

THE MOLECULAR WEIGHT DISTRIBUTION PROBLEM AND REPTATION MIXING RULES

R. S. ANDERSSSEN¹ and M. WESTCOTT¹

Dedicated to David Elliott on the occasion of his 65th birthday

(Received 16 March 1998)

Abstract

Mixing rules model how the physical properties of a polymer, such as its relaxation modulus $G(t)$, depend on the distribution $w(m)$ of its molecular weights m . They are of practical importance because, among other things, they allow estimates of the molecular weight distribution (MWD) $w(m)$ of a polymer to be determined from measurements of its physical properties including the relaxation modulus. The two most common mixing rules are “single” and “double” reptation. Various derivations for these rules have been published. In this paper, a conditional probability formulation is given which identifies that the fundamental essence of “double” reptation is the discrete binary nature of the “entanglements”, which are assumed to occur in the corresponding topological model of the underlying polymer dynamics. In addition, various methods for determining the MWD are reviewed, and the computation of linear functionals of the MWD motivated and briefly examined.

1. Introduction

In the study of macromolecules, the single most important concept is, from various practical points of view including molecular characterization, their molecular weight distributions (MWD) $w(m)$. The key role played by the higher molecular weight components in determining the properties of synthetic polymers and bio-polymers, such as grain flour doughs, is well documented (see, for example, Dealy and Wissburn [4], Doi and Edwards [5] and MacRitchie [14]). Three examples are discussed in Section 2 with the dual purpose of motivating the material examined in this paper and presenting appropriate background.

In the study of polymer dynamics, there is a strong interplay between theory and experiment. The nature of the theories developed to date (Larson [12]) is a direct re-

¹CSIRO Mathematical and Information Sciences, GPO Box 664, Canberra ACT 2601, Australia.

© Australian Mathematical Society 2000, Serial-fee code 0334-2700/00

flection of the constraints imposed by the results obtained from various measurements performed on different polymers such as single and double step-strain experiments as well as extensional experiments. From a theoretical perspective, much effort has been devoted to the formulation of realistic constitutive relationships including the integral constitutive relationships of Rivlin and Sawyers, K-BKZ, and Wagner (Bird *et al.* [2]). From a practical and industrial angle, there is a need to formulate relationships between the measurable physical and mechanical properties of polymers and their MWD. Because these relationships aim to characterize how the various molecular weight components in a polymer combine to yield an observed property, they are commonly referred to as *mixing rules*.

With the advent of metallocene catalyst technology, it is now possible to economically produce, in commercial quantities, general-purpose polymers such as polyethylene and polypropylene with precisely controlled MWD. This ability to control the MWD challenges the rheologist to establish appropriate mixing rules, which can be exploited to specifically *design* a polymer's MWD so that improved processibility and physical properties are achieved.

The formulation of mixing rules is a fairly controversial matter. All molecular motions in a condensed phase, such as a polymer melt or concentrated solution, are necessarily *cooperative* by virtue of the close packing and strong interaction between adjacent molecules. This fact potentially makes the construction of mixing rules a complex process and has spawned the search for simplified models which characterize the essence of polymer dynamics in a particular context. Idealized models, such as the tube and reptation concept of de Gennes (Doi and Edwards [5]), ignore the complexity of local cooperative motion by arguing that these interactions are unimportant on sufficiently long time scales. In particular, Doi and Edwards [5] introduced the concept of single (tube) reptation to derive theoretical relationships between the relaxation modulus $G(t)$ and the MWD for a polymer (where t denotes time).

Because of the failure of the single reptation theory to adequately predict key experimental data, des Cloiseaux [3] (and, independently, Tsenoglou [17, 18]) formulated the idea of double reptation. The conceptual differences between single and double reptation are not well understood because of the ways in which they have been derived. For example, the derivation given by Tsenoglou is algebraically complex whereas that of des Cloiseaux is physical and intuitive. In fact, Mead [16] has stated "*The fundamental essence of "double reptation" is that the "entanglements" are modelled as discrete binary contacts, though this is not obvious or completely accepted*". Consequently, a formulation for these reptation mixing rules is required which exposes more explicitly the underlying topological processes of the molecular dynamics being assumed. This is the primary goal of this paper.

The remainder of the paper is organized in the following way. Three examples of

the importance of the MWD in applications are examined in Section 2, to provide motivation as well as present appropriate background. A brief review of various methodologies for the determination of the MWD of a polymer from a variety of experimental measurements is given in Section 3, along with a discussion of the evaluation of linear functionals defined on the MWD. The formulation of the single and double reptation rules using a conditional probabilistic argument is given in Section 4.

2. Background and exemplification

2.1. Rheological mixing rules As explained above, a relationship between a measured mechanical or physical property of a polydisperse polymer (ensemble of macromolecules with more than one molecular weight) and its MWD is called a *mixing rule*. The mechanical properties are a manifestation of the microscopic composition of the material. For linear flexible polymer melts, it has been established theoretically that this composition can be generically characterized by the MWD of the polymer. Physically, this result derives from the notion that polymers are so much larger than ordinary molecules that the specific details of the chemical appendages decorating the chain are averaged out and the dominant feature remaining is the intrinsic topology of the chain.

In general, it must be assumed that each component of the MWD will contribute to the observed mechanical properties. So a rheological property is often defined in terms of the MWD $w(m)$ as a first-kind Fredholm integral equation

$$g(t) = \int_0^{\infty} k(m, t)w(m) dm, \quad (1)$$

with the kernel $k(m, t)$ weighting the MWD in a manner which reflects the relative contribution of each component of the MWD to the property under consideration. When the measurement corresponds to the relaxation modulus $G(t)$, one obtains for single reptation the mixing rule

$$g(t) = G(t), \quad k(m, t) = F(m, t), \quad (2)$$

while for double reptation one has

$$g(t) = \sqrt{G(t)}, \quad k(m, t) = \sqrt{F(m, t)}, \quad (3)$$

where $F(m, t)$ denotes the normalized relaxation function. For a monodisperse relaxation function characterized by a single time constant $\tau(m)$, one has

$$F(m, t) = \exp(-t/\tau(m)). \quad (4)$$

In a recent paper, Anderssen and Mead [1] generalized the reptation mixing rule concept through the introduction of a parameter γ such that

$$g(t) = [G(t)]^{1/(1+\gamma)}, \quad k(m, t) = [F(m, t)]^{1/(1+\gamma)}, \quad 0 \leq \gamma. \quad (5)$$

The motivation for the introduction of this parameterization was two-fold: it represents a sensible mathematical expedient, since it includes single and double reptation as the special cases when $\gamma = 0$ and $\gamma = 1$, respectively; and it can be given, on the basis of recent research (see, for example, Maier *et al.* [15]), a strong rheological and physical justification.

2.2. Molecular weight scaling of rheological properties Numerous authors (such as Zeichner and Patel [21], Locati and Gargani [13] and Wasserman [19]) have established that key rheological properties of synthetic polymers, such as the zero-shear viscosity and the steady-state recoverable compliance, have natural molecular weight scalings (MW-scalings). For example, for a variety of polymers, the following MW-scaling, with parameterization K , p and q , holds for the zero-shear viscosity η_0 ; namely,

$$\eta_0 = K(M_w)^p(Q)^q, \quad Q = M_w/M_n,$$

where M_w and M_n denote, respectively, the weight-averaged and the number-averaged MWD. In addition, Wasserman [19] has hypothesized the following MW-scaling law

$$\eta_0 = K(M_w)^p \left(\frac{M_2(w)}{M_1(w)^2} \right)^q,$$

where $M_\alpha(w)$ denotes the α -moment of the MWD, namely,

$$M_\alpha(w) = \int_0^\infty m^\alpha w(m) dm. \quad (6)$$

For various reasons, scaling plays a central role in both experimental and theoretical polymer science. On the one hand, it indicates how various experimental rheological data might be modelled. On the other, it represents a way in which to constrain the choice of theoretical models of polymer dynamics.

By analogy with the definitions of zero-shear viscosity and steady-state recoverable compliance (Dealy and Wissburn [4]), one can define a rheological parameter as any algebraic expression which is a function of the moments

$$M_\alpha(G) = \int_0^\infty t^\alpha G(t) dt$$

for various choices of the parameter α . Normally, the algebraic expressions will be simple ratios of such moments as typified by the following formulas for the zero-shear viscosity η_0 and the steady-state recoverable compliance J_e^0 :

$$\eta_0 = M_0(G), \quad J_e^0 = M_1(G)/(M_0(G))^2.$$

It follows naturally from this definition that the problem of the molecular weight scaling of rheological parameters reduces to an examination of the molecular weight scaling of the moments $M_\alpha(G)$. This has been pursued in some detail in a recent paper by Anderssen and Mead [1]. However, if necessary, one could extend the above definition of a rheological parameter to be any algebraic expression which is a function of moments of the form

$$\int_0^\infty \phi(t)G(t) dt,$$

for various choices of the function $\phi(t)$. Consequently, in the study of polymer dynamics, various linear functionals such as $M_\alpha(G)$ and $M_\alpha(w)$ must be evaluated from observational data. Ramifications of this fact are examined in Section 3.

2.3. Glutenin sub-units and the breeding of new wheat varieties Experimental evidence, in terms of correlations, has confirmed that the glutenin proteins in wheat flour dough play a crucial role in determining baking performance and quality (MacRitchie [14]). The amount and nature of the glutenin in a dough are determined by the wheat variety and, hence, the genes which distinguish one variety from another. As far as the glutenin proteins are concerned, the genes control the expression (production) of the lower and higher molecular weight glutenin monomers (glutenin sub-units) which, through disulphide (valency) bonding, combine in some unknown preferential stochastic manner to form the ensemble of glutenin protein polymers which characterize a given wheat variety. The actual proportion of the glutenin with respect to the other components within a wheat endosperm, which includes other proteins, starches and lipids, will be a function of the environmental conditions in which the wheat is grown as well as its genetics. The types of lower and higher molecular weight glutenin sub-units, as well as the ratios in which they are expressed, change from one wheat variety to the next. Consequently, if one wishes to breed new strains of wheat through genetic manipulation, then there is a need to understand (a) which genes control the types and ratios of the glutenin sub-units, (b) the molecular weights of the glutenin proteins expressed by a particular set of genes, and (c) the relationship (correlations) between the MWD of the glutenin present in a given wheat variety and baking performance. Among other things, this process will require estimates to be made of the MWD of the glutenin.

However, since the MWD of an ensemble of macromolecules cannot be determined directly, some appropriate indirect measurement procedure must be applied. A wide

variety of procedures have been developed, including size exclusion high performance liquid chromatography (size exclusion HPLC), field flow fractionation (FFF), equilibrium sedimentation (through centrifuging) and the inversion of mixing rules. A brief review of these methods, including their essential mathematical differences, is given in the next section.

3. MWD inversion methodologies

Though a wide variety of procedures can be applied to recover an estimate of the MWD of a given polymer, the focus here is on the following four methods: size exclusion HPLC, field flow fractionation (FFF), equilibrium sedimentation (through centrifuging) and the inversion of mixing rules which take the form of a first-kind Fredholm integral equation such as (1). These four methods have been chosen because they illustrate quite different aspects of the ways in which an MWD can be recovered from observational data.

The first three correspond to different implementations of the separation-and-measurement ansatz:

1. **The Separation.** Develop an accurate separation strategy which allows
 - (a) the original complex material to be separated into easily characterized components in terms of how they are measured; and
 - (b) the measurements performed on the separated components to be easily and readily converted to the information required.
2. **The Measurement.** Formulate a mathematical model which allows the required information to be defined in terms of the measurements.

Clearly, the success of any separation-and-measurement procedure will depend on the nature of the trade-off achieved in terms of

- (i) the **Accuracy** (closeness) with which the separated components can be measured (in terms of the complexity of the mathematical model which defines the measurements as a function of the required information); and
- (ii) the **Efficiency** (stability) with which the separation can be performed without an undue loss of information.

Within this context, any measure of the complexity of a mathematical model must reflect the extent to which the measurements have smoothed out the specific information required and, hence, the extent to which the model is improperly posed.

For example, when the mathematical model corresponds to a first-kind integral equation (such as (1)), the degree to which the model is improperly posed can be characterised in terms of smoothness of the kernel. Intuitively, the smoother the kernel the more improperly posed the corresponding integral equation model, since

the smoothing applied by the kernel to the required information will be greater. In fact, as is clear from Elliott [6], the first-kind integral equations with Cauchy singular kernels cease to be improperly posed and behave more like second-kind integral equations.

The philosophy behind such separation-and-measurement procedures is that the more *accurate* the measurement step is in terms of the simplicity of the mathematical model involved, the less improperly posed will be the underlying formulation relating the measurements to the phenomenon of interest. Thus, the purpose of the separation step, assuming that it can be performed *efficiently* (without any major loss of information), is that it yields measurements for which there is a simple and direct relationship connecting them to the required information.

In both the Size Exclusion HPLC and the FFF techniques, the basic separation process is *elution (elutriation)*, though the technical and physical implementation details vary greatly depending on the type of information being sought. The Encyclopaedia Britannica [22, p. 161] states

“Elutriation is a method of separation of particles. The particles are placed in a vertical tube in which water (or other fluid) is flowing slowly upwards. The particles fall through the water at speeds that vary with their sizes and densities. If the flow rate of the water is slowly increased, the most slowly sinking particles will be swept upwards with the fluid flow and removed from the tube. Intermediate particles will remain stationary, and the largest or densest particles will continue to migrate downwards. The flow can again be increased to remove the next size of particles. Thus, by careful control of flow through the tube, particles can be separated according to size.”

Size exclusion HPLC In this type of elution procedure, the “other fluid” is a static gel, which impedes the downward migration of particles on the basis of their effective hydrodynamic diameters, which are directly related to their molecular lengths (weights). Compared with electrophoresis methods, where the largest particles accumulate in bands at the top of the column and the smallest at the bottom, size exclusion HPLC works in the opposite manner with all particles passing through the column with the smallest particles exiting last and the largest exiting first. For an ensemble of particles consisting of separate monodisperse fractions, the size exclusion HPLC separation yields as measurements the residence times of each of the monodisperse fraction along with their relative concentrations. Within a cereal chemistry context, such as a study of the genetics of glutenin sub-units, one is often only interested in the existence or otherwise of a monomer of a particular molecular weight. Consequently, the measurement process reduces to one of simply identifying the various peaks in the observed elution curve. Genetic decision-making is thereby reduced to categorical process of comparing the HPLC curves corresponding to different wheat varieties. If some estimate of the molecular weights in the various bands is required, then

monodisperse standards of known molecular weights can be added which introduce additional peaks in the observed curves. A qualitative assessment of the molecular weights of particular monomers can then be inferred from the relative position of the corresponding bands and the bands produced by the standards. In this situation, the nature of the information required allows the mathematical modelling involved to be reduced to comparison and correlation. Here, the *accuracy* of the method is high if all that is required for decision-making purposes is a comparative assessment of various size exclusion HPLC curves, while its *efficiency* will depend heavily on the design and manufacture of the gel and the column, and the care with which the experiments are performed.

Field flow fractionation In this type of elution procedure, the separation is not achieved through a changing vertical flow, but through a cross-field flow being superimposed on a vertical (or horizontal) forward channel flow. The tube is replaced by a long and wide, but thin, ribbon-like channel. The direction of the forward flow is along the length of the channel, with the cross-field flow perpendicular to the length and width of the channel and, therefore, occurring through the thinnest section of the channel. It is the introduction of this cross-field flow modification by Giddings [11] which allowed elution separation to be placed on a more quantitative foundation. In the fluid flowing along the length of the ribbon-like channel, a parabolic-like profile forms into which the particles to be separated are inserted. Then, because of the back diffusion of the particles against the cross-field flow, the lower hydrodynamic diameter and, thus, lower molecular weight particles attain an equilibrium distribution in the higher velocity sections of the profile, while the larger hydrodynamic diameter and, thus, larger molecular weight particles attain an equilibrium distribution in the lower velocity sections of the profile. One then measures the residence times of the various groups of particles as they exit from the channel. The residence times will correlate positively with the hydrodynamic diameters and, thus, the molecular weights of the particles (assumed to be sphere-like). From Stokes law and the Stokes-Einstein relation, a formula relating the hydrodynamic diameters of the particles to the elution times can be derived. These hydrodynamic diameters can then be reinterpreted as molecular weights, either directly through the formulation of appropriate mathematical models, or indirectly through the use of standards with known molecular weights. For the determination of an MWD, the *accuracy* of FFF is encapsulated in the correctness of the mathematical model which is invoked to convert the residence times to hydrodynamic diameters and hence to molecular weights, while the *efficiency* of FFF depends on the success of the separation in terms of how correctly the residence times and concentrations represent the polydispersity of the polymer being tested. If all that is required is some qualitative comparison of the residence times against those for some standard, then the associated *accuracy* and *efficiency* are similar to that for the

size exclusion HPLC. In an FFF analysis, the *efficiency* is impaired in situations where there is not a consistent correlation between the measured hydrodynamic diameters of the particles and their corresponding molecular weights. Such an inconsistency can occur when the macromolecules being examined in an FFF experiment have a conformation different to the calibration standard, or when comparing two different MWDs of macromolecules with quite different conformation properties.

Equilibrium sedimentation In this situation, the separation is achieved through centrifuging a sample of the polymer in solution. The measurements are the concentrations $c(\xi)$ of the polymer at the positions (distances) ξ from the centre of the centrifuge. If it is assumed that the effect of the centrifuging can be modelled as equilibrium sedimentation, then the resulting relationship (Fujita's equation) relating the measurements to the required MWD takes the form [8]

$$f(\xi) = \int_0^{m_{\max}} \frac{\lambda m \exp(-\lambda m \xi)}{1 - \exp(-\lambda m)} w(m) dm, \quad f(\xi) = c(\xi)/c_0,$$

where

- c_0 := the initial concentration of the polymer;
- ξ := $(r_b^2 - r^2)/(r_b^2 - r_a^2)$;
- r := the radial distance from the centre of the centrifuge;
- r_a := the radial distance to the meniscus;
- r_b := the radial distance to the bottom;
- λ := $(1 - V\rho)\omega^2(r_b^2 - r_a^2)/(2RT)$;
- ω := the angular velocity of the centrifuge;
- ρ := the density of the solution;
- V := the partial specific volume of the polymer;
- T := the absolute temperature; and
- R := the universal gas constant.

Because of the strongly improperly posed nature of Fujita's equation, this is an example of a situation where the separation has not achieved much. Even though a separation has been achieved, one is still left with the need to apply regularization, or similar techniques, in order to obtain meaningful information about the MWD of the polymer from the numerical inversion of this equation with respect to given measurements of $f(\xi)$ [9]. Here, for the determination of an MWD, the *accuracy* is quite poor, while the *efficiency* is good, because of the quality of modern centrifuge devices.

Inversion of first-kind Fredholm integral equation mixing rules The alternative strategy to separation-and-measurement is to focus on a measurement which is relatively easy to perform and for which there is a corresponding mathematical model

connecting such measurements to the MWD. In the current context, this leads back to the inversion of mixing rules which take the form of the first-kind Fredholm integral equation (1). Such an approach involves the following steps: (i) measurement of the relaxation modulus $G(t)$; (ii) formulation of the model relating $G(t)$ to $w(m)$ (that is, the appropriate mixing rule); and (iii) the inversion of this model to recover an estimate of $w(m)$. However, as indicated above and explained in some detail in Mead [16], in many practical contexts, it is not $w(m)$ which is required for decision-making purposes, but some linear functional defined on $w(m)$ such as the moments entering the experimentally derived and hypothesized MW-scalings discussed briefly in Section 2. A more detailed discussion of the merits of computing appropriate linear functionals defined on $w(m)$, rather than $w(m)$ itself, can be found in Anderssen and Mead [1]. On the other hand, Wood-Adams and Dealy [20] have examined the limitations associated with inverting viscosity measurements in order to obtain estimates of $w(m)$. In such procedures, the *accuracy* is marginal, while the *efficiency*, because of the quality of modern rheological instruments, is quite high.

The trade-off between a more direct experimental approach and an indirect mathematical modelling alternative is aptly illustrated by comparing the separation-and-measurement procedures with the mixing rule alternatives. In the former, the goal, where possible, is to obtain measurements which approximate closely (with a high *accuracy*) the required solution, so that the mathematical relationship which relates the measurements to the solution is relatively simple, and therefore quite *efficient* to solve computationally more or less as it stands. The challenge is to perform the measurements with a minimal loss of information, with the design of experiments and instruments becoming the prime consideration. In the latter, one performs careful measurements where the loss of information about the phenomenon being examined is minimal, but where the relationship which relates the measurements to the required solution is improperly posed because of the smoothing which has been performed on the solution in order to produce the measurements. The challenge is to invert the relationship in a way which allows the maximum amount of information about the solution to be recovered from the measurements. Here, the prime consideration becomes the choice of the stabilization which is applied to invert the relationship in an *efficient* (and stable) manner. Consequently, the choice of a preferred methodology represents a balancing which must be managed between experimental and mathematical complexity, with respect to the type of measurements being performed and the solution being sought.

4. A conditional probabilistic derivation for single and double reptation

Initially, it is necessary to recall some background about the single reptation concept. For this purpose, because it relates naturally to the subsequent deliberations

below, the derivation given by des Cloiseaux [3] is followed. Consider a polydisperse polymer melt. It will be a mixture of various monodisperse molecular chains A , of molecular weight m_A and relaxation times τ_A , with N_A denoting the number of chains A , and N the total number of chains. For the molecules A , which are assumed to relax in their individual tubes of influence, the expected proportion of their initial tube lengths, which has not been renewed after time t (that is, the expected proportion of the unrelaxed stress remaining after time t) is given by (de Gennes [10])

$$p_A(t) = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{(2n+1)^2 t}{\tau_A}\right], \quad \tau_A \propto m_A^3. \quad (7)$$

Probabilistically, $p_A(t)$ corresponds to the probability that a randomly chosen point on the tube is still in its original stress state at time t . If it is assumed that the number of stress contacts (simple (single) “entanglements”) is proportional to the number of monomers, then the mean fraction of unrelaxed stress, after a time t , must be proportional to

$$m_s(t) = \sum_A \phi_A p_A(t), \quad (8)$$

where $\phi_A \sim (N_A/N)$ is the volume fraction of the chains A in the polymer, and the subscript s stands for “single” reptation. Doi and Edwards [5] assumed that the (stress) relaxation modulus $G(t)$ is proportional to $m_s(t)$ and thereby concluded that

$$G(t) = G_0 m_s(t), \quad G_0 = \text{constant}. \quad (9)$$

It is now a simple matter to go to the limit of a continuous distribution of molecular weights for the polydisperse melt, and thereby derive the single reptation model given above in (1) and (2) with the normalized relaxation function given by the first term in the expansion (7); namely, (4).

We are now in a position to derive the single and double reptation mixing rules using purely conditional probabilistic arguments. What is interesting is that the form of $m_s(t)$ can be derived without the need to invoke any assumptions about the number of stress contacts being proportional to the number of monomers. In addition, that argument can be generalized to derive the corresponding mean fraction of unrelaxed stress, after a time t , for double reptation, if it is simply assumed that the “entanglements” are discrete binary contacts. The consequences of this fact are quite important. Either one is deriving the correct model but from within a framework which is not valid for the phenomenon under consideration, or the conditional probability framework yields an independent basis from which to interpret single and double reptation, and therefore a natural framework from within which to formalize and generalize the reptation concept.

The single and double reptation derivations for mixing rules are based on different models of the actual “entanglements” occurring in a polymer. It is therefore necessary to make this distinction clear in the subsequent deliberations. In particular, the single reptation “entanglements” will be referred to as *s-entanglements* while the double will be referred to as *d-entanglements*.

The single reptation probabilistic derivation The starting point is to simply define $m_s(t)$ to be the probability of an *s-entanglement* at time t ; namely,

$$m_s(t) = \Pr(s\text{-entanglement at time } t).$$

The only assumptions which are made are that

(Sa) the *s-entanglements* are mutually exclusive (exactly one occurs) events; and
 (Sb) the conditional probability $\Pr(s\text{-entanglement at time } t \mid \text{chain } A)$ is equal to $p_A(t)$.

On the basis of (Sa), it follows from the Law of Total Probability (Feller [7, p. 116]) that

$$m_s(t) = \sum_A \Pr(\text{entanglement at time } t \& \text{ chains } A)$$

and, hence, from the basic formula for conditional probability, that

$$m_s(t) = \sum_A \Pr(\text{entanglement at time } t \mid \text{chains } A) \Pr(\text{chains } A).$$

However, on applying assumption (Sb) that $\Pr(\text{entanglement at time } t \mid \text{chains } A) = p_A(t)$ and that $\Pr(\text{chains } A) = N_A/N$, it follows that

$$m_s(t) = \sum_A p_A(t)(N_A/N).$$

The result (8) now follows on recalling that $\phi_A \sim N_A/N$, which, as explained above, yields the standard single reptation model, on applying the appropriate limiting argument.

The double reptation probabilistic derivation The starting point is to again define $m_d(t)$, the counterpart of $m_s(t)$ when discrete binary events between different chains are assumed to be the basis for the “entanglements”, to be the probability of a *d-entanglement* at time t ; namely,

$$m_d(t) = \Pr(d\text{-entanglement at time } t).$$

The only assumptions which are made are that

(Da) along any polymer chain, the d -entanglements are mutually exclusive events; and

(Db) each polymer chain operates independently of any other (the occurrence of one is not influenced by any of the others); from which it follows that

$$\Pr(d\text{-entanglement at time } t \mid \text{chains } A\&B) \\ = \Pr(d\text{-entanglement at time } t \mid \text{chain } A) \Pr(d\text{-entanglement at time } t \mid \text{chain } B)$$

and

(Dc) the conditional probability $\Pr(d\text{-entanglement at time } t \mid \text{chain } A)$ is equal to $p_A(t)$.

On the basis of (Da), it follows from the Law of Total Probability that

$$m_d(t) = \sum_{A,B} \Pr(d\text{-entanglement at time } t \text{ between chains } A\&B)$$

and, hence, from the basic formula for conditional probability, that

$$m_d(t) = \sum_{A \neq B} + \sum_{A=B} \Pr(d\text{-entanglement at time } t \mid \text{chains } A\&B) \times \Pr(\text{chains } A\&B).$$

Applying assumptions (Db) and (Dc), it follows that

$$m_d(t) = \sum_{A \neq B} p_A(t)p_B(t)(N_A/N)(N_B/N) + \sum_{A=B} p_A^2(t)N_A(N_A - 1)/N(N - 1).$$

On recalling that $\phi_A \sim N_A/N$ and $\phi_B \sim N_B/N$, the last expression becomes

$$m_d(t) = \sum_{A,B} \phi_A \phi_B p_A(t)p_B(t) = [m_s(t)]^2$$

and, hence, on invoking the assumption that the relaxation modulus will now be proportional to $m_d(t)$ (the natural counterpart to (9)),

$$G(t) = G_0 m_d(t) = G_0 [m_s(t)]^2.$$

It is now a simple matter to go to the limit of a continuous distribution of molecular weights for the polydisperse melt and thereby derive the double reptation model given above in (1) and (3) with the normalized relaxation function given by (4).

Acknowledgement

In various ways, the structure and content of this paper has benefitted from discussions with Professor Dave Mead and Dr Mike Southan, which the authors acknowledge with thanks.

Note added in Proofs

A novel and significant contribution to the analysis of the molecular weight distribution problem has been made by W. Thimm, C. Friedrich, M. Marth and J. Honerkamp, "On the Rose spectrum and the determination of the molecular weight distribution from rheological data", *J. Rheology* **44** (2000), 429–438.

References

- [1] R. S. Anderssen and D. W. Mead, "On the recovery of molecular weight functionals from double reptation models", *J. Non-Newtonian Fluid Mech.* **68** (1997) 291–301.
- [2] R. B. Bird, R. C. Armstrong and O. Hassager, *Dynamics of Polymeric Liquids*, Vol. 1 (John Wiley and Sons, New York, 1987).
- [3] J. des Cloiseaux, "Double reptation vs. single reptation of polymer melts", *Europhys. Lett.* **5** (1988) 437–442.
- [4] J. M. Dealy and K. F. Wissburn, *Melt Rheology and its Role in Plastics Processing* (van Nostrand Reinholdt, New York, 1990).
- [5] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, 1986).
- [6] D. Elliott, "The numerical treatment of singular integral equations—a review", in *Treatment of Integral Equations by Numerical Methods* (eds C. T. H. Baker and G. F. Miller), (Academic Press, London, 1982) 297–312.
- [7] W. Feller, *An Introduction to Probability Theory and its Applications*, Vol. 1 (John Wiley and Sons, 1968).
- [8] H. Fujita, *Mathematical Theory of Sedimentation Analysis* (Academic Press, New York, 1962).
- [9] M. Gehatia and D. R. Wiff, "Determination of a molecular weight distribution from equilibrium sedimentation by applying regularizing functions", *Euro. Polymer J.* **8** (1972) 585–597.
- [10] P. G. de Gennes, "Reptation of a polymer chain in the presence of fixed obstacles", *J. Chem. Phys.* **55** (1971) 572.
- [11] J. C. Giddings, "Field-flow fractionation: analysis of macromolecular, colloidal and particulate materials", *Science* **260** (1993) 1456–1465.
- [12] R. G. Larson, *Constitutive Equations for Polymer Melts and Solutions* (Butters worths, Boston, 1988).
- [13] G. Locati and L. Gargani, "Dependence of zero-shear viscosity on molecular weight distribution", *J. Polym. Sci., Polym. Lett. Ed.* **11** (1973) 95–101.
- [14] F. MacRitchie, "Mechanical degradation of gluten proteins during high speed mixing of dough", *J. Polym. Sci., Polym. Symp.* **49** (1975) 85–90.
- [15] D. Maier, A. Eckstein, J. Honerkamp and Chr. Friedrich, "A new mixing rule for polystyrene to calculate the MWD from rheological data", *J. Rheology* **42** (1998) 1153–1173.
- [16] D. W. Mead, "Determination of molecular weight distributions of linear flexible polymers from linear viscoelastic material functions", *J. Rheology* **38** (1994) 1797–1827.
- [17] C. Tsenoglou, "Viscoelasticity of binary homopolymer blends", *ACS Polymer preprints* **28** (1987) 185–186.
- [18] C. Tsenoglou, "Molecular weight polydispersity effects on the viscoelasticity of entangled polymers", *Macromolecules* **24** (1991) 1762–1767.
- [19] S. H. Wasserman, "The relationship between polydispersity and linear viscoelasticity in entangled polymer melts", Ph. D. Thesis, Princeton University, 1994.

- [20] P. M. Wood-Adams and J. M. Dealy, "Use of rheological measurements to estimate the molecular weight distribution of linear polyethylene", *J. Rheology* **40** (1996) 761–778.
- [21] G. R. Zeichner and P. D. Patel, "A comprehensive evaluation of polypropylene melt rheology", in *Proc. 2nd World Conf. of Chem. Eng.*, Volume VI, (Montreal, Canada, 1981) 333–337.
- [22] *The Encyclopaedia Britannica*, Vol. 4 (Enc. Brit. Inc., Chicago, 1983), p. 161.