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Applications of Monte Carlo method to nonlinear regression of rheological data

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In rheological study, it is often to determine the parameters of rheological models from experimental data. Since both rheological data and values of the parameters vary in logarithmic scale and the number of the parameters is quite large, conventional method of nonlinear regression such as Levenberg-Marquardt (LM) method is usually ineffective. The gradient-based method such as LM is apt to be caught in local minima which give unphysical values of the parameters whenever the initial guess of the parameters is far from the global optimum. Although this problem could be solved by simulated annealing (SA), the Monte Carlo (MC) method needs adjustable parameter which could be determined in ad hoc manner. We suggest a simplified version of SA, a kind of MC methods which results in effective values of the parameters of most complicated rheological models such as the Carreau-Yasuda model of steady shear viscosity, discrete relaxation spectrum and zero-shear viscosity as a function of concentration and molecular weight.

Keywords: Monte Carlo method, Caurreu-Yasuda model, discrete relaxation spectrum, scailing theory, nonlinear regression

1. Introduction

In polymer rheology, a number of mathematical models have been developed. Although most of them are known to agree with experimental data quite well, they consist of a number of parameters which vary in logarithmic scale and are not negative. Determination of the parameters from experimental data can be done by nonlinear regression. Levenberg-Marquardt (LM) algorithm is one of the most popular methods of nonlinear regression and is equipped in commercialized softwares for scientific graph such as SigmaPlot$^{\text{TM}}$ and Origin$^{\text{TM}}$. However, the results from LM algorithm are often disappointing because the algorithm depends largely on the initial guess on the parameters. Even if the user of the LM algorithm is an expert of rheology, unphysical results might be obtained. Cho (2016) suggested that logarithmic rescaling of parameters and the object function is helpful for the nonlinear regression. In summary, use of LM algorithm needs a process of trial and errors because (1) the variations of viscoelastic functions and their arguments are logarithmic; (2) the variations of the parameters are also logarithmic; (3) the number of the parameters is quite large; (4) the LM algorithm depends largely on initial values of the parameters which should be given according to the experience of the user.

Simulated annealing (SA) algorithm was developed by Kirkpatrick *et al.* (1983) and is known as one of the most effective algorithms for the regression problems which have a number of parameters (Aarts and Korst, 1989). This algorithm gives a good approximation of the global minimum of optimization problems which cannot be solved practically by a brute-force method. It is a kind of Monte Carlo method which generates a number of sets of parameters randomly and selects a most probable set of parameters according to the principle analogous to those of statistical mechanics. Details of SA algorithm are found in Press *et al*. (2002). To the authors' knowledge, Jensen (2002) would be the first which applied the SA algorithm to rheological problem.

The heating-and-cooling process in SA algorithm is apt to take unnecessarily long calculation time even if the number of parameters is not too much large. Furthermore, additional parameter is needed to control the heating-and-cooling. We guess that the algorithm could be effective even if the heating-and-cooling process is omitted. Because modern personal computer is sufficiently fast, we adopted such a simplified version of SA algorithm. We applied the simple MC method to various rheological problems such as steady shear viscosity model called the Carreau-Yasuda model (Bird *et al*., 1987), discrete relaxation spectrum and scaling theory of zero-shear viscosity of polymer solutions. It is expected that our algorithm would be effective for other rheological problems, too.

2. Monte Carlo algorithm

2.1. Parameter transform and measure of errors

We are interested in nonlinear regression for a nonlinear rheological equation with N parameters whose values vary in logarithmic scale. Let denote the viscoelastic function as $f(\mathbf{x};\mathbf{q})$ where $\mathbf{x} = (x_1, x_2, ..., x_L)$ represents the indepen-

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dent variables and $\mathbf{q} = (q_1, q_2, ..., q_N)$ represents the parameters. Since most viscoelastic functions are not negative, we shall be concentrated on a positive function which may vary in logarithmic scale as its arguments. Because of these characteristics of rheological data, the model function and parameters satisfy the followings:

$$0<x_k<\infty \text{ for } k=1, 2, ..., L, \tag{1}$$

$$0<q_k<\infty \text{ for } k=1, 2, ..., N, \tag{2}$$

and

$$f(\mathbf{x}, \mathbf{q}) \geq 0 \text{ for } \forall \mathbf{x} \text{ and } \forall \mathbf{q}. \tag{3}$$

Since parameters vary in logarithmic scale, it is more convenient to use the transform:

$$\theta_k = \log q_k. \tag{4}$$

Note that this transform of parameters prevents the occurrence of negative values of q_k since $q_k = \exp(\theta_k)$. Even though one may not know the optimum values of q_k, it is usual that most rheologists know the order of magnitude of q_k. Hence, the transform of Eq. (4) is a valuable tool for the regression with the constraints of $q_k > 0$.

Regression analysis gives the optimum values of the parameters from the minimization of the sum of square errors (SSE) such that

$$\chi^2 \equiv \sum_{\alpha=1}^{M} [y_\alpha - f(\mathbf{x}_\alpha;\boldsymbol{\theta})]^2. \tag{5}$$

However, this measure of error is not effective for rheological data because data y_α vary in logarithmic scale. Hence, most rheologists are interested in

$$\chi^2_{\mathrm{rel}} \equiv \sum_{\alpha=1}^{M} \left[1 - \frac{f(\mathbf{x}_\alpha;\boldsymbol{\theta})}{y_\alpha}\right]^2 \tag{6}$$

or

$$\mathrm{SSE} \equiv \sum_{\alpha=1}^{M} \left[\log \frac{f(\mathbf{x}_\alpha;\boldsymbol{\theta})}{y_\alpha}\right]^2. \tag{7}$$

Here, we prefer to use Eq. (7): Logarithmic sum of square errors. In order to estimate the accuracy of the regression, we will use the coefficient of determination which is defined as

$$R^2 \equiv 1 - \frac{\mathrm{SSE}}{\mathrm{SST}} \tag{8}$$

where SST is the total sum of square defined as

$$\mathrm{SST} = \sum_{\alpha=1}^{M} [\log y_\alpha - \langle \log y \rangle]^2 \tag{9}$$

where $\langle \log y \rangle$ is the mean of $\log y_\alpha$. If the model function $f(\mathbf{x}_\alpha;\boldsymbol{\theta})$ is suitable for the description of the data then it is usual that $0 \leq R^2 \leq 1$. The perfect fit of the data gives $R^2 = 1$.

2.2. Description of the algorithm

Regression is to seek the point in the parameter space which minimizes the sum of square errors. Instead of brute-force seeking, we generate N_R random numbers for θ_k within a given interval. The random number can be generated from uniform distribution and the interval is given from the knowledge of the order of magnitude of q_k. Among the N_R sets of parameters, we can find the parameter sets whose coefficients of determination are larger than a certain value, say R_C. We shall call the sets of parameters the accepted set of parameters. The average of R^2's and upper and lower bounds of parameters ($\theta_k^{\max}$ and $\theta_k^{\min}$) are calculated from the accepted sets of parameters. The average of R^2 is used as R_C for the next iteration and so are $\theta_k^{\max}$ and $\theta_k^{\min}$ for the new intervals of parameters. Repetition of the Monte Carlo seeking results in reduction of the width of the intervals of parameters. Finally we observe that $\theta_k^{\max} - \theta_k^{\min}$ goes to zero for all k and R^2 goes to unity if the initial intervals of parameters include the optimum values of parameters and we are lucky. We repeat the MC seeking by N_iter times. The first N_iter times of MC seeking is called the initial MC seeking.

Since MC seeking is a statistical process, the generated sets of parameters may miss the optimum point of the parameter space. In this case, although $\theta_k^{\max} - \theta_k^{\min}$ goes to zero during the initial MC seeking, R^2 is still much smaller than unity. To overcome this problem, we restart the Monte Carlo seeking with the new intervals defined as follows:

$$\theta_k^{\min} - \Delta\theta_k < \theta_k < \theta_k^{\max} + \Delta\theta_k \tag{10}$$

where $\theta_k^{\min}$ and $\theta_k^{\max}$ are the lower and upper bounds of parameters in the accepted sets of previous N_iter times of Monte Carlo seeking and $\Delta\theta_k$ is newly given values which controls the width of the interval of parameters. This process is called the refining MC seeking. A few times of the refining MC seeking gives acceptably high value of R^2. Then we succeed in the nonlinear regression.

In the next sections, we shall apply the MC method to various examples of rheological data: Those of steady shear viscosity at various shear rates and temperatures; those of dynamic moduli for discrete relaxation time spectrum; those of zero-shear viscosity of polymer solution as a function of concentration and molecular weight.

3. Steady Shear Viscosity Model

Steady shear viscosity of polymer melts is known to agree very well with the Carreau-Yasuda model (Bird *et al.*, 1987). Setting the shear viscosity at infinite shear rate as zero, the Carreau-Yasuda model is expressed by

$$\eta(\dot\gamma, T) = \frac{\eta_0(T)}{\{1 + [\eta_0(T)\dot\gamma/\sigma_0]^a\}^b} \tag{11}$$

where $\eta_o(T)$ is the zero-shear viscosity which is a function of temperature such as

$$\eta_o(T) = K\exp\left(\frac{T_A}{T}\right). \tag{12}$$

Note that T is the absolute temperature and T_A is called the activation temperature which can also be expressed by $T_A = E_A/R$ where R is the gas constant and K can be interpreted by the zero-shear viscosity at infinite temperature.

The Carreau-Yasuda model consists of five positive parameters: a; b; σ_o; K; T_A. The model manifests that

$$\eta(\dot{\gamma},T) \approx \begin{cases} \eta_o(T) & \text{for } \dfrac{\eta_o(T)}{\sigma_o}\dot{\gamma} << 1 \\ \dfrac{\eta_o(T)}{[\eta_o(T)\dot{\gamma}/\sigma_o]^{ab}} & \text{for } \dfrac{\eta_o(T)}{\sigma_o}\dot{\gamma} >> 1 \end{cases}. \tag{13}$$

If the interval of shear rates is wide enough to include the conditions of Eq. (13), we can collect the values of $\eta_o(T)$ for the temperatures and can determine the values of K and T_A by using the Arrhenius plot: The plot of log η_o versus T^{-1}. Furthermore the collection of data at high shear rates gives the determination of ab and $\eta_o^{1-ab}\sigma_o^{-ab}$. However, it is usual that the interval of shear rate $\dot{\gamma}_{\min} < \dot{\gamma} < \dot{\gamma}_{\max}$ cannot include the all conditions of Eq. (13) for any temperature. Usual experimental data look like Fig. 1.

We generated the data of Fig. 1 by using the following values of parameters:

$$a = 0.7;\ b = 0.5;\ \sigma_o = 2500 \text{ Pa};$$
$$T_A = 10{,}000 \text{ K};\ K = 5\times10^{-6} \text{ Pa·s}. \tag{14}$$

If Eq. (11) is used without the transform of parameters such as Eq. (4), then gradient-based method such as Levenberg-Marquardt method cannot give reasonable results since escape from a local minimum is nearly impossible. Even if Eq. (11) is used with the transform, then the deterministic nature of LM method gives the parameters of a local minimum instead of the global minimum whenever the initial condition is near the local minimum. Before testing the MC method, we investigate the dependence of LM method on initial guess and the results are listed in Table 1.

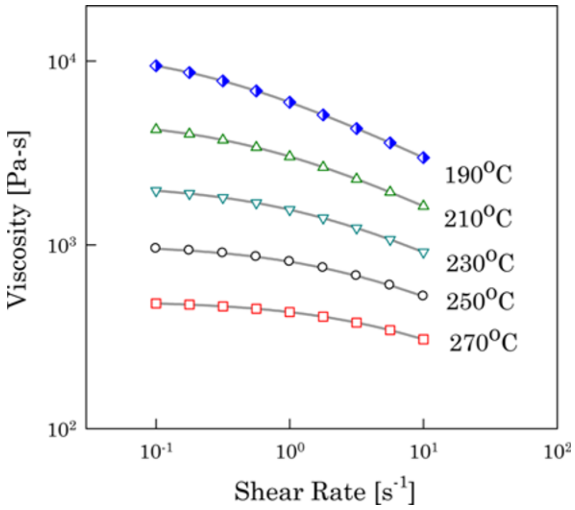

Fig. 1. (Color online) Hypothetical shear viscosity and regression by Monte Carlo method. The symbols represent the viscosities calculated from the parameter values of Eq. (14) and the line represents the viscosity calculated from the parameter values obtained from Monte Carlo method (Table 2, n = 6).

As shown in Table 1, LM method gives unrealistic results in some cases depending on initial guess. For example, b is negative and σ_o is far from the original value. However, the MC method finds the optimum values within the ranges which guarantee the physical meanings of the parameters.

We conducted the Monte Carlo method with the following initial intervals for various numbers of parameter sets: $N_R = 10^4$, 3.5×10^4 and 5×10^5.

$$0 < a < 1;\ 0 < b < 1;\ 0 < \log\sigma_o < 10;$$
$$0 < \log T_A < 10;\ -10 < \log K < 0. \tag{15}$$

The number of parameter sets N_R means that we generate N_R random numbers for each parameter according to the interval of Eq. (15). Since the number of parameters is 5 in this case, the total number of random numbers for each iteration step is $5N_R$. Although this number is huge, a modern personal computer has sufficiently high speed to

Table 1. Initial guesses and regression results of Levenberg-Marquardt method.

	Initial Guess	Regression Results	Initial Guess	Regression Results	Initial Guess	Regression Results
a	0.5	0.4127	0.5	24.04	0.5	0.7000
b	0.5	0.4127	0.5	–52.52	0.5	0.5000
σ_o	$\log\sigma_o = 12$	0.6983	$\log\sigma_o = 8$	1.280×10^{98}	$\log\sigma_o = 9$	2500
T_A	$\log T_A = 11$	9,957	$\log T_A = 8$	8,258	$\log T_A = 9$	9,997
K	$\log K = -12$	0.0254	$\log K = -8$	1.046×10^{-4}	$\log K = -9$	4.980×10^{-6}
R^2	0.9892		0.9209		1.000	
Decision	Unrealistic		Unrealistic		Realistic	

Table 2. Regression results of Monte Carlo method.

N_R	a	b	σ_o	T_A	K	R^2
10,000	0.6341	0.5049	3002	9004	3.48×10^{-6}	0.8655
	0.6161	0.6012	3911	9558	1.19×10^{-6}	0.9723
	0.6418	0.5567	3487	9495	1.33×10^{-6}	0.9649
	0.5906	0.6276	4653	9243	2.20×10^{-6}	0.9215
	0.5909	0.6387	4650	9374	1.70×10^{-6}	0.9454
relative error	**12.2%**	**17.2%**	**57.6%**	**6.65%**	**60.4%**	
35,000	0.6656	0.5452	2873	1.000×10^4	5.02×10^{-6}	1.000
	0.6850	0.5181	2637	1.000×10^4	5.00×10^{-6}	1.000
	0.6559	0.5577	2961	1.000×10^4	5.01×10^{-6}	1.000
	0.6940	0.5071	2553	1.000×10^4	5.00×10^{-6}	1.000
	0.6858	0.5168	2623	1.000×10^4	5.00×10^{-6}	1.000
relative error	**3.25%**	**5.80%**	**9.18%**	**0.02%**	**0.12%**	
50,000	0.7	0.5	2500	1.000×10^4	5.00×10^{-6}	1.000
	0.7	0.5	2500	1.000×10^4	5.00×10^{-6}	1.000
	0.7	0.5	2500	1.000×10^4	5.00×10^{-6}	1.000
	0.7	0.5	2500	1.000×10^4	5.00×10^{-6}	1.000
	0.7	0.5	2500	1.000×10^4	5.00×10^{-6}	1.000
relative error	**0%**	**0%**	**0%**	**0%**	**0%**	

finish the calculation within a minute. The results of the MC method are listed in Table 2.

As shown in Table 2, the accuracy of the MC regression increases, as N_R increases. The relative error of parameter is defined as $100(1-\theta/\theta^*)$, where θ and θ^* are, respectively, the calculated and original values of parameter. Although the MC method is originally statistical, Table 2 shows that if N_R is sufficiently large then statistical nature of the MC regression is reduced quite largely.

One of the most interesting features of the Carreau-Yassuda model is the shear rate-temperature superposition of the plot of the reduced viscosity ($\tilde{\eta}$) and shear rates ($\tilde{\dot{\gamma}}$) defined as follows:

$$\tilde{\eta} \equiv \frac{\eta(\dot{\gamma},T)}{\eta_o(T)}; \quad \tilde{\dot{\gamma}} \equiv \frac{\eta_o(T)}{\sigma_o}\dot{\gamma}. \tag{16}$$

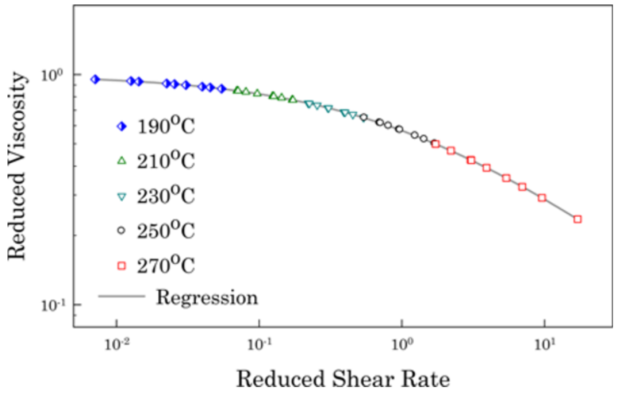

Fig. 2. (Color online) Master curve of the shear viscosity of Fig. 1. The reduced viscosity is $\eta(\dot{\gamma},T)\eta_o(T)$ and the reduced shear rate is $\eta_o(T)\dot{\gamma}/\sigma_o$.

From the determined parameters, we can calculate the reduced viscosity and shear rate of the raw data. Figure 2 shows the superposition.

4. Discrete Relaxation Spectrum

4.1. A brief review on studies of relaxation spectrum

Relaxation spectrum cannot be measured directly but it can be calculated from measureable viscoelastic functions such as relaxation and dynamic moduli. Although relaxation spectrum is one of the best ways to convert a viscoelastic function to another when data range is finite (He *et al*., 2004), it would be useless if it cannot be determined uniquely from data. Because of the ill-posedness of the problem (Honerkamp, 1989), there has been doubt on the uniqueness of relaxation spectrum (Malkin and Masalova, 2001). However, it was proven by Fuoss and Kirkwood (1941) that continuous relaxation spectrum is uniquely determined from dynamic moduli. Although continuous spectrum is unique, it does not mean that discrete spectrum is unique. In our opinion, discrete spectrum is an approximation of the continuous spectrum (Bae and Cho, 2016).

In the beginning of the study of algorithms of relaxation spectrum, the ill-posedness of the problem was not recognized. One of the algorithms of these times is that of Tobolsky and Murakami (1959). After the work of Honerkamp and Weese (1989), ill-posedness has been considered in development of algorithms of continuous spectrum (Bae and Cho, 2015; Cho and Park, 2013; Cho, 2013; Honerkamp and Weese, 1993; Stadler and Bailly, 2009).

As for discrete spectrum, one of the most remarkable algorithms was developed by Baumgärtel and Winter (1989), which is known as IRIS. Although the performance of the algorithm is amazing, mathematical analysis on how the algorithm works well was not studied rigorously. It can be said that IRIS is based on nonlinear regression of least square. On the other hand, Fulchiron *et al.* (1993) and Simhambhatla and Leonov (1993) are the algorithms based on Padé-Laplace method. Although the Padé-Laplace method is found on more rigorous mathematical basis, success of this algorithm depends largely on how accurately the Laplace transform of relaxation modulus could be obtained from experimental data. Note that experimental data are measured in a finite range of time (or frequency) while the Laplace transform should be calculated from the integration over the whole time: $0 \le t < \infty$ (or $0 \le \omega < \infty$).

Although continuous spectrum is unique, it is questionable whether discrete spectrum is unique. Since discrete spectrum can be considered as an approximation of continuous spectrum, it is not important to concerns its uniqueness. Malkin and Masalova (2001) tested various algorithms for discrete spectrum and found that different algorithms give different discrete spectra although they generate almost identical dynamic moduli. On the other hand, Bae and Cho (2015) showed that various algorithms for continuous spectrum give nearly identical spectra from the same data. This implies that continuous spectrum can be used for the identification of materials while discrete spectrum cannot. However, discrete spectrum is more convenient than continuous one because of simplicity of calculation. If someone wants to calculate nonlinear flow behavior of viscoelastic fluid with a nonlinear viscoelastic constitutive equation which consists of relaxation spectrum and genuine nonlinear parameters, then discrete spectrum is more convenient than continuous one.

From the viewpoint of regression, determination of discrete spectrum should avoid the results of negative values of relaxation times and intensities. Since these give rise to difficulty in numerical method, Cho (2010) applied wavelet function. However, this algorithm is not stable for the errors in the experimental data. Algorithm of Bae and Cho (2016) avoids the unrealistic results by use of continuous spectrum as the constraints on relaxation intensities. Their method is based on the notion that discrete spectrum is an approximation of the continuous spectrum. Monte Carlo method is one of the most effective regression methods to obey the constraints of positive parameters $G_k \ge 0$ and $\lambda_k \ge 0$. Jensen (2002) applied the simulated annealing algorithm and showed that the algorithm is very effective.

4.2. Fundamental theories of relaxation spectrum

Discrete spectrum is a set of relaxation intensities G_k and relaxation times λ_k. Relaxation and dynamic moduli are expressed in terms of discrete spectrum as follows:

$$G(t) = \sum_{k=1}^{N} G_k e^{-t/\lambda_k}, \tag{17}$$

$$G'(\omega) = \sum_{k=1}^{N} G_k \frac{\lambda_k^2 \omega^2}{1+\lambda_k^2 \omega^2}, \tag{18}$$

and

$$G''(\omega) = \sum_{k=1}^{N} G_k \frac{\lambda_k \omega}{1+\lambda_k^2 \omega^2}. \tag{19}$$

The number of relaxation times N is another parameter to characterize discrete spectrum. As N increases, the spectrum can fit relaxation and dynamic moduli with better precision. Since one of the merits of discrete spectrum is its simplicity, the lower N is the better. To find discrete spectrum looks like a nonlinear regression which minimizes the following sum of square error:

$$\chi^2 = \chi_e^2 + \chi_v^2 \tag{20}$$

where

$$\chi_e^2 = \sum_{\alpha=1}^{M} \left[1 - \frac{1}{G'(\omega_\alpha)} \sum_{k=1}^{N} G_k \frac{\lambda_k^2 \omega_\alpha^2}{1+\lambda_k^2 \omega_\alpha^2} \right]^2 \tag{21}$$

and

$$\chi_v^2 = \sum_{\alpha=1}^{M} \left[1 - \frac{1}{G''(\omega_\alpha)} \sum_{k=1}^{N} G_k \frac{\lambda_k \omega_\alpha}{1+\lambda_k^2 \omega_\alpha^2} \right]^2. \tag{22}$$

Note that M is the number of data. If χ^2 is plotted as a function of N, it is often found that χ^2 decreases steeply as N increases and it becomes nearly a constant if N is sufficiently high. Thus we can often find that the double logarithmic plot of χ^2 versus N looks like a letter L. This phenomenological result might give a criterion on N (Jensen, 2002).

4.3. Results of the algorithm

Since both relaxation intensities G_k and relaxation times λ_k have positive values, we generate random numbers g_k and τ_k which are to be used for the positive parameters by $G_k = \exp(g_k)$ and $\lambda_k = \exp(\tau_k)$. Without loss of generality, we adopt the ordering such as $\lambda_1 < \lambda_2 < \cdots < \lambda_N$. To assign the initial range of τ_k, we select N values of $\tau_k^{(\mathrm{node})}$ which are located uniformly in the interval of $(-\log\omega_{\max}, -\log\omega_{\min})$. We take step size defined as $\Delta\tau = \log(\omega_{\max}/\omega_{\min})^{-b/N}$. Then the initial intervals for the random numbers of τ_k are assigned as follows:

$$\tau_k^{(\mathrm{node})} - \Delta\tau \le \tau_k \le \tau_k^{(\mathrm{node})} + \Delta\tau. \tag{23}$$

The real number b may be chosen as $b = 3/2$ or $b = 1$. The initial intervals of relaxation intensities may be given by

$$\log G''_{\min} - c \le g_k \le \log G''_{\max} + c. \tag{24}$$

Table 3. Comparison with simulated annealing method.

The Original Spectrum		SA (Jensen (2002))		This Study	
λ_k (s)	G_k (Pa)	$\left\lvert 1-\frac{\lambda_k^{\mathrm{calc}}}{\lambda_k^{\mathrm{exact}}}\right\rvert$	$\left\lvert 1-\frac{G_k^{\mathrm{calc}}}{G_k^{\mathrm{exact}}}\right\rvert$	$\left\lvert 1-\frac{\lambda_k^{\mathrm{calc}}}{\lambda_k^{\mathrm{exact}}}\right\rvert$	$\left\lvert 1-\frac{G_k^{\mathrm{calc}}}{G_k^{\mathrm{exact}}}\right\rvert$
8.983×10^{-4}	1.118×10^{5}	0	0	6.443×10^{-3}	1.213×10^{-3}
7.242×10^{-3}	2.302×10^{4}	1.381×10^{-6}	4.345×10^{-9}	4.062×10^{-2}	1.594×10^{-2}
3.430×10^{-2}	7.770×10^{3}	0	0	1.038×10^{-1}	5.010×10^{-2}
1.532×10^{-1}	2.253×10^{3}	0	0	8.198×10^{-2}	1.441×10^{-1}
9.013×10^{-1}	2.663×10^{2}	0	0	2.335×10^{-2}	5.989×10^{-2}
4.222×10^{0}	8.633×10^{0}	9.473×10^{-9}	0	6.185×10^{-3}	4.359×10^{-3}

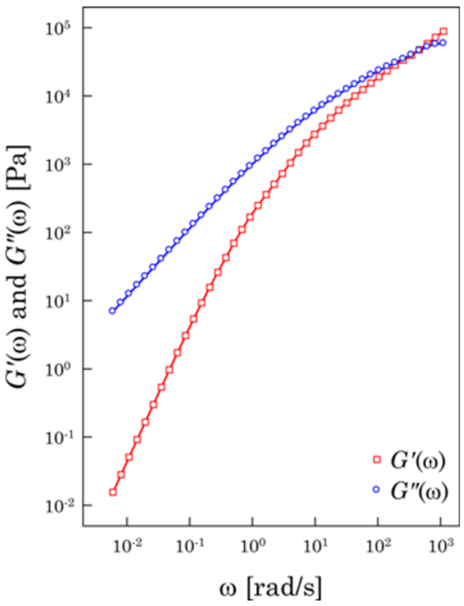

Fig. 3. (Color online) Hypothetical data of dynamic moduli fitted with the inferred discrete spectrum of Table 3.

The real number c may be chosen as 0 or 1.

We generate hypothetical data of dynamic moduli from the discrete relaxation spectrum which was tested by Jensen (2002), which are listed in Table 3. The data dynamic moduli are shown in Fig. 3 with the ones calculated from the inferred discrete spectrum.

Table 3 shows that SA algorithm is much better than the simplified MC algorithm. However, discrete spectrum is an approximation and Fig. 3 shows that the dynamic moduli calculated from the spectra in Table 3 are nearly identical. Although the uniqueness of continuous spectrum can be used for the identification of materials, the purpose of discrete spectrum may be considered as a convenient way to calculate nonlinear flow behavior as mentioned in the Section 4.1.

5. Scaling Theory of Polymer Solution

Rheological properties of polymer solution depend on not only molecular weight of polymer but also its concentration. When the concentration of polymer solution is very low, dilute solution, each polymer chains are forming a coil and exist away from others. Then physical properties of the solution become colligative properties proportional to volume fraction ϕ. The zero-shear viscosity of the solution η_{o} has the following relation with volume fraction.

$$\eta_{\mathrm{o}}-\eta_{\mathrm{s}}\approx\frac{5}{2}\eta_{\mathrm{s}}\phi\quad\text{for}\quad\phi<<\phi^{*}\,. \tag{25}$$

η_{s} is the viscosity of the solvent. As the concentration increases, the distance between the two polymer chains becomes close, and when the distance between the center of mass of the adjacent two polymer chains becomes equal to the sum of the radius of gyration of the two polymer chains, the polymer chains overlap. The concentration at this state is called the overlap concentration and is denoted by ϕ^{*}. If polymer chain is long enough to form entanglement, further increase of concentration results in entanglement of polymer chains. The concentration at the onset of entanglement is called the entanglement concentration and is denoted by ϕ_{e}. It is obvious that $\phi_{\mathrm{e}}>\phi^{*}$. The concentration regime of $\phi>\phi^{*}$ is called semi-dilute regime (Rubinstein and Colby, 2003).

In the semi-dilute regime, the zero-shear viscosity has the following relations with volume fraction:

$$\eta_{\mathrm{o}}-\eta_{\mathrm{s}}\propto\phi^{\beta}\quad\text{for}\quad\phi^{*}<\phi<\phi_{\mathrm{e}} \tag{26}$$

and

$$\eta_{\mathrm{o}}-\eta_{\mathrm{s}}\propto\phi^{\gamma}\quad\text{for}\quad\phi_{\mathrm{e}}<\phi\,. \tag{27}$$

These relations, Eqs. (25) - (27), are valid for flexible polymer chains and can be written in a single equation:

$$\begin{gathered}\eta_{\mathrm{o}}-\eta_{\mathrm{s}}=\alpha c\left[1+\left(\frac{c}{c^{*}}\right)^{n_1}\right]^{\frac{\beta-1}{n_1}}\left[1+\left(\frac{c}{c_{\mathrm{e}}}\right)^{n_2}\right]^{\frac{\gamma-\beta}{n_2}};\\ \alpha=aM_w;\ c^{*}=\frac{k_1}{M_w^{\mu_1}};\ c_{\mathrm{e}}=\frac{k_2}{M_w^{\mu_2}}\,.\end{gathered} \tag{28}$$

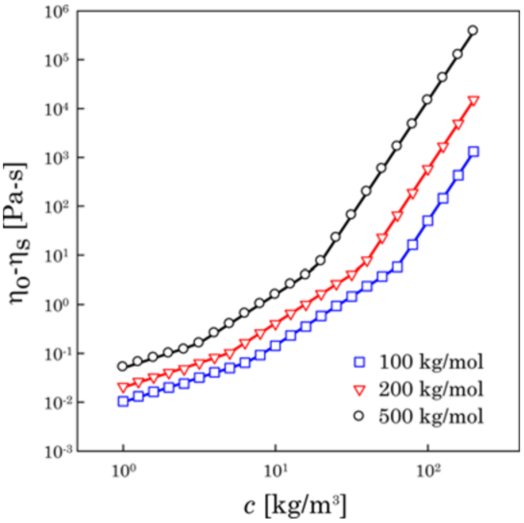

Fig. 4. (Color online) Hypothetical specific viscosity which contains 5% numerical error and nonlinear regression results.

c is mass concentration which has a relation with volume fraction and density of polymer ρ_p, $c = \rho_p\phi$. The exponents μ_k are constants which describe the molecular weight dependence of the two characteristic concentrations. According to the theory of polymer physics, the values of μ_1 and μ_2 of θ solution are known as 0.5 and 0.75. The exponents n_k are dimensionless numbers that control how the slope changes when $\log(\eta_o - \eta_s)$ is plotted as a function of $\log c$. The exponents β and γ are the slopes in the regimes of $\phi^* < \phi < \phi_e$ and $\phi_e < \phi$, respectively in $\log c$-$\log(\eta_o - \eta_s)$ plot. For θ solution, it is known that $\beta = 2$ and $\gamma = 14/3$. The change of the slope is very sharp if the molecular weight of the polymer in the solution is extremely high. However, when the molecular weight of the polymer is not very high, the transition of the slope occurs very smoothly. This phenomenon seems to be originated from that the difference between the overlap and entanglement concentrations decreases as the molecular weight decreases. Therefore, if the molecular weight of the polymer is not high enough, it may not be effective to determine the overlap concentration and the entanglement concentration at the intersection points obtained by regression of each regime.

We generated the data of Fig. 4 by using the values of parameters in Table 4 whose molecular weights are 100 kg/mol, 200 kg/mol, and 500 kg/mol, respectively. To verify that the MC algorithm finds the parameters reliably even in the case of data which contain errors, statistical random errors of 5% were added.

Table 4 shows that MC regression accurately finds the parameter values of η_s, μ_1, and μ_2, which have the physical meanings, up to two significant digits. For all other parameters, their values were obtained with a maximum error of 5% except n_1 and k_1. The value of R^2 was 0.99998 and the graphic result of the regression is shown in Fig. 4. Therefore, MC method finds the parameter values fairly accurately even in the data containing errors.

Table 4. Comparison of parameter values used for data generation and parameter values obtained from MC regression.

	Original value	Regression result
η_s	0.15	0.15
a	1.00×10^{-4}	1.00×10^{-4}
n_1	50.00	53.66
n_2	100.00	103.76
k_1	70.00	65.63
k_2	2000.00	2064.61
μ_1	0.50	0.50
μ_2	0.75	0.75

6. Conclusion

We have tested simplified Monte Carlo method to various rheological problems which need nonlinear regression with a number of parameters which vary in logarithmic scales. Although the simplified MC method omits heating and cooling processes of simulated annealing method, the simplified MC method gives acceptable results. Since the simplified MC method is simple in both mathematical and numerical aspects, we expect that our method is more practical.

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