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## The relaxation spectrum of polymer length distributions

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**Résumé.** — Nous faisons l'étude théorique du comportement d'un système de « polymères vivants » (polymères qui peuvent se casser et recombiner de manière réversible), dont la distribution de poids moléculaire (MWD) est perturbée à partir de l'état d'équilibre et relaxe ensuite. On considère deux types de cinétique chimique : (a) scission unimoléculaire réversible et (b) interéchange d'extrémités (les deux correspondent à des MWD à l'équilibre exponentielles). En prenant des formes simples pour les kernels qui donnent le taux de réaction, nous déduisons des fonctions réponse qui déterminent la relaxation du système après une perturbation arbitraire (petite) de la MWD. En général, ceci correspond à une décroissance compliquée, non exponentielle. Pourtant, dans le cas particulier d'un saut de température ou de pression, qui conserve la forme exponentielle de la MWD mais déplace sa moyenne, on prévoit une décroissance simple exponentielle dans le cas de la scission unimoléculaire tandis qu'il n'y a pas de décroissance dans le cas de l'interéchange d'extrémités. Nous pensons que nos résultats s'appliquent à l'interprétation des sauts T observés dans des expériences avec des micelles flexibles en forme de ver.

**Abstract.** — We study theoretically the behaviour of a system of « living polymers » (polymers that can break and recombine reversibly) whose molecular weight distribution (MWD) is perturbed from equilibrium and then allowed to relax. Two classes of chemical kinetics are considered : (a) reversible unimolecular scission, and (b) end-interchange. (Both yield equilibrium MWD's that are exponential). Assuming simple forms for the reaction-rate kernels in each case, we derive response functions that determine the relaxation of the system after an arbitrary (small) initial perturbation to the MWD. This is in general a complicated, non-exponential decay. However, for the special case of a temperature or pressure jump, which preserves the exponential form of the MWD but shifts its mean, a single exponential decay is predicted for the unimolecular scission case, whereas there is no decay at all in the case of end interchange. We expect our results to be relevant to the interpretation of T-jump experiments on flexible wormlike micelles.

### 1. Introduction.

A standard experimental method in the study of micellization kinetics involves applying a sudden change in temperature ( $T$ ) or pressure ( $P$ ) and observing the relaxation of the micelle size distribution to the new equilibrium state [1-8]. (The relaxation can be monitored using probes such as light scattering.) One interesting class of micellar systems (including CTAB/KBr/H<sub>2</sub>O [9, 10]) are those in which very long, flexible, wormlike micelles exist [9-20].

Even at very low concentrations of amphiphile, these can form a tangled mass of chains whose viscoelastic properties have recently been the focus of intense experimental and theoretical study (for a review see Ref. [21]). It is now recognised that reversible breaking down of the micelles can play an important role in determining the terminal time  $\tau_S$  for stress relaxation [10, 12, 14, 16, 19-21]. Reference [19] describes a theoretical model for stress relaxation, in which an important parameter is the characteristic *breaking time*  $\tau_b$  of the chains (the mean waiting time for a chain of the average length to undergo a scission or end-interchange somewhere along its length). According to the model of references [19-21], the terminal time  $\tau_S$  need not coincide with  $\tau_b$  [12], but can instead be much longer. Specifically the model predicts  $\tau_S \sim (\tau_b \tau_r)^{1/2}$ , where  $\tau_r$  is the reptation (disentanglement) time [22] of a system of hypothetical unbreakable chains with the correct mean molecular weight. [This result assumes  $\tau_b \ll \tau_r$ , in the opposite limit ;  $\tau_S$  is simply  $\tau_r$  [19].]

To test these ideas unambiguously, it is essential to have an independent experimental determination of the breaking time  $\tau_b$ . An obvious candidate is the T-jump method, and data on the CTAB/KBr system should be available soon [23]. (There is already data on some closely related though perhaps more rod-like systems [12] ; in these, the relaxation time after T-jump and the terminal time are found to be rather close.) More generally one can imagine any experiment in which the distribution of polymer lengths is disturbed and then allowed to relax to equilibrium. It is clear that some definite model for the kinetics of micellar breakdown is needed before data from these experiments can be interpreted. For example, in the dilute regime, light scattering probes the weight-average molecular weight. Theoretically one can ask whether the decay of this quantity should be single exponential, and if so, how does the decay time relate to  $\tau_b$ .

The answers to these questions must depend on the type of chemical kinetics that are present. In what follows, we study in detail two simple cases, (a) reversible unimolecular scission, and (b) end-interchange. In both cases we assume for simplicity that reactions occur with equal probability for all monomers and/or chain ends in the system, and thus neglect any dependence on chain length of the microscopic reaction rates for scission, fusion, or interchange processes. This assumption is appropriate in the entangled regime when reaction rates are determined by the local motion of subsections of chain, and not the diffusion of polymers over distances large compared to their gyration radii. In fact, for the unimolecular scission case it is sufficient to assume that the forward reaction (scission) occurs at the same rate for any bond in the system ; the principle of detailed balance, in conjunction with the known equilibrium length distribution [20] then ensures that the recombination rate constant must also be chain-length independent.

With these simplifications we are able to calculate Greens functions that determine, for the two classes of kinetics, the relaxation of an arbitrary (material preserving) small perturbation in the MWD. The particular perturbation corresponding to a T-jump is found to be a very special case : for reversible scission kinetics (case a) we find that the entire perturbation decays exponentially, whereas for interchange kinetics (case b) it does not decay at all. This means that T-jump provides a direct and robust measure of  $\tau_b$  for reversible scission but provides no information relevant to end interchange. When both are present, T-jump provides in principle a way of measuring the reaction rate for scission which is not affected by the simultaneous presence of end interchange processes.

Throughout our analysis, we ignore the so-called « fast » process whereby polymeric micelles equilibrate with the ambient density of free monomers in the system [1-8]. This involves reactions where single monomers are added or removed one by one from a chain end. We expect that, for long polymers, these processes are rather inefficient for relaxing the main part of the MWD and can therefore be ignored for our purposes. This is corroborated

experimentally by the observation of single-exponential stress relaxation [10], which is predicted theoretically *only* when kinetics of types (a) or (b) are dominant in causing significant length-changes for a long polymer [20, 21].

## 2. Reversible scission.

We first study a system of simple long chain polymers of variable length  $L$  (which we take to be a continuous parameter) that are allowed to react according to the processes of unimolecular scission, and its reverse (which involves recombination of two chains by fusion of one end of each chain). We describe the MWD as a number density  $C(L)$ , such that  $C(L) dL$  chains have length between  $L$  and  $L + dL$ . The processes to be considered are :

(i) *Unimolecular scission.* — This process is characterized by a rate constant  $k$  per unit time per unit arc length, which is the same for all polymers and is independent of time.

(ii) *Bimolecular recombination.* — Any two chains may combine by bondine end-to-end. The rate of this reaction is independent of time and is assumed proportional to the product of the concentrations  $C(L)$  for the two reacting chain species. (The collision rate is presumed independent of the lengths of the chains involved, as discusses in Sect. 1.) The process is governed by a second rate constant  $k'$ .

Using the two processes detailed in (i) and (ii) above we can write a rate equation governing the time evolution of the polymer length distribution

$$\dot{C}(L) = -kLC(L) + 2k \int_L^\infty C(L') dL' + \frac{1}{2}k' \int_0^\infty \int_0^\infty C(L') C(L'') \delta(L' + L'' - L) dL' dL'' - k' C(L) \int_0^\infty C(L') dL'. \quad (1)$$

The first term describes the loss by scission of chains of length  $L$ , and the second the creation of such chains by scission of longer chains. (A factor 2 occurs since there are two points on a longer chain at which scission can occur to give a chain of length  $L$ .) The third term is the creation of a chain of length  $L$  by combination of chains of length  $L'$  and  $L''$  and the fourth is the loss of chains of length  $L$  by combination with another chain.

Without loss of generality we now choose units so that the arc-length density per unit volume is equal to unity :

$$\rho = \int_0^\infty LC(L) dL = 1. \quad (2)$$

Using this relation it is easily confirmed that the steady state solution  $C_0(L)$  of equation (1) is the exponential MWD.

$$C_0(L) = \frac{1}{\bar{L}^2} \exp(-L/\bar{L}). \quad (3)$$

Where the mean chain length is related to the rate constants as follows :

$$\bar{L} = \frac{1}{\int_0^\infty C_0(L') dL'} = \sqrt{\frac{k'}{2k}}. \quad (4)$$

As usual, this implies a restriction on the ratio  $k'/k$ , which is determined by the equilibrium statistical mechanics of the system. In simple models, one finds  $\bar{L} \propto \exp \frac{E}{2 k_B T}$  where  $E$  is the scission.

The form (3) is more general, however, and should arise universally for chains in the semidilute (entangled) regime [20, 24]. It follows that the sole effect of a sudden temperature jump is to prepare a system which has the MWD of equation (3) but with the « wrong » value of  $\bar{L}$ . The same applies to a jump in any other thermodynamic variable that influences the chain length, for example a pressure jump.

We now take the limit of a small perturbation to the equilibrium distribution, writing  $C(L, t) = C_0(L) + \Delta(L, t)$  with  $\Delta(L, t)$  a small quantity. Substituting into equation (1) we obtain,

$$\dot{\Delta}(L, t) = -k(L + 2\bar{L})\Delta(L, t) + 2k \left[ \int_0^L \Delta(L', t) e^{-(L-L')/L} dL' + \int_L^\infty \Delta(L', t) dL' - e^{-L/L} \int_0^\infty \Delta(L', t) dL' \right]. \quad (5)$$

**2.1 GENERAL SOLUTION.** — To make this equation more tractable for a general perturbation we take the Laplace transform of equation (5). After some manipulation we obtain

$$\dot{\varepsilon}(\mu, t) = k \frac{\partial}{\partial \mu} \varepsilon(\mu, t) + f(\mu) \varepsilon(\mu, t) + g(\mu) \varepsilon(0, t) \quad (6)$$

with  $\varepsilon(\mu, t) \equiv \int_0^\infty e^{-\mu L} \Delta(L, t) dL$ . In equation (6)

$$f(\mu) = 2k \left[ \frac{1}{\mu + 1/\bar{L}} - \bar{L} - \frac{1}{\mu} \right] \quad (7a)$$

$$g(\mu) = 2k \left[ \frac{1}{\mu} - \frac{1}{\mu + 1/\bar{L}} \right]. \quad (7b)$$

To solve the differential equation (6) we must specify the initial perturbation  $\Delta(L, 0)$ , and also impose a boundary condition at  $\mu = 0$ . The correct boundary condition is found by conservation of material, which implies,

$$\int_0^\infty L \Delta(L, 0) dL = \frac{\partial}{\partial \mu} \varepsilon(\mu, t) |_{\mu=0} = 0. \quad (8)$$

We now note that  $\varepsilon(0, t) = \int_0^\infty \Delta(L, t) dL$  is the total number of excess chains at time  $t$ . To obtain an equation for the time dependence of this quantity, we may let  $\mu = 0$  in equations (6-7b); using also the boundary condition, equation (8), we obtain

$$\varepsilon(0, t) = \varepsilon(0, 0) e^{-2kLt}. \quad (9)$$

This result can now be substituted into the right hand side of equation 6, allowing an explicit solution for all  $\mu$ . The solution, which may be checked by direct substitution, is as follows :

$$\varepsilon(\mu, t) = \int_0^t [g(\mu + k(t - t')) \varepsilon(0, t') + \delta(t') \varepsilon(\mu + k(t - t'), 0)] \times \exp \left[ \int_{t'}^t f(\mu + k(t - t'')) dt'' \right] dt'. \quad (10)$$

Now substituting in the explicit forms (7a, 7b) for the functions  $f$  and  $g$  and performing the relevant time integrals, we obtain the following solution, where, for notational convenience, we have introduced the parameters  $\alpha = 1/\bar{L}$  and  $\beta = kt$  :

$$\varepsilon(\mu, t) = e^{-2kLt} \left( \frac{\mu}{\mu + \alpha} \right)^2 \times \left\{ \left( \frac{2\mu + \alpha}{\mu^2} - \frac{2(\mu + \beta) + \alpha}{(\mu + \beta)^2} \right) \alpha \varepsilon(0, 0) + \varepsilon(\mu + \beta, 0) \left( \frac{\mu + \beta + \alpha}{\mu + \beta} \right)^2 \right\}. \quad (11)$$

This result contains complete information about the linear response of the polymer length distribution  $C(L)$  to a small external perturbation. It is useful to introduce a Greens function  $\Delta_\ell(L, t)$ . The general solution for arbitrary initial condition may then be written

$$\Delta_2(L, t) = \int d\ell \Delta_2(\ell, 0) \Delta_{2,\ell}(L, t). \quad (12)$$

(It should be noted that the delta function initial condition does not conserve the total amount of material, and thus contradicts the assumption leading to boundary condition (8). However, the resulting Greens function is valid when used in equation (12) so long as the initial perturbation  $\Delta(\ell, 0)$  preserves material.)

We may introduce  $\varepsilon_\ell(\mu, t)$  defined as the Laplace transform of  $\Delta_\ell(L, t)$ . By taking the Laplace transform of the delta-function initial condition we find  $\varepsilon_\ell(\mu, 0) = \exp(-\mu\ell)$  and  $\varepsilon_\ell(0, 0) = 1$ . Substitution of these results into (11) yields

$$\varepsilon_\ell(\mu, t) = e^{-2\beta L} \left( \frac{\mu}{\mu + \alpha} \right)^2 \times \left\{ \left( \frac{2\mu + \alpha}{\mu^2} - \frac{2(\mu + \beta) + \alpha}{(\mu + \beta)^2} \right) \alpha + e^{-(\mu + \beta)\ell} \left( \frac{\mu + \beta + \alpha}{\mu + \beta} \right)^2 \right\}. \quad (13)$$

To obtain the Greens function in  $L$ -space,  $\Delta_\ell(L, t)$  we may invert this expression by complex contour integration. Introducing the usual theta function  $\theta(x) = [1 + \text{sign}(x)]/2$ , we obtain (after some algebra)

$$\Delta_\ell(L, t) = e^{-2\beta L} \frac{\alpha\beta}{(\alpha - \beta)^3} [\gamma(L) - e^{-\beta\ell} \theta(L - \ell) \gamma(L - \ell)] + e^{-2\beta L} e^{-\beta\ell} \delta(L - \ell). \quad (14)$$

With  $\gamma(L) = 2(\alpha^2 - \alpha\beta + \beta^2)(e^{-\beta L} - e^{-\alpha L}) - \alpha\beta L(\alpha - \beta)(e^{-\beta L} + e^{-\alpha L})$ . This Greens function allows the time development of an arbitrary initial perturbation  $\Delta(L, 0)$  to be evaluated as a simple integral (Eq. (12)).

**2.2 THE CASE OF A TEMPERATURE JUMP.** — Up to this point we have made no assumptions about the form of the initial perturbation  $\Delta(L, 0)$  other than it is small in some sense. We now consider what form of perturbation is obtained after an instantaneous temperature or pressure jump. As discussed following equation (4) above, such a jump prepares the system

with an initial length distribution appropriate to a shifted average chain length :  $\bar{L}$  to  $\bar{L} + \xi$ . We assume that  $\xi$  is small, i.e. terms of order  $(\xi^2)$  are negligible. Then using the Taylor expansion of  $C_0(L)$  with respect to  $\bar{L}$ ,  $\Delta(L, 0)$  is easily identified :

$$C(L, 0) = C_0(L) + \xi \frac{\partial}{\partial \bar{L}} C_0(L) \quad (15)$$

$$\Rightarrow \Delta(L, 0) = \eta (L - 2 \bar{L}) e^{-L/\bar{L}} \quad (16)$$

with  $\eta = \xi / \bar{L}^4$ .

Substitution of the expression (16) into equation (5) reveals this  $\Delta(L, 0)$  to be an eigenfunction of the time evolution operator, with eigenvalue  $1/2 k\bar{L}$ . Hence the initial perturbation decays with a single exponential relaxation :  $\Delta(L, t) = \Delta(L, 0) \exp[-t/\tau]$ , where,

$$\tau = \frac{1}{2 k\bar{L}}. \quad (17)$$

This result may be confirmed by convoluting the initial distribution obeying equation (16) with the Green function given in equation (14). The parameter  $\tau$  is precisely half the « breaking time » introduced earlier.

We see that the temperature jump amounts to a very special choice of disturbance (an eigenfunction of the integral operator in Eq. (5)) which is ideally suited to the measurement of the breaking time  $2\tau$ . Our prediction of single exponential decay for this case is supported by preliminary experimental data on wormlike micelles [23] (see also Refs. [12-14]). Note that the result depends on our assumption of a length independent recombination constant  $k'$ , which, as stated before, should be a good approximation throughout the semidilute (entangled) regime for flexible polymeric objects.

For a more general perturbation from equilibrium, not of the form of equation (16), a single exponential decay cannot usually be expected. We have not looked for other eigenfunctions of our time evolution equation (5) but it would be surprising to find any others corresponding to such a simply realized experimental procedure. Nonetheless it would be interesting to study experimentally other ways of perturbing the polymer length distribution.

### 3. The role of end-interchange processes.

In this section we examine the behaviour of a system which is allowed to evolve according to the process of end interchange only. The equation governing the time evolution of  $C(L)$  is as follows :

$$\begin{aligned} \dot{C}(L) = & -k'' LC(L) \int_0^\infty C(L') dL' - k'' C(L) \int_0^\infty L' C(L') dL' + \\ & + k'' \int_{L'=0}^L \int_{L''=L-L'}^\infty C(L') C(L'') dL' dL'' + k'' \int_{L'=0}^\infty \int_{L''=L}^\infty C(L') C(L'') dL' dL''. \end{aligned} \quad (18)$$

Here the first term represents the destruction of chains of length  $L$  by chains of any length « biting into them » somewhere in the chemical sequence. The second term represents the destruction of a chain of length  $L$  by the process of that chain biting into any other chain. The third term represents the process whereby a chain of length  $L'$  bites into one of length

$L''$  and carries off a part of length  $L - L'$  (thus creating a chain of length  $L$ ). The fourth involves a similar event in which the left over part of the bitten chain is of length  $L$ .

The processes described by the third and fourth terms are shown in figure 1.

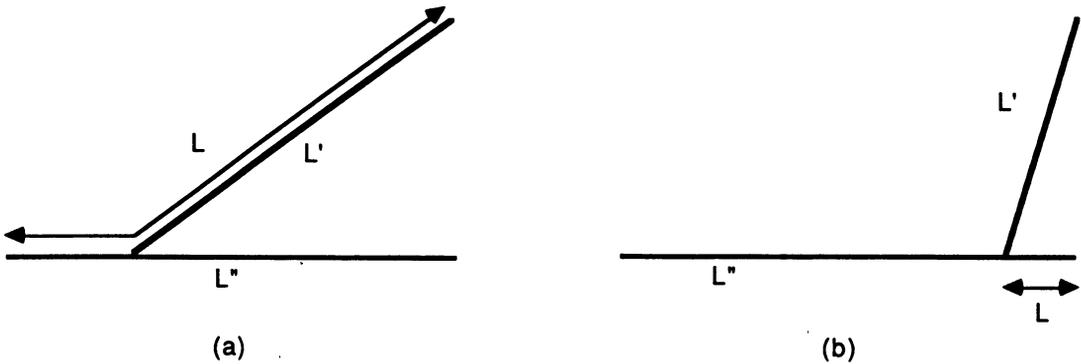


Fig. 1. — Diagrams representing the processes described by (a) the third and (b) the fourth terms in equation (18).

As before we choose units so that equation (2) applies. In this case, we can confirm at once that equation (18) has a steady state solution for *any*  $C(L)$  obeying equation (3). This is directly related to the fact that end-interchange reactions conserve chain number [25]. It implies that any thermodynamic perturbation, which takes the equilibrium distribution  $C_0(L)$  to a new distribution also of the form (3) (but with a different  $\bar{L}$ ), will not relax with time under end-interchange reactions alone. This is a remarkable result ; while it is expected that the conservation of chain number should lead to a zero mode of the time evolution equations, it is surprising that this mode should exactly correspond to the experimentally imposed perturbation in a T-jump.

Since, for the particular initial conditions corresponding to a T-jump, end interchange reactions lead to no time evolution whatever, it is clear that when end-interchange and reversible scission processes *both* are present, only the latter play a role in T-jump relaxation. This means that the single exponential relaxation with time constant  $\tau$  obeying equation (17) is retained even if end-interchange reactions are relatively fast. In this case one can enter a regime in which the T-jump relaxation is governed by reversible scission, whereas the breaking time of the average chain is controlled almost entirely by end-interchange. Thus, indiscriminate interpretation of T-jump data could lead to very misleading estimates of the breaking time (which is the quantity relevant to stress relaxation processes, at least according to the model of Ref. [19]).

Returning to the case where we consider only end-interchange kinetics we write, with  $C_0(L)$  defined as before and  $\Delta$  small,  $C(L, T) = C_0(L) + \Delta(L, t)$  and substitute into equation (18) to obtain an equation for the time evolution of  $\Delta$ . After taking the Laplace transform of this equation in  $\Delta$  we obtain a differential equation, similar to equation (6), which we can later solve for  $\varepsilon(\mu, t)$ . Specifically,

$$\dot{\varepsilon}(\mu, t) = k'' \alpha \frac{\partial}{\partial \mu} \varepsilon(\mu, t) - \frac{k''(2 \alpha^2 + \mu \alpha + \mu^2)}{\mu(\mu + \alpha)} \varepsilon(\mu, t) + \frac{k''(3 \alpha^2 \mu + 2 \alpha \mu^2 + 2 \alpha^3)}{\mu(\mu + \alpha)^2} \varepsilon(0, t). \quad (19)$$

Now for an arbitrary  $\Delta(L, 0)$  decompose as,

$$\Delta(L, 0) = \Delta_1(L) + \Delta_2(L, 0) \quad (20)$$

with

$$\Delta_1(L) = \eta(L - 2\bar{L}) e^{-\alpha L} \quad (21)$$

where we choose our value of  $\eta$  such that the following condition on  $\Delta_2$  is satisfied :

$$\int_0^\infty \Delta_2(L, 0) dL = 0. \quad (22)$$

In this way the decomposition of our initial perturbation is determined. The motivation for this decomposition is more easily understood once it is observed that  $\Delta_1$  is a zero mode of the equation for the time evolution of  $\Delta$ . This is because any  $C(L)$  of the form equation (3) is a solution of equation (18) with  $\dot{C}(L) = 0$  and a perturbation  $\Delta_1$  obeying equation (21) merely represents the transformation of  $C(L)$  from one exponential to another, each obeying equation (3) but with a slightly different mean chain length. The remainder  $\Delta_2$  is chosen so as to have zero excess chain number. By linearity, we see that time dependence of  $\Delta$  is then entirely in the second part since  $\Delta_1$  does not evolve in time :

$$\Delta(L, t) = \Delta_1(L) + \Delta_2(L, t) \quad (23)$$

and since the total number of excess chains is conserved, equation (22) continues to hold for all time :

$$\int_0^\infty \Delta_2(L, t) dL = 0. \quad (24)$$

Thus all of the time dependence of the problem is contained in the second part of the decomposition,  $\Delta_2$ . To calculate this, we first note that the Laplace transform of equation (24) gives us directly that  $\varepsilon_2(0, t) \equiv 0$ . By arguments that directly parallel those leading to equation (10), we then find the following equation for the evolution of  $\varepsilon_2(L, t)$  :

$$\varepsilon_2(\mu, t) = \varepsilon_2((\mu + \alpha k'' t), 0) e^{-k'' t} \left[ \frac{\mu(\mu + \alpha k'' t + \alpha)}{(\mu + \alpha)(\mu + \alpha k'' t)} \right]^2. \quad (25)$$

From this we may calculate a Greens function corresponding to the initial condition  $\Delta_{2,\ell}(L, 0) = \delta(L - \ell)$  :

$$\Delta_{2,\ell}(L, t) = e^{-k'' t} \frac{\alpha\beta}{(\alpha - \beta)^3} [-e^{-\beta\ell} \theta(L - \ell) \gamma(L - \ell)] + e^{-k'' t} e^{-\beta\ell} \delta(L - \ell) \quad (26)$$

where we have redefined  $\beta = \alpha k'' t$ . It should be noted that the initial condition of the Greens function, a delta function, does not have zero excess chain number and hence is not a legitimate choice for  $\Delta_2$ . However, the resulting Greens function is valid when used to compute  $\Delta_2(L, t)$  according to,

$$\Delta_2(L, t) = \int d\ell \Delta_2(\ell, 0) \Delta_{2,\ell}(L, t) \quad (27)$$

so long as the initial perturbation  $\Delta_2(L, 0)$  is correctly chosen to obey equation (24).

#### 4. Conclusions.

Within the framework of a simple model for reaction kinetics, two Greens functions have been derived for the separate reaction mechanisms of (a) reversible scission and (b) end-interchange. These allow calculation of the time evolution of any material-conserving small perturbation in the length distribution of reversibly breakable polymers. A special case is the initial perturbation corresponding to a shift in the mean chain length, as caused by a sudden jump in a thermodynamic variable such as temperature. For this case we predict single exponential decay of the entire perturbation with the characteristic time

$$\tau = \frac{1}{2k\bar{L}}$$

where  $k$  is the reaction rate (per unit length) for unimolecular scission. End-interchange reactions play no part in the relaxation after T-jump, since the perturbation in question is a zero mode of the linearized time evolution equations for end-interchange.

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