NMR line shapes of a gas of nuclear spin-$\frac{1}{2}$ molecules in fluctuating nano-containers

E.B. Fel’dman and M.G. Rudavets

Institute of Problems of Chemical Physics,
Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region,
Russia

Abstract

Reported in this paper is the impact of the fluctuations of the geometry of the nano-meter gas containers in the medium on the NMR line shape of the gas inside of the nano-containers. We calculate exactly the NMR line shape of the gas of spin-$\frac{1}{2}$ carrying molecules for two typical dynamics of the nano-container volume and the orientation with respect to the external magnetic field: (i) for a Gaussian stochastic dynamics, and (ii) for the regular harmonic vibrations. For the Gaussian ensemble of static disordered containers having an infinite correlation time, $\tau_c \to \infty$, the overall line shape is shown to obey a logarithmic low frequency asymptotics, $I(\omega) = \text{const} \times \ln(\frac{1}{\omega})$, at $\omega \to 0$, and exponentially decaying asymptotics in a high frequency domain. For the Gaussian ensemble of the rapidly fluctuating containers of a finite $\tau_c$, the overall line shape has a bell-shaped profile with $\sim \omega^{-4}$ far wing behaviour. In addition, we calculate exactly a satellite structure of the NMR line shape when the nano-bubbles in a liquid are affected by the harmonic deformations due to the acoustic waves.

PACS numbers 05.30.-d, 76.20.+q
1 Introduction

The systems we are studying in this paper are of interest due to the recent experiments [1] in which NMR responses from the H$_2$ gas confined in the nano-meter porous hydrogenated silicon have been used for measuring the size and the orientation of the nano-scale pores [2]. The accessibility of these measurements is relied on the explicit dependence of the line width of the NMR line shape on the confining volume and on the orientation of the ordered pores with respect to the strong external magnetic field. When a gas of spin-carrying molecules is confined within a nano-meter sized region, the motionally averaged (effective) dipolar interactions between the nuclear spins take on the finite values due to the spatial averaging of the dipolar interactions over the finite (nano-meter sized) region, hence, allowing the estimation of the line width [1] by the Van-Fleck formula. In addition, the motionally averaged (effective) dipolar interactions lead immediately to the exactly solvable effective spin Hamiltonian (see Sec. 2 below) allowing the exact calculation of time dependent NMR responses. In our previous paper [3] we calculated the time course of the longitudinal polarization of a gas of nuclear spin-\(^{1/2}\) carrying molecules confined in the static nano-containers. The purpose of the current paper is to extend the developed formalism for predictions of the NMR line shape in the presence of the dynamical nano-containers. The example systems we are exploring here are the cavitation bubbles that could be produced in experiments like those in sonoluminescence [4], the gas vesicles emerging in the non-invasive measurements of the liquid flow by the NMR tomography [5], [6], the bubbles in blood [7], the gas bubbles under the nucleation in the course of liquid-to-gas phase transitions [8], nano-sized free-volume holes of polymers, rubber, etc. under the elastic deformations, the gas containers within the vibrating nano-tubes [9], [10].

It is common that the NMR signals offer the spectroscopic way of the measuring of the characteristic sizes and the relaxation times of the container that surrounds and traps the nuclear spins [11], [12]. In studying the NMR signals from the $N$ spin ensemble with no special symmetry, the exponential with the number $N$ of allowed unknown basis set of the spin Hamiltonian is to be incorporated to describe the NMR signals completely. However, the complexity of the spin Hamiltonian is greatly reduced when the nuclei are subjected to the fast thermal motion within the nano-meter container. Under these conditions it arises a vast difference of the NMR time scale $t_{nmr} = 10^{-4} - 10^{-5}$ sec, that characterizes the flip-flop transitions at the nearest proton-
proton distances, and of the motional time scale, \( t_m = 10^{-11} - 10^{-12} \) sec, relevant for the round trip of the hydrogen molecules within the nano-meter container at room temperature. The presence of a reliable small parameter

\[
\varepsilon = \frac{t_m}{t_{nmr}} \approx 10^{-7}
\]

(1)

allows to average the underlying dipolar Hamiltonian over the spin spatial coordinates on the coarse-grained time intervals \( \Delta t \) obeying the inequality

\[
t_m \ll \Delta t \ll t_{nmr},
\]

(2)

giving rise to the motionally averaged spin Hamiltonian \( H \) (see Eq-s (3) and (4) of Sec. 2) with a unique spacing independent effective dipolar coupling \([1], [3]\). The exact spectrum of the motionally averaged spin Hamiltonian \( H \) has led to the development of the methods for characterizing the exact NMR spin dynamics, especially the non-ergodic spin dynamics and the line shape \([3]\).

We mention also the recent studies \([13], [14]\) in the area of the NMR responses from a confined gas in the framework of the phenomenological Bloch-Torrey equation as well as the NMR measurements \([15], [16], [17]\) revealing the reduction of the atomic mobility with respect to the bulk mobility due to the confinement effect. Although the previous papers have been largely concerned with the NMR measurements in the static nano-containers, the methods developed can be taken over for the cases of "flexible" walls of nano-containers. The point is that the dynamics of the surface of a typical bubbling behavior in liquids occurs at a millisecond time scale \([4]\), i.e. at the same time scale which is relevant for the NMR spectroscopy. In Section 2, we give a general formalism of the free induction decay (FID) for an arbitrary moving nano-containers. This is followed by analysis in Section 3 of the FID and the line shape for the Gaussian temporary fluctuations of the volume and of the orientation of the nano-containers. Our concern in the Section 3 is the line shape for a wide range of the correlation times and the amplitudes of the fluctuations of the nano-containers. Section 4 gives the line shape from the nano-containers subjected to a regular harmonic vibrations at a single frequency as well as the line shape from the nano-containers subjected to the harmonic vibrations with the Gaussian distributions of the frequencies. Finally, Section 5 summarizes the major conclusions of the calculations.
2 Line shape of a gas within nano-containers with a time-dependent volume

Consider a gas of $N$ spin-$\frac{1}{2}$ carrying molecules confined in a moving nano-containers in the strong external magnetic field $B$. On the coarse-grained time intervals $\Delta t$ [2] the effective spin dynamics is described by the motionally averaged spin Hamiltonian

$$H = \omega_0 I_z + \frac{1}{2}D(t)(3I_z^2 - I^2),$$

where the $\omega_0 = \gamma_p B$ with $\gamma_p$ standing for the proton gyromagnetic ratio, the nuclear spins are specified by the spin-$\frac{1}{2}$ operators $I_{i\alpha}$, $i = 1, \ldots, N$, ($\alpha = x, y, z$), the operators $I_{\alpha} = \sum_{i=1}^{N} I_{i\alpha}$, are referred to as the projections of the total spin operator onto the $x, y, z$ axes, respectively. Next, we assigned $I^2 = I_x^2 + I_y^2 + I_z^2$ to the square of the total nuclear spin operator. Finally, the motionally average (effective) dipolar coupling between all $\left(\begin{array}{c} N \\ 2 \end{array}\right)$ pairs of the spins in the nano-container is

$$D(t) = \frac{\gamma_p^2 \hbar f(t)}{V(t)}(3\cos^2 \theta(t) - 1).$$

Here, the $V(t)$ is the volume of the nano-container, the dimensionless form-factor $f(t)$ depends on the shape of the nano-container and $\theta(t)$ denotes the time dependent orientation of the nano-container with respect to the external magnetic field $\vec{B}$, see Fig. 1. The equivalence of the effective coupling $D$ for all the pairs of the nuclear spins is due to the fact that all the nuclei inside the nano-container are involved in the equivalent fast thermal motion inside the nano-container over the long NMR time scale $t_{nmr}$. In the absence of the nano-container’s motion, the nuclear motion inside the static nano-container gives rise to the unique motionally averaged spin coupling $D$ [1], [3]. The analytical dependence of the coupling $D$ on the nano-container’s volume $V$ admits an immediate extension of the coupling $D$ to the case of the time dependent volume $V$ by invoking the adiabatic framework [2], i.e. by regarding the motion of the nano-container to be slow as compared to the fast thermal motion of the nuclei within the nano-container.

The explicit form of the function $f(t)$ for the ellipsoidal container is in Ref. [3]. For the static containers of the nano-meter volume, $V \sim 10^3 \text{Å}^3$, the effective coupling in Eq. [1] is evaluated as $10^3$ times smaller than the
characteristic flip-flop coupling ($\sim t_{\text{nmr}}^{-1} = \gamma_0^2 h/a_0^3 \sim 10^4 - 10^5$ Hz) of two protons at a nearest separation $a_0 \sim 1\text{Å}$. This reduction of the dipolar coupling is referred to as the fast motionally narrowing (in $10^3$ times) of the line shape as compared to the line shape of the static nearest protons.

The line shape is the Fourier transform of the FID \[ F(t) = \text{tr} \{ \rho(t) I_- \} / \text{tr} \{ I_+ I_- \}, \tag{5} \]

where $I_\pm = I_x \pm iI_y$ and $\rho(0) = I_+$ is the initial density matrix in the high temperature approximation \[ 18 \]. The density matrix $\rho(t)$ of the $N$-spin ensemble in the rotating reference frame obeys the Liouville-von Neumann (L-vN) equation ($\hbar = 1$)

$$i \frac{\partial}{\partial t} \rho = \frac{1}{2} D(t) (3I_z^2 - I^2), \rho \tag{6}$$

In solving L-vN equation (6), we introduce the phase shift,

$$\varphi(t) = \frac{1}{2} \int_0^t dt' D(t'), \tag{7}$$

then, the L-vN equation (6) is solved to be

$$\rho(t) = e^{i\varphi(t) H} I_+ e^{-i\varphi(t) H} = e^{i3\varphi(t)(2I_z - 1)} I_+. \tag{8}$$

In deriving (8), we put $H = 3I_z^2 - I^2$, use the commutators $[I_\alpha, I^2] = 0$ and the identity

$$e^{i3\varphi(t) I_+} e^{-i3\varphi(t) I_+} = e^{i3\varphi(2I_z - 1)} I_+. \tag{9}$$

The trace in Eq. (5) is easily performed in the total occupancy number representation of $\mathcal{N}!/(N_\uparrow!N_\downarrow!)$-fold degenerate basis set $|N_\uparrow, N_\downarrow\rangle$, where $N = N_\uparrow + N_\downarrow$ and $I_z = \frac{1}{2} (N_\uparrow - N_\downarrow)$. The trace gives the sought FID for an arbitrary time-dependent coupling $D(t)$,

$$F(t) = \left( \cos(3\varphi(t)) \right)^{N-1}. \tag{10}$$

On the NMR reasonable time scale $t \leq t_{\text{nmr}} \sim 10^{-4}$ sec, we get $\langle D \rangle t \leq 10^{-2}$, so $\varphi(t) \ll 1$ and the FID, $F(t)$, of Eq. (10) transforms into

$$F(t) = e^{(N-1) \ln(\cos(3\varphi(t)))} \simeq e^{-\frac{N}{2}(3\varphi(t))^2} \tag{11}$$
for a large number of spins, $N \gg 1$, in the nano-container. The FID, $F(t)$, of Eq. (11) involves the effective coupling $D(t)$ of Eq. (4) as the input parameter to the phase shift $\varphi(t)$ of Eq. (7). Varying of the function $D(t)$ yields a variety of the models of the NMR line shape which are commonly discriminated into the two major groups, viz. the models of the homogeneous or inhomogeneous line width \[11, 12\]. In the following, we explore the FID for two dynamical scenarios of the container motion, for a stochastic Gaussian dynamics (Section 3) and for the regular harmonic oscillations (Section 4).

3 Line shape from fluctuating nano-containers

When the nano-sized containers are sensitive to the fluctuations of the environment, we are free to calculate the line shape by assuming the Gaussian fluctuations of the coupling $D(t)$ (4),

$$D(t) = \langle D \rangle + \delta D(t),$$

(12)

with the $\delta D(t)$ standing for the Gaussian random noise characterized by the first two moments

$$\langle \delta D(t) \rangle = 0, \quad \langle \delta D(t_1) \delta D(t_2) \rangle = \langle (\delta D)^2 \rangle C(|t_1 - t_2|),$$

(13)

where $\langle (\delta D)^2 \rangle$ is the variance of the fluctuations and the $C(t)$ denotes the correlation function, for example, $C(t) = \exp(-t/\tau_c)$, with $\tau_c$ being the correlation time. The averaging of the function $F(t)$ over the Gaussian fluctuations $\delta D(t)$ is carried in two steps: first, we rewrite the FID, $F(t)$, of Eq. (11) by introducing the Gaussian parameterization,

$$F(t) = \int_{-\infty}^{+\infty} \frac{dx}{\sqrt{\pi}} e^{-x^2 - 3ix\sqrt{2N} \varphi(t)},$$

(14)

this is followed by the second step of applying the formula for the averaging, see e.g. \[11, 12\], of the function $F(t)$ of Eq. (14) over the random Gaussian process $\delta D(t)$ entering the phase $\varphi(t)$ of Eq. (7),

$$\left\langle \exp \left( -i\kappa \int_0^t \delta D(t') dt' \right) \right\rangle_{\delta D} = \exp \left( -\kappa^2 \langle (\delta D)^2 \rangle T^2(t) \right),$$

$$T^2(t) = \int_0^t (t - t') C(t') dt',$$

(15)
with the constant $\kappa = 3x\sqrt{N/2}$. Averaging by Eq-s. (15), (14) gives the sought FID

$$F(t) = \exp\left(-\frac{\nu^2/4}{1 + \alpha\nu^2 T^2(t)}\right), \quad \alpha = \frac{\langle(\delta D)^2\rangle}{\langle D \rangle^2}, \quad \nu = 3\langle D \rangle \sqrt{\frac{N}{2}}.$$ (16)

As it stands, the FID, $F(t)$, of Eq. (16) encodes an information on the mean volume and the mean orientation of the cavity with respect to the external magnetic field as well as on the fluctuations of the cavity.

If the fluctuations were absent ($\alpha = 0$ in Eq. (16)) then the FID, $F(t)$, of Eq. (16) forms the line shape,

$$I(\omega) = \frac{1}{\pi} \int_{0}^{\infty} F(t) \cos \omega t \, dt$$ (17)

of the Gaussian type, $I(\omega) = \frac{1}{\nu\sqrt{\pi}} \exp\left(-\frac{\omega^2}{\nu^2}\right)$. Fluctuations of the cavity ($\alpha \neq 0$ in Eq. (16)), result in the broadening of the line shape so that the second moment, see e.g. (11), reads

$$M_2 = -\frac{d^2 F(t)}{d(t)^2} \bigg|_{t=0} = \frac{9N}{4} \left[\langle D \rangle^2 + \langle(\delta D)^2\rangle\right].$$ (18)

In deriving the second moment, use is made of the expression $T^2$ in Eq. (15) and the property $C(0) = 1$.

To make the calculations of the line shape $I(\omega)$ more explicit, we take the exponential correlation function, $C(t) = \exp(-t/\tau_c)$. It follows

$$T^2(t) = \tau_c^2 \left(\exp(-t/\tau_c) + \frac{t}{\tau_c} - 1\right).$$ (19)

In the analysis of the FID, $F(t)$, of Eq. (16) with the function $T^2(t)$ of Eq. (19), it seems very useful to consider the temporary fluctuations on two very different time scales.

When $\tau_c^2\langle(\delta D)^2\rangle \ll 1$, the function $T^2(t)$ is $T^2(t) = \tau_c t$ for times $t \gg \tau_c$, so that the FID of Eq. (16) reads $F(t) = \exp\left(-\frac{1}{4\alpha\tau_c t}\right)\sqrt{1 + \alpha\tau_c\nu^2 t}$, and its Fourier transform of Eq. (17) admits the following representation

$$I(\omega) = \frac{1}{\alpha\sqrt{\pi} \tau_c \nu^2} \text{Re}\left(e^{\frac{z^2}{2}} \text{erfc}(\sqrt{z})\right), \quad z = (2\alpha\tau_c\nu)^{-2} + i\omega(\alpha\tau_c\nu^2)^{-1}.$$ (20)
in terms of the function $\text{erfc}$ [19]. The function $I(\omega)$ of Eq. (20) has a bell-shaped profile with an intermediate Lorentzian asymptotics $I(\omega) = \frac{1}{\pi} \frac{1}{\Gamma^2 + \omega^2}$ where $\Gamma = (4\alpha\tau_c)^{-1}$ (see in [19] the asymptotics of the function $\text{erfc}(\sqrt{z})$ at $|\sqrt{z}| \gg 1$ or $\tau_c \to 0$). Far wing calculations of the line shape $I(\omega)$ require the FID $F(t)$ at $0 \leq t < \tau_c$, which is provided by the function $T^2(t)$ of Eq. (19) at $t \to 0$. The sought asymptotics of the line shape $I(\omega)$ can be evaluated as

$$I(\omega) \sim \frac{9N}{4\pi} \omega^{-4} (\langle \delta D \rangle^2)^{1/2}, \quad \omega \to \infty$$

(21)

on integrating the line shape $I(\omega)$ of Eq. (17) four times by parts and employing the derivatives $F'(0) = 0$, $C'(0) = -\tau_c^{-1}$.

On the other hand, when $\tau_c^2 \langle \langle \delta D \rangle^2 \rangle \gg 1$, the function $T^2(t)$ becomes $T^2(t) = t^2/2$ for $0 \leq t \leq \tau_c \to \infty$. The function $T^2(t)$ leads immediately to the slowing down of the FID of Eq. (16) in the form $F(t) = \exp(-\frac{1}{2\alpha})/\sqrt{1 + \frac{1}{2} \alpha \nu^2 t^2}$. Consequently, one is left with the line shape

$$I(\omega) = \frac{e^{-1/2\alpha}}{\pi \nu \sqrt{\omega \sqrt{2\alpha}}} K_0 \left( \frac{\omega \sqrt{2\alpha}}{\nu \sqrt{\alpha}} \right), \quad \omega \to 0,$$

(22)

and

$$I(\omega) = \frac{e^{-1/2\alpha}}{\sqrt{\pi \nu \sqrt{2\alpha} \omega}} \frac{1}{\sqrt{\omega}} \exp \left( -\frac{\omega \sqrt{2\alpha}}{\nu \sqrt{\alpha}} \right), \quad \omega \to \infty.$$

(23)

In deriving the $I(\omega)$ of Eq.-s (22) and (23), use is made of the integral representation of the modified Bessel function $K_0(x)$ and its asymptotics [19]. In order to shed light on the slowing down of the FID $F(t)$ at $t \to \infty$ (and, thus, on the logarithmic singularity of the line shape $I(\omega)$ at $\omega \to 0$ in eq. (22)), we regard a disordered almost static (frozen at $\tau_c \to \infty$) distribution of the nano-containers with the various volumes. The FID from an individual nano-container is described by the Gaussian-in-time function with the relaxation rate $\nu = 3D \sqrt{N/2}$. The main contribution to the sum of the individual FID’s weighted by the Gaussian probability density $(2\pi \langle D^2 \rangle)^{-1/2} e^{-D^2/2\langle D^2 \rangle}$ of the static fluctuations of the coupling $D$ comes from the fluctuations having the
$D = 0$, i.e. from the containers with a large volume or oriented at the magic angle $\arccos(1/\sqrt{3})$ (see the expression for the coupling $D$ of Eq. (4)). The FIDs from the large cavities are slowly damping providing a slow damping of the overall signal $F(t) \sim 1/t$ at $t \to \infty$ rather than the Gaussian-in-time asymptotics. Notice that the slowing down of the overall FID from the Gaussian ensemble of the static fluctuating nano-containers akin the slowing down of the unimolecular decay on the static disordered traps [20], [21]. Fig. 2 is aimed to show the appearance of a low frequency singularity of the line shape while increasing $\tau_c$ to infinity. The line shape for fixed $\tau_c \nu = 10$ at the various $\alpha$ is displayed on Fig. 3. In addition to having the broad shape, the line shape $I(\omega)$ shows the singularity at the zero frequency asymptotics at the large fluctuations $\alpha$.

It is worth to gather a small number of characteristic quantities involved in the Figure 3; for $N = 500$ spin-$\frac{1}{2}$ molecules ($\gamma^2 h = 2\pi \cdot 120$ Hz $\cdot$ nm$^3$) within $V = 45$ nm$^3$ nano-container and the form-factor $f(t) \sim 2$ of Eq. (4), the motionally average dipolar interaction is evaluated as $\langle D \rangle = 2\pi \cdot 5.3$ Hz, thus, $\nu = 0.25 \cdot 10^3$ Hz and $\tau_c = \nu^{-1} \simeq 4 \cdot 10^{-3}$ s.

The lessons drawn from this Section are that the fluctuations of the nano-containers give rise to the deviation of the line shape from the standard Gaussian and the Lorentzian shapes, and that for almost static disordered nano-containers at $\tau_c^2 \langle (\delta D)^2 \rangle \gg 1$, the line shape $I(\omega)$ gets narrower at $\omega \to 0$ and broader at $\omega \to \infty$ as compared to the bell-shaped profile occurring for frequently fluctuating nano-containers at $\tau_c^2 \langle (\delta D)^2 \rangle \ll 1$.

## 4 Line shape from vibrating nano-containers

Acoustic waves in the liquid surrounding the nano-bubbles can induce synchronized harmonic vibrations of the nano-bubble volumes and their orientations [4], thus, affect the NMR line shape if the acoustic waves are at the NMR relevant frequency domain $1 - 10$ kHz. The same physical picture of the NMR responses should appear for a gas within the vibrating nano-tubes [9], [10]. For all these vibrating nano-containers, we can regard the coupling $D(t)$ of Eq. (4) to be a harmonic function of the time,

$$D(t) = \langle D \rangle (1 + \varepsilon \cos(\Omega t))$$

(24)

with parameter $\varepsilon < 1$ assuming a weak vibrations of the nano-bubble volumes and the orientations. On the NMR time scale $t \sim 10^{-3}$ sec, the phase shift
\( \varphi(t) \) of Eq. (4) becomes
\[
\varphi(t) = \frac{1}{2} \langle D \rangle (t + \frac{\varepsilon}{\Omega} \sin(\Omega t)),
\]
so that \( \varphi(t) \ll 1 \) and the signal \( F(t) \) of Eq. (10) again transforms into the
\[
F(t) = e^{-\frac{1}{2}(\varepsilon^2 N \varphi(t))^2}, \quad \text{(see Eq. (11)).}
\]
For a weak vibrations, it is enough to expand the function \( F(t) \) in the powers of the parameter \( \varepsilon \) keeping only the terms up to \( \varepsilon^2 \) and linear in a small factor \( \nu^2 = \frac{9}{2} \langle D \rangle^2 N \), (by Eq. (4), the coupling \( \langle D \rangle \sim 1/N \)), giving
\[
F(t) = e^{-\frac{t^2 \nu^2}{4}} \left( 1 - \frac{\nu^2 t}{2 \Omega} \sin(\Omega t) - \varepsilon^2 \left( \frac{\nu}{2 \Omega} \right)^2 \sin^2(\Omega t) \right). \tag{26}
\]
The Fourier transformation brings the signal \( F(t) \) of Eq. (26) into the line shape
\[
I(\omega, \Omega) = \frac{1}{\nu \sqrt{\pi}} e^{-\frac{\omega^2}{\nu^2}} + \sum_{i=1,2} \left( I_i(\omega, \Omega) + I_i(-\omega, \Omega) \right),
\]
\[
I_1(\omega, \Omega) = -\frac{\varepsilon^2}{2 \nu \sqrt{\pi}} \left( 1 + \frac{\omega}{\Omega} \right) e^{-\frac{(\omega+\Omega)^2}{\nu^2}},
\]
\[
I_2(\omega, \Omega) = \frac{\varepsilon^2}{4 \nu \sqrt{\pi}} \left( \frac{\nu}{2 \Omega} \right)^2 e^{-\frac{(\omega+2\Omega)^2}{\nu^2}}. \tag{27}
\]
In the absence of the bubble vibrations (\( \varepsilon = 0 \)), the line shape \( I(\omega, \Omega) \) exhibits the motionally narrowed peak at frequency \( \omega = 0 \) with the line width \( 2\nu \). Weak bubble vibrations at the single frequency \( \Omega \) leads to the appearance of the symmetric satellite pairs of the line shape \( I(\omega, \Omega) \) (27) at the multiple frequencies \( \omega = \pm \Omega, \pm 2\Omega \). By accounting for the \( n \)-th term in the powers of the amplitude \( \varepsilon \), the satellite pairs at frequencies \( \omega = \pm n\Omega, n = 3, 4, \ldots \) arise.

Now, let an ensemble of many individual gas bubbles is spread over the liquid having a random local vibrational frequency \( \Omega \) due to an intimate fluctuations of the liquid. Under these conditions, the nuclei belonging to different bubbles are (indirectly) subjected to a different local vibrational frequency resulting to the inhomogeneous broadening of the NMR spectrum. We think of the ensemble of the bubbles as a single bubble affected by the vibrations with a continuous Gaussian distribution of frequencies
\[
D(\Omega) = A_0 \Omega^2 e^{-\frac{(\Omega-\Omega_0)^2}{2\Delta^2}} \quad \text{with} \quad A_0 = \frac{1}{\sqrt{\pi} \Delta \left( \frac{1}{2} \Delta^2 + \Omega_0^2 \right)} \tag{28}
\]
ensuring the normalization $\int_{-\infty}^{\infty} d\Omega D(\Omega) = 1$. The pre-factor $\Omega^2$ in Eq. (28) is taken for ease of performing the averaging of the line shape $I(\omega, \Omega)$ of Eq. (27) over the distribution $D(\Omega)$ of Eq. (28),

$$\langle I(\omega) \rangle = \int_{-\infty}^{\infty} d\Omega D(\Omega) I(\omega, \Omega),$$  \hspace{1cm} (29)$$
yielding

$$\langle I(\omega) \rangle = \frac{1}{\nu \sqrt{\pi}} e^{-\frac{\omega^2}{\nu^2}} + \sum_{i=1,2} \left( G_i(\omega) + G_i(-\omega) \right),$$

$$G_1(\omega) = -\frac{\varepsilon}{2 \nu (1 + \delta^2)^{3/2}} \left( \frac{1}{2} + \frac{(\Omega_0 - \omega \delta^2)}{\Delta^2 (1 + \delta^2)} (\Omega_0 + \omega) \right) e^{-\frac{(\omega + \Omega_0)^2}{\nu^2 + \Delta^2}},$$

$$G_2(\omega) = \frac{\varepsilon^2}{16} \frac{A_0 \nu \Delta}{(1 + \delta^2)^{1/2}} e^{-\frac{(\omega + 2\Omega_0)^2}{\nu^2 + 4 \Delta^2}},$$  \hspace{1cm} (30)$$
with $\delta = \Delta/\nu$. The overall line shape $\langle I(\omega) \rangle$ of Eq. (30) is still narrow at $\omega = 0$ and reveals the two symmetric satellite pairs at frequencies $\omega = \pm \Omega_0$, $\pm 2\Omega_0$ having a broad line width $2\sqrt{\nu^2 + \Delta^2}$ and $2\sqrt{\nu^2 + 4 \Delta^2}$, respectively, see Fig. 4.

In general, the satellite pair of the amplitude $\varepsilon^n$ is described (to within the pre-exponential factor) by the Gaussian shape with the line width $2\sqrt{\nu^2 + n^2 \Delta^2} \sim 2n\Delta$, i.e. $2n$ times larger than the dispersion, $\Delta$, of the frequencies in the spectral density $D(\Omega)$ of Eq. (28). Thus, the position of the $n$-th satellite pair at $\omega = \pm n\Omega_0$ and the broadening of the $n$-th satellite, $2n\Delta$, provide the NMR spectroscopic characterization of the nano-bubble vibrations happening at the mean vibrational frequency $\Omega_0$ and with the dispersion of the frequencies $\Delta$.

5 Conclusion

The focus in the paper is on the exact NMR line shape theory of a gas of spin-1/2 carrying molecules confined within the fluctuating nano-containers. Two typical dynamics of the nano-containers was treated, viz. the Gaussian stochastic dynamics and the regular harmonic vibrations.

(1). Of the variety of the Gaussian random fluctuations of the nano-containers, the most striking fluctuation effect on the NMR line shape is due to the fluctuations at the large correlation times, $\tau_c \to \infty$, (for almost frozen
disordered ensemble of the various nano-containers) and at the large amplitudes of the fluctuations of the volume and orientation of the nano-containers. Under these conditions, the NMR line shape behaves as $I(\omega) = \text{const} \times \ln \frac{1}{\omega}$ at $\omega \to 0$ and exponentially decaying at the large frequencies, $\omega \to \infty$. Alternatively, when the conditions are specified by the small correlation times, $\tau_c \to 0$, or at the small amplitudes, $\alpha$, of the Gaussian fluctuations of the nano-containers, then the line shape has the bell-shaped profile with the power law $\sim \omega^{-4}$ at far wings. The line width and its precise shape specify the mean volume, the mean orientation of the cavities as well as the deviation of the volumes and the orientations from the mean values.

(2). If the driving sources of the vibrations support the harmonic vibrations of the bubble volumes and of the orientations at a single frequency $\Omega$, then the line shape has the spike satellite pairs with a narrow line width $2\nu$ at the frequencies $\omega = \pm n\Omega$, $n = 1, 2, \ldots$ around the central spike at $\omega = 0$. For the Gaussian distribution of driving frequencies with the mean $\Omega_0$ and the dispersion $\Delta$, the central spike at $\omega = 0$ remains to be narrowed with the line width $2\nu$, however, the satellite pairs at $\omega = \pm n\Omega_0$, are subjected to broadening in the way that the $n$-th pair has the line width $\sim 2n\Delta$.

The upshot is that the paper demonstrates how the fluctuation dynamics in the medium can be characterized by the NMR spectroscopy of the gas within the fluctuating nano-containers.

Acknowledgments

Thanks are expressed to I.I. Maximov for the help in preparing the manuscript. Financial support was provided by the Russian Foundation of Basic Research (RFBR No. 04-03-32528).

References

[1] J. Baugh, A. Kleinhammes, D. Han, Q. Wang, and Y. Wu, Science 294 (2001) 1505.
[2] S. Inagaki, S. Guan, T. Ohsuna and O. Terasaki, Nature 416 (2002) 304.
[3] E.B. Fel’dman and M.G. Rudavets, JETP 98 (2004) 207; E.B.Fel’dman and M.G.Rudavets, ArXive e-print quant-ph/0306055.
[4] M. P. Brenner, S. Hilgenfeldt and D. Lohse, Rev. Mod. Phys., 74 (2002) 425.

[5] I. V. Koptyug and R. Z. Sagdeev, Russ. Chem. Rev. 71 (2002) 789.

[6] F. Rioual, T. Biben and C. Misbah, ArXive e-print physics/0401159.

[7] E. A. Brujan, Europhys. Lett., 50 (2000) 437.

[8] V. V. Klimov and V. S. Letokhov, Chem. Phys. Lett. 301 (1999) 441.

[9] D. A. Dikin, X. Chen, W. Ding, G. J. Wagner and R. S. Ruoff, J. Appl. Phys. 93 (2003) 226.

[10] P. Poncharal, Z. L. Wang, D. Ugarte and W. A. de Heer, Science 283 (1999) 1513.

[11] A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford, 1961.

[12] R. Kubo, Adv. Chem. Phys. 15 (1969) 101.

[13] L. J. Zielinski, P. N. Sen, J. Chem. Phys. 119 (2003) 1096.

[14] S. Axelrod and P. N. Sen, J. Chem. Phys. 114 (2003) 6879.

[15] S. Granic, Science 253 (1991) 1374.

[16] J.-P. Korb, L. Malier, F. Cros, S. Xu, J. Jonas, Phys. Rev. Lett. 77 (1996) 2312.

[17] M. Weber, A. Klemm, R. Kimmich, Phys. Rev. Lett. 86 (2001) 4302.

[18] M. Goldman, Spin Temperature and Nuclear Magnetic Resonance in Solids, Clarendon Press, Oxford, 1961.

[19] M. Abramowitz and I. A. Stegun, Handbook of Mathematical Functions, Dover, New York, 1965.

[20] B. Ya. Balagurov and V. G. Vaks, Zh. Eksp. Teor. Fiz. 65 (1973) 1939.

[21] P. Grassberger and I. Procaccia, J. Chem. Phys. 77 (1982) 6281.
Captions to figures.

Fig. 1. Cartoon of the two positions of the nano-container which is moving in a liquid undergoing the deformations of the volume and/or the variation of the orientation \( \theta(t) \) with the time. The nano-container confines the gas of nuclear spin-\( \frac{1}{2} \) molecules uniformly spread inside the nano-container.

Fig. 2. The line shapes \( I(\omega) \) of Eq. (17) are calculated by the Fourier transform of the FID \( F(t) \) of Eq. (16) with the function \( T^2(t) \) of Eq. (19) for the various values of the combination \( \tau_c \nu \). The parameters \( \nu \) and the \( \alpha = 1 \) are from Eq. (16).

Fig. 3. The line shapes \( I(\omega) \) of Eq. (17) for the FID \( F(t) \) of Eq. (16) with the function \( T^2(t) \) of Eq. (19) at the fixed \( \tau_c \nu = 10 \), but the amplitude of the fluctuations are allowed to vary from \( \alpha = 0.01 \) to \( \alpha = 100 \).

Fig. 4. The absolute value of the homogeneous (dashed-dot) and inhomogeneous (solid) NMR line shapes of the vibrating bubbles with the nuclear spin-\( \frac{1}{2} \) molecules inside. The absolute value of the inhomogeneous line shape \( |\langle I(\omega) \rangle| \) from Eq. (30) is shown for the parameters \( \varepsilon = 5 \), \( \Delta = 2 \), \( \Omega_0 = 2\pi \), with all the frequencies being in the units of the frequency \( \nu \) of Eq. (16).
\[
\frac{\omega}{(2\pi \nu)}
\]

\[\alpha = 1\]

\[\tau_c \nu = 0.01\]

\[= 1\]

\[= 100\]
\[ |\langle I \rangle| \]

\[ \omega / (2\pi \nu) \]