THE USE OF GAUSS-HERMITE QUADRATURE IN THE DETERMINATION OF THE MOLECULAR WEIGHT DISTRIBUTION OF LINEAR POLYMERS BY RHEOMETRY

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Abstract - The molecular weight distribution (MWD) and its parameters are of the fundamental importance in the characterization of polymers. Therefore, the development of techniques for faster MWD determination is a relevant issue. This paper aims at implementing one of the relaxation models from double reptation theory proposed in the literature and analyzing the numeric strategy for the evaluation of the integrals appearing in the relaxation model. The inverse problem, i.e., the determination of the MWD from rheological data using a specified relaxation model and an imposed distribution function was approximated. Concerning the numerical strategy for the evaluation of the integrals appearing in the relaxation models, the use of Gauss-Hermite quadrature using a new change of variables was proposed. In the test of samples of polyethylene with polydispersities less than 10, the application of this methodology led to MWD curves which provided a good fit of the experimental SEC data.
Keywords: Rheology; Inverse Problem; Gauss-Hermite Quadrature.

INTRODUCTION

The characterization of a polymer in terms of molecular weight distribution (MWD) requires not only the determination of a single average value but also additional moments of this distribution. This characterization is of fundamental practical importance because the MWD has a direct influence on the processability and final properties of a polymeric material, being one of the key variables in the control of polymerization processes.

Although the MWD is usually determined by gel permeation chromatography (GPC), some limitations of this technique, such as cost and time consumption, have led to the study of alternative methods for its determination. In this context, methods based on the use of relaxation models, which describe the linear viscoelastic properties of polymers as a function of the MWD, have received great attention in the literature.

One of the first techniques that emerged in the literature to determine the MWD from rheological data was proposed by Tuminello (1986). In this

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technique, the conversion of dynamic elastic modulus data ($G'(\omega)$) into distribution curves of molecular weight was done by a simple analytical expression, obtained from considerations regarding the relation between the relaxation mechanisms of polymer melts and the MWD. However, the distribution curves obtained by this method were characterized by presenting artificial multimodality, i.e., multimodality not found in the analysis by GPC. Applying a similar methodology for data of relaxation modulus $G(t)$, Tuminello and Mc Grory (1990) also reported artificial bimodality for some samples.

Recently, methods based on reptation and double reptation theories have been presented (Wasserman, 1995; Léonardi, 1999; Léonardi *et al.,* 2002; van Ruymbeke *et al.,* 2002a; Peirotti and Deiber, 2003; Guzmán *et al.*, 2005; Nobile and Cocchini. 2008; Friedrich *et al.*. 2009). To obtain the MWD by these methods, it is necessary to calculate the relaxation spectrum from $G'(\omega)$ and $G''(\omega)$ experimental data, impose a distribution function to represent the MWD, select a molecular model that incorporates the concept of double reptation to represent the relaxation process of the polymer molecules, and approximate an inverse problem to obtain the parameters of the distribution function selected to represent the MWD from experimental data of dynamic moduli.

The use of an arbitrary distribution function is based on the idea that the MWD is the result of random events that occur during the polymerization reaction and is controlled by the characteristics and conditions of the polymerization process. Consequently, it is expected that common characteristics are found between the MWD of different polymers. Several mathematical functions have been used in the literature to describe the molecular weight distribution of polymers (Rogosic *et al.,* 1996; Fried, 2003) including the *Flory-Schulz*, the *Gaussian* distribution and the Generalized Exponential (GEX) function (Gloor, 1983), with GEX standing out in terms of goodness of fit to experimental data of MWD derived from techniques like GPC.

Regarding the approximation of the inverse problem involved, two different approaches are usually used in these methods: i) explicit calculation of the relaxation spectrum, and ii) use of the parametric method proposed by Schwarzl (1971) in order to avoid the explicit calculation of the relaxation spectrum. For the explicit calculation of the relaxation spectrum, the application of *Tikhonov* regularization is suggested in the literature (Honerkamp and Weese, 1989; Weese, 1992). In the parametric approach, the dynamic moduli G′ and G′′ are obtained through the inversion of $G(t)$ by using the *Schwarzl* relations

(van Ruymbeke *et al*., 2002a), derived from approximations by Fourier transforms.

Besides the intrinsic ill-posedness in the approximation of the inverse problem of retrieving the parameters of the molecular weight distribution from the molecular models for the moduli (van Ruymbeke *et al.,* 2002b; Léonardi *et al.,* 1998; Léonardi, 1999; Léonardi *et al.,* 2002; van Ruymbeke *et al.,* 2002a; Peirotti and Deiber, 2003; Cocchini and Nobile, 2003; Llorens *et al.,* 2003), another key point in these methods is the efficiency of the numerical scheme used to evaluate the integrals which appear in the mixing rules used to apply the molecular models to polydisperse samples. These integrals relate the shear relaxation modulus of the entangled polymer with the MWD and have to be calculated recursively in the approximation of the inverse problem, which is basically an optimization problem. However, there is little information in the literature concerning specifically the influence of the integration method on the performance of the methods for rheological data-based determination of MWD.

Due to the intrinsic characteristics of the problem under consideration, the use of integration methods based on orthogonal polynomials appears as an interesting alternative. Orthogonal polynomials are widely used in the approximation of inverse problems in the areas of physics and mathematics. In polymer engineering, they are used in the prediction of the evolution of the MWD during polymerization reactions through the solution of chemical kinetics models, representing the MWD as a series of Laguerre (Saidel and Katz, 1968) or Lagrange (Seferlis and Kiparissides, 2002) polynomials*,* whose weight function is the *Flory-Schulz* distribution (Coni Jr., 1992). Peirotti and Deiber (2003) developed a procedure to estimate the density distribution function (DDF) $f_w(M)$ from the double reptation mixing rule for binary and polydisperse blends using data of relaxation moduli. Their approach uses the normal and gamma functions to represent the DDF, expanding these distribution functions in Hermite and Laguerre polynomials, respectively, to evaluate the double reptation mixing rule. However, further research is required to find both a robust algorithm and a complete relaxation law to consider multimodal and highly polyidisperse samples.

In the present work, the *Schawrzl* parametric approach (Schwarzl, 1971), considering the *des Cloizeaux* relaxation model (des Cloizeaux, 1990) and the Generalized Exponential (GEX) distribution function with the double reptation mixing rule, was used in the inverse problem for the determination of the MWD from rheological data. A variable transfor-

mation was proposed for the GEX distribution function in order to allow the use of Gauss-Hermite quadrature to evaluate the integrals appearing in the mixing rules required for the determination of the MWD and the results obtained with the proposed strategy are compared to those obtained with the classical trapezoidal integration method. The MWDs obtained by applying the proposed methodology were compared with size-exclusion chromatography data of commercial samples of polyethylene with polydispersities less than 10. This polydispersity index limit was defined according to preliminary tests which indicated that the methodology based on the *des Cloizeaux* model is not appropriate for high polydispersity indexes. Additionally, within this range of polydispersity, theoretical and experimental data are available in the literature for comparison purposes.

METHODOLOGY

Inverse Problem for the Determination of the MWD

The inverse problem for the determination of the MWD was written using well-established strategies described in the literature. Firstly, to apply the theory of double reptation to polydisperse polymers, it is necessary to specify a mixing rule for prediction of rheological properties of the polydisperse polymer sample from the contribution of the individual molecules. The following double reptation mixing rule (van Ruymbeke *et al.*, 2002b; Tsenoglou, 1991; Léonardi *et al.*, 2000; Vega *et al.*, 2012) was used:

$$G(t) = G_N^0 \left[\int_{LL}^{+\infty} F^{\frac{1}{\beta}}(t,M) P(M) \, dM \right]^{\beta} \qquad (1)$$

where G_N^0 is the plateau modulus, LL is the lower limit of molecular weight for the integration, $F(t,M)$ is a kernel function describing the relaxation behaviour of a monodisperse polymer of molecular weight M, $P(M)$ is the distribution function used to represent the MWD of the sample, and $P(M) \, dM$ is the normalized probability of finding a chain with molecular weight between M and $M + dM$.

In the original model of the double reptation (des Cloizeaux, 1988) the value of the exponent β in Equation 1 is 2, but different values have been suggested in the literature (van Ruymbeke *et al.*, 2002b; Maier *et al.*, 1998). In this work, as suggested by van Ruymbeke *et al.* (2002b), $\beta = 2.25$ was used.

Regarding the lower limit of the integral (*LL*), the use of either M_e (van Ruymbeke *et al.*, 2002b) or $2M_e$ (Léonardi *et al.*, 1998; Léonardi, 1999; Léonardi *et al.*, 1998; Léonardi *et al.*, 2000; Léonardi *et al.*, 2002) has been suggested in the literature. The molecular model of des Cloizeaux (1990) was used to represent the relaxation process of the polymer molecules. This model, which considers the diffusion mechanism of stress points along the chain, is able to better describe the mechanisms of reptation combined with the fluctuations of the tube length. It is given by:

$$F^{\frac{1}{\beta}}(t,M) = \frac{8}{\pi^2} \sum_{i\,ODD} \frac{1}{i^2} \exp\left(-i^2 U(t,M)\right) \qquad (2)$$

where i_{ODD} means the sum over odd numbers of i, and $U(t,M)$ is evaluated as:

$$U(t,M) = \frac{t}{\lambda_{rept}(M)} + \frac{M^*}{M} g\left(\frac{Mt}{M^*\lambda_{rept}(M)}\right) \qquad (3)$$

where g can be approximated as in the following equation, according to van Ruymbeke *et al.* (2002b):

$$g(q) = -q + q^{0.5}[q + (\pi q)^{0.5} + \pi]^{0.5} \qquad (4)$$

and λ_{rept} is given by $\lambda_{rept} = KM^3$. The parameter M^* is related to the molecular weight between entanglements (M_e) and the parameter K, which can be determined from experimental measures of viscosity as a function of the molecular weight, depends on the nature of the material and on the temperature. More details on the *des Cloizeaux* model can be found in the literature (des Cloizeaux, 1990; Maier *et al.*, 1998; van Ruymbeke *et al.*, 2002b).

The GEX function was used as the imposed MWD distribution, in the functional form proposed by Léonardi *et al.* (2002):

$$P(M) = \frac{m}{M_{ref}\,\Gamma\left(\frac{k+1}{m}\right)} \left(\frac{M}{M_{ref}}\right)^k$$

$$\exp\left[-\left(\frac{M}{M_{ref}}\right)^m\right] \qquad (5)$$

where m, k and M_{ref} are the parameters which define the distribution and Γ is the gamma function. Based

on these parameters, the expressions for the three first moments of a MWD described by the GEX function can be expressed as (Léonardi *et al.,* 2002; van Ruymbeke *et al.,* 2002a; Cocchini and Nobile; 2003):

$$\overline{M}_n = M_{ref} \frac{\Gamma\left(\dfrac{k+1}{m}\right)}{\Gamma\left(\dfrac{k}{m}\right)} \tag{6}$$

$$\overline{M}_w = M_{ref} \frac{\Gamma\left(\dfrac{k+2}{m}\right)}{\Gamma\left(\dfrac{k+1}{m}\right)} \tag{7}$$

$$\overline{M}_z = M_{ref} \frac{\Gamma\left(\dfrac{k+3}{m}\right)}{\Gamma\left(\dfrac{k+2}{m}\right)} \tag{8}$$

and the polydispersity index is given by:

$$PD = \frac{\overline{M}_w}{\overline{M}_n} = \frac{\Gamma\left(\dfrac{k+2}{m}\right)\Gamma\left(\dfrac{k}{m}\right)}{\Gamma\left(\dfrac{k+1}{m}\right)^2} \tag{9}$$

Formulation of the Parameter Estimation Problem

The optimal GEX parameters were determined by a χ^2 minimization procedure, using the following objective function:

$$\chi^2 = \min_{(k,m,M_{ref},M)} \left\{ \frac{1}{2N_E} \sum_{i=1}^{N_E} \left[\left(\frac{G'_{E_i} - G'_{M_i}}{G'_{E_i}}\right)^2 + \left(\frac{G''_{E_i} - G''_{M_i}}{G''_{E_i}}\right)^2 \right] \right\} \tag{10}$$

where G'_{E_i} and G''_{E_i} are the experimental data measured at the frequencies ω_i for $i = 1, 2, 3 \dots N_E$, N_E is the number of points in the frequency set, and G'_{M_i} and G''_{M_i} are the theoretical values of the moduli at each frequency ω_i. As suggested by van Ruymbeke *et al.* (2002a), G'_{M_i} and G''_{M_i} were calculated from the relaxation modulus $G(t)$ using the *Schwarzl* relations (Schwarzl, 1971):

$$G'_M(\omega) \sim G(t) + a_1\left[G(4t) - G(8t)\right]$$
$$+ a_2\left[G(2t) - G(4t)\right]$$
$$+ a_3\left[G(t) - G(2t)\right]$$
$$+ a_4\left[G(t/2) - G(t)\right]$$
$$+ a_5\left[G(t/4) - G(t/2)\right] \tag{11}$$
$$+ a_6\left[G(t/8) - G(t/4)\right]$$
$$+ a_7\left[G(t/16) - G(t/8)\right]$$
$$+ a_8\left[G(t/64) - G(t/32)\right] + \dots$$

$$G''_M(\omega) \sim -b_1\left[G(2t) - G(4t)\right]$$
$$+ b_2\left[G(t) - G(2t)\right]$$
$$+ b_3\left[G(t/2) - G(t)\right]$$
$$+ b_4\left[G(t/4) - G(t/2)\right]$$
$$+ b_5\left[G(t/8) - G(t/4)\right] \tag{12}$$
$$+ b_6\left[G(t/16) - G(t/8)\right]$$
$$+ b_7\left[G(t/64) - G(t/32)\right]$$
$$+ b_8\left[G(t/256) - G(t/128)\right] + \dots$$

where $a_{i's}$ and $b_{i's}$ are the coefficients that define the parametric method and can be checked in the work of Schwarzl (1971). The value of t used in the calculation is equal to the inverse of the frequency at a given point. The values of $G(t)$ were obtained using Equations (1)-(5), with the integrals appearing in Eq. (1) being evaluated either by the conventional trapezoidal rule or by the Gauss-Hermite quadrature proposed in the next section.

Due to the large range of possible values for the GEX parameters k, m, and M_{ref}, and the observed correlation among these parameters, the optimization problem described by Eq. (10) was solved considering an auxiliary parameter ζ:

$$\zeta = \frac{1}{M_{ref}{}^m} \tag{13}$$

which implies:

$$M_{ref} = \zeta^{-\frac{1}{m}} \tag{14}$$

Approximation of the Integral Relating the Shear Relaxation Modulus by Gauss-Hermite Quadrature

Based on the orthogonality of Hermite polynomials with respect to the weight function $\omega(x) = \exp(-x^2)$ in the interval $(-\infty, +\infty)$, Gauss quadrature can be used to approximate the following integral:

$$\int_{-\infty}^{+\infty} \omega(x) f(x) \, dx \approx \sum_{i=1}^{N_{quad}} w_i f(x_i) \tag{15}$$

where the abscissas x_i are the roots of the Hermite polynomial of degree N_{quad}, and w_i are the weights of the quadrature. This integral is exact when $f(x)$ is a polynomial of degree less than $2 N_{quad}$ (Abramowitz and Stegun, 1972; Press *et al.,* 1988). To apply the Gauss-Hermite quadrature in approximating the inverse problem, the first step is to rewrite the GEX function (Equation 5) in terms of a weight function $\omega(x) = \exp(-x^2)$ to later apply the double reptation mixing rule (Equation 1). By defining the following terms:

$$\Delta = \left[\frac{\Gamma\left(\frac{k+2}{m}\right)}{\Gamma\left(\frac{k}{m}\right)} \right]^{1/2} = \frac{\sqrt{\bar{M}_n \, \bar{M}_w}}{M_{ref}} \tag{16}$$

$$\phi = c\sqrt{\ln(PD)} \tag{17}$$

and

$$x = \frac{\ln\left(\frac{M}{M_{ref}\Delta}\right)}{\phi} \tag{18}$$

where c in Eq. (17) is a scaling constant used to regulate the distribution of the quadrature points in the range of molecular weights of interest, the GEX function can be expressed by the following equation:

$$P(x) = \frac{m}{M_{ref}\,\Gamma\left(\frac{k+1}{m}\right)} \Delta^k$$
$$\exp\left[k\phi x - \Delta^m \exp(m\phi x) \right] \tag{19}$$

Equation (19) can be written in terms of the weight function $\omega(x)$ as follows:

$$P(x) = g(x) \exp(-x^2) \tag{20}$$

where:

$$g(x) = \frac{m}{M_{ref}\,\Gamma\left(\frac{k+1}{m}\right)} \Delta^k$$
$$\exp\left[k\phi x - \Delta^m \exp(m\phi x) + x^2 \right] \tag{21}$$

Then the Gauss-Hermite quadrature can be applied to calculate the relaxation module $G(t)$ represented by the double reptation mixing rule. First, $P(M)\,dM$ is written as $P(x)\,dx$:

$$P(M)\,dM = M_{ref}\Delta \exp(\phi x)\,\phi P(x)\,dx \tag{22}$$

Thus, applying this change of variable to the double reptation mixing rule, Eq. (1), results in:

$$G(t) = G_N^0 \left[\int_{-\infty}^{+\infty} g^*(x) \exp(-x^2) dx \right]^\beta \tag{23}$$

where:

$$g^*(x) = g(x) F^{\frac{1}{\beta}}(t,x) M_{ref}\Delta \exp(\phi x)\phi \tag{24}$$

The double reptation mixing rule can then be calculated in terms of Gauss-Hermite quadrature by the following equation:

$$G(t) \approx G_N^0 \left[\sum_{i=1}^{N_{quad}} w_i g^*(x_i) \right]^\beta \tag{25}$$

It is important to remark that the application of the quadrature scheme proposed in this paper for the mixing rule (Eq. 25) requires the determination of the appropriate number of quadrature points and the specification of the constant c, while in the trapezoidal rule the number of subintervals and minimum and maximum values of molecular weight have to be specified as tuning parameters for the numerical integration procedure.

Direct Problem

Before treating the inverse problem described previously, a direct problem was analyzed in order to verify the implementation of molecular models used in this work. This direct problem consisted of calculating the linear viscoelastic properties of a reference sample by using the molecular weight distribution, obtained from its specific GEX function, in the double reptation mixing rule. A polystyrene sample characterized by van Ruymbeke *et al.* (2002a) was used as reference in this analysis, since for this sample both the rheometric data and the GEX function parameters were available.

Materials and Rheological Measurements

Two commercial grades of high density polyethylene (HDPE) were used. These samples, named PE1 (homopolymer used for injection) and PE2 (copolymer used for injection), were kindly provided by the Technology and Innovation Centre of *BRASKEM* S.A., as well as their GPC curves The referred GPC analyses were performed in a Waters model GPC/V2000 liquid chromatograph with RI detection, viscosimetric detector (DV), four columns (Toso-Hass HT[3], HT[4], HT[5], and HT[6]) and a pre-column (500Å), using narrow PS standards for calibration purposes and a standard polydisperse polyethylene to check the calibration curve. The size-exclusion chromatography (SEC) was carried out at 140 °C in 1,2,4-trichlorobenzene enhanced with BHT. Since both PE1 and PE2 are produced by a catalytic process which does not generate long chain branches (LCBs), the GPC/SEC results for these two materials are expected to be free of any systematic error due to the presence of LCBs. The values of number and weight average molecular weight and polydispersity index of these polyethylenes are presented in Table 1.

Table 1: Available information of the samples studied.

Sample	Available information	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	$\bar{M}_w / \bar{M}_n$
PE1	HDPE, homopolymer, injection	21000	70000	3.3
PE2	HDPE, copolymer, injection	14000	80000	5.7

Since the parameters β (Equation (1)), K (Equation (3)), plateau modulus (G_N^0) and molecular weight between entanglements (M_e) are not dependent on the molecular weight distribution, a single value of each of these parameters was used for both samples of HDPE. These values were obtained from the literature (van Ruymbeke *et al.,* 2002a; van Ruymbeke *et al.,* 2002b; Léonardi *et al.,* 2000) and are shown in Table 2.

Table 2: Constants of the des Cloizeaux model (Equations (1)-(3)) for HDPE at 190 °C.

Parameter	Value	Parameter	Value
β	2.25	M^* [g/mol]	7.0×10^4
α	3	M_e [g/mol]	1500
K [s(mol/g)$^\alpha$]	1.4×10^{-17}	G_N^0 [Pa]	2.6×10^6

Dynamic storage and loss moduli were determined using a strain-controlled rheometer (*Rheoplus* from Anton Paar) in the dynamic mode with a parallel plate geometry (25 mm diameter) at 190 °C. Linearity of the viscoelastic regime was checked by strain sweep tests. In order to obtain linear viscoelasticity measurements, strains of 5.5% for PE1 and 4.5% for PE2 were used for all the subsequent tests. The angular frequency sweep interval was 0.1-500 rads^{-1}.

RESULTS

Check of the Implemented Routines with the Direct Problem

The three sets of parameters k, m, and M_{ref} presented by van Ruymbeke *et al.* (2002a) for their polystyrene sample PS1 were applied in the implemented routines to calculate the dynamic moduli of this sample using the *des Cloizeaux* model. Although the three set of parameters provided quite similar results, as reported by van Ruymbeke *et al.* (2002a), all curves of moduli obtained with the implemented routines presented a systematic error characterized by a negative displacement in relation to the experimental data. This systematic error can be observed in the dashed lines of Figure 1, calculated with the parameter set $k = 11.245$, $m = 3.922$, and $M_{ref} = 272.960$. It is important to mention that these systematic deviations are not observed in the work of van Ruymbeke *et al.* (2002a).

The discrepancy observed in Figure 1, i.e., the vertical shift of about 5/4 for the predicted dynamic moduli (G' and G'') compared to the experimental data, can be related to an uncertainty in the plateau modulus (G_N^0), which is very difficult to measure experimentally. Therefore, if the value of the plateau modulus corrected by the factor 5/4 is considered, an adequate

representation of the experimental data is observed (solid lines of Figure 1). This correction in the plateau modulus was used in all the remaining calculations.
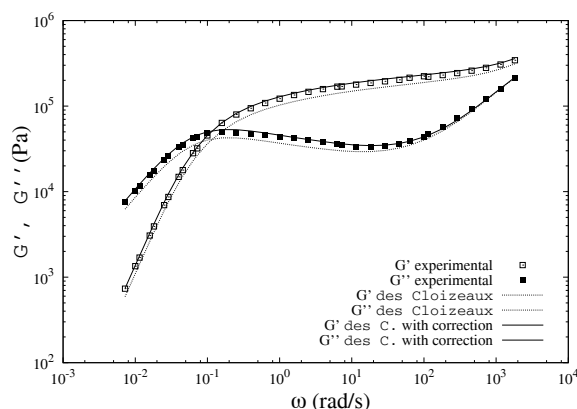

Figure 1: Experimental values of G' and G'' and values predicted by the direct problem using the GEX function with parameters k, m and M_{ref}.

Performance of the Gauss-Hermite Quadrature in the Approximation of the Inverse Problem

The inverse problem was approximated for the samples PE1 and PE2 using the trapezoidal rule and Gauss-Hermite quadrature. In the case of the trapezoidal rule, M_e was adopted as the lower limit of integration and a molecular weight of 10^7 g/mol was used as the upper limit of integration and the integration points were equally spaced on a logarithm scale. In order to make a comparison between these integration procedures, the number of points, N, used to represent the molecular weight distribution was varied in the interval ranging from 12 to 55 points.

The parameters k, m and ζ were estimated using the *Nelder-Mead* algorithm as implemented in the function *fminsearch* of MATLAB 5.3 (*The MathWorks, Inc.*) with multiple starting points to skip possible local minima, followed by the Levenberg-Marquardt algorithm implemented in the function *lsqnonlin* of MATLAB 5.3 to refine the solution. The iterations converged when the absolute change in two successive χ^2 values was less than 10^{-6}. A comparison between the estimated MWD and the results of characterization by GPC was carried out, and the dynamic moduli G' and G'' were predicted through the double reptation mixing rule and *Schwarzl* relations (Schwarzl, 1971) and compared with experimental data. For this purpose, the optimization results were expressed in terms of the following parameters: (i) relative difference between estimated

and experimental (GPC) values of the average molecular weights $\bar{M}_n$ and $\bar{M}_w$ ($\%E\bar{M}_n$ and $\%E\bar{M}_w$, respectively), (ii) root mean square error (*RMSE*) and (iii) the estimated relative integration error ($EI_{method,i}$). These parameters were defined as follows:

$$\%E\bar{M}_n = \left| \frac{\bar{M}_{n,calculated} - \bar{M}_{n,GPC}}{\bar{M}_{n,GPC}} \right| \times 100 \qquad (26)$$

$$\%E\bar{M}_w = \left| \frac{\bar{M}_{w,calculated} - \bar{M}_{w,GPC}}{\bar{M}_{w,GPC}} \right| \times 100 \qquad (27)$$

$$RMSE = \sqrt{\frac{1}{N_E}\sum_{i=1}^{N_E}\left[\left(\frac{G'_{E_i} - G'_{M_i}}{G'_{E_i}}\right)^2 + \left(\frac{G''_{E_i} - G''_{M_i}}{G''_{E_i}}\right)^2\right] + \frac{\%E\bar{M}_n}{100} + \frac{\%E\bar{M}_w}{100}} \qquad (28)$$

$$EI_{method,i} = \frac{\left|I_{G-H,55} - I_{method,i}\right|}{I_{G-H,55}} \qquad (29)$$

where G'_{E_i} and G'_{M_i} are the experimental and predicted values of G', G''_{E_i} and G''_{M_i} are the experimental and predicted values of G'', $I_{G-H,55}$ is the value of the integral that represents the area under the MWD curve obtained with the Gauss-Hermite methodology using 55 quadrature points, and $I_{method,i}$ is the value of this integral obtained with the specified method (*G-H*: Gauss Hermite quadrature, or *TRAPZ*: trapezoidal rule) and i points of quadrature. $I_{G-H,55}$ was taken as representative of the exact value of the integral. Eq. (28) is similar to that presented by Borg and Pääkkönen (2009), differing in the fact that the number of experiments (N_E) is inside the square root to take the average of the square errors.

The problem was assessed using the criteria described above and, after preliminary tests, the appropriate number of points of molecular weight necessary to represent the MWD of each sample was chosen.

Figures 2-5 present the evolution of the parameters used to evaluate the optimization as a function of the number of quadrature points used. The results presented in these figures were obtained

using the *Nelder-Mead* algorithm and values of the Gauss-Hermite quadrature scale constant c (Eq. 15) of 1/2 for PE1 and 1/3 for PE2, according to the following procedure: (i) testing different initial estimates for $N = 8$, it was found that the sets $k = 5$, $m = 0.15$, $\zeta = 8$ for PE1 and $k = 0.5$, $m = 0.5$, $\zeta = 0.1$ for PE2 provide the best fit of the GPC data; (ii) the solution for the subsequent values of N tested (up to 55) was found using the optimal set of parameters found in the previous step as initial estimates.

Figure 2 shows the variation of $\%E\bar{M}_n$ with the number of points of molecular weights for PE1 and PE2 considering the trapezoidal rule and Gauss-Hermite quadrature. It is possible to observe that, for both samples, a limiting value of $\%E\bar{M}_n$ is obtained with the Gauss-Hermite quadrature for a high number of quadrature points, indicating convergence of the integration method. This limiting value of $\%E\bar{M}_n$ was close to 0% and was reached with $N = 12$ for sample PE1, while for PE2 it was around 4% and was reached with $N = 16$. On the other hand, the data of Figure 2 show that the trapezoidal rule provided

slower convergence, in such a way that a number of quadrature points higher than the maximum used here (55) would be required to achieve the limiting values of $\%E\bar{M}_n$ obtained with the Gauss-Hermite quadrature. Figures 3 and 4 show that the behaviours of the Gauss-Hermite quadrature and the trapezoidal rule in terms of the resulting values of $\%E\bar{M}_w$ and *RMSE* are basically the same as described for $\%E\bar{M}_n$, except that the limiting values obtained by the Gauss-Hermite for $\%E\bar{M}_w$ (4% for PE1 and 15% for PE2) were higher than those corresponding to $\%E\bar{M}_n$. However, in both cases the values found in the present work are of the same order of magnitude as those obtained by Léonardi *et al* (2002) ($E\bar{M}_{n\%} = 2.46$ and $E\bar{M}_{w\%} = 6.45$) in studying the inverse problem for another HDPE of polydispersity index 4.6. Furthermore, Léonardi (1999) obtained $E\bar{M}_{n\%} = 14.36$ and $E\bar{M}_{w\%} = 19.59$ for a HDPE sample of polydispersity index 6.42, applying the GEX function and the DRMD (Double Reptation with Molecular Dynamics) model.
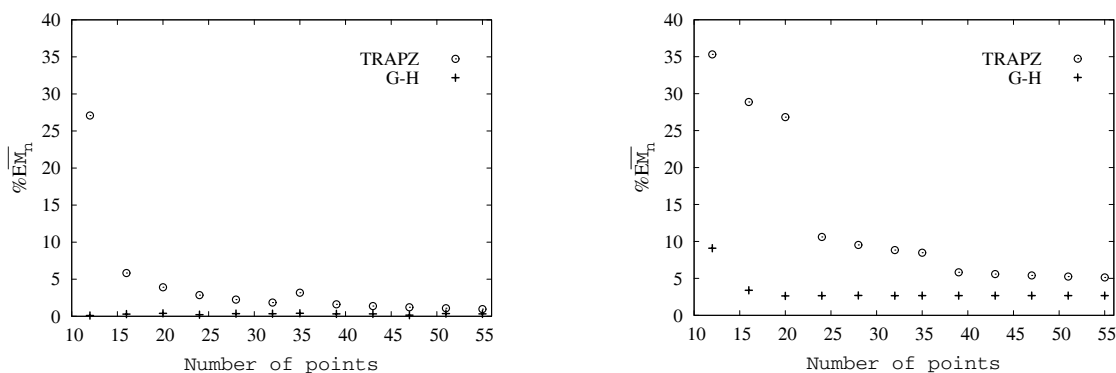

Figure 2: $\%E\bar{M}_n$ *versus* number of points of molecular weight for PE1 (on the left) and PE2 (on the right) samples using the trapezoidal rule and Gauss-Hermite quadrature.
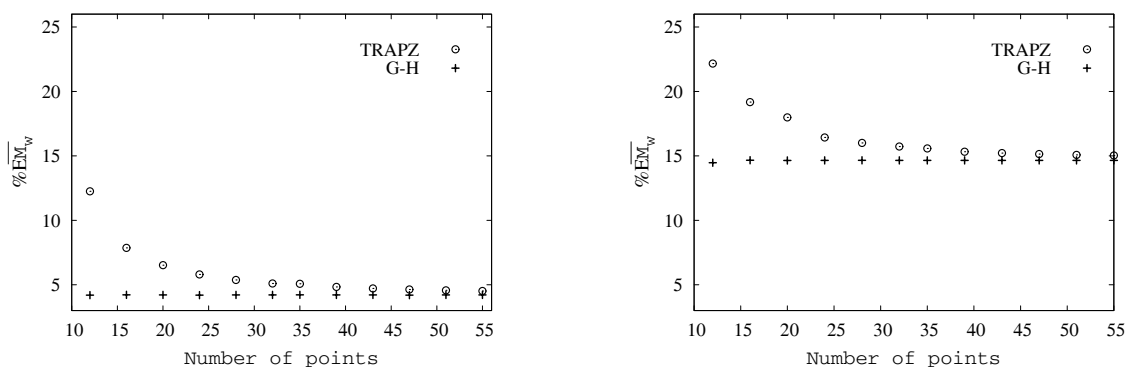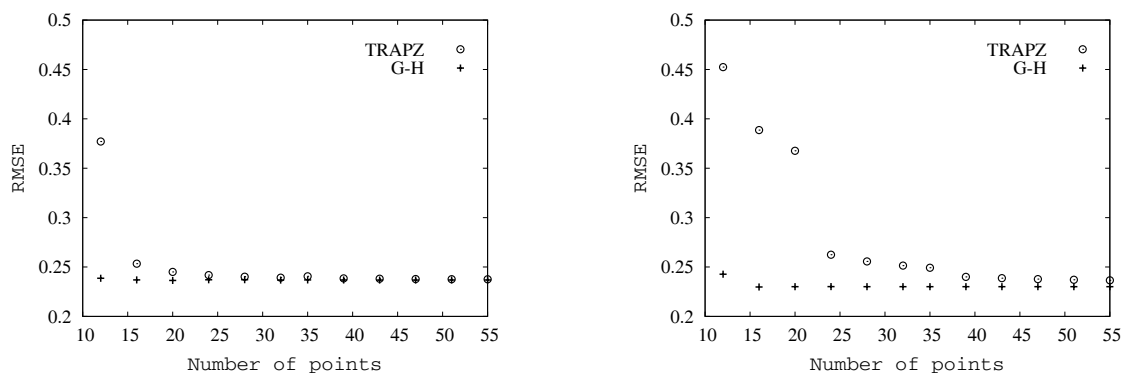

Figure 3: $\%E\bar{M}_w$ *versus* number of points of molecular weight for PE1 (on the left) and PE2 (on the right) samples using the trapezoidal rule and Gauss-Hermite quadrature.

Figure 4: *RMSE versus* number of points of molecular weight for PE1 (on the left) and PE2 (on the right) samples using the trapezoidal rule and Gauss-Hermite quadrature.

The slower convergence of the trapezoidal rule with relation to the Gauss-Hermite in terms of the parameters $\%E\bar{M}_n$, $\%E\bar{M}_w$ and *RMSE* can be explained directly based on the intrinsic variation presented by each method regarding the gain in precision resulting from an increase in the number of points of integration. As can be seen in Figure 5, the values of $EI_{G-H,i}$ decrease rapidly to values close to zero as the number of points of molecular weight increase, while for $EI_{TRAPZ,i}$ the decrease with the number points is much lower, mainly after around 20 points, limiting the accuracy which can be obtained.

Based on the previous discussion of the results presented in Figures 2-5, the results of the trapezoidal rule with $N = 55$, for both PE1 and PE2, and of the Gauss-Hermite quadrature with $N = 12$ for PE1 and $N = 16$ for PE2 were taken as reference in the subsequent analysis, where experimental and predicted data of MWD and moduli are compared. The values of $N = 12$ for PE1 and $N = 16$ for PE2

correspond to the minimal number of quadrature points required in the Gauss-Hermite quadrature to provide the same accuracy obtained when N tends to infinity. It is important to observe that these results indicate a trend of increase in the number of quadrature points needed to represent the MWD when the polydispersity index of the samples increases. In the case of the trapezoidal rule, the value of $N = 55$ was taken as a tradeoff between accuracy and computational effort based on the fact that a much larger number of integration points is required to achieve the same accuracy provided by the Gauss-Hermite quadrature.

The values obtained with the trapezoidal rule ($N = 55$) and the Gauss-Hermite quadrature ($N = 12$ for PE1 and $N = 16$ for PE2) for the GEX parameters and their standard deviation, the average molecular weights, and the parameters $\%E\bar{M}_n$, $\%E\bar{M}_w$ and *RMSE* are shown in Table 3. Concerning the parameter M_{ref}, according to Gloor (1983), it is related to the molecular weight, and is always a positive value.
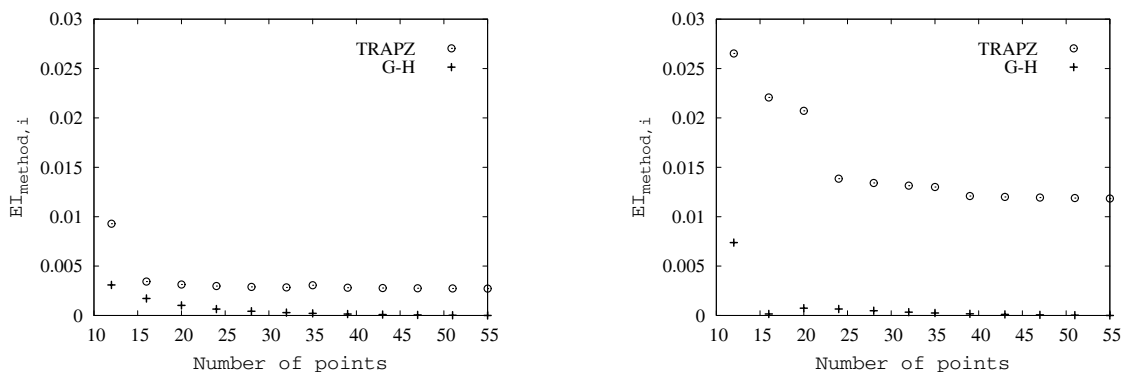

Figure 5: $EI_{TRAPZ,i}$ and $EI_{G-H,i}$ *versus* number of points of molecular weight for PE1 (on the left) and PE2 (on the right) samples using the trapezoidal rule and Gauss-Hermite quadrature.

Table 3: Approximate solutions of the inverse problem for PE1 and PE2 samples using the GEX function

PE1	55 points - TRAPZ	$k = 4.144$ $m = 0.1704$ $\zeta = 4.9081$ $M_{ref} = 8.8124 \times 10^{-5}$	$\sigma_k = 0.10945$ $\sigma_m = 0.0031738$ $\sigma_\zeta = 0.37222$ $RMSE = 0.2375$	$\bar{M}_n = 20796$ $\bar{M}_w = 66837$ $\bar{M}_w / \bar{M}_n = 3.2$	$\%E\bar{M}_n = 0.97$ $\%E\bar{M}_w = 4.52$
	12 points - G-H	$k = 4.16303$ $m = 0.17056$ $\zeta = 4.9067$ $M_{ref} = 8.9115 \times 10^{-5}$	$\sigma_k = 0.09302$ $\sigma_m = 0.002714$ $\sigma_\zeta = 0.31615$ $RMSE = 0.2386$	$\bar{M}_n = 20979$ $\bar{M}_w = 67062$ $\bar{M}_w / \bar{M}_n = 3.2$	$\%E\bar{M}_n = 0.10$ $\%E\bar{M}_w = 4.20$
PE2	55 points - TRAPZ	$k = 2.7864$ $m = 0.1674$ $\zeta = 3.8857$ $M_{ref} = 3.0181 \times 10^{-4}$	$\sigma_k = 0.02467$ $\sigma_m = 0.0009381$ $\sigma_\zeta = 0.08626$ $RMSE = 0.2365$	$\bar{M}_n = 13282$ $\bar{M}_w = 67976$ $\bar{M}_w / \bar{M}_n = 5.1$	$\%E\bar{M}_n = 5.13$ $\%E\bar{M}_w = 15.03$
	16 points - G-H	$k = 2.9597$ $m = 0.16101$ $\zeta = 4.5207$ $M_{ref} = 8.5279 \times 10^{-5}$	$\sigma_k = 0.02936$ $\sigma_m = 0.001035$ $\sigma_\zeta = 0.1130$ $RMSE = 0.2298$	$\bar{M}_n = 13525$ $\bar{M}_w = 68269$ $\bar{M}_w / \bar{M}_n = 5.0$	$\%E\bar{M}_n = 3.39$ $\%E\bar{M}_w = 14.66$

Our results indicate that this parameter behaves just as an adjustment factor and does not present physical significance, which is in agreement with the results reported by Cocchini and Nobile (2003), who reported values between 5.28×10^{-10} and 1.97×10^{4} for the parameter M_{ref} in the approximation of the inverse problem for samples of polypropylene, polyacetal, and mixtures of polystyrenes of different molecular weights. This can be explained on the basis that the ratio between the gamma functions in Eqs. (6)-(8) can be either much larger or much smaller than one, allowing M_{ref} to be of a different order of magnitude with relation to the molecular weight and the observed correlation between the parameters m and M_{ref} as given by Eq. (13).

The MWD curve obtained with the GEX parameters reported in Table 3 is compared with experimental data in Figures 6 and 8, where the GPC curves were used as a benchmark for a better understanding of which solved problem should be used. However, this is not the best criterion for assessing the quality of the results, since it is desirable to reach a methodology that is able to reliably determine the MWD without previous knowledge of the average molecular weights for comparison of the results. Because of that, a better evaluation of the molecular models and methodologies used to perform a detailed comparative study between these methods to assess the influence of the main parameters involved is of great importance. As seen from Figures 7 and 9, the estimated parameters do not perfectly fit the dynamic moduli. However, despite the model deficiency in reproducing accurately the data of G′ in the region of low frequency,

the accuracy achieved is still sufficient to obtain a good prediction of the MWD.
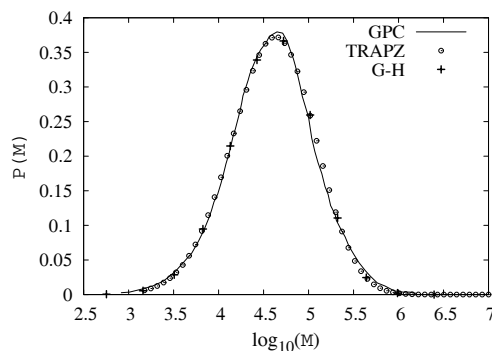

Figure 6: MWD of PE1 sample obtained by GPC and estimated by *Schawrzl* relations (55 points with the trapezoidal rule and 12 points with Gauss-Hermite quadrature).
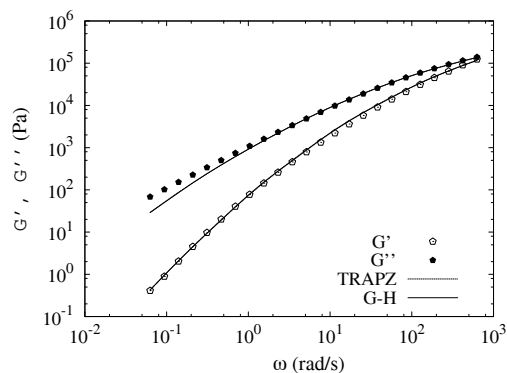

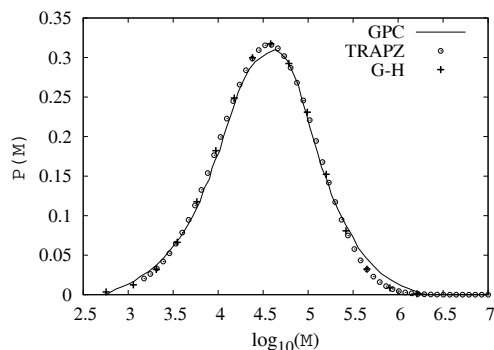**Figure 7**: Experimental and predicted dynamic moduli of sample PE1.

Figure 8: MWD of sample PE2 obtained by GPC and estimated by *Schawrzl* relations (55 points with trapezoidal rule and 16 points with Gauss-Hermite quadrature).
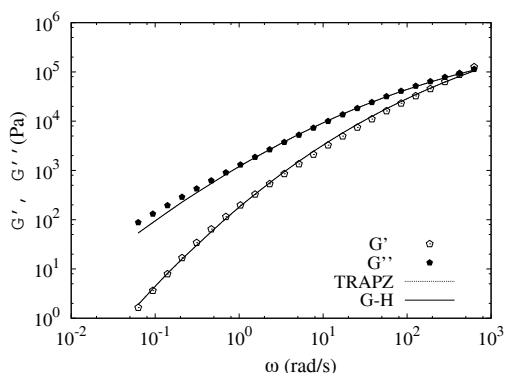

Figure 9: Experimental and predicted dynamic modules of sample PE2.

CONCLUSIONS

The methodology using Gauss-Hermite quadrature for determining the MWD through a *Schawrzl* parametric approach considering the *des Cloizeaux* model and GEX function with the double reptation mixing rule was applied to commercial samples of HDPE. In testing the developed methodology for polymer samples with polydispersity index less than 10, it was possible to estimate MWD curves and their parameters with good agreement with experimental data from GPC. The inverse problem behaviour was similar for samples with the same polydispersity index found in the literature.

The proposed change of variable in the GEX function to apply the Gauss-Hermite quadrature for solving the integral of the double reptation mixing rule was assessed. There was a tendency to increase the number of quadrature points needed to represent the MWD with increasing polydispersity index of the samples. Compared to the trapezoidal rule, the

Gauss-Hermite quadrature was found to present faster convergence with the increase of the number of integration points, providing more accurate results. This characteristic of integration accuracy can contribute to increase the potential of the prediction of MWD from dynamic rheometry as a tool to be used for practical applications.

NOMENCLATURE

a	Coefficients that define the parametric method	
b	Coefficients that define the parametric method	
c	Scale constant used to regulate the distribution of the quadrature points	
$\%E\bar{M}_n$	Relative difference between estimated average molecular weights and those obtained by GPC	-
$\%E\bar{M}_w$		-
$f(x)$	Polynomial of degree less than 2 N_{quad}	-
$F(t,M)$	Kernel function describing the relaxation behaviour of a monodisperse polymer	-
G'	Elastic modulus	Pa [kg.m^{-1}s^{-2}]
G''	Viscous modulus	Pa [kg.m^{-1}s^{-2}]
$G(t)$	Relaxation module	Pa [kg.m^{-1}s^{-2}]
G_N^0	Plateau modulus	Pa [kg.m^{-1}s^{-2}]
k	Parameter which define the GEX distribution	-
K	Constant related to the temperature and the structure of the material	s(mol/g)$^\alpha$

m	Parameter which define the GEX distribution	-
M	Molecular weight	$g.mol^{-1}$
M_e	Molecular weight between entanglements	$g.mol^{-1}$
M_{ref}	Parameter which define the GEX distribution	$g.mol^{-1}$
M^*	Parameter of des Cloizeaux model related to the molecular weight between entanglements (M_e)	$g.mol^{-1}$
$\bar{M}_n$	Number average molar mass	$g.mol^{-1}$
$\bar{M}_w$	Weight average molar mass	$g.mol^{-1}$
$\bar{M}_w / \bar{M}_n$	Polydispersity index	-
$\bar{M}_z$	Z average molar mass	$g.mol^{-1}$
N	Number of points of molecular weight	-
N_{quad}	Number of quadrature points	-
$P(M)$	Distribution function used to represent the MWD	-
t	Time	s
w_i	Weights of the quadrature	-
x	Roots of the Hermite polynomial	-

Greek Letters

α	Constant related with the structure of the material and with the temperature	-
β	The exponent of the double reptation mixing rule	-
Γ	Gamma Function	
Δ	Term written in terms of function parameters GEX	-
λ_{rept}	Relaxation Time	s
ζ	Auxiliary parameter	-
ϕ	Term written in terms of function parameters GEX	-
χ^2	Value of the objective function	-
ω_i	Experimental frequency	rad/s
$\omega(x)$	Weight function	-

Subscripts

Ei	Experimental data	
Mi	Theoretical values predicted by the model	

$G'G$	Considering simultaneous contribution of G´ and G´´	
ODD	Summation of all the odd integers	

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