

The relaxation time for our polymers is estimated with [30–32]

$$\lambda_{\text{Zimm}} \approx \frac{\eta_s R_g^3}{k_B T}. \quad (1)$$

Here λ_{Zimm} is the Zimm relaxation time estimate [52] and η_s the solvent viscosity that immerses the individual polymer coils of radius of gyration R_g . The solvent frictionally slows down relaxation which is itself driven at a given thermal energy $k_B T$ which sets the level of agitation causing polymers to collapse into a random globular coil.

It should be noted that in studies of viscoelastic fluids and their instabilities high viscosity solvents are most often used [1], as this both increases the relaxation time due to the scaling with η_s and reduces the effects of diffusion which will tend to reduce contrast if dye is used for visualization. For EOF driven fluids velocity will scale inversely with η_s , the effect of increasing viscosity will therefore both increase relaxation time *and* reduce the achievable flow rates in such a manner that the effects will cancel leaving the De number unchanged. We initially attempted flows of high viscosity solvents ($\approx 65\%$ sugar and equivalent glycerine), however we found it difficult to work with such flows due to long start up times and low achievable velocities making it difficult to study the flows. Joule heating effects further complicate highly viscous flows. As low viscosity solvents are most often used for microfluidic applications, De is not expected to change in a significant manner with changing viscosity for EOF flows, and experimental studies were complicated by the use of high viscosity solvents we moved to our low viscosity solvent.

Dynamic Light Scattering experiments (Brookhaven Instruments 200SM) for 120 ppm of the HMW sample gives a hydrodynamic radius of 296 nm while the LMW sample at 120 ppm has a radius of 137 nm. Using the experimental relationship [34] between the radius of gyration R_g and the hydrodynamic radius R_h for polyacrylamide ($R_h = 0.68R_g$; close to the Kirkwood-Riesman prediction [35] of $R_h = 0.665R_g$) allows us to determine the relaxation times of 0.025 and 0.0025 s for the HMW and LMW samples, respectively. Using the Mark-Houwink parameters [36] for PAAm in pure water gives relaxation times of 0.028 and 0.0029 s. The similarity in predicted relaxation times indicates that the addition of 20% MeOH has only a mild effect on the radius of gyration. We take the relaxation times as 0.03 and 0.003s.