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Entangled Polymeric Liquids: Nonstandard Statistical Thermodynamics of a Subchain between Entanglement Points and a New Calculation of the Strain Measure Tensor

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ABSTRACT: In entangled polymeric liquids, a subchain between two entanglements is an open system, which can exchange Kuhn segments with its neighboring subchains along the given polymer. A subchain is also a small, nonmacroscopic system, in a thermodynamic sense, because the number of segments belonging to it is small. Fluctuations are not negligible, then, and must be properly accounted for. Here, it is demonstrated that the adoption of nonstandard (small system) statistical thermodynamics for the description of the subchain behavior leads to significant corrections to classical Doi−Edwards formulas. The strain measure tensor for step deformations is recalculated in the nonstandard approach and shown to be in excellent agreement with available step shear data.

1. Introduction

There is no doubt that our current understanding of the flow behavior of concentrated polymeric liquids, and of their rheological constitutive equation, rests upon the physical picture and the concepts originally laid down by deGennes, Doi, and Edwards in the 1970s.[1−5] For the simplest polymeric system, namely a monodisperse system made up of linear flexible polymers, these authors argued that "transverse" motions of any given chain are in fact impeded, because of the uncrossability constraints due to the other chains; hence, "longitudinal" motions (reptation) do prevail. The actual multichain dynamics of these systems can thus be effectively described through one-chain models, where at any time a Brownian chain lives in a 1D cage representing the constraints (entanglements). Borrowing from classical formulas from rubber physics, then, with the force along a (primitive) chain coming from entropic elasticity, a complete constitutive equation for the stress tensor can be derived, which is a major accomplishment in the statistical mechanics of polymers.[6] Among the many successes of the theory, the parameter-free calculations for the strain-dependent response to step-strain deformations deserve to be mentioned, giving a shear damping function quite close to the data.

The basic theory of polymer dynamics has been much extended in later years, demonstrating how deep and fruitful was the original insight. Modes of entangled motion beyond pure reptation can now be efficiently described. We refer here to chain length fluctuations, at equilibrium[7] and in the linear range,[8] chain stretch and retraction in fast and/or fastly varying flows,[9,10] and constraint release and renewal (CRR), both of reptative and convective origin,[11−15] at the level of cooperative motions. Theoretical predictions and experiments have progressively become closer, of course. Essentially quantitative predictions are available for linear viscoelastic properties, e.g., for the 3.4 power law for the M dependence (at finite molecular weigths) of zero-shear viscosity, or for the curves of the G' and G'' moduli vs oscillation frequency. In the nonlinear range, qualitative and semiquantitative agreement with experiments is now achieved in most situations. By way of example, the well-known overly severe shear thinning of viscosity calculated from Doi−Edwards theory, and seemingly not shown by the data, has been recently amended by introducing the convective CRR mechanism cited above into the descriptions of high rate dynamics. To be fair, it must be noted here that most improvements over the original Doi−Edwards theory in the nonlinear range are obtained at the expense of the introduction of at least one additional parameter (besides the characteristic "cage dimension" r_0), measuring CRR efficiency.[12−15] New parameters appear to be required, really, in view of the cooperative nature of CRR, as compared to the one-chain nature of these dynamical models. Be it as it may, a widespread consensus has nowadays been gained that this kind of models correctly portrays the physics of polymer dynamics and that the remaining discrepancies between predictions and experiments can be decreased by further refinements and extensions of the theory.

Going back to the foundational level, a topic that has been consistently overlooked so far, despite its potential relevance, is that of *finite size effects at the subchain scale length r*. In fact, finite size effects were repeatedly studied in past years, but always with regard to the finite length L_0 of the whole chain: we mentioned before how chain length fluctuations were very soon added to the basic Doi−Edwards theory. Conversely, and somewhat paradoxically, no detailed theoretical investigations on this subject have been performed at the very characteristic length of entangled polymeric systems, namely, the span r of a subchain connecting two consecutive entanglements along a given primitive chain. This situation is incongruous, in the author's opinion, for the following reason. It is extensively reported in the literature that, in polymer melts at equilibrium, the characteristic length is $r_0 \approx 1-10$ nm, depending on the detailed chemistry.[16] Accordingly, the (average) number n_0 of Kuhn segments in a subchain is estimated as $n_0 \approx 10-100$. Thus, a subchain in a melt is a "small", nonmacroscopic system, with a rather small number of "particles" (the Kuhn segments). An

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analogous conclusion can be reached for a subchain in polymeric solutions.[17] The *thermodynamic limit*[18] is not expected to hold for such small systems, and deviations from standard statistical mechanics and thermodynamics can certainly be anticipated. By necessity, a special theoretical treatment is then required for a subchain in entangled polymeric liquids. Indeed, this is the motivation of the present paper.

In general terms, statistical mechanics is not restricted to macroscopic systems, and examples of (even elderly) calculations for finite systems are commonplace. On the other hand, a corresponding small system thermodynamics framework has long been lacking. The foundations of the thermodynamics of small systems were actually given in the 1960s by Hill in a now classic book.[19] Since then, experiments and theory have gradually progressed, with an outburst of activity quite recently, linked to the rapidly growing interest in "nano"-scale phenomena.[20] Applications to the behavior of a subchain in entangled polymeric liquids have not yet been proposed, however, as far as the author is aware. In tackling just this problem in the present paper, and apart from dealing with conceptual issues, we will also present detailed calculations for a specific rheological example, namely, the step-strain deformation. It will be shown that finite size effects at the subchain length scale have considerable consequences on the macroscopic material's response, modifying the original strain measure tensor by Doi and Edwards. We here anticipate that virtually absolute agreement with available data is obtained for the newly calculated shear damping function, for both melts and solutions.

Before ending the Introduction, it seems worth signaling to the reader the two modeling postulations that we adopted in this paper. First, only the so-called "slip-link" one-chain model is dealt with here, to describe the constraints over a given chain. In the slip-link model,[3] small rings are placed at discrete points along the chain, and in fact, they represent the only (topological) interaction among chains. The slip-link model is the geometrically simplest existing one-chain model, with the single characteristic length r_0. In the other most popular representation of constraints, the so-called "tube" model, two characteristic lengths are perforce required, i.e., in the longitudinal and the transverse directions of the primitive chain. A tube radius dynamics is then also needed, which is matter of debate since Doi and Edwards original papers. Second, we choose to avoid considering all modes of entangled motion other than "pure" reptation: in particular, CRR is here neglected. This choice, if perhaps somehow unrealistic, again corresponds to the option of maximum simplicity and brings back to the spirit of the earliest Doi–Edwards theory.[2–5] We would also like to emphasize that, in any event, the description of CRR dynamics is still a "work in progress", so to speak. Concerning the present paper, inclusion of CRR would certainly cause some difficulties in the evaluation of the free energy, as we will explain later. We presently prefer to discuss the new "small system" topic in the more familiar frame of the original theory.

The paper is organized as follows. In section 2, we revisit Doi–Edwards statistical thermodynamics, which is then extended to account for the "smallness" of the subchains in section 3. The *inner equilibrium assumption* on which pure reptative theories are based is also explicitly discussed in these sections. In the three following sections, the consequences of the new approach are examined. Specifically, the new damping function for step-strain deformations is calculated in section 5 for melts, and in section 6 for solutions, and compared to shear step data available in the literature. A short section with a few additional comments closes the paper.

2. Doi–Edwards Thermodynamics Revisited

In the Doi–Edwards slip-link model for entangled polymer melts[3], it is assumed that slip-links per se do not undergo any Brownian motion, and move affinely with the macroscopic deformation. Also, the interactions between different subchains are neglected, except at the slip-links. Of course, the system cannot consist of independent, *strictly* noninteracting subchains, because no equilibration would ever be attained in such a case. Rather, it is implied that "weak" interactions only occur, so as to allow for energy and mass exchanges (see below) up to an *inner equilibrium*. Under these assumptions, a free energy can be attributed to each subchain, which only depends on the generalized coordinates of the subchain itself. Then, for a Gaussian subchain of span r between two non-Brownian slip-links, and by adopting classical formulas of rubber elasticity, we write

$$a = \frac{3k_BT}{2l^2}\frac{r^2}{n} \tag{1}$$

$$f = \frac{\partial a}{\partial r} = \frac{3k_BT}{l^2}\frac{r}{n} \tag{2}$$

for the local (i.e., along the chain) free energy and intrachain tension, respectively. In eqs 1, 2, k_BT is the Boltzmann constant times temperature, l is the Kuhn segment length, and n is the number of Kuhn segments in the subchain. Notice that, in eqs 1 and 2, the subchain is depicted as a standard thermodynamic system, which in the thermodynamic limit $n,r \to \infty$, with n/r = const, properly gives an extensive free energy $a \propto (r^2/n^2)n$, and an intensive force f.

Since mass exchanges through slip-links can occur along a chain, the number n of Kuhn segments in a subchain is not fixed. In their theory, Doi and Edwards simply assumed that a constant linear density of Kuhn segments is maintained along any chain "i" (for example), equal to its equilibrium value:

$$\begin{cases} \dfrac{n_\alpha^{(i)}}{r_\alpha^{(i)}} = \dfrac{n_\beta^{(i)}}{r_\beta^{(i)}} \\ \dfrac{n_\alpha^{(i)}}{r_\alpha^{(i)}} = \dfrac{n_0}{r_0} = \dfrac{\sqrt{n_0}}{l} \end{cases} \tag{3}$$

(The rightmost equality in the second part of eq 3 comes from the well-known relationship $r_0 = \sqrt{n_0}l$.) It should be pointed out that the condition expressed by the second of eq 3 was in fact a calculated result in the original papers, for the peculiar case of an infinitely long chain partially "trapped" in a long straight tube (i.e., with $r_\alpha \gg r_0$). However, it was not proven at that time that linear density constancy also holds for ordinary entangled chains, as Doi and Edwards explicitly acknowledged.[3] It has also to be stressed that eq 3 is not valid at any time during the dynamics of the entangled polymeric liquid. Indeed, for eq 3 to be valid, inner equilibration must have already occurred, so that all mass fluxes have ceased, within a certain characteristic time τ_{eq}. Doi–Edwards original dynamics is then concerned only with "slow" motions, i.e., "(any) motion whose characteristic time scale is much longer than τ_{eq}" (quoted from ref 5).

By inserting eq 3 into eq 2, the celebrated formula is obtained:

$$f_\alpha^{(i)} = \frac{3k_BT}{\sqrt{n_0}l} = f_0 \tag{4}$$

This gives a constant tension along any chain, equal to its equilibrium value f_0. Thus, in the slip-link system, the intramolecular force is assumed to be always relaxed, even if the conformation of the primitive chain is in a nonequilibrium state. Notice in this regard that, again from eq 3, also the arc length L of the primitive chain always stays at its equilibrium value, L_0. Indeed, by calling Z and Z_0 the actual and the equilibrium number of subchains in a chain, respectively, it is

$$L^{(i)} \equiv \sum_\alpha^{Z^{(i)}} r_\alpha^{(i)} = \frac{r_0}{n_0}\sum_\alpha^{Z^{(i)}} n_\alpha^{(i)} = r_0Z_0 \equiv L_0 \tag{5}$$

(The obvious relationship $\sum_\alpha^{Z^{(i)}} n_\alpha^{(i)} = n_0Z_0$ has been used.) There is no length stretch in the caged chain, because the external deformation does not build up any "extra" tension (see eq 4). The conditions expressed by eqs 3 and 4 are equivalent, of course, and in fact they are used interchangeably by Doi and Edwards. From eqs 4 and 5, however, one can at once identify the inner equilibration time τ_{eq} introduced above with the retraction time of the polymer chain, i.e., the Rouse time τ_R.

We now proceed to restate Doi–Edwards assumption of inner equilibrium in a still different form. To this purpose, let us write down the fundamental thermodynamic equation (at constant temperature) of a subchain:

$$\mathrm{d}a = f\,\mathrm{d}r - \mu\,\mathrm{d}n \tag{6}$$

Indeed, the subchain is an open system, which can exchange Kuhn segments with its neighboring subchains along the given polymer, and this exchange is ruled by a chemical potential μ. It is

$$\mu = -\frac{\partial a}{\partial n} = \frac{3k_BT}{2l^2}\frac{r^2}{n^2} \tag{7}$$

By comparing eqs 3 and 7, we obtain

$$\begin{cases} \mu_\alpha^{(i)} = \mu_\beta^{(i)} \\ \mu_\alpha^{(i)} = \mu_0 = \dfrac{3k_BT}{2n_0} \end{cases} \tag{8}$$

The first part of eq 8 has a clear physical meaning. At inner equilibrium, mass exchanges among subchains have come to an end. As is well-known, the requirement that mass fluxes be nil corresponds to the general thermodynamic requirement that the chemical potential is constant: in our case, the chemical potential has to be constant throughout the polymer chain, i.e., $\mu_\alpha^{(i)} = \mu_\beta^{(i)}$.[21] We think that the (first) condition of inner equilibrium is better stated in this latter form than by imposing a constant linear density (i.e., $n_\alpha^{(i)}/r_\alpha^{(i)} = n_\beta^{(i)}/r_\beta^{(i)}$, eq 3) or a constant intrachain tension (i.e., $f_\alpha^{(i)} = f_\beta^{(i)}$, eq 4), although these three conditions are mathematically equivalent from the standpoint of Doi–Edwards theory. Later in this paper, it will be shown that these conditions are in fact no more equivalent when the subchain is appropriately considered as a small thermodynamic system.

Finally, it is instructive to shortly discuss the calculation of the total free energy density of the entangled polymeric liquid. The free energy $A^{(i)}$ of a chain "i" is first calculated as

$$A^{(i)} \equiv \sum_\alpha^{Z^{(i)}} \frac{3k_BT}{2l^2}\frac{r_\alpha^{(i)2}}{n_\alpha^{(i)}} = \frac{3k_BT}{2l^2}\frac{{r_0}^2}{{n_0}^2}\sum_\alpha^{Z^{(i)}} n_\alpha^{(i)} = \frac{3k_BT}{2}Z_0 \tag{9}$$

where the condition $r_\alpha^{(i)}/n_\alpha^{(i)} = r_0/n_0$ (from eq 3) has been used. It is seen from eq 9 that the free energy of any chain stays at its equilibrium value, whatever the actual chain conformation, provided that inner equilibration has been attained. The actual total free energy density A is then simply obtained by multiplying $A^{(i)}$ times the number C_0 of primitive chains per unit volume:

$$A = C_0Z_0\frac{3k_BT}{2} \tag{10}$$

Since C_0Z_0 is the equilibrium number of subchains per unit volume, and $3k_BT/2$ can be regarded as the energy of a noninteracting subchain (associated with the subchain center-of-mass degrees of freedom), eq 10 actually gives the total free energy of the entangled melt just as that of an ideal gas of subchains. It seems also worth emphasizing explicitly that the actual free energy of the system, if inner equilibrium holds, is always equal to its equilibrium value A_0, which is a profound and often overlooked outcome of classical Doi–Edwards theory.[6] In fact, in their theory, this result is a direct consequence of two assumptions: (i) the non-Brownian nature of the slip-links, which leads to eq 1, and (ii) the absence of any chain stretch (which keeps the length of the primitive chain at L_0, eq 5).

By using the definition of the chemical potential given in eq 7, the total free energy density of the entangled liquid can readily be calculated as

$$A = C_0Z_0n_0\mu \tag{11}$$

under the single assumption $\mu_\alpha^{(i)} = \mu_\beta^{(j)} \equiv \mu$ (which is less restrictive than the assumption of eq 8). Then, from eq 11, eq 8 is rewritten as

$$\begin{cases} \mu_\alpha^{(i)} = \mu_\beta^{(j)} \\ A = A_0 \end{cases} \tag{12}$$

We believe that eq 12 is the most transparent form for the inner equilibrium conditions of Doi–Edwards thermodynamics. In words, the chemical potential per Kuhn segment must be the same everywhere (i.e., in all chains), and the total free energy must stay at its equilibrium value. Equation 12 will be our only assumption in the rest of this paper.

3. Nonstandard Statistical Thermodynamics of a Subchain and the Inner Equilibrium Assumption

In statistical thermodynamics, the "appropriate" ensemble to be used to study the subchain behavior is the grand canonical ensemble, because the subchain is an open system. The grand canonical partition function Ξ of a Gaussian subchain in a chemical potential μ is given by

$$\Xi(r,\mu,T) = \int_0^\infty \mathrm{d}n \, \exp\left(-\frac{\mu n}{k_B T}\right) Z_n^{(G)}(r,T) \tag{13}$$

where $Z_n^{(G)}$ is the classical Gaussian partition function at a fixed n:

$$Z_n^{(G)}(r,T) = \Omega^n(T)\frac{1}{n^{3/2}} \exp\left(-\frac{3}{2l^2}\frac{r^2}{n}\right) \tag{14}$$

Notice that, in eq 14, the n dependence of the preexponential factor is accurately given, as it is needed to perform the integration of eq 13. (Ω in the preexponential factor is a quantity dependent on T only;[22] its explicit expression is not required in the following.) The grand canonical partition function of eq 13 is simply a weighted sum of partition functions over all the possible populations n of the given subchain, with an exponentially decreasing weight function parametrically controlled by the chemical potential. For the sake of precision, the upper limit of integration in eq 13 should be the degree of polymerization $Z_0 n_0$ of the chain molecule, rather than infinity, but the just noted approximation has only very minor effects. On the other hand, analytic integration of eq 13 (plus eq 14) is straightforward, giving[23,24]

$$\Xi(r,\mu,T) = \frac{l}{r} \exp\left(-\sqrt{6}\sqrt{\frac{\mu + \omega(T)}{k_B T}}\frac{r}{l}\right) \tag{15}$$

with $\omega(T) \equiv -k_B T \ln(\Omega(T))$. The latter equation for Ξ, eq 15, will then be used in the following.

For the grand canonical ensemble, and under isothermal conditions, the equation linking the characteristic function Ξ with the appropriate thermodynamic quantities, i.e., the so-called fundamental statistical-thermodynamical equation, is

$$\mathrm{d}(-k_B T \ln \Xi) = \bar{f}\,\mathrm{d}r + \bar{n}\,\mathrm{d}\mu \tag{16}$$

The overbar symbol in eq 16 is meant to indicate that the particle number $\bar{n}$ and the force $\bar{f}$ are both average values, to be calculated over all possible populations of the given subchain. Notice that, at the level of generality of eq 16, nothing is stated concerning the dependency of $\bar{n}$ and $\bar{f}$ on the characteristic variables (r,μ,T) of the grand canonical ensemble. Still, in eq 16, we emphasize that it holds true both in standard and nonstandard statistical thermodynamics, i.e., either in the thermodynamic limit or not.[19] This is crucial, since we are just going to utilize that equation for a nonstandard case. From eqs 15 and 16, we get[23,24]

$$\bar{n} = -\frac{\partial k_B T \ln \Xi}{\partial \mu} = \frac{r}{l}\sqrt{\frac{3k_B T}{2(\mu + \omega(T))}} \tag{17}$$

$$\bar{f} = -\frac{\partial k_B T \ln \Xi}{\partial r} = \frac{k_B T}{l}\left(\frac{l}{r} + 3\sqrt{\frac{2(\mu + \omega(T))}{3k_B T}}\right) \tag{18}$$

With eq 17, it is seen that the grand canonical formalism naturally gives a constant linear density $\bar{n}/r$ of Kuhn segments along any chain, as in Doi–Edwards theory, provided that the chemical potential is constant (i.e., provided that the first part of eq 12 holds). At variance with Doi–Edwards theory, however, the tension $\bar{f}$ along a chain is not constant, as it depends on the span r of the subchain under observation. In other words, the intrachain force of eq 18 is not an intensive quantity (compare with eq 2). The latter feature is an immediate consequence of the fact that the subchain is a small open system, as highlighted in the Introduction; hence, effects of the fluctuations in the Kuhn segments' number are directly observable. In fact, a constant tension in the caged chain is only recovered from eq 18 in the thermodynamic limit, where $r \to \infty$. Out of this limit, we find that the inner equilibrium conditions $f_\alpha^{(i)} = f_\beta^{(j)}$ and $\mu_\alpha^{(i)} = \mu_\beta^{(j)}$, discussed at some length in the previous section, are not equivalent. We maintain the condition $\mu_\alpha^{(i)} = \mu_\beta^{(j)} \equiv \mu$ on the chemical potential as our assumption.

To entirely detail the assumption of inner equilibration, as dictated by eq 12, the explicit expression of the total free energy density A is now required. However, since each individual system of the ensemble (i.e., each subchain) is in our case a small system, where the conventional identifications of "extensive" and "intensive" properties should be abandoned, writing the total free energy A as a sum of individual free energies requires some care. The correct procedure to be followed was devised by Hill,[19] and is here simply adapted for the subchains' system of our interest. The final formula for A in whatever actual configuration (of chemical potential μ and temperature T) of the entangled polymeric liquid is

$$A = -C_0 Z_0 n_0\left(\sqrt{\frac{2(\mu + \omega(T))}{3k_B T}}\frac{l}{\langle r\rangle}\langle k_B T \ln \Xi\rangle + \mu\right) \tag{19}$$

where the symbol $\langle\ldots\rangle$ indicates an average over all the subchains. By inserting eq 15 for the grand partition function Ξ into eq 19 and by adding $C_0 Z_0 n_0 \omega(T)$ (this will prove convenient later), with some manipulation, we then get

$$A = k_B T C_0 Z_0 n_0\left(\sqrt{\frac{2(\mu + \omega(T))}{3k_B T}}\frac{l}{\langle r\rangle}\left\langle \ln\frac{r}{l}\right\rangle + \frac{\mu + \omega(T)}{k_B T}\right) \tag{20}$$

(The latter equation gives a free energy differing from that of eq 19 only for a constant, in isothermal conditions. The same symbol A is used in the two equations.) Equation 20 for the total free energy density is the key result of the present paper. It is immediately seen that, by neglecting the first term in eq 20, eq 11 is recovered, save for the $C_0 Z_0 n_0 \omega(T)$ constant, only depending on temperature. Thus, the first term in bracket in eq 20 is a *new* free energy contribution, due in fact to the nonnegiglible fluctuations in the Kuhn segments' number occurring in the individual subchains. Further, notice that a nondimensional generalized chemical potential $\hat{\mu} \equiv 2(\mu + \omega(T))/3k_B T$ naturally appears in the free energy A and, under isothermal conditions, becomes the effective independent variable in the grand canonical scheme. Specifically, the condition $\mu_\alpha^{(i)} = \mu_\beta^{(j)} \equiv \mu$ now becomes $\hat{\mu}_\alpha^{(i)} = \hat{\mu}_\beta^{(j)} \equiv \hat{\mu}$. Third, and the most important, eq 20 together with eq 12 leads to the following inference:

$$\begin{cases} \hat{\mu}_\alpha^{(i)} = \hat{\mu}_\beta^{(j)} \equiv \hat{\mu} \\ A = A_0 \end{cases} \Rightarrow \hat{\mu} = \mathscr{F}(\text{deformation history}) \qquad (21)$$

Indeed, since the averages $\langle ... \rangle$ in eq 20 depend on the imposed deformation history, and A must stay at its equilibrium value A_0 by the inner equilibration hypothesis, the chemical potential $\hat{\mu}$ is bound to vary, and is in general a *functional* $\mathscr{F}$ over the past deformations.

We emphasize that the result expressed by eq 21 comes solely from finite size effects at the subchain level. In the absence of the first term in the free energy expression, eq 20, inner equilibration would imply $\hat{\mu} = \hat{\mu}_0$, i.e., Doi–Edwards original result. On the other hand, under the same assumption of Doi–Edwards theory, eq 12, but properly accounting for the "smallness" of n_0, the unescapable conclusion is reached that the chemical potential $\hat{\mu}$ depends on the actual configuration of the polymeric liquid. This new result represents the crucial advancement with respect to our previous work on the same subject.[23,24] In the rest of the present paper, we will investigate the consequences of this result.

4. Effects of Step Deformations

When dealing with eqs 20 and 21, it is convenient to introduce the nondimensional subchain span $x = r/r_0$ and chemical potential $y = \hat{\mu}/\hat{\mu}_0$, that is, variables normalized in terms of the full equilibrium values r_0 and $\hat{\mu}_0$, respectively. Therefore, the inner equilibrium condition $A = A_0$ reduces to

$$y + \frac{2}{3}\frac{\langle \ln x \rangle + \ln\sqrt{n_0}}{\langle x \rangle}\sqrt{y} - \left(1 + \frac{2}{3}\ln\sqrt{n_0}\right) = 0 \qquad (22)$$

i.e., an algebraic quadratic equation (in $\sqrt{y}$), with "coefficients" depending on the deformation history (through the averages $\langle x \rangle$ and $\langle \ln x \rangle$), and, parametrically, on the full equilibrium number n_0 of Kuhn segments in a subchain. Notice that the logarithmic terms in eq 22 appear only because of the newly calculated "correction" for the free energy: the standard result would instead be $y=1$. In this regard, notice that the appearance of n_0 in eq 22 will lead to different nonequilibrium results for different polymeric melts, at variance with Doi and Edwards theory, which should apply universally. (See below for the case of polymeric solutions.) This point will be thoroughly illustrated in the following.

We proceed now to calculate the effects of the simplest conceivable imposed deformation history, namely, a step deformation. To this end, we will assume (as Doi and Edwards did) that "affinity" holds, i.e., that any subchain end-to-end vector joining two consecutive sliplinks is deformed by the macroscopic deformation gradient tensor $\mathbf{E}$. Thus, it is $r\mathbf{u} = \mathbf{E}\cdot r_0\mathbf{u}_0$, where $\mathbf{u} = \mathbf{E}\cdot\mathbf{u}_0/|\mathbf{E}\cdot\mathbf{u}_0|$ and $\mathbf{u}_0$ are unit vectors giving the actual and the original direction, respectively, of the given subchain, and $r = r_0|\mathbf{E}\cdot\mathbf{u}_0|$ (hence $x = |\mathbf{E}\cdot\mathbf{u}_0|$). At undistorted equilibrium, the $\mathbf{u}_0$ vectors are randomly distributed. Thus, the averages in eq 22 simply become angular integrations over the isotropic $\mathbf{u}_0$ distribution existing prior to deformation.

Let us consider the step shear case, with γ the imposed shear strain. The variation of the normalized chemical potential y with γ, as calculated from eq 22, is reported in Figure 1, for two "realistic" values of n_0 (10 and 100 for the lower and upper curve, respectively). Starting with a zero derivative, $y(\gamma;n_0)$ monotonically increases with the imposed strain, to level off at the asymptotic value $1 + (2\ \ln\sqrt{n_0})/3$. Then, significant deviations of y from unity are calculated at shear strains definitely accessible in experiments. As an example, for $\gamma = 3$, it is $y(n_0 = 10) = 1.13$ and $y(n_0 = 100) = 1.35$. Similar trends and comparable variations of y with strain are found in step elongational deformations (not reported). It remains to be shown, however, how the predicted variation in y will affect experimentally observable quantities.

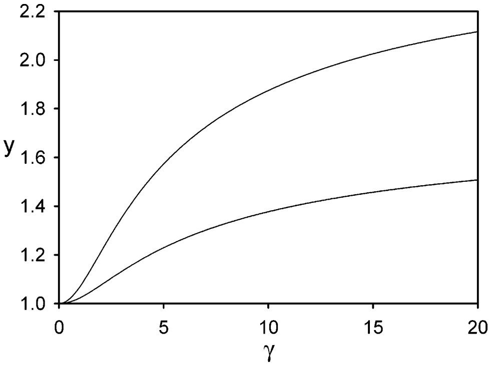

Figure 1. Nondimensional chemical potential as a function of strain in step shear deformation. Upper and lower curves refer to $n_0 = 100$ and 10, respectively.

It is of interest to look again at the arc length $L^{(i)}$ of a primitive chain. Using eq 17, and the relationship $r_0 = \sqrt{n_0}l$, we readily calculate

$$L^{(i)} \equiv \sum_{\alpha}^{Z^{(i)}} r_\alpha^{(i)} = l\sqrt{\hat{\mu}}\sum_{\alpha}^{Z^{(i)}} \bar{n}_\alpha{}^{(i)} = l\sqrt{\hat{\mu}}Z_0 n_0 = Z_0 r_0\sqrt{n_0\hat{\mu}} \equiv L_0\sqrt{y} \qquad (23)$$

to be compared with eq 5 of the standard theory. It so appears from eq 23 that a primitive chain, at inner equilibrium after a step strain, is elongated with respect to its full equilibrium length L_0, in a manner depending on the actual configuration of the entire system. It seems appropriate to mention that an idea of "partial retraction" of a chain at τ_{eq}, depending on some measure of deformation of the system, has been systematically pursued in recent years by Wagner and co-workers,[25] who generalized an older idea by Marrucci,[26] in the context of "tube" models. Here, however, the lengthening of the chains is linked to fluctuation effects at the subchain level, rather than to assumptions on tube diameter variations.

Another quantity of interest at the primitive chain scale is the average number $[Z]$ of subchains per chain, i.e., the ensemble average of $Z^{(i)}$. (The symbol [...] is used to indicate the average of a *chain* quantity.) To evaluate $[Z]$, first note that, with N the total number of chains in the ensemble, it is

$$[Z] \equiv \frac{\sum_i Z^{(i)}}{N} = \frac{\sum_i Z^{(i)}}{N}\,\frac{NZ_0 n_0}{\sum_i \sum_{\alpha}^{Z^{(i)}} \bar{n}_\alpha^{(i)}} \equiv \frac{Z_0 n_0}{\langle \bar{n} \rangle} \qquad (24)$$

By using now the averaged version of eq 17 for $\langle \bar{n} \rangle$, and again the relationship $r_0 = \sqrt{n_0}l$, it is readily calculated that

$$[Z] = \frac{Z_0 n_0}{\langle \bar{n} \rangle} = \frac{Z_0 n_0 l}{\langle r \rangle}\sqrt{\hat{\mu}} = \frac{Z_0}{\langle x \rangle}\sqrt{y} \qquad (25)$$

With respect to the original Doi–Edwards theory, therefore, we find a less drastic decrease in $[Z]$ with increasing step deformation, because of the mitigating effect due to the contemporary increase of the chemical potential.

For the sake of clarity, we remind the reader that the just found physical effects, namely, the lengthening of the primitive chain and the deacrease of its average number of subchains, have been computed here for step-strain deformations, under the assumptions of affinity and of inner equilibration. Situations of continuous flows, possibly with nonaffine deformations occurring, are beyond the purpose of the present paper.

5. Strain Measure Tensor. Shear Damping Function

We are ready to calculate the macroscopic mechanical response of the polymeric liquid, i.e., its stress tensor, as determined through the above-discussed nonstandard statistical thermodynamics of the subchains. In ample generality, the (intrachain) stress tensor $\mathbf{T}$ of an entangled polymeric system is given by:[6]

$$\mathbf{T} = \zeta\langle \mathbf{fr} \rangle \qquad (26)$$

with $\mathbf{r}$ and $\mathbf{f}$ the vectorial span and force of the subchain, and ζ the *actual* numeral density of subchains. Under the inner equilibrium assumption, it is $\zeta = C_0[Z]$, and $\mathbf{f} = \bar{f}\mathbf{u}$ ($\mathbf{u}$ is the subchain current direction), with $[Z]$ and $\bar{f}$ from eqs 25 and 18, respectively. By substitution, we then obtain

$$\mathbf{T} = k_B T C_0 Z_0 n_0 \frac{l}{\langle r \rangle}\sqrt{\hat{\mu}}\left(\langle \mathbf{uu} \rangle + 3\sqrt{\hat{\mu}}\left\langle \frac{r}{l}\mathbf{uu} \right\rangle\right) \qquad (27)$$

or, in terms of the (x, y) variables introduced in the previous section

$$\mathbf{T} = k_B T \zeta_0 \frac{\sqrt{y}}{\langle x \rangle}(\langle \mathbf{uu} \rangle + 3\sqrt{y}\langle x\mathbf{uu} \rangle) \qquad (28)$$

($\zeta_0 = C_0 Z_0$ is the *equilibrium* numeral density of subchains.) Thus, the stress tensor consists of *two* additive contributions, one of them never considered until now (with only one exception, see refs 23 and 24), directly stemming from fluctuation effects at the subchain scale. The relative weight of these two contribution is ruled by the newly introduced function $y(x)$, given by eq 22, itself again generated by fluctuations. Incidentally, we mention here that eq 27 or eq 28 for the stress tensor can also be readily deduced by affine variation of the total free energy A (see eqs 19 and 20) and that for this stress tensor it has previously been shown that the stress optical rule holds.[24]

Consider now the step-strain case. As it is well-known, some time after a step deformation experiments invariably indicate the so-called time-strain separability, i.e., factorization of the stress in a deformation-dependent tensor times a time-dependent decay (a "memory function"). Time-strain separability is readily interpreted in caged-chain models, and for monodisperse systems, by imagining that the chain, soon after the deformation, rapidly "rearranges" in its new cage, to reptate out only at later times. In Doi–Edwards model, the fast process is taken to be a 1D Rouse-like relaxation, ending up at $\tilde{t} = \tau_R$, with a constant tension along the chain (see eq 4). In our interpretation, the fast rearrangement is identified with the attaining of "inner equilibrium", i.e., of a constant chemical potential along the chain, which is completed at $\tilde{t} = \tau_{eq}$. (Although $\tau_{eq} \approx \tau_R$ is certainly expected, the two characteristic times need not to coincide.) In both cases, the fast reorganization of the caged chain fully determines the tensorial response as $\mathbf{T}(\tilde{t})$. To explicitly calculate $\mathbf{T}(\tilde{t})$ from eq 28, observe that, under the assumption of "affinity" of the deformations, it is

$$\langle \mathbf{uu} \rangle = \left\langle \frac{\mathbf{E}\cdot\mathbf{u}_0\mathbf{E}\cdot\mathbf{u}_0}{|\mathbf{E}\cdot\mathbf{u}_0|^2} \right\rangle_0 \equiv \mathbf{Q}_{DE}^{(IAA)} \qquad (29)$$

$$\frac{1}{\langle x \rangle}\langle x\mathbf{uu} \rangle = \frac{1}{\langle |\mathbf{E}\cdot\mathbf{u}_0| \rangle_0}\left\langle \frac{\mathbf{E}\cdot\mathbf{u}_0\mathbf{E}\cdot\mathbf{u}_0}{|\mathbf{E}\cdot\mathbf{u}_0|} \right\rangle_0 \equiv \mathbf{Q}_{DE} \qquad (30)$$

where both tensors $\mathbf{Q}_{DE}^{(IAA)}$ and $\mathbf{Q}_{DE}$ had in fact previously been introduced by Doi and Edwards.[6] Hence, it is

$$\frac{\mathbf{T}(\tilde{t})}{k_B T \zeta_0} = \frac{\sqrt{y}}{\langle x \rangle}\mathbf{Q}_{DE}^{(IAA)} + 3y\mathbf{Q}_{DE} \equiv \mathbf{Q} \qquad (31)$$

The nondimensional tensor $\mathbf{Q}$ of eq 31 is the new strain measure tensor proposed here. Notice that, without the term containing $\mathbf{Q}_{DE}^{(IAA)}$ (which comes from fluctuations), and with $y = 1$, tensor $\mathbf{Q}$ reduces to the "rigorous" Doi–Edwards strain measure $3\mathbf{Q}_{DE}$. Notice also that, with $y = 1$, eq 31 would give the strain measure tensor deduced in refs 23 and 24. As discussed above, however, a strain dependent y is in fact dictated by the inner equilibrium condition, eq 12.

In step shear, let X be the shearing direction, and Y the direction normal to the shear planes. In the linear limit (small strain), we easily calculate $Q_{XY}(\gamma) = \gamma$. Thus, the shear elastic modulus turns out from eq 31 to be exactly equal to that of a (nonBrownian) rubber, i.e., $G = k_B T \zeta_0$, and different from the Doi–Edwards modulus $G_{DE} = 4k_B T \zeta_0/5$, as already discussed elsewhere.[23] We mention this result here just because the correct relationship between G and the (molar) entanglement molecular weight M_e, hence n_0, will be required below, to perform comparisons with experiments.

Going to the nonlinear material response, the so-called damping function $h(\gamma) \equiv Q_{XY}(\gamma)/Q_{XY}(\gamma \rightarrow 0)$ has to be considered. The most striking feature of the new $h(\gamma)$, as calculated from eq 31, is the dependence on n_0, which is a direct consequence of the inner equilibrium condition, eq 22 of the previous section. In fact, we have now a family of damping functions (parametric in n_0), rather than an universal damping function, as in Doi–Edwards theory. All of these new damping functions are found to be less strain thinning than $h_{DE}(\gamma)$, in agreement with the observations, thus significantly correcting the results reported in refs 23 and 24, based on the assumption $y = 1$. In Figure 2, two plots of $h(\gamma)$ are shown up to $\gamma = 20$, with $n_0 = 10$ and 100 for the lower and upper curve, respectively. Both curves are strain thinning, but they are also clearly distinct from each other. This differentiation should be experimentally observable on

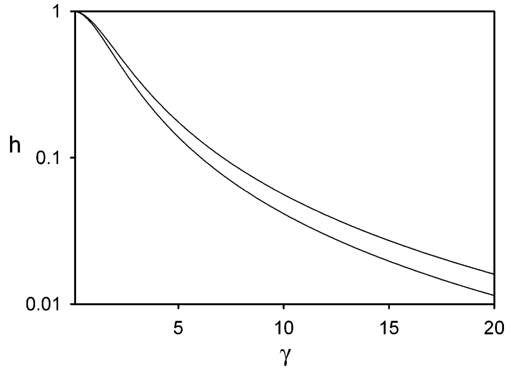

Figure 2. Shear damping functions. As in Figure 1, upper and lower curves refer to $n_0 = 100$ and 10, respectively.

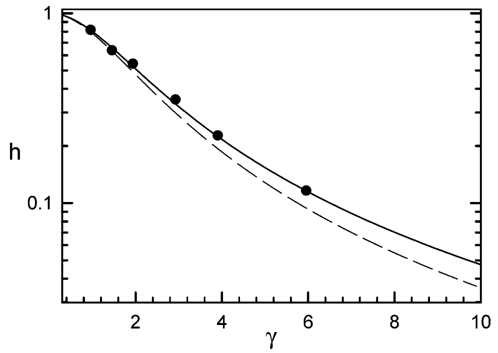

Figure 3. Calculated and experimental damping functions. Data on polystyrene melt from Urakawa et al.[27] Dashed curve is from Doi–Edwards theory. The continuous line is the new damping function, with $n_0 = 23$, as required for polystyrene.

properly chosen polymer melts, by measurements at large strains.

As a matter of fact, however, such data are not available in the literature (see e.g., ref 27), either because the melts investigated are rather polydisperse or because the maximum imposed shear strain is relatively low. We have been able to find out only one data set with the appropriate requisites, for a polystyrene melt studied by Urakawa et al.[28] Their sample is with $M_W = 2.5 \times 10^5$ g/mol, and with a low polydispersity index $M_W/M_n = 1.1$. From the elastic modulus equation $G = k_B T \zeta_0$, M_e is deduced at once, as $M_e = \rho \mathscr{R} T/G$, with ρ the polymer mass density, and $\mathscr{R}$ the gas constant. Independent measurements (at 140 °C) give $\rho = 0.97$ g/cm^3 and $G = 0.20$ MPa;[16] hence $M_e \approx 17000$ g/mol (±5% variations are estimated with temperature variations of ±20 °C). Notice that $Z_0 \approx 15$; hence, the melt is well entangled. Finally, the number n_0 of Kuhn segments between two entanglements is calculated from the relationship $n_0 = (0.82)^2 j(M_e/m)/C_\infty$,[29] where the 0.82 factor enters for all polymers with a carbon backbone, and, for polystyrene, it is $j = 2$ (j is the number of carbon–carbon bonds per monomer), $m = 104$ (m is the monomer molecular weight), and $C_\infty = 9.6$ (C_∞ is the so-called "characteristic ratio" of the polymer, which can be independently measured or calculated[30]). Thus, we get $n_0 = 23 \pm 1$, to be inserted in our calculation of the entangled polystyrene damping function.

In Figure 3, the polystyrene damping function data taken from Urakawa et al. (at 160 °C) are shown, together with the newly calculated $h(\gamma; n_0 = 23)$, and with the classical, universal $h_{DE}(\gamma)$. It is apparent that the new theory performs better than Doi–Edwards theory. Consider, for example, the comparison at the maximum available experimental strain ($\gamma = 6$): it is $h_{DE} = 0.09$, and $h = 0.11$, the latter value being indistinguishable from the datum. Although an estimate of the experimental error for the Urakawa et al. data is not given in the original paper,[28] and hence data might in actual fact be slightly different from those reported, we think that the improved agreement between theory and experiments is authentic, though further experiments are certainly required. Once more, we would like to emphasize that these promising results have been obtained with no additional parameters with respect to the original Doi–Edwards theory, since n_0 is independently calculated.

6. A Simple Extension to Solutions

So far, we have been considering polymer melts only. In this section, based on well-known, simple scaling arguments,[17,31] an extension to solutions is proposed. Specifically, the case of semidilute entangled solutions will be dealt with, for both good and Θ solvents. Some comparison with experiments will also be presented.

In semidilute solutions, the most important length scale is the correlation length ξ, identifying a typical distance above which excluded volume (and hydrodynamic) interactions are screened out. A chain part of dimension ξ, made up of g Kuhn segments, behaves then as if in dilute solution, hence it is $\xi = g^\alpha l$, with the α exponent depending on solvent quality ($\alpha = {}^3/_5$ and ${}^1/_2$ in good and Θ solvents, respectively). Since chains are overlapping, the correlation volumes ξ^3 ("blobs") are space filling, and the *current* volume fraction ϕ of the polymer solution is written as $\phi = gl^3/\xi^3$. Thus, in general, both g and ξ vary with ϕ, and for the correlation length it is

$$\xi = l\phi^{-\alpha/(3\alpha-1)} = \begin{cases} l\phi^{-3/4} & \text{good} \\ l\phi^{-1} & \Theta \end{cases} \qquad (32)$$

On length scales larger than ξ, the chain is a random walk of correlation blobs. In entangled semidilute solutions, the entanglement strand R_0 is itself a random walk, made up of ν_0 blobs (ν_0 is as yet unknown), hence $R_0 = \sqrt{\nu_0}\,\xi$.

To extend the results of the previous sections to solutions, we simply assume that the correlation length ξ is the "elementary" length scale, in place of the Kuhn segment l, distinctive of melts. Correspondingly, all other melt-based quantities are also changed, and the physics is just "scaled up". Thus, for example, the canonical partition function of a subchain R between entanglements is always Gaussian, as in eq 14, but with (n,l,r) replaced by (ν,ξ,R). By weigthed integration over the number of blobs ν, rather than over the number n of Kuhn segments like in eq 13, hence with mass exchanges through slip-links occurring "in blob units", the subchain grand canonical partition function becomes

$$\Xi(R,\hat{\mu},T) = \frac{\xi}{R}\exp\left(-3\sqrt{\hat{\mu}}\frac{R}{\xi}\right) \qquad (33)$$

(dependent on ϕ), and so on. The resulting expression for the total free energy density (see eq 20) should be noticed, which in terms of the above introduced variables x and y (here it is $x = R/R_0$) reads

$$A = k_B T C_0 Z_0 \left(\frac{\langle \ln x \rangle - \ln \sqrt{\nu_0}}{\langle x \rangle} \sqrt{y} + \frac{3}{2} y \right) \quad (34)$$

(compare with eq 22). The latter equation, together with the condition $A = A_0$ of inner equilibrium, give the variation of the chemical potential y with the deformation history, parametric in ν_0.

The equilibrium number of blobs per entanglement strand remains to be found. From the random walk relationship $\nu_0 = R_0^2/\xi^2$, and from eq 32, ν_0 is obtained once the equilibrium dimension R_0 of the subchain is known. There has been a long debate on the prediction of R_0 in semidilute solutions, but a certain degree of consensus has recently been gained on the following expression:[31]

$$R_0 = r_0 F(\phi) = \begin{cases} \sqrt{n_0} l \phi^{-3/4} & \text{good} \\ \sqrt{n_0} l \phi^{-2/3} & \Theta \end{cases} \quad (35)$$

We then calculate

$$\nu_0 = \begin{cases} n_0 & \text{good} \\ n_0 \phi^{2/3} & \Theta \end{cases} \quad (36)$$

According to eq 36, the equilibrium number ν_0 of blobs per subchain in semidilute entangled solutions in good solvents is *equal* to the equilibrium number n_0 of Kuhn segments per subchain in the melt. In short, a good solvent solution is a melt of blobs. By using this result in our theory (e.g., in eq 34), we conclude that, for a given polymer, the damping functions of the melt and of its semidilute solutions (by varying ϕ) in good solvents must exactly coincide. Testing this prediction is not easy, of course. Indeed, since $\phi \ll 1$ in the semidilute regime, very high molecular weigth polymers have to be used in experiments, to attain fully entangled solutions. Moreover, in well entangled systems, wall slip problems often arise in step deformations, spuriously affecting the measurements. To date, the most complete available data set is that by Sanchez-Reyes and Archer,[32] with ultrahigh molecular weigth polystyrene solutions in diethylphthalate (a good solvent), at various concentrations $0.015 < \phi < 0.08$. Special care was taken by those authors to remove wall slip effects, by grafting the shearing surfaces of micrometer-sized glass beads. With their modified cone-and-plate apparatus, Sanchez-Reyes and Archer were able to explore the materials response up to very large strains ($\gamma_{MAX} = 18$).

In Figure 4, data taken from ref 32 are reported, together with the classical Doi–Edwards damping function and the prediction from the theory presented here. On the basis of the above discussion, we put $\nu_0 = n_0 = 23$ in our calculations: the $h(\gamma)$ of Figure 3 is exactly the same as that of Figure 2. The agreement between data and the new predictions is excellent, especially at large strain ($\gamma > 5$, for example), and the improvement over Doi–Edwards damping function is clear. It should be indicated, however, that a remaining (small) discrepancy at intermediate strain values exists, where solution data are systematically somewhat below the predictions. The reason for this discrepancy is presently unknown.

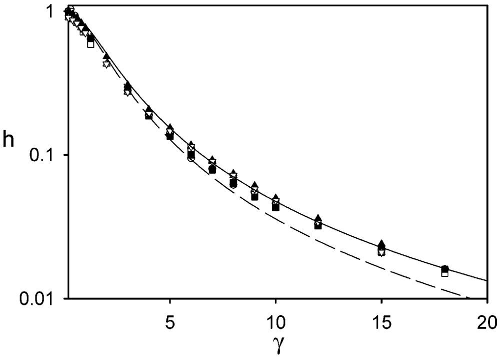

Figure 4. Calculated and experimental damping functions for semidilute solutions in a good solvent. Data from ref 32, at different volume fractions ($0.015 < \phi < 0.08$) of polystyrene in diethylphthalate. Dashed and continuous lines as in Figure 3. The newly calculated damping function is for $\nu_0 = n_0 = 23$, as required for good solvent semidilute polystyrene solutions.

Finally, we would like to call attention to another result of the theory, for semidilute solutions in Θ solvents. For these solutions, we get $\nu_0 = n_0\phi^{2/3}$ (eq 36); hence, the damping function should become dependent on concentration, i.e., dependent on the degree of entanglement of the polymer chain. We are unaware of experiments for possibly testing such a prediction.

7. Closing Remarks

In this work, we examined some consequences of the fact that, in entangled polymeric liquids, a subchain between two entanglement points is not a macroscopic system, in its thermodynamic limit. Instead, the subchain is a small system, open to Kuhn segments exchanges through its extremity slip-links, and the nonnegligible fluctuations in its own (small) Kuhn segments number must be accounted for. To this end, the nonstandard statistical mechanics and thermodynamics[19] of a subchain have been here formulated, and the original Doi–Edwards assumption of inner equilibration restated in detail. It has been found that the macroscopic mechanical response of the entangled liquid depends explicitly on specific polymer characteristics, namely, on the number of "elementary units" (Kuhn segments or blobs) in the subchain. As a worked example, the calculation of the new shear damping function has been presented, together with some comparison to available data.

The parallel results on the first and second normal stress differences N_1 and N_2 (still in step strain) were not explicitly considered for the following reasons. On one hand, from the approach proposed here, these quantities are predicted to explicitly depend on n_0 (over and beyond the n_0 dependence of the elastic modulus), but we were unable to find published data to test such predictions. On the other hand, for the important quantity $\Psi = -N_2/N_1$, the n_0 dependence is in fact numerically irrelevant, and the new results are undistinguishable from those with $y = 1$, already reported in refs 23 and 24. As discussed in those papers, the agreement of the predicted Ψ with the few available data also improved with respect to the classical Doi–Edwards prediction, and the present advanced version of the new theory preserves that result. Finally, coming again to the first normal stress difference N_1 in step shear, it seems worth to signal that the well-known Lodge–Meissner rule $N_1 = \gamma T_{XY}$ is readily demonstrated to hold for our new stress tensor, eq 31, in both the old (i.e., with $y = 1^{23,24}$) and the new version of the theory.

From the standpoint of theory, it is appropriate to give now some additional comments on the delicate problem of constraint release and renewal (CRR), a dynamical mechanism entirely neglected in this paper. Indeed, our new theoretical treatment is a direct extension of Doi−Edwards original theory,[2−6] hence, with no CRR. Let us specifically consider the inner equilibration hypothesis, discussed in sections 2 and 3 above. Such hypothesis is neatly formulated through the condition $A = A_0$ on the total free energy density, and its consequences are readily deduced, given the simple mathematical form of A. Yet it is apparent that, if one wants to somehow introduce CRR into these one-chain models, the expression for the total free energy will radically change. CRR amounts to say that there is a pseudo-Brownian creation and destruction of slip-links, with an “intensity” depending on the externally imposed flow history. No one knows how to write down the energetics of these processes, however, because the creation and destruction “rules” are in fact essentially arbitrary. As an example, in their version of CRR dynamics Mc Leish and co-workers state that “the number of entanglements per chain ... does not change”,[33] which of course is a (strong) additional condition on the dynamics. In the opinion of the author, this issue cannot be settled in one-chain theories. Numerical simulations of physical networks of reptating chains might be of help in the future.[34]

On the other hand, we speculate that the special case of CRR in step deformations is more understandable, as follows. After the affine step displacement of the slip-links, the inner equilibration process implies the retraction of all the chains. On a given chain, “external” slip-links are then vacated by retraction of the chain itself, and some “internal” slip-links are also lost, because of the retraction of the surrounding chains. The disappearance of an internal slip-link s_i is a *constraint release* event. In a naïve picture of constraint release, the disappearance of s_i would lead to a “straightening” of the primitive chain between s_{i-1} and s_{i+1}, and to one subchain “lost”. However, *constraint renewal* can also occur on the released portion of primitive chain between s_{i-1} and s_{i+1}, simply because a previously “hidden” obstacle, i.e., another primitive chain, is caught on the way to the straight, locally relaxed state.[35] A little reflection makes it clear that these constraint renewal events are the more probable the more the subchains had been elongated (on average) by the deformation. The newly appeared slip-link s'_i is within a distance r_0 (or R_0) from the disappeared s_i, because the density of primitive chains is always constant, and the number of subchains is left unchanged. Thus, at large strains, constraint release and constraint renewal somehow compensate with each other, there is no loss of subchains (except for those lost by retraction from the extremities, and already accounted for, see eq 25), and there is no net loss of average orientation. The resulting stress after a step deformation, and the damping function, are therefore well computed even if CRR is neglected, as we observed in this paper.

Going back to the comparison with experiments, we have found excellent agreement between damping function data and predictions, both for melts and solutions, up to the largest imposed strain. These results may help clear up a persistent discrepancy between Doi−Edwards original theory and data. Indeed, it is well-known that the Doi−Edwards damping function shows too much strain thinning. By accounting for fluctuations at the subchain level, we remedy this deficiency. To further validate the theory, carefully designed experiments on polymeric systems with different n_0 values are strongly in demand. This is left for future work.

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