A MODIFICATION OF BERGMANN'S METHOD OF THE DECOMPOSITION NMR SPECTRA OF POLYMERS

J. UHRIN[1]), J. MURÍN[1]), D. OLČÁK[1]), Košice

Broad-line NMR spectra in solid polymers could often be decomposed into elementary components reflecting different kinds of mobility of macromolecular chains in a polymer. For this purpose the Bergmann method is frequently used. The influence of the modulation on the components is also considered in this method. This paper deals with some numerical-mathematical problems of decomposition of broad-line NMR spectra with the aim to spend up the convergence of the numerical method.

МОДИФИКАЦИЯ БЕРГМАНОВСКОГО МЕТОДА РАЗЛОЖЕНИЯ ЯМР-СПЕКТРОВ ПОЛИМЕРОВ

Широкие линейчатые ЯМР-спектры твердых полимеров могут быть часто разложены на элементарные составляющие, соответствующие разным типам подвижности макромолекулярных цепочек в полимере. Для этой цели часто используется метод Бергмана. Рассмотрено также влияние модуляции на составляющие. Кроме того, в работе исследуется математическая проблема разложения широких линейчатых ШМР-спектров с целью улучшения сходимости рядов, используемых в численных расчетах.

I. INTRODUCTION

In studying the partially crystalline polymers by broadline proton NMR-measurements one can frequently observe that the NMR spectrum changes its shape when the temperature of the sample varies. Various kinds of molecular motion (e.g. atomic groups, macromolecular chains and macromolecular segments of different lengths) activated at different temperatures are responsible for changes in the NMR spectra. Molecular mobility depends not only on temperature, but also on the molecular composition of macromolecular chains and on their spatial arrangement (crystalline and noncrystalline areas). If the molecular mobility in individual structural areas differs, the NMR spectrum is a superposition of two or

[1]) Department of Physics, Technical University, Park Komenského 2, 041 20 KOŠICE, Czechoslovakia.

three NMR lines differing in intensities, widths and in shapes. These component lines correspond to the resonating nuclei situated in regions with different molecular mobility. Decomposition of the NMR spectra into elementary components is very important for studying both molecular motion and structure (its heterogeneity) of the polymer. The main information obtained from such analysis is (1) relative number of resonating nuclei belonging to different regions (it is derived from the areas under the component lines), (2) the parameters of the individual lines such as the width, shape and the second moment, give us a possibility of modelling molecular motions in these regions.

The first line shape analysis of the partially crystalline polymer was carried out by Wilson and Pake [1]. They observed a spectrum consisting of superimposed broad and narrow resonance lines which they assigned to rigid crystalline and mobile amorphous material, respectively. Many later authors have extended and improved this method of separation [2—10, 14]. Recently the method elaborated by Bergmann has frequently been used [6, 7]. In this paper we are dealing with the problem of the decomposition of NMR spectra according to the Bergmann method. Our intention is focused on numerical problems of the spectral analysis.

II. THEORETICAL DESCRIPTION OF THE EFFECT OF MODULATION ON THE LINE SHAPE

The absorption line is supposed to be in the form of the analytical function $Y(x')$, where x' stands for the induction of magnetic field, which consists of two parts: the static magnetic field x and the modulating field $H\cos\omega t$. The shape of the line is described by the function [7]:

$$Y(x') = Y(x + H\cos\omega t). \tag{1}$$

Extending this function to the Fourier series we obtain

$$Y(x + H\cos\vartheta) = \frac{A_0 x}{2} + \sum_{n=1}^{\infty} A_n(x)\cos n\vartheta, \quad (\vartheta = \omega t) \tag{2}$$

$$A_n(x) = \frac{2}{\pi}\int_0^{\pi} Y(x + H\cos\vartheta)\cos n\vartheta \, \mathrm{d}\vartheta. \tag{3}$$

Taking into account a normalization of the absorption spectrum

$$\int_{-\infty}^{+\infty} Y(x)\,\mathrm{d}x = 1 \tag{4}$$

the normalizing factor in eq. (3) has the form

$$Q_n = \frac{H^n}{2^{n-1}n!}. \tag{5}$$

If we develop the function $Y(x + H\cos\vartheta)$ into the Taylor series in point x and $A_n(x)$ is divided by Q_n, we obtain

$$\frac{A_n(x)}{Q_n} = K_n(x) = \frac{n!\,2^n}{\pi H^n}\int_0^{\pi}\left[Y(x) + Y'(x)H\cos\vartheta + \ldots + \frac{1}{n!}Y^{(n)}H^n\cos^n\vartheta + \ldots\right]\cos n\vartheta \, \mathrm{d}\vartheta = \frac{n!\,2^n}{\pi H^n}\int_0^{\pi}\frac{1}{n!}Y^{(n)}H^n\cos^n\vartheta\cos n\vartheta \, \mathrm{d}\vartheta, \tag{6}$$

e.g. for small modulation amplitudes $K_n(x) = Y^{(n)}(x)$. In most events the first derivation of the absorption signal is recorded, hence the function

$$y(x) = K_1(x), \quad y(x) = 2/\pi H\int_0^{\pi} Y(x + H\cos\vartheta)\cos\vartheta \, \mathrm{d}\vartheta$$

describes the first derivation of the absorption line with respect to the influence of the modulation field H. After integration per partes one can obtain

$$y(x) = \frac{2}{\pi}\int_0^{\pi} Y'(x + H\cos\vartheta)\sin^2\vartheta \, \mathrm{d}\vartheta. \tag{7}$$

III. THE NUMERICAL METHOD OF THE DECOMPOSITION OF THE SPECTRUM

We suppose the occurrence of three simple lines in the spectrum. There are narrow, medium and broad lines. For the narrow line the Lorentzian lineshape was taken

$$Y_L(x, \beta_L^N) = \frac{1}{\pi\beta_L^N}\frac{1}{1 + \left(\frac{x}{\beta_L^N}\right)^2} \tag{8}$$

for the medium line the normalized product of the Gaussian and Lorentzian lines

$$Y_{GL}(x, \beta_L^M, \beta_G^M) = R\frac{\exp\left[-\left(\frac{x}{\beta_G^M}\right)^2\right]}{1 + \left(\frac{x}{\beta_L^M}\right)^2} \tag{9}$$

where R is the factor which serves the normalization

$$R = [\pi\beta_L^M \exp(\gamma)^2 \operatorname{erfc}(\gamma)]^{-1}, \quad \gamma = \beta_L^M/\beta_G^M$$

and the broad line is given by the experimental values at low temperature. The presumed form of the line-shape enables a variation by the scaling factor s

$$Y_{LT}(x, s)=\frac{1}{s} Y\left(\frac{x}{s}\right). \tag{10}$$

The resulting function which fits the experimental spectrum with regard to the modulation field is

$$Y'_T(x, p)=\frac{2}{\pi}\int_0^{\pi}[w_L Y'_L(\eta, \beta_L^N)+w_{GL}Y'_{GL}(\eta, \beta_L^M, \beta_G^M)+ \\ +w_{LT}Y'_{LT}(\eta, s)]\sin^2\vartheta\,\mathrm{d}\vartheta=\frac{2}{\pi}\int_0^{\pi} f(\eta, p)\sin^2\vartheta\,\mathrm{d}\vartheta, \tag{11}$$

where $\eta=x+H\cos\vartheta$ and the "vector" p substitutes the parameters of the lines β_L^N, β_L^M, β_G^M, s and the weight factors w_L, w_{GL} and w_{LT}. The function f depends on the weight factor in a linear way.

In our case the experimental spectrum is obtained in equidistant steps and all experimental values are interpreted like values with an equal probability. Minimization of the Φ function

$$\Phi=\sum_{i=1}^{N}[Y'_T(x_i, p)-Y'_E(x_i)]^2\Delta x_i \tag{12}$$

enables us to find the optimal vector p. The Y'_E in (12) denotes the experimental line after normalization

$$\int_{-\infty}^{+\infty} Y_E(x)\,\mathrm{d}x=[xY_E(x)]_{-\infty}^{+\infty}-\int_{-\infty}^{+\infty} xY'_E(x)\,\mathrm{d}x=1 \tag{13}$$

when the first term on the right-hand side is supposed to be zero.

For the minimization process a method similar to the Marquardt method [11] was used, which is in fact a combination of the Newton method and the gradient method.

Let $\Psi_i=Y'_T(x_i, p)-Y'_E(x_i)$. In the Hessian matrix $\mathcal{G}$ of the function Φ

$$\mathcal{G}_{\alpha\beta}=\frac{\partial^2\Phi}{\partial p_\alpha\partial p_\beta}=2\sum_{i=1}^{N}\frac{\partial\Psi_i}{p_\alpha}\frac{\partial\Psi_i}{p_\beta}\Delta x_i+ \\ +2\sum_{i=1}^{N}\Psi_i\frac{\partial^2\Psi_i}{\partial p_\alpha\partial p_\beta}\Delta x_i \tag{14}$$

the second sum is neglected because the process of the numerical derivation increases the errors [12] and a further reason for neglecting is the fact that the matrix $\mathcal{G}$ represented only by the first sum is a positive definite matrix.

The gradient of the Φ function is

$$g_\alpha=2\sum_{i=1}^{N}\Psi_i\frac{\partial\Psi_i}{\partial p_\alpha}\Delta x_i. \tag{15}$$

For each evaluation of Ψ_i in (14) and (15) it is necessary to compute the integral by (11) and so the choice of the optimal numerical method of integration is essential

$$Y'_T(x, p)=\frac{2}{\pi}\int_0^{\pi} f(x+H\cos\vartheta)\sin^2\vartheta\,\mathrm{d}\vartheta= \\ =\frac{2}{\pi}\int_{-1}^{1}\frac{f(x+Ht)(1-t^2)}{\sqrt{1-t^2}}\,\mathrm{d}t. \tag{16}$$

This form of the integrand suggests that the Chebyshew–Gauss method of integration is usable [12]

$$Y'_T(x, p)=\frac{2}{n}\sum_{i=1}^{n} f(x+Ht_i)(1-t_i^2)+E, \tag{17}$$

where $t_i=\cos(2i-1)\pi/2n$ and E is the error of the numerical integration. The error can be expressed by

$$E=\frac{2\pi}{2^{2n}2n!}g(\tau)^{(2n)} \tag{18}$$

where $g=f(x+H\tau)(1-\tau^2)$, $\tau\in(-1, 1)$. For the Lorentz curve (narrow) the $2n$-th derivation is

$$\frac{\mathrm{d}^{2n}Y_L}{\mathrm{d}t^{2n}}=\left(\frac{H}{\beta_L^N}\right)^{2n}\frac{(2n)!}{\pi\beta_L^N[z^2+1]^{(2n+1)/2}}\sin[(2n+1)\varphi],$$

Z denotes $z=\eta/\beta_L^N=(x+Ht)/\beta_L^N$ and $\varphi=\operatorname{arc\,tg}\beta_L^N/(x+Ht)$. After evaluating the $2n$-th derivation

$$\frac{\mathrm{d}^{2n}}{\mathrm{d}t^{2n}}[Y_L(x+Ht)(1-t^2)]=\frac{(2n)!}{H\pi\beta_L^N(z^2+1)^n}\left(\frac{H}{\beta_L^N}\right)^{2n-1} \\ \times\left[(t^2-1)\left(\frac{H}{\beta_L^N}\right)^2\frac{2n+1}{z^2+1}\sin(2n+2)\varphi-4nt\frac{H}{\beta_L^N}\times\right. \\ \left.\times\frac{\sin(2n+1)\varphi}{(z^2+1)^{1/2}}+(2n-1)\sin(2n\varphi)\right],$$

we obtain the estimation for error $E(z\to 0,\ \varphi\to\pi/2)$

$$E\leqslant\frac{8n}{\beta_L^N H}\left(\frac{H}{2\beta_L^N}\right)^{2n}. \tag{19}$$

This means that the Chebyshev–Gauss method leads to a rapid convergence when the modulation field is smaller than the line-width. If $H\sim 10^{-1}\,\beta_L^N$ only 6—10 (or less) points of the Chebyshev–Gauss method are sufficient.

Newton's method leads to convergence near the minimum where the function has a quadratic behaviour. The equations for correction are linear

$$\mathcal{G}\delta p = -g, \quad \delta p = -\mathcal{G}^{-1}g \tag{20}$$

but in the region far from the minimum the correction-vector is taken co-linear with the gradient and its orientation is antiparallel to that of the gradient

$$\delta p = -\lambda g, \tag{21}$$

where λ is a positive constant with an unknown value. A compromise between Newton's method and the steepest descent method is obtained when the matrix $\mathcal{G}+\lambda\mathcal{I}$ ($\mathcal{I}$ is unit matrix) substitutes the matrix $\mathcal{G}$. Then the equations for corrections are

$$(\mathcal{G}+\lambda\mathcal{I})\,\delta p = -g. \tag{22}$$

For $\lambda = 0$ we have Newton's method and for a λ much bigger than the biggest eigenvalue of $\mathcal{G}$ the matrix equations (22) give the same corrections as equation (21). For a λ too big the vector of the corrections lies in a "*resonable*" direction, but the length of this vector is small and that is why the progress in convergence is slight. Indeed the length of the vector is

$$|\delta p| = \sqrt{\sum_i \left(\frac{g_i'}{\Lambda_{ii}+\lambda}\right)^2} \tag{23}$$

where $g' = \mathcal{U}^+ g$. The matrix $\mathcal{G}$ is transformed into a diagonal form by the matrix $\mathcal{U}$ and Λ_{ii} are (positive) eigenvalues of the matrix $\mathcal{G}$. In our opinion it is useful to substitute the vector of the correction $\delta p^{(n)}$ by the vector $\delta p^{(n)}\chi_n(\lambda)$ where $\chi_n(\lambda)$ is an upward function under the conditions $1 \leq \chi_n(\lambda) \leq K$, $\chi_n(0) = 1$.

In our case the function $\chi_n(\lambda)$ was taken in the form

$$\chi_n(\lambda) = \frac{1}{M}\sum_{i=1}^{M}\chi_{n,i}(\lambda) \tag{24}$$

$\chi_{n,i}(\lambda) = \chi_{n-1,i}(\lambda) + C$ if the $\delta p_i^{(n)}$ changes the sign in the n-th iteration in comparison with $\delta p_i^{(n-1)}$ and $\chi_{n,i} = 1$ if the sign is the same. The constant $C = \min(\lambda, K)$. For $\lambda \to 0$ e.g. in the region of the minimum $\chi_n(\lambda) = 1$ and the length of the corrections is determined by Newton's method.

The criterium for the convergence is the condition $\Phi_{n+1} < \Phi_n$, where Φ_n is the value (12) at the n-th iteration. Unlike the algorithm in [11] the following strategy was suitable for our computations.

i) $\lambda_n = \dfrac{\lambda_{n-1}}{\vartheta}$ $\quad \Phi_{n+1} \leq \Phi_n$

ii) $\lambda_n = \vartheta'\lambda_{n-1}$ $\quad \Phi_{n+1} > \Phi_n$

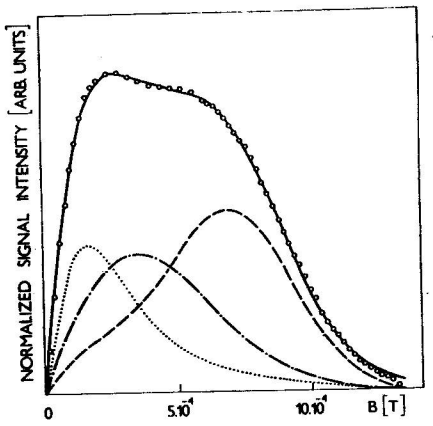

Fig. 1. Decomposition of the NMR spectrum of the copolymer 2-dimethyleneamine and 1-ethylester of methacrylic acid at the temperature 225 K. The low temperature spectrum was measured at 100 K. Experimental points (-∘-), calculated spectrum (——), narrow component — Lorentzian (.....), medium component — Gauss–Lorentz curve (-.-.-), low-temperature spectrum (- - -). Weight factors are: $w_L = 0.20$, $w_{GL} = 0.26$, $w_{LT} = 0.54$, the parameters of the spectrum are: $\beta_L^N = 2.78$ G, $\beta_L^M = 9.74$ G, $\beta_G^M = 5.78$ G and $s = 0.916$. The amplitude of modulation $B_m = 0.4$ G.

$\vartheta > 1$ ($\vartheta \doteq 1.3$—1.5) $r \doteq 3$—5 and step ii) is repeated until the event i is achieved. The Hessian matrix is preserved in memory because the ii) event may occur. The function $\chi_n(\lambda) = 1$ for all events ii).

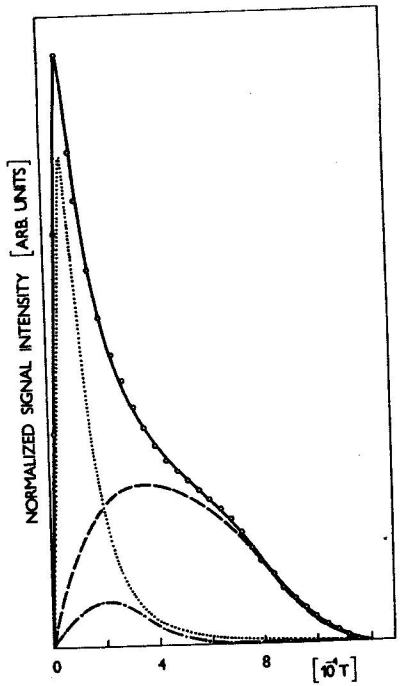

Fig. 2. Decomposition of the NMR spectrum of a polypropylene sample (denoted as PP-17). Temperature 340 K, low temperature spectrum was measured at 195 K. Components are drawn in the same manner as in Fig. 1. Parameters of the spectra are: $w_L = 0.19$, $w_{GL} = 0.05$, $w_{LT} = 0.75$, $\beta_L^N = 1.06$ G, $\beta_L^M = 8.5$ G, $\beta_G^M = 2.97$ G and $s = 0.93$. Modulation $B_m = 0.35$ G.

The derivation by the weight factor was evaluated directly and the next derivations in a numerical way. For our aims the rational approximation of the erfc(γ) [13] was suitable. This approximation reduced considerably the operation time.

Computations were executed by a EC 1033 computer.

In Fig. 1 and 2 are illustrative examples. The function Φ decreases from $\sim 10^{-2}$ to 10^{-6} during iterations.

The weight factor must obey the condition $w_L + w_{GL} + w_{LT} = 1$, hence the number of independent parameters is lower, but we did not apply this condition because all lines were normalized. If the sum of the weight factor is far from the value 1, the process converges to a "*non-physical*" minimum. Small deviations from the value 1 can occur in practice because the experimental and low-temperature spectra are normalized in the limited interval but the Lorentz curve and the Gauss–Lorentz curve in the unlimited interval.

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