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Research Article

Modelling Polymers as Compressible Elastic Spheres in Couette Flow

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Abstract. A model of polymer chains as compressible elastic spheres in flow is presented. The spherical polymer blobs are assumed to compress in simple Couette flow in accord with recent rheo-optic measurements on semi-dilute solutions. The experimentally determined decrease in radius with increasing shear rate is predicted by the model. Furthermore, the model predicts power law exponents for the viscosity-shear rate within the range of measured values for polymer chains.

Keywords. Semi-dilute Polymer solutions, Couette Flow, compression, modelling, power law.

INTRODUCTION

The rheology of polymers is of both fundamental interest and considerable practical importance.¹⁻⁴ Predicting the flow behaviour of polymeric solutions from the fundamental physics of the individual chains has long been the quest of soft condensed matter.^{5,6} The combination of statistical mechanics and fluid mechanics has been used to predict polymer rheology.^{7,8} Kuhn was the first to develop a model of chains in flow.⁹ He modelled the chains as beads on a spring in which the beads account for the hydrodynamic forces and the spring embodies the elastic nature of the chain. He also developed the first statistical mechanical model that enabled the calculation of the effective spring constant from the chain properties.⁹ Kuhn's 1933 *Kolloid Z.* paper also showed that the chains experience both extensional and compressive hydrodynamic forces as they tumble in flow in so called Jeffery Orbits.¹⁰ Interestingly, since Kuhn's original paper, the compressive forces have been ignored and only extension is assumed to occur. The dumbbell model presented by Kuhn enables the hydrodynamic forces to be evaluated and the steady state condition of the forces to be equated as a function of the angle around the vorticity axis. Since Kuhn's pioneering work, an essential assumption of polymer dynamics is that the single molecule response to applied stress may be used to interpret the observed macroscopic material behaviour.^{2,4,6} The elegant models of single polymer chains which assume that the chain can be described as

a random walk on a periodic lattice have been successful in predicting a number of the key properties of polymers.^{5,6} Furthermore, the inclusion of excluded volume to the ideal chain has enabled prediction of the solution size of polymers.^{3,11,12} The entropy of the chain is derived in terms of the end-to-end vector of the random chains.² This model forms the basis of rubber elasticity and is used to incorporate elasticity in models of flow where chain deformation results in entropy reduction and elasticity.¹³ The *theory of rubber elasticity* (based on the same physical assumptions) predicts the elastic behaviour of rubbers over a wide strain range.¹³ Importantly, the “*Rubber Theory*” predicts both the compressive and extensional behaviour of rubbers. This agreement between the theory and experiment, albeit at effectively “infinite” molecular weight and high polymer concentration with excluded volume interactions neglected, gives confidence that the fundamental tenets of the theory are correct. However, due to their complexity there exist very few simulations of polymer solutions and melts in the semi-dilute and concentrated regimes.^{8,14-16}

A general assumption used in models of polymers in flow is that the chains extend in response to the hydrodynamic forces.¹⁴⁻¹⁶ Recent experimental evidence shows that synthetic polymer chains compress in Couette flow at semi-dilute concentrations.¹⁷⁻¹⁹ Recent studies on semi-dilute DNA solutions shows that extension and tumbling occurs.^{20,21} It appears that the general assumption of chain extension in flow may not be valid for concentrations above critical overlap in Couette flow.^{18,19,22,23} Furthermore, recent Brownian dynamics simulations for dilute solutions predict chain compression by neglecting excluded volume effects and including hydrodynamic interactions.^{24,25} While these simulations have been done for dilute chains, the neglect of excluded volume effects is consistent with concentrated solution behaviour. The inclusion of hydrodynamic interactions in concentrated solution where they are screened is not however consistent with the physics of concentrated solutions. Many of the models and experiments presented in the literature are for purely extensional flows.^{2,26} Recent simulations on the blood borne protein von Willebrand Factor (vWF) show that in Couette flow the vWF chain tumbles when exposed to high shear rates to extend and then refold. When exposed to relatively low extensional shear rates, the vWF unfolds and extends.²⁷⁻²⁹

In light of recent experimental evidence showing chain compression in Couette flow, a new model is presented where the chains compress in response to the hydrodynamic forces. We also note that coil compression is an elastic event which leads to reduced friction in the system and is therefore consistent with the shear thinning

and visco-elasticity observed for polymer solutions in simple flow. Purely extensional flow results in an increasing extensional viscosity with shear rate.³⁰

RESULTS

The shear rate dependence of the end-to-end distance, r , has been measured for polymethyl methacrylate (PMMA) using fluorescence resonance energy transfer (FRET) tagged chains in laminar Couette flow.²² The conformation of poly-4-butoxy-carbonyl-methylurethane (4-BCMU) in flow has been measured using absorption spectroscopy where the change in segment length with shear is used to determine the change in polymer size.¹⁸ The results of the previous studies are re-plotted on a log-log scale in Figure 1 below. Both polymers show a decrease in the end-to-end distance with increasing shear rate. Reversibility was observed upon cessation of shear for all shear rates measured.^{18,22}

The results presented in Figure 1 are from two different rheo-optical experiments for two different polymeric systems. The data for PMMA was collected using time resolved FRET measurements on end tagged PMMA as a molecular tracer in a matrix of untagged PMMA

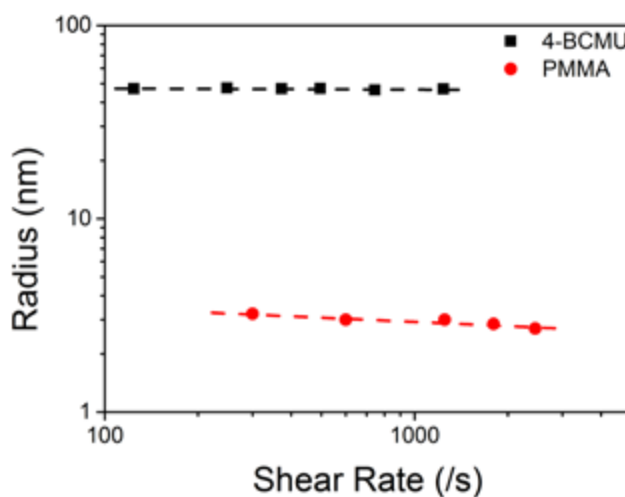


Figure 1. Measured end-to-end distance plotted as $\log r$ versus \log shear rate. ata for 800kD 4-BCMU.¹⁸ has the fitted equation: $\log(r) = -0.0046\log(\dot{\gamma}) + 1.7$ with the coefficient of determination: $R^2 = 0.23$. Data for 49kD FRET tagged PMMA in Couette flow²² shows the fitted equation: $\log(r) = -0.0072\log(\dot{\gamma}) + 0.69$ with $R^2 = 0.88$. The lines of best fit yield an inverse 0.07 ± 0.02 power of the radius with shear rate for the PMMA and 0.0042 ± 0.002 for the 4-BCMU. The error bars are approximately the size of the symbols. The error associated with each point is: $\sim 5\%$ in the shear rate due to the radius/gap ratio of the Couette cell. For the 4-BCMU the un-sheared size of the chain is 49 ± 1 nm and for PMMA the size is 4 ± 0.1 nm.

at $\sim 2C^*$. The data for 4-BCMU is taken from reference 1 where the segment lengths of the 4-BCMU are measured to decrease with increasing shear rate at a polymer concentration of $\sim 1.6C^*$.¹⁸ Calculation of the average segment length and conversion to an end-to-end distance using the equation $r = aN^{1/2}$ yields the results presented in Figure 1 for 4-BCMU. Here N is the number of segments and a the segment length as taken from literature values.¹⁸ Both data sets show a decreasing radius with shear rate with a power law behaviour.

THEORY

The polymers are modelled as space filling, spherical elastic objects at semi-dilute concentration. The spheres are compressible and may change their volume through deformation. The flow is defined as simple Couette flow where the spherical blobs are exposed to a uniform velocity gradient at low Reynolds number, $R_e = vr/\eta$ for neutral buoyancy spheres. In view of recent experimental evidence showing that polymer chains compress in Couette flow (see Figure 1), we assume that the translational hydrodynamic forces on the sphere act to compress the chain in accord with the experimental evidence.^{17,22,31} The semi-dilute concentration is such that the spherical blobs are in contact with each other and compress in flow. We postulate that the reason compression rather than extension dominates the flow response of these polymers is due to the crowding of the single chain by the neighbouring chains in semi-dilute solution. The tumbling motion of the chains results in a time average compressive hydrodynamic force on the sphere in semi-dilute solutions.

For the semi-dilute solutions, the blobs experience both rotational and compressive forces in flow. The rotational force (torque) acts to make the compressive hydrodynamic forces on the sphere uniform. As such the hydrodynamic translational force acts isotropically inward on the blob and is opposed by the elastic force. The force acting on each half space in the Couette flow acts in the opposite direction and is simply one half of the Stokes' drag on the sphere. Goldman, Cox and Brenner^{32,33} determined the hydrodynamic force on a sphere in Couette flow at low Reynolds number as:

$$F_y^{s*} = F_y^s / 6\pi\eta r U \quad (1)$$

Here F is the force with the subscript y defining the direction of the translational motion in the unperturbed shear rate s , r is the sphere radius, U the fluid velocity and η the solvent viscosity.

Equation 1 defines the force on the sphere at distances from the walls greater than the radius as:

$$f_{hyd} = 6\pi\eta r U \quad (2)$$

The torque on the sphere, Faxen's Law, was also determined as:³³

$$T_x^{s*} = T_x^s / 8\pi\eta r^3 \Omega \quad (3)$$

where T is the torque on the sphere, with the superscript s defining the undisturbed shear rate, the subscript x is the vorticity axis and Ω is the rotational velocity.

The local forces may then be equated under steady state flow. The elastic and hydrodynamic forces on sphere then act to change the radius in flow. The forces are used in the following treatment as at each point in the system the hydrodynamic and elastic forces oppose each other. In order for the system to reach steady state, the

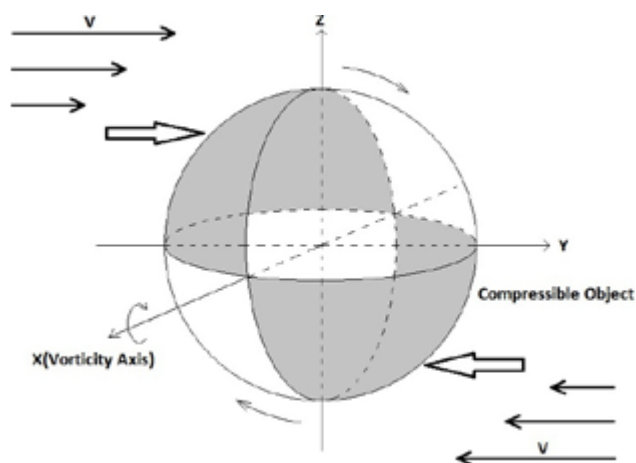


Figure 2. Schematic showing the polymer represented as a sphere in Couette flow. At semi-dilute concentrations each sphere is in "contact with the surrounding spheres. The shaded area shows the region which experiences a compressive force from the flow. The upper half experiences a compressive force from left to right while the bottom right hand part of the image experiences a similar compressive force from the flow from right to left. Each surface experiences a compressive force equal to one half the Stokes' drag on a sphere. The total compressive force is then equal to $f_{compressive} = f_{hyd} = 6\pi\eta r U$ where η is the solution viscosity, r the sphere radius and U the velocity difference across the sphere in the direction shown. The sphere also experiences a torque around the vorticity axis. This rotational motion causes a tumbling which yields an averaged symmetric compression on the blobs in flow. At each point across the surface the hydrodynamic force is equal to the elastic force under steady shear. Local fluctuations will occur with the system reaching an average reduced size of the coil with increasing shear rate and commensurate hydrodynamic force. The arrows pointing inward on the blob represent the local hydrodynamic compressive force.

completely isotropic forces throughout the solution are equivalent. Obviously, the forces will fluctuate around the steady state average as the blobs rotate around the vorticity axis in the shear field. In steady state flow the hydrodynamic and elastic forces are then equated:

$$f_{el} = f_{hyd} \quad (4)$$

Where the magnitude of the elastic force for the blob is taken from the theory of rubber elasticity and has a similar form as that reported previously:^{13,34}

$$f_{el} = E \times Area = \frac{3nk_B T}{r} \quad (5)$$

Where E is the Young's modulus of the blob, k_B is Boltzmann's constant, T the absolute temperature and r the sphere radius. The elastic force so described embodies the entropic nature of the chain. Here we define n as the number of chain interactions (usually assumed to be entanglements) where n may be assumed to be constant for finite deformation. The *theory of rubber elasticity defines* n as the number of cross links in the gel.¹³ Note that the theory of rubber elasticity introduces an r_0 term into equation 5 to allow for compression and the finite size of the chain in the quiescent state.¹³ Neumann has previously suggested that the inability to account for r_0 in the Hookean force law used in models of polymers in flow arbitrarily restricts the chain to extension.^{35,36} Indeed the neglect of the r_0 term results in a Hookean response of the chains that is not physically correct in that the radius is zero at zero force and infinite at infinite extension. The formalism introduced by Neumann has the correct limiting behaviour for the force law in both extension and compression. Compression of the chains to point size would require an infinite force as would large stretching.

At each localised point, we assume that the elastic force acting normal to the surface of the blob as shown in Figure 2 opposes the hydrodynamic force.

The hydrodynamic force on the spherical blob is developed from equation 2 above using the assumption that the velocity in Couette flow U defines the shear rate as:

$$\dot{\gamma} = U / 2r \quad (6)$$

Then

$$f_{hyd} = 6\pi\eta\dot{\gamma}r^2 \quad (7)$$

Here the viscosity of the polymer solution is η , $\dot{\gamma}$ the shear rate experienced by the chain and r the average end-to-end vector of the chain as defined above. It is assumed that the end-to-end distance is equivalent to the

radius of the sphere that experiences the hydrodynamic force. The hydrodynamic force varies as r^2 in accord with the original derivation of the hydrodynamic drag on a dumbbell derived by Kuhn.⁹

To first order the viscosity of the solution, is approximated by a modified version of Einstein's equation:

$$\eta \sim \eta_0 \phi \quad (8)$$

Where the η_0 is the effective solvent viscosity and ϕ the volume fraction of the chains. We assume that the effective solvent viscosity composed of solvent and the surrounding polymers. The polymer chains in flow act as compressible objects where the (incompressible solvent) may exchange freely throughout the system. The solution viscosity will depend on the polymer volume fraction and the shear rate. We assume that η_0 is also proportional to the volume fraction ϕ so that:

$$\eta \sim \phi^m \quad (9)$$

De Gennes and later Rubinstein and Colby have derived the volume fraction dependence for the viscosity of semi-dilute solutions using scaling arguments and determined that $m = 2$. Furthermore, experimental data confirms the scaling arguments for polyethylene oxide in the semi-dilute concentration range.^{2,37} By assuming $\phi \sim r^3$ by substitution into equation 5 we obtain the following:

$$\eta \sim r^{3m} \quad (10)$$

Equating the hydrodynamic and elastic forces on the spherical object in flow;

$$\frac{3nk_B T}{r} = 6\pi r^{3m} \eta \dot{\gamma} r^2 \quad (11)$$

Yields:

$$nk_B T \sim \dot{\gamma} r^{3(m+1)} \quad (12)$$

so that

$$r \sim nk_B T \dot{\gamma}^{-1/3(m+1)} \quad (13)$$

The generally accepted power law model is of the form:

$$\eta \sim \dot{\gamma}^n \quad (14)$$

Values of n reported for polymeric systems range between $p \sim -0.2$ to -1.0 .³⁸⁻⁴⁰ Interpretation of the data

presented by Stratton indicates that for monodisperse polystyrene, $p = -0.82$.⁴⁰ The value of $p = -2/3$ predicted by the model is well within the range of accepted values for shear thinning polymers.³⁸

The viscosity-shear rate in model developed has the power law form:

$$\eta \sim \dot{\gamma}^{-m/(m+1)} \quad (15)$$

The dependence of the radius with shear rate for $m = 2$ is then:

$$r \sim k_B T \dot{\gamma}^{-1/9} \quad (16)$$

and

$$\eta \sim \dot{\gamma}^{-2/3} \quad (17)$$

Thus the model predicts values for the power law model in accord with those determined experimentally for polymer solutions and hard sphere suspensions.^{39,40}

DISCUSSION

The measured dependence of the decrease in the radius with increasing shear rate (power law of -0.09 ± 0.02) is in close agreement with the model prediction of $-1/9$ (-0.11) (Equation 16) when $m = 2$ is used for the volume fraction power law of the viscosity for the PMMA data.

Furthermore, the model predicts a power law for the shear thinning viscosity of $-2/3$ (-0.67) that is within the range observed for polymer solutions which have been found to lie within the range of -1.0 to -0.2 .³⁸⁻⁴⁰ Using the approximation that the viscosity follows a volume fraction squared behavior allows the model to fit both the power law behavior of the radius and viscosity with shear rate for PMMA. Expansion of the Einstein Equation involves the addition of higher order terms in the volume fraction as attributed to Batchelor.³³ Any correction to the viscosity-volume fraction dependence would presumably require higher order terms ($m > 2$) that would yield lower values of the predicted power law at higher concentrations. Indeed, scaling arguments predict that the viscosity follows a $14/3$ power of the volume fraction at concentrations above the entanglement concentration.³⁷ The measured viscosity-molecular weight behavior for a range of polymers is consistent with the volume fraction dependence used in Equation 7.⁴¹ Furthermore, de Gennes and later Rubinstein and Colby have modeled the viscosity-polymer volume fraction dependence described

in Equation 9 using scaling arguments to show that $m = 2$ in the semi-dilute concentration range.^{2,37} This relationship between the volume fraction of the polymer and the effective solvent viscosity enables the macroscopic viscosity-shear rate power law to be predicted (Equation 15). The predicted and measured decrease in radius with shear rate for the PMMA are in excellent agreement when the second order dependence of the viscosity on volume fraction ($m = 2$) is used. Fitting the BCMU data requires that m is approximately 1 ($m = 1.0015$). This suggests a power law for the viscosity of $\sim -1/2$. Equation 7 yields an unbounded radius (and viscosity) as the shear rate tends to zero so that a modified form of the above equations must be used at low shear rates. The form of the equations at low shear rates will be similar to the Cross equation for shear thinning.³⁹ The recently measured shear induced phase separation observed in semi-dilute polymer solutions may be explained by chain compression in flow where the solutions appear to be more heterogeneous as reflected in the scattering measurements. The observed compression in flow lays the foundation for an explanation of the observed shear induced phase changes observed for polymer solutions.^{42,43}

Furthermore, it is noted that the model predicts a value of $p = -1/2$ and a radius dependence of the shear rate with a power of $-1/6$ for dilute solutions where it is assumed that the viscosity is proportional to the volume fraction. A review of the literature on the power law behavior observed for polymer solutions of differing volume fraction would be appropriate in validating the current model. The power law of the viscosity with volume fraction is used as an adjustable parameter in the model and suggests possible reasons for the different power law behavior reported in the literature for the same polymer systems.

CONCLUSIONS

The model for polymers in flow is presented where the chains behave as elastically deformable spheres that compress in simple shear flow at semi-dilute concentrations. Equating the elastic and hydrodynamic forces on the blob enables the power law observed for shear thinning and the reduction in end-to-end distance with shear rate to be predicted over the range of shear thinning. Physically the model is consistent with the observed rheology of polymer solutions in Couette flow which is attributed here to compression of the chains in flow rather than the previously assumed extension. Development of the model using the assumption that the chains compress enables a simple analytical prediction of polymer visco-elastic behavior including the power law for shear thinning.

AUTHORS' CONTRIBUTIONS

DX undertook data analysis and contributed to writing the paper. DD contributed to writing the paper and developed the model.

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