

Soft Matter

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: K. Sozanski, A. Wisniewska, T. Piasecki, K. Waszczuk, A. Ochab-Marcinek, T. Gotszalk and R. Holyst, *Soft Matter*, 2014, DOI: 10.1039/C4SM01280A.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Depletion Layer in Polymer Solutions at an Interface Oscillating at the Subnano- to Submicrometer Scale[†]

Krzysztof Sozanski,^a Agnieszka Wisniewska,^a Tomasz Piasecki,^b Karol Waszczuk,^b Anna Ochab-Marcinek,^a Teodor Gotszalk,^b and Robert Holyst^{*a}

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

Mobility of segments of polymer mesh in a solution determines the dynamic response of the depletion layer (DL) to mechanic stimuli. This phenomenon can be used to vastly decrease the local viscosity experienced by any device performing periodic motion at the nano- and microscale in complex liquids. We refined the vibrating quartz tuning fork (QTF) method to probe the viscosity of model aqueous solutions of polyethylene glycol, covering a broad range of molecular weights (3 kDa – 1 MDa) and QTF oscillation amplitudes (50 pm – 100 nm). For semidilute solutions of PEGs of high molecular weight, we found a drop of the local viscosity, up to two orders of magnitude below the bulk value. We propose a simple explanation based on the notion of depletion layer, strongly supported by rheometry and dynamic light scattering results. We show that it is possible to directly probe the viscosity of the DL and increase its thickness far above the equilibrium value. The key role is played by the rate of relaxation of the entangled system. The relevance of this paradigm ranges from basic research on dynamics of entangled systems to design of energy-efficient nanomachines operating in crowded environment.

1 Introduction

One of the key concepts in polymer science is the dependence of physical properties of a polymer system on the length-scale at which observations are made.¹ An important manifestation of such scale-related phenomena is the significant decrease of polymer concentration in solution in proximity of a non-adsorbing surface, known as the depletion layer (DL).² Although its thickness is of the order of the gyration radius of a polymer coil^{3,4} (which is usually in the nm range), its existence has profound consequences for e.g. colloid stability and flocculation,⁵ mobility in complex systems,⁶ and rates of biochemical reactions.⁷ Until now, depletion layer has been viewed and modeled exclusively as a static phenomenon, occurring at the surface of an immobile plane/sphere^{4,8} or around a diffusing particle,^{5,9,10} complementing the viscosity scaling paradigm.^{11–14} Even in case of diffusion studies, an implicit assumption has been made that depletion is an equilibrium state and its size and properties can be therefore treated as constant.

The equilibrium interfacial depletion layer at a flat surface

has already been directly observed by optical methods.^{3,15–17} However, none of these experiments allowed to probe the dynamics of the DL or capture the response of the polymer to mechanical stimuli. To induce and probe changes in the polymer structure at a vibrating interface, a system generating fast mechanical oscillations of precisely controlled amplitude in the nanometric range is required. The total displaced surface should be relatively large to diminish the edge effects and slip at the side surfaces, approximating a flat interface model. A novel instrument we designed, based on a quartz tuning fork (QTF), fulfills both these requirements.

QTF is a mass-produced vibrating piezoelectric device, usually used as a frequency reference in digital real time clocks. It is manufactured with hermetic vacuum housing, which may be however removed to expose the piezoelectric element. When excited using an electric signal at resonance frequency, QTF vibrates in flexural mode in which its prongs move perpendicular to their side surfaces. It can serve as both actuator and detector, offering very good stability of resonance frequency, small dimensions and low price. Therefore, numerous scientific applications of such devices have recently been developed, including specific biosensors,¹⁸ humidity sensors¹⁹, or even atomic force microscopy actuators.²⁰ Particular attention is given to their uses in measurements of density and viscosity of liquids.^{21–24} Such sensors can be very accurate, as damping of the vibrations of a QTF immersed in a fluid strongly depends on the viscosity of the medium.^{23–25} However, we have not found any papers mentioning attempts of application

[†] Electronic Supplementary Information (ESI) available: Exact molecular masses and PDI of the PEGs used, additional results of bulk viscosity, QTF and DLS measurements. See DOI: 10.1039/b000000x/

^a Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland. Fax: 4822 343 3333; Tel: 48 22 343 3123; E-mail: rholyst@ichf.edu.pl

^b Faculty of Microsystem Electronics and Photonics, Wrocław University of Technology, Janiszewskiego 11/17, 50-372 Wrocław, Poland.

of QTFs for determination of intrinsic dynamics of polymer systems.

The principle of QTF is similar to quartz crystal microbalance (QCM), the main difference being that the QCM vibrations occur along the direction parallel to its surface. QCM has been used as a sensor for viscosity of simple liquids²⁶ as well as polymer solutions.^{27,28} For polymers of large molecular mass a significant decrease in viscosity compared to the bulk value has been observed, which the authors attributed to the adsorption of polymer on the microbalance surface.^{27,28} However, it should be noted that in case of QCM only shear parallel to the surface can be observed, while the QTF is a 3D object immersed in the liquid. Shear stress – same as in case of the QCM – does appear at its side walls. However, in case of the QTF, an additional effect plays the key role in oscillation damping, which is forced flow of the liquid at the face of the prong perpendicular to the direction of its motion. Significant quantities of the liquid are displaced during the QTF motion, which is not the case for the QCM. Moreover, the two devices operate in very different frequency ranges (*ca.* 30 kHz for the QTF, compared to several up to hundreds of MHz for the QCM). Physically different phenomena may therefore be observed in these two cases.

The main inconvenience of QTF applied as a liquid viscosity sensor is significant parasitic capacitance and leakage current due to direct exposition of the electrodes to the investigated liquid. Suppression of these effects requires use of custom QTFs with buried electrodes²³ or sophisticated measurement methods.^{29,30} Despite that, QTF is a highly interesting sensor because of its great sensitivity to the liquid density and viscous friction.^{21,23,25,31} Its relatively low resonance frequency makes the necessary electronics and digital signal processing simpler. Moreover, the amplitude of the QTF oscillations can be precisely controlled by adjusting the excitation voltage.

In this manuscript, we present a systematic analysis of viscosity measurements performed by means of a quartz tuning fork for a broad range of aqueous polyethylene glycol solutions. We confront the obtained data with standard rheometric measurements, revealing differences of up to two orders of magnitude. Precisely controlling the amplitude of oscillations of the QTF over more than three orders of magnitude (tens of pm up to 100 nm), we scanned the polymer systems to see whether the spatial extent of motion influences the response of the polymer mesh. To put the results in the perspective of polymer dynamics, we performed dynamic light scattering measurements of characteristic relaxation times at different wave vectors. Merging all the data, we propose a versatile description of the dynamics of the depletion layer and its response to mechanical stimuli, opening new perspective for the emerging science of nanorheology of macromolecular systems.

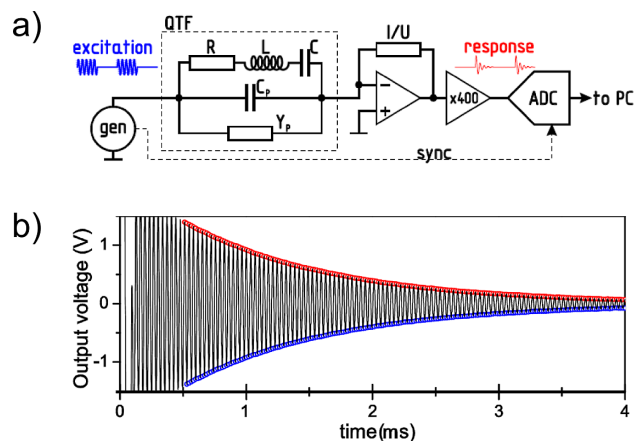


Fig. 1 a) Block diagram of the device using modulated excitation signal to measure the vibrations of the QTF. Shown are: the excitation signal, the electric equivalent circuit of the QTF in conductive liquid, current-to-voltage converter, amplifier, and analog-to-digital converter. b) Exemplary registered current generated by a QTF oscillating in water during its ringdown after excitation with 100 mV(RMS) voltage. The parameters of the exponential decay of vibrations are the time constant t_c and the initial amplitude of vibrations A_i .

2 Experimental Details

2.1 QTF Measurement System

The liquids we studied were aqueous solutions of polymers. Even highly purified water is electrically conductive to some extent, which makes typical electric measurements of the QTF vibration curve difficult or even impossible to perform.²⁵ To overcome this limitation, a novel method for QTF excitation and measurement of vibrations was used.²⁹ The simplified schematic of the measurement setup employing this technique is shown in Fig. 1a. In this method, the excitation signal is modulated in a series of sinusoidal bursts. It allows to minimize the influence of the current resulting from the conductivity of the liquid, represented by Y_p in Fig. 1a, on the total measured current.²⁹

During a burst, QTF vibrations are excited. When the excitation voltage is switched off, the vibrations decay and the current generated due to the piezoelectric effect in the QTF is measured using the current-to-voltage converter. Its output is then amplified, which results in the effective ratio of current-to-voltage conversion of 0.4 V/nA. Signal is processed using an analog-to-digital converter and analyzed using custom-written software. The software controls the measurement and calculates the parameters of the exponential decay of the vibrations caused by the viscosity-dependent damping. To improve the signal-to-noise ratio, hundreds of excitation–decay cycles are recorded during a single experimental run. Exem-

plary recording of the ringdown current is shown in Fig. 1b.

The initial value of the amplitude of the current generated by QTF (A_i) is used to calculate the amplitude of physical vibrations of the QTF during the excitation. It is only possible if the QTF used in the experiments has a known value of the electromechanical coupling coefficient α . For a QTF vibrating at the radial frequency ω ,

$$\frac{I}{\omega} = \alpha \cdot x, \quad (1)$$

where I is the amplitude of the current generated by the QTF and x is the displacement amplitude of the QTF prongs.³² We estimated the actual value of α in simultaneous electrical and optical measurements. We used Agilent 4294A impedance analyzer to excite the QTF with known voltage and determine the components of the QTF equivalent circuit elements. It allowed to evaluate the QTF resonance frequency and the magnitude of the QTF current at the resonance. At the same time, the magnitude of the vibrations was measured using the SIOS SP-S 120 Standard laser vibrometer. The QTFs that we used in the experiments were characterized by $\alpha = 16.8 \mu\text{C/m}$, while the amplitudes of vibrations obtained during the experiments ranged from tens of pm to 100 nm.

The time constant t_c of the exponential decay of the vibrations is correlated with the damping coefficient γ and viscosity η . Both modeling³³ and previous measurements²⁴ imply that $t_c \propto \eta^{-\frac{1}{2}}$. Here, we evaluate η by comparison of the decay time constants of the QTF measured in the sample t_c and in pure water $t_{c_{H_2O}}$, which served as a reference:

$$\eta = \eta_{H_2O} \left(\frac{t_{c_{H_2O}}}{t_c} \right)^2 \quad (2)$$

The core of the measurement system was enclosed in a steel box, wherein temperature was monitored with a thermocouple and kept at 298 ± 1 K.

2.2 Rheometry and Dynamic Light Scattering

Reference viscosity measurements of the polymer solutions were performed on a Malvern Kinexus Pro rotational rheometer, at a temperature of 298 ± 0.1 K. We adjusted the applied system geometry to the rheological properties of different samples. For samples of low expected viscosity (similar to pure water), we used a double-cylinder geometry: inside cylinder diameter 24 mm, outside cylinder diameter 27 mm, gap between lower and upper geometry 1 mm. For more viscous solutions we applied a cone-plate geometry: cone diameter 50 mm, angle 1° , plate diameter 60 mm, gap between geometries 0.03 mm. Homogeneous samples were poured onto the geometry rather than applied with a syringe not to induce formation of air bubbles within the liquid and equilibrated afterwards to ensure stable, uniform temperature across

the whole volume. For each sample, we first performed measurements at controlled shear rate to find the appropriate range of shear stress, where stable, purely viscous response was observed (usually, *ca.* 0.01 to 10 Pa). Subsequently, we performed measurements at controlled shear stress. Dynamic viscosity at zero shear, which is used throughout the whole article, was calculated by linear extrapolation of thus obtained data to 0. This step could also be regarded as an averaging procedure, since the measured viscosity value did not depend substantially on the shear stress within the investigated range.

We carried out the dynamic light scattering (DLS) measurements with a custom-assembled setup, based on a Stabilitel 2017 argon ion laser (514 nm wavelength), a Brookhaven BI-200SM goniometer, and Contin software for data analysis. All experiments were performed at 298 K, at a range of angles within the 30° to 150° limits. For each angle (i.e. wave vector), we analyzed autocorrelation of scattered photons as a function of time (sample curves can be found in the ESI[†]) and obtained polymer relaxation times from fitting of the correlation function. If there was a necessity for using a two-component fit (which was the case for high molecular mass polymers), we took only the slow mode into account for further analysis. The fast mode is generally ascribed to the internal dynamics of the chain and rearrangement within a single blob^{34,35} and therefore was not relevant in a situation where the whole entangled system is pushed by the oscillating wall.

2.3 Polymers Used

We used polyethylene glycol (PEG) aqueous solutions as well described, neutral polymer model system. Most polymers were obtained as molecular mass standards (low polydispersity) from Polymer Standard Service (Mainz, Germany); some regular PEGs of higher polydispersity (Sigma-Aldrich) were also tested. Detailed data on molecular weights and PDI are available in the ESI[†]. Overall, we investigated solutions of PEGs ranging from 3 kDa to 1 MDa, of concentrations falling mostly in the semidilute regime, with some samples from the dilute regime. Solutions were prepared in deionized water (good solvent conditions were fully satisfied) and stirred overnight on a magnetic stirrer to assure uniformity of the samples.

3 Results and Discussion

First, reference measurements of viscosity of the PEG solutions were performed by means of regular rheometry. Five PEG molecular mass standards were investigated; for each of the polymers, solutions of three different concentrations were prepared. Additionally, few measurements for broad-distribution PEGs were made. The obtained viscosity values ranged from less than 1 to over 150 mPa·s. The results agreed

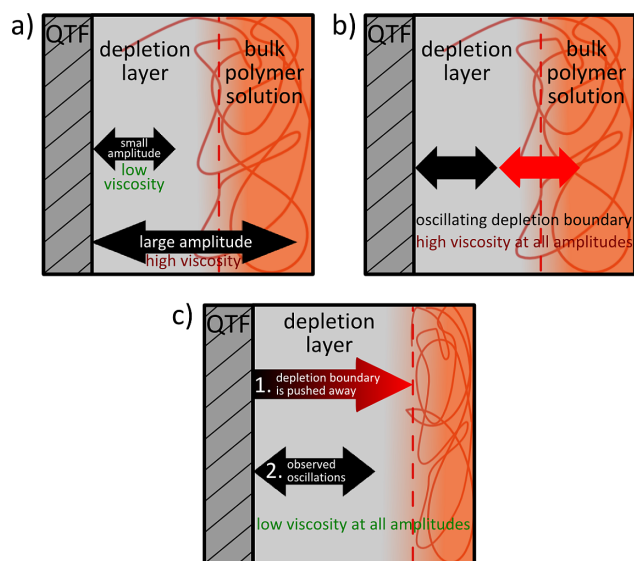


Fig. 2 Different considered models of depletion layer at an oscillating wall in a polymer solution. (a) The depletion layer is static, viscosity at small oscillation amplitudes is of the order of solvent viscosity, strongly increasing when the amplitude exceeds the DL thickness; (b) Due to hydrodynamic forces, the depletion layer moves together with the wall, therefore bulk viscosity is observed irrespective of the oscillation amplitude (the DL moves as if it was an intrinsic element of the QTF); (c) The oscillating wall forces broadening of the depletion layer, so that its thickness corresponds to the oscillation amplitude (polymer chains are pushed away from the surface and don't relax fast enough to fill the available space).

very well with the previously postulated scaling formula for viscosity of complex liquids³⁶ – confrontation with the scaling equation, along with the exact numbers for all the investigated solutions, is available in the ESI[†]. To investigate the viscoelasticity of the solutions, we performed oscillatory rheometric measurements (Malvern Kinexus Pro). Attempting to determine the linear viscoelastic region, we recorded the G' storage modulus at variable amplitude of the rheometer geometry oscillations and frequency of 1 Hz, which is a standard value for such experiments. Irrespective of the shear strain, the measured values of G' were below the sensitivity of the apparatus (only the inertia of the geometry was observed). This suggested purely viscous behavior of the bulk samples, which was in line with the fact that in rotational measurements the recorded viscosity did not change with the shear rate.

While preparing the QTF experiments, we took different hypotheses concerning the response of the polymer system to the oscillations into account, three of which are schematically depicted in Fig. 2. Being able to roughly predict the thickness of the DL^{4,16} (which was of the order of the gyration radius, i.e. ranged from *ca.* 2 to 70 nm for different polymers), we

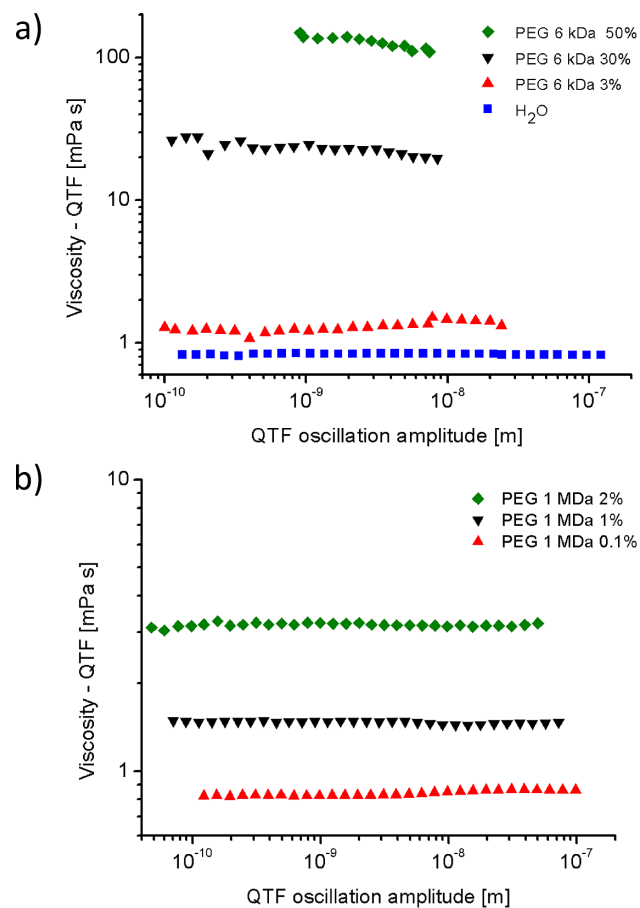


Fig. 3 Viscosity measured by the QTF in solutions of (a) PEG 6kDa; (b) 1 MDa plotted against the fork oscillation amplitude. Results of calibration measurements in deionized water are also given in graph (a). Bulk viscosities of solutions denoted with symbols matching in both graphs (e.g. 6 kDa 50% and 1 MDa 2%) are roughly the same. Analogous results for other investigated solutions can be found in the ESI[†].

designed the experiments so that the amplitude of the oscillations of the QTF would in all cases range from above to below this value. We gave particular attention to measuring the viscosity experienced at low amplitudes. Effectively, it came down to an amplitude range from tens of picometers to *ca.* 100 nanometers. If the depletion zone boundary did not follow the oscillations nor rearrange in any way (static depletion layer), a distinct crossover should be visible: for small displacements, the fork would experience the low viscosity of the DL (similar to the solvent viscosity), while for displacements exceeding the thickness of the DL, a much higher viscosity of bulk polymer solution would be observed (see Fig. 2a). Moreover, for large initial amplitudes a double-exponential decay would be expected: first, heavy damping in the polymer would take place, followed by slow decay when the oscilla-

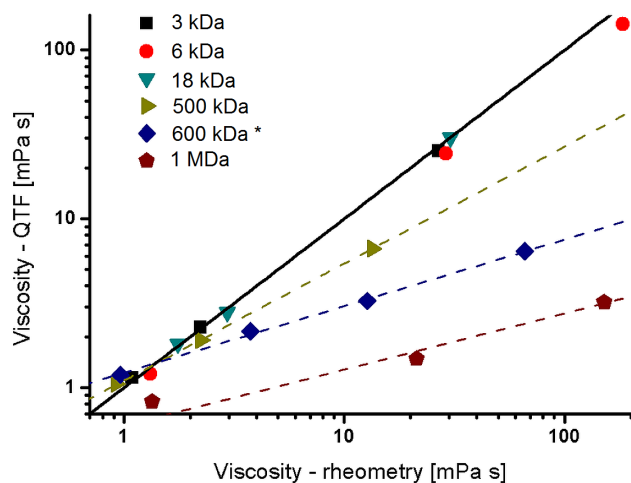


Fig. 4 Log-log plot comparing viscosities measured by regular rheometry and QTF. For polymers of $M_w < 20$ kDa very good conformity is observed, whereas for high M_w PEGs significant differences appear. Dashed lines are drawn as a guide for the eye, connecting points corresponding to solutions of the same polymer at different concentrations.

tion amplitude decreased into the depletion zone. However, this was not the case: all the decay patterns fitted perfectly to a single-exponential decay. We did not observe a meaningful dependence of the measured viscosity on the initial amplitude for any of the samples (appropriate graphs for 3 kDa and 1 MDa PEGs are presented in Fig. 3; analogous data for other investigated polymers can be found in the ESI[†]).

For all solutions of polymers of $M_w < 20$ kDa we obtained very good agreement between the results from QTF and rheometry measurements. The method proved therefore accurate even for solutions of viscosity two orders of magnitude greater than the viscosity of water.

An interesting observation was made for solutions of high M_w polymers (500 and 600 kDa, 1 MDa). Although the viscosity measured with the QTF did not depend on the oscillation amplitude, it was overall much lower than the reference bulk value. For example, in the case of the 2% solution of 1 MDa PEG, the observed discrepancy was fifty-fold. A comparison of viscosities measured with QTF and rheometry is presented in Fig. 4.

The observed discrepancy between QTF-measured and bulk viscosity for solutions of high- M_w PEGs could not be explained by analysis of static structure of the mesh. Therefore, we decided to investigate the dynamics of the polymer solutions using dynamic light scattering (DLS). In all solutions of low M_w polymers (up to 18 kDa), a single-component fit of the correlation function matched the results very well. However, in semidilute solutions of high M_w PEGs two distinct relaxation modes were observed. The fast mode was ascribed

to local relaxation of polymer chains³⁴ within a single blob of the size corresponding to the correlation length.³⁵ This was in line with our observation, supported by literature data,³⁷ that the fast mode relaxation time shortened with increasing polymer concentration: as the concentration increased, the correlation length (and, consequently, the blob size) decreased, restricting the length-scale and time-scale of the basic relaxation mode. Contrarily, for the slow mode we observed an increase in relaxation times with polymer concentration. Although the exact interpretation of the origin of the slow mode is still debated, it is generally related to the hindered motions of the entire entangled chains.³⁸ Therefore, it reflects the ability of the polymer mesh to react to the displacements of the QTF prongs.

For each of the samples, we performed DLS measurements at 7 different θ angles, ranging from 30° to 150°. Therefore, the length of the wave vector q covered the range of *ca.* 30 to 120 nm ($q = 4\pi n \sin(\theta/2)\lambda^{-1}$, where n – refractive index, $\lambda = 514$ nm – laser wavelength). We obtained relaxation times τ_0 from fitting of the autocorrelation curves and plotted τ_0^{-1} against q^2 for each of the investigated solutions. Characteristic diffusion coefficients D were calculated as slopes of the linear $\tau_0^{-1}(q^2)$ plots. According to the suggested interpretation of the long relaxation mode, D in the semidilute solutions refers to motion of large segments of the entangled polymer system, providing information about the dynamics of the mesh.

The frequency of QTF vibrations was fixed in the preformed experiments (resonance frequency was determined by the geometry of the fork prongs) and the oscillation period τ_{osc} was equal to 37 ± 2 μs . The slight shifts of τ_{osc} were due to differences in sample density and no indication of polymer adsorption on the QTF surface was observed. To incorporate the DLS results into the interpretation of QTF measurements, we used the diffusion coefficients to calculate root mean square displacement of polymer mesh segments, d_{RMS} occurring during a single τ_{osc} period:

$$d_{\text{RMS}} = (6D\tau_{\text{osc}})^{1/2}. \quad (3)$$

d_{RMS} is a measure of the extent of space, at which polymer relaxation can be expected during the QTF oscillation period. Another key factor is the thickness of the equilibrium DL, which determines the extent of space at which a decrease of polymer concentration is observed at equilibrium conditions. As the DL boundary is not well defined, as a rough approximation we assume that the thickness of the DL equals R_g .

A direct relation between the decrease of QTF-measured local viscosity of entangled solutions of high- M_w polymers and the geometric parameters d_{RMS} and R_g can be observed, which is depicted in Fig. 5. There is a straightforward physical justification for such dependence. Let us consider the limiting case for long polymer chains, when $d_{\text{RMS}} \ll R_g$, *i.e.*

the mesh relaxes very slowly and the depletion region is relatively broad. At low initial amplitudes of QTF oscillations ($A_i \ll R_g$), the DL/bulk boundary can be treated as stationary. The QTF moves within the DL, experiencing viscosity similar as in pure solvent. However, when A_i approaches or exceeds R_g , the QTF-measured viscosity does not increase. This can be explained by the „dynamic depletion” phenomenon: during the initial phase of forced oscillations, the polymer is pushed away and the DL is broadened (*cf.* Fig. 2c). As the relaxation of the polymer mesh is slow, it does not follow the motion of the QTF. Therefore, only the low viscosity of the DL is observed.

When $d_{\text{RMS}} \gg R_g$, the polymer chains are mobile and the mesh can follow the movement of the QTF in an extent sufficient for dynamic reconstruction of the DL. Even at small amplitudes ($A_i < R_g$) the DL/bulk boundary is not immobile: it follows the oscillations of the QTF to keep the equilibrium thickness of the DL at any given point of the oscillation cycle. Such assumption is fully supported by experimental data: for all QTF measurements in the $d_{\text{RMS}} > R_g$ regime (*i.e.* for polymers of $M_w < 20$ kDa), bulk viscosity was reproduced within a 15% error margin, irrespective of the amplitude. Unfortunately, due to technical limitations we were not able to perform measurement at A_i exceeding d_{RMS} for the low- M_w polymers (where d_{RMS} is of the order of hundreds of nm – see Table S3 in the ESI[†]). However, the limiting case for high amplitudes of QTF oscillations in PEG solutions is simple newtonian flow at high shear rate, characterized by the bulk solution viscosity. Therefore, no significant changes of effective viscosity at high amplitudes should be expected.

4 Conclusions

In the experiments presented hereby, the quartz tuning fork can be treated as a macroscopic object (approximation of a flat wall) moving in a polymer solution at nanoscopic amplitudes. Viscosity measurements performed using a QTF oscillating at different amplitudes (covering nearly three orders of magnitude and crossing the key length-scales in polymer solutions: coil radius and correlation length) revealed no dependence of the experienced viscosity on the amplitude. In solutions of relatively short polymer chains, bulk viscosity was well reproduced. This showed the utility of the improved QTF technique for measurements of viscosity of such liquids.

In case of high- M_w polymers a significant (even 50-fold) decrease of QTF-measured viscosity versus the bulk value was observed. We used dynamic light scattering to capture the internal dynamics of the polymer mesh and correlated the drop of the effective viscosity with the mobility of mesh segments and thickness of the depletion layer. We proved that if the relaxation of the polymer system is overrun by the motion of the fork, the DL/bulk boundary can be treated as station-

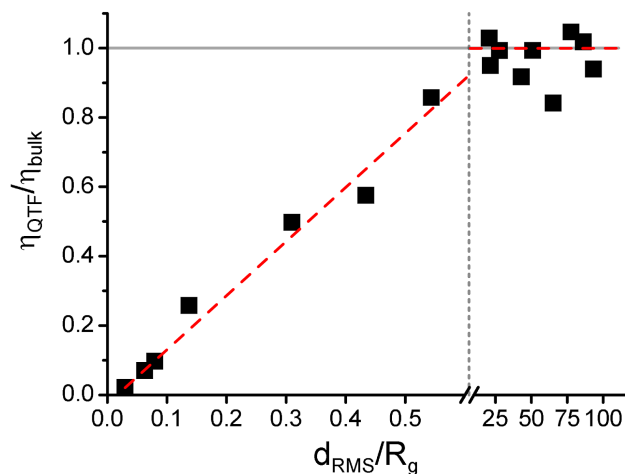


Fig. 5 QTF-measured viscosity of entangled polymer solutions strongly decreases when d_{RMS} , *i.e.* root mean square displacement of a polymer unit during one QTF oscillation period, drops below the thickness of the depletion layer (roughly approximated by the polymer gyration radius, R_g). In this regime, the DL/bulk solution boundary approaches a stationary state, while the QTF moves inside the DL. Oscillation amplitude is not relevant: even if $A_i \gg R_g$, the DL is broadened to A_i during the initial period of the experiment (forced QTF oscillations), while its return to the equilibrium state is relatively slow at low d_{RMS} . Please mind the break at the horizontal axis. Dashed red line is drawn as a guide for the eye.

ary and the oscillator measures the viscosity of the depletion layer. Furthermore, at high oscillation amplitudes a significant broadening of the DL can be forced, as the polymer chains are pushed away from the QTF surface. Due to slow diffusion of segments of heavily entangled mesh of long polymer chains, the DL does not return to its equilibrium thickness until the oscillation amplitude drops well below R_g .

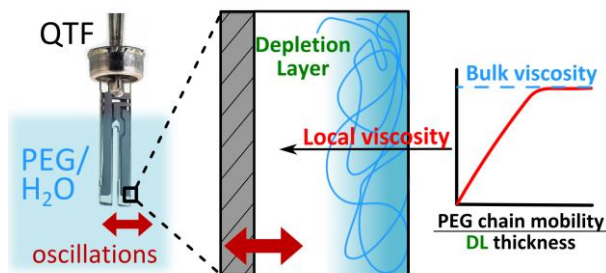
Experimental observation of the dynamic properties of the depletion layer proves that not only the length-scale domain should be considered in the description of the structure of complex liquids, but – in case of any dynamic systems – also the time-domain. This opens a perspective for new studies on the dynamic in nanorheology as well as in-depth analysis of the nature of slow relaxation modes in polymer systems. The presented paradigm should also prove important in research on micro- and nanosized machines operating in crowded environment; both the engineered and natural ones. If the rate of the repetitive/oscillating motion of such machines is high enough to overrun the relaxation dynamics of the surrounding mesh, they should experience greatly reduced mechanical resistance of the environment, which would result in their facilitated operation and lower energy consumption.

Acknowledgments

K.S. acknowledges financial support of the Ministry of Science of Poland within the Diamond Grant program DI2011 015341. A.O.M. is supported by the National Science Centre grant No. 2011/01/D/ST3/00751 (SONATA grant). R.H. and A.W. acknowledge the National Science Center for funding the project from the funds granted on the basis of the decision number 2011/02/A/ST3/00143 (Maestro grant).

References

- 1 P.-G. de Gennes, *Scaling Concepts In Polymer Physics*, Cornell University Press, 1979.
- 2 J. F. Joanny, L. Leibler and P.-G. de Gennes, *J. Polym. Sci. Pol. Phys.*, 1979, **17**, 1073–1084.
- 3 D. Auserre, H. Hervet and F. Rondelez, *Macromolecules*, 1986, **19**, 85–88.
- 4 G. J. Fleer, A. M. Skvortsov and R. Tuinier, *Macromolecules*, 2003, **36**, 7857–7872.
- 5 P. Jenkins and M. Snowden, *Adv. Colloid. Interfac.*, 1996, **68**, 57–96.
- 6 R. Tuinier, J. K. G. Dhont and T. H. Fan, *Europhys. Lett.*, 2006, **75**, 929–935.
- 7 S. Hou, N. Ziebac, T. Kalwarczyk, T. S. Kaminski, S. A. Wieczorek and R. Holyst, *Soft Matter*, 2011, **7**, 3092–3099.
- 8 B. Vincent, *Colloid. Surface.*, 1990, **50**, 241–249.
- 9 T. Odijk, *Macromolecules*, 1996, **29**, 1842–1843.
- 10 A. Ochab-Marcinek, S. A. Wieczorek, N. Ziebac and R. Holyst, *Soft Matter*, 2012, **8**, 11173–11179.
- 11 R. Holyst, A. Bielejewska, J. Szymanski, A. Wilk, A. Patkowski, J. Gapinski, A. Zywocinski, T. Kalwarczyk, E. Kalwarczyk, M. Tabaka, N. Ziebac and S. A. Wieczorek, *Phys. Chem. Chem. Phys.*, 2009, **11**, 9025–9032.
- 12 N. Ziebac, S. A. Wieczorek, T. Kalwarczyk, M. Fialkowski and R. Holyst, *Soft Matter*, 2011, **7**, 7181–7186.
- 13 A. Ochab-Marcinek and R. Holyst, *Soft Matter*, 2011, **7**, 7366–7374.
- 14 K. Sozanski, A. Wisniewska, T. Kalwarczyk and R. Holyst, *Phys. Rev. Lett.*, 2013, **111**, 228301.
- 15 C. Allain, D. Auserre and F. Rondelez, *Phys. Rev. Lett.*, 1982, **49**, 1694–1697.
- 16 D. Auserre, J. Edwards, J. Lecourtier, H. Hervet and F. Rondelez, *Europhys. Lett.*, 1991, **14**, 33–38.
- 17 A. Cuenca and H. Bodiguel, *Phys. Rev. Lett.*, 2013, **110**, 108304.
- 18 X. D. Su, C. C. Dai, J. Zhang and S. J. O'Shea, *Biosens. Bioelectron.*, 2002, **17**, 111–117.
- 19 X. Zhou, T. Jiang, J. Zhang, X. Wang and Z. Zhu, *Sensor. Actuator. B-Chem.*, 2007, **123**, 299–305.
- 20 F. J. Giessibl, M. Herz and J. Mannhart, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 12006–12010.
- 21 L. F. Matsiev, 1999 IEEE Ultrasonics Symposium Proceedings, 1999, pp. 457–460.
- 22 J. Zhang, C. C. Dai, X. D. Su and S. J. O'Shea, *Sensor. Actuator. B-Chem.*, 2002, **84**, 123–128.
- 23 Y. Liu, R. DiFoggio, K. Sanderlin, L. Perez and J. Zhao, *Sensor. Actuator. A-Phys.*, 2011, **167**, 347–353.
- 24 K. Waszczuk, T. Piasecki, K. Nitsch and T. Gotszalk, *Sensor. Actuator. B-Chem.*, 2011, **160**, 517–523.
- 25 L. Matsiev, 2000 IEEE Ultrasonics Symposium Proceedings, 2000, pp. 427–434.
- 26 I. D. Avramov, *Meas. Sci. Technol.*, 2009, **20**, 124006.
- 27 P. Wang, J. Fang, Y. Hou, X. Du and D.-M. Zhu, *J. Phys. Chem. C*, 2009, **113**, 729–735.
- 28 S. Qin, X. Tang, L. Zhu, Y. Wei, X. Du and D.-M. Zhu, *J. Colloid. Interf. Sci.*, 2012, **383**, 208–214.
- 29 K. Waszczuk, T. Piasecki, K. Nitsch and T. Gotszalk, *Meas. Sci. Technol.*, 2013, **24**, 085304.
- 30 J. Toledo, T. Manzaneque, J. Hernando-García, J. Vazquez, A. Ababneh, H. Seidel, M. Lapuerta and J. L. Sánchez-Rojas, *Comparison of quartz tuning forks and AlN-based extensional microresonators for viscosity measurements in oil/fuel mixtures*, 2013.
- 31 A. Agoston, F. Keplinger and B. Jakoby, *Sensor. Actuator. A-Phys.*, 2005, **123–124**, 82–86.
- 32 Y. Qin and R. Reifengerger, *Review of Scientific Instruments*, 2007, **78**, 063704–063704–7.
- 33 H. Hosaka, K. Itao and S. Kuroda, *Sensors and Actuators A: Physical*, 1995, **49**, 87–95.
- 34 T. Nicolai, W. Brown, S. Hvidt and K. Heller, *Macromolecules*, 1990, **23**, 5088–5096.
- 35 J. Li, Y. Lu, G. Zhang, W. Li and C. Wu, *Chinese J. Polym. Sci.*, 2008, **26**, 465–473.
- 36 T. Kalwarczyk, N. Ziebac, A. Bielejewska, E. Zaboklicka, K. Koynov, J. Szymanski, A. Wilk, A. Patkowski, J. Gapinski, H.-J. Butt and R. Holyst, *Nano Lett.*, 2011, **11**, 2157–2163.
- 37 P. Stepanek, C. Konak and J. Jakes, *Polym. Bull.*, 1986, **16**, 67–73.
- 38 J. Li, T. Ngai and C. Wu, *Polym. J.*, 2010, **42**, 609–625.



We experimentally investigate the dynamics of the interfacial region of polymer solutions – depletion layer. Viscosity experienced by the oscillator is even two orders of magnitude lower than the bulk value.