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the oscillation. The first normal stress difference obtained in this way changes sign from positive to negative as Γ in increased, in qualitative agreement with the experimentally measured values. This behavior has also been reported by Marrucci and co-workers[26] in their two-dimensional calculations. In the lowest shear-rate regime in which the averaged value of N_1 is positive, we find the averaged value of N_2 to be negative and comparable to or greater in magnitude than the averaged value of N_1.

We also compute the effect of shear on the steady-state rheological properties of solutions of rodlike polymers that are isotropic at equilibrium. We find for the Onsager excluded-volume potential that shear can induce a discontinuous transition to a nematic phase only if the concentration is so high that the isotropic phase becomes metastable at equilibrium, the stable equilibrium being that of coexisting nematic and isotropic phases. This result may explain why shear-induced transitions have not been seen experimentally in lyotropic solutions.

References and Notes

(1) Kiss, G.; Porter, R. S. *J. Polym. Sci., Polym. Symp.* **1978,** *No. 65,* 193.
(2) Kiss, G.; Porter, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1980,** *18,* 361.
(3) Navard, P. *J. Polym. Sci., Polym. Phys. Ed.* **1986,** *24,* 435.
(4) Moldenaers, P.; Mewis, J. *J. Rheol.* **1986,** *30,* 567.
(5) Marrucci, G.; Maffettone, P. L. *Macromolecules* **1989,** *22,* 4076.
(6) Doi, M. *J. Polym. Sci., Polym. Phys. Ed.* **1981,** *19,* 229.
(7) Onsager, L. *Ann. N.Y. Acad. Sci.* **1949,** *51,* 627.
(8) Maier, W.; Saupe, A. *Z. Naturforsch.* **1958,** *13A,* 564; **1959,** *14A,* 882; **1960,** *15A,* 287.
(9) Marrucci, G.; Ciferri, A. *J. Polym. Sci., Polym. Lett. Ed.* **1977,** *15,* 643.
(10) Thirumalai, D. *J. Chem. Phys.* **1986,** *84,* 5869.
(11) Mead, D. W.; Larson, R. G. *Macromolecules* **1990,** *23,* 2524.
(12) See, H.; Doi, M.; Larson, R. G. *J. Chem. Phys.* **1990,** *92,* 792.
(13) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978,** *74,* 918.
(14) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics;* Oxford University Press: New York, 1986.
(15) Larson, R. G. In *Recent Developments in Structural Continua;* Longman: London, 1990; Vol. 2.
(16) Lekkerkerker, H. N. W.; Coulon, P.; van der Haegen, R.; Deblieck, R. *J. Chem. Phys.* **1984,** *80,* 3427.
(17) Kuzuu, N.; Doi, M. *J. Phys. Soc. Jpn.* **1984,** *53,* 1031.
(18) Hinch, E. J.; Leal, L. G. *J. Fluid Mech.* **1976,** *76,* 187.
(19) Gähwiller, C. H. *Phys. Rev. Lett.* **1972,** *28,* 1554.
(20) Carlsson, T. *Mol. Cryst. Liq. Cryst.* **1984,** *104,* 207.
(21) Frank, R. C. *Discuss. Faraday Soc.* **1958,** *25,* 19.
(22) Mewis, J.; Moldenaers, P. *Mol. Cryst. Liq. Cryst.* **1987,** *153,* 291.
(23) Moldenaers, P. Ph.D. Thesis, Katholiecke Universiteit Leuven, 1987.
(24) Larson, R. G.; Mead, D. W. *J. Rheol.* **1989,** 33, 185.
(25) Hill, R. *Proc. Phys. Soc. London* **1952,** *A65,* 349.
(26) Marrucci, G. Presentation at the 61st Annual Meeting of the Society of Rheology, Montreal, Canada, Oct 21–26, 1989.
(27) Abe, A.; Yamazaki, T. *Macromolecules* **1989,** *22,* 2145.
(28) Wee, E. L.; Miller, W. G. *J. Phys. Chem.* **1971,** *75,* 1446.
(29) Keentok, M.; Georgescu, A. G.; Sherwood, A. A.; Tanner, R. I. *J. Non-Newtonian Fluid Mech.* **1980,** *6,* 303.
(30) Ramachandran, S.; Gao, H. W.; Christiansen, E. B. *Macromolecules* **1985,** *18,* 695.
(31) Magda, J. J.; Baek, S.-G.; de Vries, L.; Larson, R. G., manuscript in preparation.

Relaxation of Entangled Polymers in Melts

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ABSTRACT: In this paper, a theoretical study of the relaxation of entangled polymers in melts is presented, the aim being to reproduce experimental results in a precise manner. The reptation concept introduced by de Gennes is used for this purpose but with strong modifications. Several results are obtained. First, a phenomenological approach is used to confirm the validity of the "double reptation" principle that enables us to deduce the relaxation of a mixture of very long polymers and of moderately long polymers from the relaxation of each species considered separately. This assumption being well verified, the problem reduces to the relaxation of monodisperse polymers. Then, it is shown that the relaxation of such polymers can be deduced from the motions of stress points on the chains. It is assumed that the diffusion constant of a point depends on its position on the chain. Moreover, the fact that sliding motion as well as diffusive motion may simultaneously contribute to reptation is taken into account. Three related models are presented, exactly solved, and discussed. One model gives results in good agreement with experiments (on polybutadiene), and this model, which incorporates diffusion and sliding effects, is especially simple from a mathematical point of view since it belongs to a class of easily tractable models whose study seems promising.

I. Introduction

In order to describe relaxation processes in polymer melts made of long polymers, P.-G. de Gennes[1] introduced the reptation concept in 1971, and this idea was later developed by M. Doi and S. F. Edwards.[2] Our problem here is to calculate the stress relaxation function $G(t)$ (where t is time), but in practice the experimentalists measure $G''(\omega)$ and $G'(\omega)$.

$$G''(\omega) = \omega \int_0^\infty \mathrm{d}t \cos \omega t \, G(t) \quad \text{(loss modulus)}$$

$$G'(\omega) = \omega \int_0^\infty \mathrm{d}t \sin \omega t \, G(t) \qquad (1)$$

Simple diffusion reptation can be used in the context of the tube model to obtain an expression for $G(t)$. After time t, a part of the initial tube remains unchanged; let

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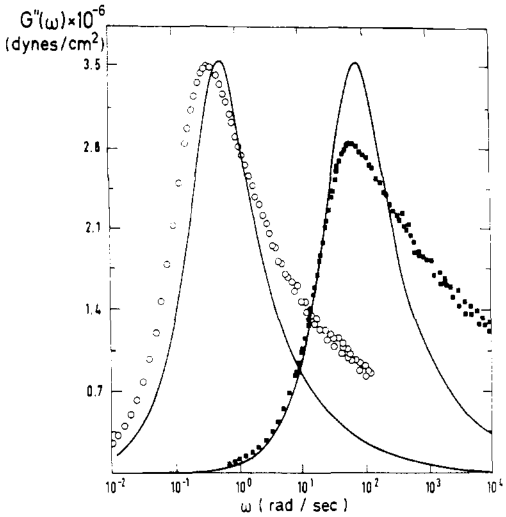

Figure 1. A simultaneous fit of loss modulus data for two monodisperse polybutadiene samples by the "simple reptation" model of de Gennes, Doi, and Edwards. The curves correspond to eqs 2 and 3. Open circles are data for M_L = 355 000; filled squares are data for M_S = 70 900 (obtained from measurements by R. Colby[3]). The peak on the left-hand side corresponds to the larger mass. It is assumed that $\tau_L/\tau_S = (M_L/M_S)^3$. The theoretical curves correspond to the values τ_L = 2.7 and $G_0 = 8.4 \times 10^6$ dyn/cm².

$p(t)$ be the corresponding average fraction; for a monodisperse melt, we can write

$$G(t)/G_0 = p(t) \qquad (2)$$

(with $p(0) = 1$).

Moreover, it is not difficult to show that if pure diffusion is the renewal mechanism, $p(t)$ has the form[1,2]

$$p(t) = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-(2n+1)^2 t/\tau] \qquad (3)$$

where τ, the main relaxation time of a polymer in the melt, is proportional to M^3 (here M is the molecular mass). This prediction is compared in Figure 1, with results obtained by R. Colby[3] (in 1987) for two monodisperse samples of masses 355 000 and 70 900. We see that we cannot have a good fit: the experimental curves are broader than predicted,[4] and the broadening increases when the molecular mass decreases. It is clear that one relaxation time is not sufficient to describe the process. We need another dimensionless parameter (e.g. the mean number of entanglements per polymer). More precisely, this necessity results from the fact that the curves representing $G''(\omega)$ for the two samples cannot be deduced from each other by translation. Thus, the de Gennes–Doi–Edwards model cannot be considered as completely successful, even for strongly entangled monodisperse polymers.

The discrepancy is much worse if we consider polydisperse polymer melts. In this case, the single tube model gives

$$G(t) = \sum_A \varphi_A p_A(t) \qquad (4)$$

where φ_A is the volume fraction of polymers of mass M_A and where $p_A(t)$ is given by

$$p_A(t) = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-(2n+1)^2 t/\tau_A] \qquad (5)$$

with $\tau_A \propto M_A{}^3$ (and $p_A(0) = 1$).

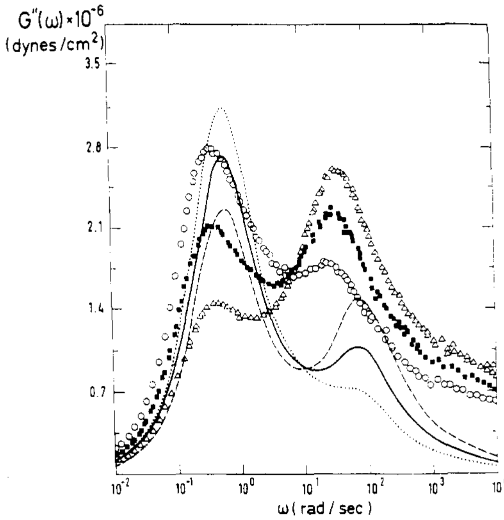

Figure 2. Predictions of the "simple reptation" model of de Gennes, Doi, and Edwards are experimental data obtained from experiments by R. Colby[3] for three different polymer blends. The curves correspond to eqs 4 and 5 with τ_L = 2.7 and $G_0 = 8.4 \times 10^6$ dyn/cm², as in Figure 1. In the following, φ_L is the volume fraction of the longer polymers (M_L = 355 000) and $\varphi_S = 1 - \varphi_L$ is the volume fraction of the shorter ones (M_S = 70 900). The dotted line is the prediction and the open circles are the data for φ_L = 0.882; the solid line and filled squares are for φ_L = 0.768; the dashed line and open triangles are for φ_L = 0.638.

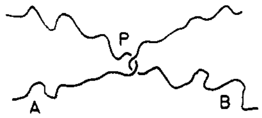

Figure 3. The polymers A and B are entangled, and there is a stress point at P. The stress disappears if either A or B reptates entirely through P.

This experimental prediction is compared in Figure 2 with the experimental results obtained by Colby[3] for three different polybutadiene blends, made by mixing polymers of molecular masses 355 000 and 70 900. Clearly, the theory is unadequate.

In 1988, the author showed that the situation can be greatly improved by using the "double reptation" concept.[5] The idea is simple. At a stress point, two polymers, A and B, are entangled (see Figure 3), and this entanglement persists if and only if one polymer reptates through this point: we have a two-body process. The consequence of this simple remark is that the stress relaxation function must be given by an expression of the form

$$G(t)/G_0 = [\sum_A \varphi_A p_A(t)]^2 \qquad (6)$$

This assumption was called "double reptation" by the author, and it must be understood that the reptation motion may simultaneously involve diffusion and sliding processes which both contribute to $p(t)$. Now, we can use the simplest approximation, i.e. replace $p_A(t)$ by expression 5 and compare the result with the same experimental curves. For monodisperse samples, the result is shown in Figure 4, and we see that the fit is slightly better because the theoretical curve is broader. For polydisperse samples, the results are shown on Figure 5, and the improvement is spectacular as was previously indicated.[5]

Incidentally, we note that eq 6 implies the equality

$$G(0) = G_0$$

where G_0 is a constant, independent of the molecular mass

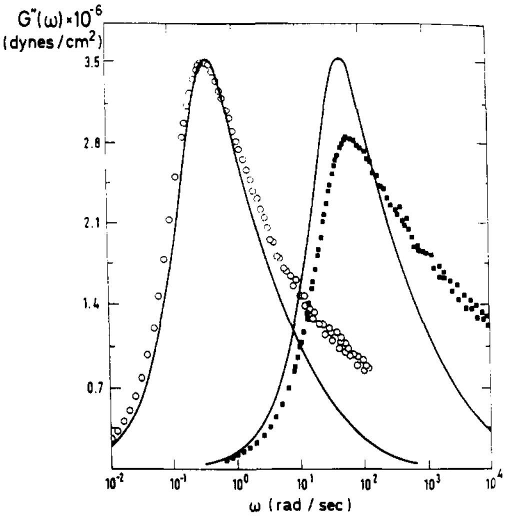

Figure 4. Simultaneous fit of loss modulus data obtained by applying the "double reptation" principle to the Doi–Edwards model. The curves correspond to eqs 6 and 5. The experimental data are the same as those on Figure 1. The theoretical curves correspond to the values $\tau_L = 5.9$ s and $G_0 = 9.6 \times 10^6$ dyn/cm^2. The fit is slightly better than in Figure 1.

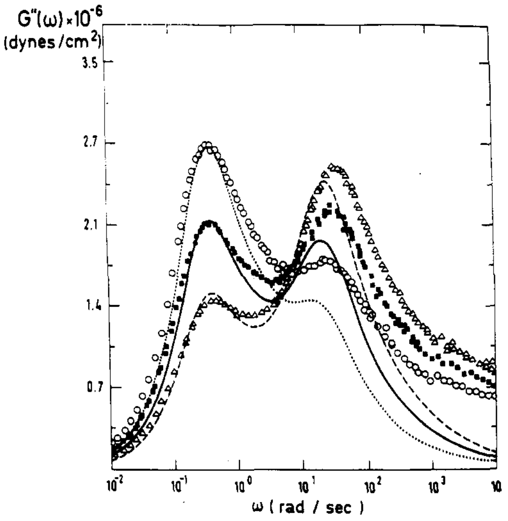

Figure 5. Predictions obtained by applying the "double reptation" principle to the Doi–Edwards model, and experimental data for blends. The curves correspond to eqs 6 and 5. The experimental data are the same as on Figure 1. The dotted line is the prediction and the open circles are the data for $\varphi_L = 0.882$; the solid line and filled squares are for $\varphi_L = 0.768$; the dashed line and open triangles are for $\varphi_L = 0.638$. The fit is much better than in Figure 3.

M. Consequently, the loss modulus $G''(\omega)$ must obey the sum rule

$$\int_0^\infty \frac{d\omega}{\omega} G''(\omega) = G_0 \frac{\pi}{2}$$

This means that the area under the curves representing $G''(\omega)$ against log ω does not depend on the molecular mass of the polymers, and experimentally this fact is well verified. This remark also indicates that the broadening and flattening of the curves, which are observed for low molecular masses, are not independent effects.

Now two questions arise: (1) Is eq 6 always valid? More precisely, we can reformulate this question as follows. Assuming that eq 6 applies to monodisperse melts, we can always determine a function $p_A(t)$ for each molecular mass M_A so as to get a good representation of the relaxation of polymers of species A (we write $G_A(t) = [p_A(t)]^2$); then, can we predict the relaxation of polymer blends with the same accuracy by using eq 6 and the *same* functions $p_A(t)$? (2) Is it possible to find a model giving the right $p_A(t)$ for each A? The aim of this paper is to answer these questions, and, in both cases, we give a positive answer.

Thus, in section II, we probe the validity of eq 6 by using a phenomenological representation of the Colby results for monodisperse samples. In section III, we discuss the physics of the reptation concept in connection with other approaches. In section IV, we examine how the usual reptation approach can be modified in order to provide an accurate description of the relaxation properties of monodisperse melts. In section V, we present a coordinate transformation which serves to treat the models presented in the second part of the paper. In section VI, we study a class of easily tractable models that incorporate diffusion and sliding and will be called basic diffusion models (BD). In section VII, we deduce these models from a very simple Langevin equation. A simple soluble model (BD1) belonging to this BD class is described in detail in section VIII, and we show that it leads to a good representation of reality. In section IX, this BD1 model is compared to another diffusion model (VD1) which is also soluble. In section X, the BD1 model is compared with another soluble model (UDS1) for which sliding is large. Comparisons between these similar models lead us to a better understanding of the whole process, and we note that the best fit is obtained with the BD1 model, a fact which a priori was not obvious.

Finally, in section XI, we summarize and discuss our results.

II. The Double Reptation Principle

In this section, we want to establish the validity of the double reptation principle. For this purpose, we represent $p_A(t)$ by an expression of the form

$$p_A(t) = K(\beta_A) \sum_{n=0}^{\infty} \frac{1}{(2n+1)^{2-\beta_A}} \exp[-(2n+1)^2 t/\tau_A] \quad (7)$$

(with $p_A(0) = 1$, this condition determines $K(\beta_A)$). For the longer polymer (L) of mass $M_L = 355\,000$, we take $\beta_L = 0.25$ and $\tau_L = 6.70$ and, for the shorter one (S) of mass $M_S = 70\,900$, we take $\beta_S = 0.43$ and $\tau_S = 0.0404$ with the global factor $G_0 = 11.3 \times 10^6$. Thus, for this model, $\tau_L/\tau_S = 165.9$ which is larger than $(M_L/M_S)^3 = 125.5$.

These values and eq 6 enable us to fit the experimental curves corresponding to monodisperse samples as shown in Figure 6. Now, we use *the same constants* and *the same formula* to predict the relaxation of polymer blends. The results appear in Figure 7. Again, we obtain a very good fit.

As a consequence, we see that we may trust eq 6: the "double reptation" assumption seems (at least for entangled polymers) to be an extremely good approximation.

However, the reader may raise an objection and ask whether the same conclusion could be deduced from the study of other polymers. Thus polystyrene blends made of very long chains and of shorter ones have been studied by H. Watanabe and T. Kotaka in two publications[6,7] and the discussions contained in these papers seem to imply that simple reptation (the tube model) has to be used to interpret the experiments. However, this idea can be checked by looking at Figure 2 in the first paper.[6] This figure shows curves representing $G''(\omega)$ versus log ω, and if the simple reptation idea was correct, all these curves would cross at the same point because in that case, $G''(\omega)$ would be linear with respect to concentrations. This is not what the experiment indicates as the reader can

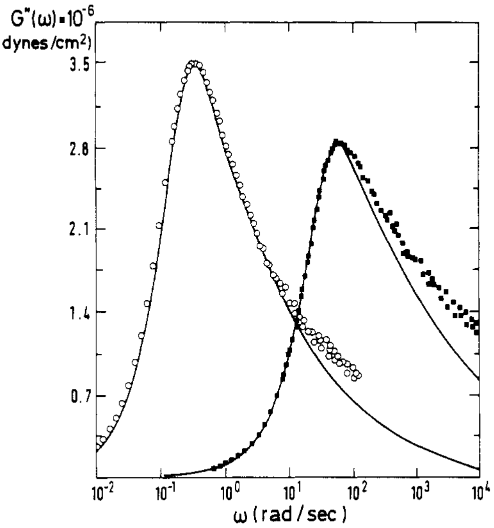

Figure 6. A phenomenological fit of loss modulus data for two monodisperse polybutadiene samples. The curves correspond to eqs 6 and 7. For the longer polymers (M_L = 355 000), we take β_L = 0.25 and τ_L = 6.70; for the shorter ones (M_S = 70 900), we take β_S = 0.43 and τ_S = 0.0404. We have a rather good fit.

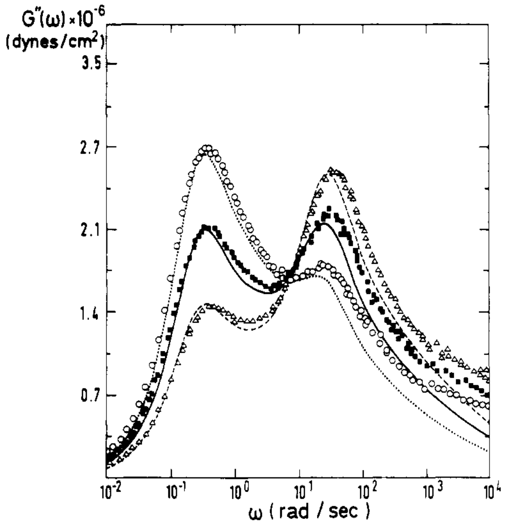

Figure 7. Predictions deduced from the phenomenological fit and experimental data for blends. The curves correspond to eqs 6 and 7. The values of β_L, τ_L, β_S, and τ_S are the same as those for Figure 4. The dotted line is the prediction and the open circles the data for φ_L = 0.882; the solid line and filled squares for φ_L = 0.768; the dashed line and open triangles for φ_L = 0.638. We note that the fit is practically as good for the blends as it was for the monodisperse samples. This fact clearly proves the validity of the "double reptation" principle.

easily verify, and the discrepancy corresponds to a factor 1.4 or 1.5 (i.e. a large factor: 1.4 as compared to 1). Thus, the experiments by H. Watanabe and T. Kotaka[6] show clearly that the simple reptation assumption is not valid. Actually, they may be compatible with the double reptation idea, but this has not been checked!

III. How Can We Compare the Double Reptation Principle with Apparently Similar Approaches?

From a mathematical point of view, our eq 6 is practically the same as a relaxation equation introduced by G. Marucci[8] in 1985 and used by many scientists.[9] However, the underlying ideas are completely different.

In fact, G. Marucci suggested that constraint release can be accounted for by letting the tube diameter increase when the surrounding chain reptates. Thus, for a monodisperse sample, his formula reads

$$G(t)/G_0 = [p(t)]^{\alpha}$$

where α is not very different from 2, but not necessarily an integer. Thus, Marucci's approach can be considered as a modified one-body process, and the derivation of his equation is semiempirical.

On the contrary, the double reptation principle consists in recognizing that relaxation in a polymer melt is a genuine two-body process. Accordingly, the derivation of eq 6 is transparent. The basic assumptions are the following. (1) At a stress point, two chains A and B exert a force on each other. (2) The stress points do not move. (3) The amount of stress produced by a deformation does not depend on the molecular masses of the polymers in the sample (G_0 is a constant). (4) The stress relaxation function is proportional to the number of original stress points still remaining at time t. (5) The probability that the stress points associated with polymer A and B remain at time t is equal to the product $p_A(t)p_B(t)$, and this simple but reasonable assumption leads immediately to eq 6.

IV. How Can We Describe the Physical Relaxation Process in Mathematical Terms?

Before trying to improve eq 3, let us recall how it can be derived. It is assumed that a polymer chain has a diffusive reptation motion along itself and that the diffusion coefficient is $D = D_0/L$ where L is the length of the polymer and D_0 a constant. We want to calculate the probability $p(t)$ that a stress point that is on the chain at time zero remains on it after a time t. To calculate $p(t)$, instead of assuming that the stress point is fixed and that the chain reptates, we can consider that the chain is fixed and that the stress point moves along the chain (relative motion). Now let $x(t)$ be the coordinate of a stress point on the chain (the coordinates of the end points of the chain are $x = 0$ and $x = L$). Let $P(t;x,x_0)$ be the probability that $x(t) = x$ $(0 < x < L)$ when $x(0) = x_0$ $(0 < x_0 < L)$. Clearly, we have

$$p(t) = \frac{1}{L}\int_0^L \mathrm{d}x \int_0^L \mathrm{d}x_0\, P(t;x,x_0) \qquad (8)$$

On the other hand, the function $P(t;x,x_0)$ obeys the diffusion equation

$$\frac{\partial}{\partial t}P(t;x,x_0) = D\frac{\partial^2}{\partial x^2}P(t;x,x_0) \qquad (9)$$

with the boundary conditions

$$P(0;x,x_0) = \delta(x - x_0) \qquad (10)$$

$$P(t;0,x_0) = P(t;L,x_0) = 0 \qquad (11)$$

(absorption at the end points).

The solution of the preceding equation is

$$P(t;x,x_0) = \sum_{n=1}^{\infty} \sin\frac{n\pi x}{L} \sin\frac{n\pi x_0}{L} \exp[-n^2 t/\tau] \qquad (12)$$

where τ is given by

$$\frac{1}{\tau} = \frac{D\pi^2}{L^2} = \frac{D_0\pi^2}{L^3} \qquad (13)$$

Thus, by combining eq 8 and 12, we obtain the classical result (3).

It is not at all obvious that the theory could be improved by developing the same line of thought. Thus, the author made attempts in various directions, but they were unsuccessful. For instance, the idea that polydispersion could play an important role in the interpretation of the experiments had to be rejected. Finally, the author came to the following conclusions: (1) it is reasonable to assume that the motion of a chain along a stress point can always be simulated by a motion of the stress point on the chain; (2) a realistic representation of the motion of a stress point on a chain can be obtained by modidying eq 9.

In principle, the internal relaxation modes of the polymers should play an important role but we know, from the work of M. Doi,[10] that it is quite difficult to take them into account in a proper way. With our present approach, the problem is greatly simplified because the preceding assumptions amount explicitly to the elimination of these modes. Now, only two variables remain, namely, time t and the coordinate x of the stress point along the chain.

Thus, in the following, it is assumed that eq 8 remains valid as well as the boundary conditions (10) and (11) but that eq 9 is replaced by the conservation equation

$$\frac{\partial}{\partial t}P(t;x,x_0) = -\frac{\partial}{\partial x}J(t;x,x_0) \qquad (14)$$

where the current $J(t;x,x_0)$ is of the form

$$J(t;x,x_0) = -\left[D(t,x)\frac{\partial}{\partial x} + F(t,x) \right] P(x;x_0,t) \qquad (15)$$

From this equation, we would like to obtain $p(t)$ as the sum of a series

$$p(t) = \sum_{n=0}^{\infty} A_n \exp(-t/\tau_n) \qquad (16)$$

where the A_n and τ_n have to be determined. Diffusion is represented in the right-hand side of eq 15 by the first term and sliding by the second one.

Now we have to find adequate expressions for $D(t,x)$ and $F(t,x)$. Moreover, we note that such functions need not be well-defined, and a priori one could believe that they are random variables! Consequently, we shall now consider various possibilities.

A very simple assumption consists in assuming that the relaxation process can be reduced to a pure time-dependent diffusion process and arguments could be found in favor of this idea. Then eqs 14 and 15 would reduce to

$$\frac{\partial P}{\partial t}(t;x,x_0) = D(t)\frac{\partial^2}{\partial x^2}P(t;x,x_0) \qquad (17)$$

This equation can be solved easily and leads to the result

$$p(t) = \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 \frac{\pi^2}{L^2} \int_0^t \mathrm{d}t'\, D(t') \right] \qquad (18)$$

Unfortunately, this expression seems rather far from the phenomenological formula given by (7) and it has serious drawbacks. We see that, if $D(t)$ has an explicit dependence with respect to t, the time symmetry is broken. In principle, there is nothing wrong with such an assumption since we can consider that this time symmetry breaking is related to the fact that the initial strain (producing with stress) is applied at time zero. However, assuming that $D(t)$ is a function with a strong dependence with respect to t implies not only that the strain modifies the conformation of the chains but also that this strain has a strong influence on their dynamical properties, a possibility which is hard to believe.

In order to avoid this time symmetry breaking, one might assume on the contrary that $D(t)$ is a stationary random variable and that $p(t)$ has to be averaged; unfortunately this approach does not work. In fact, it is not difficult to show that the random effects would contribute to a broadening of $G''(\omega)$ for small ω (long times); it cannot lead to the broadening for large ω (short times) which is observed. Thus the present simple assumption can be discarded.

Incidentally, one could perhaps avoid time symmetry breaking by introducing retardation effects, but in this case, simple diffusion equations like (15) cannot be used and then the problem becomes more complex.

In order to avoid these difficulties, we can, on the contrary, assume, that $D(x,t)$ and $F(t,x)$ do not depend on t and it will be shown, in the following section, that this approach is successful. In this case, eq 14 and 15 reduce to the simpler equation

$$\frac{\partial}{\partial t}P(t;x,x_0) = \frac{\partial}{\partial x}\left[D(x)\frac{\partial}{\partial x} + F(x) \right] P(t;x,x_0) \qquad (19)$$

where the "diffusion function" $D(x)$ and the "sliding function" $F(x)$ obey the parity conditions

$$D(L-x) = D(x)$$
$$F(L-x) = -F(x) \qquad (20)$$

Now the time symmetry is not broken, but the reader many wonder why $D(x)$ and $F(x)$ depend on x, and how on a time scale shorter than the Rouse time a section of the chain can "know" how far it is from the chain ends. These questions can be answered as follows.

First, we must realize that the dependence with respect to x takes into account retardation effects in a hidden way. A point which at time zero is located near the extremities of the polymer reaches these extremities more quickly than a point initially located in the central part; therefore, this point is more sensitive to the strong short time effects and consequently its average diffusion coefficient is larger.

Moreover, it is not absurd to believe that a chain has a structure which depends on x. As a chain in a melt is quasi Brownian in spite of excluded-volume effects, it must happen frequently that segments belonging to the same chain touch one another. This effect is probably larger in the central part of the chain, and it may have an influence on the local dynamical properties of the chain. In other terms, the effective tube width may depend on the distance from the tube ends.

We may also remark, that when static properties do not play a role, a point on the chain can still "know" its position on the chain because the Rouse times are much shorter than the times involved in the reptation process.

Now let us try to understand the physical meaning of the sliding function $F(x)$. We may say that when we have a stress, we have forces, and that these forces can induce sliding effects, but this statement lacks precision. The origin of $F(x)$ can be understood better by reading section VII in which the "basic diffusion" model is derived from a Langevin equation; then we see that, in the case under consideration, the existence of $F(x)$ is related to the fact that $D(x)$ depends on x.

In order to solve the preceding equations, we can introduce the eigenfunctions $\varphi_n(x)$ and the eigenvalues E_n which are solutions of the equations

$$\frac{\partial}{\partial x}D(x)\left[\frac{\partial}{\partial x} + \frac{F(x)}{D(x)} \right]\varphi(x) + E\varphi(x) = 0 \qquad (21)$$

(with $\varphi(x) = \varphi(L) = 0$).

The eigenfunctions $\varphi_n(x)$ are not orthonormal but can be transformed into orthonormal functions by setting

$$\tilde{\varphi}_n(x) = \exp\left(\frac{-V(x)}{2} \right)\varphi_n(x) \qquad (22)$$

where $V(x)$ obeys the equation

$$V'(x) = F(x)/D(x) \tag{23}$$

These functions are solutions of the equation

$$\left[\frac{\partial}{\partial x} - \frac{F(x)}{2D(x)}\right]D(x)\left[\frac{\partial}{\partial x} + \frac{F(x)}{2D(x)}\right]\tilde{\varphi}(x) + E\tilde{\varphi}(x) = 0 \tag{24}$$

which is of the form $H\tilde{\varphi} - E\tilde{\varphi} = 0$ where H is Hermitian. Thus, we may assume that the functions $\tilde{\varphi}_n(x)$ form an orthonormal set. Now, we can introduce the functions $\bar{\varphi}_n(x)$ defined by

$$\bar{\varphi}_n(x) = \exp(-V(x))\varphi_n(x) = \exp\left[-\frac{V(x)}{2}\right]\tilde{\varphi}(x) \tag{25}$$

These functions are solutions of the equation

$$\left[\frac{\partial}{\partial x} - \frac{F(x)}{D(x)}\right]D(x)\frac{\partial}{\partial x}\bar{\varphi}(x) + E\bar{\varphi}(x) = 0 \tag{26}$$

and thus eqs 21 and 26 are conjugate. The functions $\varphi_n(x)$ and $\bar{\varphi}_n(x)$ form a biorthogonal set

$$\int_0^L \mathrm{d}x\ \bar{\varphi}_n(x)\varphi_m(x) = \int_0^L \mathrm{d}x\ \tilde{\varphi}_n(x)\tilde{\varphi}_m(x) = \delta_{nm} \tag{27}$$

Now, it is easy to see that the solution of eq 19 which obeys the boundary condition

$$P(0;x,x_0) = \delta(x - x_0)$$

is given by

$$P(t;x,x_0) = \sum_{n=0}^{\infty}\varphi_n(x)\bar{\varphi}_n(x_0)e^{-E_nt} \tag{28}$$

In the following, we assume that n takes the value $n = 1, 2, ..., \infty$ (with $E_{n+1} > E_n$) where $(n - 1)$ is the number of zeros of $\varphi_n(x)$ between 0 and L. As eq 21 is invariant under the transformation $x \rightarrow (L - x)$, the eigenfunctions obey the parity conditions

$$\begin{aligned}\varphi_{2p+1}(L - x) &= \varphi_{2p+1}(x)\\ \bar{\varphi}_{2p+1}(L - x) &= \bar{\varphi}_{2p+1}(x)\\ \varphi_{2p}(L - x) &= -\varphi_{2p}(x)\\ \bar{\varphi}_{2p}(L - x) &= -\bar{\varphi}_{2p}(x)\end{aligned} \tag{29}$$

Then eq 16 reads

$$p(t) = \sum_{n=1}^{\infty}A_ne^{-E_{2n+1}t} \tag{30}$$

where A_n is given by eqs 8 and 28

$$A_n = \frac{1}{L}\left[\int_0^L \mathrm{d}x\ \varphi_{2n+1}(x)\right]\left[\int_0^L \mathrm{d}x_0\ \bar{\varphi}_{2n+1}(x_0)\right] \tag{31}$$

We now have to choose proper expressions for $D(x)$ and $F(x)$; in particular these functions must depend on a one dimensionless parameter (a function of the number of entanglements per polymer).

V. A Useful Coordinate Transformation and Its Application to Soluble Models

In order to solve equations of type (19), it will be useful to replace the coordinate x $(0 < x < L)$ by a new coordinate η $(0 < \eta < \pi)$.

We consider a function, $a(x)$ (with $a(L - x) = a(x)$) normalized by the condition

$$a(L/2) = 1 \tag{32}$$

We also introduce the constant c by setting

$$c = \frac{1}{L}\int_0^L \frac{\mathrm{d}x}{a(x)} \tag{33}$$

The variable η is defined by the equation

$$\frac{\mathrm{d}\eta}{\mathrm{d}x} = \frac{\pi}{Lca(x)} \tag{34}$$

and the boundary conditions

$$\begin{aligned}\eta(x = 0) &= 0\\ \eta(x = L) &= \pi\end{aligned} \tag{35}$$

which are compatible with eq 33.

We now introduce the function $b(\eta)$ by writing

$$b(\eta) = ca(x) \tag{36}$$

The preceding transformation can be expressed in terms of $b(\eta)$ since according to the preceding equations, we have

$$\begin{aligned}\frac{\mathrm{d}\eta}{\mathrm{d}x} &= \frac{\pi}{Lb(\eta)}\\ \int_0^{\pi}\mathrm{d}\eta\ b(\eta) &= \pi\\ b(\pi/2) &= c\end{aligned} \tag{37}$$

This notation will be sufficient to define all the models that will be introduced in the following sections. However, in order to get exact solutions, i.e. explicit expressions for the A_n, we need more explicit expressions for the functions $a(x)$ and $b(\eta)$. In fact, to define the three soluble models (BD1, VD1, and VDS1) that will be presented in the next sections, we shall always use the same functions $a(x,\beta)$ and $b(\eta,\beta)$ (here β is an arbitrary exponent that is a function of the number of entanglements per polymer). By definition, we set

$$b(\eta,\beta) = \frac{c(\beta)}{[\sin \eta]^{\beta}} = c(\beta)a(x,\beta) \tag{38}$$

where $c(\beta)$ is given by (see eq 37)

$$\frac{1}{c(\beta)} = \frac{1}{\pi}\int_0^{\pi}\frac{\mathrm{d}\eta}{[\sin \eta]^{\beta}} \tag{39}$$

Actually, we have

$$c(\beta) = \pi^{1/2}\frac{\left(-\frac{\beta}{2}\right)!}{\left(-\frac{1}{2} - \frac{\beta}{2}\right)!} \tag{40}$$

(See Appendix A: $c(\beta) = \pi/K_{0,-1-\beta}$.)

VI. The Basic Diffusion Models (BD): A Class of Easily Tractable Equations

By definition, a basic diffusion model is defined by an equation of the form

$$\frac{\partial}{\partial t}P(t;x,x_0) = \frac{\partial}{\partial x}\left[A(x)\frac{\partial}{\partial x}[A(x)P(t;x,x_0)]\right] \tag{41}$$

which is a special case of eq 19 (here we have $D(x) = A^2(x)$ and $F(x) = A'(x)A(x)$).

As we shall see, such equations are important for several reasons and particularly because they can be reduced to the simple diffusion equation (eq 9); thus, they can be solved easily and have the same relaxation spectrum as the simple diffusion equation.

In the present case, eqs 26 and 25 become

$$A(x)\frac{\partial}{\partial x}\left(A(x)\frac{\partial\bar{\varphi}(x)}{\partial x}\right) + E\bar{\varphi}(x) = 0 \tag{42}$$

$$\bar{\varphi}(x) \propto A(x)\varphi(x)$$

Now, we may set

$$D(x) = A^2(x) = Da^2(x) \qquad (43)$$

where D is defined by the requirement $a(L/2) = 1$. (See eq 32.)

Let us remark that, until now, the amplitudes of the functions $\bar{\varphi}_n(x)$ (or $\varphi_n(x)$) were arbitrary. Let us fix them by writing

$$\bar{\varphi}_n(x) = ca(x)\varphi(x) \qquad (44)$$

where c is given by eq 33.

The preceding definitions and the notation introduced in section V can be used to transform eq 42. Setting

$$\psi_n(\eta) = (L/\pi)^{1/2}\bar{\varphi}_n(x) \qquad (45)$$

and noting that

$$a(x)\frac{\partial}{\partial x} = \frac{\pi}{L}\frac{\partial}{\partial \eta}$$

we immediately see that the eigenfunctions $\psi_{\mathrm{n}}(\eta)$ are solutions of the equation

$$\frac{D\pi^2}{L^2}\frac{\partial^2}{\partial \eta^2}\psi(\eta) + E\psi(\eta) = 0 \qquad (46)$$

Moreover, according to eqs 44, 34, and 45, we have

$$\int_0^L \mathrm{d}x\ \varphi_n(x)\bar{\varphi}_m(x) = \int_0^L \frac{\mathrm{d}x}{ca(x)}\bar{\varphi}_n(x)\bar{\varphi}_m(x) = \int_0^\pi \mathrm{d}\eta\ \psi_n(\eta)\psi_m(\eta)$$

Therefore, eq 27 leads to the normalization condition

$$\int_0^\pi \mathrm{d}\eta\ \psi_n(\eta)\psi_m(\eta) = \delta_{nm}$$

Accordingly, the solutions of eq 46 are

$$\psi_n(y) = (2/\pi)^{1/2}\sin n\eta$$

$$E_n = D\frac{\pi^2}{L}n^2 = n^2/\tau \qquad (47)$$

Our aim is to calculate $p(t)$, which is given by eqs 30 and 31. We note that (see eqs 45, 37, and 47)

$$\frac{1}{L^{1/2}}\int_0^L \mathrm{d}x\ \bar{\varphi}_{2n+1}(x) = \frac{1}{\pi^{1/2}}\int_0^\pi \mathrm{d}\eta\ b(\eta)\psi_{2n+1}(\eta) = \frac{2^{1/2}}{\pi}\int_0^\pi \mathrm{d}\eta\ b(\eta)\sin\,[(2n+1)\eta]$$

$$\frac{1}{L^{1/2}}\int_0^L \mathrm{d}x\ \varphi_{2n+1}(x) = \frac{1}{\pi^{1/2}}\int_0^\pi \mathrm{d}\eta\ \psi_{2n+1}(\eta) = \frac{2^{1/2}}{\pi}\frac{1}{2n+1}$$

Now, using the preceding equalities and eqs 30 and 31, we can write an explicit expression for $p(t)$

$$p(t) = \sum_{n=0}^{\infty} A_n \exp[-(2n+1)^2 t/\tau]$$

$$A_n = \frac{4}{\pi^2}\frac{1}{2n+1}\int_0^\pi \mathrm{d}\eta\ b(\eta)\sin\,[(2n+1)\eta] \qquad (48)$$

To establish the preceding formalism, we assumed that the density of stress points on the chain at time zero is uniform and the the diffusion process is nonuniform. We note incidentally that the same eq 48 could be obtained by assuming, on the contrary, that we have uniform diffusion (with a constant coefficient D) and that, at time zero, the probability distribution of stress on the chain is $(\pi/2)b(\pi x/L)$. However, this second interpretation does not seem realistic.

VII. Derivation of the Basic Diffusion Model (BD) from a Langevin Equation

In statistical mechanism, it is well-known that diffusion equations can be derived from Langevin equations[11] and that these Langevin equations provide a kind of microscopic interpretation of the diffusion process. Therefore it is useful to know the form of the Langevin equation which corresponds to eq 41 and which defines the basic diffusion process.

Actually, as we shall see, this equation has the very simple form

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A(x)f(t) \qquad (49)$$

where $f(t)$ is a Gaussian random function whose statistical properties are determined by the average

$$\langle f(t)f(t')\rangle = 2\delta(t-t')$$

(white noise).

By applying standard techniques, let us show how eq 41 can be deduced from eq 49. We start by remarking that the basic ingredients for the derivation are the mean values

$$\langle x(t+\tau) - x(t)\rangle_{x(t)=x} \simeq \tau\lambda(x)$$

$$\langle [x(t+\tau) - x(t)]^2\rangle_{x(t)=x} \simeq \tau\mu(x)$$

where τ is a small time increment whereas $\lambda(x)$ and $\mu(x)$ are quantities that we shall now calculate. We note however that this calculation is not completely trivial because $x(t)$ and $f(t)$ are not independent variables.

Equation 49 can be written in the form

$$x(t+\tau) - x(t) = \int_t^{t+\tau}\mathrm{d}t'\ A(x,t')f(t')$$

On the other hand, we have

$$\begin{aligned} A(x(t')) - A(x(t)) &= \int_t^{t'}\mathrm{d}t''\ \frac{\partial}{\partial t''}A(x(t'')) \\ &\simeq A'(x(t))\int_t^{t'}\mathrm{d}t''\ \frac{\mathrm{d}x(t'')}{\mathrm{d}t''} \\ &\simeq A'(x(t))\int_t^{t'}\mathrm{d}t''\ A(x(t''))f(t'') \end{aligned}$$

Consequently, we may write

$$x(t+\tau) - x(t) \simeq A'(x(t))A(x(t))\int_t^{t+\tau}\mathrm{d}t'\int_t^{t'}\mathrm{d}t''\ f(t')f(t'') \qquad (50)$$

As $\delta(t)$ can be considered as a symmetric functions we can assume that

$$\int_t^{t'}\mathrm{d}t'\ \langle f(t')f(t'')\rangle = 1 \qquad (51)$$

(This is a delicate point!) Finally, by averaging eq 50, we obtain

$$\langle x(t+\tau) - x(t)\rangle_{x(t)=x} = \tau A'(x)A(x) \qquad (52)$$

On the other hand, we have

$$\begin{aligned} [x(t+\tau) - x(t)]^2 &= \int_t^{t+\tau}\mathrm{d}t'\int_t^{t+\tau}\mathrm{d}t''\ A(x(t'))A(x(t''))f(t')f(t'') \\ &\simeq A^2(x(t))\int_t^{t+\tau}\mathrm{d}t'\int_t^{t+\tau}\mathrm{d}t''\ f(t')f(t'') \qquad (53) \end{aligned}$$

and by averaging eq 53, we obtain

$$\langle [x(t+\tau) - x(t)]^2\rangle_{x(t)=x} = 2\tau A^2(x) \qquad (54)$$

Thus, we find

$$\lambda(x) = A'(x)A(x)$$
$$\mu(x) = 2A^2(x) \tag{55}$$

Of course, the previous deviation is not completely trivial, but it is possible to convince oneself that it is correct. Now let us consider an arbitrary function $\mathcal{O}(x)$. For given initial conditions (at $t = 0$) concerning the value of $x(0)$, we can, at time t, define the average $\langle \mathcal{O}(x(t)) \rangle$, and it is not difficult to see that this quantity obeys the equation

$$\left\langle \frac{\partial}{\partial t}\mathcal{O}(x(t)) \right\rangle_{x(t)=x} = \lambda(x)\left\langle \frac{\partial}{\partial x}\mathcal{O}(x(t)) \right\rangle_{x(t)=x} + \frac{\mu(x)}{2}\left\langle \frac{\partial^2}{\partial x^2}\mathcal{O}(x(t)) \right\rangle_{x(t)=x} \tag{56}$$

Let us now introduce the probability distribution $P(t;x)$ of x at time t. For any function $\mathcal{O}(x)$, we have

$$\langle \mathcal{O}(x) \rangle = \int_0^L \mathrm{d}x\, P(t;x)\mathcal{O}(x)$$

This eq 56 gives

$$\int_0^L \mathrm{d}x\, \frac{\partial P(t;x)}{\partial t}\mathcal{O}(x) = \int_0^L \mathrm{d}x\, P(t;x)\left\langle -\lambda(x)\frac{\partial}{\partial x}\mathcal{O}(x) + \frac{\mu(x)}{2}\frac{\partial^2}{\partial x^2}\mathcal{O}(x) \right\rangle = \int_0^L \mathrm{d}x\, \mathcal{O}(x)\left\{ \frac{\partial}{\partial x}[\lambda(x)P(t;x)] + \frac{1}{2}\frac{\partial^2}{\partial x^2}[\mu(x)P(t;x)] \right\}$$

Now, integrating by parts, and remarking that $\mathcal{O}(x)$ is completely arbitrary, we get

$$\frac{\partial}{\partial t}P(t;x) = \frac{\partial}{\partial x}\left[\lambda(x)P(t;x) + \frac{1}{2}\mu(x)\frac{\partial}{\partial x}P(t;x) \right]$$

Finally, replacing $\lambda(x)$ and $\mu(x)$ by their explicit expressions given by eq 55, we obtain

$$\frac{\partial}{\partial t}P(t;x) = \frac{\partial}{\partial x}\left[A'(x)A(x)P(t;x) + A^2(x)\frac{\partial}{\partial x}P(t;x) \right] = \frac{\partial}{\partial x}\left[\mathrm{A}(x)\frac{\partial}{\partial x}[A(x)P(t;x)] \right]$$

This equation is the same as eq 41, and this fact shows that eq 49 is the Langevin equation corresponding to the basic diffusion model.

Incidentally, we see that the preceding equation contains a diffusion term and a sliding term. We introduced such terms before but we observe now that both of them are consequences of the simple equation (49).

Thus, the basic diffusion models are valuable not only because they are easily tractable but also because they can be interpreted in a rather simple manner.

VIII. A Soluble "Basic Diffusion" Model (BD1)

A simple soluble model belonging to the BD class described in the preceding section will now be treated in detail. To define this model (BD1), we set

$$b(\eta,\beta) = \frac{c(\beta)}{[\sin \eta]^{\beta}} \quad (0 < \beta < 1) \tag{57}$$

(see eq 38), and, in eq 43, we replace $a(x)$ by the corresponding function $a(x,\beta)$

$$D(x) \equiv D(x,\beta) = Da^2(x,\beta) \tag{58}$$

(see Section V).

We note that the factor D which appears in equation 58 is the value of the diffusion coefficient at the center of the polymer; we assume that it coincides with the usual diffusion constant (de Gennes, Doi-Edwards model) and that the relation

$$D = D_0/L \tag{59}$$

still holds. We believe that this simple assumption is realistic (but other assumptions could be made!). Consequently, relation 13 (between τ and D) remains unchanged.

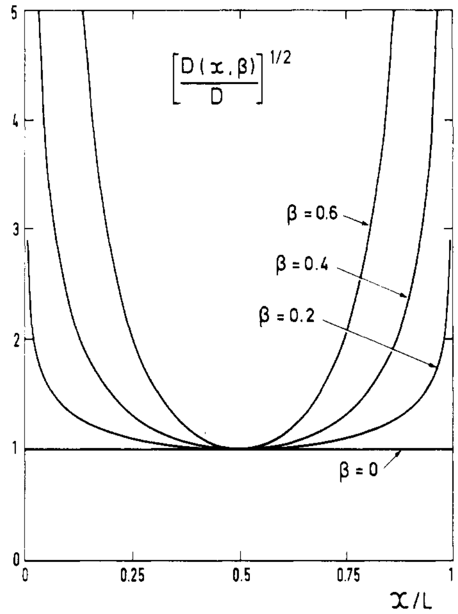

Figure 8. Plot of $a(x,\beta) = [D(x,\beta)/D]^{1/2}$ against x/L. This function is used to define diffusion and sliding both for the BD1 model and for the BD1 model. We note that $a(x,\beta)$ becomes infinite for $x = 0$ and $x = L$.

The model is now completely determined and the function $a(x,\beta) \equiv [D(x,\beta)/D]^{1/2}$ is plotted against x/L on Figure 8 for several values of β. We see that $D(x,\beta)$ is singular at $x = 0$ and $x = L$; thus, using relations introduced in section IV, we can show that for small x

$$D(x,\beta) \propto (x/L)^{-2\beta/(1+\beta)} \tag{60}$$

This is the price that one has to pay in order to get functions $A_n(\beta)$ which decrease like $n^{-(2-\beta)}$, when $n \to \infty$ (i.e. more slowly that n^{-2}).

Our model is soluble and this means that we can derive exact expressions for the coefficients $A_n(\beta)$. According to eqs 48 and 57, we have

$$A_n(\beta) = \frac{4}{\pi^2}\frac{c(\beta)}{2n+1}\int_0^{\pi}\mathrm{d}\eta\, \frac{\sin (2n+1)\eta}{[\sin \eta]^{\beta}}$$

Let us now consider the integrals

$$K_{n,p} = \int_0^{\pi}\mathrm{d}x\, \sin (2n+1)x\, [\sin x]^p$$

where n and p are integers. Recurrence methods can be used to calculate these quantities (see Appendix A), and we find

$$K_{n,p} = \pi^{1/2}\frac{\left(\frac{p}{2}\right)!\left(n - \frac{1}{2} - \frac{p}{2}\right)!}{\left(-\frac{1}{2} - \frac{p}{2}\right)!\left(n + \frac{1}{2} + \frac{p}{2}\right)!} \tag{61}$$

Using Carlson's theorem,[12] we can extend this formula to noninteger values of p by analytic continuation in the domain where the integrals converge. Thus, we may write

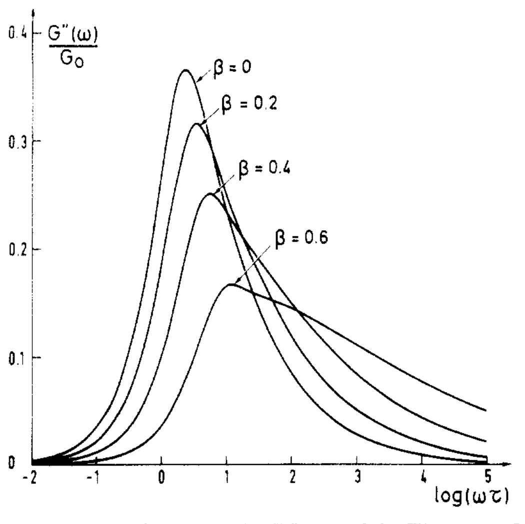

Figure 9. Loss modulus for the BD1 model. The ratio $G''(\omega)/G_0$ is plotted against log ($\omega\tau$) for several values of β; the exponent β is a function of the molecular mass M, i.e. the number of entanglements per polymer. On the other hand, τ is the main relaxation time and we assume that it is proportional to M^3.

$$A_n(\beta) = \frac{4}{\pi^2}\frac{c(\beta)}{2n+1}K_{n,-\beta}$$

where $c(\beta)$ is given by eq 40 and $K_{n,-\beta}$ by eq 61. Finally, for the BD1 model, we obtain the result

$$p(t) = \sum_{n=0}^{\infty} A_n(\beta) \exp[-(2n+1)^2 t/\tau]$$

$$A_n(\beta) = \frac{4}{\pi}\,\frac{\left[\left(-\frac{\beta}{2}\right)!\right]^2}{\left(-\frac{1}{2}-\frac{\beta}{2}\right)!\left(-\frac{1}{2}+\frac{\beta}{2}\right)!}\,\frac{\left(n-\frac{1}{2}+\frac{\beta}{2}\right)!}{(2n+1)\left(n+\frac{1}{2}-\frac{\beta}{2}\right)!} \qquad (62)$$

For a monodisperse melt

$$G(t)/G_0 = [p(t)]^2$$

and, from this equality, we can calculate $G''(\omega)/G_0$ for the BD1 model; this quantity is a function of $\omega\tau$ and is plotted against log ($\omega\tau$) on Figure 9, for several values of β. We observe that, when β increases, the corresponding curve becomes broader and that the top of the curve moves toward the right. Both effects are exactly what we need, and we also note that the shape of our theoretical curves is very similar to the shape of the curves defined by the experimental data.

Now, we can try to fit the Colby results. For the long polymer (L) of mass M_L = 355 000, we take β_L = 0.30 and τ_L = 12.5, and for the shorter one (S) of mass M_S = 70 900, we take β = 0.45 and $\tau_S = \tau_L(M_S/M_L)^3$ ($\simeq$0.1) (this shorter polymer must be considered as rather long; we remain far from the Rouse regime!). We introduce a global factor $G_0 = 12.3 \times 10^6$. Thus, we note that τ_S is not adjusted but deduced from theoretical considerations.

These values and eq 6 with $p(t)$ given by eq 62 enable us to fit the experimental curves corresponding to the monodisperse samples as shown on Figure 10. The fit is very good even better than with the phenomenological formula. In particular, the peaks appear simultaneously at the right place.

Now, we use the same constants and the same formula to predict the relaxation of the polymer blends. The results appear on Figure 11. Again, we have a rather good fit. In fact, the results are not quite as good as those of the phenomenological model in some regions, but better in other ones.

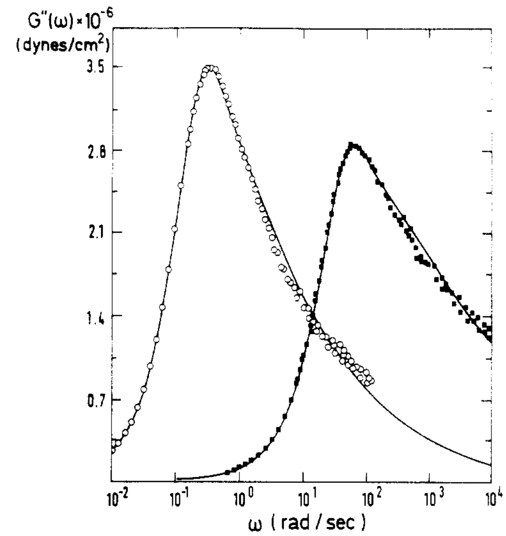

Figure 10. BD1 model: simultaneous fit of loss modulus data for two monodisperse polybutadiene samples. The curves correspond to eq 50. It is assumed that $\tau_L/\tau_S = (M_L/M_S)^3$. The curves are drawn for τ_L = 12.5 and $G_0 = 12.3 \times 10^6$ dynes/cm^2. The only dimensionless parameters are β_L = 0.30 and β_S = 0.45 which lead to the best fit.

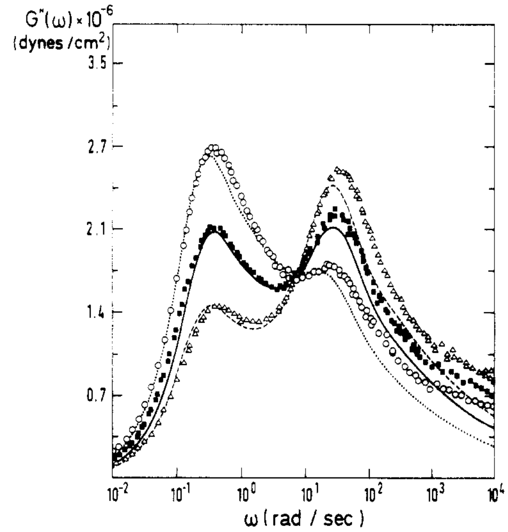

Figure 11. BD1 model: predictions and experimental data for three polymer blends. The curves correspond to eq 50. As in Figure 10, we have τ_L = 12.5, $G_0 = 12.3 \times 10^6$ dyn/cm^2, β_L = 0.30, and β_S = 0.45. The dotted line is the prediction and the open circles are the data for φ_L = 0.882; the solid line and filled squares for φ_L = 0.768; the dashed line and open triangles for φ_L = 0.638.

Thus, the model can be considered as successful. Still, an uncertainty remains because we do not know exactly how the exponent β depends on M.

IX. A Soluble "Variable Diffusion" Model (VD1)

At this point, if the reader is satisfied with our simple BD1 model, he may stop and jump directly to the conclusion. However, he might think that the theoretical interpretation presented in section VII is not a sufficient proof if the validity of the BD models, that these models were introduced mainly for reasons of mathematical convenience, and that diffusion equations containing only a purely diffusive term might be more adequate. This is why we shall now present a model of this type which otherwise is very similar to the BD1 model and also soluble.

The general equation is of the form

$$\frac{\partial}{\partial t}P(t;x,x_0) = \frac{\partial}{\partial x}\left[D(x)\frac{\partial}{\partial x}P(t;x,x_0)\right] \qquad (63)$$

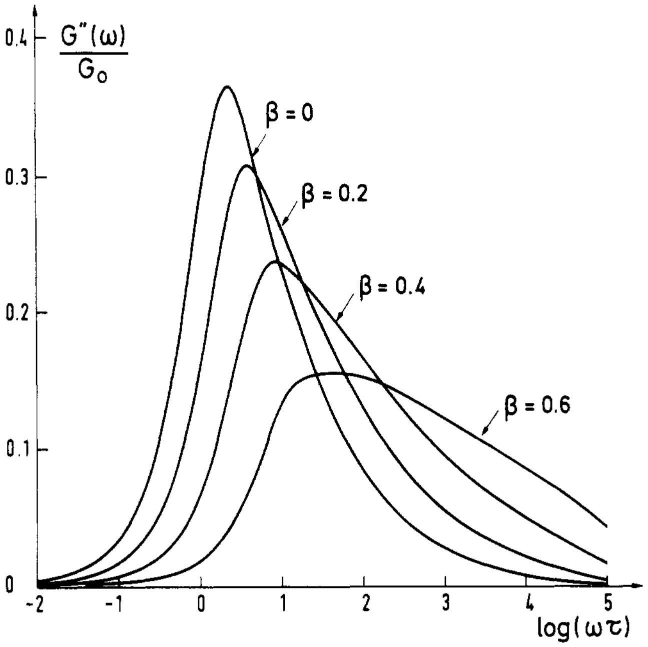

Figure 12. Loss modulus for the VD1 model. The ratio $G''(\omega)/G_0$ is plotted against log ($\omega\tau$) for several values of β. Here τ is the main relaxation time.

Its solution is

$$P(t;x,x_0) = \sum_{n=0}^{\infty} \varphi_n(x)\varphi_n(x_0)e^{-E_n t} \tag{64}$$

where the orthonormal functions $\varphi_n(x)$ are eigenfunctions of the equation

$$\frac{\partial}{\partial x}\left(D(x)\frac{\partial\varphi(x)}{\partial x}\right) + E\varphi(x) = 0 \tag{65}$$

(now $\bar{\varphi}_n(x) \equiv \varphi(x)$ and we have $F(x) = 0$ and $V(x) = 0$).

To define the VD1 model, we write

$$D(x,\beta) = Da^2(x,\beta)$$

where $a(x,\beta)$ is the function introduced in section VI. Again, the system is soluble and its solution is given in Appendix B. The function $p(t)$ is equal to the integral

$$p(t) = \int_0^L \mathrm{d}x \int_0^L \mathrm{d}x_0\, P(t;x,x_0) \tag{66}$$

and finally, for this VD1 model, the result is given by eq B-19 which reads

$$P(t) = \sum_{n=0}^{\infty} A_n(\beta) \exp[-(2n+1)(2n+1+\beta)t/\tau]$$

$$A_n(\beta) =$$

$$\frac{4}{\pi^{3/2}} \frac{\left(\frac{\beta}{2}\right)!}{\left(-\frac{1}{2}+\frac{\beta}{2}\right)!} \frac{\left(2n+1+\frac{\beta}{2}\right)}{(2n+1)(2n+1+\beta)} \frac{\left(n-\frac{1}{2}\right)!\left(n+\frac{\beta}{2}\right)!}{n!\left(n+\frac{1}{2}+\frac{\beta}{2}\right)!} \tag{67}$$

a result which can be compared with the eq 62 concerning the BD1 model.

For a monodisperse melt, we have

$$G(t)/G_0 = [p(t)]^2$$

as before, and from this equality, we can calculate $G''(\omega)/G_0$ for the VD1 model; this quantity is a function of $\omega\tau$ and is plotted against log ($\omega\tau$) on Figure 12, for several values of β.

We can now compare Figure 12 and Figure 9. We see that for the VD1 model, the displacement of the peaks toward the right is larger than for the BD1 model and therefore is a little too large to fit the experimental results. Moreover, we note that the shape of the curves for the VD1 model is not really suitable: the curves are too rounded on the right-hand side near the top. The VD1 model remains acceptable, but the BD1 model is better. This result seems to indicate that the reptation process must include correlated diffusion and sliding contributions.

X. A Soluble Model with "Uniform Diffusion and Sliding" (UDS1)

Now, the reader may raise another question? It is necessary to use a model in which the diffusion constant depends on x? To reproduce the experimental curves, is it not sufficient to introduce a certain amount of sliding? Fortunately, an exactly soluble model of this kind is directly related to the BD1 and VD1 models. So, we shall now describe it, in order to be able to answer the preceding question.

The basic equation defining this UDS1 model is the following (see eq 19 in section IV)

$$\frac{\partial P}{\partial t}(t;x,x_0) = D\frac{\partial}{\partial x}\left[\frac{\partial}{\partial x} + \beta\frac{(\pi/L)}{tg(\pi x/L)}\right]P(t;x,x_0) \tag{68}$$

Its solution has the form

$$P(t;x,x_0) = \sum_{n=0}^{\infty} \varphi_n(x)\bar{\varphi}_n(x_0)e^{-E_n t} \tag{69}$$

where the eigenfunctions $\varphi_n(x)$ and $\bar{\varphi}_n(x)$ form a biorthogonal system. These functions are solutions of the equations

$$D\frac{\partial}{\partial x}\left[\frac{\partial}{\partial x} + \frac{\beta(\pi/L)}{tg(\pi x/L)}\right]\varphi(x) + E\varphi(x) = 0$$

$$D\left[\frac{\partial}{\partial x} - \frac{\beta(\pi/L)}{tg(\pi x/L)}\right]\frac{\partial}{\partial x}\bar{\varphi}(x) + E\bar{\varphi}(x) = 0$$

Again the system is soluble and its solution is given in Appendix C; we write

$$p(t) = \frac{1}{L}\int_0^L \mathrm{d}x \int_0^L \mathrm{d}x_0\, P(t;x,x_0) \tag{70}$$

and, for this UDS1 model, the result is

$$p(t) = \sum_{n=0}^{\infty} A_n(\beta) \exp[-(2n+1)(2n+1+\beta)t/\tau]$$

$$A_n(\beta) =$$

$$\frac{4}{\pi^{3/2}} \frac{\left[\left(\frac{\beta}{2}\right)!\right]^2}{\beta!}\left(2n+1+\frac{\beta}{2}\right)\frac{(2n+\theta)!}{(2n+1)!}\left[\frac{\left(n-\frac{1}{2}\right)!}{\left(n+\frac{1}{2}+\frac{\beta}{2}\right)!}\right]^2 \tag{71}$$

a result which can be compared with eq 62 concerning the BD1 model and with eq 67 concerning the VD1 model.

At first sight, this UDS1 model looks similar to the preceding ones but there is a great difference. For the BD1 and VD1 models, $A_n(\beta)$ decreases like $n^{-(2-\beta)}$ when $n \to \infty$; on the contrary for the UDS1 model, $A_n(\beta)$ decreases like n^{-2}. This unpleasant feature of the UDS1 model appears clearly when one calculates $G''(\omega)/G_0$ for a monodisperse melt by using the formula

$$G(t)/G_0 = [p(t)]^2$$

This quantity is plotted against ln ($\omega\tau$) on Figure 13, for several values of β. We see that a large shift of the top

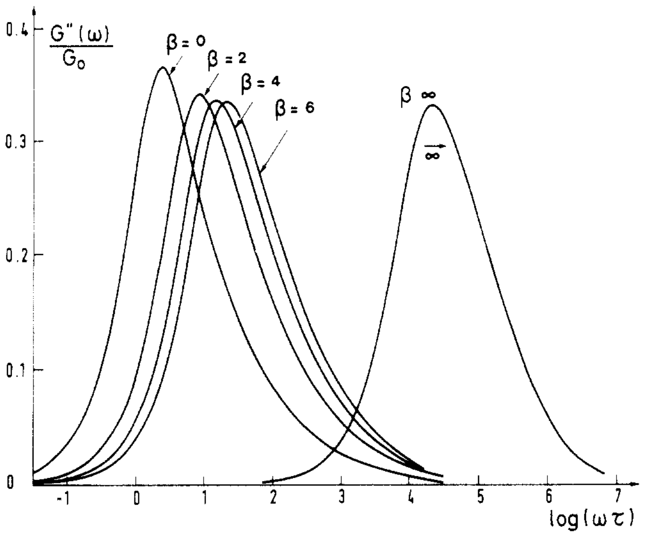

Figure 13. Loss modulus for the UDS1 model. The ratio $G''(\omega)/G_0$ is plotted against log $(\omega\tau)$ for several values of β. Here τ is the (main) relaxation time.

of the curves toward the right may occur but that the broadening and flattening of the curves always remains very small. The UDS1 model is completely unrealistic, and we see that, to reproduce the experimental results, we need equations in which the diffusion constant is strongly singular at $x = 0$ and $x = L$, as was already pointed out at the beginning of section VIII.

XI. Summary and Conclusion

The results obtained in this paper can be summarized as follows:

(1) The relaxation of polymer melts can be analyzed in the framework of the "double reptation" principle (eq 16) which seems to be an extremely good approximation.

(2) Relaxation is a consequence of the motions of the polymers but we can simulate the effects thus produced, by assuming that the stress points move along the polymers.

(3) This motion of a point on a polymer can be described by using a time-independent equation whose type is given by eq 19; the point may diffuse and slide along the polymers, these two possibilities corresponding to two different terms in the equation.

(4) Three exactly soluble models are presented in the paper, namely, a "basic diffusion" model (BD1), a "variable diffusion" model (VD1), and a "uniform diffusion with sliding" model (UDS1).

(5) The BD1 model is characterized by the equation

$$\frac{\partial P}{\partial t} = D\frac{\partial}{\partial x}\left[a(x,\beta)\frac{\partial}{\partial x}[a(x,\beta)P] \right]$$

where $a(x,\beta)$ is a function which becomes infinite for $x = 0$ and $x = L$ and which is defined in section V. The BD1 model belongs to a class of easily tractable models (the BD class described in section VI) which have the same relaxation times as the simple reptation model (and the Rouse model). In other words, for all BD models $\tau_n = \tau/n^2$ for the nth mode. Moreover, these models correspond to very simple Langevin equations.

The BD1 model is our best soluble model and leads to a good fit with the experimental data. However, here we did not study the dependence of β upon the mass of the polymers and the model remains semiphenomenological.

(6) The VD1 model is characterized by the equation

$$\frac{\partial P}{\partial t} = D\frac{\partial}{\partial x}\left[a^2(x,\beta)\frac{\partial}{\partial x}P \right]$$

and here $a(x,\beta)$ is the same function as the $a(x,\beta)$ of the BD1 model. The VD1 model is solved with the help of hypergeometric functions. Now there is a β-dependent shift of the relaxation times. The model gives results that are similar to those obtained with the BD1 model but not quite as good. This fact indicates that purely diffusive reptation is not sufficient to describe reality; sliding effects must be (explicitly or implicitly) taken into account.

(7) The UDS1 model is characterized by the equation

$$\frac{\partial P}{\partial t} = D\frac{\partial}{\partial x}\left(\frac{\partial P}{\partial x} - \beta\frac{\pi/L}{tg(\pi x/L)}P\right)$$

The first term on the right-hand side is a simple diffusion term; the second one introduces singular sliding effects. This model is directly related to the VD1 model and can be solved in the same manner; the relaxation times of the VD1 and UDS1 models are the same. However the results obtained with the USD1 model are quite different and completely unrealistic. This seems to indicate that we need singular diffusion at $x = 0$ and $x = L$ (and perhaps more singular sliding) in order to get an adequate description of reality.

Now, we should try to justify the BD1 model and we should also examine how β depends on the molecular mass of the polymer. However, this is a new problem and we shall not consider it here. Moreover, the best model from a theoretical point of view might differ from the BD1 model. However, we believe that it should belong to the BD-type like the BD1 model.

We must also extend the theory to the Rouse domain, and one has to check that the "double reptation" principle remains valid. Moreover, when we shall be able to incorporate Rouse relaxation in our equations, we shall at the same time find the dependence of the viscosity upon M (the famous 3.4 law!).

Thus, much work remains to be done, concerning the relaxation of polymer melts; however we have established principles that tell us how one must proceed further; this may lead to new significant progress in this field.

Appendix A. Calculation of $K_{n,p}$

We want to calculate the integrals

$$K_{n,p} = \int_0^\pi \mathrm{d}x \sin(2n+1)x\,[\sin x]^p \qquad (n, p \text{ integers})$$

We can first calculate $K_{0,p}$. By transforming the corresponding equation, we obtain the recurrence relation

$$K_{0,p} = \frac{p}{p+1}K_{0,p-2}$$

with $K_{0,0} = 2$ and $K_{0,-1} = \pi$. From it, we deduce

$$K_{0,p} = \pi^{1/2}\frac{\left(\frac{p}{2}\right)!}{\left(\frac{1}{2}+\frac{p}{2}\right)!} \tag{A-1}$$

Then, by transforming the integral which defines $K_{n,p}$, we obtain the recurrence relation

$$K_{n,p} = K_{n-1,p} + 2\left(\frac{2n-p-3}{p+2}\right)K_{n-1,p+1} \tag{A-2}$$

Now, from (A-1) and (A-2), we deduce

$$K_{n,p} = \pi^{1/2}\frac{\left(\frac{p}{2}\right)!\left(n-\frac{1}{2}-\frac{p}{2}\right)!}{\left(-\frac{1}{2}-\frac{p}{2}\right)!\left(n+\frac{1}{2}+\frac{p}{2}\right)!} \qquad \text{(A-3)}$$

We note that Carlson's theorem[12] shows that (A-1) and (A-3) can be applied for noninteger values of p.

Appendix B. VD1 Model: Solution and Calculation of $p(t)$

The VD1 model was presented at the beginning of section IX. To solve this model, one has to calculate the eigenvalues E_n and the orthonormal eigenfunctions $\varphi_n(x)$, solutions of the equation

$$\frac{\partial}{\partial x}\left[Da^2(x,\beta)\frac{\partial}{\partial x}\right]\varphi(x) + E\varphi(x) = 0 \qquad \text{(B-1)}$$

with the boundary conditions

$$\varphi(0) = \varphi(L) = 0 \qquad \text{(B-2)}$$

where $a(x,\beta)$ is the function introduce in section V.

Then, according to eqs 30 and 31, the function $p(t)$ is given by the equalities

$$p(t) = \sum_{n=1}^{\infty} A_n e^{-E_{2n+1}t}$$

$$A_n = \frac{1}{L}\left[\int_0^L \mathrm{d}x\ \varphi_{2n+1}(x)\right]^2 \qquad \text{(B-3)}$$

(Here $\bar{\varphi}_n(x) \equiv \varphi_n(x)$ because the operator $(\partial/\partial x)a^2(x,\beta)\cdot(\partial/\partial x)$ is Hermitian.)

Now we recall that to define $a(x,\beta)$, we introduced a new variable η $(0 < \eta < \pi)$ by setting

$$\frac{\mathrm{d}\eta}{\mathrm{d}x} = \frac{\pi}{b(\eta,\beta)} \qquad \text{(B-4)}$$

$$b(\eta,\beta) = \frac{c(\beta)}{(\sin\eta)^\beta} \qquad \text{(B-5)}$$

where $c(\beta)$ is given by eq 40. Then $a(x,\beta)$ is defined by the equality

$$a(x,\beta) = \frac{b(\eta,\beta)}{c(\beta)} = \frac{1}{(\sin\eta)^\beta}$$

In order to solve eq B-1, we set

$$\psi(\eta) \propto \varphi(x) \qquad \text{(B-6)}$$

Then using the operator equalities

$$a(x,\beta)\frac{\partial}{\partial x} = \frac{\pi}{L}\frac{\partial}{\partial\eta}$$

$$\frac{\partial}{\partial x}a(x,\beta) = \frac{\pi}{L}\frac{1}{b(\eta,\beta)}\frac{\partial}{\partial\eta}b(\eta,\beta) = \frac{\pi}{L}\left[\frac{\partial}{\partial\eta} - \frac{\beta}{tg\eta}\right]$$

we transform eq B-2 into

$$\left(\frac{\partial}{\partial\eta} - \frac{\beta}{tg\eta}\right)\frac{\partial}{\partial\eta}\bar{\psi}(\eta) + \epsilon\bar{\psi}(\eta) \qquad \text{(B-7)}$$

$$E = \frac{D\pi^2}{L^2}\epsilon = \epsilon/\tau \qquad \text{(B-8)}$$

(we use the same notation as in section IV).

On the other hand $A_n(\beta)$, given by eq B-3 can be expressed in terms of the eigenfunctions $\bar{\psi}_n(\eta)$. According to eq B-3, B-4, and B-6, we have

$$A_n = \frac{1}{\pi}\frac{\left[\int_0^\pi \mathrm{d}\eta\ b(\eta,\beta)\bar{\psi}_{2n+1}(\eta)\right]^2}{\int_0^\pi \mathrm{d}\eta\ b(\eta,\beta)[\bar{\psi}_{2n+1}(\eta)]^2}$$

and more explicitly (see eq B-5)

$$A_n = \frac{c(\beta)}{\pi}\frac{\left[\int_0^\pi \mathrm{d}\eta\ [\sin\eta]^{-\beta}\bar{\psi}_{2n+1}(\eta)\right]^2}{\int_0^\pi \mathrm{d}\eta\ [\sin\eta]^{-\beta}[\bar{\psi}_{2n+1}(\eta)]^2} \qquad \text{(B-9)}$$

A final transformation will enable us to solve eq B-7. We set

$$z = \sin^2(\nu/2) \qquad (0 < z < 1)$$

$$\bar{\psi}(\eta) = [z(1-z)]^{(1/2)+(\beta/2)}F(z) \qquad \text{(B-10)}$$

Then, we have

$$\frac{\partial}{\partial\eta} = [z(1-z)]^{1/2}\frac{\partial}{\partial z}$$

$$\frac{1}{tg\eta} = \frac{1-2z}{2[z(1-z)]^{1/2}}$$

Thus, eq B-7 is transformed into

$$z(1-z)\frac{\partial^2 F}{\partial z^2} + \left(\frac{3}{2}+\frac{\beta}{2}\right)(1-2z)\frac{\partial F}{\partial z} + (\epsilon - 1 - \beta)F = 0 \qquad \text{(B-11)}$$

Now, we can use the fact that the hypergeometric function[13]

$$F(a,b;c;z) = \frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)}\int_0^1 \mathrm{d}t\ t^{b-1}(1-t)^{c-b-1}(1-z)^{-a} \qquad \text{(B-12)}$$

is a solution of the equation

$$z(1-z)\frac{\partial^2 F}{\partial z^2}[c - (a+b+1)z]\frac{\partial F}{\partial z} - abF = 0 \qquad \text{(B-13)}$$

To reproduce eq B-11, we have only to choose the values

$$b = 2 + \beta - a$$

$$c = \frac{3}{2} + \frac{\beta}{2}$$

$$\epsilon = a(a - 2 - \beta) + 1 + \beta$$

where a must be determined by boundary conditions.

The hypergeometric functions $F_n(z) \equiv F(a,2+\beta-a;{}^3/_2+(\beta/2);z)$ which correspond to the functions $\psi_{2n+1}(\eta)$ are given by the conditions

$$F_n(1) = 1 \qquad (\text{since } F_N(0) = 1) \qquad \text{(B-14)}$$

On the other hand, from eq B-12, we get[14]

$$F(a,b;c;1) = \frac{\Gamma(c)\Gamma(c-a)}{\Gamma(a+b)}$$

$(\Gamma(x+1) = x!)$. The preceding equation gives

$$F_n(1) = \frac{\left(\frac{1}{2}+\frac{\beta}{2}\right)!\left(-\frac{3}{2}-\frac{\beta}{2}\right)!}{\left(\frac{1}{2}+\frac{\beta}{2}-a\right)!\left(-\frac{3}{2}-\frac{\beta}{2}+a\right)!}$$

and since, for any z, we have[15]

$$(-z)!(z-1)! = \pi/\sin\pi z$$

we get

$$F_n(1) = \frac{\sin \pi\left(\frac{1}{2} + \frac{\beta}{2}\right)}{\sin \pi\left(\frac{1}{2} + \frac{\beta}{2} - a\right)}$$

A solution of this equation is

$$a = -2n \qquad (n = \text{integer})$$
$$b = 2 + \beta + 2n$$

and another solution would be obtained by permuting a and b. However, we can forget this second solution because it would lead to exactly the same results as the first one. Finally, we obtain

$$F_n(z) \equiv F(-2n,2+\beta+2n;{}^3/_2+(\beta/2);z)$$
$$\epsilon_n = (2n + 1)(2n + 1 + \beta) \qquad \text{(B-15)}$$

(Incidentally we note that the functions $F_n(z)$ are Gegenbauer polynomials.[16])

We have now to calculate the corresponding values of $A_n(\beta)$. Starting from eq B-9 and using eq B-10, we can express $A_n(\beta)$ in terms of $F_n(z)$. A simple calculation gives

$$A_n(\beta) = \frac{c(\beta)}{\pi 2^\beta} \frac{[\int_0^1 \mathrm{d}z\, F_n(z)]^2}{\int_0^1 \mathrm{d}z\, [z(1 - z)]^{(1/2)+(\beta/2)} F_n(z)} \qquad \text{(B-16)}$$

The integrals which appear in this formula can be calculated exactly (see Appendices D and F) and we find

$$\int_0^1 \mathrm{d}z\, F_n(z) = \frac{1 + \beta}{(2n + 1)(2n + 1 + \beta)} \qquad \text{(B-17)}$$

$$\int_0^1 \mathrm{d}z\, [z(1 - z)]^{(1/2)+(\beta/2)} F_n(z) = \frac{\pi}{2^{3+2\theta}}\left[\frac{(\beta + 1)!}{\left(\frac{\beta}{2}\right)!}\right]^2 \frac{(2n)!}{\left(2n + 1 + \frac{\beta}{2}\right)(2n + 1 + \beta)} \qquad \text{(B-18)}$$

Finally, for the VD1 model, we obtain

$$p(t) = \sum_{n=0}^{\infty} A_n(\beta) \exp[-(2n + 1)(2n + 1 + \beta)t/\tau]$$

$$A_n(\beta) = \frac{4}{\pi^{3/2}} \frac{\left(\frac{\beta}{2}\right)!}{\left(-\frac{1}{2} + \frac{\beta}{2}\right)!} \frac{\left(2n + 1 + \frac{\beta}{2}\right)}{(2n + 1)(2n + 1 + \beta)} \times \frac{\left(n - \frac{1}{2}\right)!\left(n + \frac{\beta}{2}\right)!}{n!\left(n + \frac{1}{2} + \frac{\beta}{2}\right)!} \qquad \text{(B-19)}$$

Appendix C. UDS1 Model: Solution and Calculation of *p*(*t*)

The UDS1 model was presented at the beginning of section X. To solve this model, one has to calculate the eigenvalues E_n and the biorthogonal set of functions $\varphi_n(x)$ and $\bar{\varphi}_n(x)$, solutions of the coupled equations

$$D\frac{\partial}{\partial x}\left[\frac{\partial}{\partial x} + \beta\frac{\pi/L}{tg(\pi/L)}\right]\varphi(x) + E\varphi(x) = 0$$
$$D\left[\frac{\partial}{\partial x} - \beta\frac{\pi/L}{tg(\pi/L)}\right]\frac{\partial}{\partial x}\bar{\varphi}(x) + E\bar{\varphi}(x) = 0 \qquad \text{(C-1)}$$

with the boundary conditions

$$\varphi(0) = \varphi(L) = 0$$

We can also write

$$\varphi(x) = [\sin (\pi x/L)]^{-\beta}\bar{\varphi}(x)$$

in agreement with eqs 22 and 23.

Then according to eqs 30 and 31, the function $p(t)$ is given by the equalities

$$p(t) = \sum_1^{\infty} A_n e^{-E_{2n+1}t} \qquad \text{(C-2)}$$

$$A_n = \frac{1}{L}[\int_0^L \mathrm{d}x\, \varphi_{2n+1}(x)][\int_0^L \mathrm{d}x\, \bar{\varphi}_{2n+1}(x)] \qquad \text{(C-3)}$$

Now, let us set

$$\eta = \pi x/L \qquad \psi(\eta) \propto \varphi(x) \qquad \bar{\psi}(\eta) \propto \bar{\varphi}(x)$$
$$E = \frac{DL^2}{\pi^2}\epsilon$$

We have

$$\psi(\eta) \propto [\sin \eta]^{-\beta}\bar{\psi}(\eta) \qquad \text{(C-4)}$$

and the functions $\psi(\eta)$ and $\bar{\psi}(\eta)$ obey and the equations

$$\frac{\partial}{\partial \eta}\left(\frac{\partial}{\partial \eta} + \frac{\beta}{tg\eta}\right)\psi(\eta) + \epsilon\psi(\eta) = 0$$
$$\left(\frac{\partial}{\partial \eta} - \frac{\beta}{tg\eta}\right)\frac{\partial}{\partial \eta}\bar{\psi}(\eta) + \epsilon\bar{\psi}(\eta) = 0 \qquad \text{(C-5)}$$

Moreover, eq C-2 can be written in the form

$$A_n(\beta) = \frac{1}{\pi} \frac{[\int_0^\pi \mathrm{d}\eta\, \bar{\psi}_{2n+1}(\eta)][\int_0^\pi \mathrm{d}\eta\, \bar{\psi}_{2n+1}(\eta)]}{\int_0^\pi \mathrm{d}\eta\, \bar{\psi}(\eta)\psi(\eta)} = \frac{[\int_0^\pi \mathrm{d}\eta\, \bar{\psi}_{2n+1}(\eta)][\int_0^\pi \mathrm{d}\eta\, [\sin \eta]^{-\beta}\psi_{2n+1}(\eta)]}{\int_0^\pi \mathrm{d}\eta\, [\sin \eta]^{-\beta}[\psi_{2n+1}(\eta)]^2} \qquad \text{(C-6)}$$

Now, we remark that eq C-5 coincide with eq B-7 of Appendix B and can be solved in the same way. Again, we set (see eq B-10)

$$z = \sin^2 (\eta/2)$$
$$\bar{\psi}(\eta) = [z(1 - z)]^{(1/2)+(\beta/2)}F(z) \qquad \text{(C-7)}$$

The eigenfunctions and eigenvalues are the same as those of Appendix B. Again, we find (see eq 59)

$$F_n(z) \equiv F\left(-2n,2+\beta+2n;\frac{3}{2}+(\beta/2);z\right)$$
$$\epsilon_n = (2n + 1)(2n + 1 + \beta)$$

Finally, starting from eq C-6 and using eq C-7, we can express $A_n(\beta)$ in terms of $F_n(z)$, and we obtain

$$A_n(\beta) = \frac{1}{\pi} \frac{[\int_0^1 \mathrm{d}z\, [z(1 - z)]^{\beta/2}F_n(z)][\int_0^1 \mathrm{d}z\, F_n(z)]}{\int_0^1 \mathrm{d}z\, [z(1 - z)]^{(1/2)+\beta/2}[F_n(z)]^2} \qquad \text{(C-8)}$$

The integrals $\int_0^1 \mathrm{d}z\, F_n(z)$ and $\int_0^1 \mathrm{d}z\, [z(1 - z)]^{(1/2)+\beta/2} \cdot [F_n(z)]^2$ were used previously and are given by eqs B-17 and B-18, respectively. A calculation of the third integral leads to the result (see Appendix C)

$$\int_0^1 \mathrm{d}z\, [z(1 - z)]^{3/2}F_n(z) = \frac{(1 + \beta)!}{2^{2+2\beta}}\left[\frac{\left(n - \frac{1}{2}\right)!}{\left(n + \frac{1}{2} + \frac{\beta}{2}\right)!}\right]^2 \qquad \text{(C-9)}$$

Finally, by putting the values of these integrals in eq C-8, we obtain the value of $A_n(\beta)$ for the UDS1 model. The final expressions are

$$p(t) = \sum_{n=0}^{\infty} A_n(\beta) \exp[-(2n + 1)(2n + 1 + \beta)t/\tau]$$

$$A_n(\beta) = \frac{4}{\pi^{3/2}} \frac{\left[\left(\frac{\beta}{2}\right)!\right]^2}{\beta!}\left(2n + 1 + \frac{\beta}{2}\right)\frac{(2n + \theta)!}{(2n + 1)!} \times \left[\frac{\left(n - \frac{1}{2}\right)!}{\left(n + \frac{1}{2} + \frac{\beta}{2}\right)!}\right]^2 \quad \text{(C-10)}$$

Appendix D. Calculation of I_n

We want to calculate the integral

$$I_n = \int_0^1 \mathrm{d}z\, F_n(z) \quad \text{(D-1)}$$

where $F_n(z)$ is a solution of the equation

$$z(1 - z)F_n''(z) + \left(\frac{3}{2} + \frac{\beta}{2}\right)(1 - 2z)F_n'(z) + [(2n + 1)(2n + 1 + \beta) - 1 - \beta]F_n(\beta) = 0 \quad \text{(D-2)}$$

and obeys the boundary conditions

$$F_n(0) = F_n(1) = 1 \quad \text{(D-3)}$$

Equation D-2 can be written in the form

$$\frac{\partial}{\partial z}[z(1 - z)F_n'(z)] + \left(\frac{1}{2} + \frac{\beta}{2}\right)\frac{\partial}{\partial z}[(1 - 2z)F_n(z)] + (2n + 1)(2n + 1 + \beta)F_n(z) = 0 \quad \text{(D-4)}$$

Let us integrate this equation with respect to z from $z = 0$ to $z = 1$; we obtain

$$\left(\frac{1}{2} + \frac{\beta}{2}\right)[-F_n(1) - F_n(0)] + (2n + 1)(2n + 1 + \beta)\int_0^1 \mathrm{d}z\, F_n(z) = 0$$

Thus, using the boundary conditions (D-3), we find

$$I_n = \frac{1 + \theta}{(2n + 1)(2n + 1 + \theta)} \quad \text{(D-5)}$$

Incidentally, we note that $F_n(z)$ is a hypergeometric function ($F_n(z) \equiv F(-2n,2+\beta+2n;\, ^3/_2+\beta/2;z)$), which can be represented by a simple series. Therefore, we could also derive (D-5) by integrating this series term by term.

Appendix E. Calculation of I_n

We want to calculate the integral

$$\bar{I}_n = \int_0^1 \mathrm{d}z\, [z(1 - z)]^{\beta/2}F_n(z) \quad \text{(E-1)}$$

where $F_n(z)$ is defined by eqs D-2 and D-3 of Appendix D.

Let us define the integral

$$I_n(\alpha) = \int_0^1 \mathrm{d}z\, [z(1 - z)]^{\alpha}F_n(z) \quad \text{(E-2)}$$

which is a function of α and β. We know that

$$I_n(0) = I_n = \frac{1 + \beta}{(2n + 1)(2n + 1 + \beta)}$$

(see Appendix A), and, first, we shall derive a recurrence formula that will enable us to calculate $I_n(\alpha)$ for integer values of α.

Let us start from eq D-4

$$\frac{\partial}{\partial z}[z(1 - z)F_n'(z)] + \left(\frac{1}{2} + \frac{\beta}{2}\right)\frac{\partial}{\partial z}[(1 - 2z)F_n(z)] + (2n + 1)(2n + 1 + \beta)F_n(z) = 0$$

Let us multiply this equation by $[z(1 - z)]^{\alpha}$; after a few transformations, we obtain

$$\frac{\partial}{\partial z}[z(1 - z)F_n'(z)] + \left(\frac{1}{2} + \frac{\beta}{2} - \alpha\right)\frac{\partial}{\partial z}[(z(1 - z))^{\alpha}(1 - 2z)F_n(z)] + \left[(2n + 1)(2n + 1 + \beta) - 2\alpha(2\alpha - \beta) - \frac{\alpha(1 + \beta - 2\alpha)}{2z(1 - z)}\right][z(1 - z)]^{\alpha}F(z) = 0$$

Let us integrate this equation with respect to z from $z = 0$ to $z = 1$. We obtain

$$[(2n + 1)(2n + 1 + \beta) - 2\alpha(2\alpha - \beta)]I_n(\alpha) - \frac{\alpha}{2}(1 + \beta - 2\alpha)I_n(\alpha - 1) = 0$$

or more simply

$$\frac{I_n(\alpha)}{I_n(\alpha - 1)} = \frac{\alpha\left(\alpha - \frac{1}{2} - \frac{\beta}{2}\right)}{4\left(\alpha + n + \frac{1}{2}\right)\left(\alpha - n - \frac{1}{2} - \frac{\beta}{2}\right)}$$

Let us now assume that α is an integer. By recurrence, we obtain

$$I_n(\alpha) = \frac{1 + \beta}{4^{\alpha+1}} \frac{\left(n - \frac{1}{2}\right)!\left(-n - \frac{1}{2} - \frac{\beta}{2}\right)!}{\left(-\frac{1}{2} - \frac{\beta}{2}\right)!\left(n + \frac{1}{2} + \frac{\beta}{2}\right)} \frac{\alpha!\left(\alpha - \frac{1}{2} - \frac{\beta}{2}\right)!}{\left(\alpha + n + \frac{1}{2}\right)!\left(\alpha - n - \frac{1}{2} - \frac{\beta}{2}\right)!} \quad \text{(E-3)}$$

This formula can be extrapolated to real values of α with $\alpha > -1$, and according to Carlson's theorem,[12] this extrapolation is unique.

Now, we can calculate $\bar{I}_n = I_n(\beta/2)$. By putting $\alpha = \beta/2$ in the preceding equation and with the help of the identity[15]

$$\left(\frac{1}{2} + \frac{\beta}{2}\right)!\left(\frac{\beta}{2}\right)! = \frac{\pi^{1/2}}{2^{1+\beta}}(1 + \beta)!$$

we obtain the final result

$$\bar{I}_n = \frac{(1 + \beta)!}{4^{1+\beta}}\left[\frac{\left(n - \frac{1}{2}\right)!}{\left(n + \frac{1}{2} + \frac{\beta}{2}\right)}\right]^2 \quad \text{(E-4)}$$

Appendix F. Calculation of J_n

We want to calculate the integral

$$J_n = \int_0^1 \mathrm{d}z\, [z(1 - z)]^{(1/2)+(\beta/2)}[F_n(z)]^2 \quad \text{(F-1)}$$

where $F_n(z)$ is defined by eqs D-2 and D-3 of Appendix

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D which imply that $F_n(z)$ is a hypergeometric function

$$F_n(z) \equiv F\left(-2n,2+\beta+2n;\frac{3}{2}+(\beta/2);z\right)$$

To obtain the value of J_n, we shall use the fact that $F_n(z)$ is a Gegenbauer polynomial, since we have[16]

$$C^{\lambda}_{2n}(t) = \frac{(2\lambda + 2n - 1)!}{(2n)!(2\lambda - 1)!}F\left(2\lambda+2n,-2n;\lambda+\frac{1}{2};\frac{1 - t}{2}\right)$$

which for $\lambda = 1 + \beta/2$ gives

$$F_n(z) = \frac{(1 + \beta)'(2n)!}{(2n + 1 + \beta)}c^{1+\theta/2}_{2n}(1 - 2z) \qquad \text{(F-2)}$$

Now, we consider the classical formula[17]

$$\int_{-1}^{1}\mathrm{d}t\ (1 - t^2)^{\lambda-1/2}[c^{\lambda}_{n}(t)]^2 = \frac{2^{-2\lambda}}{[(\lambda - 1)!]^2}\frac{2\pi(2\lambda + n - 1)!}{(n + \lambda)n!}$$

By setting $t = 1 - 2z$ and by choosing for λ the value $\lambda = 1/\beta/2$, we transform the preceding formula into

$$\int_{0}^{1}\mathrm{d}z\ z(1 - z)^{(1/2)+(\beta/2)}[C^{1+\beta/2}_{2n}(1 - 2z)]^2 = \frac{\pi 2^{-3-2\beta}}{\left[\left(\frac{\beta}{2}\right)!\right]^2}\frac{(2n + 1 + \beta)!}{\left(2n + ! + \frac{\beta}{2}\right)(2n)!} \qquad \text{(F-3)}$$

Finally, by combining eqs D-2 and D-3, we obtain the result

$$J_n = \frac{\pi 2^{-3-2\beta}}{\left[\left(\frac{\beta}{2}\right)!\right]^2}\frac{[(\beta + 1)!]^2(2n)!}{\left(2n + 1 + \frac{\beta}{2}\right)!\left(2n + 1 + \frac{\beta}{2}\right)!} \qquad \text{(F-4)}$$

References and Notes

(1) de Gennes, P.-G. *J. Chem. Phys.* **1971,** *55,* 572.

(2) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans.* **1978,** *74,* 1789, 1802, 1818. *The Theory of Polymer Dynamics*; Clarendon Press; Oxford, 1986; Chapter 6.

(3) Rubinstein, M.; Colby, R. *J. Chem. Phys.* **1988,** *89,* 5291.

(4) Doi and Edwards already noted this fact in their book (see ref 2).

(5) des Cloizeaux, J. *Europhys. Lett.* **1988,** *5,* 437 (note that in this paper, Figures 1 and 6 have been unduly permuted but not their captions). The double reptation concept is clearly formulated in this publication, but the same idea also appears in other papers: see discussion in section III.

(6) Watanabe, H.; Kotaka, T. *Macromolecules* **1984,** *17,* 2316.

(7) Watanabe, H.; Kotaka, T. *Macromolecules* **1987,** *20,* 530.

(8) Marucci, G. *J. Polym. Sci., Polym. Phys. Ed.* **1985,** *23,* 159.

(9) Viovy, J. L. *J. Phys. (Les Ulis, Fr.)* **1985,** *46,* 847. Rubinstein, M.; Helfand, E.; Pearson, D. S. *Macromolecules* **1987,** *20,* 822 (see also ref 2). Cassagnau, Ph. Thèse de Doctorat-Université de Pau et des Pays de l'Adour, 1988. Ball, R. C.; McLeish, T. C. B. *Macromolecules* **1989,** *22,* 1911.

(10) Doi, M. *J. Polym. Sci. Lett.* **1981,** *19,* 265. Doi, M. *J. Polym. Sci., Polym. Phys. Ed.* **1983,** *21,* 667.

(11) Kirkwood, J. G. *Selected Topics in Statistical Mechanics*; Zwanzig, R. W., Ed.; Gordon and Breach: London, 1967. *Selected Papers on Noise and Stochastic Processes*; Wax, N., Ed.; Dover: New York, 1954.

(12) Titchmarsh, E. C. *The Theory of Functions*, 2nd ed.; Oxford University Press: London, 1939; Section 5.8, p 185.

(13) Erdelyi, A., et al. *Higher Transcendental Functions*; McGraw-Hill: New York, 1953; Vol. I, Chapter II, p 56.

(14) Gradshtein, I. S.; Ryzhik, I. M. *Table of Integrals, Series and Products*; Academic Press: New York, 1965; pp 948, 950.

(15) Jahnke, E., Emde, F. *Tables of Functions*, 4th ed.; Dover: New York, 1945; p 11.

(16) See ref 9, pp 1029 and 1030.

(17) See ref 9, p 827.

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Equilibrium Morphology of Block Copolymer Melts. 3

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ABSTRACT: The field theoretical approach for block copolymer melts developed in our earlier work (Kawasaki, K.; et al. *Macromolecules* **1988,** *21,* 2972) was recast in such a way as to avoid power series expansion in the concentration variable. The general scaling behavior was found, which naturally gives rise to the well-known two-thirds power law of the domain size. The theory is related to other approaches by Helfand and co-workers and by Semenov. Numerical consequences of the theory are also presented that clearly demonstrate approach to the correct asymptotic behavior.

1. Introduction

In the first two of the present series to be referred to as OK[1] and KOK,[2] respectively, we have described attempts to extend Leibler's field theoretical formulation of block copolymer melts[3] to include strong segregation regime in microphase-separated states. The free energy functional, $H\{\psi\}$, was obtained as a functional power series in the local order parameter field, $\psi(\mathbf{r})$. Despite the apparent success of OK in predicting the morphological phase diagram in the strong segregation region when the series was terminated in the fourth order, the higher order terms were found to contribute at least equally in KOK, and validity of the expansion was questioned. The present paper is motivated by our desire to find an alternate approach free from the convergence question of the series expansion approach of OK and KOK.

We start from the formal field theoretical framework of KOK where the functional power series of $H\{\psi\}$ is divided into short-range and long-range contributions, the latter described in terms of the Gaussian chain statistics (section 2). Instead of expanding the long-range contribution in the power series as in KOK, we express it by introducing the field conjugate to $\psi(\mathbf{r})$, which is self-consistently determined for given $\psi(\mathbf{r})$ (section 3). In section 4 we derive the general scaling properties, a consequence of which is that the linear dimension of domains in microphase-separated states scales as two-thirds the power of the polymerization index in the strong segregation limit. The theory is applied to the lamellar phase in section 5 and

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