Modeling Sub-Continuum Effects on the Mechanical Properties of Ultrathin Macromolecular Layers

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ABSTRACT

This paper makes progress on the prediction of mechanical modulus and mechanical relaxation time of macromolecular materials at small length and time scales. Fundamental studies of large molecules in confined geometries inform predictions of macroscopic materials behavior. A modified Einstein relation for diffusion of small particles relates macromolecular monomer and chain lengths to mechanical properties. Measurement of viscosity in thin polymer layers show marked increase in viscosity in polymer layers thinner than the polymer radius of gyration. This modeling enables analysis of measurements of the near zero shear rate viscosity in thin macromolecular layers. The intermolecular diffusion time constants, which also depend upon macromolecular size and confinement effects, govern the mechanical relaxation time. This work aims to connect fundamental macromolecular physics with nanometer-scale process and device development.

Keywords: mechanical properties, macromolecule, polymer film, molecular confinement, MEMS, NEMS

1 INTRODUCTION

Macromolecular systems offer opportunities for nanoengineering because of their ease of manufacture [1], functionality including the ability to conduct electricity and emit light [2], and usefulness as mechanical elements in nano electro-mechanical systems (NEMS) [3-5]. The physical properties of thin polymer films can differ from bulk properties at lengths comparable to or thinner than the radius of gyration of a molecule in bulk polymer [6]. Examples of polymer orientation, confinement, and frustration at small scales are observed as shifts in measured glass transition temperature T_g, [7, 8], changes in polymer thermophysical properties [10], or changes in mechanical viscoelastic properties [11, 12].

The length scale for a macromolecule is the radius of gyration, R_g, defined as the root mean squared distance between the centroid of a molecule and each of its monomers [6]. For polymer structures with one or more feature of size near or below the polymer radius of gyration, the molecule is confined and partially oriented along the direction of the layer, illustrated in Fig. 1. The partial molecular orientation can affect the mechanical properties

of this structure by increasing the layer mechanical modulus or the viscosity [13], complicating the design of macromolecular nanosystems.
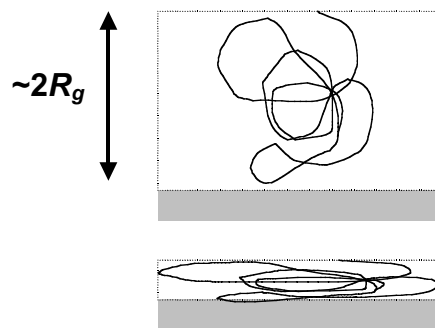

Figure 1: The lowest energy state of a macromolecule is in the 'rolled-up' conformation. The size of the molecule is given by R_g, the radius of gyration (top). When the layer thickness is less than R_g, the molecule is confined and oriented in the layer direction (bottom).

In general, studies of mechanical phenomena in thin macromolecular layers seek to combine understanding of molecular phenomena with more macroscopically observed phenomena.

The local mobility of large molecules in a thin film depends upon molecular confinement and proximity to nearby surfaces. The diffusion of polymer layers in a supported thin film structure can be substantially reduced due to the presence of a nearby surface [14-17]. Inter-polymer friction coefficients in thin Polystyrene (PS) films can be 10^2 to 10^3 times greater than the bulk coefficients, depending upon the support material [14]. Molecular confinement induced by the presence of the bounding surface causes reduced diffusion, and the surface chemistry of the bounding medium can increase or decrease the diffusivity. The self-diffusivity of polymers is also thickness dependant, demonstrating a factor of two reduction in PS films at thickness well above R_g [15]. Zheng [16] reports over an order of magnitude reduction in self-diffusivity of PS films at distances up to $10\ R_g$ away from a bounding interface, and Lin [17] reports similar reduction in Poly Methyl Methacrylate (PMMA) films, but only up to distances of $4\ R_g$ from the bounding surface.

Mechanical motion in thin polymer films is also restricted by confinement and bounding effects [11, 13].

Polyphenylmethylsiloxane films sandwiched between atomically flat mica surfaces demonstrate strong rubber elasticity at thickness below five to six R_g when subjected to small oscillatory motions [11]. This elasticity could be due to 'bridging' of polymer molecules with portions of individual molecule near both sandwiching surfaces [18]. A qualitative measure of shear compliance in PS films sandwiched between aluminum surfaces showed a reduction to 60% of the bulk value for the thinnest films. A two-fluid model of polymer motion near interfaces proposes that some molecules are trapped near a bounding surface while molecules away from the bounding surface or near a free surface have a different mobility [19] and experiments support this model [8, 20]. More detailed models consider a local mobility, varying near interfaces but not discontinuously [9,14].

While much past research has studied the fundamentals of the mechanical behavior in thin macromolecular materials, the performance and reliability of devices made from these materials have received little attention. This paper distills previous fundamental findings into rules for engineering calculation of materials properties for NEMS. The target application of this work is nanoscale manufacturing and reliability of macromolecular NEMS in general, and an advanced, atomic force microscope (AFM) based data storage system in particular [13]. Figure 2 shows nanometer-scale data bits written into a thin polymer film. In this image, the data bits and the polymer film into which they are written are smaller than the polymer radius of gyration. An important result of the present work will be to improve understanding of the bit writing process.

Following the Introduction, which includes a review of fundamental studies on the mechanical properties of ultrathin polymer films, an approach is presented for bridging molecular scaling arguments to macroscopic mechanical properties. A relation for the prediction of near steady-state viscosity of a thin polymer film allows reduction of experimental data in terms of intrinsic polymer properties. Finally, the approach predicts the size-dependant mechanical relaxation time of the thin polymer film.
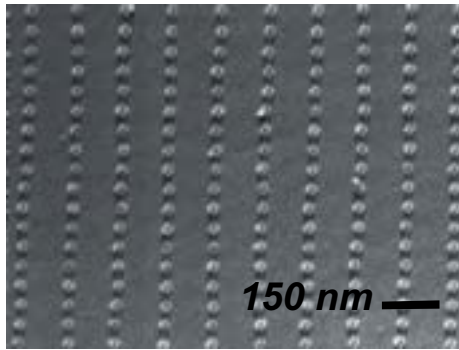

Figure 2: Thermomechanically written data bits in a 35 nm PMMA film [3]. The formation and stability of these data bits depend strongly upon the film properties [13].

2 MOLECULAR VIEW OF STEADY-STATE VISCOSITY

Macromolecular NEMS components experience mechanical phenomena at small time and length scales. The present work considers a model of the polymer at close to steady state to predict the near zero shear rate viscosity. A second, more refined model considers size effects on mechanical relaxation time.

Two relaxation mechanisms determine polymer molecular motion: a) monomer migration, which depends upon the free volume near each monomer and cooperative motion of nearby monomers, and b) reptation of the polymer chain, which requires migration of the polymer end. DeGennes [3] proposed a model of local macromolecular motion known as reptation, in which macromolecules in a condensed system move along the path of their own molecular backbone. More force or longer time is required for a macromolecule to locally move perpendicular to its path compared to motion through reptation. DeGennes [21] has suggested that for free-standing or uncapped thin films, chain reptation will be the dominant molecular transport mode. Doi and Edwards [22] suggest that this is true for long time scales.

For scaling analysis, we follow the approach and notation of Doi and Edwards [22]. A Stokes-Einstein relation for the self-diffusion of a macromolecule relates diffusivity to viscosity, and is implicit in the Rousse model of macromolecule reptation [22]. In general, diffusivity D is given by $D=L^2/\tau$ where L is characteristic length and τ is characteristic time. This model assumes that complete translation of a molecule is a motion approximately equivalent to reptation of the entire chain. A characteristic molecular length is L. At lengths less than L and at times less than τ, we expect molecular diffusivity, and therefore viscosity, to differ from bulk values.

The Rouse model of polymer dynamics considers the ratio of the total chain length to the actual path of the chain as a, which is also approximately the distance between entanglements. A chain polymer has monomer-monomer spacing b measured in the axial chain direction. It is possible to calculate steady-state viscosity as [22]

$$\eta_0 = \frac{c\zeta N^3 b^6}{\pi^2 a^4}$$

Where η_0 is steady-state viscosity, c is a constant accounting for intrinsic material properties. As the chain length N is proportional to M, the molecular weight, $\eta_o \sim M^3$. The polymer radius of gyration is given by $R_g^2 = Nb^2$. The lengths L, a, and b are related $L = Nb^2/a$. Therefore

$$\eta_0 = \frac{c\zeta}{\pi^2 a} L^3$$

Where L is the length scale for molecular diffusion. We conclude that $\eta_o \sim L^3$. This well-known scaling argument can now be applied to understanding macromolecular diffusion in confined geometries, for example in macromolecular layers where the layer thickness is comparable to or less than L.

3 MOLECULAR VIEW OF MECHANICAL RELAXATION TIME

Two temporal effects will modify the mechanical behavior of macromolcular materials. For mechanical displacements in bulk macromolecular materials at the shortest times, mechanical information does not have time to diffuse along the length of the macromolecule, resulting in a 'glassy' or amorphous response [5]. This response is at timescales where molecular diffusion is limited to $L<a$ [22, 23].

The timescale for reptation is associated with the diffusion time constant $\tau = L^2/D$. For confined macromolecular materials where the effective diffusion length scale $L_{eff}<L$, there will be an effective time $\tau_{eff}<\tau$ at reptation onset. This time τ can be thought of as the primary mechanical relaxation time. While it is possible to simply write $\tau_{eff}= L_{eff}^2/D$, it is also possible to predict from first principles [22]

$$\tau = \frac{c\zeta N^3 b^4}{\pi^2 k_B T a^2}$$

Where k_B is Boltzman's constant and T is absolute temperature. Or rewriting as in Section 2

$$\tau = \frac{c\zeta N}{\pi^2 k_B T}L^2$$

At constant molecular weight, $\tau \sim L^2$ or $\tau_{eff} \sim L_{eff}^2$. For varying molecular weight, the relation is $\tau \sim ML^2$ or $\tau_{eff} \sim ML_{eff}^2$. While this relation is well-known for bulk macromolecular materials, little attention has been given to studying mechanical relaxation in confined macromolecular systems.

4 EXPERIMENT

A method for measuring the viscous properties of a macromolecular layer was proposed by Hamsdorff [24] and later applied to thin polymer films by Dürig [13]. In this experiment, a laser diffraction technique measures the time required to melt polymer nanostructures to half their original volume. The polymer is PMMA of molecular weight $\sim 3 \times 10^5$ and $R_g \sim 35$nm. Polymer films of thicknesses 35 nm, 70 nm, and 300 nm are tested. Figure 3 shows scanning probe images of nanostructured polymer layers. Fig. 4 shows measured relaxation time [25].
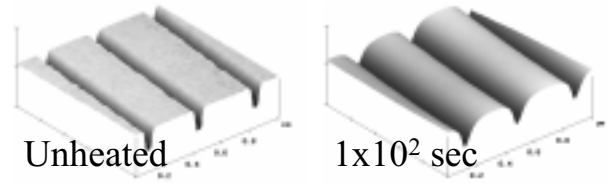

Figure 3: AFM images of melting nanostructures in a polymer surface. The trenches have a periodicity of 360 nm, the polymer has thickness 35 nm.
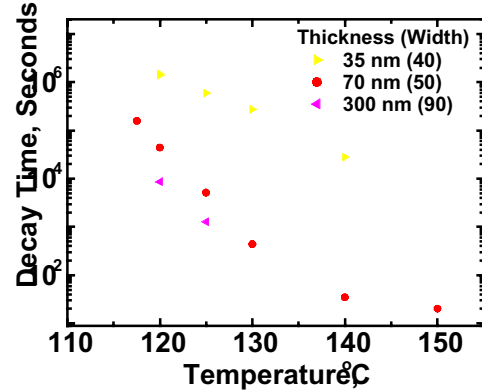

Figure 4: Time required for the polymer nanostructues of Fig. 3 to melt to 50% of unheated volume as a function of temperature [25].

If the surface-tension driving force that causes polymer flow during melting is constant during the measurement, and the flow is at low Reynolds number, the viscosity scales with film thickness h, surface tension stress σ, decay time t_{decay}, structure periodicity p, and structure width w [26].

$$\eta_0 = \frac{2h^2 \sigma t_{decay}}{w(p-w)}$$

Assuming the surface tension is constant at 0.03 N /m [26], Table 1 lists the measured viscosity at 120 ºC.

The measured viscosity in Table 1 is consistent with the tabulated value for engine oil at near room temperature, $O(10^0)$ Pa-sec, and for Low Density Polyethylene at 180 ºC is $O(10^3)$ [26]. Table 1 additionally lists the effective diffusion coefficient length scale, L_{eff}.

Thickness	MeasuredViscosity	L_{eff}
35 nm	1.15×10^4 Pa-sec	$0.45 R_g$
70	1.07×10^3	$0.93 R_g$
300	8.57×10^2	R_g

Table 1: Measured viscosity and estimated L_{eff} for three thicknesses of PMMA at 120 ºC.

5   SUMMARY AND CONCLUSION

This paper reviews past literature on macromolecular motion and makes progress on predicting mechanical properties of macromolecular materials at small length scales. Scaling arguments show the size and molecular weight dependence of the zero-shear rate viscosity and the mechanical relaxation time. Table 2 summarizes these scaling arguments.

Parameter	Molecular Weight Dependence	Size Dependence
η_0	M^3	L^3
τ	M^3	ML^2

Table 2: Summary of Viscosity and mechanical relaxation time dependence on molecular weight and size confinement effects.

The scaling arguments summarized in Table 2 aid in understanding measurement of zero shear-rate viscosity in thin polymer layers. The increase in measured viscosity by over an order of magnitude corresponds to a reduction of diffusion length by approximately 50%. This change in diffusion length compares well with literature data taken by other measurement methods.

To the best of our knowledge, the independent measurement of length scale effects on relaxation time in NEMS has not been reported in the literature. There exists an opportunity for scientific inquiry in this area, which is required for the design of NEMS made from advanced materials. The polymer properties predicted by this work aid in the modeling of thermomechanical nanostructure formation and stability. This work further seeks to impact the design of polymer-based sensors, organic optoelectronics, and microcontact imprinting.

ACKNOWLEGEMENT

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