

Microrheometry for Studying the Rheology and Dynamics of Polymers near Interfaces

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Abstract

The design of an instrument capable of opto-mechanical studies of the rheology of viscoelastic polymeric fluids near solid interfaces is described. The instrument probes the ‘meso-scale’ (length scales of $O(\mu\text{m})$) and bridges the gap between molecular-scale devices such as the Surface Force Apparatus (SFA) and conventional rheometers. The high viscosity materials and intermediate length scales probed with the current device are of direct relevance to industrial coating and thin film polymer processing operations, in addition to fundamental investigations of slip and interfacial instabilities. The device utilises small fluid samples (of the order of $1 \mu\text{L}$), allows a wide range of viscosities (and thus molecular weights) to be investigated and can also be used with different substrate materials & surface coatings. Direct optical access to the sample also permits in-situ rheo-optical studies of material response under different loading conditions and flow histories.

1. Introduction

The conformational and dynamical behaviour of polymers near surfaces is of vital interest to the polymer processing industry. Problems associated with extrusion and film processing and fundamental studies of adhesion or the understanding of new biochemical systems all require a need to develop a clear picture of how macromolecules behave near interfaces. Of particular interest are the behaviour of polymer melts as they are processed under strong shearing conditions and the onset of viscoelastic flow instabilities. These instabilities lead to unstable flow and extrudate distortion which have been attributed (at least in part) to the violation of the no-slip condition at the polymer-metal interface [1,2]. We do not pursue a detailed review of these phenomena; however we note that there is still considerable discussion in the literature over the mechanism and cause of these effects [2-7].

The physical models for these phenomena typically invoke molecular, or micro-mechanical, arguments. The resulting failure modes predicted by these models vary considerably, and lead to unstable motions with markedly different spatial and temporal characteristics. For example, in support of evidence for a critical stress-induced slip (predicted by most bulk techniques such as capillary rheometry [3,8,9]), various authors [9,10] have argued that a cohesive failure is the most likely

mechanism. Here chain disentanglement occurs between the adsorbed layer and the bulk, and hence the slip plane is close to, but not at, the interface. However, a recent study by Mackay and Henson [11] suggests that slippage can occur at any stress and the authors argue that a critical stress is more likely to be a result of sensitivity limitations when attempting to measure these small stresses using a conventional bulk technique. Forcible desorption of the entangled polymers from the surface due to the externally imposed flow (effectively an adhesive failure) has also been blamed for apparent wall slip [12]. Significantly, both explanations predict that the dynamics of such events are connected to the conformational changes induced in the layer of molecules adjacent to the substrate. The polymer chains nearest the wall are expected to have markedly different relaxation times (and hence effective viscosities) from the entangled macromolecules in the bulk melt [13]. This effect is increasingly important as the molecular weight and degree of entanglement of the chains increases [14]. It is therefore of both practical and theoretical interest to examine the non-equilibrium behavior of high molecular weight polymer chains at solid-melt interfaces, and the associated dynamical slip or ‘stick-slip’ events that are involved in the development of ‘sharkskin’ and, eventually, gross melt fracture [15]. It is worth emphasising that these conformational changes will also affect the linear viscoelastic properties of the system [13]. However, experimental investigations of slip at small strain amplitudes are extremely limited and most slip studies to date have focussed on steady shear or large amplitude oscillatory behaviour.

Over the past two decades, numerous experimental and theoretical tools have been developed to investigate the tribology and rheology of sheared fluid films, and are summarised in Fig. 1. The macroscopic continuum mechanics of microstructured fluids is now well-developed and constitutive equations exist which can accurately model the non-Newtonian behaviour of polymeric fluids undergoing deformation [16,17]. These theories are verified by mechanical measurements from various torsional and pressure-driven rheometers. At the microscopic level, molecular dynamics and kinetic

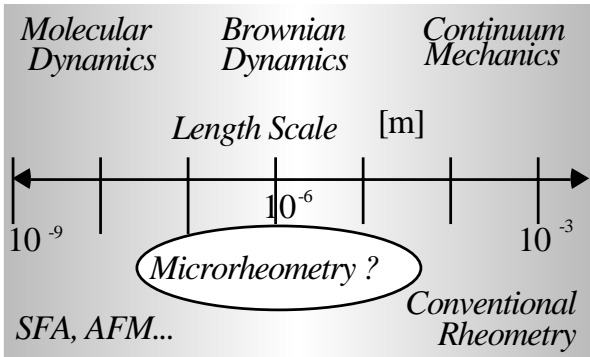


Figure 1: Schematic representation of the mesoscale regime

theory can be used to model the material response [18,19]. These predictions are paralleled by instruments designed specifically to study these very short length scales such as the Surface Forces Apparatus (SFA) pioneered by Israelachvili and Tabor [20] and refined by others [21,22]. The SFA has revolutionised the experimental study of very thin (1 nm – 1 µm) lubricating fluid films, although it is primarily used for oligomeric materials (*e.g.* short chain alkanes), small "ideal" molecules (*e.g.* OMCTS) or tethered polymer brushes [23]. Interpretation of rheological data obtained from the SFA is complicated by the non-viscometric nature of the deformation.

Many industrial processing operations involving complex fluids fall in an intermediate or ‘meso’-scale domain (see Fig. 1). Here the contour length of the polymer, the ultimate thickness of the processed film and the characteristic surface roughness of the experimental geometry may *all* be on the scale of 0.1 – 10 µm. On the numerical side, the large gap between continuum mechanical descriptions of polymeric fluids and molecular dynamic simulations of single chains has been bridged recently by hybrid stochastic techniques such as Brownian Dynamics [24,25] and by Stokesian Dynamics [26]. These techniques are computationally effective at intermediate or ‘meso’ length scales and capable of predicting the complex dynamical response of fluids with microstructure. However with the exception of the work of Granick and co-workers [27,28], there are few established experimental techniques

capable of performing quantitative rheometric measurements on this meso-scale. This paper describes one approach to building a "microrheometer" designed specifically to span this "mesoscopic" regime.

The slip dynamics have been investigated by numerous authors using instruments at both ends of the spectrum depicted in Fig. 1. For example the SFA has been used to investigate friction and stick-slip events on the nanometer scale in short chain molecules [29]. Henson and Mackay [30] adapted a bulk rheometer to look at small gaps, and have refined it sufficiently that it is now arguably almost a mesoscopic technique; although as these authors point out their approach does have restrictions [11]. Mhetar and Archer [5] used a novel optical technique seeding the fluid with tracer particles to measure the velocity profile directly. Migler et al. have used the transport of fluorescently tagged fluid to look at fluid motion at an interface [12] by the use of an evanescent wave approach. Each of these devices is accompanied by problems in the interpretation of the data. The ideal device would generate a well defined and controllable flow whilst providing a wide range of mechanical deformation and simultaneously permitting optical access to the sample. Below we present one possible embodiment of such a device.

2. Description of the Microrheometer

The design of the *Microrheometer* is shown in Fig. 2 and is conceptually simple. Two glass 'optical flats' (Newport Inc.) polished to $\lambda/10$ or better comprise the rheometer plates and are arranged parallel to each other with the fluid sample placed between them. A simple shearing flow (see Fig. 3) is generated by translating one of the plates laterally. Plane Couette flow is the simplest homogeneous deformation to generate experimentally and analyse theoretically [16], but there are two practical challenges for this type of device. Firstly, the plates must be parallel to within a negligible fraction of the gap and secondly, the motion of the plate must be in the plane of the plate.

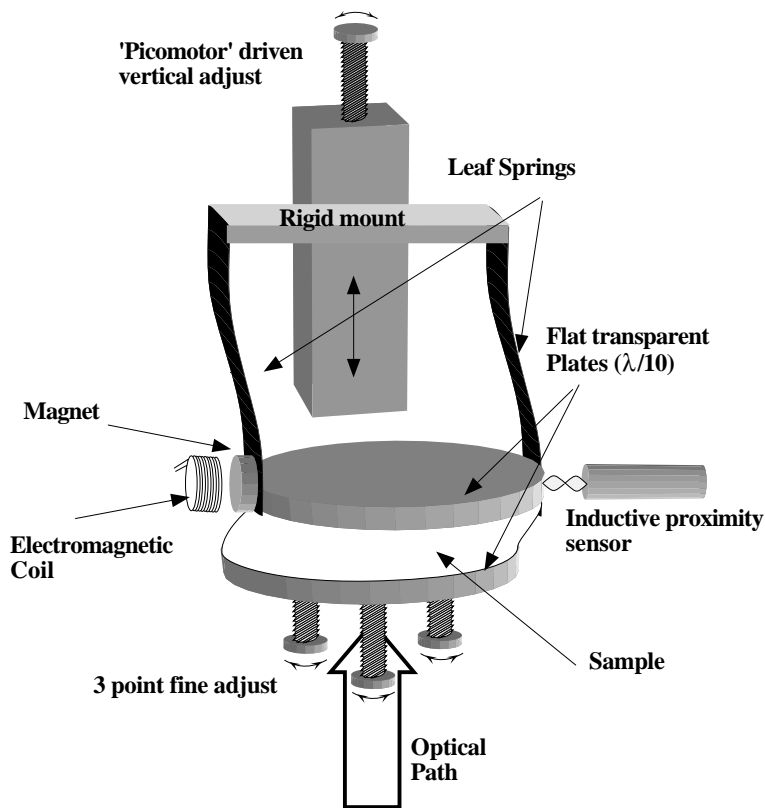


Figure 2: Schematic diagram of the construction of the microrheometer

We employ an approach similar to that used in SFA studies of friction and tribology [31-33]. The translating plate is mounted on a double cantilever spring system. Provided the deflection is very much less than the lever-arm, the resulting motion is constrained to be within the plane of the plate and is therefore effectively one-dimensional. Traditional SFA's use piezoelectric "bimorphs" as a drive mechanism and are consequently very stiff. We therefore chose an alternative approach utilising an electromagnetic drive with a solenoid coil and rare earth magnet, plus weak leaf springs. This ensures that the instrument rigidity is as low as possible and does not dominate over the sample properties - a particular problem for Newtonian fluids and small applied stresses. Hence we can use larger gaps (*cf.* conventional SFA separations of $O(\text{nm})$) and study the

static & dynamic properties of much lower viscosity materials than would otherwise be possible. An inductive sensor (Kaman Electronics) is used to track the lateral displacement of the surface (and hence, for a known gap, the nominal strain in the sample) with a resolution of 5 nm/√Hz and range of 50 μm. The abilities and sensitivities of the device are summarised in Table 1.

Table 1: The parameter space of the microrheometer

Parameter	Value	Comment
Plate Size (diameter)	0.013 m	Currently, 5mm - 0.02m possible
Gap Range	500 nm — 500 μm	Practical lower limit ~ 5 μm
Sample Size	0.07 μL — 40 μL	Governed by parameters above
Temperature Range	Ambient	The design has been specifically considered with higher (~200 °C) temperatures in mind - since we measure the gap absolutely thermal expansion is not a problem
Stress Range	8 mPa — 1 kPa	This is drive current limited so different drive electronics would significantly increase the range
Dynamic Range (oscillatory)	<1 mHz — 500 Hz	Governed by the stiffness of the springs and mass of surface. Note resonance currently at 50 Hz
Velocity Range (steady shear)	~1 nm/s ? - 1 mm/s	The lower limit at the moment is drift limited
	Gap = 1 μm	Gap = 500 μm
Strain Range (gap dependent)	0.5% — 5000%	0.001% — 10%
Strain Rate Range	2×10 ⁻⁶ s ⁻¹ — 2 s ⁻¹	1×10 ⁻³ s ⁻¹ — 1000 s ⁻¹
Viscosity Range	4 mPa.s — 500×10 ⁶ Pa.s	8×10 ⁻⁶ Pa.s — 1×10 ⁶ Pa.s

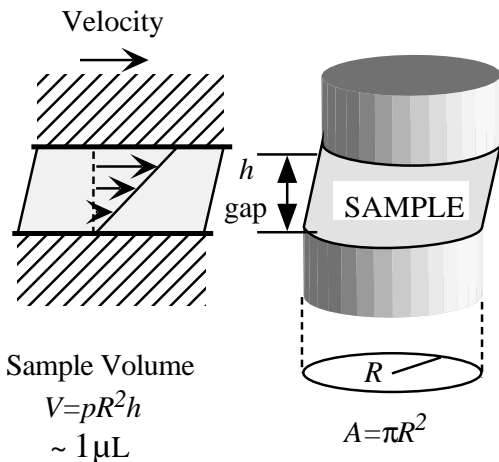


Figure 3: Planar Couette flow geometry

The upper fixture is mounted on a linear stage (Newport Inc.) and driven by a ‘picomotor’ (New Focus Inc.). This allows us to position the top surface with a smallest step size of 30 nm over a range of 1 cm with no drift. Alignment of the surfaces is achieved by a three-point adjustment using high accuracy micrometers. Transmission interferometry through the optically-transparent plates (for this purpose the plates are silvered) allows the absolute separation and parallelism to be determined in a manner similar to the SFA [20]. The application of interferometry to our experimental apparatus is shown schematically in Fig. 4 and is discussed at length by Dhinojwala and Granick [34].

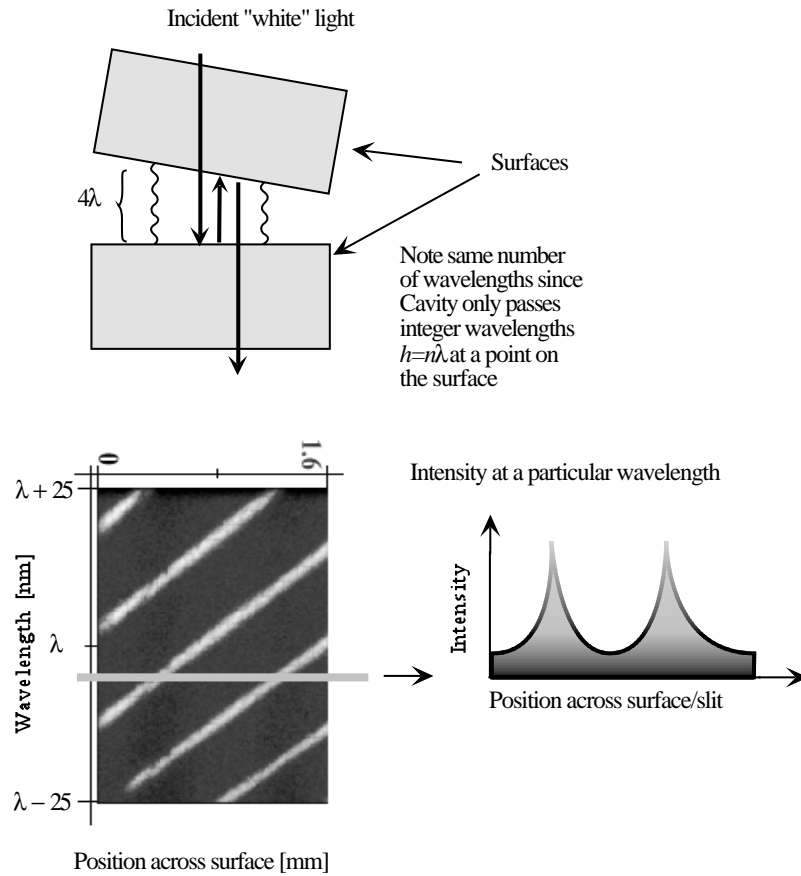


Figure 4: The use of white light interferometry for the determination of parallelism and plate separation. Only integer wavelengths are passed in a reflective cavity. Hence at a particular gap only certain wavelength orders are passed (integers n and $n+1$ for adjacent wavelengths). With varying gap and a fixed order the wavelength must change. The spectrometer therefore gives a 1D slice across the surface versus wavelength. Absolute gap and parallelism are consequently easily obtained from the wavelengths at order n and $n+1$.

3. Calibration of the Apparatus

The sliding plate apparatus described above is designed to operate as a controlled stress instrument; *i.e.* a known force is applied and the resulting displacement detected. However the instrument has a finite compliance arising from the leaf springs. To extract quantitative information from the experimental data, two issues must be addressed. Firstly, the intrinsic response (due to inertia, and compliance) of the instrument must be considered. Secondly, the experimental observables must be converted to instrument-independent material functions. Hence, once the effect of the moving mass is removed, the drive force and detected displacement are converted into a true shear stress and a nominal shear strain in the fluid. The complex viscosity of the material is then determined directly. This analysis is straightforward for the planar geometry described in the present paper, but it is a particular problem for the surface force instruments due to their curved surfaces.

In our instrument, a known force, $F(t)$, is applied and the resulting displacement, $X(t)$, detected. For the case of Small Amplitude Oscillatory Shear (SAOS) the deformation of the system can be modelled as a second order differential equation:

$$m \frac{d^2 X(t)}{dt^2} + (D + d) \frac{dX(t)}{dt} + (K + k)X(t) = F(t) \tag{1}$$

where m is the mass of the moving plate, and the parameters D , d and K , k are the damping coefficient and spring constants respectively. The lower case parameters represent the non-zero properties of the instrument itself and upper case variables represent the fluid response. In SAOS experiments, the drive force is given by $F(t)=F_0\cos(\omega t)$ and, after an initial transient, the resulting displacement is of the form $X(t)=X_0\cos(\omega t + \phi)$ where ϕ is a phase angle shift that can be determined accurately using a lock-in amplifier (EG&G model 7260). The lock-in amplifier not only allows a wide frequency range ($1 \text{ mHz} < \omega < 1 \text{ kHz}$) and dynamic range (-120 dB in principle) but also allows an additional harmonic to be determined in parallel. This is useful for the detection of non-linearities in the dynamic response. The sample response (D , K) is determined using the difference between a calibration run with no sample (run 1 - measured values $\{k\},\{d\}$) and a second run with a sample between the plates (run 2 - measured values $\{D+d\},\{K+k\}$). The instrument response can always be described by a simple (and ideal) Voigt model of a linear spring and dashpot in parallel. The Voigt sample model used here to characterise the fluid works well for SAOS, but for steady shear, Large Amplitude Oscillatory Shear (LAOS) or step impulses, different mechanical models are required.

The effective compliance of the apparatus/sample ensemble is of course strongly geometry dependent. However, for plane Couette flow, there is a simple geometric relation that connects the measured complex rigidity K^* to the complex modulus G^* . The true linear viscoelastic modulus of the material is given by:

$$K + j\omega D \equiv K^* = \frac{1}{p} G^* = \frac{1}{p} (G' + j\omega G'') \quad (2)$$

where $j = \sqrt{-1}$ and the geometric factor is simply $p = h/A$ with h the plate separation and A the plate area. There is no analogous simple relation for torsional shear flow in the parallel plate geometry or for the complex flows realised between the opposed curved interfaces in the SFA.

4. Effect of Gap Separation on Material Response

4.1 Mode of deformation

Microrheometers of the form described above can be used to probe gap-dependent material responses under a wide range of deformation histories including (but not limited to) SAOS, Large Amplitude Oscillatory Shear (LAOS) and steady shear. Slip and other non-linear effects have been studied in the latter two modes (see *e.g.* [3,5]) but to our knowledge no experimental studies of slip have been performed using SAOS. For this reason in the present paper we will concentrate on the effects of gap variations on the viscoelastic response for a polymer melt. We also aim to show that in the large gap limit, the microrheometer measurements agree well with conventional bulk rheometry.

4.2 Small Amplitude Oscillatory Shear

Scaling predictions have recently been presented for the dynamical behavior of high molecular weight polymer melts in confined geometries [13] which have not yet been investigated experimentally. For small chain deformations, the apparent linear viscoelastic properties in a confined geometry are predicted to vary with the degree of the polymer adsorption. The slip velocity is given in terms of the gap and the adsorption conditions by:

$$U_s \sim \frac{U}{\left[2 + (\tau_1 h / \tau_0 a N)\right]} \quad (3)$$

Here U_s is the wall slip velocity, U is the rate of displacement of the moving plate, h the gap and aN the contour length of the polymer molecule. The relaxation times of the polymer in the bulk and at the wall are τ_0 and τ_1 respectively. In general $\tau_1 \neq \tau_0$ due to the different physico-chemical environment at the interface. For large gaps and/or strong adsorption *i.e.* $\tau_1 h \gg \tau_0 aN$ there is negligible slip. As the gap is decreased, or the relaxation times changed, the wall slip increases to a theoretical maximum of $U/2$. The consequences of this apparent slip on the linear viscoelastic properties of the melt are summarised in Fig. 5. For strong adsorption and large gaps the model reduces to Rouse dynamics of a free chain [19]. As the ratio $(\tau_1 h / \tau_0 aN)$ decreases the dynamical response of the fluid is modified by the slip and an additional intermediate regime occurs in which $G' \sim \omega^{1/2}$. This dependence of the material function on the adsorption conditions arises as a result of the change in relaxation times (and hence the apparent viscosities) of the layer of molecules closest to the walls. Such predictions can be directly tested in our apparatus by varying the plate separation and surface chemistry of the fixtures.

If the viscosity is independent of the gap, the measured rheological properties should remain constant as the gap is reduced. However as indicated in Eqn. 2 the true moduli are directly connected to the measured compliance of the material (which is gap-dependent). In Fig. 6a modulus data obtained for a polydimethylsiloxane (PDMS, $M_w=139,000$) are plotted over a range of gaps h ($10 \mu\text{m} \leq h \leq 70 \mu\text{m}$) and compared to oscillatory shear data obtained from a commercial cone-and-plate rheometer (TA instruments CSL²-500). These data were obtained before implementation of the interferometric gap determination. For frequencies in the range $10 \text{ rad/s} \leq \omega \leq 200 \text{ rad/s}$ both techniques are in excellent agreement. The storage modulus does deviate at lower frequencies since the fluid is only weakly viscoelastic and G' is not reliably detectable over the compliance of the instrument. At high frequencies there is a systematic deviation in both G' & G'' and smaller gaps result in lower values of the moduli. We believe this is an artefact of proximity to resonance which occurs at $\omega_c \sim 180 \text{ rad/s}$.

The only fit made to this data is a single constant offset h_0 applied to the nominal gap values. The reasons for this are as follows. If the inverse of the measured compliance values (see Eqn. 2) are

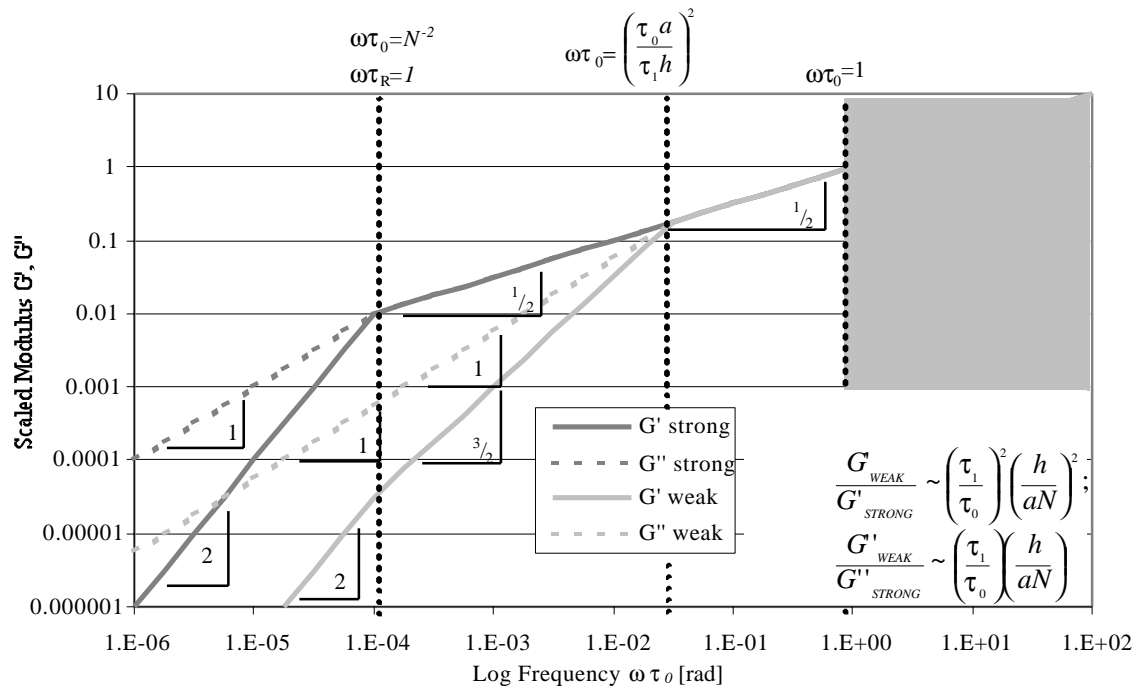


Figure 5: Asymptotic predictions of scaling theories for the SAOS behaviour of confined polymers (adapted from [13]). For representative purposes we use the following parameter values $\tau_0=1 \text{ s}$; $\tau_1=5 \text{ s}$; $a=10^{-6} \text{ m}$; $h=10^{-6} \text{ m}$; $N=100$.

plotted against the gap for a Newtonian fluid they should vary linearly (the gradient is the modulus) and must intersect the axis at the origin. If the line is not straight there is a gap effect. The experimental data at $\omega = 1$ rad/s shown in Fig. 6a are replotted in this manner in Fig. 6b. At gaps $h \geq 10 \mu\text{m}$ the data vary linearly, indicating no gap effect. At smaller gaps, two effects become evident. The first is a non zero offset which is the same for the real and imaginary parts of the complex compliance). This value of $h_0 = 7 \mu\text{m}$ indicates an error in the determination of "zero" gap and was the correction value applied to the data in Fig. 6a. Such zero-gap errors in microrheometry only shift the measured data vertically along the y-axis. The second item to note from Fig. 6b is the deviation from linearity at small separations. This can be attributed to a finite normal compliance of the instrument resulting in a load sensitive gap error. Both these problems are eliminated by the implementation of the interferometric gap determination approach and such in-situ determinations of the true gap are essential if microrheometric measurements are to be used in a quantitative manner.

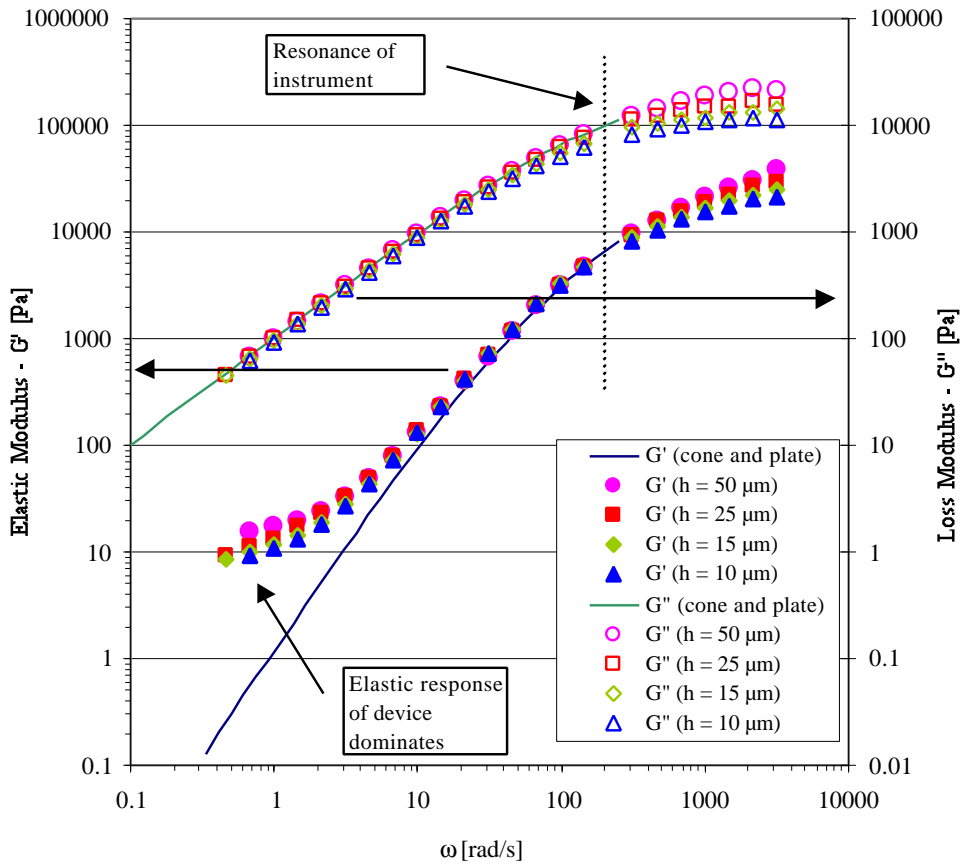


Figure 6: a) Microrheometer data at a variety of gaps for PDMS with a weight average molecular weight $M_w = 139,000$ g/mol. Cone and plate data overlaid from a TA Instruments CSL²-500. All data were taken at room temperature ($T_o = 25^\circ\text{C}$).

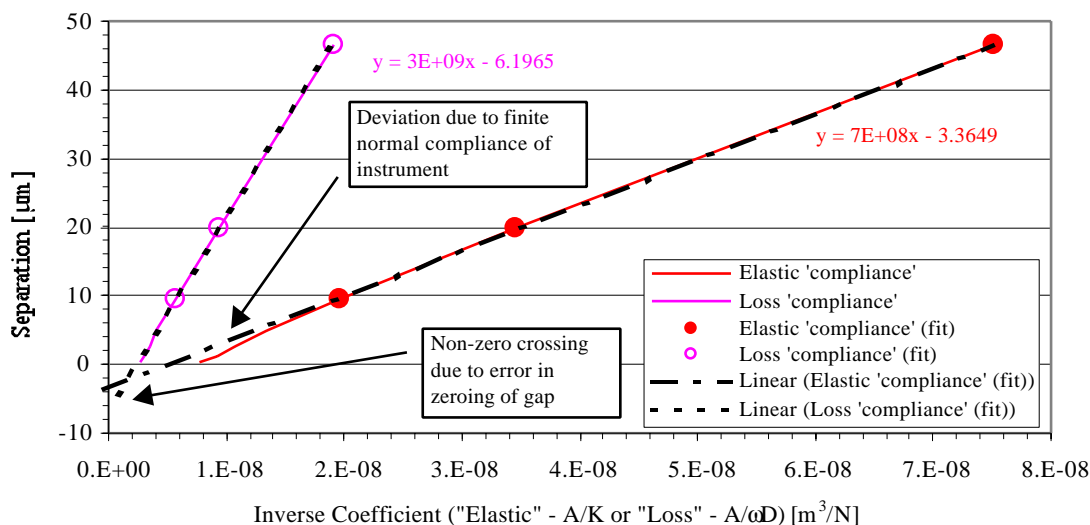


Figure 6: b) The apparent sample compliance from Fig. 6a at $\omega = 1$ rad/s plotted against gap. This form of plot highlights gap dependent effects.

5. Conclusions

In this paper we have discussed the concept of microrheometric instruments capable of studying the behaviour of polymer melts in confined geometries where the polymeric length scale is on the same order as the experimental length scales. We have outlined the design considerations and construction issues faced in building a microrheometer. We have emphasised the problems associated with the requirement for parallelism and the necessity for an absolute measure of the gap. We have also clearly demonstrated that these problems are solvable and allow the design of a parallel plate rheometer capable of operating at very small separations. In the present configuration, the instrument is driven electromagnetically, allowing us to keep the lateral compliance within reasonable limits. Strain is derived from an inductive position sensor and, by adjusting the stiffness of the leaf springs, a broad range of fluid properties can be accessed. From the data presented we show that the apparatus is capable of probing rheological properties down to gaps of less than ten microns. In addition the device can also be used as a conventional rheometer for esoteric materials in which large samples are not available [35]. The use of interferometry provides an absolute measure of the gap and the parallelism and hence removes any uncertainty about gap variations during the course of an experiment. Conversely a measurement of normal displacement during imposed shearing deformation could be used to obtain the normal force exerted by the fluid during the deformation (if the vertical compliance is calibrated). We plan to report on such enhancements in the future. Also the instrument has been designed with the specific intention of supporting higher sample temperatures and leaving the sample optically accessible for opto-rheological experiments. Current research activities in our laboratory include a detailed investigation of the change in apparent viscosity in an homologous series of polymer melts as the gap is varied. We are also investigating the effects of various surface finishes and chemistry (*e.g.* fluorocarbon sprays, roughness, silanisation) on the rheological behaviour of the confined film.

6. References

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