Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information (ESI) for:
Depletion Layer in Polymer Solutions at an Interface Oscillating at the Subnano- to Submicrometer Scale

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1 Polymer Characterization

In all experiments we used polyethylene glycol as a well-described, water-soluble, non-adsorbing, neutral model polymer. For molecular weight standards, purchased from Polymer Standard Service GmbH (Mainz, Germany), gel permeation chromatography (GPC) measurements were performed by the manufacturer and suitable data was provided. The data on polymers standards used in the experiments is collected in Table S1.

Table S1 Weight-average molecular masses and polydispersity indices (PDI) for PEG molecular weight standards used in the experiments.

Designation	M_{w} [Da]	PDI
3 kDa	3060	1.09
6 kDa	6550	1.06
18 kDa	17900	1.20
500 kDa	496000	1.46
1 MDa	941000	1.07

We also used two non-standardized PEGs of average molecular mass ca. 600 kDa, purchased from Sigma-Aldrich. As the exact M_{w} is not of primary concern for the subject (both bulk viscosity and relaxation times were measured for each of the prepared solution separately, no interpolation or fitting of data with respect to M_{w} was necessary), we did not perform chromatographic measurements for this polymer. However, much higher polydispersity (PDI ¿ 2) should be expected than in case of the M_{w} standards.

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2 Bulk Viscosity Data

Precise rheomertic measurement were performed to establish the macroscopic viscosity of the polymer solutions. The results are presented in Table S2. The obtained values were confronted with the previously published viscosity scaling equation for polymer solutions:[1,2]

$$\ln\left(\frac{\eta}{\eta_0}\right) = b\left(\frac{R_\mathrm{h}}{\xi}\right)^a, \tag{S1}$$

where η, η_0 – viscosities of polymer solution and pure solvent, respectively; a, b – parameters of the order of unity; R_h – hydrodynamic radius of the polymer coils; ξ – correlation length. ξ is proportional to $(c/c^*)^{-\beta}$, where c – polymer concentration; c^* – overlap concentration; β – constant, for good solvent conditions equal 0.75.[3] Parameter a in Equation S1 is proportional to the ratio of hydrodynamic and gyration radii of a polymer coil, $a\beta \propto R_\mathrm{h}/R_\mathrm{g}$, although its physical meaning and implications are still under discussion.[4]. Parameter b is temperature-dependent and can be adapted to put the equation in terms of activation energy for solution flow.[5] The parameters, universal for all semi-dilute PEG systems, were established experimentally in our previous work.[2] The results presented hereby proved fully consistent with the scaling equation, as can be seen in Figure S1, which confirms proper characterization of the molecular masses. For PEGs of M_w below 20 kDa, QTF-measured viscosity reproduces the bulk values. This means that for systems characterized by sufficiently fast relaxation times, the QTF method can be used to measure bulk viscosity and the obtained values would still follow the general scaling relations.

Table S2 Bulk viscosity of the investigated PEG solutions. All measurements were performed at 298 K, with deionized water as solvent. An asterisk denotes non-standardized polymers of broad M_w distribution

Polymer	% w/w	Bulk viscosity [mPa·s]
3 kDa	3%	1.09
	10%	2.23
	40%	26.8
6 kDa	3%	1.32
	30%	28.9
	50%	184
18 kDa	3%	1.76
	5%	2.94
	20%	30.4
500 kDa	0.1%	0.92
	0.5%	2.23
	2%	13.4
600 kDa*	0.1%	0.96
	0.5%	3.74
	1%	12.7
	2%	66.2
1 MDa	0.1%	1.34
	1%	21.3
	2%	152

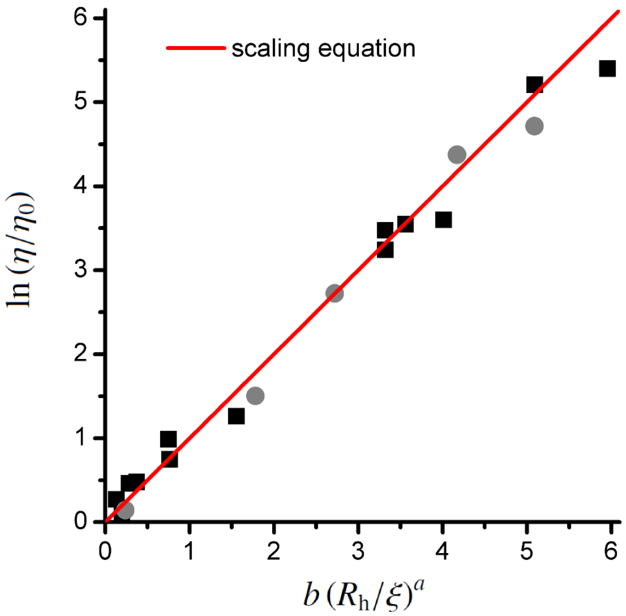

Figure S1 Experimental data on bulk viscosity overlaid with the viscosity scaling equation (Equation S1). Full consistency is observed. Gray circles correspond to non-standardized polymers of broad M_w distribution

3 QTF-Measured Viscosity vs. Oscillation Amplitude

In all the investigated polymer solutions, we performed QTF measurements in a wide range of oscillation amplitudes. The limits were dictated by the signal/noise ratio decreasing for extremely small amplitudes and possible distortions at high values of stimulating voltage. Exemplary results for 3 kDa and 1 MDa PEGs can be found in the main text (Figure 4); analogous data for other samples are presented in Figure S2. Irrespective of the parameters of the different investigated systems (R_h, ξ), no dependence of effective viscosity on the oscillation amplitude can be found.

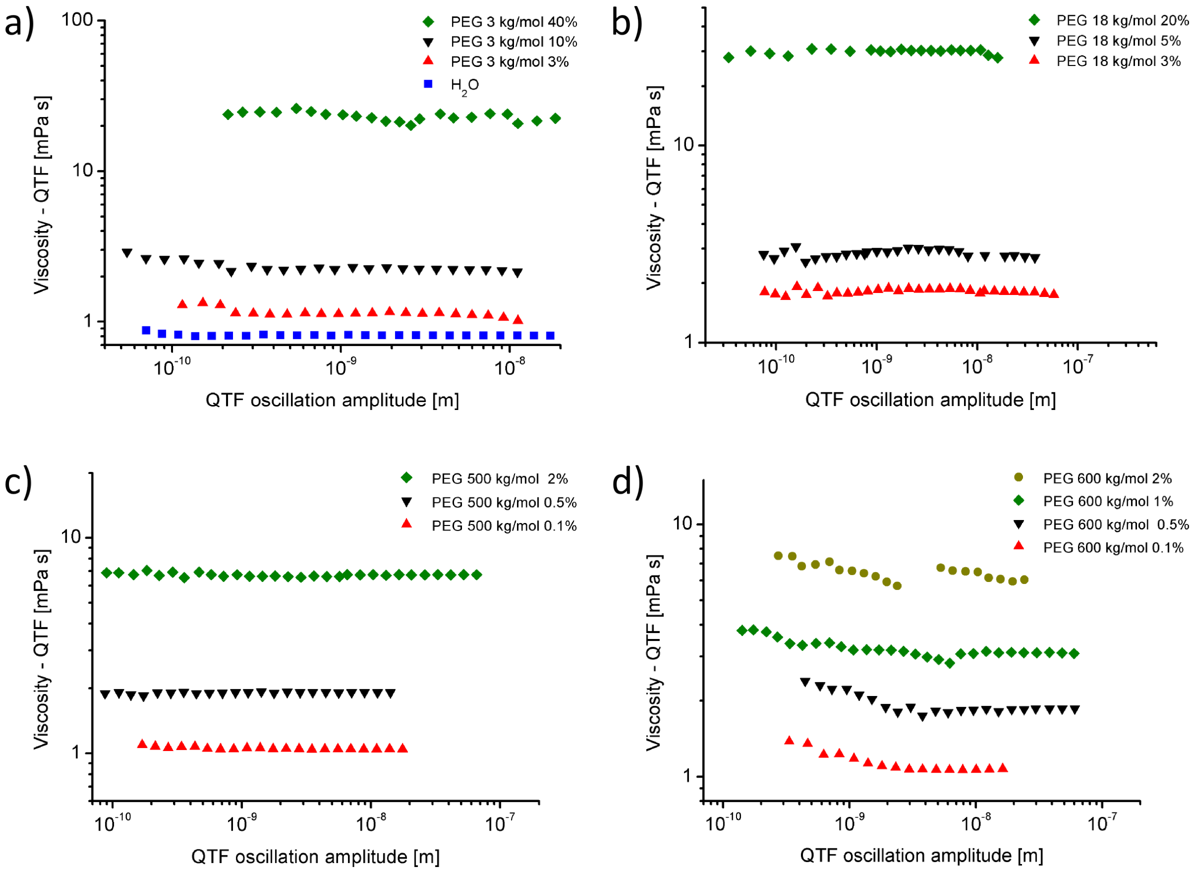

Figure S2 Results of viscosity measurements performed with the QTF oscillating at different amplitudes. PEG solutions: (a) 6 kDa; (b) 18 kDa; (c) 500 kDa; (d) 600 kDa (non-standardized M_w)

4 Relaxation Modes in DLS

For solutions of polymers of low molecular masses (up to 18 kDa), only a single relaxation mode was observed and monoexponential fitting was performed (see exemplary correlation curve in Figure S3a). However, for semi-dilute solutions of polymers of high molecular weight two distinct modes were observed (Figure S3b). The values of characteristic diffusion coefficients obtained for the investigated samples are given in Table S3. The fast mode is ascribed to the internal dynamics of the chains and rearrangement within a single blob[6,7], while the slow mode is generally related to the hindered motion of the entangled chains.[8] Such interpretation is in line withe the observed concentration dependence of the measured D values. In case of the fast mode, D increases with concentration (blobs get smaller, which prevails over the overall viscosity increase and enhances blob mobility). On the other hand, D of the slow mode decreases with concentration (the polymer mesh becomes thicker and motion of whole chains or their large segments is hindered). For small polymers, both phenomena (movement within blobs and of mesh segments) occur at similar length- and time-scales and cannot be easily distinguished. In the 500 kDa 0.1% solution only one mode was observed due to the fact that the solution fell in the dilute concentration regime and therefore the chains were not interpenetrated (separate coils occurred in the solution rather than a polymer mesh).

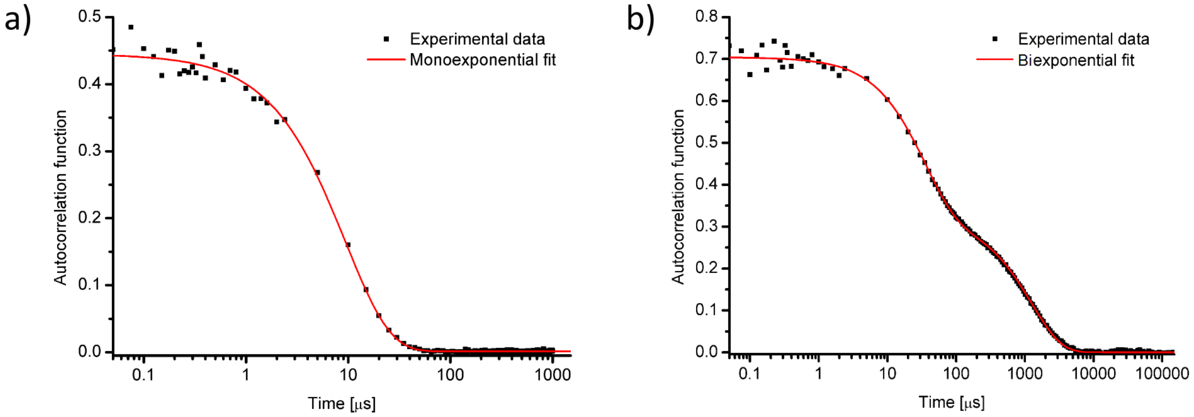

Figure S3 Sample dynamic light scattering (DLS) correlation curves obtained at $\theta = 90$deg for PEG solutions: a) 18 kDa, 5%, monoexponential decay; b) 500 kDa, 2%, double-exponential decay

Table S3 Diffusion coefficients D (both slow and fast mode) obtained from DLS measurements for different PEG solutions. For each sample, autocorrelation of scattered photons was captured at 7 different θ angles (30 – 150°), i.e. at different wave vectors q. Fitting of mono- or biexponential models yielded characteristic correlation times τ_0. D values were calculated as slopes of the linear $\tau_0^{-1}(q^2)$ plots. d_{RMS} (root mean square displacement) was calculated as $d_{\mathrm{RMS}} = (6D\tau_{\mathrm{osc}})^{1/2}$, where τ_{osc} is the QTF oscillation period (~37 μs). d_{RMS} is a measure of space explore by segments of the polymer mesh during a single QTF oscillation period; therefore, for high-M_{w} PEGs it concerns only the slow diffusion mode. Asterisk denotes non-standardized polymer of broad M_{w} distribution

Polymer	% w/w	D_1 [μm^2 s^{-1}]	D_2 [μm^2 s^{-1}]	d_{RMS} [nm]
3 kDa	3%	146.8	–	181
	10%	180.7	–	200
	40%	211.3	–	217
6 kDa	3%	109.2	–	156
	30%	250.2	–	236
	50%	225.1	–	224
18 kDa	3%	81.6	–	135
	5%	87.7	–	140
	20%	148.2	–	181
500 kDa	0.1%	11.0	–	49.4
	0.5%	36.0	2.70	24.5
	2%	47.5	0.88	14.0
600 kDa*	0.1%	22.6	4.51	31.6
	0.5%	23.0	2.14	21.8
	1%	25.5	0.21	6.9
	2%	30.3	0.073	4.0
1 MDa	0.1%	11.9	1.02	15.1
	1%	24.9	0.077	4.1
	2%	38.3	0.017	2.0

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