvious but nevertheless necessary remark. Note that in the main presented formulae for the dynamic susceptibility the normalization factor is chosen so that $\chi$ is defined per unit volume of the particle substance. So, such a form renders a “specific” susceptibility. To get a susceptibility of a particle, one has to multiply this quantity by the particle volume $V_m$. But proceeding to calculation of the susceptibility of a disperse system we should remember that in fact any of the obtained expressions depends parametrically upon the orientation of the particle anisotropy axis. Therefore, evaluation of $\chi$ for a particle assembly (say, ferrocolloid), besides a trivial scaling by particle numerical concentration $n$, demands the knowledge of the easy-axes distribution function and the averaging over it. This circumstance should be taken into account while solving any particular problem concerning magnetic properties of a composite media formed by anisotropic particles. In below—see Section 6—we shall address in detail the orientational averaging over the random distribution of the axes (non-homogeneous broadening) while studying FMR in a super-paramagnet in the presence of a strong external field. There it will be clear that such a kind of averaging may yield the results which are far from trivial.

However, for the intrinsic FMR the case of random spread of particle axes is, perhaps, the most simple one. Indeed, since we consider all the particles to be identical, i.e., possess equal values of the parameters $\sigma$ and $\alpha$, that means that their magnetic response characteristics are also the same. Moreover, the susceptibilities $\chi_\parallel$ and $\chi_\perp$ per se do not depend upon the angle $\vartheta$ between vectors $n$ (anisotropy axis) and $h$ (external field) otherwise than via simple angular weight factors. That enables us to write

$$
\chi(\vartheta) = \phi (\chi_\parallel \cos^2 \vartheta + \chi_\perp \sin^2 \vartheta),
$$

where $\phi = nV_m$ is the volume concentration of the magnetic substance in the composite. Averaging over the three-dimensional random distribution immediately gives

$$
\overline{\chi} = \frac{1}{3}(\chi_\parallel + 2\chi_\perp). \tag{4.46}
$$

For the case of $\sigma \ll 1$ for the static susceptibility of such an assembly from Eqs. (4.35) and (4.45) we get

$$
\chi^{(0)} = n\mu^2/3k_BT,
$$
which proves that for the susceptibility of a random assembly the expansion in $\sigma \ll 1$ begins at least with the second-order correction.
5 Magnetic resonance in the external field.
I. Isotropic superparamagnet

In this short section we shall consider another limiting case of FMR—magnetic resonance in an isotropic superparamagnet subjected to sufficiently strong external field. Obviously this case is an idealization for materials with rather low anisotropy. The goal of our study is to find out to what extent the superparamagnetic behavior of the particle magnetic moment modifies its precessional motion. In the absence of fluctuations the latter, if described by the Landau-Lifshitz equation (1.36), is very simple. At the damping parameter $\alpha \to 0$ it is the Larmor precession with the fundamental frequency $\omega_H = \gamma H$ and decrement $\alpha \omega_H$, where $H$ is the strength of the external field.

A great simplification in the problem under solution is that since, assuming magnetic isotropy, we set $K = \sigma = 0$, the resulting dynamic susceptibility would not depend upon the particle orientation and due to that no additional averaging would be required.

On our way to quantitative description, the step-by-step repetition of considerations of Section 4.1 lead us to Eq. (4.5) where now we should set

$$U = -\mu H (\mathbf{e} \cdot \mathbf{h}),$$

and thus get the corresponding KERD in the form

$$2\tau_D \frac{\partial W}{\partial t} = -\tilde{J} W \left( \tilde{J} + \frac{1}{\alpha} \frac{\partial}{\partial \mathbf{e}} \right) \left[ \xi (\mathbf{e} \cdot \mathbf{h}) - \ln W \right]. \quad (5.1)$$

In a constant field $\mathbf{H} = H \mathbf{h}$ the stationary normalized solution of Eq. (5.1) is the already familiar Langevin distribution (2.13) which for the equilibrium magnetization of the particle yields

$$M_0 = I \langle e \rangle_0 = I \int e W_0 de = IL(\xi) h,$$

where the argument $\xi = \mu H/k_B T$ is defined with respect to the static field.

In a non-equilibrium situation the observed magnetization is determined by the average of the “microscopic” variable $\mathbf{e}$ taken with the distribution function $W$ from Eq. (5.1). The corresponding moment equation follows from Eq. (4.22) at $\sigma = 0$ and reads

$$2\tau_D \frac{d}{dt} \langle \mathbf{e} \rangle = -\frac{1}{\alpha} \left( \langle \mathbf{e} \times \xi \rangle - 2\langle \mathbf{e} \rangle - \langle (\mathbf{e} \times (\mathbf{e} \times \xi)) \rangle \right), \quad (5.2)$$

As always, this equation is not closed and needs some approximation in order to obtain the analytical solution. To split the higher moments, we may apply the effective-field method in its most simple form (3.21):

$$W_e = W_0 \left[ 1 + a_i (e_i - \langle e_i \rangle_0) \right], \quad (5.3)$$

i.e., reducing the number of auxiliary variables to one vector quantity denoted by $\mathbf{v}$. Averaging of $\mathbf{e}$ with this distribution function yields

$$\langle e_i \rangle = \langle e_i \rangle_0 + \langle (e_i e_k)_0 - \langle e_i \rangle_0 (e_k)_0 \rangle a_k. \quad (5.4)$$

Note that in its general form the last representation almost exactly coincides with Eq. (4.30) from the previous section. This is natural, since in every linear effective-field
1.5 The effective-field method. The general feature of the effective-field method is that it allows one to consider the expansion of a non-equilibrium solution with respect to a small parameter which has the meaning of some field. The essential difference, however, is located in the form of the equilibrium distribution function. For example, here, unlike the case of intrinsic FMR, \( W_0 \) has no \( e \leftrightarrow -e \) symmetry, and so the odd equilibrium moments do not vanish.

In order to find the dynamic susceptibility of a particle, we should consider the non-equilibrium part of its magnetization \( m = I(\langle e \rangle - \langle e \rangle_0) \) induced by a radio-frequency field \( H_1(t) \) with the amplitude \( H_1 \ll H \), or in the dimensionless form—\( \xi_1 \ll \xi \), where \( \xi_1 = \mu H_1 / k_B T \). So we have to treat vectors \( a \) and \( \xi_1 \) as the quantities of the same (small) order of magnitude. Taking this into account, after substitution of expression (5.3) into Eq. (5.4) we get

\[
2 \tau_D \frac{d}{dt} \left( \langle e_i e_k \rangle_0 - \langle e_i \rangle_0 \langle e_k \rangle_0 \right) - a_k - a_i + \xi_1 i + \left( a_k - \xi_1 k \right) \langle e_i e_k \rangle_0 - \frac{1}{\alpha} e^{ikl} \left( a_k - \xi_1 k \right) \langle e_l \rangle_0.
\]

This tensor equation with the aid of formula (5.4) and representation of the equilibrium moments (2.16) is not so difficult to transform into the equation for the non-equilibrium magnetization [47]:

\[
\frac{d}{dt} m = -\gamma (m \times H) - \frac{1}{\tau_\parallel} H_2 (m \cdot H) - \frac{1}{\tau_\perp} H_2 (H \times (m \times H)) + I_0 H [\gamma (H_1 \times H) + \frac{1}{\tau_\parallel} H_2 (H_1 \cdot H) + \frac{1}{\tau_\perp} H_2 (H \times H_1)],
\]

where \( I_0 = I_L(\xi_1) \) and the indices assigned to the relaxation times

\[
\tau_\parallel = \frac{\tau_D}{\xi_1}, \quad \tau_\perp = \frac{2L_1 - L \tau_D}{\xi_1}.
\]

The obtained equation looks very much alike that for the magnetization in the rigid dipole model—cf. Eqs. (3.12) and (3.13). This resemblance by no means would seem occasional, if to remember the discussion about "internal" and "external" superparamagnetism given in Section 1.2. Just due to this similarity the relaxation terms in the last equation and those of the rigid dipole model have exactly the same form. The difference occurs in the way the constant and the field of the rigid dipole model affect the equilibrium moments.
and at $\xi \gg 1$

$$
\tau_\parallel = \frac{1}{2} \tau_\perp, \quad \tau_\perp = 2\tau_D/\xi = (\alpha \omega_H)^{-1},
$$

where $\omega_H = \gamma H$.

Therefore, in weak fields ($H \ll k_B T/\mu$) the magnetization relaxation time depends only on the magnetic volume and temperature of the particle: $\tau_\parallel \approx \tau_\perp \approx \tau_D \propto V_m/T$. Conversely, for the opposite case ($H \gg k_B T/\mu$), the time of decay of the free precession of the magnetic moment in a field $H$ is determined only by the strength of the latter: $\tau_\parallel \sim \tau_\perp \propto H^{-1}$. Thus one concludes that as the ratio $V_m/T$ (at constant $H$) diminishes, the same occurs to the relaxation times, and the absorption line of FMR widens.

Let us evaluate the dynamic susceptibility of an isotropic superparamagnetic particle in a linearly polarized oscillating field $H_1 \propto e^{-i\omega t}$. Setting in Eq. (5.6) $H_\perp H$ and $m_i = \chi_{ik}(\omega) H_{ik}$, for the susceptibility in the direction of the radio-frequency field we get

$$
\chi = \frac{IL}{H} \frac{\omega_H^2 (1 + \alpha_e^2) - i\alpha_e \omega H}{\omega_H^2 (1 + \alpha_e^2) - \omega^2 - 2i\alpha_e \omega H},
$$

(5.8)

where we have introduced the effective constant of the precession damping

$$
\alpha_e = \frac{\xi - L}{\xi L} \alpha.
$$

(5.9)

The two last formulae retrieve a very compact and easy to observe description of FMR in the isotropic case. Eq. (5.8) in its form completely coincides with the conventional Landau-Lifshitz susceptibility except that the damping parameter $\alpha$ is replaced by the effective value $\alpha_e$ “dressed” with the Langevin argument $\xi$ dependent factor. Insofar $\alpha_e$ accumulates and renders all the effect of superparamagnetism on the magnetic moment motion; its asymptotic forms are

$$
\alpha_e = \begin{cases} 
2\alpha/\xi & \text{for } \xi \ll 1, \\
\alpha & \text{for } \xi \gg 1.
\end{cases}
$$

(5.10)

Fig. 5.1 shows this function in the intermediate $\xi$ range and proves that $\alpha_e(\xi)$ monotonically ascends at $\xi \to 0$ and asymptotically approaches from above its finite value $\alpha$ at $\xi \to \infty$. So, if $\xi \gg 1$ (strong fields and/or massive particle), then Eq. (5.8) exactly coincides with the standard expression yielded by the Landau-Lifshitz equation. In the case $\xi \ll 1$ (weak fields and/or small particle) the susceptibility looses its resonance character. Substituting the corresponding asymptotic value of $\alpha_e$ into Eq. (5.9), one finds

$$
\chi = \frac{\mu I}{3k_B T} \frac{1}{1 - i\omega \tau_D}.
$$

(5.11)

Note that here, like in Section 4.3, the susceptibility is defined for a unit volume of the particle substance. To obtain the susceptibility of the non-interacting particle assembly one should multiply Eqs. (5.9) and (5.11) by the particle magnetic volume fraction $\phi = nV_m$. In result, the coefficient in Eq. (5.11) transforms into the already well-known quantity—initial superparamagnetic susceptibility $\chi_0 = n\mu^2/3k_B T$ of Eq. (3.9).

Therefore, with the diminution of the thermal Langevin argument $\xi = \mu H/k_B T$ the dispersion $(\chi')$ and absorption $(\chi'')$ lines of FMR of an isotropic particle deform: being
regular Lorentzians at $\xi \gg 1$ they become simple Debye relaxational ones in the intense fluctuations range $\xi \ll 1$.

In usual technique for FMR measurements the frequency of the spectrometer $\omega$ is constant, and the controlled changeable parameters being the magnetizing field strength $H$ and temperature $T$. In Fig. 5.2 there are presented the field-strength dependencies of the real $\chi'$ and imaginary $\chi''$ parts of the complex susceptibility evaluated with the aid of formula Eq. (5.8) for two reference values of the dimensionless inverse temperature $\beta = IV_m\omega/\gamma k_BT$; in this scaling $\beta = 1$ corresponds to room temperature at $I = 10^3 \, G$ and $\omega = 10^{10} \, s^{-1}$ for the particles with the magnetic core diameter $\approx 5 \, nm$. The non-Lorentzian character of the susceptibility at small $\beta$ is most distinctive if to look at the lines of $\chi'$: at $\beta < 0.65$ these curves do not have any nodes at all, see Fig. 5.2a.

Calculation of the susceptibility lines shows that the resonance field $H_{res}$, corresponding to the maximum of the imaginary part of $\chi$:

$$\chi''_{res}(H_{res}) = \max\{\chi''(H)\},$$

but weakly depends upon $\beta$. Much more sensitive to the change of this parameter are $\chi''_{res}$ itself and the absorption line width $\Delta H$ at the level $\chi''_{res}/2$. In the limit $\beta \to \infty$ (or $T/V_m \to 0$) the absorption line shape is determined by the Landau-Lifshitz equation, and thus

$$\chi''_{res} = \gamma I/2\alpha\omega_H, \quad \Delta H/H_{res} = 2\alpha.$$ 

When the particle volume decreases (the ratio $T/V_m$ grows), the absorption peak height diminishes whereas the linewidth increases.

Though one have to be cautious when applying the results of so simple a model to any experiment on real disperse ferromagnets, we would like to refer to at least one situation that looks very close to the above-considered one. In paper [55] there were studied dilute colloidal suspensions of ferromagnetic metals, the particles of which were spherical and less than $10 \, nm$ in diameter. The observed FMR lines turned out to be
Figure 5.2: Dynamic susceptibility of an isotropic superparamagnet. Solid lines: $\chi''(\xi)$, dashed lines: $\chi'(\xi)$ at $\alpha = 0.1$; the field-independent Langevin parameter $\beta = 0.5$ (Fig. a) and $\beta = 10.0$ (Fig. b)

extremely wide comparing with those for massive specimens. For example, at $H \simeq 3000$ Oe the linewidth $\Delta H$ was 1400 Oe for iron and 1000 Oe for nickel that is by an order of magnitude greater than the intrinsic anisotropy fields in these metals. Moreover, in both cases the gyromagnetic ratios evaluated upon the position of the resonance peaks of $\chi''(H)$ curves did not differ (within the experimental accuracy) from those measured on massive iron and nickel.
6 Magnetic resonance in the external field. II. Anisotropic superparamagnet

Now we shall extend the theory of the preceding section on the case of an anisotropic superparamagnet. If to recall the considerations of Sections 4.2 and 5, it becomes clear that the desired generalized description should essentially include averaging over both orientational degrees of freedom of the particles, i.e., the internal one (the magnetic moment $\mu$) and the external one (the particle axis orientation $n$). In order to be particular, here we restrict ourselves to a situation, where the distribution $f(n)$ is a given function, namely, a constant. The substance corresponding to such a condition is a solid dispersed ferromagnet with random distribution of the particle axes. Actual objects with such a structure are, for example, dispersively solidified alloys of Cu-Co type (see [25,26]), granular iron-containing films [56] and bulk specimens [57], polymerized or frozen magnetic fluids, etc.

The usual experimental situation in performing FMR measurements, is the one where the fixed frequency of excitation lies in the range $\omega/2\pi \simeq 10$ GHz. The resonance line is observed and recorded with the variation of the magnetizing field strength $H$. Since for the frequencies used, the resonance condition takes place at $H_{\text{res}} \simeq \omega/\gamma \approx 3 \cdot 10^3$ Oe, we may assume that the external field $H$ is always much greater than the anisotropy field $H_a$. This, in turn, means that for a theoretical study of FMR in an anisotropic superparamagnet an approximation $H_a/H \ll 1$ would be an appropriate and sufficiently general one. Therefore, the results of Section 5 can serve as the zero-order approximation for the perturbation expansion in parameter $H_a/H$.

The following treatment is based mostly on that given in Ref. [58]. Referring to it, we would also like to draw the reader’s attention to the fact, that the representation of vectors and tensors via their spherical components, as it is done in Ref. [58], provides much more compact way of analytical studies than that based on the Cartesian representations, which we have used previously.

Let us begin with the KERD (4.5), which introducing for the sake of convenience the operator $\hat{P} = \hat{J} + (1/\alpha) \partial/\partial e$, we rewrite it as

$$2\tau_D \frac{\partial W}{\partial t} = \hat{J} W \hat{P} \left( \frac{U}{k_B T} + \ln W \right). \quad (6.1)$$

In the case of fixed orientation of particle axes this equation is valid for any form of the magnetic energy $U$. Under steady-state conditions, when the external magnetic field is $H = \text{const}(t)$, its equilibrium solution is [cf. Eq. (4.8)]

$$W_0 = Z_0^{-1} \exp(-U_0/k_B T), \quad Z_0 = \int \exp(-U_0/k_B T) \, de, \quad (6.2)$$

where $U_0$ is time-independent. The quantity we are interested in FMR studies, is the non-equilibrium part of the macroscopic magnetic moment:

$$m = \mu \left( \langle e \rangle - \langle e \rangle_0 \right). \quad (6.3)$$

Here, as usual, the indexless brackets denote statistical averaging with the distribution function $W(t)$ from Eq. (6.1) whereas those with the subscript refer to the equilibrium
The equation of motion for the vector $\mathbf{m}$ is obtained by multiplying of Eq. (6.1) by $\mu \mathbf{e}$ from the left and the subsequent integration over the angular coordinates of $\mathbf{e}$:

$$2\tau_D \frac{\partial m_i}{\partial t} = -\mu \left[ \langle \hat{P}_k \left( \frac{U}{k_B T} + \ln W \right) \hat{J}_k e_i \rangle \right] ;$$

(6.4)

the parentheses indicate that each operator acts only onto the function standing alongside it.

We take the effective-field representation of the solution of Eq. (6.4) in the form similar to (5.3), assuming that the unknown vector coefficient $a$ is linear in the parameter $\mu h/k_B T$, where $h$ is the amplitude of the alternating field. So we have

$$W = W_0 \left[ 1 + \left( \frac{4\pi}{3} \right)^{\frac{1}{2}} a_k (Y^*_1 - \langle Y^*_1 \rangle_0) \right].$$

(6.5)

The spherical harmonics $Y_{1k}$ has appeared in Eq. (6.5) because from now on we are using the representation of vectors and tensors via their spherical components. For example, for the unit vector $\mathbf{e}$ one has

$$e_k = (4\pi/3)^{\frac{1}{2}} Y_{1k}(\theta, \varphi), \quad \langle e_k \rangle = (4\pi/3)^{\frac{1}{2}} \int Y_{1k} W d\Gamma,$$

where $k = 0, \pm 1$ and $d\Gamma = \sin \theta d\theta d\varphi$ is the spherical angle element.

Substituting Eq. (6.5) into (6.3) we get the analogue of the linear relation (5.4) which now reads

$$m_k = \mu N_{kq} a_q, \quad N_{kq} = (4\pi/3)^{\frac{1}{2}} \left[ \langle Y_{1k} Y^*_1 \rangle_0 - \langle Y_{1k} \rangle_0 \langle Y^*_1 \rangle_0 \right].$$

(6.6)

Taking the average of the right-hand side of Eq. (6.3) with the distribution function (6.5), linearizing the result with respect to the small parameter $\mu h/k_B T$, and after that eliminating $a_i$ with the aid of Eq. (6.6), we arrive at the equation

$$2\tau_D \frac{\partial}{\partial t} m_k + \Lambda_{kq} m_q = \frac{\mu^2}{k_B T} R_{kq} h_q,$$

(6.7)

where the matrix coefficients

$$\Lambda_{kq} = R_{kp} N_{pq}, \quad R_{kq} = (4\pi/3) \left( \langle \hat{J}_s Y_{1k} \rangle \langle \hat{P}_s Y^*_1 \rangle \right)_0,$$

(6.8)

comprise only the averages taken with the equilibrium distribution.

### 6.1 Free oscillations of the magnetic moment

As the first step we shall use Eq. (6.7) to determine the resonant frequency and the decay rate of the precession of an individual particle. So we set $h = 0$ and evaluate the eigenvalues of the matrix $\Lambda_{kq}$ from (6.8). We direct the coordinate axis $Oz$ along the direction of the magnetizing field $\mathbf{H}$ and introduce the notation $x = \cos \theta$ for the polar coordinate of the vector $\mathbf{e}$.

The matrix elements are easily found if to use the identities

$$\langle \hat{J}_k \hat{u} \rangle \langle \hat{J}_k \hat{v} \rangle = \frac{\partial u}{\partial \theta} \frac{\partial v}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial u}{\partial \varphi} \frac{\partial v}{\partial \varphi}, \quad \langle \hat{J}_k \hat{u} \rangle \langle \nabla_k \hat{v} \rangle = \frac{1}{\sin \theta} \left[ \frac{\partial u}{\partial \theta} \frac{\partial v}{\partial \varphi} - \frac{\partial u}{\partial \varphi} \frac{\partial v}{\partial \theta} \right],$$

where $\hat{J}_k$ and $\hat{P}_k$ are the angular momentum and angular momentum operators, respectively.
where \( u \) and \( v \) are arbitrary angular functions. For the diagonal components of matrices \( N_{kp} \) and \( R_{kp} \) from Eqs. (6.7) and (6.9) we find

\[
N_0 \equiv N_{00} = \langle x^2 \rangle_0 = \langle x \rangle_0^2, \quad N_{\pm} \equiv N_{\pm1,\pm1} = \frac{1}{2} (1 - \langle x^2 \rangle_0),
\]

\[
R_0 \equiv R_{00} = 1 - \langle x^2 \rangle_0, \quad R_{\pm} \equiv R_{\pm\pm} = \frac{1}{2} [1 + \langle x^2 \rangle_0 \mp (2i/\alpha) \langle x \rangle_0].
\]

The results of the zero in \( H_a/H \) approximation, i.e., those of Section 5, are recovered if we set \( U_0 = -\mu (e \cdot H) \). In this case due to the axial symmetry of the equilibrium distribution function \( W_0 \) the matrices \( N_{kp} \) and \( R_{kp} \) are diagonal and their non-zero elements

\[
N_0 = \frac{dL}{d\xi}, \quad N_{\pm} = \frac{L}{\xi}, \quad R_0 = \frac{2L}{\xi}, \quad R_{\pm} = 1 - \frac{L}{\xi} \mp \frac{iL}{\alpha},
\]

are simple combinations of the Langevin function \( L \) and its argument \( \xi = \mu H/k_B T \). Using these formulae, for the eigenvalues \( \lambda_k \) introduced by representation \( \Lambda_{kj} = \lambda_k \delta_{kj} \), from Eqs. (6.8)–(6.10) one finds

\[
\lambda_0 = 2 \frac{d \ln \xi}{d \ln L}, \quad \lambda_{\pm} = \frac{\xi}{L} - 1 \mp \frac{i\xi}{\alpha}.
\]

Substitution of (6.11) into Eq. (6.7) for \( h = 0 \) yields the frequency of the free precession and the relaxation time of the perpendicular to the magnetizing field component of the magnetic moment:

\[
\omega_H = |\text{Im}\lambda_{\pm}|/2\tau_D = \xi/2\alpha \tau_D = \gamma H, \quad \tau_{\perp} = 2\tau_D/\text{Re}\lambda_{\pm} = 2\tau_D L(\xi - L)^{-1} = (\alpha_\epsilon \gamma H)^{-1},
\]

which are exactly the results presented by formulas (5.7)–(5.9) of Section 5.

Now we are ready to add the contribution of the particle anisotropy to the equilibrium energy setting \( U_0 = -\mu (e \cdot H) + U_a \). From the very beginning it is convenient to employ for \( U_a \) the representation via the spherical functions, proposed in [59]:

\[
U_a = -V_m \sum_{j \text{ even}}^{\infty} K_j \Phi_j (e), \quad \Phi_j = \sum_{m=-j}^{j} b_m Y_{jm} (\vartheta', \varphi'),
\]

where \( K_j \) are the anisotropy constants, \( b_m \) are numerical coefficients, and \( \vartheta' \) and \( \varphi' \) are the angular coordinates of the magnetic moment vector relative to the system attached to the particle anisotropy axes.

Under the assumption of weak anisotropy \( (H_a/H \sim U_a/\mu H) \), the first order corrections to the eigenvalues of Eq. (6.7) can be found if we use for the equilibrium distribution function the expression

\[
W_e = W_0 \left\{ 1 + \frac{V_m}{k_B T} \sum_j K_j [\Phi_j (e) - \langle \Phi_j (e) \rangle_0] \right\},
\]

where \( W_0 \) is the Langevin distribution function (6.2) with \( U_0 = -\mu (e \cdot H) \). Allowance for contributions linear in \( K_j \) does not alter the diagonality of the matrix \( \Lambda_{kp} \). Hence,
the calculation of the decrements $\lambda_k$ reduces to evaluation of the equilibrium moments $\langle x \rangle_e$ and $\langle x^2 \rangle_e$ with the distribution function (6.14) and substituting them into Eq. (6.9) instead of $\langle x \rangle_0$ and $\langle x^2 \rangle_0$, respectively.

However this step may not be done immediately, since beforehand one has to transform the angular coefficients $\Phi_j(e)$ of the expansion (6.13) to the reference coordinate framework, in which the polar axis is aligned with the direction of the magnetizing field $H$. Since we shall need only tensor contractions of $\Phi_j$ with functions which do not depend upon the azimuthal coordinates, for our requirements the integral relations given in [59] would suffice:

\[
\langle P_j(x) \Phi_j'(e) \rangle_0 = \langle P_j(x) P_j'(x) \rangle_0 \Phi_j'(\Gamma),
\]

(6.15)

where $P_j(x)$ is the Legendre function of the argument $x = \cos \vartheta$, and $\Phi_j'(\Gamma)$ stands for the angular representation of $\Phi$ in the coordinate system aligned with $H$.

Calculations with the distribution function (6.14) yield the following expressions for the eigenvalues of the matrix $\Lambda_{kp}$:

\[
\lambda_k = \lambda_k^{(0)} + \Delta \lambda_k = \lambda_k^{(0)} + (\Delta R_k - \lambda_k^{(0)} \Delta N_k)/N_k^{(0)},
\]

(6.16)

where $\lambda_k^{(0)}$ and $N_k^{(0)}$ should be taken from Eqs. (6.10) and (6.11). Evaluating the corrections entering Eq. (6.16), one finds

\[
\Delta R_0 = -(V_m/k_B T) \sum_j K_j \Phi_j(\Gamma) \langle x^2 P_j \rangle_0,
\]

(6.17a)

\[
\Delta R_\pm = -(V_m/2k_B T) \sum_j K_j \Phi_j(\Gamma) \langle \{x^2 \mp 2(i/\alpha)x\} P_j \rangle_0,
\]

(6.17b)

\[
\Delta N_0 = (V_m/k_B T) \sum_j K_j \Phi_j(\Gamma) \langle (x^2 - 2\langle x \rangle_0) P_j \rangle_0,
\]

\[
\Delta N_\pm = \Delta R_0.
\]

Substitution of Eqs. (6.17) into (6.16) gives

\[
R_+ = \left(1 - \frac{L}{\xi} - \frac{iL}{\alpha} \right) + \frac{V_m}{k_B T} \sum_j K_j \Phi_j \left\{ \frac{j(j+1)}{2\xi^2} - \frac{1}{\xi} \frac{dL_j}{d\xi} - \frac{i}{\alpha} \frac{dL_j}{d\xi} \right\}.
\]

(6.18)

This expression leads to the final representation of the eigenvalues corresponding to the precessional normal modes:

\[
\lambda_\pm = \left\{ \frac{\xi}{L} - 1 + \frac{V_m}{k_B T} \sum_j \frac{1}{L^2} \left[ \frac{j(j+1)}{2} L_j - \xi \frac{dL_j}{d\xi} \right] K_j \Phi_j \right\} \mp
\]

\[
\mp i \left\{ \frac{\xi}{\alpha} + \frac{V_m}{\alpha k_B T} \sum_j \frac{j(j+1)}{2} \frac{L_j}{L} K_j \Phi_j \right\},
\]

(6.19)

where we have introduced the family of the Langevin functions by relation $L_j = \langle P_j(x) \rangle_0$, so that $L_1 = L$; note that the function $L_2$, that we have used in Section 3.4 also complies with the given definition.

One can find the free precession parameters of an anisotropic superparamagnet substituting Eq. (6.19) into the definitions (6.12). We shall do this for the two most popular kinds of magnetic anisotropy, namely, uniaxial ($j = 2$, $K_2 \equiv K_u$) and cubic
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(j = 4, K_4 \equiv K_c). In these cases each of the sums, entering the expressions (6.18), (6.19) has only one non-zero term:

\[ K_j \Phi_j = \begin{cases} 
\frac{2}{3} K_u P_2(\cos \vartheta) \delta_{2j}, \\
\frac{2\pi}{15} K_c \left[ Y_{40}(\vartheta, \varphi) + \left( \frac{5}{11} \right)^2 (Y_{44}(\vartheta, \varphi) + Y_{4-4}(\vartheta, \varphi)) \right] \delta_{4j}.
\end{cases} \]

(6.20)

Here the angle \( \Gamma = \{ \vartheta, \varphi \} \) determines the direction of the anisotropy axis of the particle in the coordinate system with the polar axis along the external field \( \mathbf{H} \). With the aid of Eq. (6.20), formulas (6.19) for the eigenfrequencies of the magnetic moment precession take the form

\[ \omega_0^{(u)} = \gamma \left[ H + \frac{2K_u}{I} \frac{L_2}{L} P_2(\cos \vartheta) \right], \]

\[ \omega_0^{(c)} = \gamma \left[ H + \frac{2K_c}{I} \frac{L_4}{L} \left( 1 - \frac{5}{4} \sin^2 2\vartheta - \frac{5}{4} \sin^2 \vartheta \sin^2 2\varphi \right) \right]. \]

(6.21)

We want to point out to an expected, but nevertheless remarkable, prediction of formulas (6.21). According to them, in fine ferromagnetic particles thermal fluctuations (the Néel superparamagnetism) induce “dressing” of the anisotropy constant of the type \( \tilde{K}_j = K_j (L_j / L) \). Due to that effect, at \( \xi < 1 \) (high-temperature range) the observed anisotropy contribution to the FMR lines “melts” according to the law \( \tilde{K}_j \propto \xi^{-1} \).

6.2 FMR in an assembly of randomly oriented superparamagnetic particles

To find the response of the particle magnetic moment to a weak oscillating field \( \mathbf{h} \), it is necessary to return to equation (6.7) and use its full (with the non-zero right-hand side) form. As it is well-known, the fundamental characteristics of FMR is the dynamic susceptibility \( \chi_+ \) determined with respect to the circularly polarized field

\[ \mathbf{h} = \left( h_0 / \sqrt{2} \right) (\cos \omega t, \sin \omega t, 0), \]

whose direction of rotation coincides with that of the magnetic moment precession. The imaginary-exponent form of representation of \( \mathbf{h} \) is very simple:

\[ \mathbf{h} = (h, 0, 0), \quad h = h_0 \exp(i\omega t). \]

(6.22)

After substituting expressions (6.22) into Eqs. (6.7) and (6.8), one gets the dynamic susceptibility of the particle:

\[ \chi_+(\omega) = \left( \mu^2 / k_B T \right) R_+ (2i\omega \tau_D + \lambda_+)^{-1}, \]

(6.23)

where \( R_+ \) and \( \lambda_+ \) are defined by formulae (6.18) and (6.19). Considering the above-presented relations, one should not forget that the function \( \chi_+(\omega) \) depends upon the angular coordinates of the particle anisotropy axis as on the parameters.

In a solid dispersed ferromagnet the orientation distribution of the particle axes—the orientational texture of the specimen—is fixed. The type of such a texture usually is determined by conditions under which the substance had been prepared. As an example,
we can point out to magnetic fluids polymerized without or in the presence of external magnetic field [41,60]. There the orientational texture is the function of the direction and strength of the field imposed on a specimen during solidification, see [61]. We shall describe the orientational texture of a fine-particle assembly by a distribution function \( f(\Gamma) \) normalized by the condition

\[
\int f(\Gamma) \, d\Gamma = n,
\]

where \( n \) is the number of the particles per unit volume of the substance. To obtain a susceptibility of such an assembly, one has to take the average

\[
\chi_+ = \int \chi_+(\Gamma) \, d\Gamma
\]

(6.24)
of the quantity (6.23) over the orientational texture. For an ideally ordered system, where \( f(\Gamma) = n\delta(\Gamma - \Gamma_0) \), the averaging reduces to multiplying by \( n \), so that \( \chi_+ = n\chi_+ \). In all other cases one needs to perform integration (6.24).

Our objective here is to calculate the susceptibility of an assembly of randomly oriented particles, the situation often encountered in experiment. Let us begin with simple qualitative considerations. Note, that in a system of randomly oriented particles the spread of resonant frequencies caused by the orientational spread of the anisotropy field directions is maximum. The corresponding contribution to the FMR linewidth is about \( \Delta\omega \sim \gamma H_a \sim \gamma K/I \) and is often much larger than the intrinsic linewidth \( \Delta\omega \sim \alpha \gamma H \) of the ferromagnetic material. This orientational “inhomogeneous” broadening strongly affects the observable magnetic spectra of polycrystalline ferrites. A theory of inhomogeneous FMR line broadening (independent grain model), not taking into account superparamagnetic effects, was developed in Ref. [45]. Since formula 6.23) has been obtained as a result of the solution of the kinetic equation, it means that now we are able to extend the theory of Ref. [45] to the case of fine-particle assembly and find out the temperature-induced FMR line transformation. For all we know from the preceding sections of this Chapter, with the temperature growth the inhomogeneous broadening should be replaced by the homogeneous superparamagnetic one.

Fortunately, it is not so difficult to calculate the integral (6.24) with the function (6.23). Moreover, for the case of uniaxial anisotropy, it can be done analytically. Substitution of Eqs. (6.18), (6.22) and (6.23) into Eq. (6.24), after cumbersome but elementary calculations yields

\[
\chi_+ = \frac{n\mu^2}{k_B T} \left\{ \frac{B}{D} + \frac{[2A - B - B \arctan \left[ \frac{3D}{(2C - D)} \right]^{1/2}]}{[3D/(2C - D)]^{1/2}} \right\},
\]

(6.25)

where the arctan function and square roots should be dealt with as the analytical continuations of the corresponding real quantities, since the coefficients

\[
A = 1 - \left( \frac{1}{\xi} + \frac{i}{\alpha} \right) L, \quad B = \frac{2KuV}{3k_BT} \left[ \frac{3}{\xi^2} - \left( \frac{1}{\xi} + \frac{i}{\alpha} \right) \frac{dL_2}{d\xi} \right],
\]

(6.26)

\[
C = 2i\omega\tau_D + \left( \frac{\xi}{L} - 1 \right) - \frac{i}{\alpha} \xi, \quad D = \frac{2KuV}{3k_BT} \frac{1}{L^2} \left( 3 - \xi \frac{d}{d\xi} - 3\frac{i}{\alpha} L \right) L_2.
\]

occur to be complex.
Let us look at the limiting cases of formula (6.26). To be specific, we shall take the imaginary part of the susceptibility (absorption line) $\chi''$ as the function which we shall look after. For $K_u \to 0$ (isotropic particles) we return immediately to the result of Section 5:

$$\chi'' = \frac{n\mu^2}{k_BT} \frac{Re A \cdot Im C - Im A \cdot Re C}{|C|^2} = \gamma n\mu L(\xi) \frac{\alpha\omega}{(\omega - \omega_H)^2 + \alpha^2\omega_H^2},$$

cf. Eq. (5.8).

Another limiting case deals with the magnetic particles with vanishingly small damping constant (intrinsic FMR linewidth): $\alpha \to 0$. In this situation only those particles, for which the resonance condition Eq. (6.21) holds, contribute to the observed susceptibility. Particles with the anisotropy axes perpendicular to the magnetizing field ($\vartheta = \pi/2$) have the lowest resonant frequency

$$\omega_r = \omega_H(1 - \varepsilon L_2/L),$$

where $\varepsilon = K_u/IH \sim H_a/H$ is the dimensionless parameter which we assume to be less than unity—see the beginning of the section. The presented formula for the “transverse” $\omega_r$ marks the left-hand edge of the absorption line as plotted vs. frequency. Its right-hand edge is formed by the particles with $\vartheta = 0$ which have $\omega_r = \omega_H(1 + 2\varepsilon L_2/L)$. Thus the inhomogeneous broadening of the absorption line in a uniaxial randomly oriented superparamagnet is

$$\Delta \omega = 3\varepsilon \omega_H L_2/L.$$ (6.27)

For $\chi''$ inside the frequency interval (6.27) the limiting transition in formula (6.25) yields

$$\chi'' = \frac{\pi n\mu L}{2H} \frac{1 + (1 - L^2/L_2)(1 - \omega/\omega_H)}{[3|\varepsilon|(L_2/L)(\omega/\omega_H + \varepsilon L_2/L - 1)]^{1/2}}.$$ (6.28)

In particular, it follows from Eq. (6.28) that the absorption lines for particle assemblies with positive and negative anisotropies ($\varepsilon > 0$ and $\varepsilon < 0$) transform into each other if reflected with respect to the axis $\omega = \omega_H$. At low temperatures ($\xi \to 0$) from Eq. (6.28) there follows the expression

$$\chi'' = \frac{\pi n\mu L}{2H} \frac{1}{[3|\varepsilon|(|\omega/\omega_H + \varepsilon - 1|)]^{1/2}},$$

defined inside the frequency interval $1 - \varepsilon < \omega/\omega_H < 1 + 2\varepsilon$. The last equation which is the result of a double limiting transition ($\alpha \to 0$, $\xi \to 0$) yields the results by Morrison and Karayianis [45] for an assembly of randomly oriented uniaxial particles.

Figures 6.1 and 6.2 present the results of numerical evaluation of $\chi''$ for finite values of $\alpha$, $\varepsilon$, and $\xi$ for the systems of particles with uniaxial as well as cubic anisotropy. It is worth to remind here that we consider the situation, typical to the majority of FMR experiments, where the frequency $\omega$ and amplitude $h$ of the alternating field are fixed, whereas the varied quantities are the dimensionless strength of the magnetizing field $\gamma H/\omega$ and the parameter $\xi_0 = IVm\omega/\gamma k_BT$, which, in the same way as $\xi$ depends upon the temperature and particle volume, but unlike the latter is independent of $H$. In all here presented calculations it has been set $\alpha = 10^{-2}$. The dimensionless anisotropy parameter
Figure 6.1: Absorption lines $\chi''_+$ (left column) and their derivatives (right column) for an assembly of superparamagnetic particles with positive uniaxial anisotropy ($\varepsilon = 0.1$) for the values of the Langevin parameter: $\xi_0 = 1$ (a), 2 (b), 5 (c), and 50 (d); the precession damping parameter $\alpha = 10^{-2}$
Figure 6.2: Absorption lines $\chi''_+ (\text{left column})$ and their derivatives (right column) for an assembly of superparamagnetic particles with positive cubic anisotropy ($\varepsilon = 0.1$) for the values of the Langevin parameter: $\xi_0 = 1$ (a), 2 (b), 10 (c), and 50 (d); the precession damping parameter $\alpha = 10^{-2}$.
has been defined according to relation $\varepsilon = K\gamma/I\omega$, which also makes it field-independent; the constant $K$ was set equal either to $K_u$ for the uniaxial case, or—to $K_c$ for the cubic one.

Let us evaluate the characteristic ranges of $\xi_0$ and $\varepsilon$, setting $I \simeq 500$ G and $K \sim 10^8$ erg/cm$^3$ (magnetite), and $\omega = 2\pi \cdot 10^{10}$ rad/sec, i.e. the spectrometer wavelength is 3 cm. Using these values and $\gamma = 2 \cdot 10^7$ erg/Oe, we find that $\xi_0$ varies from $\sim 1$ (particles of diameter $\sim 5$ nm, temperature $\sim 400$ K) to $\sim 100$ (particles of diameter $\sim 15$ nm, temperature $\sim 100$ K). The corresponding estimation of the size-independent anisotropy parameter yields $|\varepsilon| \simeq 0.1$. These numbers enable one to correlate the FMR spectra given in Figs. 6.1 and 6.2 to real dispersed ferromagnets.

For convenience and clarity we present here not only the families of the absorption lines $\chi''_+$, but also their derivatives $d\chi''_+/dH$. The latter are in fact the actual signal recorded by a spectrometer, and are mostly plausible to determine the FMR linewidth $\Delta H$. This quantity (also called a “peak-to-peak width”) is defined as the distance along the field-strength axis between the two extrema (maximum and minimum) of the function $d\chi''_+/dH$, located on opposite sides of the point $d\chi''_+/dH = 0$, which are farthest from it. Remark that, if determined according by this definition, the width of the classical symmetrical Lorentzian line (5.8) is $\Delta H = 2\omega /\sqrt{3}\gamma$.

Figures 6.1 and 6.2 display the transformation of the FMR spectra with the decrease of temperature. At high temperatures the homogeneous superparamagnetic broadening of the line is so intense that there is almost no trace of the anisotropic nature of the particles observed—see panels a in Figs. 6.1 and 6.2. In this situation the line is symmetrical, smooth, and its maximum lies at $\gamma H/\omega = 1$, as it should be for FMR in an isotropic system. As the temperature falls down, the effect of thermal fluctuations reduces, and the inhomogeneous broadening becomes to show up. Eventually—see panels d in Figs. 6.1 and 6.2—the line acquires the classical polycrystalline shape [45] with distinctive steep edges and width $\Delta H = 3|\varepsilon|\omega/\gamma$. From consideration of the $d\chi''_+/dH$ curves we deduce that the cited evolution of the absorption lines yields a non-monotonic temperature dependence of the linewidth. For low ($\xi_0 \gg 1$) temperatures $\Delta H$ is large due to the spread of the anisotropy axes directions of the particles. With the temperature growth the superparamagnetic tendency to impart isotropy to the magnet causes $\Delta H$ to decrease, but in the intense fluctuational range ($\xi_0 \ll 1$) this tendency, having become dominating, leads to an infinite broadening. This considerations are illustrated by Figs. 6.3a,b obtained by numerical calculations with formulas (6.25)–(6.26). For comparison, in the same figures the asymptotic dependencies

$$\gamma \Delta_s H = 2\alpha_e /\sqrt{3}$$

for superparamagnetic broadening ($K \to 0$) and

$$\gamma \Delta_u H = 3|\varepsilon|L_2/L$$

and

$$\gamma \Delta_c H = 10|\varepsilon|L_4/3L,$$

are shown.

Let us, after [58], estimate the position of the minimum in the curves of Figs. 6.3. For the case of uniaxial anisotropy one should take the explicit form of different contributions to the linewidth, namely,

$$\Delta_s H = \frac{2}{\sqrt{3}} \frac{\alpha \omega \xi_0 - L}{\gamma \xi_0 L}, \quad \Delta_u H = 3 \frac{|\varepsilon| \omega L_2}{\gamma L},$$

for superparamagnetic broadening ($K \to 0$) and

$$\gamma \Delta_u H = 3|\varepsilon|L_2/L$$

and

$$\gamma \Delta_c H = 10|\varepsilon|L_4/3L,$$
Yu. L. Raikher and M. I. Shliomis. The effective-field method.

Figure 6.3: FMR linewidth for an assembly of randomly oriented superparamagnetic particles (determined as the peak-to-peak distance in the external field scale) as a function of the parameter $\xi_0 \propto 1/T$ for the cases of uniaxial (a) and cubic (b) anisotropy for $|\varepsilon| = 0.1$ and $\alpha = 0.1$. Solid curves: numerical calculation, dashed ones: asymptotic linewidth dependencies $\Delta_s H$ (1) and $\Delta_u H$ (2 in Fig. a), $\Delta_c H$ (2 in Fig. b)

and rearrange them for $\xi_0 < 1$. An expansion yields

$$\Delta_s H = \frac{4}{\sqrt{3}} \cdot \frac{\omega}{\gamma} \frac{\alpha}{\xi_0}, \quad \Delta_u H = \frac{3}{5} \frac{|\varepsilon|\omega}{\gamma} \xi_0.$$

Setting $\Delta_s H = \Delta_u H$, one obtains for the parameters of the point of minimum:

$$\xi_0^{(\text{min})} = 2 \left( \frac{5\alpha/3^{3/2}}{\omega |\varepsilon|} \right)^{1/2}, \quad (\gamma/\omega)H^{(\text{min})} = 4 \left( \frac{3^{3/2}\alpha |\varepsilon|/5}{\omega} \right)^{1/2}.$$

Transforming this into a dimensional estimate, one gets for the temperature corresponding to the minimal linewidth $T^{(\text{min})} \approx (V_m/k_B)(K I \omega/\alpha\gamma)^{1/2}$. Thus we see that the boundary point $T^{(\text{min})}$ which separates the ranges of “fluctuational” and “dynamic” behavior of the particle magnetic moment grows proportional to the particle volume. Substituting of the above-mentioned values of the magnetic and size parameters gives for magnetite $T^{(\text{min})} \approx 5 \text{ K}$ (grains with diameter $\sim 5 \text{ nm}$) and $T^{(\text{min})} \approx 150 \text{ K}$ (grains with diameter $\sim 15 \text{ nm}$).

Transformations of the FMR lines affect as well the position of the maximum (peak) on the $\chi''(H)$ curve that is conventionally ascribed to the resonance field-strength $H_{\text{res}}$. The function $H_{\text{res}}(\xi_0)$ is shown in Fig. 6.4. From there it follows that, depending upon the actual type of the magnetic anisotropy of the grains, change of temperature might have either increasing or decreasing effect on the resonance field of a disperse ferromagnet.

In conclusion we remark that the scope of magnetic fluid and disperse ferromagnet problems, where the developed approach might be useful, is by no means limited by the ones, detailed consideration of which we have presented in this Chapter. As an example of forthcoming interesting result we would like to point out to the study of FMR in a magnetic fluid [62]. In this situation both orientational distribution functions—that of
the magnetic moment and that of the anisotropy axes—are affected by the changes in temperature and magnetic field strength.

Figure 6.4: Resonance field determined as the position of the peak of $\chi''(H)$ as a function of the parameter $\xi_0 \propto 1/T$ for uniaxial (curves 1) and cubic (curves 2) anisotropies; $\varepsilon = 0.1$ (solid lines), $\varepsilon = -0.1$ (dashed lines)
7 Suspensions of particles with finite anisotropy. Dynamics of field-induced birefringence

This section gives a glimpse on the manifestations of a finite internal magnetic anisotropy of ferroparticles, i.e., “internal” superparamagnetism, on their orientational behavior in suspensions under the influence of the low-frequency alternating field. To some extent, the model which we consider here opposes the “rigid dipole” one which we have studied in Chapter 1.

(It is not so difficult to find out that the set of limiting cases opposing the “rigid dipole” approach comprises at least two different models. Besides the “soft dipole” approximation, as we may call the one developed in below, corresponding to the case $\sigma < 1$, there should be a model describing the situation for large but nevertheless finite $\sigma$. As a matter of fact, just such a theory had been developed and verified in [63, 64]. However, this last model is essentially non-linear (it takes into account the hysteresis transitions of the magnetic moment occurring in the ferroparticles with high internal potential barriers), and due to that does not allow the effective-field approximation. Because of that here we restrict our dealing with it to a mere reference.)

Let us following the paper [65], consider a suspension of weakly anisotropic particles ($\sigma < 1$) and remind the estimates of the relaxation times of the “internal” ($\tau_B$) and “external” ($\tau_D$) superparamagnetism. According to formulas (1.8) and (1.21), their ratio is $\tau_D/\tau_B \approx I/6\alpha\gamma\eta$, where $\eta$ is the viscosity of the liquid matrix. For classical magnetic fluids of the magnetite-in-kerosene kind ($I \simeq 500$ G, $V_m \simeq 5 \cdot 10^{-19}$ cm$^3$, $\eta \simeq 2 \cdot 10^{-2}$ Ps), we have $\tau_D/\tau_B \leq 10^{-2}$. In an alternating field the “internal” superparamagnetism dominates in the frequency range $0 < \omega < 1/\tau_D$. Since, as it has been explained in Section 1, the values of $\tau_D$ lie somewhere between $10^{-9}$ and $10^{-7}$ s, the so defined “low-frequency” range is sufficiently wide.

Under condition $\omega \tau_D \ll 1$ the internal distribution function of the particle magnetic moment may be taken in its equilibrium form

$$W(e) \propto \exp \left[ \mu(e \cdot H(t))/k_B T \right]. \quad (7.1)$$

Now we use this function to average the orientational magnetic energy (4.6)

$$U = -\mu H(e \cdot h) - KV_m(e \cdot n)^2, \quad (7.2)$$

of a uniaxial single-domain particle over the fast internal variables, i.e., the angular coordinates of the magnetic moment. The so obtained from Eqs. (7.1)–(7.2) partially-equilibrium energy function is

$$\bar{U} = -KV_m L_2(t)(n \cdot h), \quad L_2(t) = 1 - 3L(\xi)/\xi, \quad \xi = \mu H(t)/k_B T; \quad (7.3)$$

here $n$ and $h$ are the unit vectors of the particle anisotropy axis and the external field $H(t) = H(t) h$, respectively; the Langevin function parametrically, through its argument, depends upon time.

Note that formula (7.3) does not include the magnetic moment vector $e$. The latter, being the fast variable, has been adiabatically eliminated with the aid of averaging. In its present form function $\bar{U}$ explicitly refers to the orientational influence of an alternating
external field onto the orientation of the particle easy magnetization axes. The orientational distribution \( P(n, t) \) of the latter in the system under consideration is described by the KERD \[63\]

\[
2\tau_B \frac{\partial P}{\partial t} = \hat{J} P \hat{J} \left( \frac{U}{k_B T} + \ln P \right), \tag{7.4}
\]

where the infinitesimal rotation operator \( \hat{J} = (n \times \partial/\partial n) \) is defined with respect to the angular coordinates of the particle axis \( n \). (It is not really necessary to go into details of the derivation of Eq. (7.4), since they are very much alike those for the KERD’s already considered in the preceding Chapters.)

To “materialize” the results of our present study we shall assume, as in Section 3.4, that we have a suspensions of slightly non-spherical particles, and in each of them the easy magnetization axis coincides with the major geometrical one. The effective-field approximation, pertinent to the this case, where the only observable variable is the second-rank tensor \( n_i n_k \), is

\[
P_e = \frac{1}{4\pi} \left[ 1 + b_{ik} \left( n_i n_k - \frac{1}{3} \delta_{ik} \right) \right]; \tag{7.5}
\]
here, as usual, the tensor \( b_{ik} \) is independent of \( n \). Note that in Eq. (7.5) from the very beginning we have taken the equilibrium distribution function to be isotropic: \( P_0(n) = 1/4\pi \); due to which the customarily \( \langle n_i n_k \rangle_0 \) term in the parentheses has reduced to the Kronecker’s delta. The justification of this is apparent. If \( \sigma \) were exactly zero (ideal magnetically isotropic particles), there would have been no coupling between the magnetic moments and the particle axes, so the distribution of the latter would have been isotropic, whatever is the external magnetic field imposed on the system. Since we work under assumption that the parameter \( \sigma = KV_m/k_B T < 1 \) and suppose that the presence of the anisotropy but slightly changes the behavior of the suspension, then the distribution \( P(n) = \text{const} \) is the only reasonable choice of the basic state.

Using representation (7.5) with \( b_{ik} \sim \sigma \) for linearization of Eq. (7.4), and fulfilling the procedure of derivation of the macroscopic equation of motion very close to that described in Sections 2.2 and 5, we arrive at the equation

\[
\frac{1}{3} \tau_B \frac{\partial S_{ik}}{\partial t} = -S_{ik} + \frac{1}{5} \sigma L_2(t) \left( h_i h_k - \frac{1}{3} \delta_{ik} \right), \tag{7.6}
\]

for the orientation tensor of a suspension, which has been introduced and discussed in Section 3.5. Adopting the same coordinate system (\( z \)-axis parallel to the direction of the linearly polarized external field), we recover formula (3.39) for the difference of the refraction indices of the suspension:

\[
\Delta n = n_{||} - n_{\perp} = \frac{3}{4} \kappa \phi n_0 S_{zz}; \tag{7.7}
\]

for the explanation of the parameters—see Section 3.4.

In a periodic field \( H(t) = H_0 \cos \omega t \) the solution of equation (7.6) is easy, if one sets \( \xi_0 = \mu H_0/k_B T < 1 \). Substitution of the result into Eq. (7.7), yields the expression

\[
\Delta n = \frac{1}{3} \kappa \phi n_0 \left( \frac{\sigma \xi_0}{10} \right)^2 \left[ 1 + \frac{\cos(2\omega t - \psi)}{1 + \frac{4}{9} \omega^2 \tau_B^2} \right], \tag{7.8}
\]
that describes the birefringence modulation of the magnetic fluid; here the phase lag angle is $\psi = \arctan \frac{2}{3} \omega \tau_B$.

If the conventional method of birefringence measurement is used, then the intensity $Q$ of the transmitted light is given by the well-known formula (3.36). For the set-up angle $\beta = \pi/4$, as in Section 3.4, one has

$$Q = Q_0 \sin^2(\delta/2), \quad (7.9)$$

with the optical phase lag $\delta$ defined by Eqs. (3.35) or (3.40). Substituting Eq. (7.8) into (7.9), after the standard transformations [39] for the intensity of the transmitted light we get the Fourier series

$$\frac{Q(t)}{Q_0} = \frac{1}{2} \left[ 1 - J_0(b) \cos a - 2 \sum_{m=1}^{\infty} (-1)^m J_m(b) \cos mx \cos \left( \frac{\pi m}{2} - a \right) \right], \quad (7.10)$$

where

$$a = \pi l \kappa \phi_0 (\sigma \xi_0)^2 / 150 \lambda, \quad b = a / \sqrt{1 + \frac{4}{5} \omega^2 \tau_B^2}, \quad x = \frac{2}{3} \omega \tau_B,$$

and $J_m$ is the Bessel function of the index $m$.

As it follows from Eq. (7.10), the spectrum of the signal $Q(t)$ incorporates only the even (multiples of $2\omega$) harmonics; the amplitude $Q_a^{(2\omega)}$ of the alternating part having the frequency $2\omega$ and the constant component $Q_c$ of the light flux are, respectively:

$$Q_a^{(2\omega)} / Q_0 = J_1(b) \sin a, \quad Q_c / Q_0 = \frac{1}{2} [1 - J_0(b) \cos a]. \quad (7.11)$$

At $\xi_0 < 1$, when the parameter $a$ may be assumed small, Eq. (7.11) yields simple dispersion dependencies

$$\frac{Q_a^{(2\omega)}}{Q_0} = \frac{a^2}{2 \sqrt{1 + \frac{4}{5} \omega^2 \tau_B^2}}, \quad \frac{Q_c}{Q_0} = \frac{a^2}{4} \left[ \frac{1}{2(1 + \frac{4}{5} \omega^2 \tau_B^2)} \right], \quad (7.12)$$

convenient to be verified experimentally.

The corresponding data, taken from Ref. [65], is shown in Fig. 7.1; for actual details of fitting of Eqs. (7.12) to the measured dependencies and discussion of the causes of the observed deviations—see the cited paper.
Figure 7.1: Frequency dependence of the intensities of the light, transmitted through a layer of magnetic fluid subjected to the action of an alternating magnetic field: $Q_a^{(2\omega)}$ (curve 1 and filled circles), $Q_c$ (curve 2 and crossed circles)
References


Appendix. Some properties of the function $R(\sigma)$

From the definition (2.10) of function $R(\sigma)$:

$$R(\sigma) = \int_0^1 e^{\sigma x^2} \, dx$$  \hspace{1cm} (A.1)

there follows the expression for its derivatives at the zero point:

$$\left( \frac{d^n R}{d\sigma^n} \right)_{\sigma=0} = \frac{1}{2n+1}.$$  \hspace{1cm} (A.2)

Therefore in case of $\sigma \ll 1$ we have

$$R = 1 + \frac{1}{3} \sigma, \quad R' = \frac{1}{3} + \frac{1}{5} \sigma, \quad R'' = \frac{1}{5} + \frac{1}{7} \sigma, \quad R''' = \frac{1}{7} + \frac{1}{9} \sigma.$$  

In order to find the asymptotic expansion for $R$ at large values of $\sigma$, we shall use the equation for this function

$$R' = (e^\sigma - R) / 2\sigma,$$  \hspace{1cm} (A.3)

which is obtained from Eq.(A.1) by differentiating with respect to $\sigma$ and following integrating of the right-hand side over $x$. Substituting into Eq.(A.3) the representation

$$R = e^\sigma f / 2\sigma,$$

Eq.(A.3) transforms into equation

$$f' + \left( 1 - \frac{1}{2\sigma} \right) f = 1$$

for the function $f$. Transiting there to the argument $\rho = \sigma^{-1}$, yields

$$-\rho^2 \frac{df}{d\rho} + \left( 1 - \frac{\rho}{2} \right) f = 1.$$  \hspace{1cm} (A.4)

Solution of the last equation is sought in the form of a series

$$f = \sum_a a_n \rho^n.$$  \hspace{1cm} (A.5)

For coefficients $a_n$ from Eq. (A.4) we get a recursive formula

$$a_n = \left( n - \frac{1}{2} \right) a_{n-1}, \quad a_0 = 1.$$  \hspace{1cm} (A.6)

Substituting Eqs. (A.5) and (A.6) into Eq. (A.3), we arrive at the expansion

$$R = \frac{e^\sigma}{2\sigma} \left( 1 + \frac{1}{2\sigma} + \frac{3}{4\sigma^2} + \ldots + \frac{(2n-1)!!}{2^n \sigma^n} + \ldots \right).$$  \hspace{1cm} (A.7)

Differentiating this formula with respect to $\sigma$, one finds the asymptotic ($\sigma \gg 1$) expressions for the derivatives

$$R' = \frac{e^\sigma}{2\sigma} \left( 1 - \frac{1}{2\sigma} - \frac{1}{4\sigma^2} + \ldots \right);$$  \hspace{1cm} (A.8)

$$R'' = \frac{e^\sigma}{2\sigma} \left( 1 - \frac{3}{2\sigma} + \frac{3}{4\sigma^2} + \ldots \right);$$  \hspace{1cm} (A.9)

$$R''' = \frac{e^\sigma}{2\sigma} \left( 1 - \frac{5}{2\sigma} + \frac{15}{4\sigma^2} + \ldots \right).$$  \hspace{1cm} (A.10)