Profile of an inhomogeneously broadened NMR line in a dilute system of monopoles

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The profile of an NMR line is calculated for the case when the inhomogeneous field can be represented as the field generated by randomly distributed magnetic charges. It is shown that magnetic suspensions in an external field exhibit structure described by this model. The good agreement between the computed and measured line profiles allows the geometric parameters of the structure to be determined.

1. INTRODUCTION

The problem of an inhomogeneously broadened magnetic resonance line in magnetically dilute systems,[1] in which the spatially inhomogeneous magnetic field is produced by randomly distributed magnetic dipoles (paramagnetic centers), is well known in NMR and EPR. By magnetically dilute we mean a system described by a lattice model with a small fraction of sites occupied by magnetic impurities or, equivalently, a continuum model with point sources of the field. In the low-density limit the spatial correlations arising in the distribution of separate magnetic centers due to the presence of the excluded volume become weak and it can be assumed that the magnetic impurities are distributed statistically independently of one another, which simplifies the problem. This problem can be solved for the case of a dilute system of dipoles by Anderson's statistical method.[1] The profile of the magnetic resonance line is found to be a Lorentzian whose width is proportional to the concentration of magnetic centers.

This result is applicable not only to magnetic resonance spectroscopy but also other types of spectroscopy, and the field which results in shifts of the resonance frequencies can be of any nature—electric or, as in the case of, for example, NQR or IR spectroscopy, mechanical stresses generated by point defects in the crystal lattice.[2] The profile of an inhomogeneously broadened line depends strongly on how the field decays away from the source. This is most easily seen in the high-frequency asymptotic behavior of the line profile $I(\omega)$. Let the frequency shift decrease away from an isolated source as $r^{-\alpha}$ (the angular dependence in this case is unimportant). Since isolated, close sources make the main contribution in the line wing, it can be assumed that $I(\omega)d\omega \propto r^2dr$, whence

$$I(\omega) \propto \omega^{-(3/\alpha+1)}. \tag{1}$$

For dipoles ($\alpha=3$) we obtain the Lorentzian asymptotic frequency behavior $I(\omega) \sim \omega^{-2}$.

In the present paper the line profile is calculated for the case when the field generated by the sources is coulombic, r^{-2}. As one can see from Eq. (1), in this case the asymptotic behavior is of the form $I(\omega) \propto \omega^{-5/2}$. A possible realization of this situation in magnetic resonance is a diamagnetic matrix with a low volume fraction of the ferromagnetic material, distributed in the form of long thin rods ($L/d \gg 1$, where L is the length and d is the diameter) magnetized along the long axis. For $L^3n \gg 1$ (n is the rod concentration) and a random arrangement of the rods the magnetic field dispersed in the matrix is identical to the magnetic field of randomly distributed magnetic charges (monopoles) pinned to the ends of the rods. The results of an experimental study of this system are presented in the final section of this paper.

2. CALCULATION OF THE LINE PROFILE

Consider a system of magnetic charges m_i, randomly distributed in space. The line profile is determined by the distribution function of the resonance frequencies. For magnetic resonance in a strong field only the projection of the local field on the external field leads to a frequency shift. Let the external field be oriented along the z axis. Then we must calculate the spatial distribution function of the z component of the local field $\mathbf{h}=\Sigma\mathbf{h}_i$, $\mathbf{h}_i=m_i\mathbf{r}_i/|\mathbf{r}_i|^3$. This is equivalent to calculating the distribution averaged over the configurations of the system at a prescribed point. Magnetic neutrality implies that the prescribed point can be taken as the origin of coordinates.

A similar problem was investigated in detail by Chandrasekhar[3] in connection with the calculation of the distribution of the gravitational field in a system of stars. Chandrasekhar found that the distribution function of the magnitude of the field is

$$W(|\mathbf{h}|)=H(|\mathbf{h}|/h_N)/h_N, \tag{2}$$

where $H(y)$ is the Holtzmark distribution

$$H(y)=\frac{2}{\pi y}\int_0^\infty \exp[-(x/y)^{3/2}]x \sin xdx, \tag{3}$$

and the normal field is given by the expression

$$h_N=2\pi(4/15)^{2/3}(\langle m_i^{3/2}\rangle n)^{2/3}, \tag{4}$$

where n is the concentration of field sources. We note that this problem has a higher-order symmetry than the dipole problem. For polarized dipole moments there arises a shift of the line center that is not associated with the presence of an average demagnetizing field,[4] while for charges of the same sign the line remains symmetric with respect to a change in sign of the frequency ω. Thus for charges of different signs m_i in Eq. (4) can be replaced by $|m_i|$, and

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n will be the total concentration of positive and negative charges. On account of the spherical symmetry, we can switch from the distribution of the magnitude to the distribution of the z component. Finally, the expression for the line profile assumes the form

$$I(\omega)=\frac{1}{\pi}\int_{\omega}^{\infty}\frac{dy}{y^2}\int_0^{\infty}\exp[-(x/y)^{3/2}]x\sin xdx, \quad (5)$$

where ω is expressed in units of the normal frequency $\omega_N=\gamma h_N$ and γ is the gyromagnetic ratio. The presence of oscillations make this expression inconvenient for numerical computation. It can be put into a much simpler form by Fourier transforming, integrating by parts, and transforming the resulting integrals. A more direct method is to calculate directly the distribution function for the z-component. Omitting some details, we give this derivation below.

To simplify the formulas we drop the m_i distribution, since it enters the final expression in just as simple a form as in Eq. (4). As in Ref. 3, we employ the Markov technique. Since the contributions from separate monopoles are statistically independent, the characteristic distribution function (Fourier transform) can be written as a product of the corresponding single-particle characteristic functions. In NMR the characteristic function for the line profile is the free-induction signal $G(t)$, which can be written as $(m_i=1)$

$$G(t)=\lim_{R\to\infty}\left[\frac{1}{V}\int_0^R e^{i\omega t}d^3r\right]^{Vn}, \quad (6)$$

where $V=(4/3)\pi R^3$, $\omega=r^{-2}\cos\varphi$, and φ is the angle between **r** and the z axis. In order to eliminate the divergence in the upper limit, we add and substract unity in the bracketed expression:

$$G(t)=\lim_{R\to\infty}\left[1-\frac{1}{V}\int_0^R(1-e^{i\omega t})d^3r\right]^{Vn}$$
$$=\lim_{R\to\infty}\left[1-\frac{1}{V}\int_0^{\infty}(1-e^{i\omega t})d^3r\right]^{Vn}=\exp[-nC(t)], \quad (7)$$

where

$$C(t)=\int_0^{\infty}d^3r(1-e^{i\omega t})=(4/15)t^{3/2}(2\pi)^{3/2}. \quad (8)$$

Thus the final expression for the free-induction signal has the form

$$G(t)=\exp[-(\omega_N t)^{3/2}], \quad (9)$$

$$\omega_N=2\pi\gamma(4/15)^{2/3}(\langle|m_i|^{3/2}\rangle n)^{2/3}, \quad (10)$$

and the desired line profile is the Fourier cosine transform of this expression.

3. PROFILE OF THE NMR LINE OF THE BINDER IN MAGNETIC SUSPENSIONS

Description of the samples

The profile of the NMR line of the binder in two samples of ferrolacquers (FLs), employed in the production of floppy disks and manufactured using PM-1 and Magnox-371 magnetic powders, was measured experimentally. The binder consisted mainly of a mixture of É-05/M2 resin, ethyl cellulose, toluene, isophorone, and cyclohexonone in different quantities ($\approx$20 wt.%). (The NMR lines of the binder itself were narrow enough that they could be neglected in this problem). The powder concentration was 5 vol.%. The preparation of the ferrolacquer included operations such as dispersion in a bead mill and filtering. Investigations of the morphological characteristics of the powders (prepared by washing from an oligomeric matrix using a heptane-acetone mixture) with the help of electron microscopy gave the following results (l_{av} is the average length, d_{av} is the average diameter, and n_a is the number of attachments):

Powder	l_{av}, Å	d_{av}, Å	l_{av}/d_{av}	n_a, %
PM-1	2720	570	4.8	25
Magnox-371	2690	540	5.0	18

Here the number of junctions is the percentage ratio of the number of branchings of the particles to the total number of particles.[1] The number of attachments reflects, though not completely, the density of defects of the powders.

The NMR spectra were obtained at 60 MHz by Fourier transforming half of the echo in the sequence $90_x-\tau-180_y$ ($\tau=50$ μsec).

Model of the structure

For a random arrangement of ferromagnetic particles in the matrix the width and profile of the NMR line of the binder can be calculated using the Anderson technique.[1] However, the measured line width was found to be two orders of magnitude smaller than expected for a random arrangement of particles, i.e., the average magnetic field dispersed in the matrix is extremely weak. This indicates that the magnetic particles are gathered into long clusters, oriented and magnetized in the direction of the external field. If L is the length of such filaments and d is the diameter, then when the the two conditions $L/d\gg1$ and $L^3n\gg1$, hold simultaneously the field dispersed in the matrix is the field generated by a dilute system of magnetic charges (the second condition expresses the fact that near one end of a filament the influence of the other end is negligible compared with the influence of the ends of the other filaments: near one pole of the magnet the system "forgets" that the other pole exists). Substituting $n\sim v/Ld^2$ (where v is the volume fraction of the particles) into the second condition, we rewrite it as $(L/d)^2\gg1/v$, whence it is obvious that the second condition is stronger and incorporates the first condition. As will become clear in our discussion of the experiment, this condition is satisfied with a large margin in the experimental systems studied.

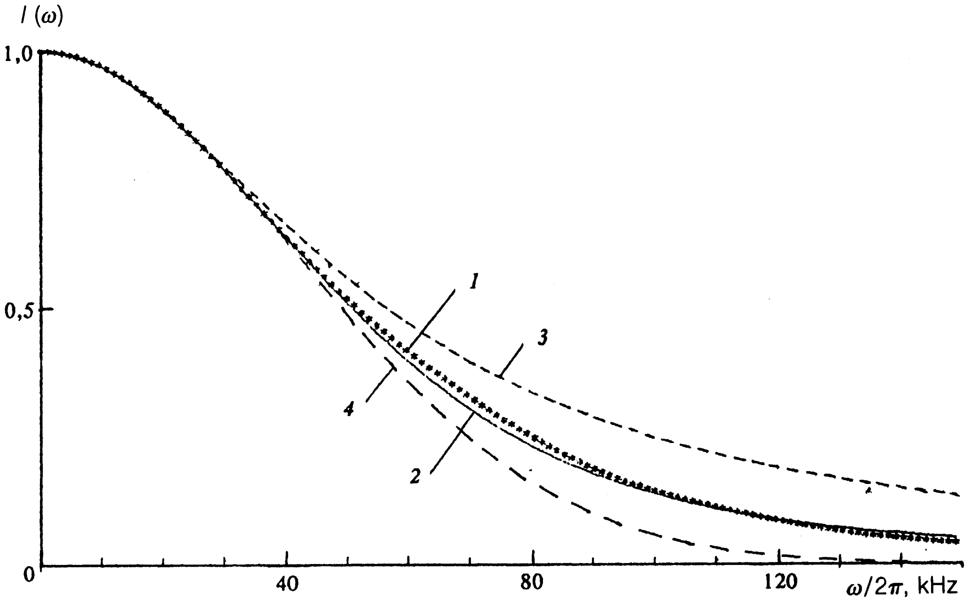

FIG. 1. NMR line profile for a suspension with Magnox powder: *1*—experiment, *2*—Fourier transform of the expression (9), *3*—Lorentzian, *4*—Gaussian.

The magnetic charge at the end of a filament is determined from the condition of flux conservation

$$m = B_s d^2/16, \tag{11}$$

where B_s is the saturation induction ($\sim$0.4 T for $\gamma - Fe_2O_3$). The concentration of filament ends is

$$n = v \frac{8}{\pi L d^2}. \tag{12}$$

Comparing Eqs. (11) and (12) to Eq. (10) we obtain

$$\frac{L}{d} = \frac{v}{\pi} \left(0.65 \frac{B_s}{h_N} \right)^{3/2}, \tag{13}$$

i.e., this geometric characteristic is simply expressed in terms of the line width $\omega_N = \gamma h_N$.

Experimental results

Figures 1 and 2 display the profiles of NMR lines of the binder for PM-1 and Magnox-371 powders, respectively. The theoretical curves are the Fourier transform of the expression (9). Lorentzian and Gaussian curves are shown for comparison. The agreement between the theoretical curves and the experimental data is good. This indicates that the model chosen adequately describes the structure of the suspension. The values of the normal frequencies and parameters of the structure were found to be as follows (n_{av} is the average number of particles per cluster):

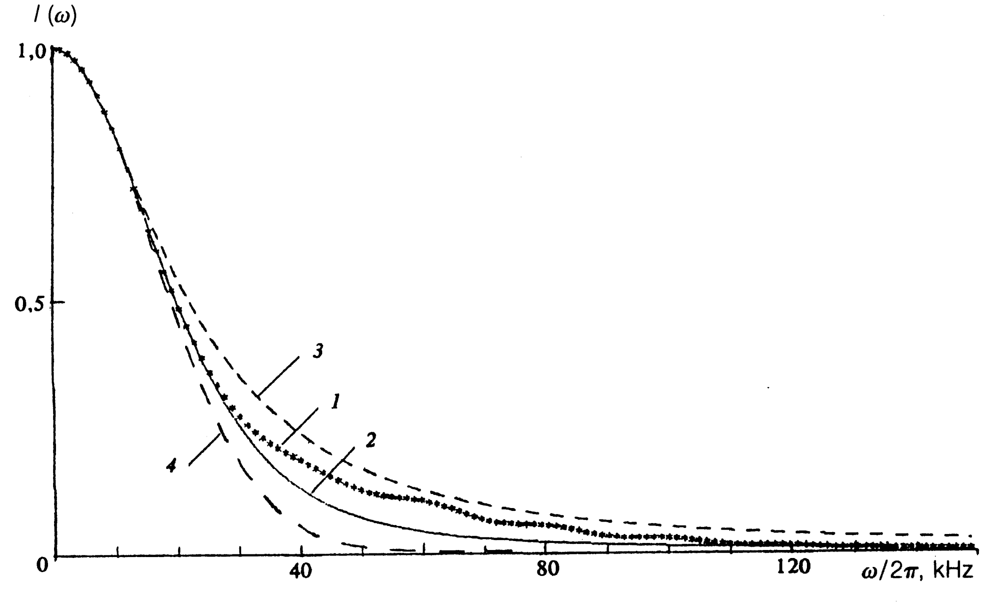

FIG. 2. NMR line profile for a suspension with PM-1 powder: *1*—experiment, *2*—Fourier transform of the expression (9), *3*—Lorentzian, *4*—Gaussian.

Powder	$\omega/2\pi$, Hz	L/d	n_{av}
PM-1	35150	89	19
Magnox-371	14260	344	69

The differences between the two samples are probably connected with the high density of defects in PM-1, preventing particles from lining up into long filaments.

4. CONCLUSIONS

The model considered in this paper is one of the few examples in which a nontrivial profile of a magnetic resonance line can be calculated exactly. This makes it possible to determine, by comparing with experiment, the quantitative values of the model parameters. Investigation of one possible class of objects—magnetic suspensions—showed that a magnetically dilute system of monopoles provides a good model of the magnetic field dispersed in the matrix. We now have a unique possibility for using the NMR method to study the structure of suspensions and kinetics of cluster formation, which is very difficult to do by any other methods due to the smallness of the number of participating particles.

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[1)] A. V. Raevskii kindly provided the electron microscopy data.

[1] A. Abragam, *The Principles of Nuclear Magnetism*, Oxford University Press, New York, 1983, Chap. 5.
[2] L. V. Berlyand, N. V. Chukanov, and V. A. Dubovitsky, Chem. Phys. Lett. **181**, 450 (1991).
[3] S. Chandrasekhar, *Stochastic, Statistical, and Hydromagnetic Problems in Physics and Astronomy*, University of Chicago Press, Chicago, 1985.
[4] F. S. Dzheparov and E. K. Khenner, Fiz. Tverd. Tela **28**, 2180 (1986) Sov. Phys. Solid State **28**, 1218 (1986)].

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