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Research article

Medium Amplitude Field Susceptometry (MAFS) for magnetic nanoparticles

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ABSTRACT

The linear dynamic susceptibility is arguably the most important property to specify the magnetization dynamics of a given system. Therefore, this quantity has been studied in great detail and the corresponding measurements known as susceptometry are well-established. Notwithstanding its relevance, the linear susceptibility is inherently limited to describe the magnetization response to weak external fields only. Here, we suggest the framework of Medium Amplitude Field Susceptometry (MAFS) to study the non-linear response which complements the linear susceptibility and provides additional information on the magnetic properties of the system and is applicable to magnetic fields of medium amplitudes. In particular, we introduce the general third-order nonlinear susceptibility $\hat{\chi}_3$ as a central quantity that completely specifies the lowest-order non-linear response to arbitrary time-dependent magnetic fields. We show that response functions in medium amplitude oscillatory magnetic fields and parallel superposition susceptometry are contained in $\hat{\chi}_3$ as special cases. Also included in $\hat{\chi}_3$ are interesting intermodulation effects when the system is probed by a superposition of oscillating magnetic fields with different frequencies. We work out the explicit form of $\hat{\chi}_3$ for several model systems for the dynamics of magnetic nanoparticles (MNPs). We expect this unifying framework to be not only of theoretical interest, but also useful for a deeper characterization of MNP systems, giving additional information on their suitability for various applications.

1. Introduction

The linear susceptibility is a fundamental material parameter that fully encodes the magnetization response of a system to arbitrary time-dependent magnetic fields [1,2]. An important restriction to the above is that the amplitudes of the applied fields must be small enough. Because of its importance, measuring the linear susceptibility has become a standard characterization method for magnetic systems [3]. Indeed, developments in alternating current (AC) susceptometry now allow us to measure the susceptibility over a very wide frequency range [4–6]. From a theoretical point of view, linear response theory provides not only a solid foundation of the linear susceptibility, but also suggests different approaches for their measurements, such as step-changes in the magnetic field strength, oscillatory magnetic fields or, via the fluctuation–dissipation theorem, from equilibrium magnetization fluctuations. The remarkable result of linear response theory is that all these different methods ultimately measure the same quantity, i.e. the linear susceptibility [2].

With their strong magnetization response, magnetic nanoparticles (MNPs) are particularly interesting model systems that have attracted a considerable body of experimental and theoretical work [3]. In addition, numerous engineering and biomedical applications of MNPs are currently being explored and developed [7–11]. Many of these applications use MNPs as field-controlled materials or otherwise rely on their field-dependent properties. Therefore, there is great interest in the response of MNPs to general time-dependent fields. Due to their superparamagnetic nature, "moderate" field strengths are routinely accessible experimentally that drive MNP systems beyond the linear response regime.

While it is generally acknowledged that nonlinear responses contain a wealth of additional information on a system, they are also difficult to quantify in general. Some applications such as magnetic particle spectroscopy explicitly probe non-linear responses in terms of amplitudes of higher harmonics, typically by large amplitude oscillatory magnetic fields [12]. Thus, one approach is to use AC susceptometry with medium or large amplitudes to measure higher order susceptibilities. This approach has been used e.g. in superconductors [13]. In the context of MNPs and ferrofluids, using small amplitude oscillatory magnetic fields, the linear dynamic susceptibility has been studied intensively (see e.g. Refs. [3,5] and references therein) and can be considered to be understood quantitatively for not too strong interactions, at least for thermally blocked MNPs (see e.g. Refs. [3,14] and references therein). In contrast, the nonlinear susceptibilities of MNPs are much less well understood. Besides magnetic particle spectroscopy, only few dedicated experimental studies on the nonlinear susceptibilities of MNPs have appeared so far [15,16]. Recent theoretical approaches used perturbation methods based on the Clausius–

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Mossotti equation and the mean-spherical approximation [17,18] to calculate nonlinear susceptibilities. In AC fields, however, these approaches miss dissipative contributions. Only very recently did some studies appear that numerically calculated the nonlinear response based on kinetic models for the magnetization dynamics [19–22]. Raikher and Stepanov were able to calculate the third order response to AC fields from a kinetic model and compared a low-frequency approximation to experimental data [23,24].

Here, instead, we propose the third-order nonlinear susceptibility $\hat{\chi}_3$ as a new relevant material property that fully describes the nonlinear response of magnetic systems to arbitrary time-dependent fields of moderate amplitudes. We call this approach Medium Amplitude Field Susceptometry (MAFS) to emphasize the extension of classical linear susceptometry to magnetic fields of medium amplitude. Thereby, we aim to transfer a recent development in rheology [25] to magnetic systems. We discuss general properties of the third-order nonlinear susceptibility and show that Medium Amplitude Oscillatory Field (MAOF) susceptibilities and Parallel Superposition (PS) susceptibilities are contained in $\hat{\chi}_3$ as special cases. We also discuss the phenomenon of intermodulation, where nonlinearities of the magnetization dynamics react to a superposition of two oscillating magnetic fields with different frequencies by producing a response at several linear combinations of the input frequencies. In addition, we illustrate the general framework for some commonly used models of MNP dynamics. Thereby, we derive and discuss explicit expressions of $\hat{\chi}_3$ for these models.

The paper is organized as follows. The general approach to nonlinear susceptibilities employed here is presented in Section 2 together with the specialization to particular cases such as MAOF and PS. In Sections 3 and 4, the third-order dynamic susceptibilities defined in Section 2 are illustrated for different models of MNP dynamics within the rigid-dipole approximation and for immobile MNPs, respectively. Details of the derivation are given in the Appendix. Finally, some conclusions are offered in Section 5.

2. Theory and general relations

Consider a paramagnetic material (e.g. a collection of MNPs) where a magnetization M can be induced by an applied magnetic field H. The magnetization law $M_{\rm eq} = M_{\rm eq}(H)$ gives the equilibrium magnetization resulting from a static magnetic field. For time-dependent magnetic fields $H = H(t)$, however, the induced magnetization is in general also time-dependent, $M = M(t)$. When the field amplitude is sufficiently small, the relation between M and H is linear and can be written as

$$M(t) = \int_{-\infty}^{t} \chi(t-t_1)H(t_1)\mathrm{d}t_1, \qquad |H| \text{ small}, \tag{1}$$

with the material function $\chi(t)$ known as the linear magnetic susceptibility.

When the amplitude of the magnetic field increases, the linear relation (1) breaks down since the magnetization depends nonlinearly on the magnetic field. Expanding this dependence in a Volterra series in the magnetic field, the time-dependent magnetization can be expressed in the form [26–28]

$$M(t) = \sum_{n=1}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \chi_n(\tau_1,\ldots,\tau_n) \prod_{j=1}^{n} H(t-\tau_j)\mathrm{d}\tau_j \tag{2}$$

which holds for general paramagnetic materials with time-independent magnetic properties. The functions $\chi_n(t_1,\ldots,t_n)$ are called the nth order Volterra kernels. The first term of the series in Eq. (2) is the linear magnetic susceptibility appearing in Eq. (1), $\chi_1(t) = \chi(t)\Theta(t)$ with $\Theta(x)$ the Heaviside step function ensuring causality.

It should be noted that nonlinear relations of the form (2) are well studied mathematically [29] and have been employed in other contexts such as rheology [25] and engineering [28]. Strictly speaking, convergence of the series (2) cannot be guaranteed for arbitrary time-dependent fields $H(t)$, but for a rather large class [26] that encompasses most situations of interest for magnetic systems. Since specifying an infinite number of response functions χ_n is impractical, the Volterra series (2) is most useful if the first few terms are dominant. This is the situation considered here.

2.1. Field switch

When switching on a magnetic field of constant strength H at time $t = 0$, $H(t) = H\Theta(t)$ with $\Theta(x)$ the Heaviside step function, the magnetization response from Eq. (2) can be written as

$$M(t) = \sum_{n=1}^{\infty} H^n R_n^{\rm on}(t) \tag{3}$$

with the nth order relaxation function for switching on,

$$R_n^{\rm on}(t) = \int_{-\infty}^{t} \cdots \int_{-\infty}^{t} \chi_n(\tau_1,\ldots,\tau_n) \prod_{j=1}^{n} \mathrm{d}\tau_j. \tag{4}$$

If instead a magnetic field of strength H was applied in the infinite past and switched off at time $t = 0$, $H(t) = H(1-\Theta(t))$, the magnetization relaxation is given by

$$M(t) = \sum_{n=1}^{\infty} H^n R_n^{\rm off}(t) \tag{5}$$

with the nth order relaxation function for switching off,

$$R_n^{\rm off}(t) = \int_{t}^{\infty} \cdots \int_{t}^{\infty} \chi_n(\tau_1,\ldots,\tau_n) \prod_{j=1}^{n} \mathrm{d}\tau_j. \tag{6}$$

For long times, $\lim_{t\to\infty} R_n^{\rm off}(t) = 0$, describing the relaxation to the isotropic state with vanishing magnetization.

2.2. Generalized frequency response function

With the success of AC susceptometry, it is very common and convenient to study the linear susceptibility not in the time but in the frequency domain [3]. Define the Fourier transform of the magnetization as

$$\hat{M}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}t\, e^{-i\omega t} M(t) \tag{7}$$

and similarly for the magnetic field $\hat{H}(\omega)$. The corresponding backtransform is given by

$$M(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}\omega\, e^{i\omega t} \hat{M}(\omega). \tag{8}$$

Taking the Fourier transform of Eq. (2), the nonlinear magnetization response can equivalently be formulated in the frequency domain as

$$\hat{M}(\omega) = \sum_{n=1}^{\infty} \frac{1}{(2\pi)^{n-1}} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \hat{\chi}_n(\omega_1,\ldots,\omega_n) \times \delta(\omega - \sum_{j=1}^{n}\omega_j) \prod_{k=1}^{n} \hat{H}(\omega_k)\mathrm{d}\omega_k, \tag{9}$$

with the nth order complex susceptibility defined by

$$\hat{\chi}_n(\omega_1,\ldots,\omega_n) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\sum_{k=1}^{n} i\omega_k t_k} \chi_n(t_1,\ldots,t_n) \prod_{k=1}^{n} \mathrm{d}t_k \tag{10}$$

To first order, $\hat{\chi}_1(\omega) = \hat{\chi}(\omega)$ is the well-known complex magnetic susceptibility, which is the one-sided Fourier transform of the linear susceptibility $\chi(t)$. The general nth order complex susceptibility $\hat{\chi}_n$ is the Fourier transform of the nth order susceptibility χ_n introduced in Eq. (2) with respect to all n time arguments. This quantity is also known as nth frequency-domain kernel [29].

Before we proceed, it is worth to establish a number of general properties of $\hat{\chi}_n$. First, upon changing the sign of the applied field $\hat{H}(\omega) \to -\hat{H}(\omega)$, we expect that the magnetization also changes its sign, $\hat{M}(\omega) \to -\hat{M}(\omega)$. Therefore, only terms with n odd should appear in the series (2) and (9). We note in passing that exceptions to this rule have been observed in various superconducting systems, the origin of which is still being debated [13]. Second, since $\hat{H}(\omega)$ and $\hat{M}(\omega)$ are Fourier transforms of real-valued functions, their complex conjugate must satisfy $\hat{H}^*(\omega) = \hat{H}(-\omega)$ and $\hat{M}^*(\omega) = \hat{M}(-\omega)$. The same property also applies to the kernels, leading to

$$\chi_n'(-\omega_1,\dots,-\omega_n) = \chi_n'(\omega_1,\dots,\omega_n)$$
$$\chi_n''(-\omega_1,\dots,-\omega_n) = -\chi_n''(\omega_1,\dots,\omega_n), \tag{11}$$

where $\chi_n'(\omega_1,\dots,\omega_n)$ and $\chi_n''(\omega_1,\dots,\omega_n)$ are the real and imaginary part of $\hat{\chi}_n(\omega_1,\dots,\omega_n)$, respectively. Eqs. (11) generalize well-known properties of the linear susceptibility in that the in-phase responses χ_n' are time-reversal invariant, whereas the out-of-phase quantities χ_n'' indicate losses and change sign. Additionally, we find from Eq. (11) that $\chi_n''(0,\dots,0) = 0$, i.e. no magnetic losses for time-independent magnetic fields. The in-phase contributions χ_n' are even functions of the frequencies and therefore not constraint.

Since only odd terms appear in Eq. (9), the first terms of the series read

$$\hat{M}(\omega) = \hat{\chi}_1(\omega)\hat{H}(\omega) + \frac{1}{(2\pi)^2}\int_{-\infty}^{\infty}\mathrm{d}\omega_1\int_{-\infty}^{\infty}\mathrm{d}\omega_2\int_{-\infty}^{\infty}\mathrm{d}\omega_3$$
$$\times\,\delta(\omega - \sum_{j=1}^{3}\omega_j)\hat{\chi}_3(\omega_1,\omega_2,\omega_3)\hat{H}(\omega_1)\hat{H}(\omega_2)\hat{H}(\omega_3)$$
$$+\,\mathcal{O}(\hat{H}^5), \tag{12}$$

with $\hat{\chi}_3(\omega_1,\omega_2,\omega_3)$ the third-order complex susceptibility. In the following, we will be interested mostly in this quantity.

2.3. Medium amplitude oscillatory fields (MAOF)

For the special case of oscillating magnetic fields

$$H(t) = H\cos(\omega_0 t) \tag{13}$$

of medium amplitude H and given frequency ω_0, Eq. (12) takes a simple form so that the magnetization response (2) becomes

$$M(t) = \Re\left\{He^{i\omega_0 t}[\hat{\chi}_1(\omega_0) + \frac{3}{4}H^2\hat{\chi}_3(\omega_0,\omega_0,-\omega_0)]\right\}$$
$$+\,\frac{3}{4}H^3\Re\{e^{3i\omega_0 t}\hat{\chi}_3(\omega_0,\omega_0,\omega_0)\} + \mathcal{O}(H^5), \tag{14}$$

where $\Re A$ denotes the real part of the complex quantity A. Explicitly writing out the real part, Eq. (14) can be written as

$$M(t) = H[\chi'(\omega)\cos(\omega t) + \chi''(\omega)\sin(\omega t)]$$
$$+\,H^3[\chi_{31}'(\omega)\cos(\omega t) + \chi_{31}''(\omega)\sin(\omega t)$$
$$+\,\chi_{33}'(\omega)\cos(3\omega t) + \chi_{33}''(\omega)\sin(3\omega t)] + \mathcal{O}(H^5), \tag{15}$$

where χ_{33}' and χ_{33}'' are the in-phase (real part) and out-of-phase (imaginary part) contributions to the third harmonic, whereas χ_{31}' and χ_{31}'' give the third-order corrections to the linear susceptibilities χ' and χ'', respectively. For medium amplitudes H, the third-order terms given in Eq. (15) specify the magnetization response, whereas higher order terms need to be retained in the expansion for larger amplitudes.

Comparison of Eq. (14) to Eq. (15) allows us to identify the third-order in-phase and out-of-phase AC-susceptibilities in terms of $\hat{\chi}_3$ as

$$\chi_{31}'(\omega) = \frac{3}{4}\Re\hat{\chi}_3(\omega,\omega,-\omega) \tag{16}$$

$$\chi_{31}''(\omega) = -\frac{3}{4}\Im\hat{\chi}_3(\omega,\omega,-\omega) \tag{17}$$

$$\chi_{33}'(\omega) = \frac{1}{4}\Re\hat{\chi}_3(\omega,\omega,\omega) \tag{18}$$

$$\chi_{33}''(\omega) = -\frac{1}{4}\Im\hat{\chi}_3(\omega,\omega,\omega), \tag{19}$$

with $\Im A$ the imaginary part of the complex quantity A.

2.4. Parallel superposition (PS) susceptometry

A different method of probing the response of MNP systems has been proposed by using a superposition of AC and DC fields. Such studies have been used e.g. to determine field-dependent relaxation times parallel and perpendicular to an applied field [30,31].

Here, we consider only the special case where both fields are oriented parallel to each other. Consider a static field of strength H_0 superimposed parallel to an oscillating field,

$$H(t) = H_0 + H_1\cos(\omega_0 t) \tag{20}$$

Eq. (20) formally generalizes MAOF, discussed in Section 2.3. Therefore, it may seem that MAOF is a particular case of PS susceptometry for $H_0 = 0$. This, however, is misleading since in PS the amplitude H_1 is small compared to H_0.

Inserting the particular time-dependent field (20) into Eq. (9), the resulting magnetization response can be expressed as

$$M(t) = H_0\chi_0^{\mathrm{PS}} + H_1\left(\Re\{\chi_{||}^{\mathrm{PS}}e^{i\omega_0 t}\} + \Re\{\chi_2^{\mathrm{PS}}e^{2i\omega_0 t}\}\right), \tag{21}$$

with the static susceptibility

$$\chi_0^{\mathrm{PS}}(H_0,H_1,\omega) = \chi_1(0) + H_0^2\hat{\chi}_3(0,0,0) + \frac{3}{2}H_1^2\hat{\chi}_3(\omega,-\omega,0), \tag{22}$$

the parallel susceptibility

$$\chi_{||}^{\mathrm{PS}}(H_0,\omega) = \chi_1(\omega) + 3H_0^2\hat{\chi}_3(\omega,0,0), \tag{23}$$

and the second harmonic susceptibility

$$\chi_2^{\mathrm{PS}}(H_0,H_1,\omega) = \frac{3}{2}H_0H_1\hat{\chi}_3(\omega,\omega,0). \tag{24}$$

As mentioned above, the amplitude H_1 is considered small in PS and therefore terms $\mathcal{O}(H_1^3)$ are neglected. Note that the magnetization response (21) in PS oscillates with the excitation frequency ω_0 as well as with the second harmonic $2\omega_0$, but no third harmonic for small H_1. Traditional PS measurements almost exclusively focus on the first harmonic, Eq. (23), and extract the dependence on the magnitude H_0 of the static field [30,31], whereas the second harmonic response is typically not reported. We also point out that PS probes different linear combinations of $\hat{\chi}_1$ and $\hat{\chi}_3$ as well as different combinations of the arguments of $\hat{\chi}_3(\omega_1,\omega_2,\omega_3)$ than MAOF. Therefore, PS and MAOF indeed provide complementary information for medium amplitude fields.

2.5. Intermodulation

Instead of probing the system at a single frequency ω_0 as in Eq. (13), one can impose a more complex time-dependent excitation field with I frequencies $n_m\omega_0$,

$$H(t) = H\sum_{m=1}^{I}\cos(n_m\omega_0 t). \tag{25}$$

Due to nonlinearities, the system's response is not limited to first and third harmonics but contains a number of linear combinations of the excitation frequencies. This phenomenon is called intermodulation and is well studied e.g. in microwave systems [32].

For illustration, let us consider the simplest case of $I = 2$, i.e. the superposition of two frequencies, $n_1\omega_0$ and $n_2\omega_0$. In this case, we find from Eq. (12) that the medium-amplitude magnetization response contains the frequencies $n_1\omega_0$, $n_2\omega_3$, $3n_1\omega_0$, $3n_2\omega_0$, $(2n_1+n_2)\omega_0$, $(n_1+2n_2)\omega_0$, $|2n_1-n_2|\omega_0$, $|n_1-2n_2|\omega_0$. For $n_1 = n_2$, this reduces to the first and third harmonic, as expected. Choosing $n_2 = 4n_1$, however, the response comprises eight different frequencies $\omega_k = k\omega_0$ with $k \in I_\omega$ where $I_\omega = \{1,2,3,4,6,7,9,12\}$. We want to point out that such intermodulation effects are naturally included in Eq. (12) but are not routinely captured in standard approaches that study responses to medium-amplitude oscillatory fields. Within the present framework, the response is described from Eq. (12) as

$$\hat{M}(\omega) = 2\pi H[\hat{\chi}_1(\omega_0)\delta(\omega-\omega_0) + \hat{\chi}_1(4\omega_0)\delta(\omega-4\omega_0)]$$

$$+ 2\pi H^3 \sum_{k\in I_\omega} \hat{\chi}^I_{3,k}(\omega_0)\delta(\omega-\omega_k) \quad (26)$$

where the functions $\hat{\chi}^I_{3,k}(\omega)$ are defined as

$$\hat{\chi}^I_{3,1}(\omega) = \frac{3}{4}\hat{\chi}_3(\omega,\omega,-\omega) + \frac{3}{2}\hat{\chi}_3(4\omega,-4\omega,\omega) \quad (27)$$

$$\hat{\chi}^I_{3,2}(\omega) = \frac{3}{4}\hat{\chi}_3(4\omega,-\omega,-\omega) \quad (28)$$

$$\hat{\chi}^I_{3,3}(\omega) = \frac{1}{4}\hat{\chi}_3(\omega,\omega,\omega) \quad (29)$$

$$\hat{\chi}^I_{3,4}(\omega) = \frac{3}{4}\hat{\chi}_3(4\omega,4\omega,-4\omega) + \frac{3}{2}\hat{\chi}_3(4\omega,\omega,-\omega) \quad (30)$$

$$\hat{\chi}^I_{3,6}(\omega) = \frac{3}{4}\hat{\chi}_3(4\omega,\omega,\omega) \quad (31)$$

$$\hat{\chi}^I_{3,7}(\omega) = \frac{3}{4}\hat{\chi}_3(4\omega,4\omega,-\omega) \quad (32)$$

$$\hat{\chi}^I_{3,9}(\omega) = \frac{3}{4}\hat{\chi}_3(4\omega,4\omega,\omega) \quad (33)$$

$$\hat{\chi}^I_{3,12}(\omega) = \frac{1}{4}\hat{\chi}_3(4\omega,4\omega,4\omega) \quad (34)$$

Note that $\hat{\chi}^I_{3,3} = \hat{\chi}_{33}(\omega)$ and $\hat{\chi}^I_{3,12}(\omega) = \hat{\chi}_{33}(4\omega)$ are the same susceptibilities that appear within MAOF. The remaining susceptibilities, however, do not appear in MAOF or PS and provide new information on the system.

3. Illustration of nonlinear susceptibilities for thermally blocked MNPs

Having established the general theory and formalism in Section 2, we now exemplify and illustrate these quantities for specific models of MNP dynamics that are frequently used in the literature. But before doing so, we want to emphasize that the above formalism applies regardless of the underlying model, the particular relaxation mechanisms or dipolar interaction strength and concentration regimes.

In this section, we consider for simplicity only models for the ultra-dilute regime where interactions between MNPs can be neglected. In addition, the models investigated in this section apply to thermally blocked MNPs where Néel relaxation can be neglected. The models we consider are the Fokker–Planck Equation (FPE) model, the Effective Field Approximation (EFA), and Shliomis' 2001 magnetization equation (Sh01). Details of these models as well as a derivation of the third order susceptibilities can be found in Appendices B, C and E. The opposite case of immobile MNPs where Néel processes are the only relaxation mechanism is considered in Section 4.

We first specialize to the response to medium amplitude oscillatory fields (MAOF). The corresponding susceptibilities $\hat{\chi}_{3k}(\omega)$ for $k \in \{1,3\}$ are defined in Section 2.3. The susceptibilities $\hat{\chi}_{31}$ give the $\mathcal{O}(H^3)$ correction to the harmonic response at the excitation frequency ω_0. The susceptibilities $\hat{\chi}_{33}$ on the other hand determine the nonlinear response at the frequency $3\omega_0$. Fig. 1(a) and (b) show the real and imaginary part of $\hat{\chi}_{3k}$, respectively. For low frequencies, $\chi'_{3k}(\omega)$ approach the quasi-static limiting values $\chi'_{31}(0) = (3/4)\hat{\chi}_3^{\rm qs}$, $\chi'_{33}(0) = (1/4)\hat{\chi}_3^{\rm qs}$, where $\hat{\chi}_3^{\rm qs}$ denotes the third-order static susceptibility. See Appendix A and Eq. (A.1) for a discussion of the quasi-static limit and a derivation of $\hat{\chi}_3^{\rm qs}$.

We want to emphasize that the scaled susceptibilities $\hat{\chi}_{3k}(\omega)/\hat{\chi}_3^{\rm qs}$ are functions of frequency ω only, independent of MNP properties. Fig. 1 shows the predictions of three models for the MNP dynamics denoted as FPE, EFA and Sh01 (see Appendices B, C and E). From Fig. 1 we find that all three models give the same qualitative predictions, with close agreement between FPE and EFA and somewhat larger differences for the Sh01 model. The in-phase susceptibilities χ'_{3k} show approximately the inverse behavior of the linear counterpart, i.e. starting from negative values of the quasi-static susceptibility at low frequencies, $\chi'_{3k}(\omega)$ increase with increasing frequency ω until fast approaching zero as ω^{-4} for $\omega\tau_{\rm B} \gtrsim 10$. Similarly, the shape of the out-of-phase susceptibilities χ''_{3k} is similar to the linear counterpart but with a negative sign and the minima occurring at frequencies slightly lower than $\tau_{\rm B}^{-1}$. Their approach to zero for large frequency is governed by the power law ω^{-3} for $\omega\tau_{\rm B} \gg 1$. Since the susceptibilities χ''_{3k} govern magnetic losses in oscillating fields, the corresponding reduction of magnetic losses are relevant for magnetic fluid hyperthermia applications as they are detrimental to the heating efficiency.

Next, we study the three nonlinear susceptibilities related to parallel superposition (PS) susceptometry defined and discussed in Section 2.4. The quantity $\hat{\chi}_3(\omega,-\omega,0)$ appearing in Eq. (22) is real-valued and governs the correction to the static susceptibility. The susceptibility $\hat{\chi}_3(\omega,0,0)$ determines the nonlinear contribution to the parallel susceptibility at the excitation frequency ω, Eq. (23), while $\hat{\chi}_3(\omega,\omega,0)$ governs the parallel response at the second harmonic, see Eq. (24). Fig. 2(a) and (b) show the real and imaginary part of these PS susceptibilities, respectively. For low frequencies, the real parts of these susceptibilities all approach the same quasi-static value $\hat{\chi}_3^{\rm qs}$ as expected. The increase of these susceptibilities with increasing frequency is similar to χ'_{3k} seen in Fig. 1, but approaching zero at somewhat larger frequencies. It is only the second-harmonic susceptibility $\chi'_3(\omega,\omega,0)$ that shows a pronounced overshoot around $\omega\tau_{\rm B} \approx 1$, whereas the overshoot for $\chi'_3(\omega,0,0)$ is tiny and absent for $\chi'_3(\omega,-\omega,0)$. The imaginary parts of the susceptibility, $\chi''(\omega,0,0)$ and $\chi''_3(\omega,\omega,0)$ show a slight asymmetric single peak at frequencies below $\tau_{\rm B}^{-1}$. Positive values of these susceptibilities imply enhanced magnetic losses which could be of interest in magnetic fluid hyperthermia applications. Indeed an additional DC field was found to improve the heating power [33,34]. Same as found for MAOF, the three models give qualitatively similar predictions, with good quantitative agreement between FPE and EFA, while Sh01 model shows somewhat larger deviations.

A full visualization of the third-order nonlinear susceptibility $\hat{\chi}_3(\omega_1,\omega_2,\omega_3)$ is very difficult since it is a function of three independent frequencies. Fig. 3 shows contour plots of the real and imaginary part of $\hat{\chi}_3$ for the submanifold with $\omega_3 = \omega_1$, i.e. only two independent frequencies are considered for this plot. The dashed lines in Fig. 3 show the one-dimensional cross sections $\omega_2 = \omega_1$ and $\omega_2 = 0$ of $\hat{\chi}_3$ that are probed by MAOF and PS, respectively As seen from Fig. 3, the maxima and minima of $\hat{\chi}_3$ manifest themselves differently for different cross sections. In particular, the more asymmetric shape of the imaginary part of the susceptibility in PS compared to MAOF can be understood by Fig. 3(b).

Fig. 4(a) and (b) show the real and imaginary part, respectively, of the susceptibilities (27)–(34) associated with intermodulation effects as discussed in Section 2.5. In the low-frequency limit, the intermodulation susceptibilities approach one of three limiting values, $\hat{\chi}^I_{3,1}(0) = \hat{\chi}^I_{3,4}(0) = (9/4)\hat{\chi}_3^{\rm qs}$, $\hat{\chi}^I_{3,2}(0) = \hat{\chi}^I_{3,6}(0) = \hat{\chi}^I_{3,7}(0) = \hat{\chi}^I_{3,9}(0) = (3/4)\hat{\chi}_3^{\rm qs}$, and $\hat{\chi}^I_{3,3}(0) = \hat{\chi}^I_{3,12}(0) = (1/4)\hat{\chi}_3^{\rm qs}$. Therefore, the real parts of $\hat{\chi}^I_{3,k}$ all start with negative values for low frequencies. Fig. 4 shows that $\Re\hat{\chi}^I_{3,k}$ cross the zero axis at some frequency between $\omega\tau_{\rm B} = 0.1$ and 2, develop a small maximum before rapidly decaying to zero at frequencies $\omega\tau_{\rm B} > 10$.

4. Illustration of nonlinear susceptibilities for immobile MNPs

In Section 3 we considered models within the rigid-dipole (thermally blocked) approximation where Brownian particle rotation is the only magnetization relaxation mechanism. Here, instead, we consider the opposite limit of immobile MNPs where magnetization relaxation is exclusively caused by internal, Néel processes. While many systems show a combination of Brownian and Néel relaxation [3,35,36], it is helpful to consider these processes separately.

For immobile MNPs, there are less analytical results available in the literature concerning the magnetization dynamics compared to the rigid-dipole approximation. Although the stochastic Landau–Lifshitz–Gilbert equation is generally considered a well-defined starting point [37], extracting useful results for the magnetization relaxation remains a challenge due to the time-scale separation involved. In

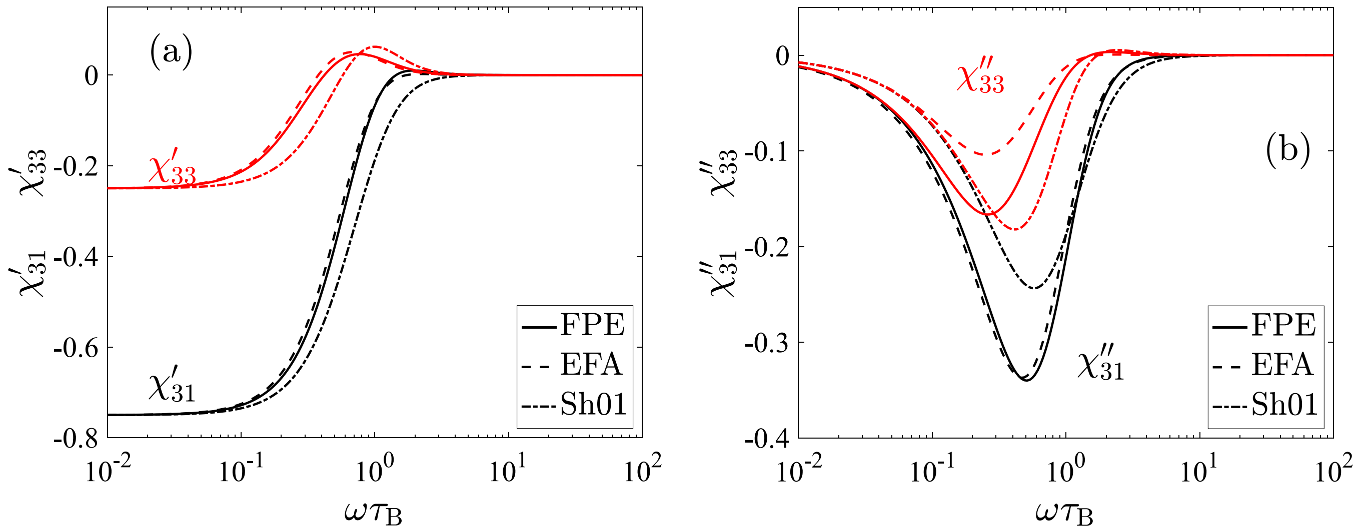

Fig. 1. The nonlinear susceptibilities χ'_{31} and χ'_{33} (a) and χ''_{31} and χ''_{33} (b) are shown as a function of reduced frequency on a semi-logarithmic axis. Susceptibilities are scaled with $|\hat{\chi}_3^{qs}|$. Solid, dashed and dot-dashed lines correspond to the FPE model, Eq. (E.17), the EFA, Eq. (C.4), and Shliomis 2001 approximation, Eq. (B.6), respectively.

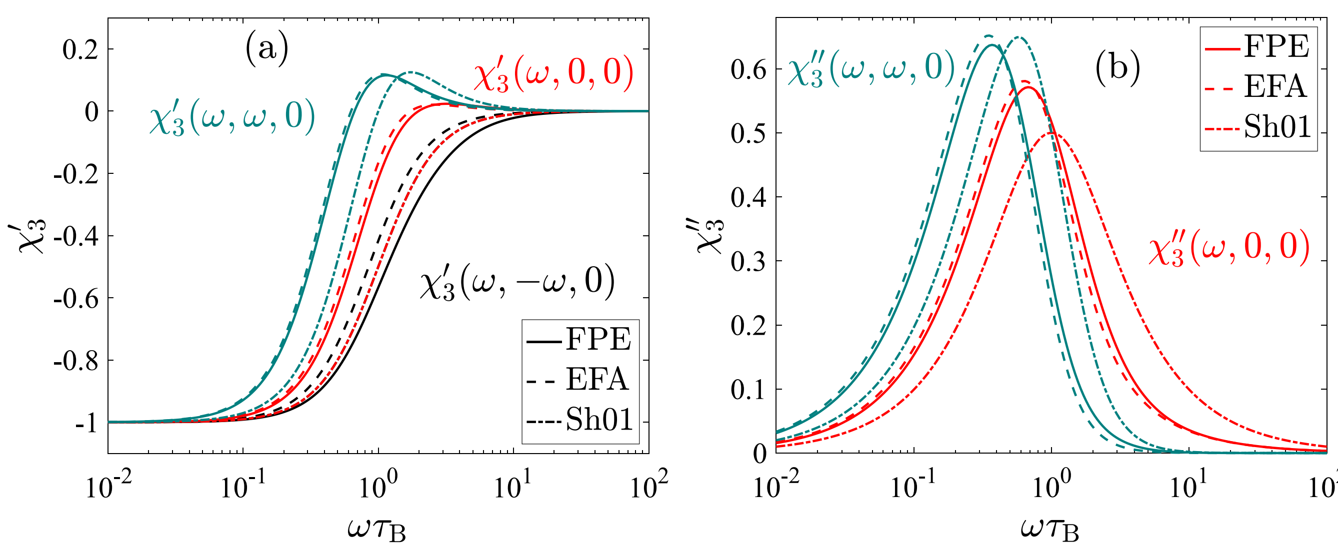

Fig. 2. The real (a) and imaginary (b) part of the third order complex susceptibilities $\hat{\chi}_3$ related to PS, Eq. (21), normalized by $|\hat{\chi}_3^{qs}|$ are shown as a function of dimensionless frequency $\omega\tau_B$ on a semi-logarithmic scale. Line styles are the same as in Fig. 1. Note that $\hat{\chi}_3(\omega,-\omega,0)$ is real.

Ref. [23], the authors proposed analytical expressions for the third-order susceptibility by an ad hoc transfer of results obtained for the rigid dipole approximation. Here, instead, we use a simplified model in terms of thermally activated magnetization reversals that mimic Néel relaxation for sufficiently large anisotropy barriers [38,39]. In these Monte-Carlo type models, the magnetization is restricted to point either parallel or anti-parallel to the particle's easy axis with a probability of switching between the two that is governed by an Arrhenius rate. The magnetization response for the resulting two-state model can be worked out analytically. See Appendix F for details. As an example, we show in Fig. 5 the third-order susceptibilities χ'_{33} and χ''_{33} governing the third harmonic response for MAOF. We observe that χ'_{33} and χ''_{33} look qualitatively similar to the rigid-dipole case shown in Fig. 1. Therefore, the ad hoc expression proposed in Ref. [23] provides a rather good approximation to the result of the Monte-Carlo type model. One qualitative difference between the two is the prediction of a maximum of χ''_{33} at around $\omega\tau_N \approx 2$ which is absent in the Monte-Carlo type model. Note that the Monte-Carlo type model predicts a much slower decay for the high-frequency behavior of immobile MNPs $\chi'_{33} \sim \omega^{-2}$ and $\chi''_{33} \sim \omega^{-1}$ for $\omega\tau_N \gg 1$ compared to exponents −4 and −3, respectively, found above for thermally blocked particles.

5. Conclusions

We here propose Medium Amplitude Field Susceptometry (MAFS) as an extension of classical, linear susceptometry for a more in-depth characterization of the magnetization dynamics. In particular, we introduce the third-order complex dynamic susceptibility $\hat{\chi}_3(\omega_1,\omega_2,\omega_3)$

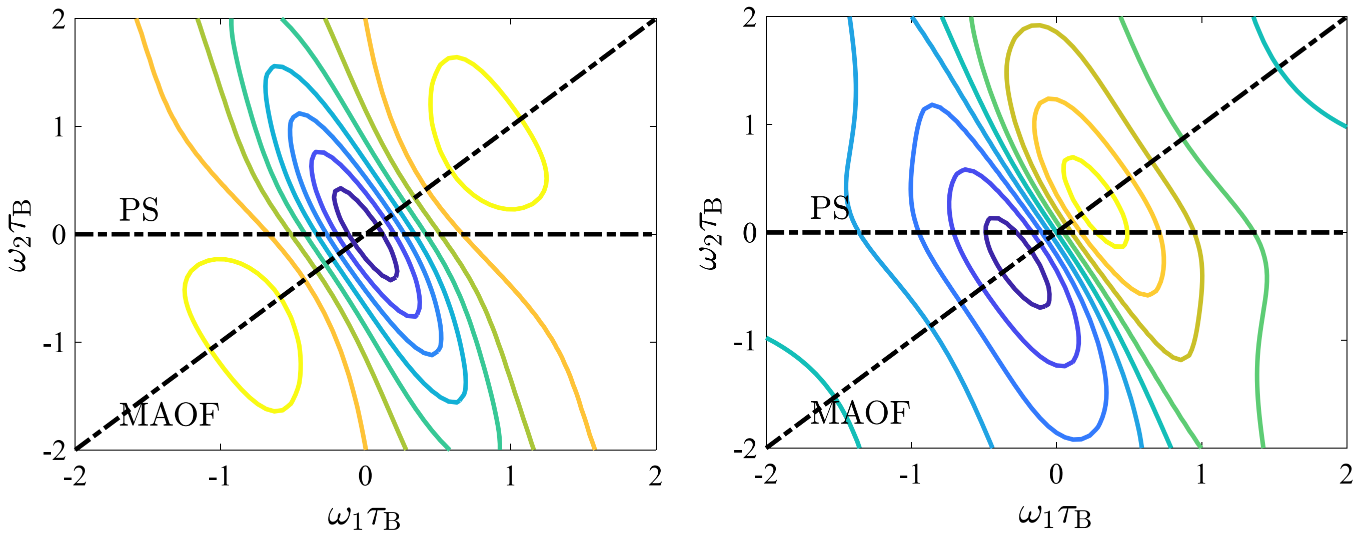

Fig. 3. Contour plots of the real (left) and imaginary (right) part of the third-order complex non-linear susceptibility $\hat{\chi}_3(\omega_1, \omega_2, \omega_1)$. MAOF and PS probe one-dimensional cross-sections of this quantity, indicated by dash-dotted lines.

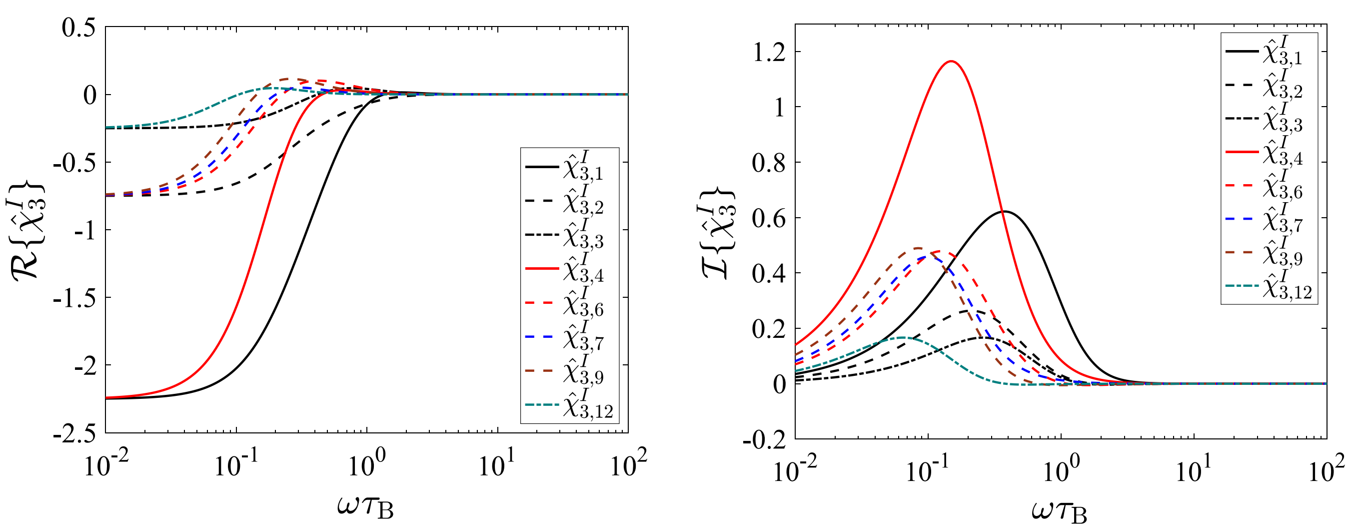

Fig. 4. The real (a) and imaginary (b) part of the third order complex intermodulation susceptibilities $\hat{\chi}^I_{3,k}$ normalized by $|\hat{\chi}_3^{qs}|$ are shown as a function of dimensionless frequency $\omega\tau_B$ on a semi-logarithmic scale. Results are shown for the FPE model, Eq. (E.17). The real (imaginary) parts are all negative (positive) at low frequencies.

as the central new quantity that completely determines the magnetization dynamics to arbitrary time-dependent fields of medium amplitude. For example, medium amplitude oscillatory field and parallel superposition susceptibility are contained within $\hat{\chi}_3(\omega_1, \omega_2, \omega_3)$ as particular one-dimensional cross-sections through the three-dimensional $(\omega_1, \omega_2, \omega_3)$-frequency space. More generally, the three frequency arguments correspond to three possibly different frequencies present in the applied magnetic field. Therefore, all three frequencies are identical in magnitude for the response to a harmonically oscillating field, whereas in parallel superposition, one frequency argument is zero, corresponding to the contribution of the time-independent field. Thus, MAFS provides a unifying framework of these different response functions. In addition, intermodulation effects are naturally described within MAFS, where a superposition of magnetic field frequencies lead to magnetization responses at several linear combinations of the input frequencies.

The medium field range considered here can be defined operationally for oscillating fields as the regime where the fifth order harmonic response is negligible compared to the third. For static fields, the third order response can be considered to be valid up to Langevin parameters of around 1, where the deviation from the Langevin function remains below 1%.

Since there is an ongoing discussion in the literature about the appropriate form of the magnetization equation for MNPs, we illustrate the general theory and framework for several models of the magnetization dynamics of MNPs. For these models, we calculate explicit expressions for the third order complex dynamic susceptibility $\hat{\chi}_3(\omega_1, \omega_2, \omega_3)$. For simplicity, we restrict ourselves to models for non-interacting MNPs that are either thermally blocked or immobile. In particular, we consider the Fokker–Planck Equation (FPE) model, the effective field approximation (EFA) and Shliomis 2001 (Sh01) magnetization equation. All three models are found to give qualitatively similar results for the third-order susceptibilities, with the EFA model agreeing more closely to FPE than Sh01. Similar conclusions concerning MAOF have been drawn in Ref. [21]. That EFA gives good approximations to FPE results has also been found in the context of magnetoviscosity [40].

Let us point out again that MAFS is not limited to the above models but instead offers a general framework for any nonlinear magnetization

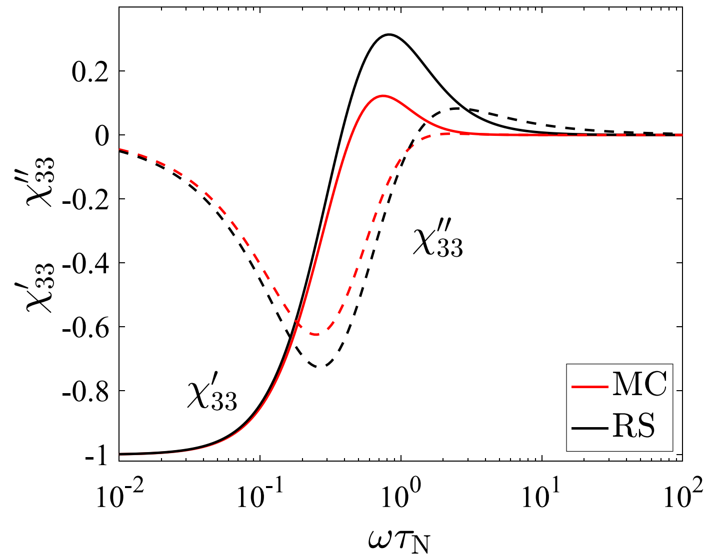

Fig. 5. The frequency dependence of the real (χ'_{33}) and imaginary (χ''_{33}) part of the third order complex susceptibilities are shown as solid and dashed lines, respectively. Results of the Monte-Carlo (MC) type model, Eqs. (F.7) and (F.8) are shown as red lines while black lines correspond to the results of Raikher and Stepanov (RS), Ref. [23].

equation. It will be interesting to work out the effect of interparticle interactions as well as the combination of Brownian and Néel relaxation on the form of $\hat{\chi}_3(\omega_1,\omega_2,\omega_3)$.

We also want to emphasize that MAFS offers a wealth of additional information in addition to classical AC susceptometry. As we have demonstrated in Section 3, MAFS is able to distinguish between different models of the magnetization dynamics with identical linear dynamic susceptibilities.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Patrick Ilg reports financial support was provided by Engineering and Physical Sciences Research Council. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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Appendix A. Quasi-static approximation

Consider first the quasi-static approach. This approach has been used e.g. in Ref. [18] within the mean-spherical approximation to calculate interaction effects on the nonlinear response. Here, for simplicity, we restrict ourselves to the non-interacting case.

Consider general time-dependent magnetic fields $H(t)$ that vary slowly enough such that the instantaneous magnetization at every time can be approximated by the equilibrium relation $M(t) = M_{\rm sat}L(h(t))$ with $M_{\rm sat} = n\mu$ the saturation magnetization, n the number density of MNPs and μ their magnetic moment. $L(x) = \coth(x) - 1/x$ denotes the Langevin function and the dimensionless field is defined by $h(t) = \mu H(t)/k_BT$ with k_BT the thermal energy. For fields with medium amplitudes, the Langevin function can be approximated by $L(x) = x/3 - x^3/45 + \mathcal{O}(x^5)$. Inserting these relations and taking the Fourier-transform, the magnetization can be expressed in the form Eq. (12) where the linear susceptibility is independent of frequency, $\hat{\chi}_1^{\rm qs}(\omega) = \chi_{\rm L}$, with the Langevin susceptibility $\chi_{\rm L} = n\mu^2/(3k_BT)$. For the third-order contribution we find

$$\hat{\chi}_3^{\rm qs} = -\frac{\chi_{\rm L} q}{15}, \tag{A.1}$$

with $q = \mu^2/(k_BT)^2$. Thus, $\hat{\chi}_1^{\rm qs}$ and $\hat{\chi}_3^{\rm qs}$ are both real-valued and independent of frequency. Therefore, as remarked earlier, the quasi-static approximation disregards dissipation effects and can be considered as the zero-frequency limit of the dynamical theory.

Appendix B. Shliomis '01 magnetization equation

We deliberately skip the classical magnetization equation proposed by Shliomis in 1971 [41] and still widely used today since it reduces to a linear relaxation for the present case with the magnetization parallel to the applied field direction. Therefore, nonlinear susceptibilities are not present in this model, $\hat{\chi}_3^{\rm Sh71} = 0$.

In 2001, Shliomis suggested a modified magnetization equation to improve some of the shortcomings of the original model [42]. The modified theory is formulated in terms of a dimensionless effective field $\xi_e(t)$ that governs the instantaneous magnetization via $M(t) = M_{\rm sat}L(\xi_e(t))$. In absence of flow and with the magnetization parallel to the external field direction, the dynamics of the effective field simplifies to [42]

$$\dot{\xi}_e = -\frac{1}{\tau_B}(\xi_e - h), \tag{B.1}$$

where τ_B denotes the Brownian relaxation time. This model is intended for thermally blocked MNPs where Néel relaxation can be neglected. Assuming the system was at equilibrium at some early initial time $t_0 \to -\infty$ we can write the general solution to Eq. (B.1) as

$$\xi_e(t) = \frac{1}{\tau_B}\int_{-\infty}^{t} dt'\, e^{-(t-t')/\tau_B} h(t'). \tag{B.2}$$

Expanding the Langevin function $L(x)$ in a Taylor series, we can write the resulting magnetization in the form (2) with the linear susceptibility given by a single-exponential relaxation,

$$\chi_1(t) = \Theta(t)\frac{e^{-t/\tau_B}}{\tau_B}, \tag{B.3}$$

with $\Theta(t)$ the Heaviside step function and the third-order susceptibility given by

$$\chi_3^{\rm Sh01}(\tau_1,\tau_2,\tau_3) = -\frac{\chi_L q}{15\tau_B^3}\Theta(\tau_1)\Theta(\tau_2)\Theta(\tau_3)e^{-(\tau_1+\tau_2+\tau_3)/\tau_B} \tag{B.4}$$

Taking Fourier transforms, we arrive at the well-known Debye form for the linear susceptibility

$$\hat{\chi}_1(\omega) = \frac{\chi_L}{1+i\omega\tau_B} \equiv \chi_L\psi(\omega) \tag{B.5}$$

where for convenience of notation we defined the dimensionless function $\psi(x) \equiv [1+ix\tau_B]^{-1}$ with the property $\psi(0)=1$. For the third-order nonlinear susceptibility we find from Eq. (B.4)

$$\hat{\chi}_3^{\rm Sh01}(\omega_1,\omega_2,\omega_3) = \hat{\chi}_3^{\rm qs}\psi(\omega_1)\psi(\omega_2)\psi(\omega_3). \tag{B.6}$$

In the zero-frequency limit, Eq. (B.6) recovers the quasi-static approximation as it should, $\hat{\chi}_3^{\rm Sh01}(0,0,0) = -\chi_L q/15 = \hat{\chi}_3^{\rm qs}$. Using Eqs. (16)–(19), we can derive explicit expressions for the nonlinear AC-susceptibilities within the Sh01 model,

$$\frac{\chi'_{31}(\omega)}{\chi_L q} = \frac{-1-(\omega\tau_B)^2}{20[1+(\omega\tau_B)^2]^3} \tag{B.7}$$

$$\frac{\chi''_{31}(\omega)}{\chi_L q} = \frac{-(\omega\tau_B)-(\omega\tau_B)^3}{20[1+(\omega\tau_B)^2]^3} \tag{B.8}$$

$$\frac{\chi'_{33}(\omega)}{\chi_L q} = \frac{-1+3(\omega\tau_B)^2}{60[1+(\omega\tau_B)^2]^3} \tag{B.9}$$

$$\frac{\chi''_{33}(\omega)}{\chi_L q} = \frac{-3(\omega\tau_B)+(\omega\tau_B)^3}{60[1+(\omega\tau_B)^2]^3} \tag{B.10}$$

with $\chi''_{31}(0) = \chi''_{33}(0) = 0$ as they should.

Appendix C. MRS74 EFA

Martsenyuk, Raikher, Shliomis [43] employed the so-called effective field approximation (EFA) to arrive at a magnetization equation that simplifies to

$$\dot{M} = -\frac{1}{\tau_B}\left(1-\frac{h(t)}{\xi_e}\right)M \tag{C.1}$$

for the case where the magnetization is parallel to the magnetic field direction. As in Appendix B, ξ_e denotes the effective field that allows to express the magnetization as $M(t) = M_{\rm sat}L(\xi_e(t))$. Historically, Shliomis proposed the magnetization equation discussed in Appendix B as a simplification of Eq. (C.1).

Expressing the effective field as $\xi_e = L^{-1}(m)$, where $m = M/M_{\rm sat}$, and using the known series expansion of the inverse Langevin function [44]

$$L^{-1}(x) = 3x + \frac{9}{5}x^3 + \mathcal{O}(x^5), \tag{C.2}$$

we find that Eq. (C.1) can be rewritten as

$$m + \tau_B\dot{m} = \frac{h(t)}{3} - \frac{h(t)}{5}m^2 + \mathcal{O}(hm^4). \tag{C.3}$$

Taking the Fourier-transform (7) of Eq. (C.3) and using a perturbative solution, we recover the Debye susceptibility (B.5) for χ_1 and find the third-order nonlinear susceptibility within EFA to be given by

$$\hat{\chi}_3^{\rm EFA}(\omega_1,\omega_2,\omega_3) = \hat{\chi}_3^{\rm qs}\mathbb{S}\psi(\omega_1)\psi(\omega_2)\psi(\omega_1+\omega_2+\omega_3), \tag{C.4}$$

where $\psi(x)$ is defined in Eq. (B.5) and $\mathbb{S}$ denotes the symmetrization operator acting on the arguments $\omega_1,\omega_2,\omega_3$. For example, $\mathbb{S}\psi(\omega_1)\psi(\omega_2) = (\psi(\omega_1)\psi(\omega_2)+\psi(\omega_1)\psi(\omega_3)+\psi(\omega_2)\psi(\omega_3))/3$. From Eq. (C.4), the nonlinear AC-susceptibilities are obtained from Eqs. (16)–(19) as

$$\frac{\chi'_{31}(\omega)}{\chi_L q} = \frac{-3+(\omega\tau_B)^2}{60[1+(\omega\tau_B)^2]^3} \tag{C.5}$$

$$\frac{\chi''_{31}(\omega)}{\chi_L q} = \frac{-5(\omega\tau_B)-(\omega\tau_B)^3}{60[1+(\omega\tau_B)^2]^3} \tag{C.6}$$

$$\frac{\chi'_{33}(\omega)}{\chi_L q} = \frac{-1+7(\omega\tau_B)^2}{60[1+(\omega\tau_B)^2]^2[1+9(\omega\tau_B)^2]} \tag{C.7}$$

$$\frac{\chi''_{33}(\omega)}{\chi_L q} = \frac{-5(\omega\tau_B)+3(\omega\tau_B)^3}{60[1+(\omega\tau_B)^2]^2[1+9(\omega\tau_B)^2]} \tag{C.8}$$

Note that the low-frequency limit $\omega\tau_B \to 0$ recovers the quasi-static result given in Eq. (A.1), $\hat{\chi}_3^{\rm EFA}(0,0,0) = \hat{\chi}_3^{\rm qs} = -\chi_L q/15$ and $\chi''_{31}(0) = \chi''_{33}(0) = 0$. Eqs. (C.7), (C.8) agree with the result obtained in Ref. [24] from a perturbation analysis.

For the case of PS considered in Section 2.4, we find the quadratic contribution to the parallel susceptibility to be given by

$$3\hat{\chi}_3^{\rm EFA}(\omega,0,0) = \hat{\chi}^{\rm qs}\frac{3+i\omega\tau_B}{(1+i\omega\tau_B)^2}. \tag{C.9}$$

The contribution Eq. (C.9) is consistent up to quadratic order in the static field with the familiar expression for the parallel susceptibility within EFA [40],

$$\chi_{||}^{\rm EFA}(\omega,h_0) = \chi_L\frac{3L'(h_0)}{1+i\omega\tau_{||}(h_0)}, \tag{C.10}$$

where $h_0 = \mu H_0/k_BT$, $L'(x)$ the derivative of the Langevin function and the field-dependent parallel relaxation time is given by $\tau_{||}(h) = \tau_B hL'(h)/L(h)$.

Appendix D. Müller and Liu

Based on nonequilibrium thermodynamics, Müller and Liu proposed an alternative magnetization equation with a richer structure [45]. For the present case of longitudinal dynamics, their magnetization equation simplifies to

$$\dot{M} = -\zeta(H_e - H), \tag{D.1}$$

where H_e is the effective field, $\xi_e = \mu H_e/k_BT$. Following Leschhorn and Lücke,[46] we identify their transport coefficient as $\zeta = 3\chi_L/(\tau_B F)$ where $F = L^{-1}(m)/m$. Using the expansion (C.2) of the inverse Langevin function, the magnetization Eq. (D.1) becomes identical to Eq. (C.3) obtained within EFA. Therefore, also the third order nonlinear response of the Müller and Liu equation coincides with Eq. (C.4) obtained from the EFA magnetization Eq. (C.1).

Appendix E. Fokker–Planck equation (FPE) model

E.1. Model definition

In their classical work,[43] Martsenyuk et al. proposed to model the rotational dynamics of individual MNPs on the level of kinetic theory. Let $f(\mathbf{e};t)$ denote the time-dependent probability density of finding the magnetization orientation $\mathbf{e}$ at time t. For non-interacting rigid dipoles, the rotational dynamics is governed by rotational diffusion and the torque due to applied magnetic field fields [43]

$$2\tau_B\frac{\partial}{\partial t}f = -\mathcal{L}\cdot[(\mathbf{e}\times\mathbf{h})f - \mathcal{L}f], \tag{E.1}$$

where $\mathcal{L} \equiv \mathbf{e}\times\partial/\partial\mathbf{e}$ denotes the rotational operator. Several works have investigated the FPE (E.1) using analytical and numerical methods (see e.g. Refs. [21,47,48]). However, we are not aware of comprehensive analytical results of this model for the nonlinear dynamic response. Historically, EFA (see Appendix C) and Sh01 (see Appendix B) were developed to simplify the FPE model.

E.2. Time-dependent perturbation theory

Time-dependent perturbation theory is a powerful method that is frequently used in nonequilibrium statistical mechanics [1]. The general connection of Volterra series with regular perturbation methods has been investigated in Ref. [49].

Consider the time-dependent probability density f that obeys a kinetic equation of the form

$$\frac{\partial}{\partial t} f(t) = (\mathrm{L}_0 + h(t)\mathrm{L}_1) f(t). \tag{E.2}$$

For simplicity of notation, the phase space variable in f is suppressed in the following. In Eq. (E.2), $h(t)$ denotes the time-dependent field. The operators L_0 and L_1 describe the time evolution of the unperturbed system and the influence of an applied field, respectively.

Using the Dyson decomposition, the formal solution to the kinetic Eq. (E.2) from an initial condition $f(t_0)$ at time t_0 up to the current time $t > t_0$ can be written as [1,50]

$$f(t) = e^{(t-t_0)\mathrm{L}_0} f(t_0) + \int_{t_0}^{t} \mathrm{d}t'\, e^{(t-t')\mathrm{L}_0} h(t')\mathrm{L}_1 f(t'). \tag{E.3}$$

Repeatedly substituting the Dyson decomposition on the right hand side of Eq. (E.3) generates a series expansion of the solution,

$$f(t) = \sum_{n=0}^{\infty} f^{(n)}(t), \tag{E.4}$$

with the first member the unperturbed propagation

$$f^{(0)}(t) = e^{(t-t_0)\mathrm{L}_0} f(t_0) \tag{E.5}$$

and the recursion relation

$$f^{(n+1)}(t) = \int_{t_0}^{t} \mathrm{d}t'\, e^{(t-t')\mathrm{L}_0} h(t')\mathrm{L}_1 f^{(n)}(t'). \tag{E.6}$$

Note that the nth member of the series (E.4) obeys $f^{(n)} = \mathcal{O}(h^n)$. Thus, the perturbation series Eq. (E.4) generates a power series in the field h.

For the special case of equilibrium initial conditions of the unperturbed system, $f(t_0) = f_0$ with $\mathrm{L}_0 f_0 = 0$, we find $f^{(0)}(t) = f_0$, i.e. the unperturbed system remains in equilibrium, slightly simplifying the above series.

E.3. Perturbation theory for rigid dipoles

The FPE equation for non-interacting rigid dipoles (E.1) can be represented in the form (E.2) with

$$\mathrm{L}_0 f = \frac{1}{2\tau_\mathrm{B}} \mathscr{L}^2 f \tag{E.7}$$

$$\mathrm{L}_1 f = -\frac{1}{2\tau_\mathrm{B}} \mathscr{L} \cdot [(\mathbf{e} \times \hat{\mathbf{h}}) f], \tag{E.8}$$

where $\hat{\mathbf{h}} = \mathbf{h}/h$ denotes the unit vector in the direction of the magnetic field. For the unperturbed system, L_0 describes free rotational diffusion with the Brownian rotational relaxation time τ_B. The stationary solution for the unperturbed system is the isotropic state, $f_0 = 1/(4\pi)$ with $\mathrm{L}_0 f_0 = 0$. In the presence of a magnetic field, L_1 describes precessional motion.

Substituting Eqs. (E.7) and (E.8) into (E.6) we find the first order contribution given by

$$f^{(1)}(\mathbf{e};t) = \frac{1}{4\pi} \int_{t_0}^{t} \frac{\mathrm{d}t_1}{\tau_\mathrm{B}} e^{-(t-t_1)/\tau_\mathrm{B}} h(t_1) P_1(\mathbf{e}\cdot\hat{\mathbf{h}}), \tag{E.9}$$

with $P_1(x) = x$ the first order Legendre polynomial. Linear response theory is based on Eq. (E.9) as has been employed e.g. in Ref. [47]. The second order contribution is obtained from Eq. (E.6) for $n = 1$ and reads

$$f^{(2)}(t) = \frac{1}{4\pi} \int_{t_0}^{t} \frac{\mathrm{d}t_1}{\tau_\mathrm{B}} \int_{t_0}^{t_1} \frac{\mathrm{d}t_2}{\tau_\mathrm{B}} K_2(t-t_1, t_1-t_2) h(t_1) h(t_2) \tag{E.10}$$

with the two-point kernel function

$$K_2(\tau_1,\tau_2) = e^{-3\tau_1/\tau_\mathrm{B}} e^{-\tau_2/\tau_\mathrm{B}} P_2(\mathbf{e}\cdot\hat{\mathbf{h}}) \tag{E.11}$$

with $P_2(x) = (3x^2-1)/2$ the second order Legendre polynomial. Finally, the third order term obtained from Eq. (E.6) for $n = 2$ becomes

$$f^{(3)}(t) = \frac{1}{4\pi} \int_{t_0}^{t} \frac{\mathrm{d}t_1}{\tau_\mathrm{B}} \int_{t_0}^{t_1} \frac{\mathrm{d}t_2}{\tau_\mathrm{B}} \int_{t_0}^{t_2} \frac{\mathrm{d}t_3}{\tau_\mathrm{B}} K_3(t-t_1, t_1-t_2, t_2-t_3) h(t_1) h(t_2) h(t_3) \tag{E.12}$$

with the three-point kernel function

$$K_3(\tau_1,\tau_2,\tau_3) = e^{-3\tau_2/\tau_\mathrm{B}} e^{-\tau_3/\tau_\mathrm{B}} [6e^{-6\tau_1/\tau_\mathrm{B}} P_3 - e^{-\tau_1/\tau_\mathrm{B}} P_1] \tag{E.13}$$

For ease of notation, we have suppressed the argument $(\mathbf{e}\cdot\hat{\mathbf{h}})$ of the Legendre polynomials P_1 and P_3 in Eq. (E.13). Truncating the expansion (E.4) at $n = 3$ allows us to discuss the third-order nonlinear response to magnetic fields.

With the probability density $f(\mathbf{e};t)$ at hand, the instantaneous magnetization parallel to the field direction can be calculated from

$$M(t) = M_\mathrm{sat} \int (\mathbf{e}\cdot\hat{\mathbf{h}}) f(\mathbf{e};t) \mathrm{d}\mathbf{e}. \tag{E.14}$$

Inserting the expansion (E.4) together with the results (E.9)–(E.12) into Eq. (E.14), the integration over the magnetization orientation can be performed to find

$$M(t) = \frac{1}{3} M_\mathrm{sat} \Bigg[\int_{t_0}^{t} \frac{\mathrm{d}t_1}{\tau_\mathrm{B}} e^{-(t-t_1)/\tau_\mathrm{B}} h(t_1) - \frac{1}{5} \int_{t_0}^{t} \frac{\mathrm{d}t_1}{\tau_\mathrm{B}} \int_{t_0}^{t_1} \frac{\mathrm{d}t_2}{\tau_\mathrm{B}} \int_{t_0}^{t_2} \frac{\mathrm{d}t_3}{\tau_\mathrm{B}} e^{-(t-t_1)/\tau_\mathrm{B}} e^{-3(t_1-t_2)/\tau_\mathrm{B}} e^{-(t_2-t_3)/\tau_\mathrm{B}} h(t_1) h(t_2) h(t_3) + \mathcal{O}(h^5) \Bigg] \tag{E.15}$$

Note that due to orthogonality of Legendre polynomials, terms quadratic in the magnetic field are absent in Eq. (E.15).

To rewrite Eq. (E.15) in the form of the Volterra series (2), we let $t_0 \to -\infty$ and change integration variables from t_j to $\tau_j = t - t_j$ to find the linear susceptibility $\chi_1(t)$ to be given again by Eq. (B.3). It is reassuring that the different models all agree within the linear response regime. For the third-order dynamic susceptibility we find

$$\chi_3^\mathrm{FPE}(\tau_1,\tau_2,\tau_3) = -\frac{\chi_\mathrm{L} q}{5\tau_\mathrm{B}^3} \mathrm{S}\Theta(\tau_1)\Theta(\tau_2-\tau_1)\Theta(\tau_3-\tau_2) e^{-\tau_1/\tau_\mathrm{B}} e^{-3(\tau_2-\tau_1)/\tau_\mathrm{B}} e^{-(\tau_3-\tau_2)/\tau_\mathrm{B}} \tag{E.16}$$

with S the symmetrization operator introduced above.

Performing the Fourier transformation of Eq. (E.16) we find the third-order complex susceptibility for the FPE model to be given by

$$\hat{\chi}_3^\mathrm{FPE}(\omega_1,\omega_2,\omega_3) = \hat{\chi}_3^\mathrm{qs} \mathrm{S}\psi(\omega_3)\psi((\omega_2+\omega_3)/3)\psi(\omega_1+\omega_2+\omega_3) \tag{E.17}$$

where the function $\psi(x)$ was defined above from the Debye model in Eq. (B.5) and S the symmetrization operator introduced in Appendix C. Note the close resemblance of Eq. (E.17) to the EFA result (C.4).

For the special case of MAOF discussed in Section 2.3, the susceptibility governing the third harmonic is obtained from Eq. (E.17) as

$$\frac{\chi'_{31}(\omega)}{\chi_\mathrm{L} q} = \frac{-27 + 13(\omega\tau_\mathrm{B})^2}{60[1+(\omega\tau_\mathrm{B})^2]^2[9+4(\omega\tau_\mathrm{B})^2]} \tag{E.18}$$

$$\frac{\chi''_{31}(\omega)}{\chi_\mathrm{L} q} = -\frac{42(\omega\tau_\mathrm{B}) + 2(\omega\tau_\mathrm{B})^3}{60[1+(\omega\tau_\mathrm{B})^2]^2[9+4(\omega\tau_\mathrm{B})^2]} \tag{E.19}$$

$$\frac{\chi'_{33}(\omega)}{\chi_\mathrm{L} q} = \frac{-3 + 17(\omega\tau_\mathrm{B})^2}{20[1+(\omega\tau_\mathrm{B})^2][9+4(\omega\tau_\mathrm{B})^2][1+9(\omega\tau_\mathrm{B})^2]} \tag{E.20}$$

$$\frac{\chi''_{33}(\omega)}{\chi_\mathrm{L} q} = \frac{-14\omega\tau_\mathrm{B} + 6(\omega\tau_\mathrm{B})^3}{20[1+(\omega\tau_\mathrm{B})^2][9+4(\omega\tau_\mathrm{B})^2][1+9(\omega\tau_\mathrm{B})^2]}. \tag{E.21}$$

Eqs. (E.20) and (E.21) agree with the result obtained in Ref. [23] via a different method.

For the case of PS considered in Section 2.4, we find

$$3\hat{\chi}_3^{\rm FPE}(\omega,0,0) = \hat{\chi}^{\rm qs}\frac{9-(\omega\tau_{\rm B})^2+7i\omega\tau_{\rm B}}{(1+i\omega\tau_{\rm B})^2(3+i\omega\tau_{\rm B})}. \tag{E.22}$$

Note that this result looks qualitatively different from the one obtained within EFA, Eq. (C.9). Nevertheless, both equations give rather similar results, see Fig. 2.

Appendix F. Immobile and magnetically hard MNPs

The stochastic Landau–Lifshitz–Gilbert equation is often considered the most appropriate model for the magnetization dynamics of immobile MNPs [37]. However, for magnetically hard MNPs, the huge time scale separation makes this model very impractical for numerical as well as analytical studies. Raikher and Stepanov, for example, proposed an ad hoc approximation to the third order MAOF susceptibility $\hat{\chi}_{33}$ to simplify the lengthy and cumbersome expressions [23].

Here, instead, we consider simplified models in terms of jump processes that can be simulated efficiently via Monte-Carlo methods (see e.g. [38,39] and references therein). If $p_\pm(t)$ denote the probability that the magnetization of a given MNP is oriented parallel/anti-parallel to its easy axis, these approaches postulate a simple rate equation of the form $\dot{p}_+ = r_- p_- - r_+ p_+$. The coefficients $r_\pm$ denote the rate with which the magnetization reverses. Assuming thermal activation with Arrhenius rates and using $p_+(t)+p_-(t)=1$, the magnetization equation reads [35]

$$\tau_{\rm N}\dot{m} = -m\cosh(h(t)) + \sinh(h(t)). \tag{F.1}$$

In this section, $h(t)$ denotes the projection of the instantaneous dimensionless magnetic field on the (frozen) easy axis orientation.

The magnetization Eq. (F.1) can formally be solved for any field $h(t)$,

$$m(t) = m(0)e^{-g(t)} + \int_0^t e^{-(g(t)-g(t'))}\sinh(h(t'))\frac{{\rm d}t'}{\tau_{\rm N}} \tag{F.2}$$

with $g(t) = \int_0^t \cosh(h(t')){\rm d}t'/\tau_{\rm N}$. Expanding this expression for weak fields, we can write the magnetization response in the form (2) with an exponential decay for the linear susceptibility,

$$\chi_1(t) = \Theta(t)\frac{1}{\tau_{\rm N}}e^{-t/\tau_{\rm N}}, \tag{F.3}$$

and the third order non-linear susceptibility

$$\chi_3^{\rm MC}(\tau_1,\tau_2,\tau_3) = \chi_1(\tau_1)\delta(\tau_3-\tau_2)\left[\frac{1}{6}\delta(\tau_2-\tau_1) - \frac{1}{2\tau_{\rm N}}\Theta(\tau_2)\Theta(\tau_1-\tau_2)\right]. \tag{F.4}$$

The linear susceptibility (F.3) is given again by a Debye law

$$\hat{\chi}_1(\omega) = \frac{3\chi_{\rm L}}{1+i\omega\tau_{\rm N}}, \tag{F.5}$$

formally identical to Eq. (B.5) with the characteristic relaxation time given by $\tau_{\rm N}$. Note the extra factor 3 in the nominator compared to Eq. (B.5). Eq. (F.5) applies to samples with their easy axis perfectly aligned with the applied magnetic field. For randomly oriented MNPs, an additional average over the random axis orientations needs to be performed. Therefore, the relevant amplitudes of the magnetic field are reduced by a corresponding factor.

Fourier transforming Eq. (F.4), we obtain the third order nonlinear susceptibility for this model in the form

$$\hat{\chi}_3^{\rm MC}(\omega_1,\omega_2,\omega_3) = \frac{1}{2}\chi_{\rm L}q\frac{1-3{\rm S}[1+i\omega_1\tau_{\rm N}]^{-1}}{1+i(\omega_1+\omega_2+\omega_3)\tau_{\rm N}}. \tag{F.6}$$

Note that the quasi-static response is given by $\hat{\chi}_3^{\rm MC}(0,0,0) = -\chi_{\rm L}q$, a factor 15 larger than for the mobile case since the response is not tied to the Langevin magnetization law.

Using Eqs. (18), (19), the third order susceptibilities for MAOF predicted by this model read

$$\chi'_{33}(\omega) = -\frac{\chi_{\rm L}q}{8}\frac{2-10(\omega\tau_{\rm N})^2}{[1+(\omega\tau_{\rm N})^2][1+9(\omega\tau_{\rm N})^2]} \tag{F.7}$$

$$\chi''_{33}(\omega) = -\frac{\chi_{\rm L}q}{8}\frac{\omega\tau_{\rm N}(9-3(\omega\tau_{\rm N})^2)}{[1+(\omega\tau_{\rm N})^2][1+9(\omega\tau_{\rm N})^2]} \tag{F.8}$$

These formulae are very similar to the ad hoc approximation proposed in Ref. [23], with only small differences in the numerical prefactors in the nominators.

We also note that the quadratic contribution to the PS parallel susceptibility

$$3\hat{\chi}_3^{\rm MC}(\omega,0,0) = -\frac{3}{2}\chi_{\rm L}q\frac{2+i\omega\tau_{\rm N}}{(1+i\omega\tau_{\rm N})^2} \tag{F.9}$$

is formally very similar to Eq. (C.9) derived for thermally blocked MNPs.

References

[1] R. Kubo, M. Toda, N. Hashitsume, Statistical Physics II, in: Springer Series in Solid-State Sciences, vol. 31, Springer Berlin Heidelberg, 1991, http://dx.doi.org/10.1007/978-3-642-58244-8, URL http://link.springer.com/10.1007/978-3-642-58244-8.

[2] J.-L. Barrat, J.-P. Hansen, Basic Concepts for Simple and Complex Liquids, Cambridge University Press, 2003.

[3] S. Odenbach (Ed.), Colloidal Magnetic Fluids, in: Lecture Notes in Phys, vol. 763, Springer, Berlin, 2009.

[4] J. Tafur, A.P. Herrera, C. Rinaldi, E.J. Juan, Development and validation of a 10 kHz–1 MHz magnetic susceptometer with constant excitation field, J. Appl. Phys. 111 (7) (2012) 07E349, http://dx.doi.org/10.1063/1.3680200, URL https://pubs.aip.org/jap/article/111/7/07E349/391396/Development-and-validation-of-a-10-kHz-1-MHz.

[5] R.M. Ferguson, A.P. Khandhar, C. Jonasson, J. Blomgren, C. Johansson, K.M. Krishnan, Size-dependent relaxation properties of monodisperse magnetite nanoparticles measured over seven decades of frequency by AC susceptometry, IEEE Trans. Magn. 49 (7) (2013) 3441–3444.

[6] J.D. Hilgar, A.K. Butts, J.D. Rinehart, A method for extending AC susceptometry to long-timescale magnetic relaxation, Phys. Chem. Chem. Phys. 21 (40) (2019) 22302–22307, http://dx.doi.org/10.1039/C9CP03936H, URL https://xlink.rsc.org/?DOI=C9CP03936H.

[7] Kritika I. Roy, Therapeutic applications of magnetic nanoparticles: recent advances, Mater. Adv. 3 (20) (2022) 7425–7444, http://dx.doi.org/10.1039/D2MA00444E, URL http://xlink.rsc.org/?DOI=D2MA00444E.

[8] V. Socoliuc, M.V. Avdeev, V. Kuncser, R. Turcu, E. Tombácz, L. Vékás, Ferrofluids and bio-ferrofluids: looking back and stepping forward, Nanoscale 14 (13) (2022) 4786–4886, http://dx.doi.org/10.1039/D1NR05841J, URL http://xlink.rsc.org/?DOI=D1NR05841J.

[9] A. Coene, J. Leliaert, Magnetic nanoparticles in theranostic applications, J. Appl. Phys. 131 (16) (2022) 160902, http://dx.doi.org/10.1063/5.0085202, URL https://pubs.aip.org/jap/article/131/16/160902/2836759/Magnetic-nanoparticles-in-theranostic-applications.

[10] V.F. Cardoso, A. Francesko, C. Ribeiro, M. Bañobre-López, P. Martins, S. Lanceros-Mendez, Advances in magnetic nanoparticles for biomedical applications, Adv. Healthc. Mater. 7 (5) (2017) http://dx.doi.org/10.1002/adhm.201700845, 1700845–35, publisher: John Wiley & Sons, Ltd. URL http://doi.wiley.com/10.1002/adhm.201700845.

[11] J. Kudr, Y. Haddad, L. Richtera, Z. Heger, M. Cernak, V. Adam, O. Zitka, Magnetic nanoparticles: From design and synthesis to real world applications, Nanomaterials 7 (9) (2017) 243, http://dx.doi.org/10.3390/nano7090243, URL http://www.mdpi.com/2079-4991/7/9/243.

[12] K. Wu, D. Su, R. Saha, J. Liu, V.K. Chugh, J.-P. Wang, Magnetic particle spectroscopy: A short review of applications using magnetic nanoparticles, ACS Appl. Nano Mater. 3 (6) (2020) 4972–4989, http://dx.doi.org/10.1021/acsanm.0c00890, URL https://pubs.acs.org/doi/10.1021/acsanm.0c00890.

[13] K. Buchkov, A. Galluzzi, E. Nazarova, M. Polichetti, Complex AC magnetic susceptibility as a tool for exploring nonlinear magnetic phenomena and pinning properties in superconductors, Materials 16 (14) (2023) 4896, http://dx.doi.org/10.3390/ma16144896, URL https://www.mdpi.com/1996-1944/16/14/4896.

[14] A.O. Ivanov, P.J. Camp, Theory of the dynamic magnetic susceptibility of ferrofluids, Phys. Rev. E 98 (5) (2018) 050602, URL https://link.aps.org/doi/10.1103/PhysRevE.98.050602.

[15] T. Bitoh, K. Ohba, M. Takamatsu, T. Shirane, S. Chikazawa, Comparative study of linear and nonlinear susceptibilities of fine-particle and spin-glass systems: quantitative analysis based on the superparamagnetic blocking model, J. Magn. Magn. Mater. 154 (1) (1996) 59–65, http://dx.doi.org/10.1016/0304-8853(95)00572-2, URL https://linkinghub.elsevier.com/retrieve/pii/0304885395005722.

[16] P. Jönsson, T. Jonsson, J. García-Palacios, P. Svedlindh, Nonlinear dynamic susceptibilities of interacting and noninteracting magnetic nanoparticles, J. Magn. Magn. Mater. 222 (1) (2000) 219–226, http://dx.doi.org/10.1016/S0304-8853(00)00557-6, URL https://linkinghub.elsevier.com/retrieve/pii/S0304885300005576.
[17] G. Wang, J. Huang, Nonlinear magnetic susceptibility of ferrofluids, Chem. Phys. Lett. 421 (4) (2006) 544–548, http://dx.doi.org/10.1016/j.cplett.2006.02.010, URL https://linkinghub.elsevier.com/retrieve/pii/S0009261406001874.
[18] B. Horváth, P. Decsi, I. Szalai, Nonlinear contributions to the dynamic magnetic susceptibility of magnetic fluids, J. Mol. Liq. 359 (2022) 119279, http://dx.doi.org/10.1016/j.molliq.2022.119279, URL https://linkinghub.elsevier.com/retrieve/pii/S0167732222008170.
[19] T. Yoshida, K. Enpuku, Simulation and quantitative clarification of ac susceptibility of magnetic fluid in nonlinear brownian relaxation region, Japan. J. Appl. Phys. 48 (2009) 127002, URL https://iopscience.iop.org/article/10.1143/JJAP.48.127002.
[20] M.S. Rusanov, V.S. Zverev, E.A. Elfimova, Dynamic magnetic susceptibility of a ferrofluid: The influence of interparticle interactions and ac field amplitude, Phys. Rev. E 104 (4) (2021) 044604, http://dx.doi.org/10.1103/PhysRevE.104.044604, URL https://link.aps.org/doi/10.1103/PhysRevE.104.044604.
[21] A.A. Kuznetsov, A.F. Pshenichnikov, Nonlinear response of a dilute ferrofluid to an alternating magnetic field, J. Mol. Liq. 346 (2022) 117449, http://dx.doi.org/10.1016/j.molliq.2021.117449, URL https://linkinghub.elsevier.com/retrieve/pii/S0167732221021735.
[22] P. Ilg, Nonequilibrium response of magnetic nanoparticles to time–varying magnetic fields: contributions from Brownian and Néel processes, Phys. Rev. E 109 (2024) 034603, http://dx.doi.org/10.1103/PhysRevE.109.034603.
[23] Y.L. Raikher, V.I. Stepanov, Linear and cubic dynamic susceptibilities of superparamagnetic fine particles, Phys. Rev. B 55 (22) (1997) 15005–15017, http://dx.doi.org/10.1103/PhysRevB.55.15005, URL https://link.aps.org/doi/10.1103/PhysRevB.55.15005.
[24] Y.L. Raikher, V.I. Stepanov, Linear and nonlinear superparamagnetic relaxation at high anisotropy barriers, Phys. Rev. B 66 (21) (2002) 214406, http://dx.doi.org/10.1103/PhysRevB.66.214406, URL https://link.aps.org/doi/10.1103/PhysRevB.66.214406.
[25] K.R. Lennon, G.H. McKinley, J.W. Swan, Medium amplitude parallel superposition (MAPS) rheology. part 1: Mathematical framework and theoretical examples, J. Rheol. 64 (3) (2020) 551–579, http://dx.doi.org/10.1122/1.5132693, URL https://pubs.aip.org/sor/jor/article/64/3/551-579/241632.
[26] S. Boyd, L. Chua, Fading memory and the problem of approximating nonlinear operators with volterra series, IEEE Trans. Circuits Syst. 32 (11) (1985) 1150–1161, http://dx.doi.org/10.1109/TCS.1985.1085649, URL http://ieeexplore.ieee.org/document/1085649/.
[27] M.O. Franz, B. Schölkopf, A unifying view of wiener and volterra theory and polynomial kernel regression, Neural Comput. 18 (12) (2006) 3097–3118, http://dx.doi.org/10.1162/neco.2006.18.12.3097, URL https://direct.mit.edu/neco/article/18/12/3097-3118/7117.
[28] C. Cheng, Z. Peng, W. Zhang, G. Meng, Volterra-series-based nonlinear system modeling and its engineering applications: A state-of-the-art review, Mech. Syst. Signal Process. 87 (2017) 340–364, http://dx.doi.org/10.1016/j.ymssp.2016.10.029, URL https://linkinghub.elsevier.com/retrieve/pii/S0888327016304393.
[29] S. Boyd, L.O. Chua, C.A. Desoer, Analytical foundations of volterra series, IMA J. Math. Control Inf. 1 (3) (1984) 243–282, http://dx.doi.org/10.1093/imamci/1.3.243, URL https://academic.oup.com/imamci/article-lookup/doi/10.1093/imamci/1.3.243.
[30] J. Dieckhoff, D. Eberbeck, M. Schilling, F. Ludwig, Magnetic-field dependence of Brownian and Néel relaxation times, J. Appl. Phys. 119 (4) (2016) 043903, URL http://aip.scitation.org/doi/10.1063/1.4940724.
[31] M. Küster, H. Nádasi, A. Eremin, P.H. Boštjančič, F. Ludwig, Magnetic-field dependence of the magnetic dynamics of barium hexaferrite nanoplatelet suspensions, J. Magn. Magn. Mater. 588 (2023) 171368, http://dx.doi.org/10.1016/j.jmmm.2023.171368, URL https://linkinghub.elsevier.com/retrieve/pii/S0304885323010181.
[32] F. Bergmann, M. Letz, H. Maune, G. Jakob, Description of intermodulation generation of nonlinear responses beyond the validity of the power series expansion, Appl. Phys. Lett. 118 (1) (2021) 012902, http://dx.doi.org/10.1063/5.0034697, URL https://pubs.aip.org/aip/apl/article/118/1/012902/39889/Description-of-intermodulation-generation-of.
[33] K. Murase, H. Takata, Y. Takeuchi, S. Saito, Control of the temperature rise in magnetic hyperthermia with use of an external static magnetic field, Phys. Medica 29 (6) (2013) 624–630, http://dx.doi.org/10.1016/j.ejmp.2012.08.005, URL https://linkinghub.elsevier.com/retrieve/pii/S1120179712001287.
[34] C.M. Lucaciu, S. Nitica, I. Fizesan, L. Filip, L. Bilteanu, C. Iacovita, Enhanced magnetic hyperthermia performance of zinc ferrite nanoparticles under a parallel and a transverse bias DC magnetic field, Nanomaterials 12 (20) (2022) 3578, http://dx.doi.org/10.3390/nano12203578, URL https://www.mdpi.com/2079-4991/12/20/3578.
[35] P. Ilg, M. Kröger, Longest relaxation time versus maximum loss peak in the field-dependent longitudinal dynamics of suspended magnetic nanoparticles, Phys. Rev. B 106 (13) (2022) 134433, http://dx.doi.org/10.1103/PhysRevB.106.134433, URL https://link.aps.org/doi/10.1103/PhysRevB.106.134433.
[36] T. Yoshida, K. Enpuku, Field-dependent Néel relaxation time of magnetic nanoparticles in AC excitation fields: Boundary field between Néel- and Brownian-dominant regions, J. Appl. Phys. 135 (9) (2024) 093901, http://dx.doi.org/10.1063/5.0192306, URL https://pubs.aip.org/jap/article/135/9/093901/3268017/Field-dependent-Neel-relaxation-time-of-magnetic.
[37] T. Gilbert, Classics in magnetics a phenomenological theory of damping in ferromagnetic materials, IEEE Trans. Magn. 40 (6) (2004) 3443–3449, http://dx.doi.org/10.1109/TMAG.2004.836740, URL http://ieeexplore.ieee.org/document/1353448/.
[38] J. Carrey, B. Mehdaoui, M. Respaud, Simple models for dynamic hysteresis loop calculations of magnetic single-domain nanoparticles: Application to magnetic hyperthermia optimization, J. Appl. Phys. 109 (8) (2011) 083921, URL http://aip.scitation.org/doi/10.1063/1.3551582.
[39] P. Ilg, Diffusion-jump model for the combined Brownian and Néel relaxation dynamics of ferrofluids in the presence of external fields and flow, Phys. Rev. E 100 (2) (2019) 022608, http://dx.doi.org/10.1103/PhysRevE.100.022608.
[40] Y.L. Raikher, M.I. Shliomis, The effective field method in the orientational kinetics of magnetic fluids, in: W.T. Coffey (Ed.), Relaxation Phenomena in Condensed Matter, in: Advances in Chemical Physics, vol. 87, John Wiley & Sons, 1994, p. 595.
[41] M.I. Shliomis, Effective viscosity of magnetic suspensions, Sov. Phys.—JETP 34 (6) (1972) 1291–1294.
[42] M.I. Shliomis, Ferrohydrodynamics: Testing a third magnetization equation, Phys. Rev. E 64 (2001) 060501, URL https://link.aps.org/doi/10.1103/PhysRevE.64.060501.
[43] M.A. Martsenyuk, Y.L. Raikher, M.I. Shliomis, On the kinetics of magnetization of suspension of ferromagnetic particles, Zh. Eksp. Teor. Fiz. 65 (1973) 834, URL http://www.jetp.ras.ru/cgi-bin/dn/e_038_02_0413.pdf; Sov. Phys. JETP 38 (1974) 413.
[44] W. Kuhn, F. Grün, Beziehungen zwischen elastischen Konstanten und Dehnungsdoppelbrechung hochelastischer Stoffe, Kolloid-Zeitschrift 101 (3) (1942) 248–271, http://dx.doi.org/10.1007/BF01793684, URL http://link.springer.com/10.1007/BF01793684.
[45] H.W. Müller, M. Liu, Structure of ferrofluid dynamics, Phys. Rev. E 64 (2001) 061405, URL http://pre.aps.org/abstract/PRE/v64/i6/e061405.
[46] A. Leschhorn, M. Lücke, Magnetization of rotating ferrofluids: Predictions of different theoretical models, Z. Phys. Chem. 220 (2) (2006) 219–224, http://dx.doi.org/10.1524/zpch.2006.220.2.219, URL https://www.degruyter.com/document/doi/10.1524/zpch.2006.220.2.219/html.
[47] P. Ilg, M. Kröger, S. Hess, Magnetoviscosity and orientational order parameters of dilute ferrofluids, J. Chem. Phys. 116 (20) (2002) 9078–9088, URL http://scitation.aip.org/content/aip/journal/jcp/116/20/10.1063/1.1473656.
[48] J.H. Sánchez, C. Rinaldi, Magnetoviscosity of dilute magnetic fluids in oscillating and rotating magnetic fields, Phys. Fluids 22 (4) (2010) 043304, http://dx.doi.org/10.1063/1.3370119, URL http://aip.scitation.org/doi/10.1063/1.3370119.
[49] X.-J. Dong, Z.-K. Peng, W.-M. Zhang, G. Meng, Connection between volterra series and perturbation method in nonlinear systems analyses, Acta Mech. Sin. 30 (4) (2014) 600–606, http://dx.doi.org/10.1007/s10409-014-0010-4, URL http://link.springer.com/10.1007/s10409-014-0010-4.
[50] D.J. Evans, G. Morriss, Statistical Mechanics of Nonequilibrium Liquids, second ed., Cambridge University Press, Cambridge, 2008.