Modeling of non-stationary processes in the study of liquid media by the method of nuclear magnetic resonance in a weak field

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Abstract. The article substantiates the necessity of developing a theoretical model to study the influence of non-stationary processes on the shape of the recorded NMR signal in a weak magnetic field. Therefore, comparison of different ways of solving Bloch’s equations to describe the shape of the recorded NMR signals using a modulation technique is carried out. Moreover, mathematical models have been developed to describe the shape of the NMR signal, considering the peculiarities of its registration using modulation techniques in a weak field. Finally, the results of calculations, obtained by proposed methods, are compared with experimental data.

1. Introduction
At present, one of the urgent tasks of applied physics is the development of fast and reliable methods of express control of the state of condensed media [1−6]. Now, the main requirement for express control methods is that research or measurements by these methods should not change the physical structure and chemical composition of the studied medium. This is necessary to obtain confirmation of the identified deviation of the state of the medium from the standard in a given sample on high-resolution instruments in a stationary laboratory [3, 4, 7−10].

The results of numerous experiments have shown that the method based on the phenomenon of nuclear magnetic resonance (NMR) is the only one that meets these requirements. It does not cause irreversible changes in the structure and chemical composition of various condensed matter, unlike optical, ultrasonic, X-ray, electromagnetic, or other methods [8−16].

The only condition for its use is the presence of nuclei with magnetic moments in the medium [4, 8−10, 17−21]. There are a lot of such media, both natural and artificial. Especially a lot of them among the liquid, which almost always contains protons. Therefore, a large amount of both experimental and theoretical research in the field of NMR has been carried out by various scientists in the world. Special attention in these studies was paid to the methods of NMR signal registration in strong and medium high-uniform magnetic fields. In addition, there is active work on the theoretical description of these
processes to decipher the recorded spectra. Less attention has been paid to pulsed NMR relaxometry methods, which are mainly implemented in the medium magnetic fields with the induction of $B$ from 0.6 to 1.4 Tesla. For these methods, methods for measuring the time of longitudinal $T_1$ and transverse $T_2$ relaxation of the condensed medium based on the solution of Bloch equations were proposed. The measured values of $T_1$ and $T_2$ allow establishing unambiguously existence of a deviation from a standard state in the investigated environment [3, 8, 10, 17, 22, 23]. In some cases, for known media, such as fats or gels in their production, $T_1$ and $T_2$ values are monitored on the production line by express control.

The results of our previous studies have shown that it is extremely difficult for one person to carry out express control with the help of pulsed methods. This requires, among other things, the ability to move the NMR relaxometer (for example, on the territory of the factory), which is extremely difficult due to the large weight and size of the device. The stand-alone power supply will also have large weight and size since it must provide pulse energy of about 300 W for the implementation of the pulse technique. It is necessary to use at least 1000 pulses. Therefore, the use of such devices in the field is very difficult. Therefore, we have developed a design of a small NMR relaxometer. His weight with power supplies does not exceed 6 kg. In this device, a modulation technique is used to register the NMR signal of a weak magnetic field with $B$ less than 0.15 $T$. Results of our studies have confirmed the possibility of using a small-sized NMR relaxometer for express control of the condensed medium at the place of sampling. At the same time, the experience of operation of small-size NMR relaxometers has shown that in several cases (for example, environmental monitoring, a study of hydrocarbon compounds or biological solutions) the measured values of $T_1$ and $T_2$ are not enough for effective express control. In this case, in order to make an informed decision on the further use of the environment (especially in the study of water, and fuels and lubricants), it is necessary to determine the cause of this deviation from the standard one. Unlike in production control, in this case, there is no information about what impurity can be in the environment. Therefore, it is impossible to make a preliminary calibration of the dependence of $T_1$ and $T_2$ on the concentrations of impurities in the medium. There are only data on $T_1$ and $T_2$ for certain temperatures of the medium, which correspond to its standard state.

One of the possible solutions to this problem may be our proposed method of decoding the structure of the NMR signal. In the case of studying a medium in a weak magnetic field using a modulation technique, the signal consists of absorption and dispersion signals [22-25]. Currently, the theory of absorption and dispersion signals is well described using Bloch equations for pulse methods used in spectrometry and relaxometry. Many analytical expressions are obtained separately for NMR absorption and dispersion signals [4, 19, 22, 24-27]. It should be noted that in NMR spectrometry or relaxometry, basically all measurements are carried out on the absorption signal since it has a higher signal-to-noise ratio.

To obtain analytical expressions for the absorption and dispersion signals from the Bloch equations, a different number of approximations is made. Most of them do not meet the conditions of NMR signal registration using the modulation technique in a weak magnetic field. The main of the approximations relates to the fact that in NMR spectrometers and pulse NMR relaxometers the signals are recorded under conditions of fast adiabatic passage through resonance. For this reason, almost all theoretical solutions for the registration of the NMR signal were based on this approximation. But in a weak magnetic field, it is impossible to obtain the condition of fast adiabatic passage through resonance.

The absence of a theoretical model to describe the formation of the NMR signal in a weak magnetic field significantly reduces the efficiency of studies of condensed media. It also limits the possibilities of NMR modernization of flowmeters-relaxometers and magnetometers on the flowing liquid, in which a modulation technique is used to register the NMR signal. Therefore, the purpose of this paper is to supplement this section of the NMR theory with new knowledge. Its use will allow us to reproduce the shape of the line of the registered NMR signal under conditions of weak magnetic field modulation in the interpolar space of the NMR relaxometer, considering the peculiarities of its registration established earlier [25, 28].
2. Structure of the recorded NMR signal in a weak magnetic field

The motion of longitudinal and transverse components of the magnetization vector of the condensed medium in the NMR registration coil of the spectrometer is described by Bloch equations [29–31]:

\[
\begin{align*}
\frac{dM_x(t)}{dt} + \frac{M_x(t)}{T_2} + \Delta \omega M_x(t) &= 0 \\
\frac{dM_y(t)}{dt} + \frac{M_y(t)}{T_2} - \Delta \omega M_y(t) &= 0 \\
\frac{dM_z(t)}{dt} - \frac{M_z(t)}{T_1} - \frac{\gamma H_0 M_z(t)}{T_1} - \frac{\gamma H_1 M_z(t)}{T_1} &= 0
\end{align*}
\]

where \(\Delta \omega = \omega_0 - \omega_{\text{NMR}}\) is the detuning frequency of the NMR signal detection circuit \(\omega_{\text{NMR}}\) from the magnetization precession frequency in the field \(H_0\) \(\left(\omega_0 = \gamma H_0\right)\), \(\gamma\) is the gyromagnetic ratio of the nucleus, \(\chi_0\) is the static nuclear magnetic susceptibility, \(H_1\) is the field in the detection coil, \(T_1\) and \(T_2\) are the times of longitudinal and transverse relaxation of a liquid medium, and \(t\) is a time.

In [24, 26, 31, 32], when considering (1), the replacement of variables for the components of the magnetization vector \(M_x\) and \(M_y\) and the transition to a coordinate system rotating with frequency \(\omega_{\text{nmr}}\) were substantiated in detail. In a rotating coordinate system with new variables, equation (1) takes the following form:

\[
\begin{align*}
\frac{du(t)}{dt} + \frac{u(t)}{T_2} + \Delta \omega \cdot u(t) &= 0 \\
\frac{dv(t)}{dt} + \frac{v(t)}{T_2} - \Delta \omega \cdot v(t) &= -\gamma H_1 M_z(t) \\
\frac{dM_z(t)}{dt} + \frac{M_z(t)}{T_1} - \frac{\gamma H_1 v(t)}{T_1} &= \frac{M}{T_1}
\end{align*}
\]

where \(M = \chi_0 H\) is the magnetization of the medium under study in the magnetic field of the spectrometer, \(v(t)\) and \(u(t)\) are the absorption and dispersion signals.

In the case of using a modulation technique for registering an NMR signal in a weak magnetic field, the value of \(H\) changes as follows:

\[
H = H_0 + H_m \sin(\omega_m t)
\]

where \(H_0\) is a constant magnetic field, \(H_m\) is a modulation coil field, \(\omega_m\) is a modulation frequency.

In this case, the change in the detuning of the field frequency from the resonance in the system of Bloch equations (2), taking into account (3), will have the following form:

\[
\Delta \omega = \gamma H_0 + \gamma H_m \sin(\omega_m t) - \omega
\]

In this case, the Bloch equations (2) will have a coefficient \(\gamma H_m \sin(\omega_m t)\), which depends on the time. The presence of this coefficient makes it impossible to use the standard methods used in NMR spectroscopy for solving (2). These methods consist in the fact that the equation (2) must be reduced to Volterra integral equation by the method of Gvozdover and Magazanik [24, 32, 33]. Then you need to decompose the equations into series, determine the conditions of their convergence and limit the calculations to the first term.

In the case where the following relationship is performed:

\[
\gamma^2 H_1^2 T_1 T_2 \ll 1,
\]

there is a rapid adiabatic passage through the resonance. This corresponds to the case of NMR signal registration in spectrometers with strong and medium high-uniform magnetic fields.

Therefore, in most of the papers, when considering the modulation technique, the authors made the following approximation \(H_0 \gg \gamma H_m \sin(\omega_m t)\). Thus, assuming an insignificant effect of the modulation field on the magnitude of the magnetic field \(H_0\). This made it possible to perform an approximate solution of the Bloch equations in [24, 26, 27, 34, 35], and then introduce an additional term in their solution, which considers the modulation of the magnetic field.

The closest solution that reflects the shape of the NMR line recorded in the experiment using the modulation technique was obtained in [35]:
Considering (3), equation (6) takes the following form:

\[ U(t) = U_0 \exp \left( -\frac{t}{T_2} \right) \cos \left( \omega_0 t + \frac{1}{2} \gamma \frac{dH}{dt} t^2 \right) \]  

(6)

Analysis of the obtained line shape using (7) shows that the recorded NMR signal does not depend on the value of the \( H_1 \) field, which is the determining parameter when it is registered by the autodyne detector. For recording the NMR signal with the maximum S/N ratio from different media, the value of \( H_1 \) will be different for different media, but there is no such dependence in (6). This discrepancy does not allow to fully compare the results of theoretical calculations with the experiment.

Therefore, we have developed two variants of describing the shape of the recorded NMR signal in a weak magnetic field using a modulation technique.

In the first case, in equations (2) it is necessary to consider the peculiarities of registration of the NMR signal in the weak field using the modulation technique. One of them is that the registration of the NMR signal must be performed only at the resonance frequency \( \omega_{\text{nmr}} = \omega_0 = \gamma H_0 \). For most of the media studied, if the NMR frequency is adjusted to \( \omega_{\text{nmr}} \) from the resonance frequency \( \omega_0 \), the signal-to-noise ratio (S/N) may become less than 1.3. At this value of S/N ratio, the operation of the NMR signal accumulation scheme in NMR spectrometers and relaxometers becomes ineffective [25, 28]. This will not allow different measurements to be made with an error of no more than 1%.

With this feature in mind, ratio (4) is transformed into the following form:

\[ \Delta \omega = \gamma H_m \sin(\omega_m t) \]  

(8)

Expression (8) is a new coefficient for the Bloch equations (2). The values of \( H_m \) and \( \omega_m \) in it are determined considering the relations established in [3, 25, 28].

Another new coefficient that we introduce in the Bloch equations (2) is associated with the need to take into account the influence of the modulation of the weak magnetic field on the magnetization of the medium \( M \). Then the new ratio for \( M \) takes the following form:

\[ M = \chi_0 (H_0 + H_m \sin(\omega_m t)) \]  

(9)

After substituting the new coefficients (8) and (9) into the Bloch equations (2), they take the following form:

\[ \frac{du(t)}{dt} + \frac{u(t)}{T_2} + \gamma H_m \sin(\omega_m t) v(t) = 0, \]

\[ \frac{dv(t)}{dt} + \frac{v(t)}{T_2} - \gamma H_m \sin(\omega_m t) u(t) + \gamma H_1 M_z(t) = 0, \]

\[ \frac{dM_z(t)}{dt} + \frac{M_z(t)}{T_1} - \frac{M}{T_1} - \gamma v(t) H_1 = 0. \]  

(10)

This system of equations (10) is solved in Wolfram Mathematica for \( v(t) \), \( u(t) \) and \( M_z(t) \) components, taking into account the initial conditions:

\[ M_z(0) = \chi_0 H_0, \]

\[ u(0) = 0, \]

\[ v(0) = 0, \]

since the exact analytical solution of system (9) for the indicated components is extremely difficult to obtain.

Considering the peculiarities of the autodyne detector operation [25, 28, 34], we propose to describe the shape of the line of the detected NMR signal in a weak magnetic field \( G(t) \) by the following ratio:

\[ G(t) = F(t) \sqrt{\frac{A}{A + B} v^2(t) + \frac{B}{A + B} u^2(t)} \]  

(11)
where $v(t), u(t)$ are the absorption and dispersion signals, $A$ and $B$ are the coefficients that determine the contribution to the recorded NMR signal from the absorption and dispersion signals, and $F(t)$ is the coefficient that takes into account phase changes.

The second variant of signal description relates to the fact that different approximations are often used for processing of research results. In some cases, they allow reproducing experimental dependencies with high accuracy.

The recorded NMR signal is a damped non-periodic oscillation — "wiggles". Our previous studies have allowed us to establish that the shape of the recorded signal line can be described by the following formula:

$$U_c(t) = U_0 \exp \left(-\frac{t}{T_2}\right)f(t)$$

where $U_0$ is the maximum amplitude value of the recorded NMR signal, $T_2$ is the transverse relaxation time, $f(t)$ is a function describing the oscillatory part of the signal ("wiggles ").

Figure 1 (a, b) shows the recorded NMR signal from the water with different ways of approximation.

![Figure 1. The NMR signal from water at a temperature $T = 291.4$ K. Plot 1 is the experimental data, plot 2 is the theoretical calculation of the line shape, plots 3 and 4 are the envelopes of the experimental signal.](image)

Analysis of the line shape of the registered NMR signal (figure 1.a, plot 1) shows that it falls asymmetrically. This is due to the presence of non-stationary processes during the operation of the autodyne detector at the time of passing through the resonance. The calculation result presented in figure 1.a (plot 2) using (7) is strongly inconsistent with the experiment (plot 1). Therefore, we proposed the option to "clamp" the plot 1 (figure 1.b) between two exponents (plots 3 and 4), which have different attenuation coefficients. According to the theory of physical experiment, the formula for describing the function with different envelopes can be presented as follows:

$$u(t) = \frac{\text{env}_{\text{upper}}(t) + \text{env}_{\text{lower}}(t)}{2} + f_{\text{osc}}(t) \frac{\text{env}_{\text{upper}}(t) - \text{env}_{\text{lower}}(t)}{2}$$

where $\text{env}_{\text{upper}}(t)$ and $\text{env}_{\text{lower}}(t)$ are upper and lower envelopes correspondingly, $f_{\text{osc}}(t)$ is a function that describes oscillations.

Based on our previous experimental results, as well as data on studies conducted by other scientists in the field of NMR, an expression for $f_{\text{osc}}(t)$ in (13) can be represented in the following form:

$$f_{\text{osc}}(t) = \frac{a \exp(-bt) + c \exp(-dt)}{2} + \cos(g(t-f) + h(t-f)^2) \frac{a \exp(-bt) + c \exp(-dt)}{2},$$

where $a, c$ are dimensionless parameters, $b, d$ are attenuation coefficients ($b \sim 1/T_2$, $d$ takes into account the inhomogeneity of the magnetic field $H_0$), $g$ is a parameter having frequency dimension.
(Hz), takes into account the resonance frequency $\omega_0$, $\hbar$ is a parameter having dimension $1/s^2$, takes into account the modulation of the field, $f$ is a parameter that has the dimension of time, necessary to correct the approximation in the time axis, because the first peak of the real signal is not always set to 0.

3. Results of NMR signals calculations and their comparison with the experiment

Figure 2 presents as an example the results of comparing the peak shape ("wiggle") of the recorded NMR signal (plot 1) with the calculation of their line shape (plot 2) performed using (11). Water was used as a condensed medium at $T = 279.3$ K. The numerical values of the absorption and dispersion signals $v(t)$ and $u(t)$ were used to calculate $G(t)$. These values were obtained from the solution of the system of equations (10), and the experimental values of magnetic fields and relaxation constants $T_1$ and $T_2$ were used in the solution.

![Figure 2](image1)

**Figure 2.** The shape of the NMR signal from water. Plot 1 is the experimental data, plot 2 is the theoretical calculation.

The analysis of the dependences presented in figure 2 shows that the proposed new relation (11), which uses solutions of the Bloch equations (10) with the new coefficients established by us, allows us to reproduce the line shape of the recorded NMR signal using a modulation technique (autodyne) in a weak magnetic field with an error of no more than 3% (up to 4 peaks).

As an example, figure 3 shows the result of comparing the shape of the peaks ("wiggles") of the recorded NMR signal (figure 1) with the calculation of their line shape (figure 2), performed using (14) for tap water (figure 3.a) and a mixture of two gasolines (figure 3.b).

![Figure 3](image2)

**Figure 3.** The shape of the NMR signal line a) from water b) from a mixture of gasoline Al-95 and Al-76. Plot 1 is the experimental data, plot 2 is the theoretical data, plots 3 and 4 are the envelopes.
The analysis of the dependences presented in figure 3 shows that the approximation developed by us allows obtaining a good agreement between the theoretical and experimental forms of magnetic resonance lines. This allows it to be used for effective express control of condensed media.

4. Conclusion
According to the results of the experiments, it was found that the mathematical model developed by us for describing the shape of the NMR signal line using (11) has no restrictions on its use in express control of the state of various media. For its application, it is necessary to register an NMR signal from a medium containing a nucleus with magnetic moments. For example, a signal can be registered at the resonance frequency of protons containing in liquid. After that, it is necessary to measure the relaxation times $T_1$ and $T_2$ of the medium. Using the data obtained, it is possible to calculate the shape of the line and determine the contribution to its structure from the absorption and dispersion signals.

In the case of calculating the NMR line using a mathematical model (14), preliminary calibration is necessary. That includes calibration of values of $H_1$, $H_m$, modulation frequency $\omega_m$, etc. Calibration should be performed for different temperatures, and the nucleus of the medium, which will be used to record the NMR signal. This makes it very difficult to use this model to perform express control in the field. It is more rational to use it in a laboratory or stationary premises where the media under study are known and their temperature can be controlled more easily. In addition, these conditions require a higher degree of accuracy when conducting express control studies.

5. References
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