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Magnetic relaxation in ferronematics in the mean-field description

Yu.L. Raikher[a,b,*], V.I. Stepanov[a]

[a] Institute of Continuous Media Mechanics — the Division of Perm Federal Research Center, Russian Academy of Sciences, Ural Branch, Perm 614013, Russia
[b] Institute of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg 620083, Russia

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ABSTRACT

We demonstrate that a ferronematic (a dilute suspension of ferromagnet nanoparticles in a nematogenic matrix) may display a direct analog of Néel superparamagnetism entailed by the orienting effect of the matrix on the embedded particles. The latter are assumed to be the objects with pronounced anisometricity; in magnetic aspect, they are single-domains with strong magnetic hardness (e.g. imposed by their rod-like shape) so that the magnetic moment is fixed inside the particle body. Above the isotropic–nematic transition point, the considered system is just a ferrofluid with random distribution of the particle axes. Below the transition, the particle–matrix coupling emerges that sets the axis of each particle (and, hence, its magnetic moment) under the same angle to the director. If this alignment is along the director, then each particle falls under the action of orientational potential with two equal wells (0° and 180°) separated by the energy barrier whose height is defined by the intensity of the surface particle–matrix interaction. Provided the thermal energy is of the order of the barrier height (the material estimates readily admit that), the Brownian motion makes the particle to randomly rotate between the orientational minima. This mechanism entails spontaneous inversions of the magnetic moment as well, thus ensuring relaxation of any initially established magnetization of the ferronematic; the reference time of this process depends exponentially on the hight of the energy barrier scaled with thermal energy. Treating the nematogenic matrix with the aid of mean field model and using the linear response theory to describe the magnetodynamics of the particles, we show that the "liquid-crystalline" superparamagnetism produces an easily identifiable signature in the dynamic magnetic susceptibility spectrum of a ferronematic.

To memory of Yuriy Reznikov who had a flawless intuition in posing the problems which are really worth of being solved.

1. Introduction

1.1. Ferronematic composites

A possibility to produce dispersions of magnetic nanoparticles (MNP) in nematic liquid crystals (NLC) – the so-called ferronematics (FNs) – had been clairvoyantly predicted by Brochard and de Gennes [1]. These composites bring together the strong magnetism of MNPs with the intense and flexible optical response of NLCs to orientational deformations. Nowadays, when synthesis of thermotropic FNs ceased to be an exotic occurrence, see, Refs. [2–7], for example, the detailed investigation of their properties is the matter of not only fundamental but of direct practical interest. However, if to take a general look at the topical research work, it becomes evident that the main effort is exerted on the studies of equilibrium properties of FNs while their dynamic properties stay virtually untouched. Because of that, the time-dependent magnetic response of FNs is yet a poorly known subject. Meanwhile, besides the vital importance of this issue for predicting functioning of FN cells, it might become interesting, for example, with respect to microrheology of the carrier NLC matrices. This is the more so, that when the matrix is in the nematic phase, any motion of the embedded particles affects the orientational state of the matrix and vice versa.

Hereby, we develop a model approach to describe the magnetodynamic response of FNs to an AC field. In a pure macroscopic framework the issue was addressed in Ref. [8] for the systems where thermal fluctuations of the particle orientations are negligible. Besides, only the nematic phase state was considered. The leading line of this work is to point out a close analogy between the Néel mechanism of internal superparamagnetic relaxation in a ferromagnet nanoparticle and the behavior of fine magnetically hard particles (magnetic dipoles) embedded in and interacting with the NLC matrix. Thermal fluctuations of the particles are taken into account both

* Corresponding author.
E-mail address: raikher@icmm.ru (Y. Raikher).

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above and below the isotropic-nematic transition point. The manifestations of this "liquid-crystalline" superparamagnetism on the dynamic magnetic response of a FN are presented and analyzed.

1.2. Néel superparamagnetism

The Néel superparamagnetism results from the action of thermal fluctuations on the magnetic moment $\boldsymbol{\mu}$ of a single-domain particle. A brief outline of the basic effect is as follows. Consider a single-domain particle of a ferromagnet fixed inside a solid matrix. The inner magnetic anisotropy of this particle is of the easy-axis type with unit vectors $\boldsymbol{n}$ and $-\boldsymbol{n}$ denoting the two equivalent minima of orientation-dependent part of the magnetic energy. In the angular space, those minima are separated by the potential barrier of height $E_A^{(m)}$ equidistant from the minima. At zero temperature and in the absence of external field, vector $\boldsymbol{\mu}$, once having been set along one of the two possible directions of the anisotropy axis (e.g. $\boldsymbol{\mu} \parallel \boldsymbol{n}$), always remains there: the energy barrier forbids $\boldsymbol{\mu}$ to switch to energetically equivalent position $-\boldsymbol{n}$ whatever $E_A^{(m)}$.

At finite temperatures, where thermal fluctuations are ever present, the situation changes. There always exists some non-zero probability that a portion of energy "lended" to the magnetic moment by a fluctuation would exceed $E_A^{(m)}/kT$. Due to that, the magnetic moment would surmount the anisotropy barrier, assume the inverse orientation $\boldsymbol{\mu} \parallel -\boldsymbol{n}$, and keep it until a next sufficiently intense fluctuation comes to drive it back to $\boldsymbol{n}$. Apparently, the higher the temperature, the more frequently vector $\boldsymbol{\mu}$ would change its direction.

From the magnetic viewpoint, such re-orientation of $\boldsymbol{\mu}$ means spontaneous magnetic switching in a mechanically quiescent particle. As soon as the average time lapse $\langle \Delta t \rangle$ between the switchings becomes much shorter than the reference time of the measuring device, the particle would seem non-magnetized despite that microscopically it remains a piece of ferromagnet where all the spins are coupled and co-aligned by the exchange interaction. This effect is widely known since 1950's under the name of *superparamagnetism*. The term reflects the fact that such objects at frequencies $\omega < 1/\langle \Delta t \rangle$ respond to an applied field as true paramagnets: they possess no remanence and their magnetic susceptibility obeys the Curie law $\chi \propto 1/T$. The only difference is that the magnetic moment of a nanoparticle is 10^4–10^5 times greater than in any atomic or molecular paramagnet.

As the magnetic anisotropy energy $E_A^{(m)}$ is proportional to the nanoparticle volume (or surface), superparamagnetism is not relevant for the objects of micron size or greater since for them the ratio $E_A^{(m)}/kT$ is high, and the expectation time of magnetic switching, being proportional to $\exp(E_A^{(m)}/kT)$ is huge. On the other hand, this thermofluctuational process strongly affects the magnetodynamic properties of finely disperse ferromagnets because in nanoparticles the ratio $E_A^{(m)}/kT$ becomes small (few units or less) at the temperatures which are far below the Curie point .

1.3. "Superparamagnetism" of FN

Our goal is to show that in FNs there might exist an effect that is a close analog of the Néel superparamagnetism of nanoparticles. To justify this inference, it suffices to refer to two essential features of the FNs. First, due to their pronounced anisometricity, the embedded particles possess substantial shape magnetic anisotropy. This means that in each particle vector $\boldsymbol{\mu}$ is tightly attached to a certain internal geometric axis, so that under small-to-moderate AC fields, and, apparently, in the absence of the latter, the magnetic moment can move only together with the particle body. Second, in the nematic state of the matrix, its interaction with the particle is anisotropic, so that the angular minima of that energy single out stable orientations of the particle axis with respect to the matrix director $\boldsymbol{n}$.

To provide a simple example, let us assume that the particle is rod-like, and the minima of the particle–matrix coupling correspond to alignment of the particle axis (and its magnetic moment $\boldsymbol{\mu}$) with the matrix director $\boldsymbol{n}$. Evidently, in the absence of external magnetic field the symmetry of the nematic requires that the positions of the particle with $\boldsymbol{\mu} \parallel \boldsymbol{n}$ and $\boldsymbol{\mu} \parallel -\boldsymbol{n}$ are equivalent, so that the respective energy wells (minima) have equal depths. In the angle space, those minima are separated by a potential barrier, whose summit corresponds to transverse orientation $\boldsymbol{\mu} \perp \boldsymbol{n}$ while its height E_A depends on the strength of the particle–matrix interaction.

Therefore, the orientation energy of a magnetically hard particle embedded in an NLC is a direct analog of the above-described double-well potential of internal uniaxial magnetic anisotropy experienced by the magnetic moment of a Néel particle. If the reference energy E_A ranges a few kT units, the Brownian motion should induce orientational diffusion of the particle, its body and magnetic moment altogether. The superparamagnetism of FNs should explicitly manifest itself in their response to a probing AC field. Moreover, as E_A disappears in the isotropic state, the dynamic magnetic susceptibility of the composite should change substantially on passing the transition point.

In below, in Sections 2 and 3 we define the macroscopic order parameters and magnetization of the FN and derive the expression for single-particle energy in the mean field approximation. In Section 4, on the basis of this energy, the Fokker-Planck-like (rotary diffusion) kinetic equation is derived describing the time-dependent thermofluctuational motion of the particle in the presence of external magnetic field. In Section 5, this equation is solved and the dynamic magnetic susceptibility $\chi(\omega)$ of a FN is obtained. The low-frequency approximation for $\chi(\omega)$ that reveals the quasi-Néel behavior of the FN is presented in Section 6. There the reference values of material parameters typical for FNs are estimated and a qualitative discussion of the predicted effect is given. The detailed description and plots of the temperature dependence of the dynamic magnetic susceptibility of a FN with positive coupling parameter, i.e., the one that ensures alignment of prolate particles with the director, are given in Section 7. The concluding Section 8 renders a synopsis of the results with regard to a single known to us experiment on AC probing of a thermotropic FN.

2. Orientational order parameters of the ferronematic

We consider a FN as a stable dilute suspension of magnetic grains of anisometric shape in a nematogenic medium. As both components of this binary mixture are capable of uniaxial orientational alignment, we introduce for each elementary unit (molecule or particle) a unit vector $\boldsymbol{\nu}$ of its major axis that makes angle ϑ with the direction of the macroscopic orientation and define the macroscopic order parameters of the components as

$$\langle P_2(\vartheta_\alpha)\rangle_\alpha = 2\pi \int_0^\pi W^{(\alpha)}(\vartheta_\alpha) \cdot P_2(\cos\vartheta_\alpha) \sin\vartheta_\alpha \quad d\vartheta_\alpha, \tag{1}$$

where the second Legendre polynomial depends on the respective angle and is averaged over it with the corresponding distribution function W_α. The subscript α in Eq. (1) is either m (molecule) or p (particle); however, for brevity, in what follows index m would be omitted.

Therefore, the scalar orientational order parameters of the FN components are

$$\eta = \langle P_2(\cos\vartheta)\rangle, \quad \text{and} \quad Q = \langle P_2(\cos\vartheta_p)\rangle_p, \tag{2}$$

for the molecules and ferroparticles, respectively; the absence/presence of index alongside the brackets denotes the distribution function which is used in the respective averaging.