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Stress relaxation following uniaxial extension of polystyrene melt and oligomer dilutions

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Abstract

The Filament Stretching Rheometer has been used to measure the stress relaxation following the startup of uniaxial extensional flow, on a narrow molar mass distribution (NMMD) polystyrene melt and styrene oligomer dilutions thereof. All samples used here were characterized in molecular weight, mechanical spectroscopy and constant strain rate uniaxial extension in Huang *et al.* [1, 2]. The stress relaxation following the steady extensional stress was measured on a 285 kg/mole NMMD polystyrene and two 1.92 kg/mole styrene oligomer dilutions thereof (PS-285k, PS-285k/2k-72 and PS-285k/2k-44 in Ref. [1]). The two dilutions contained 28 and 56 weight percent oligomer, respectively. Further, the stress relaxation on a 545 kg/mole NMMD polystyrene diluted with 48 weight percent 0.972 kg/mole styrene oligomer (PS-545k/1k-52 in Ref. [2]) was measured as well. All the terminal relaxations could be predicted by a Doi and Edwards, e.g. pure configurational, type of model. At smaller time scales agreement with a molecular stress function type of constitutive representation was observed for all measured relaxations.

1 Introduction

The first studies on extensional rheology of well-defined polymer melts were performed in the seventies by Vinogradov *et al.* [3]. They introduced the guideline for the future experimental effort by measuring the startup of uniaxial extensional viscosity of nearly monodisperse polyisoprene melts. Their effort came concurrently to the emergence of the tube ideas by De Gennes [4], Doi and Edwards [5].

Vinogradov and coworkers stretched the 'dog-bone' shaped samples exponentially in time to measure the extensional force. The experiments were limited to low Hencky strain values due to sample breaking. About three decades later, the first startup and steady measurements on nearly monodisperse polystyrene melts were published by Bach *et al.* [6]. They used a filament stretching rheometer (FSR) to stretch a short cylindrical sample, and recorded the force and the mid-filament diameter which corresponds to the local strain [7]. The first FSR was developed by Sridhar *et al.* [8]. Preceding the work by Bach *et al.* [6], it was used to measure the extensional viscosity of nearly monodisperse entangled polystyrene solutions [9]. The two studies by Bach *et al.* [6] and Bhattacharjee *et al.* [9] showed a clear difference of flow

physics between pure melts and corresponding dilutions with similar number of entanglements per chain.

To bridge this gap between polymer melts and solutions, Huang *et al.* [1, 2, 10] presented extensional measurements on oligomer diluted narrow molecular weight distributed (NMMD) polystyrenes. The authors changed both the concentration and the molecular weight of the unentangled oligomers, which contain from 1.6 to 7.3 Kuhn segments. It has been found that with similar entanglement numbers per chain, the extensional viscosity of these oligomer dilutions lied between the corresponding values of a melt and a solution when the number of Kuhn segments were at least above two [1, 2, 11]. A theoretical consequence seems to be that the current tube model is missing key physical elements to predict the rheological behavior of entangled polymer systems, despite the effort to include contour length fluctuations [12], constraint release [13], chain stretch [14], convective constraint release [15] and finite extensibility [16].

Extensional measurements are sensitive to changes in material properties, particularly compared to shear flow. Recently it seems that several quantitative ideas are capable of predicting the dynamics of these entangled solutions, oligomer dilutions and pure melts [11, 17, 18, 19, 20, 21]. However, in the evaluation of theoretical ideas, it is important that the startup and steady extensions are supplemented with additional extensional measurements. Stress relaxation is a classical method, not only in shear but also following uniaxial extension. Here we present new measurements on the stress relaxation of a NMMD polystyrene melt and different oligomer dilutions following uniaxial extension.

For polymer melts, stress relaxation is experimentally straightforward using equipments such as the melt extensometer (RME) [22, 23], the Munstedt tensile rheometer (MTR) [24] and the Sentmanat extensional rheometer (SER) [25]. Basically the imposed extension is halted and the fluid is allowed to relax. However, large strain can be difficult or impossible to obtain [26] using these techniques as the samples break during extension [27]. Furthermore, during relaxation the samples may likewise lose uniformity and break [28]. In an FSR it is important to use a closed loop control algorithm [29] to ensure a exponentially decaying mid-filament diameter during extension and a constant one during relaxation [30]. It ensures a defined strain rate and at the same time avoids sample break [26] during both extension [6] and relaxation [30]. The FSR developed by Bach *et al.* [31] is equipped with a controlled temperature environment and a closed loop control scheme [6, 32]. It is applied here as all materials need to be measured above room temperature. For polymer solutions the FSR is the only rheometer to measure extensional viscosity including stress relaxation [33, 34].

2 Extensional technique

The extension technique used here has been described in details in previous papers. The FSR equipment including the thermostated environment was presented in Bach *et al.* [31]. The closed loop control between the subsequent measured strain based on sample length and mid-filament diameter was first used by Bach *et al.* [6] and has been presented more recently in details by Marín *et al.* [32]. The same methodology was applied in Nielsen *et al.* [30] to achieve a fixed mid-filament diameter during stress relaxation.

The samples were molded into cylinders with a height of L_i and a diameter of D_i . In the FSR the samples were pre-stretched to a central diameter of D_0 . During an extension the central Hencky strain of the sample is then calculated as $\epsilon(t) = -2 \ln(D(t)/D_0)$ where $\dot{\epsilon} = d\epsilon/dt$ is the

strain rate. $D(t)$ is the diameter of the mid-filament plane (the necking) of the sample.

The viscosities during startup and stress relaxation are defined as

$$\bar{\eta}^+ = \frac{\sigma_{zz} - \sigma_{rr}}{\dot{\epsilon}_0} \quad \text{and} \quad \bar{\eta}^- = \frac{\sigma_{zz} - \sigma_{rr}}{\dot{\epsilon}_0} \quad (1)$$

respectively, where the extensional stress is the difference between the axial, σ_{zz} , and radial, σ_{rr} , component of the stress tensor, $\boldsymbol{\sigma}$. The viscosity during the stress relaxation is defined using the constant extensional rate, $\dot{\epsilon}_0$, from the preceding startup flow. The sample is stress free at rest, for $t < 0$, and the constant extensional rate, $\dot{\epsilon}_0$, is applied for $t > 0$. This is followed by a fixed mid-filament diameter during the stress relaxation, which is initiated at a Hencky strain of ϵ_0 .

At small Hencky strain values a shear flow may occur. This is significant at small aspect ratios where the shear contribution may add to the measured force. The effect can be diminished using the correction factor from Rasmussen *et al.* [35]. Using this correction factor the average extensional stress is calculated as

$$\langle \sigma_{zz} - \sigma_{rr} \rangle = \frac{F(t) - m_f g / 2}{\pi D(t)^2 / 4} \cdot \frac{1}{1 + (D(t)/D_i)^{10/3} \cdot \exp(-A_i^3)/(3A_i^2)}, \quad (2)$$

where $A_i = 2L_i/D_i$ is the initial aspect ratio. The angular bracket, $\langle \sigma_{zz} - \sigma_{rr} \rangle$, denotes the average extensional stress across the mid-sample plane. All published computational FSR studies show that the deviations from ideal extension diminish at larger strain, and the above formula ensures a maximal 3% deviation from the theoretically correct evaluation at small strain values. The initial aspect ratios, A_i , of the individual samples here are all between 0.44 and 0.66. As discussed in details in Nielsen *et al.* [30], it is assumed that uniform extension in the radial direction of the mid-filament plane is accurate within a few percent error. It allows the angular bracket in Eq. (2) to be omitted.

3 Materials

In Huang *et al.* [1, 2] the NMMD polystyrenes were dissolved in the most ideal diluent, which is a shorter chain of the same polymer. The chain is short enough to not be entangled and to stay in a random configuration at all the experimental conditions. θ is the weight fraction of the long chain in the dilution. In polymer dynamics, the entanglement length (M_e) and the Kuhn step length (M_K) are established terms. An ideal dilution of a melt will change the entanglement molecular weight as $M_{e,\theta} = M_e/\theta$ and consequently the plateau modulus G_N^0 in a similarly way as $G_{e,\theta}^0 = \theta^2 G_N^0$. This is at least the case for sufficient high concentrations of the ideal diluent [1]. The Kuhn step length is assumed to be unchanged. For polystyrene the Kuhn length, defined as molecular weight, is 0.61 kg/mol according to Fang *et al.* [36]. The entanglement molecular weight M_e is more debated. It has been reported in the range of 13.3 to 18.1 kg/mol for polystyrene [37]. Table 1 lists the relevant molecular weight for the involved NMMD polystyrenes in the present work. As in Huang *et al.* [1] we have used $M_e = 13.3$ kg/mol for polystyrene.

The mechanical spectroscopy of the involved polystyrene melt and polystyrene dilutions in this work was previously measured by Huang *et al.* [1, 2]. We have listed the relevant

Table 1: Polystyrene molecular weights from Huang *et al.* [1, 2]

Name	M_w	M_w/M_n	M_w/M_K	M_w/M_e
OS-1k	0.972 kg/mole	1.12	1.6	-
OS-2k	1.92 kg/mole	1.08	3.1	-
PS-285k	285 kg/mole	1.09	-	21.4
PS-545k	545 kg/mole	1.12	-	41.0

linear dynamical parameters in Table 2 fitted by Rasmussen and Huang [11, 17]. They used the method by Baumgaertel *et al.* [38] and Baumgaertel and Winter [39], where the memory function is given as

$$M(t - t') = \int_0^{\tau_{max}} n_e G_N^0 \left[\left(\frac{\tau}{\tau_{max}} \right)^{n_e} + \left(\frac{\tau}{\tau_c} \right)^{-n_g} \right] \frac{e^{-(t-t')/\tau}}{\tau^2} d\tau. \quad (3)$$

Here τ_{max} is the maximal relaxation time. The material parameters n_e , n_g , τ_c and G_N^0 have a unique value for each type of polymer with respect to the time-temperature superposition. As in Rasmussen and Huang [11, 17], here $n_e = 0.2$ and $n_g = 0.7$ are fixed values for all the materials. The plateau modulus is $G_{e,\theta}^0 = \theta^2 \cdot T/403.15$ kPa, referred to 130°C as the reference temperature [6]. Although the τ_c theoretically has a unique value, it is sensitive to the particular glass transition temperature of which may vary. The particular τ_c value, fitted by Rasmussen and Huang [11, 17], for each of the samples is therefore also listed in Table 2.

Table 2: Parameters for the NMMD polystyrene melt and oligomer dilutions from Rasmussen and Huang [11, 17] at 130°C. θ is the weight fraction of the long polystyrene chain in the dilution. T is the temperature of the stress relaxation measurements. a_T is the time-temperature superposition shift factor from T to 130°C.

Polystyrenes	θ	M_w/M_e	τ_{max}	τ_c	T	a_T
PS-285k	1	21.4	9500 s	0.6 s	130°C	1
PS-545k/1k-52	0.52	21.3	11 s	0.0007 s	89°C	440
PS-285k/2k-72	0.72	15.4	440 s	0.09 s	120°C	8
PS-285k/2k-44	0.44	9.4	26 s	0.03 s	110°C	56

4 Stress relaxation on NMMD polymers melts

Some of the first experimental efforts on ideal polymer systems were actually the extension of a NMMD polyisoprene melt, made in the mid seventies [3]. These measurements were limited to low Hencky strain values of about 1.5, with only a few of them above a value of 2. The small Hencky strain values of the measurements limited their theoretical importance. The theoretical developments predating the extensional experiments on NMMD polystyrene melts by Bach *et al.* [6] were experimentally evaluated on either extension on dilute polymer solutions [8] or broadly distributed polymer melts [22]. Shear flow is in most cases not sensitive enough to get discrepancy between theoretical ideas. Although rheometry is an excellent tool for qualitative assessment of constitutive equations, one has to be careful not to interpret qualitative physical

mechanism. Here methods based on neutron or x-ray scattering allowing measurements of the actual configurational change of polymer chains are far more useful.

For more complex extensional flow, as stress relaxation following steady flow, only one data set measured on a 145 kg/mole polystyrene melt has been presented in the scientific literature [30]. Stress relaxation following steady flow is of particular importance in the evaluation of nonlinear relaxation involved in specific constitutive models. The steady condition maximizes the orientation and stretching of the polymer chains at a particular extensional rate. Here we present a new data set with about twice the molecular weight, i.e. 285 kg/mole, in Figure 1.

Focusing on (undiluted) monodisperse polystyrene melts, the 'interchain pressure' [40] mechanism seems to be able to qualitatively describe the steady extensional viscosity measured by Bach *et al.* [6]. This mechanism was incorporated into several frameworks [41, 42, 43] allowing a quantitative predicting of the startup and steady extensional viscosity of NMMD polystyrene melts. Particularly the model by Wagner *et al.* [41] has been shown to be capable of handling more complex extensional flow as well [44, 45]. In the method by Wagner *et al.* [41] the 'interchain pressure' was incorporated into the 'stretch evolution' constitutive framework. In this one the components of the stress tensor, σ_{ij} , are given as

$$\sigma_{ij} = \int_{-\infty}^t M(t-t') f(t, t')^2 5 \left\langle \frac{E_{in} u_n E_{jm} u_m}{|\mathbf{E} \cdot \mathbf{u}|^2} \right\rangle dt', \quad (4)$$

where $M(t-t')$ is the memory function and by definition the initial value $f(t', t') = 1$. All involved angular brackets represent an average, here on a unit sphere. It is an integral defined as $\langle \dots \rangle = 1/(4\pi) \int_{|\mathbf{u}|=1} \dots d\mathbf{u}$ where $\mathbf{u}$ is a unit vector. Analytical formulas for all involving unit sphere integrals in this paper can be found in Urakawa *et al.* [46]. The components of the displacement gradient tensor $\mathbf{E}$ are $E_{ij}(\mathbf{x}, t, t') = \partial x_i / \partial x_j'$, $i = 1, 2, 3$ and $j = 1, 2, 3$ in Cartesian coordinates. (x'_1, x'_2, x'_3) are the coordinates of a particle in the reference state displaced to the coordinates (x_1, x_2, x_3) in the present state at time t' and t respectively.

In the original model [41] the stretch evolution of the 'Interchain pressure' [40] type can be written as

$$\frac{\partial}{\partial t} f(t, t') = f(t, t') \frac{\partial}{\partial t} \langle \ln |\mathbf{E} \cdot \mathbf{u}| \rangle - \frac{f(t, t')^2 (f(t, t')^3 - 1)}{3\tau_R}, \quad (5)$$

where τ_R is the Rouse time. The value of the Rouse time from Rasmussen and Huang [17] is used here. Experimentally the Rouse time is based on a direct fitting of this model to the startup of extension and steady measurements, with a broad range of molecular weight. In Figure 1 we have shown the corresponding model predictions, as the solid lines, based on this 'interchain pressure' constitutive equation. The value of the Rouse time for PS-285k from Rasmussen and Huang [17] is $\tau_R = 474s$. The expected agreement with the experiments is seen throughout all extensional rate. It is achieved from the steady stress, representing the maximal extension of the polymer, to a complete relaxation of the 'stretch evolution' function, f , until unity. The dashed lines, where $f = 1$, represent the Doi-Edwards predictions of the extensional viscosity. Due to the higher molecular weight, and therefore a larger separation between the Rouse and reptation time of this sample compared to the one measured in Nielsen *et al.* [30], the relaxations show a clear transition to a flow which is controlled by a pure configuration stress, of the Doi and Edwards type. The measurements in Figure 1, and all the following ones, are all terminated as the lower resolution on the weight cell, used to measure the extensional force, cannot deliver a sufficient accurate measurement.

It should be noted that our use of the MSF constitutive concept is not necessary a unique theoretical representation. Other constitutive equations would be expected to result in a similar agreement, particularly the ones based on 'interchain pressure' where the nonlinear relaxation originates from the 'interchain pressure' solely [42, 43].

5 Stress relaxation on oligomer dilutions

Currently only three quantitative theories have been published considering the flow physics of oligomer diluted NMMD polystyrenes [17, 18, 21]. The first two models are both based on Eq. (4). The one published by Rasmussen and Huang [17] is based on a discrete difference between pure NMMD melts, melts diluted with oligomers with chain length longer than two Kuhn segments, and melts diluted with oligomers shorter than two Kuhn segments. For oligomers longer than two Kuhn steps, the flow physics is assumed to follow a constant interchain pressure originating from the random configured oligomer. Below two Kuhn steps a Rouse dynamics is observed [11]. The transition to steady extension flow is in all cases controlled by the classical maximal extensibility controlled by the number of Kuhn steps in-between entanglements. The recent model by Wagner [18] differs. The model parameters are controlled by the lowering of the glass transition temperature from the pure melt state due to dilution. It therefore represents a continuous model for all types of NMMD systems regardless of the type and amount of the diluent. The stretch evolution is basically a transition in-between a 'interchain pressure' [40] and a Rouse formulation. It is written as

$$\frac{\partial}{\partial t} f(t, t') = f(t, t') \frac{\partial}{\partial t} \langle \ln |\mathbf{E} \cdot \mathbf{u}| \rangle - \left(1 - \frac{2}{3} a_{T_g} \right) \frac{f(t, t') - 1}{\tau_R} - \frac{2}{3} a_{T_g} \frac{f(t, t')^2 (f(t, t')^3 - 1)}{3\tau_R}. \quad (6)$$

The values of the used Rouse times and shift factors from the lowering of the glass transition, a_{T_g} , used by Wagner [18] for the diluted systems at 130°C are listed in Table 3. Both models by Rasmussen and Huang [17] and Wagner [18] agree, with one exception discussed later, with the startup and steady data of the relevant dilutions. As the both models are based on the 'stretch evolution' Eq. (4), they will give matching predictions in stress relaxation. The model from Rasmussen and Huang [17] has though only been suggested as the explanations of the flow physics for oligomer dilutions with oligomer length of more than two Kuhn steps. The model from Wagner [18] does not have these restrictions and can be applied on all samples presented here. It includes pure melts as well as any length of the oligomers. Therefore in the following we have only included a comparison of the experimental data with the model by Wagner [18], and not with the one by Rasmussen and Huang [17].

Table 3: Parameters for the NMMD polystyrene oligomer dilutions from Wagner [18] at 130°C. θ is the weight fraction of the long polystyrene chain in the dilution.

Polystyrenes	θ	τ_R	a_{T_g}
PS-545k/1k-52	0.52	0.26s	$4.09 \cdot 10^{-4}$
PS-285k/2k-72	0.72	19.6 s	0.0906
PS-285k/2k-44	0.44	2.33 s	0.0108

Figures 2 and 3 show the startup of the extension data (from Ref. [1]) followed by stress relaxation for the 285 kg/mole polystyrene diluted with the OS-2k oligomer. The measured

sample in Figure 2 is diluted with a weight fraction of $\theta = 0.72$ (PS-285k/2k-72) and in Figure 3 with $\theta = 0.44$ (PS-285k/2k-44). As the case of the corresponding pure melt in Figure 1, all measurements were relaxed at a Hencky strain of $\epsilon_0 = 3$. In the case of the dilution with $\theta = 0.72$ in Figure 2, the relaxation was initiated at almost steady condition. In Figure 3 for the more diluted one with $\theta = 0.44$, the transition to the steady viscosity was at a slightly higher strain value than $\epsilon_0 = 3$. The value of $\epsilon_0 = 3$ was not high enough to reach the steady stress values before the relaxation was initiated. The observed relaxation follows the used 'stretch evolution' function, f , in Eq. (6), and it relaxes toward unit of f . As in Figure 1, the dashed lines here are model predictions with $f = 1$, corresponding to a Doi-Edwards e.g. a pure configuration representation. The very good agreement in-between the theoretical representation and the measurements, confirms the accuracy in the use of the representation in Eq. (6). But care needs to be taken. The particular relaxation data presented here, as well as the startup and steady, cannot distinguish the fundamental physical differences between the two published models by Rasmussen and Huang [17] and Wagner [18]. Basically the accuracy confirms that the 'molecular stretch' representation given in Eq. (4) and the general character of the function represented by Eqs. (5) and (6) seem to be a correct basis for the fluid mechanics for NMMD polymers in extension. Although it is not likely to be the only one.

Figure 4 shows the startup of the extension data (from Ref. [2]) followed by stress relaxation for a 545 kg/mole NMMD polystyrene diluted with 48 weight percent OS-1k oligomer (PS-545k/1k-52). In this case the agreement with the prediction by Eq. (6) is less convincing. This is particularly the case near the steady levels. A simpler Rouse based model [11] may in this case do it better. The OS-1k solution is more strain hardening than the OS-2k solutions. As a consequence it seems to be more problematic to reach steady viscosity [2]. Fortunately relaxation experiments can still be performed at lower strain values as done in Figure 4. As in the previous figures the measured viscosities at the initiation of the relaxation are well above a pure configuration representation of $f = 1$. Here as well the viscosity relaxes toward unit of f represented by the dashed lines.

6 Conclusions

The filament stretching rheometer was used to measure the uniaxial extensional viscosity until steady viscosity followed by stress relaxation, on a 285 kg/mole NMMD polystyrene (PS-285k) and two 1.92 kg/mole styrene oligomer dilutions with 72 and 44 weight percent polymer (PS-285k/2k-72 and PS-285k/2k-44). Further a 545 kg/mole NMMD polystyrene diluted with 0.972 kg/mole oligomer, using 52 weight percent polymer (PS-545k/1k-52), was extended to high strain values followed by stress relaxation. All terminal relaxations could be predicted from a pure configurational, e.g. of the Doi and Edwards, type of model. The stress is ultimately dominated by the contribution from the reptation dynamics changing the molecular configurations, considered on a Kuhn step level.

Particularly for the 285 kg/mole NMMD melt the relaxation on a shorter time scale, seemingly controlled by the Rouse time, was experimentally observed on a time scale of one order of magnitude lower than the reptation time. This allows a clear separation of these two effects. It supports the general idea of factorization of stress into a tensorial contribution controlled by reptation dynamics modified by a scaling factor.

The terminal relaxation of the pure configurational type has been confirmed, not only for the pure NMMD melts but also for the oligomer diluted ones. At lower time scale the recent

constitutive ideas [17, 18], both based on the experiments by Huang *et al.* [1, 2], are able to predict the startup and steady extensional viscosities of oligomer dilutions quantitatively. Both are also in reasonable agreement with stress relaxation data. Other available quantitative theories, published before the experimental work by Huang *et al.* [1, 2], are unable to reproduce the complex extension dynamics of the oligomer dilutions.

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Figure 1: The extensional viscosity during startup, $\bar{\eta}^+$ (from Ref. [1]), and stress relaxation, $\bar{\eta}^-$ as a function of the strain based time and the time, respectively. The measurements are on a 285 kg/mole polystyrene melt (PS-285k) at 130°C. The lines are the corresponding predictions to the data from Eq. (5) using the material parameters from Table 2. The Rouse time is $\tau_R = 474s$ from Ref. [17]. The dashed lines are the corresponding predictions to the data from Eq. (4) with $f = 1$ (lower curves).

Figure 2: The extensional viscosity during startup, $\bar{\eta}^+$ (from Ref. [1]), and stress relaxation, $\bar{\eta}^-$ as a function of the strain based time and the time, respectively. The measurements are on 72 weight % 285 kg/mole diluted in 1.92 kg/mole styrene oligomer (PS-285k/2k-72), measured at 120°C. The lines are the corresponding predictions to the data from Eq. (6) using the material parameters from Table 2 and 3. The dashed lines are the corresponding predictions to the data from Eq. (4) with $f = 1$ (lower curves).

Figure 3: The extensional viscosity during startup, $\bar{\eta}^+$ (from Ref. [1]), and stress relaxation, $\bar{\eta}^-$ as a function of the strain based time and the time, respectively. The measurements are on 44 weight % 285 kg/mole diluted in 1.92 kg/mole styrene oligomer (PS-285k/2k-44), measured at 110°C. The lines are the corresponding predictions to the data from Eq. (6) using the material parameters from Table 2 and 3. The dashed lines are the corresponding predictions to the data from Eq. (4) with $f = 1$ (lower curves).

Figure 4: The extensional viscosity during startup, $\bar{\eta}^+$ (from Ref. [2]), and stress relaxation, $\bar{\eta}^-$ as a function of the strain based time and the time, respectively. The measurements are on 52 weight % 545 kg/mole diluted in 0.972 kg/mole styrene oligomer (PS-545k/1k-52), measured at 89°C. The lines are the corresponding predictions to the data from Eq. (6) using the material parameters from Table 2 and 3. The dashed lines are the corresponding predictions to the data from Eq. (4) with $f = 1$ (lower curves).

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