

Classification

Physics Abstracts

82.35 — 36.20 — 05 40

Short Communication

Nonlinear Thermodynamic Relaxation in Living Polymer Systems

C.M. Marques^(1,2) and M.E. Cates⁽¹⁾⁽¹⁾ Cavendish Laboratory Madingley Road, Cambridge CB3 0HE, U.K.⁽²⁾ Institut Charles Sadron, 6 rue Boussingault, 67083 Strasbourg Cedex, France*(Received 7 March 1991, accepted 21 March 1991)*

Abstract. — We present the complete (nonlinear) solution for the response of a system of living polymers to an arbitrary thermodynamic perturbation of its equilibrium polymer size distribution. Our results are relevant for the interpretation of T-jump experiments on wormlike micelles in the concentrated regime, where very large perturbations to the equilibrium size distribution can be easily obtained.

In a recent work Turner and Cates [1] analyzed the linear relaxation spectrum of the polymer length distribution of a system of “living” polymers [2]. These polymers can break and recombine reversibly; well studied examples arise in viscoelastic surfactants phases. According to simple theory, the polymers or micelles have an equilibrium exponential length distribution (in suitable units)

$$c_0(L) = \frac{\phi}{L_0^2} \exp \{-L/L_0\} \quad (1)$$

characterized by an average length L_0 which depend on the thermodynamic variables of the system such the temperature, the pressure and the volume fraction of monomers, ϕ . In a simple model [2] $L_0 \sim \phi^{1/2} \exp \{-E/(2kT)\}$ where E is the energy to create two end-caps. Under a sudden modification of one of the thermodynamic variables (most commonly, of the temperature) the distribution $c_0(L)$ relaxes to a new equilibrium exponential distribution $c(L)$, characterized by a new average length $\bar{L}$. The characteristic time and the functional form of the relaxation of the size distribution provides information about the microscopic factors which control the kinetics of the system.

The simplest description of living polymer kinetics assumes that a chain can only change mass either by breaking in two new shorter chains or by recombining with another to form a new larger chain. This scission-recombination scheme provides a integro-differential equation for the time

evolution of $c(t, L)$

$$\begin{aligned} \dot{c}(t, L) = & -kLc(t, L) + 2k \int_L^\infty c(t, L') dL' + \\ & + k'/2 \int_0^L c(t, L') c(t, L - L') dL' - k'c(t, L) \int_0^\infty c(t, L') dL' \end{aligned} \quad (2)$$

where k and k' are respectively the scission and recombination rate constants. At equilibrium these two parameters are not independent since the principle of detailed balance imposes a constraint on their ratio. This can easily be checked by noting that the distribution (1) is indeed the stationary solution of the evolution equation (2), only under the condition $\phi \frac{k'}{2k} = L_0^2$.

If an instantaneous perturbation (a step-change in the thermodynamic conditions) is imposed on the system, the rate constants k and k' assume new equilibrium values which obey

$$\phi \frac{k'}{2k} = \bar{L}^2 \quad (3)$$

where ϕ is the volume fraction after the perturbation and $\bar{L}$ is the new equilibrium length. Assuming the modification is such that the final average length $\bar{L}$ only differs slightly from the initial average length L_0 ($\bar{L} - L_0 \ll L_0$), Turner and Cates [1] showed that $c(t, L)$ remains exponentially distributed with an average length which relaxes exponentially in time:

$$\bar{L}(t) = \bar{L} + (L_0 - \bar{L}) \exp \{-t/\tau\} \quad (4)$$

where τ is given by

$$\tau = \frac{1}{2k\bar{L}} \quad (5)$$

As expected, the relaxation time of the average length gives a measure of the microscopic breaking rate k , if an independent measure of the average length is available. The single exponential dependence, equation (4) has been well confirmed experimentally [3] by monitoring the time evolution of a light-scattering signal which probes the average length of the polymer size distribution [3,4].

It is however of experimental interest (and in fact easier from the point of view of monitoring the relaxation) to provoke rather large changes in the average length distribution. For example one can perform a large amplitude T-jump experiment on viscoelastic micellar solutions in the concentrated regime [3,5]. The challenge, from a theoretical point of view, is then to describe the complete nonlinear response of the size distribution of living polymers to an arbitrary large jump in thermodynamic parameters.

In the present work we show that $c(t, L)$ remains exponentially distributed for any amplitude of a sudden variation of the thermodynamic parameters and that this gives rise to an interesting and unusual time evolution of the average chain length. More generally, we also show that $c(t, L)$ remains exponentially distributed for any perturbation which conserves the total volume fraction of monomers (for instance, a temperature modification having an arbitrary time-dependence).

Our central observation, in considering nonlinear perturbations, is that the function

$$c(L) = \phi f^2(t) \exp \{-Lf(t)\} \quad (6)$$

is a non-linear eigenfunction of equation (2) with a (time-indexed) eigenvalue $f(t)$ that obeys

$$\frac{df}{dt} = k \left[1 - \frac{\phi k'}{2k} f^2(t) \right] \quad (7)$$

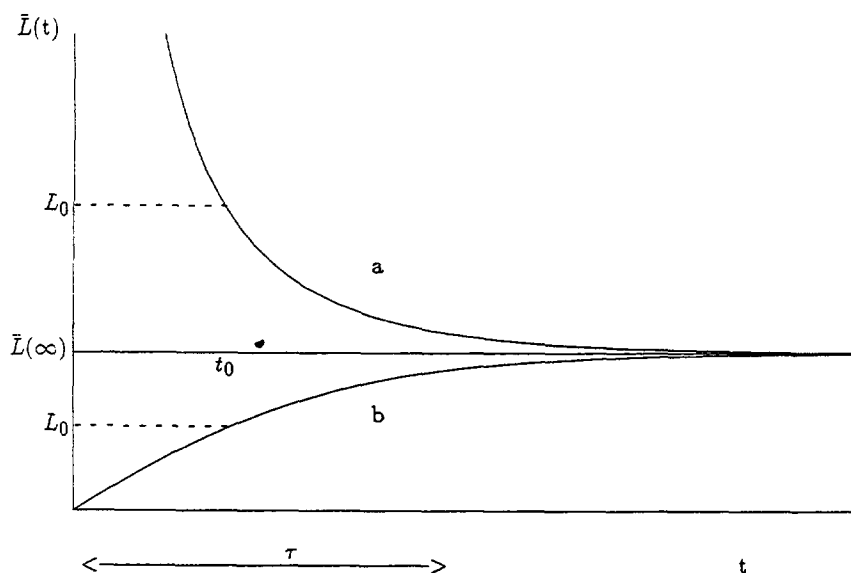


Fig. 1. — Time evolution of the average length for a living polymer system under a temperature, pressure or concentration jump. a) The initial average length L_0 is larger than final average length $\bar{L}$, b) the reverse case where $L_0 < \bar{L}$. Each experimental jump amplitude corresponds in this diagram to a particular initial time t_0 . It is also clear from the picture that for amplitudes such that $t_0 > 2\tau$ only the exponential tail of the decay curve is accessible to the experiment.

This may be checked by direct substitution.

In particular, the time evolution of $c(t, L)$ for a thermodynamic jump will be the solution of (7) with the initial condition $f(t = 0) = 1/L_0$. Making use of (3,5) we get

$$\begin{cases} f(t) = \bar{L}^{-1} \tanh \left[\frac{t + t_0}{2\tau} \right] & \text{if } L_0 > \bar{L} \\ f(t) = \bar{L}^{-1} \coth \left[\frac{t + t_0}{2\tau} \right] & \text{if } L_0 < \bar{L} \end{cases} \quad (8)$$

where the constant t_0 is given by

$$\begin{cases} t_0 = 2\tau \tanh^{-1} [\bar{L}/L_0] & \text{if } L_0 > \bar{L} \\ t_0 = 2\tau \coth^{-1} [\bar{L}/L_0] & \text{if } L_0 < \bar{L} \end{cases} \quad (9)$$

These equations fully describe the recovery following a sudden change in temperature, pressure or volume fraction. We see that the response at intermediate times $t_0 \ll t \ll 2\tau$ to a large jump does not follow an exponential decay in time. Instead the average chain length decays (or grows) like a power law in time:

$$\begin{cases} f(t) \sim \frac{t}{2\tau} & \text{for } L_0 > \bar{L} \\ f(t) \sim \frac{2\tau}{t} & \text{for } L_0 < \bar{L} \end{cases} \quad (10)$$

At long times ($t > \tau$) one recovers the exponential decay of equation (4) obtained in the linear response approximation. Likewise one can check directly from equations (8,9) that, when the imposed perturbation is small (large t_0), the decay is exponential over all timescales (see Fig. 1).

We would like to note as well that for thermodynamic perturbations of a more complicated time-dependent form the differential equation (7) still holds provided the volume fraction of monomers is constant in time. Under these conditions $c(t, L)$ remains exponentially distributed with a time dependent average length $L(t) = 1/f(t)$. To calculate this in the general case from equation (7) one would require a microscopic model for the dependence of the breaking and recombination rate constants k, k' on thermodynamic conditions. The detailed balance condition (3) relates the ratio of these to the thermodynamic parameters through the equilibrium average length but to find the response to a general perturbation the two are required separately. For the simplest case of a step-function change, the rate constant k, k' are time independent and so this complication doesn't arise.

We stress finally that these results are well adapted to probe the time relaxation of living polymers in concentrated solutions of surfactant micelles [3]. In the concentrated regime the light-scattering intensity varies very little with the temperature; its time evolution can thus in principle be monitored more easily when a large temperature jump is applied to the system. At any instant we expect the scattered signal to be related to the time-dependent average length by

$$\frac{1}{I(t)} = A + \frac{B}{\bar{L}(t)} \quad (11)$$

where the second term can be thought of as a correction arising from chain-end effects (or alternatively the translational entropy of mixing of chains). We expect then our nonlinear relaxation analysis, which predicts $\bar{L}(t)$, to be useful under these conditions. It is important to remark that the result (11) is fundamentally different from the dilute regime where A vanishes and hence $I(t) \sim \phi \bar{L}(t)$ [3,6].

Acknowledgements.

We thank S.J. Candau and M. Turner for very helpful comments. Financial support from the British French joint research program Alliance is gratefully acknowledged. This work was funded in part by EEC grant No SC1 0288 - C.

References

- [1] TURNER M.S., CATES M.E., *J. Phys. France* **51** (1990) 307.
- [2] CATES M.E., CANDAU S.J., *J. Phys. Cond. Matter* **2** (1990) 6869.
- [3] CANDAU S.J., MERIKHI F., WATON G., LEMARECHAL P., *J. Phys. France* **51** (1990) 977.
- [4] CATES M.E., MARQUES C.M., BOUCHAUD J.-P., submitted to *J. Chem. Phys.*
- [5] HOFFMANN H., LÖBL H., REHAGE H., WUNDERLICH I., *Tenside Detergents* **22** (1985) 290.
- [6] des CLOIZEAUX J., JANNINK G., *Les Polymères en Solution*, Les éditions de Physique, Les Ulis (1987).