Shear thinning in dilute and semidilute solutions of polystyrene and DNA

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The viscosity of dilute and semidilute unentangled DNA solutions, in steady simple shear flow, has been measured across a range of temperatures and concentrations. For polystyrene solutions, measurements of viscosity have been carried out in the semidilute unentangled regime, while results of prior experimental measurements in the dilute regime have been used for the purpose of data analysis, and for comparison with the behaviour of DNA solutions. Interpretation of the shear rate dependence of viscosity in terms of suitably defined non-dimensional variables, is shown to lead to master plots, independent of temperature and concentration, in each of the two concentration regimes. In the case of semidilute unentangled solutions, defining the Weissenberg number in terms of a concentration dependent large scale relaxation time is found not to lead to data collapse across different concentrations. On the other hand, the use of an alternative relaxation time, with the concentration dependence of a single correlation blob, suggests the existence of universal shear thinning behaviour at large shear rates.

I. INTRODUCTION

Two distinct regimes of behaviour are always observed in steady simple shear flows of polymer solutions when the polymer contribution to viscosity \( \eta_p \) is plotted against the shear rate \( \dot{\gamma} \), regardless of the domain of concentration. At low shear rates, the solution is essentially Newtonian, with a constant viscosity independent of shear rate, typically denoted as the zero shear rate viscosity \( \eta_0 \). Beyond a threshold value of shear rate, of magnitude roughly \( \dot{\gamma} \approx \lambda^{-1} \), where \( \lambda \) is a large scale relaxation time, the viscosity decreases with increasing shear rate, exhibiting a power law dependence on \( \dot{\gamma} \) at sufficiently large values of shear rate. In the case of dilute polymer solutions, some experimental and computational studies suggest the existence of a third regime at even higher shear rates, where the viscosity levels off and displays another Newtonian regime independent of shear rate. Though the existence of the first two regimes has been observed in all experimental studies, and predicted in many analytical and computational studies, there are significant differences in the reported exponent for the power law decay of viscosity. The source of this discrepancy is probably the result of the experimental studies being conducted under widely varying conditions of temperature (\( T \)), polymer molecular weight (\( M \)), concentration (\( c \)), and ranges of shear rate, and the theoretical studies being carried out with different polymer models and underlying assumptions. The goal of the present work is to examine if it is possible to collapse the viscosity versus shear rate data, obtained experimentally for dilute and semidilute unentangled solutions of polystyrene and DNA across a wide range of conditions, onto universal master plots by appropriately choosing variables that represent the state of the solution when it is undergoing simple shear flow. It is anticipated that such a representation of the data would lead to a more unambiguous understanding of the nature of shear thinning itself, and of the power law exponent.

At equilibrium, for dilute and semidilute solutions of polymers that are neutral, flexible and linear, it has been established that just two variables, the solvent quality \( z \) and the scaled concentration \( c/c^* \), are sufficient to collapse the static and dynamic properties of a wide variety of different polymer-solvent systems, onto master plots [1–5]. The solvent quality \( z \), which is the scaling variable that describes the temperature crossover behaviour from \( \theta \) solvents to very good solvents, combines the dependence on \( T \) and \( M \), while \( c/c^* \) (where \( c^* \) is the overlap concentration which determines the onset of the semidilute regime), combines the dependence on \( c \) and \( M \). In the presence of flow, a number of experimental and theoretical studies suggest that plotting \( \eta_0/\eta_0 \) versus \( \lambda \dot{\gamma} \) for different systems leads to a collapse of data. However, these studies are invariably limited to a particular concentration regime, and in most cases do not attempt to examine equilibrium and nonequilibrium behaviour within a common conceptual framework. In this work, we examine if the representation of viscosity versus shear rate data in terms of \( z, c/c^* \) and \( \lambda \dot{\gamma} \) (with particular attention paid to the appropriate choice of \( \lambda \)), is sufficient to reveal the underlying universal behaviour in dilute and semidilute unentangled solutions of polystyrene and DNA.

The literature on experimental, analytical and computational studies of the shear thinning of polymer solutions is very extensive, and is spread over several decades in the past. For the purpose of placing the present work in context, we discuss a few papers that highlight the essential aspects of the experimental observations and theoretical predictions that have been made over the years, starting with dilute solutions before considering semidilute unentangled polymer solutions.

Arguably the most careful experimental measurements of
the shear thinning of dilute polymer solutions were carried out nearly 50 years ago with the help of capillary viscometers. Representative examples of this work are the papers by Kotaka et al. [7], Noda et al. [8] and Suzuki et al. [9], in which the intrinsic viscosity $[\eta]$ was measured as a function of the nondimensional shear rate $\lambda Z \dot{\gamma}$, where

$$\lambda = \frac{M[\eta]_0 N_A k_B T}{N_A k_B T}$$

(1)

is a large scale relaxation time based on the zero shear rate value of the intrinsic viscosity $[\eta]_0$. Here, $\eta_s$ is the solvent viscosity, $N_A$ is the Avogadro number and $k_B$ is Boltzmann’s constant. Kotaka et al. [7] considered the behaviour of polystyrene solutions with polymers of several different molecular weights in four different solvents covering the range from $\theta$ to good solvents. Their experiments were carried out up to a maximum value of nondimensional shear rate $\lambda Z \dot{\gamma} = 5$. They observed a collapse of data when $[\eta]/[\eta]_0$ was plotted against $\lambda Z \dot{\gamma}$, for all the different molecular weights, temperatures and solvents, regardless of the quality of the solvent. They did not comment on the shear thinning exponent, nor did they observe the high shear rate constant viscosity regime. Noda et al. [8] measured the ratio $[\eta]/[\eta]_0$ for several different molecular weight samples of poly($\alpha$-methyl-styrene), and one polystyrene sample, in both $\theta$ and good solvents, for nondimensional shear rates up to a maximum value of $\lambda Z \dot{\gamma} \approx 40$. In contrast to the observation by Kotaka et al. [7], they observe a large difference in the behaviour of the polystyrene sample in good and $\theta$ solvents, for values of $\lambda Z \dot{\gamma} > O(1)$. The thinning observed in good solvents is significantly greater than in $\theta$ solvents, with the viscosity in the $\theta$ solvent levelling off to a constant value for $\lambda Z \dot{\gamma} > 5$. With regard to the dependence on molecular weight, they find that their data for the $13.6 \times 10^6$ g/mol (13.6 M) polystyrene sample in decalin (which is a $\theta$ solvent) exhibits less shear thinning than the $7.14 \times 10^6$ g/mol (7.14 M) polystyrene sample of Kotaka et al. [7] in the same solvent, with a delayed onset of shear thinning. They also observe a clear influence of molecular weight in their observations of the shear thinning of the poly($\alpha$-methyl-styrene) samples, with an increase in the threshold value of $\lambda Z \dot{\gamma}$ for shear thinning with increasing molecular weight. They report that their data does not permit them to extract a shear thinning exponent, and interestingly, they do not observe a collapse in any of their data sets. On the other hand, Suzuki et al. [9] observe data collapse for several of the polystyrene solutions considered by them when they plot $[\eta]/[\eta]_0$ against $\lambda Z \dot{\gamma}$. For instance, they find that data for the $6.2 \times 10^6$ g/mol (6.2 M) polystyrene sample in three different solvents, all at their respective $\theta$ temperatures, collapse onto a single curve, for nondimensional shear rates up to a maximum value of $\lambda Z \dot{\gamma} \approx O(2)$. Similarly to Noda et al. [8], they find that increasing the solvent quality (while keeping the molecular weight fixed), increases the degree of shear thinning. However, in direct contrast to the observation of Noda et al. [8], they find that an increase in the polymer molecular weight (by roughly a factor of 2) leaves the onset of shear thinning relatively unchanged, but increases the degree of shear thinning. It should be noted that these authors also do not comment on the shear thinning exponent, and do not observe the levelling off in the viscosity at high shear rates, for the range of shear rates examined by them.

By plotting $\eta_\text{p}/\eta_0\text{p}$ versus $\lambda^3 \dot{\gamma}$, Mochimaru [10] has shown that data reported previously in the literature for an extraordinarily broad range of polymer-solvent systems, across a wide range of molecular weights and concentrations (and a relatively narrower range of temperatures), can be collapsed onto a master plot if the large scale relaxation time $\lambda^3$ is chosen appropriately. In particular, Mochimaru [10] has shown that $\lambda^3$ can be chosen for each of these systems (regardless of the regime of concentration) such that experimental shear thinning data can be shifted onto a single curve that corresponds to the theoretical prediction of shear thinning by the FENE-P dumbbell model for dilute polymer solutions (11) (with the value of the finite-extensibility parameter $b = 50$). The experimental data typically have an upper limit to the nondimensional shear rate in the region $10^4$ to $10^5$. Since the limiting value of the power law exponent for the FENE-P dumbbell model is $-2/3$, presumably all the experimental data considered in Ref. [10] that lie on the theoretical curve conform to this exponent. It is worth mentioning here that Bird et al. [11], in their monograph on the kinetic theory of polymeric liquids, have compiled an extensive set of experimental data published previously, in order to compare experimental measurements with theoretical predictions of shear thinning by the FENE and FENE-P dumbbell models for dilute polymer solutions.

The experiments of Hua and Wu [12] represent a relatively recent examination of the shear thinning of dilute polystyrene solutions in which (rather than the intrinsic viscosity) the shear rate dependence of $\eta_\text{p}$ at finite concentrations below the overlap concentration $c^*$, has been considered. Measurements were carried out in a Couette viscometer for shear rates up to roughly $10^4$ s$^{-1}$ on polystyrene samples with four different molecular weights in dioctyl phthalate solutions at different temperatures that span $\theta$ and good solvents. Hua and Wu [12] find that data collapse, independent of temperature, can be achieved if the ratio $\eta_\text{p}/\eta_\text{p}\text{p}$ is plotted versus $\lambda^3 \dot{\gamma}$, where $\lambda^3 = 1/\gamma^*$, with $\gamma^*$ being the threshold shear rate for the onset of shear thinning. When plotted in this manner, they find that the smaller molecular weight solutions exhibit a higher degree of shear thinning. The highest molecular weight solution is found to exhibit a power law exponent equal to $-2/3$. As a result, the data appears to suggest that this limiting value is approached from above with increasing molecular weight. The highest molecular weight solution also clearly exhibits a second Newtonian plateau value for $\eta_\text{p}$, for shear rates $\gamma \gtrsim 10^4$.

The use of single molecule experiments to observe fluorescently stained DNA in order to understand the relationship between microscopic dynamics and macroscopic rheology has been pioneered by the groups of Shaqfeh and Chu [13–16]. In particular, the observation of molecular behaviour in the flow-gradient plane has led to significant new insights into the stretching and tumbling dynamics of individual molecules in simple shear flow. By making use of the relationship between the intensity of the measured image and the polymer density, Teixeira et al. [14] and Schroeder et al. [15] infer the
accessible elements of the radius of gyration tensor. Since the Giesekus expression relates moments of the polymer conformation to the stress tensor, this enables them to estimate the dependence of viscosity on shear rate. The Giesekus expression is not valid in the presence of hydrodynamic interactions. However, Schroeder et al. [15] show through Brownian dynamics simulations which incorporate hydrodynamic interactions (discussed in more detail below), that the difference between predictions of viscosity by the Giesekus and Kramers expressions are not significant. By defining the Weissenberg number by \( \dot{W} = \lambda_1 \dot{\gamma} \), where \( \lambda_1 \) is the longest relaxation time (obtained by an appropriate analysis of the relaxation of initially stretched molecules), both Teixeira et al. [14] and Schroeder et al. [15] observe that for Weissenberg numbers in the range 70 < \( \dot{W} < 1000 \), the viscosity decays according to the power law, \( \eta_s \sim \dot{W}^{-\alpha} \), with \( \alpha = 0.54 \) reported by the former, and \( \alpha = 0.53 \) by the latter.

Analytical attempts to predict the dependence of viscosity on shear rate for dilute polymer solutions date back all the way to the early development of kinetic theories for polymer solutions. Here we summarise some of these efforts, paying attention to the relationship between the underlying polymer model and the resultant prediction of shear thinning.

Using a rigid dumbbell model for the polymer molecule with hydrodynamic interactions included, Stewart and Sorensen [17] used the Galerkin method to predict the ratio \( \eta_s/\eta_0 \) as a function of shear rate. They found that beyond the initial Newtonian plateau, the viscosity decreases with increasing shear rate, and approaches the asymptotic power law exponent \(-1/3 \) as \( \dot{\gamma} \to \infty \). On the other hand, Fan [18] used the Galerkin method to show that for a FENE dumbbell model, at moderate shear rates, the curve of \( \log(\eta_s/\eta_0) \) versus \( \log(\dot{\gamma}) \) has a slope \(-0.607 \). In the special case of the FENE-P dumbbell model, it can be shown that the asymptotic power law exponent is equal to \(-2/3 \) as \( \dot{\gamma} \to \infty \) [11]. Thus the replacement of the rod with a spring as the connector between the beads leads to a significant change in the predicted value of the shear thinning exponent. None of these dumbbell models predict the second Newtonian plateau at high shear rates.

An asymptotic power law exponent of \(-2/3 \) in the limit of large Weissenberg numbers was also observed by Winkler [19], who developed a model for dilute solutions of semiflexible polymers with the polymer molecules represented by a continuous differentiable space curve (with a fixed contour length), and hydrodynamic interactions incorporated in a pre-averaged manner. Curiously, Winkler [19] found that chain stiffness had very little influence on the dependence of viscosity on shear rate.

A qualitatively different prediction of the dependence of viscosity on shear rate is obtained when hydrodynamic interactions are treated with more sophisticated approximations than the simple pre-averaging approximation introduced originally by Zimm [20] in the context of a coarse-grained bead-spring chain model for dilute polymer solutions. A detailed discussion of a hierarchy of such models is given in the review article by Prakash [21]. The most advanced approximations account for fluctuations in hydrodynamic interactions [22] [23], with a recent contribution accounting for fluctuations in both hydrodynamic interactions and in the FENE spring force law [24]. For sufficiently long chains, the shape of the viscosity versus shear rate curve predicted by these models is rather complex. When a Hookean spring force law is used, after the initial Newtonian behaviour at low shear rates, there is a relatively weak shear thinning regime over a limited range of shear rates (with no discernible power law), followed by shear thickening for a range of shear rates (whose extent depends on chain length), until a constant plateau value is reached at high shear rates. The occurrence of shear thinning followed by shear thickening predicted by these closure approximations for hydrodynamic interactions has been confirmed subsequently by exact Brownian dynamics simulations [24] [25]. The use of a FENE spring force law leads to identical behaviour, except that subsequent to the onset of shear thickening, instead of reaching a high shear rate plateau value, a second shear thinning regime is observed which continues indefinitely for increasing shear rates, and approaches power law behaviour with an exponent equal to \(-2/3 \) [26]. The initial shear thinning has been attributed to the presence of hydrodynamic interactions, while the second shear thinning regime has been associated with the finite extensibility of the chain.

A renormalisation group calculation by Öttinger [27], based on a bead-spring chain model for the polymer has shown that just the presence of excluded volume interactions alone, without either finite extensibility or hydrodynamic interactions, leads to the prediction of shear thinning in dilute polymer solutions, with a power law exponent equal to \(-0.25 \) in the limit of high shear rates. A similar exponent has been predicted by Prakash [28], who accounted for fluctuating excluded volume interactions with the help of a Gaussian approximation. These approximate predictions of the shear thinning exponent in the presence of excluded volume interactions have been validated by Brownian dynamics simulations for bead-spring chains in the long chain limit [29].

Computer simulations of the behaviour of dilute polymer solutions in shear flow, with a view to predicting viscometric functions, have been carried out with coarse-grained bead-rod and bead-spring chain models, both with and without the inclusion of hydrodynamic and excluded volume interactions. Whilst, to our knowledge, all the bead-rod chain simulations have been carried out with Brownian dynamics simulations [30] [32], bead-spring chain simulations (which use either FENE [33] [34] or wormlike chain spring force laws [15] [35]) have treated the solvent either implicitly using Brownian dynamics simulations [15] [55], or explicitly, using either nonequilibrium molecular dynamics [33] or multiparticle collision dynamics [34] simulations.

Free-draining bead-rod chain simulations, with chain lengths ranging from 20 beads [30] to 100 beads [31], predict a shear thinning exponent of \(-1/2 \) for sufficiently high shear rates. The inclusion of hydrodynamic interactions (for chains with a maximum of 20 beads) appears to decrease the exponent to a value closer to \(-0.3 \) [32]. Interestingly, Liu [30] observed that either decreasing the number of beads to 2 or using a multibead rod model leads to an exponent equal to \(-1/3 \), which is identical to the analytical prediction by Stewart and
Sorensen [17] for a rigid dumbbell model. The decrease in the predicted power law exponent is consequently purely due to the flexibility of the chain.

Two different power law regimes of shear thinning are observed in Brownian dynamics simulations of bead-spring chains with finitely extensible springs, with hydrodynamic and excluded volume interactions included [15] [35]. At intermediate Weissenberg numbers, 100 < Wi < 1000, the exponent is estimated to be close to −1/2. However, at high Weissenberg numbers, Jendrejack et al. [35] obtain an exponent equal to −2/3 (for Wi > 10^4), while Schroeder et al. [15] fit their simulation data with an exponent equal to −0.61 for Wi > 10^3. On the other hand, only a single power law regime with an exponent equal to −0.59 ± 0.02, is observed in the nonequilibrium molecular dynamics simulations of Aust et al. [33], who obtain data collapse onto a master plot when they plot their viscosity data (for different chain lengths), in terms of the ratio η/η_0 versus λ_0γ, where λ_0 is as defined above. Since the solvent is treated explicitly in these simulations, hydrodynamic interactions are automatically included. The high Weissenberg number asymptotic value of the shear thinning exponent in all these simulations is consistent with analytical results for finitely extensible chains. The multiparticle collision dynamics simulations of Ryder and Yeomans [34], who used a FENE spring force law, were not carried out to sufficiently high Weissenberg numbers in order to observe shear thinning. However, by including a bending potential which enabled them to examine the influence of chain stiffness, they find that with increasing chain stiffness, in contrast to the analytical results of Winkler [19], the viscosity shear thins with an exponent equal to −1/3, analogous to the prediction for a rigid dumbbell or multibead rod model.

A striking contrast between predictions of bead-rod and bead-spring chain simulations is that while the former predicts that the viscosity levels off at high shear rates and approaches a second constant Newtonian regime, the latter predicts that the viscosity never levels off, but rather that the power law regime persists indefinitely. These observations are valid regardless of whether hydrodynamic interactions are included or not. However, it should be noted that Petera and Muthukumar [32] seem to suggest that even in the case of bead-rod chain simulations, when both hydrodynamic and excluded volume interactions are included, the second Newtonian regime disappears, and the power law regime appears to persist, at least until the maximum value of nondimensional shear rate in their simulations of Λ_2γ ≈ 10^4. The existence of the second Newtonian regime in bead-rod simulations has been attributed to a number of different reasons. The free draining bead-rod simulations of Liu [30] show that the mean-square end-to-end distance of a chain increases with increasing shear rate until the onset of the power law regime (where the chain stretch is a maximum), followed by a continuous decrease in magnitude which coincides with the levelling off of the viscosity at high shear rates. By separating the polymer contribution to solution stress into a Brownian and a viscous contribution, Doyle et al. [31] demonstrate that power law shear thinning is caused largely by Brownian stresses, while the levelling off of viscosity at high shear rates is attributable to viscous stresses. For finitely extensible bead-spring chains, Jendrejack et al. [35] use a simple scaling argument to explain the observed power law scaling of viscosity with Weissenberg number. They first show that the viscosity scales as η/η_0 ∼ δ^3, where δ is a measure of chain length fluctuations transverse to the flow direction, and subsequently that, δ = γ^−1/3. Further, they explain the levelling off of viscosity for bead-rod chains by arguing that the predicted scaling of δ does not persist to very high shear rates due the existence of a bond length cutoff at small length scales.

While the rheological behaviour of dilute polymer solutions has been studied extensively over the years, experimental measurements [6] [13] [36] [39] and theoretical predictions [8] [39] [44] of the rheological behaviour of semidilute polymer solutions are comparatively sparse. Hur et al. [13] carried out pioneering single molecule and bulk rheological measurements on semidilute solutions of DNA in shear flow. By plotting the polymer contribution to viscosity in the Weissenberg number range, 10 < Wi < 3000, they find a power law shear thinning behaviour, η/η_0 ∼ Wi^−c, where the exponent has the values, a = 0.53, 0.43, and 0.51, for scaled concentrations, c/c_e = 1, 3, and 6, respectively, with the Weissenberg number defined in terms of the longest relaxation time, λ, as in the case of dilute solutions discussed above. Noting the similarity in dilute and semidilute solutions of the dependence of the fractional extension of a chain on strain, and the similarity in the time dependence of the power spectral density, when viewed at the same Weissenberg number, along with the similarity of shear thinning exponents, they conclude that the role of the surrounding DNA chains in a semidilute solution is to merely viscosify the solvent.

More recently, Heo and Larson [37] have examined the linear and nonlinear rheological behaviour of semidilute solutions of polystyrene in tricresyl phosphate, close to and above the entanglement concentration c_e, with a view to examining if master plots can be constructed by choosing appropriately scaling variables using the “blob” scaling arguments of de Gennes [45]. They find that in the concentration range, c_e < c < c**, where c** is the concentration above which a polymer chain obeys random walk statistics on all length scales, data for different molecular weights can be collapsed onto a universal curve when the scaled viscosity, η/η_0(c/c_e)^(3/(3−λ)), is plotted versus λcγ (in the range 10^{−4} < λcγ < 30). Here, ν is the Flory scaling exponent, and λc is the Rouse time of an entanglement strand. Interestingly, curves for different c/c_e do not collapse on top of each other. Heo and Larson [37] do not comment on the shear thinning exponent, nor the apparent decrease that is observed in the slope of the scaled viscosity curve at high values of the nondimensional shear rate.

Computing the behaviour of semidilute polymer solutions is challenging since both intra and inter molecular hydrodynamic and excluded volume interactions need to be taken into account, particularly with the former being a long-range interaction. The seminal bead-spring chain simulations by Stoltz et al. [40] (using Brownian dynamics), and Huang et al. [41] (using multiparticle collision dynamics), were the first attempts to computationally estimate viscometric functions for semidilute unentangled polymer solutions in simple shear.
flow. In both these papers, the Weissenberg number is defined as, \( \lambda_{W} = \lambda_1 \dot{\gamma} \), where \( \lambda_1 \) is the longest relaxation time obtained by fitting the decay of the mean square end-to-end distance of a chain as it relaxes from an initially extended state, to an exponential function. Huang et al. \([41]\) show explicitly from their simulations that \( \lambda_1 \), which is a function of concentration, obeys the well known scaling law, \( \lambda_1 \sim (c/c^*)^{(2-3\nu)/(3\nu-1)} \), derived from blob scaling arguments. Stoltz et al. \([40]\), in their simulations of chains with 10 beads, do not observe data collapse when they plot the scaled viscosity, \( \eta_0/\eta_0(c/c^*) \), versus \( \lambda_{W} \) for two concentrations, \( c/c^* = 1 \) and \( c/c^* = 2 \), on the same plot (though this is not entirely clear since error bars have not been reported). By converting their nondimensional simulation results to dimensional quantities (by choosing appropriate parameter values), they show that for \( c/c^* = 1 \), in the Weissenberg number range, \( 3 < \lambda_{W} < 200 \), a shear thinning exponent equal to \(-0.51\) is obtained, in close agreement with the experimental results of Hur et al. \([13]\). On the other hand, by plotting \( \eta_0/\eta_0 \) versus \( \lambda_{W} \), Huang et al. \([41]\) show that data for different values of \( c/c^* \) collapse onto a master plot, provided the chain length is held fixed. A weak dependence on chain length is observed when data for chains with 50 and 250 beads are plotted together. For large values of Weissenberg number, regardless of concentration and chain length, they observe power law shear thinning, with an exponent equal to \(-0.45\).

It is clear from the summary of experimental measurements and theoretical predictions of the shear rate dependence of the viscosity of dilute and semidilute polymer solutions given above, that there is a great deal of variation in the reported results. While there are many common elements, there are also significant differences. The aim of the present paper is to gain some understanding of the origin of these differences, and to attempt to resolve them by representing experimental data in terms of nondimensional variables that capture the underlying physics. Towards this end, we are aided by our recent experimental work in characterising the equilibrium and linear viscoelastic behaviour of DNA solutions in terms of the solvent quality \( \nu \) and the scaled concentration \( c/c^* \). Experimental measurements have been carried out on dilute and semidilute unentangled solutions of DNA with three different molecular weights, at various values of \( \nu, c/c^* \), and shear rates \( \dot{\gamma} \). We have also examined the behaviour of synthetic polystyrene solutions. In the case of dilute solutions, we have reinterpreted some of the wealth of prior experimental data on dilute polystyrene solutions in terms of the variables \( \nu, c/c^* \) and \( \lambda_{W} \dot{\gamma} \). For semidilute solutions, we have carried out experimental measurements for two different molecular weights of polystyrene dissolved in dioctyl phthalate, at various points in the space of coordinates \( \{\nu, c/c^*, \dot{\gamma}\} \). The characteristics and specific details of all the solutions are discussed in the section below.

The plan of the paper is as follows. In various subsections of section III, we briefly describe the experimental protocol for preparing the DNA and polystyrene samples, and for carrying out the viscosity measurements. In section IV, the solvent quality and overlap concentration of the DNA and polystyrene solutions studied here, and of dilute polystyrene solutions examined in prior experimental studies, is tabulated. In the latter case, details of the procedure used to estimate \( \nu \) and \( c^* \) are given in Appendix A. The shear rate dependence of dilute solutions is considered in section V, while that of semidilute solutions is considered in section VI, including the estimation of relaxation times and zero shear rate viscosities. In the case of dilute solutions, a detailed comparison is carried out of the master plots that describe the shear thinning behaviour of DNA and polystyrene solutions. In subsection VC, it is shown that the use of a conventionally defined relaxation time to construct master plots for semidilute solutions, does not lead to data collapse. A scaling argument based on blob theory is used in section VI to derive an alternative relaxation time which has a different dependence on \( c/c^* \). Some simple scaling expressions that have been derived previously for semidilute solutions at equilibrium are given in Appendix B for ease of reference. The usefulness of the alternative relaxation time in revealing the universal behaviour of semidilute solutions is examined in subsection VE. Finally, in section VI, we summarize the principal conclusions of this work.

### II. MATERIALS AND METHOD

#### A. DNA samples

Three different linear genomic DNA samples, (i) 25 kilobasepairs (kbp), (ii) \( \lambda \)-phage [48.5 kbp] and (iii) T4 bacteriophage [165.6 kbp], were used in this work at various temperatures (10 to 44.6°C) and concentrations in the dilute (0.112 to 0.0038 mg/ml) and semidilute (0.441 to 0.023 mg/ml) regimes. The 25 kbp samples were extracted, linearized, and purified from *Escherichia coli* (E. coli) stab cultures procured from Smith’s group at UCSD, who have genetically engineered special 3-300 kbp double-stranded DNA fragments. These fragments have been incorporated inside *E. coli* bacterial strains, which can be cultured to produce sufficient replicas of its DNA, which are then cut at precisely desired locations to extract the fragments. The linear genomic DNA of \( \lambda \)-phage was purchased from New England Biolabs, U.K.

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**TABLE I.** Representative properties of the 25 kbp, \( \lambda \)-phage, and T4 DNA used in this work (reproduced from Table I of Ref. \([6]\)). The contour length is estimated using the expression \( L = \text{number of basepairs} \times 0.34 \text{ nm} \); the molecular weight is calculated from \( M = \text{number of base-pairs} \times 662 \text{ g/mol} \) (where the base-pair molecular weight has been calculated for a sodium-salt of a typical DNA base-pair segment); the number of Kuhn steps from \( N_k = L/(2P) \) (where \( P \) is the persistence length, which is taken to be 50 nm), and the radius of gyration at the \( \theta \) temperature is estimated from \( R_g^2 = L/4\pi N_k \).

| DNA Size (kbp) | \( M \) (x10^6 g/mol) | \( L \) (μm) | \( N_k \) | \( R_g^2 \) (nm) |
|----------------|------------------------|-------------|----------|-----------------|
| 25             | 16.6                   | 9           | 85       | 376             |
| 48.5           | 32.1                   | 16          | 165      | 524             |
| 165.6          | 110                    | 56          | 563      | 969             |
Methylene chloride was then completely evaporated in a vacuum of polystyrene in DOP, methylene chloride was used as a solvent for polystyrene at 22°C. Samples were dissolved in DOP, which is considered a theta solvent [1.04] purchased from Varian (England). Both the polystyrene samples have been reproduced here from a similar Table in Pan et al. [6]. The DNA samples were dissolved in a solvent containing 10 mM Tris (#T1503, Sigma-Aldrich), 1 mM EDTA (#E6758, Sigma-Aldrich) and 0.5 M NaCl (#S5150, Sigma-Aldrich), which was also used for preparing subsequent dilutions. The solvent has a viscosity of 1.01 mPa.s at 20°C, which is approximately equal to the viscosity of water. For linear genomic DNAs from T4 and λ phages, with anticipated purity of high orders, concentrations of 0.24 mg/ml and 0.5 mg/ml, respectively, were used, as specified by the companies. For the 25 kbp linear DNA, the concentration of DNA (0.441 mg/ml) was determined by both UV-VIS spectrophotometry (#UV-2450, Shimadzu) and agarose gel electrophoresis, the latter by comparing with a standard DNA marker (#N0468L, New England Biolabs). The molecular weight, contour length, number of Kuhn steps, and the radius of gyration at theta-temperature, of the DNA molecules used in this work, are given in Table I [49].

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table

| Temperature (°C) | 15°C | 20°C | 25°C | 30°C | 35°C |
|-----------------|------|------|------|------|------|
| 25 kbp          |      |      |      |      |      |
| z               | 0    | 0.33 | 0.64 | 0.95 | 1.24 |
| $c^*$           | 0.123 | 0.084 | 0.068 | 0.059 | 0.052 |
| 48.5 kbp        |      |      |      |      |      |
| z               | 0    | 0.45 | 0.89 | 1.32 | 1.73 |
| $c^*$           | 0.088 | 0.055 | 0.043 | 0.037 | 0.032 |
| 165.6 kbp       |      |      |      |      |      |
| z               | 0    | 0.84 | 1.65 | 2.44 | 3.20 |
| $c^*$           | 0.048 | 0.024 | 0.018 | 0.015 | 0.013 |

B. Polystyrene samples

As discussed in the introduction, two different approaches have been adopted here with regard to polystyrene samples. In the case of dilute solutions, we have adopted the previously published results of Inagaki and coworkers [7,9]. Noda et al. [8] and Hua and Wu [12], since it is possible to convert the data reported in their work to the framework adopted in this paper, namely, representation of the results in terms of the non-dimensional variables ($z$, $c^*$, $\lambda_2/\gamma$). The conversion procedure is discussed in detail in Appendix A with some of the relevant parameters reproduced here, wherever relevant. Details of polymer sample sources, the polydispersity index, and sample preparation procedure have been given in the original references, to which we refer the reader.

In the semidilute regime, we have carried out experiments on two linear polystyrene polymers: (i) with molecular weight $1.14 \times 10^6$ g/mol (1.1 M) and a polydispersity index (PDI) = 1.09 purchased from Polymer Source Inc. (Canada) and (ii) with molecular weight $1.54 \times 10^7$ g/mol (15.4 M) (PDI = 1.04) purchased from Varian (England). Both the polystyrene samples were dissolved in DOP, which is considered a theta solvent for polystyrene at 22°C [49]. To assist with the dissolving of polystyrene in DOP, methylene chloride was used as a co-solvent and the mixture was mixed for 24 hours. Methylene chloride was then completely evaporated in a vacuum oven at 40°C over the course of several days until no further weight loss was registered.

C. Shear rheometry

A Contraves Low Shear 30 rheometer (1T/1T – cup and bob; shear rate range: 0.01–100 s⁻¹; temperature sensitivity: ± 0.1°C) has been used to obtain all the shear viscosity measurements reported in the present work. The Contraves Low Shear 30 rheometer has two main advantages: it has a zero shear rate viscosity sensitivity even at a shear rate of 0.017 s⁻¹ and thus can measure very low viscosities; and has a very small sample requirement (minimum 800 μl) [36]. These advantages are ideal for measuring the viscosities of DNA solutions. The measuring principles underlying the Contraves rheometer have been detailed in a recent study [36]. The rheometer was calibrated with Newtonian Standards (silicone oils) of known viscosities (around 10, 100 and 1000 mPa-s at 20°C), and the zero error adjustment was carried out as described earlier in Ref. [6]. Values obtained fall within 5% of the company specified values. A continuous shear ramp was avoided, and to avoid the problem of aggregation of long DNA chains, λ and T4 DNA (at their maximum concentrations) were kept at 65°C for 10 minutes and instantly put into ice for 10 minutes [36,38]. A manual delay of 30 seconds was applied at each shear rate to allow the DNA chains to relax to their equilibrium state and the sample was equilibrated for 30 minutes at each temperature. Some typically observed relaxation times are given in Table I of Ref. [6]. We have also established that the measured viscosity does not depend on rheometer geometry in the range of shear rates employed (in terms of the ‘gap’ between the cup and the bob), by measuring the viscosity of T4 DNA at two different gaps at two different temperatures, as elaborated in our earlier work [46].

III. SOLVENT QUALITY AND OVERLAP CONCENTRATION

The state of a polymer solution at equilibrium is completely determined by the solvent quality parameter $z$, defined by the
expression [2],

\[ z = k \left(1 - \frac{T_\theta}{T}\right) \sqrt{M} \]  

(2)

(where \( k \) is a chemistry dependent constant, and \( T_\theta \) is the \( \theta \)-temperature), and the overlap concentration \( c^* \), which is defined by the expression [3],

\[ c^* = \frac{M}{\left(\frac{4\pi}{3}\right) R_g^2 N_A} \]  

(3)

(where \( R_g \) is the radius of gyration). The values of \( z \) and \( c^* \) for all the solutions for which experimental measurements of viscosity have been reported in this work are tabulated below, firstly for DNA solutions, and subsequently for the various sets of polystyrene solutions.

A. DNA solutions

The value of \( z \) at any temperature and molecular weight can be determined from Eq. (2) if the values of \( k \) and \( T_\theta \) are known. The procedure for determining the value of \( k = 0.0047 \pm 0.0003 \mathrm{~g/mol} \cdot \mathrm{mol}^{-1/2} \), and \( T_\theta = 15 \ C \), for the DNA solutions used in this study, has been discussed extensively in Ref. [6]. Typical values of \( z \) for the three DNA samples used here, at various values of \( T \), are reported in Table I.

The radius of gyration can be determined from the expression \( R_g = R_g^0 \alpha_g(z) \), for any \( M \) and \( T \), where \( \alpha_g(z) \) is the universal swelling of the radius of gyration for dilute polymer solutions [2]. Since the chain conformations at the \( \theta \) temperature are expected to be ideal Gaussian chains, the analytical value for the radius of gyration at \( T_\theta \) is, \( R_g^0 = L/\sqrt{6N_k} \). We have consequently used the respective values of \( L \) and \( N_k \) for all the molecular weights used here, to determine \( R_g^0 \) (as displayed in Table I). Further, since we know \( z \), \( \alpha_g \) can be determined from the expression \( \alpha_g = (1 + a z + b z^2 + c z^3)^{m/2} \), where the constants, \( a = 9.528, b = 19.48, c = 14.92, \) and \( m = 0.1339 \) have been obtained by Brownian dynamics simulations [30]. Representative values of \( c^* \) found using this procedure, at various \( M \) and \( T \), are displayed in Table II. The validity of the values of \( R_g \) (and consequently \( c^* \)) determined by this procedure has been discussed by Pan et al. [6].

B. Polystyrene solutions

1. Ultradilute solutions in the limit \( c/c^* \to 0 \)

Inagaki and coworkers [7, 9] and Noda et al. [8] have carried out viscosity measurements on a series of dilute polystyrene solutions. Using Zimm-Crothers and Ubbelohde viscometers, they have estimated the intrinsic viscosity [\( \eta \)] by extrapolating finite concentration data to the limit of zero concentration. With this procedure, they have tabulated measured values of the ratio [\( \eta \)]/[\( \eta \)]_0 as a function of \( \lambda c \). (This data is discussed further in section [14B] below). For the present it suffices to note that since measurements are reported in the ultradilute limit, \( c/c^* \to 0 \), it is not necessary to estimate \( c^* \) for these solutions.

The solvent quality of the solutions used in Refs. [7, 8], and [9] can be determined from values of the swelling of the intrinsic viscosity, \( \alpha_g = ([\eta]_0 [\eta]_0)_0^{1/3} \), which have been reported for most of the samples. The universal swelling of the radius of gyration \( \alpha_g \), as a function of the solvent quality \( z \), has been determined by Brownian dynamics simulations for dilute polymer solutions [46], and the simulation data has been shown to satisfy the expression \( \alpha_g = (1 + a z + b z^2 + c z^3)^{m/2} \), where the values of the constants are: \( a = 5.448, b = 3.156, \)

| Solvent         | \( M \) (\( \times 10^6 \mathrm{~g/mol} \)) | \( L \) (\( \mu \mathrm{m} \)) | \( N_k \) | \( T \) (\( ^\circ \mathrm{C} \)) | \( z \)       |
|-----------------|----------------------------------------|--------------------------|--------|------------------|-----------|
| Benzene         | 7.14                                  | 17.85                    | 9917   | 13.6             |
| 1-Chlorobutane  | 3.16                                  | 7.90                     | 4389   | 9.0              |
| Toluene         | 3.16                                  | 13.9                     | 3.48   | 6.0              |
| Mix-decalin     | 13.6                                  | 34                       | 18889  | 38 \( (\theta) \)  |
|                 |                                        |                          |       | 5.1              |
|                 |                                        |                          |       | 0                |

TABLE III. Solvents, polystyrene molecular weights, contour lengths, number of Kuhn steps, temperatures and solvent qualities of the samples used in the experiments of Inagaki and coworkers. [7, 9] (superfix a) and Noda et al. [8] (superfix b). In the latter work, a mixture of cis and trans isomers of the solvent decalin has been used, with 60% of the cis isomer. Note the difference in the \( \theta \)-temperature reported for decalin in the two works. The number of Kuhn steps is estimated based on the molar mass of a Kuhn monomer for polystyrene (720 g/mol), and the contour length is calculated from the length of a single Kuhn step (1.8 nm) [5].

| Solvent         | \( M \) (\( \times 10^6 \mathrm{~g/mol} \)) | \( L \) (\( \mu \mathrm{m} \)) | \( N_k \) | \( T \) (\( ^\circ \mathrm{C} \)) |
|-----------------|----------------------------------------|--------------------------|--------|------------------|
| PS1             | 0.55                                  | 1.38                     | 764    | \( 0.044 \) 0.17 | 0.30     |
| PS2             | 0.68                                  | 1.70                     | 944    | \( 0.046 \) 0.19 | 0.33     |
| PS3             | 0.93                                  | 2.33                     | 1292   | \( 0.053 \) 0.22 | 0.38     |
| PS4             | 2                                     | 5.0                      | 2778   | \( 0.078 \) 0.33 | 0.56     |

TABLE IV. Molecular weights, contour lengths, number of Kuhn steps, solvent quality and overlap concentration (in g/ml) for dilute polystyrene samples PS1 to PS4 used in Ref. [12], at various temperatures \( T \). The contour length and the number of Kuhn steps are calculated as described in the caption to Table III.
TABLE V. Molecular weights, contour lengths, number of Kuhn steps, solvent quality parameter and overlap concentration (in mg/ml) for polystyrene solutions PS1.1M and PS15.4M, used to carry out viscosity measurements in the semidilute regime, at various temperatures. The $\theta$-temperature is taken to be 22°C. The contour length and the number of Kuhn steps are calculated as described in the caption to Table III.

| $M$ (×10^6 g/mol) | $L$ (nm) | $N_k$ | $T$ (°C) |
|------------------|---------|-------|--------|
| 156 100 50       | 2.25   | 1528  | 22     |
| 250 150 75       | 2.75   | 1528  | 30     |
| 350 200 100      | 3.25   | 1528  | 35     |

TABLE VI. Intrinsic viscosities $[\eta]_0$ (in ml/mg) for 25 kbp, λ-phase DNA, and T4 DNA at various temperatures $T$. The relaxation time $\lambda_T$ (in s) is also listed for each DNA and has been calculated from Eq. (1).

| $T$ (°C) | $[\eta]_0$ (λ-phase DNA) | $\lambda_T$ (in s) |
|---------|------------------------|-------------------|
| 15      | 0.059                  | 0.252             |
| 25      | 0.060                  | 0.307             |
| 30      | 0.067                  | 0.311             |
| 35      | 0.064                  | 0.310             |

TABLE VII. Intrinsic viscosities $[\eta]_0$ (in ml/mg) and relaxation times $\lambda_T$ (in s) for the polystyrene solutions used in Ref. [12].

| $T$ (°C) | PS1 | PS2 | PS3 | PS4 |
|---------|-----|-----|-----|-----|
| 22      | 0.072 0.0011 | 0.082 0.0015 | 0.096 0.0024 | 0.142 0.0076 |
| 25      | 0.075 0.0009 | 0.086 0.0013 | 0.101 0.0021 | 0.153 0.0067 |
| 30      | 0.083 0.0006 | 0.096 0.0008 | 0.115 0.0013 | 0.180 0.0045 |
| 35      | 0.090 0.0004 | 0.104 0.0005 | 0.125 0.0009 | 0.201 0.0031 |

### 3. Solutions at finite concentrations above $c^*$

It is necessary to evaluate the solvent quality and the overlap concentration for the two linear polystyrene polymers with molecular weights $1.14 \times 10^6$ g/mol (PS1.1M) and $1.54 \times 10^6$ g/mol (PS15.4M), which have been used for the experiments in the semidilute regime, in order to locate the samples in the space of coordinates ($z, c/c^*, \lambda_T$). The properties are evaluated from the properties of the solution in the dilute regime. The solvent quality $z$ for these solutions can be calculated using the value of $k$ for polystyrene/DOP solutions determined as discussed in Appendix A. Since the dependence on molecular weight of the intrinsic viscosity at the theta temperature is known from fitting the data reported in Ref. [12] ($[\eta]_0 \sim M^{0.52}$), the values of $[\eta]_0$ for the PS1.1M and PS15.4M solutions can be determined. Using the procedure described in Appendix A it follows that the values of $[\eta]_0$, and consequently $c^*(z)$ can be determined at the three temperatures, 22, 30, and 35°C, at which the viscosity measurements have been carried out. The values of $z$ and $c^*$ found in this manner are listed in Table IV.

### 4. Dilute solutions

For the purpose of examining the universality of the viscosity versus shear rate data for dilute polymer solutions, we need the relaxation time $\lambda_T$ in order to non-dimensionalize the shear rate, and the zero shear rate viscosity $\eta_0$ in order to non-dimensionalize the polymer contribution to viscosity. The values of these two quantities, for the various solutions considered here, are discussed below before assessing the existence of master plots.

#### A. Relaxation time $\lambda_T$ and zero shear rate viscosity $\eta_0$

#### 1. DNA solutions

By appropriately extrapolating concentration dependence functions of the zero shear rate viscosity to zero concentration, Pan et al. [46] have previously determined the intrinsic viscosity $[\eta]_0$ for the 25 kbp and T4 DNA solutions used here. For λ-phase DNA (which is not discussed in Ref. [46]), the intrinsic viscosity $[\eta]_0$ at the θ-temperature $T_0$ was determined here by following the same procedure. The value of $[\eta]_0$ for
\( \lambda \)-phage DNA at all other temperatures has been calculated using the expression \( \eta = [\eta_0]^3 = [\alpha_\eta(z)]^3 \), with \( \alpha_\eta(z) \) being the universal swelling of the viscosity radius obtained by Brownian dynamics simulations [46], discussed in section III B 1 above. It was established in Ref. [46] that the swelling of the viscosity radius of DNA solutions in the presence of excess salt can be collapsed onto universal master plots determined previously for synthetic polymer solutions. The values of \( \eta_0 \) obtained by this procedure at different temperatures, for all three samples of DNA, are listed in Table VI.

The relaxation times \( \lambda _z \), which can be easily determined from Eq. (1) using the known values of \( \eta_0 \) for all the three DNA solutions, are listed at the various experimentally relevant temperatures in Table VI.

The zero shear rate solution viscosity, \( \eta_0 \), for dilute 25 kbp and T4 DNA solutions was determined by us previously by least-square fitting the values of viscosity in the plateau region of very low shear rates (across a range of temperatures and concentrations below \( c^* \)), and extrapolating to zero shear rate [46]. Values of \( \eta_0 \) for \( \lambda \)-phage DNA have been determined here by following the same procedure. Data for all the three DNA samples, for various values of \( c/c^* \) and \( T \), are displayed in Table I of the supplementary material.
2. Polystyrene solutions

Since Inagaki and coworkers [10] and Noda et al. [11] have directly listed values of the ratio $|\eta|/|\eta|_0$ as a function of $\lambda_Z \dot{\gamma}$ in their papers, it is not necessary to evaluate $\lambda_Z$ or $\eta/\eta_0$ for their polystyrene solutions. On the other hand, as described in Appendix A, the data presented by Hua and Wu [12] can be used to determine the values of $|\eta|_0$ and $\lambda_Z$ for the solutions used in their work. These values are reproduced in Table VII for ease of reference, and for comparison with the values for DNA solutions in Table VII.

The steady state solution shear viscosity, $\eta$, was measured for the polystyrene solutions PS1 to PS4 by Hua and Wu [12] across a range of temperatures. As in the case of DNA solutions, we have extracted the zero shear rate viscosities $\eta_0$ at each temperature by least-square fitting the values of viscosity in the plateau region of very low shear rates, and extrapolating to zero shear rate. Estimating the solvent viscosity, $\eta_s$, for the dioctyl phthalate solutions (as described in Appendix A), values of the polymer contribution to steady state zero shear rate viscosity, $\eta_0$, have been obtained for all the polystyrene solutions used by Hua and Wu [12]. Data obtained in this manner, for various values of $c/c^*$ and $T$, are displayed in Table II of the supplementary material.

B. Dependence of viscosity on shear rate

The steady state solution viscosity $\eta$ of the three DNA solutions was measured as a function of shear rate $\dot{\gamma}$ for a variety of concentrations in the dilute regime, and across a temperature range in the crossover regime from $\theta$ to good solvents (15–35°C). While the dependence of $\eta$ on $\dot{\gamma}$ at fixed concentration and at various temperatures is displayed in Figs. 1(a), (c) and (e), the dependence at fixed temperature and various concentrations is shown in Figs. 1(b), (d) and (f). The general pattern of the viscosity curves is typical of the behaviour observed for polymer solutions, with a constant plateau region at low shear rates denoting Newtonian behaviour, followed by shear thinning at high shear rates. For each of the DNA, the viscosity can be seen to decrease with increasing temperature, at a fixed concentration. However, a change in the temperature does not appear to significantly affect the shear rate at which the onset of shear thinning occurs. On the other hand, at a fixed temperature, the viscosity increases with increasing concentration, and the increase in concentration appears to decrease the shear rate at which the onset of shear thinning occurs.

The data in Figs. 1(a) (along with additional measurements) is replotted in Figs. 2(a) to (c) in terms of the non-dimensional variables $\eta/\eta_0$ and $\lambda_Z \dot{\gamma}$, where the temperature dependence is represented in terms of the solvent quality $z$, and the concentration dependence in terms of the scaled concentration $c/c^*$. Though there is a degree of scatter, the data appears to collapse onto master curves, independent of solvent quality and concentration. The collapse of data for different temperatures is similar to earlier observations by Kotaka et al. [17] and Suzuki et al. [18]. In particular, the large difference be-
between the viscosity curves in $\theta$ and good solvents observed by Noda et al. [8], is not reflected in Figs. 2(a) to (c).

Several aspects of the data displayed in Figs. 2(a) to (c) are worth noting in the context of previous observations of shear thinning in dilute polymer solutions. First, the shear thinning exponent in all cases is less than $-2/3$, which is the known limiting value for finitely extensible chains. Second, none of the curves level off at the highest shear rates measured here. Finally, the onset of shear thinning occurs at higher values of $\lambda_{Z}\dot{\gamma}$ with increasing molecular weight of the DNA chains. This last observation is more clearly displayed in Fig. 3 where selected data for all the three DNA samples is plotted together in a single graph. The increase, with increasing molecular weight, in the value of $\lambda_{Z}\dot{\gamma}$ at which the viscosity begins to decrease, is in line with the earlier observations of Noda et al. [8] for poly($\alpha$-methyl-styrene). Since the largest non-dimensional shear rates measured here are of $O(10^2)$, the data in Figs. 2(a) to (c) is probably still in the crossover region, and the shear thinning exponent may approach the limiting value of $-2/3$ only at much higher shear rates. In the crossover regime, the slope of the viscosity curve varies from 0 in the Newtonian regime to $-2/3$ in the finite extensibility limit. The difference in the power law slopes for the three DNA samples is probably due to their being determined over different ranges of shear rates in the crossover regime. All these aspects are discussed in greater detail after considering the data displayed in Fig. 4.

Figure 4 displays the scaled viscosity versus non-dimensional shear rate measurements for dilute polystyrene solutions, reported previously in Refs. [7], [8], [9], and [12], in terms of the variables $z$ and $c/c^*$. It is clear that the onset of shear thinning occurs for shear rates in the range $1 \leq \lambda_{Z}\dot{\gamma} \leq 2$, independent of the molecular weight. Though there is a degree of scatter in the data (roughly of order 5% about the mean), there is considerable overlap in the non-dimensional viscosity values for $\lambda_{Z}\dot{\gamma} \lesssim O(2)$, independent of solvent quality. All the data of Kotaka et al. [7] and Suzuki et al. [9], and the data of Noda et al. [8] for the particular case of polystyrene in toluene, seem to agree with that of Hua and Wu [12] up to $\lambda_{Z}\dot{\gamma} \sim O(3)$. However, for polystyrene in decalin (which is a $\theta$-solvent), the data of Noda et al. [8] seems to suggest that shear thinning stops beyond $\lambda_{Z}\dot{\gamma} \sim O(2)$, and the viscosity levels off at higher shear rates. There is significantly more variation in the behaviour of polystyrene samples whose viscosity was measured at nondimensional shear rates greater than $\lambda_{Z}\dot{\gamma} \sim O(3)$. Firstly, the shear thinning of the 13.6 million molecular weight sample of polystyrene in toluene [8] appears to be considerably less than that of all the polystyrene samples considered by Hua and Wu [12], with the viscosity levelling off at high shear rates. Some levelling off can also be seen in the data of Hua and Wu [12] for the 2 million molecular weight samples with increasing solvent quality. At the $\theta$-temperature, the power law shear thinning exponent for the 2 million molecular weight sample seems to be at the limiting value of $-2/3$. Finally, the trend in the data of Hua and Wu [12] is clearly contradictory to that of Noda et al. [8] with regard to the influence of solvent quality. While the former predicts a decrease in shear thinning with increasing solvent quality (most apparent for the 2 million molecular weight sample), the latter predicts an increase with increasing solvent quality (note the molecular weight in the latter case is 13.6 million).

It is challenging to make sense of the wide range of behaviour displayed by the dilute polystyrene samples in Fig. 4 and the comparatively less varied behaviour observed for the dilute DNA samples considered here (displayed in Figs. 2 and 3). It is clear that, when $\eta_0/\eta_\infty$ is plotted versus $\lambda_{Z}\dot{\gamma}$ for various values of $z$ and $c/c^*$, data collapse onto master plots, independent of temperature and concentration, is observed, (i) at all values of shear rate in the case of DNA, and (ii) only for shear rates $\lambda_{Z}\dot{\gamma} \lesssim O(2)$ for polystyrene solutions. The delay in the onset of shear thinning with increasing molecular weight, which is clearly observed for DNA solutions, is not observed for polystyrene solutions, though it has been ob-
served by Noda et al. [8] for poly(α-methyl-styrene). The complex dependence of viscosity on shear rate predicted by models that include consistently-averaged, or fluctuating hydrodynamic interactions, can be invoked to understand some of the observed behaviour. According to these models, the presence of hydrodynamic interactions delays the onset of shear thinning due to finite extensibility, with the shear rate at which chains become aware of their finiteness increasing with increasing chain length. This would then explain the observed delay in the onset of shear thinning with increasing molecular weight. However, the theoretical models also predict shear thickening due to the presence of hydrodynamic interactions, but no shear thickening is apparent in the data for DNA presented here. It is worth noting that the contour lengths of most of the polystyrene samples considered here (displayed in Tables III and IV) are significantly smaller than the contour lengths of the DNA samples (see Table I). The exception is the 13.6 million molecular weight sample of Noda et al. [8], whose contour length of 34 μm lies between that of λ-phage (16 μm) and T4 DNA (56 μm). Indeed this difference from all the other polystyrene samples might explain to some extent the reduced shear thinning of this sample, with shear thinning due to finite extensibility probably occurring only at much higher shear rates.

In spite of the wealth of data that has been accumulated on the shear rate dependence of the viscosity of dilute polymer solutions, it is clear that there are yet many unanswered questions, and there is still a need for more systematic experiments that are able to clearly address the roles of excluded volume interactions, hydrodynamic interactions and finite extensibility in determining the nature of the dependence.

V. SEMIDILUTE SOLUTIONS

A. Dependence of viscosity on shear rate

Fig. 5 displays the dependence of the scaled viscosity \( \eta_p/\eta_0 \) on the shear rate \( \dot{\gamma} \), for 25 kbp, λ-phage, and T4 DNA, while Fig. 6 displays the same dependence for the two
FIG. 6. The ratio $\eta_p/\eta_{p0}$ as a function of shear rate $\dot{\gamma}$, for semidilute solutions of linear 1.1 M and 15.4 M polystyrene samples, each at a fixed absolute concentration and at different temperatures. The temperatures are indicated in the legends and the concentrations are mentioned in individual figures. The values of $c/c^*$ and $\eta_0$ corresponding to the various cases are listed in Table IV of the supplementary information.
polystyrene samples examined in this work, i.e., PS1.1M and PS15.4M, in the semidilute regime. Values of \( \eta_p \) for all the samples have been determined identically as in the case of all the other solutions considered here, and are displayed in Tables III and IV of the supplementary information, for DNA and polystyrene, respectively. Each of the subfigures in these plots corresponds to a different concentration, with the individual symbols in the subfigures representing different temperatures. All the displayed concentrations correspond to solutions in the semidilute regime, as can be confirmed from the values of \( c/c^* \) listed in Table III and IV of the supplementary information. The reason the scaled viscosity appears to increase with temperature is because of the division of \( \eta_p \) by \( \eta_{p0} \). While, as expected, \( \eta_p \) decreases with increasing temperature (see Fig. 1 (a) of the supplementary information for the behaviour of 25 kbp DNA), the shear rate dependence of \( \eta_p \) is more pronounced over the same range of shear rates, for solutions at a lower temperature.

In order to construct master plots from the data displayed in Figs. 5 and 6 it is necessary to non-dimensionalize the shear rate \( \dot{\gamma} \) by multiplying it with a suitable relaxation time. The choice of relaxation time is considered in the section below.

B. Relaxation time \( \lambda_\eta \)

It is common, both in single molecule experiments\(^{[13]}\,^{[38]}\,^{[51]}\) and in computations\(^{[40]}\,^{[41]}\,^{[44]}\) involving semidilute solutions, to define the Weissenberg number in terms of the longest relaxation time \( \lambda_1 \). In the case of bulk rheological measurements, however, it is more convenient to use a relaxation time, \( \lambda_\eta \), defined in terms of the polymer contribution to the zero shear rate viscosity\(^{[6]}\),

\[
\lambda_\eta = \frac{M \eta_{p0}}{cN_A k_B T}
\]

Note that, in the limit \( c \to 0 \), \( \lambda_\eta \to \lambda_Z \). Defining the Weissenberg number in terms of either \( \lambda_1 \) or \( \lambda_\eta \) is entirely equivalent since they both have the same dependence on concentration in the semidilute regime\(^{[6]}\,^{[38]}\), and their ratio is a universal constant\(^{[6]}\).

The values of \( \lambda_\eta \) for all the semidilute DNA and polystyrene solutions considered here can be obtained using Eq. (4), and the values of \( \eta_{p0} \) listed in Tables III and IV of the supplementary information. As noted in Appendix A, the ratio \( (\eta_{p0}/M) \) is found to depend linearly on inverse temperature \((1/T)\), for dilute DNA and polystyrene solutions. Figs. 7 (a) and (b) show that, interestingly, there appears to be a linear relationship between \( \lambda_\eta \) and \((1/T)\), for semidilute DNA and polystyrene solutions, in the range of concentrations and temperatures considered here. Additional data at other concentrations in the semidilute regime displaying similar behaviour is shown in Figs. 2 and 3 of the supplementary information.

Pan et al.\(^{[6]}\) have recently determined the universal scaling function that governs the zero shear rate viscosity of unentangled semidilute DNA solutions, in the double crossover regime defined by the variables \( \{z, c/c^*\} \). They showed that, independent of the DNA molecular weight, the zero shear rate viscosity obeys a power law, \( \eta_{p0}/\eta_{p0}^* = (c/c^*)^{(3\nu_{eff}-1)} \), where \( \eta_{p0}^* \) is the value of \( \eta_{p0} \) at \( c = c^* \), and the effective power law exponent, \( \nu_{eff} \), depends on the solvent quality \( z \). It follows from Eq. (4), that the relaxation time \( \lambda_\eta \) must obey the scaling law,

\[
\frac{\lambda_\eta}{\lambda_\eta^*} \sim \left( \frac{c}{c^*} \right)^{2-3\nu_{eff}(z)-1}
\]

where \( \lambda_\eta^* \) is the value of \( \lambda_\eta \) at \( c = c^* \). The concentration dependence of the ratio, \( \lambda_\eta/\lambda_\eta^* \), for the three different molecular
weights of DNA, is presented in Fig. 8 for four different values of the solvent quality $z$. Note that in order to maintain the same value of solvent quality across the various molecular weights, it is necessary to carry out experiments at the appropriate temperature for each molecular weight. Clearly, provided $z$ is the same, the data collapses onto universal power laws, independent of DNA molecular weight. The exponent $(2 - 3\nu_{\text{eff}})/(3\nu_{\text{eff}} - 1)$ can be calculated, at each of the values of $z$, using the values of $\nu_{\text{eff}}(z)$ determined previously by Pan et al. [6]. The lines through the symbols in Fig. 8 have been drawn with their slopes obtained in this manner. The dependence on $(c/c^*)$, predicted by the scaling law Eq. (5), is evidently obeyed.

C. Time-temperature superposition

The dependence of the scaled viscosity $\eta_p/\eta_{p0}$ on the Weissenberg number $\lambda_\eta \dot{\gamma}$ is displayed in Figs. 9 for the 25 kbp, $\lambda$-phage and T4 DNA samples, and in Fig. 10 for the 1.1 M and 15.4 M polystyrene samples, respectively. There are several striking features in these figures that we discuss in turn.

The first noticeable fact is that the various curves for $\eta_p/\eta_{p0}$ at different temperatures, but at the same concentration collapse on top of each other when the data is represented in this form, both for the DNA and the polystyrene solutions. This implies that using $\lambda_\eta$ as the relaxation time to non-dimensionalize the shear rate leads to time-temperature superposition, i.e., all the different curves seen in the individual subfigures of Figs. 9 and 10 collapse on to a single curve for each concentration, independent of temperature.

The most significant aspect of Figs. 9 for DNA and Figs. 10 for polystyrene, is that the data does not collapse on to master curves, independent of $c/c^*$ or molecular weight, as has been observed previously in simulations [41]. Nor is the slope in

FIG. 8. Universal crossover scaling of the relaxation time $\lambda_\eta$. The quantity $\lambda_\eta^c$ is defined as the value of $\lambda_\eta$ at $c = c^*$. In order to display all the measurements on a single plot, the ratios of relaxation times for the different values of $z$ have been multiplied by different fixed factors as indicated. Lines through the data have been drawn with a slope calculated using the values of $\nu_{\text{eff}}(z)$ determined previously for the zero shear rate viscosity (see Table IV in Ref. [6]).

FIG. 9. Dependence of the scaled polymer contribution to shear viscosity, $\eta_p/\eta_{p0}$, on the Weissenberg number, $\lambda_\eta \dot{\gamma}$, at different temperatures and concentrations, for (a) linear 25 kbp, (b) $\lambda$-phage, and (c) T4 DNA. The lines are least square fits of data in the shear thinning region.
FIG. 10. Dependence of the scaled polymer contribution to shear viscosity, $\eta_p/\eta_{p0}$, on the Weissengberg number, $\lambda_\gamma \dot{\gamma}$, at different temperatures and concentrations, for (a) linear 1.1 M polystyrene, and (b) linear 15.4 M polystyrene.

FIG. 11. Slope of $\eta_p/\eta_{p0}$ versus $\lambda_\gamma \dot{\gamma}$ as a function of absolute concentration $c$, obtained from the curves in Figs. 9 for DNA, and from the curves in Fig. 10 for polystyrene.

D. The derivation of an appropriate relaxation time

Within the blob scaling ansatz for semidilute solutions, the confirmation of a polymer chain at equilibrium consists of a series of 'correlation' blobs, with size $\xi_c$, such that chain segments below this length scale are under dilute solution conditions, while segment chains at larger length scales experience concentrated solution conditions. As a result, within a correlation blob, chain segments interact with each other through hydrodynamic and excluded volume interactions, while both these interactions are absent between correlation blobs themselves. On length scales larger than $\xi_c$, the absence of excluded volume interactions leads to chains obeying random walk statistics. Further, since the correlation blobs are space filling, the behaviour of an unentangled semifluid solution can be considered to be equivalent to that of a melt of Rouse chains of correlation blobs. This simple picture of semifluid solutions at equilibrium can be used to derive scaling laws for several different properties [3,45]. Here, we consider semidilute solutions in the presence of shear flow, and use the blob picture to derive what the concentration dependence of a large scale relaxation time might be. Some of the equilibrium scaling laws that are useful for this purpose are reproduced in Appendix [5] for ease of reference.

Consider a system of chains with $N$ monomers each, in the semidilute concentration regime, undergoing simple shear flow at a shear rate $\dot{\gamma}$. Under these conditions, it is envisaged...
that the chain breaks up into a series of ‘Pincus’ blobs (as depicted schematically in Fig. 12), where the blob size $\xi$ sets the length scale at which the stretching energy of the chain segment within the Pincus blob is equal to $k_B T$ \[52\]. Clearly, with the onset of flow, it is the chain of correlation blobs that breaks up into a sequence of Pincus blobs, and one can consider each Pincus blob to consist of $m$ correlation blobs. As a result, random walk statistics dictate that,\[\xi_S = \xi_c m^{1/2}\] (6)

One can obtain an estimate of $m$, and its dependence on the shear rate as follows. We know that the stretching energy of chain segment within a Pincus blob is of order $k_B T$. As a result,\[f\xi_S = k_B T\] (7)

where $f$ is the stretching force on the chain. The stretching force arises due to the drag exerted by the flowing solvent on the segment within the Pincus blob. The drag force is equal to the velocity difference across a Pincus blob times the friction coefficient of a Pincus blob, $\xi_S$. The velocity difference is equal to $\dot{\gamma}\xi_S$, and $\xi_S = m\xi_c$ (where $\xi_c$ is the friction coefficient of a correlation blob) since the correlation blobs obey Rouse dynamics. As a result, from Eq. (7),\[f = (\dot{\gamma}\xi_S)m\eta\xi_c\] (8)

Substituting Eq. (8) into Eq. (7) leads to,\[m\dot{\gamma}\xi_c^2\eta_0\xi_c = k_B T\] (9)

From Eq. (6), it follows that,\[m^2\dot{\gamma}\xi_c^3\eta_0 = k_B T\] (10)

or\[m = \left(\frac{k_B T}{\eta_0\xi_c^3}\right)^{1/2}\] (11)

Using the expression for the relaxation time of a correlation blob, $\tau_c$, in Eq. (B12), we get,\[m = (\tau_c\dot{\gamma})^{-1/2}\] (12)

The number of correlation blobs within a Pincus blob decreases with increasing shear rate, as might be expected, since the size of the Pincus blob decreases with increasing shear rate.

The recognition of the inverse shear rate dependence of the Pincus blob size is responsible for the development of a scaling model to explain shear thinning in polymer melts by Colby and coworkers \[53\]. We adopt their arguments (with some important differences) to develop an expression for the shear rate dependence of $\eta_p$ in semidilute solutions, and by this means, come up with the choice of an appropriate concentration dependent relaxation time.

According to Rouse theory, when $\tau_{\text{chain}}\dot{\gamma} < 1$, the shear viscosity of a polymer melt is given by the expression,\[\eta = k_B T\left(\frac{\tilde{c}}{N}\right)\tau_{\text{chain}}\sum_{p=1}^{N} \frac{1}{p^2}\] (13)

where $\tilde{c}$ is the number of monomers per unit volume, $N$ is the number of monomers per chain, $\tau_{\text{chain}}$ is the relaxation time of the chain, and the sum is carried out over the $N$ normal modes of the chain. It is appropriate to recall here that the ‘$p$’th mode corresponds to a segment of the chain containing $(N/p)$ monomers. Colby and coworkers \[53\] argue that in a shear flow, the chain breaks up into a series of Pincus blobs that are aligned in the flow direction, i.e., the chain forms a ‘blob’ pole, unlike when the chain ends are separated by a stretching force, in which case the chain is a directed random walk of Pincus blobs (which was the original Pincus \[52\] scenario).

Since the stretching energy is less than $k_B T$ within the Pincus blob, the conformation of the chain segment within the blob is unperturbed from its equilibrium configuration. According to Colby and coworkers, the Rouse expression for the viscosity (Eq. (13)) only applies to chain segments within the Pincus blob, since they are the ones contributing to viscous dissipation, while the segments on larger length scales are stretched and store energy elastically. Colby et al. \[53\] derive an alternative expression for the viscosity by changing the lower bound of the summation in Eq. (13) to the mode number cor-
molecular weights (25–165.6 kbp) can be collapsed onto a single master curve when represented in terms of a Weissenberg number that is based on the relaxation time defined by Eq. (13). (a) 25 kbp DNA, (b) λ-phage DNA, and (c) T4 DNA. The value of \( \nu_{\text{wv}} \) corresponding to the particular value of \( z \) has been used in the definition of the relaxation time.

**FIG. 13.** Universal shear thinning of semidilute DNA solutions, independent of concentration and solvent quality, at shear rates \( \lambda \gamma \gg 1 \), when represented in terms of a Weissenberg number that is based on the relaxation time defined by Eq. (13). (a) 25 kbp DNA, (b) λ-phage DNA, and (c) T4 DNA. The value of \( \nu_{\text{wv}} \) corresponding to the particular value of \( z \) has been used in the definition of the relaxation time.

**FIG. 14.** (a) Representative data for all three DNA molecular weights showing that the terminal slope at high shear rates decreases with increasing molecular weight. (b) Data collapse across molecular weights, concentrations and solvent quality, when the polymer contribution to viscosity \( \eta_p \) is scaled by \( \eta_s \sqrt{M} \).

 responding to the length scale of the Pincus blob. They use \( (R_{\text{eq}}/\xi_0) \) as a measure of this mode number (where \( R_{\text{eq}} \) is the mean size of the chain at equilibrium), and by using the shear rate dependence of \( \xi_0 \), they obtain a expression for the viscosity that depends on the shear rate.

In the case of semidilute solutions, for \( \tau_{\text{chain}} \gamma < 1 \), Eq. (13) takes the form (using Eq. (B3) for \( c/\nu_p \)),

\[
\eta = k_B T \left( \frac{1}{N_c \xi_0^3} \right) \tau_{\text{chain}} \sum_{p=2}^{N_c} \frac{1}{p^2}
\]

(14)

where \( N_c \) is the number of correlation blobs in a chain. For \( N_c \gg 1 \), using Eq. (B15) for \( \tau_{\text{chain}} \), this implies,

\[
\eta = \frac{k_B T \eta_s \xi_0^3}{N_c \xi_0^3} = k_B T \frac{\eta_s}{N_c \xi_0^2}
\]
or,

\[ \frac{\eta}{\eta_s} \sim N_c \sim \left( \frac{c}{c^*} \right)^{\frac{4}{3}-1} \]  

in agreement with the expression derived by Jain et al. \(^5\) for the zero shear rate viscosity of semidilute solutions.

For strong flows, as argued by Colby and coworkers \(^{53}\), \( \tau_p \dot{\gamma} < 1 \) only for the modes ‘p’ that lie within a Pincus blob. Rather than \( (R_s/\xi_S) \), we suggest that it is more appropriate to use the number of Pincus blobs in a chain, \( X \), as the lower bound of the sum in Eq. \((14)\), since the chain is divided in ‘X’ segments by the action of the flow. For low shear rates, \( X \rightarrow 1 \), since the entire chain is contained in a Pincus blob, while at high shear rates, \( X \rightarrow N_c \). Note that,

\[ X = \frac{N_c}{m} \]  

At high shear rates consequently, Eq. \((14)\) becomes,

\[ \eta = k_B T \left( \frac{1}{N_c \xi_S^3} \right) \tau_{\text{chain}} \sum_{\lambda = 0}^1 \frac{1}{p^2} \]  

Converting the sum to an integral, and carrying out the integral in the limit \( N_c \gg 1 \), we get,

\[ \eta = \frac{k_B T \eta_c}{N_c \xi_S^3} \frac{N_c}{k_B T} \frac{1}{X} \eta_s \frac{m}{N_c} = \eta_s m \]

From Eq. \((12)\), this implies that at high shear rates, for semidilute solutions,

\[ \frac{\eta}{\eta_s} = \left[ \tau_c \dot{\gamma} \right]^{\frac{1}{2}} \]  

Using the expression for \( \tau_c \) from Eq. \((B14)\), we get,

\[ \frac{\eta}{\eta_s} = \left[ \tau_0 N^{3\nu} \left( \frac{c}{c^*} \right)^{\frac{3\nu}{3\nu-1}} \right]^{\frac{1}{2}} \]

where \( \tau_0 \) is the monomer relaxation time (see Eq. \((B13)\)).

Equation \((19)\) suggests that the viscosity of a semidilute polymer solution should shear thin with a power law exponent of \(-1/2\). However, we have seen from our experimental observations that the shear thinning exponent is typically less than \(-1/2\). Nevertheless, we can conclude from Eq. \((19)\) that the dependence of the relaxation time on scaled concentration should be \( (c/c^*)^\nu/(1-3\nu) \), rather than the dependence \( (c/c^*)^{2-3\nu}/(3\nu-1) \) predicted for \( \lambda_0 \). In other words, the scaling analysis here suggests that data collapse may be achieved by using the relaxation time,

\[ \lambda = \tau_0 N^{3\nu_c} \left( \frac{c}{c^*} \right)^{3\nu_c/3\nu-1} \]  

(\( \nu_c \) is the effective exponent \( \nu_c \) has been introduced to account for differences in solvent quality), rather than \( \lambda_0 \). This hypothesis is tested in the results presented in the next subsection. It is worth noting that, using blob scaling arguments, Heo and Larson \(^{57}\) have previously obtained an identical dependence on concentration for \( \lambda_0 \), the Rouse time of an entanglement strand, with which they have successfully collapsed data in the concentration range, \( c_c < c < c^* \).

E. Universal shear thinning of semidilute solutions

The viscosity data presented earlier in Figs. \(5\) is reinterpreted in terms of the scaling variables suggested by the anal-
ysis of the previous subsection, and plotted in Figs. 13 (a), (b) and (c), for 25 kbp, λ-DNA and T4 DNA, respectively. It is immediately apparent that in each case, for $\lambda_{\gamma} \gg 1$, the viscosity collapses onto master curves, independent of $c/c^*$ and the solvent quality $z$. It should be noted that the value of $\nu_{\text{eff}}$ corresponding to the particular value of $z$ has been used in these plots. The slope of the shear thinning region seems to vary with molecular weight, with the magnitude decreasing as the molecular weight increases. This can be seen more clearly in Fig. 14 (a), where representative data for all the three DNA molecular weights are plotted side by side. It is possible that the experimental data lies in a crossover region, and that the Weissenberg numbers at which asymptotic shear thinning with exponent -0.5 is observed, have not been explored for λ-phage and T4 DNA.

We find that dividing the polymer contribution to viscosity $\eta_\text{p}$ by $\eta_\text{ρ} \sqrt{M}$ leads to a collapse of data across molecular weights, concentrations and solvent quality, as shown in Fig. 14 (b). This result is not obvious from the scaling arguments developed in section V D above. Nevertheless, it is striking, and awaits a satisfactory explanation.

An attempt to use the relaxation time given by Eq. (20) to collapse the data for the two polystyrene solutions is shown in Figs. 15 (a) and (b). Clearly, all the data is in the regime prior to the onset of significant shear thinning, and no conclusions can consequently be drawn from the lack of data collapse, which is expected only in the power law regime. More data at higher shear rates is necessary to resolve this issue.

VI. CONCLUSIONS

Measurements of the viscosity of dilute and semidilute unentangled DNA solutions in simple shear flow have been carried out over a wide range of temperatures and concentrations. While similar measurements have been made for semidilute unentangled polystyrene solutions, previously reported data on dilute polystyrene solutions has been adapted for the central purpose of this work, which is to examine (in all these cases), if universal behaviour is exhibited when a proper choice of scaling variables is made. In particular, since it is well established that the dependence of equilibrium static and dynamic properties of polymer solutions on the variables $\{T, c, M\}$, becomes universal when represented in terms of the solvent quality $z$, and the scaled concentration $c/c^*$, we examine if extending this space by adding the Weissenberg number $\lambda_{\gamma}$ as a non-dimensional variable, leads to a universal representation of non-equilibrium behaviour as well.

In order to pursue this goal, we have firstly determined the values of $z$ and $c/c^*$ for all the solutions considered here. While this has been done previously by us for the three DNA molecular weights considered here [5,56], their estimation for polystyrene solutions has been discussed here in detail (see Appendix A and Tables II, III, IV and V).

For dilute solutions, the Weissenberg number has been defined in terms the large scale relaxation time $\lambda_{\gamma}$, which is based on the zero shear rate intrinsic viscosity (see Eq. 1). Using previously reported data on intrinsic viscosities of DNA and polystyrene solutions, and estimating them with a systematic procedure (detailed in Appendix A), when they are not available, we have calculated $\lambda_{\gamma}$ for all the solutions considered here (see Tables VII and VIII). By determining the zero shear rate viscosity, $\eta_{00}$, from the shear rate independent viscosity data at low shear rates (see Tables I and II of the supplementary material), it becomes possible to plot the ratio $\eta_{\gamma}/\eta_{00}$ as a function of the Weissenberg number $\lambda_{\gamma}Z_{\gamma}$, for both the DNA and the polystyrene solutions, at various values of $z$ and $c/c^*$, in the dilute regime (see Figs. 2 and 4).

When represented in this form, the data for dilute DNA solutions clearly indicates the existence of master plots independent of $z$ and $c/c^*$. However, the onset of shear thinning occurs at higher values of $\lambda_{\gamma}Z_{\gamma}$ with increasing molecular weight of the DNA chains. Interestingly, the shear thinning exponent in all cases is less than $-2/3$, which is the known limiting value for finitely extensible chains. The behaviour is more complex in the case of dilute polystyrene solutions. While data from different groups collapse on top of each other for $\lambda_{\gamma}Z_{\gamma} \leq O(2)$, there is considerable variation in the results reported at higher shear rates, both in terms of the dependence on solvent quality and on molecular weight. It is hoped that future work will throw light on the unresolved issues that have been clearly identified here through the adoption of a common framework for describing equilibrium and non-equilibrium behaviour.

For semidilute solutions, a large scale relaxation time, $\lambda_{\gamma}$, based on the zero shear rate viscosity, has been defined (see Eq. 4), that has the same dependence on the scaled concentration $c/c^*$, as the longest relaxation time, $\lambda_1$, used previously in simulation studies [40,41,44]. Values of $\eta_{0}$ for semidilute unentangled DNA and polystyrene solutions have been determined from the shear rate independent viscosity data at low shear rates (see Tables III and IV of the supplementary material). In the double crossover regime defined by the variables $\{z, c/c^*\}$, the expectation that the ratio $\lambda_{\gamma}/\lambda_1^*$ has a power law dependence on $c/c^*$, with an effective exponent $\nu_{\text{eff}}$ that depends on $z$ (see Eq. 5), is shown to be satisfied for semidilute unentangled DNA solutions (see Fig. 8).

The use of a Weissenberg number based on $\lambda_{\gamma}$ for semidilute unentangled DNA and polystyrene solutions, collapses data at different temperatures but at the same concentration, on top of each other, establishing the existence of time-temperature superposition (see Figs. 9 and Fig. 10). The failure to collapse data for different concentrations is contrary to predictions by recent simulations [41], which find such a collapse for a Weissenberg number based on $\lambda_1$.

A scaling theory for semidilute unentangled solutions that pictures a polymer chain as a blob pole of Pincus blobs in the presence of flow, leads to the definition of a Weissenberg number which is based on a relaxation time whose concentration dependence arises from the dependence on $c/c^*$ of a single correlation blob. Remarkable data collapse, independent of solvent quality and concentration, is obtained at high shear rates when the shear rate dependence of viscosity is interpreted in terms of such a Weissenberg number.

There is clearly a need for theoretical analysis and detailed mesoscopic simulations that go beyond the simple scaling theory presented here in order to understand the complex and rich
behaviour displayed by semidilute unentangled polymer solutions. The experimental data reported here provide benchmark results for the validation and elucidation of future theoretical and computational studies.

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Appendix A: Determination of \( \{z, c^*, \lambda_2\} \) for the dilute polystyrene solutions used in Hua and Wu [12]

Hua and Wu [12] have reported viscosity measurements for four different polystyrene molecular weight samples dissolved in dioctyl phthlate (DOP). The values of the molecular weights, and the sample concentrations are reproduced in Table VIII, with the nomenclature used in their work. The DOP solvent is reported to have a viscosity of 53 mPa.s at room temperature, and is considered a \( \theta \)-solvent for polystyrene at 22°C [49]. Viscosity measurements have been carried out with a Couette rheometer at the \( \theta \) temperature, and three temperatures in the good solvent regime. The detailed procedure to represent the measurements of Hua and Wu [12] in terms of the non-dimensional variables \( (z, c/c^*, \lambda_2 \gamma) \) is discussed below.

| Sample | Molecular weight \( M \) (×10^6 g/mol) | Concentration \( c_w \) (wt%) | \( c \) (g/ml) |
|--------|-----------------------------------|------------------|---------|
| PS1    | 0.55                              | 0.40             | 0.0046  |
| PS2    | 0.68                              | 0.45             | 0.0048  |
| PS3    | 0.93                              | 0.50             | 0.0054  |
| PS4    | 2.0                               | 0.30             | 0.0028  |

Appendix B: Viscosity measurements for four different polystyrene solutions used by Hua and Wu [12]

The experimental data reported by Hua and Wu [12], the values obey the molecular weight scaling, \( [\eta]_0 \sim M^{0.52} \). As discussed in section III B 1, values of \( [\eta]_0 \) at any other temperature can be obtained from the expression, \( [\eta]_0 = [\eta]_0(\theta) [\alpha_0(z)]^3 \). In particular, one can determine the intrinsic viscosity at \( T = 35^\circ C \) for each of the four different molecular weights by guessing a value of the constant \( k \), calculating the value of \( z \) from Eq. 4, and using the universal equation for \( \alpha_0(z) \) obtained previously by BD simulations [46]. The values calculated by this procedure can then be compared with the values reported in Ref. [12] for \( T = 35^\circ C \) in order to refine the guess for the constant \( k \). Using this trial and error procedure, we find that the value \( k = 0.0055 \) leads to values of intrinsic viscosity that are within a few percent of values extracted from Fig. 1 in Ref. [12]. As a result, we take this to be the value of \( k \) for the polystyrene solutions used in Ref. [12]. Once the value of \( k \) is known, the solvent quality and intrinsic viscosity at any other temperature and molecular weight can be calculated as described above. The values of \( z \) and \( [\eta]_0 \) calculated using this procedure are given in Table IX, with an asterisk indicating that at those temperatures, \( [\eta]_0 \) has been plotted versus \( M \) in Fig. 1 of Ref. [12]. Figure 16 displays a plot of \( [\eta]_0/M \) for the four polystyrene solutions as a function of \( 1/T \). The linear dependence is in line with the recent work of Rushing and Hester [54] who have shown that this ratio scales linearly with \( 1/T \) for a number of different polymer-solvent systems, with a slope that is independent of molecular weight. A similar linear dependence was shown in our earlier work to exist for the 25 kbp and T4 DNA solutions [46].

The concentration of the dilute polystyrene solutions used by Hua and Wu [12] has been reported in terms of weight percent (reproduced here as \( c_w \) in Table VIII), rather than in g/ml, which are the units used in the current work, represented by \( c \). In order to convert to the latter, one requires the density of the solution \( \rho_{soln} \), since \( c = \rho_{soln} c_w \). The value of \( \rho_{soln} \) has not been reported in Ref. [12] for the various solu-
plotted versus $M$, at regime, $T$. The expression, $c$ straight forward to show from Eq. (A1) and the definition of solutions PS1 to PS4, which lead to values of $\rho$ are known at these temperatures (see Table IX), one can find have reported their estimate of the overlap concentration tions. However, in Table 2 of their paper, Hua and Wu [12] have reported their estimate of the overlap concentration $c_\infty$, at $T = 22^\circ C$, and at one temperature in the good solvent regime, $T = 35^\circ C$, which they state has been calculated using the expression, $c_\infty = 1/(\rho_{soln}[\eta]_0)$. Since the values of $[\eta]_0$ are known at these temperatures (see Table IX), one can find the values of $\rho_{soln}$ that lead to the reported values of $c_\infty$. We have used this procedure to find estimates of $\rho_{soln}$ for all four solutions PS1 to PS4, which lead to values of $c_\infty$ within a few percent of the reported values. These values of $\rho_{soln}$ have been used to calculate the values of concentration $c$ in g/ml, listed in Table VIII.

It is possible to use the intrinsic viscosity data for the solutions PS1 to PS4 to get more accurate estimates of the overlap concentration $c_\infty$ than those calculated by Hua and Wu [12], by making use of the universal viscosity ratio $U_{\eta R}$ defined by the expression [46],

$$U_{\eta R} = \frac{[\eta]_0 M}{(4\pi/3) R_g^3 N_A} = \frac{6}{4\pi/3} \phi \frac{N_p}{N_A}$$

where $\phi$ is the Flory-Fox constant [3]. $\phi = [\eta] M/6^{1/2} R_g^2$. It is straight forward to show from Eq. (A1) and the definition of $c^*$ that,

$$c^*(z) = \frac{U_{\eta R}(z)}{[\eta]_0(z)}$$

Pan et al. [46] have shown recently that the dependence of the universal ratio $U_{\eta R}$ on the solvent quality $z$, obtained from BD simulations and experimental measurements on synthetic polymer solutions and on 25 kbp and T4 DNA solutions, can be described very well by the expression,

$$U_{\eta R} = U_{\eta R}^0 \left( 1 + a_g z + b_g z^2 + c_g z^3 \right)^{1/2}$$

where $U_{\eta R} = 1.49$, and the suffixes on the parameters $a$, $b$, and $c$ indicate constants in the relevant expressions for the universal swelling functions $a_g(z)$ and $c_g(z)$, given in sections IIIA and IIIB respectively. Since we know the solvent quality and the intrinsic viscosity for the four polystyrene solutions at the various temperatures, the overlap concentration $c^*$ can be calculated from Eqs. (A2) and (A3). The scaled concentration $c/c^*$ can then be found using the values of $c$ listed in Table VIII for each of the solutions. Values of $c^*$ and $c/c^*$ calculated in this manner are listed in Table IX.

The large scale dilute solution relaxation time $\lambda_2$ (defined in Eq. (1)) for the polystyrene solutions PS1 to PS4 can be obtained once the solvent viscosity $\eta_s$ and its dependence on temperature is known. The latter has not been reported by Hua and Wu [12], who give the viscosity at room temperature to be 53 mPa.s. The dependence on temperature of the viscosity of dioctyl phthalate solutions has been shown by Pilaf and Labsky [55] to obey the Vogel-Fulcher equation, $\ln \eta_s = A + B/(T + C)$, with the constants $A = -2.4617$, $B = 707.86$, $C = 84.543$, and temperature $T$ in degrees centigrade. This expression leads to $\eta_s = 53$ mPa.s at $T = 25.5^\circ C$. Calculating values of $\eta_s$ at all temperatures of interest here with this expression, and using the appropriate values of $[\eta]$, the relaxation times $\lambda_2$ for the dilute polystyrene solutions used in Ref. [12], are listed in Table IX.

Appendix B: Blob scaling laws for semifluid solutions at equilibrium

The postulate that a polymer chain in a semifluid solution at equilibrium is a sequence of correlation blobs can be used to derive some simple scaling expressions for various solution properties [3, 45]. Some of these expressions are reproduced here since they are useful for the derivations in section VD.

If a chain consists of $N_c$ correlation blobs that obey random walk statistics, then

$$R_{eq} \sim \xi_c N_c^{1/2}$$

where $R_{eq}$ is the mean size of the chain at equilibrium. If $\bar{c}$ is the number of monomers per unit volume, and $N$ is the number of monomers per chain, then $(\bar{c}/N)$ is the number of polymers per unit volume, and

$$\bar{c} = \frac{N_p}{N}$$

where, $N_p$ is the total number of polymers in the system, and $V$ is the system volume. Since the correlation blobs are space filling, this implies,

$$\xi_c^3 N_c N_p = V$$
or, from Eq. (B2),
\[
\frac{\bar{c}}{N} = \frac{1}{\xi_c N_c}
\]  
(B3)

Solving for \( \xi_c^3 \) we get,
\[
\xi_c^3 = \left( \frac{N}{N_c} \right) \frac{1}{\bar{c}}
\]  
(B4)

At the overlap concentration, since \( R_{eq} = bN^\nu \), where \( b \) is the size of a monomer, and \( \nu \) is the Flory exponent, we have,
\[
\bar{c}^* \sim \frac{N}{R_{eq}} \sim b^{-3} N^{4 - 3\nu}
\]  
(B5)

Multiplying and dividing the right hand side of Eq. (B4) with \( \bar{c}^* \), and using Eq. (B5), we get
\[
\xi_c^3 = \left( \frac{N}{N_c} \right) \left( \frac{\bar{c}^*}{\bar{c}} \right) b^3 N^{3\nu - 1}
\]  
(B6)

For semidilute solutions, it can be shown that (see supplementary material in Jain et al. [5]),
\[
N_c = \left( \frac{\bar{c}}{\bar{c}^*} \right)^{\frac{1}{3\nu - 1}}
\]  
(B7)

As a result,
\[
\xi_c^3 = b^3 N^{3\nu} \left( \frac{\bar{c}}{\bar{c}^*} \right)^{\frac{1}{3\nu - 1}} \left( \frac{\bar{c}^*}{\bar{c}} \right)^{\frac{1}{3\nu - 1}}
\]
which simplifies to,
\[
\xi_c^3 = b^3 N^{3\nu} \left( \frac{c}{c^*} \right)^{\frac{1-\nu}{3\nu - 1}}
\]  
(B8)

where, we have used \( (c/c^*) \) in place of \( (\bar{c}/\bar{c}^*) \) since they are identical (\( c = \bar{c}m_k \), where \( m_k \) is the mass of a monomer).

The diffusivity of a correlation blob is given by
\[
\mathcal{D}_c = \frac{k_B T}{\zeta_c}
\]  
(B9)

where, \( \zeta_c \) is the friction coefficient for the blob. Since the chain segment within a correlation blob obeys Zimm dynamics,
\[
\zeta_c \sim \eta_s \xi_c
\]  
(B10)

and as a result,
\[
\mathcal{D}_c = \frac{k_B T}{\eta_s \xi_c}
\]  
(B11)

The relaxation time for a single blob can be derived from the expression,
\[
\tau_c = \frac{\xi_c^2}{\mathcal{D}_c} = \frac{\xi_c^2}{(k_B T/\eta_s \xi_c)}
\]
or,
\[
\tau_c = \frac{\eta_s \xi_c^3}{k_B T}
\]  
(B12)

If we define,
\[
\tau_0 = \frac{\eta_s b^3}{k_B T},
\]  
(B13)
as the monomer relaxation time, it follows from Eq. (B8) that,
\[
\tau_c = \tau_0 N^{3\nu} \left( \frac{c}{c^*} \right)^{\frac{3\nu - 1}{1 - \nu}}
\]  
(B14)

Since a single chain in a semidilute solution is equivalent to a Rouse chain of correlation blobs in a melt, it follows that the relaxation time of the chain as a whole, \( \tau_{\text{chain}} \), is given by \( [3] \)
\[
\tau_{\text{chain}} = \tau_c N_c^2
\]
or,
\[
\tau_{\text{chain}} = \left( \frac{\eta_s \xi_c^3}{k_B T} \right) N_c^2
\]  
(B15)

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