Polymers are flexible long chain molecules, of outstanding importance in diverse fields from processing of materials to biological activity. It is well known that it is possible to effectively confine some polymers to two dimensions, for example by anchoring each monomer to the interface between immiscible fluids. Polymer dynamics in two dimensions (2d) has remained relatively unexplored compared to bulk solutions, despite there being important examples both in life sciences and in technology where polymer molecules are confined to a plane. We consider the simplest situation where the chains lie flat and are free to move only in a 2d space. Such a surface layer exerts a lateral osmotic pressure $\Pi = \gamma_0 - \gamma$, which is the amount by which the surface tension $\gamma$ is reduced compared to the free interface tension $\gamma_0$. This pressure becomes significant above overlap of single chains, where it has a power-law dependence on the concentration that has been known for some time. Like its counterpart in 3d bulk solutions, this equilibrium property is well explained within the picture of the polymer semi-dilute regime as an ensemble of independent “blobs.” Despite a few decades of experiments, very little is known instead about the physical nature of the divergence of viscosity and elasticity in 2d. These dynamical properties control important processes like foam drainage and stabilization and flow in emulsions when polymers are used as surfactants. The theoretical framework to describe complex non-Newtonian flow and the dynamics of chains is well understood in 3d, but cannot be applied straightforwardly in 2d. How does the confinement to the surface, specifically a 2d effect, affect the dynamics of the system?

This Letter presents a study of the dynamics of concentration fluctuations in a wide range of polymer monolayers, performed with surface dynamic light scattering. Polymers are spread onto an interface in dilute conditions, and cannot subsequently submerge and re-surface. Under these conditions polymer chains are unable to cross each other. This is the case for many monolayer systems studied in the literature. The technique used in this work, developed by Langevin and others, see the monograph, is the only existing probe of thermal concentration fluctuations in monolayers. Despite its use on polymer monolayers by various groups, some issues concerning the data analysis have been resolved only recently, hence the data which is available for a quantitative comparison is very limited.

Isolated polymer chains are usually modelled as random walks with potential interactions. The Flory exponent $\nu$ relates the number of monomers $N$ to the radius of gyration: $R_g \sim N^{\nu}$. When the concentration in a polymer solution is increased so that individual chains are forced to overlap, the system enters a semi-dilute regime that lasts until the monomer fraction is very high. The semi-dilute region is important because for sufficiently long chains it covers a wide range of concentrations. The equilibrium properties of polymers in this regime are given both in 2d and 3d by scaling laws, with exponents related to $\nu$. In particular, fluctuations of the density of monomers are correlated over a length $\xi$, defining a region known as a “blob.” Inside the blob the chain has the same statistics as an isolated single chain, but different blobs are statistically independent. In 2d $\xi$ scales with the concentration $\Gamma$ as:

$$\xi \sim \Gamma^{\nu/(1-2\nu)},$$

decreasing from a value of the order of $R_g$ at the overlap concentration to the monomer size. Scaling of the osmotic pressure in a monolayer was first shown experimentally in ref.:

$$\Pi \sim \xi^{-2} \sim \Gamma^{\nu_{eq}}, \text{ where } \nu_{eq} = 2\nu/(2\nu - 1).$$

Figure shows equilibrium data for some of the systems studied in this work. In 2d there are well known limiting regimes: The “good solvent”, in which the chain behaves as a self-avoiding random walk, hence $\nu = 3/4$ and $\nu_{eq} = 3$, and the “$\theta$ conditions” where the effects of excluded volume balance the monomer-monomer preferential attraction. Here the Flory exponent is predicted to be $\nu = 4/7$ and the power law exponent increases to $\nu_{eq} = 8$, making this isotherm much steeper and compact.
In contrast to the bulk, where the polymer chains can interpenetrate, in the planar 2d geometry the polymers are segregated and attain disk-like configurations \( \triangledown \). Chains are corralled by their neighbors, as was observed with DNA molecules confined to a plane in ref. \[10\].

In general, the response to a deformation in an isotropic 2d material is characterized by two elastic moduli: changes in area are controlled by the dilation modulus \( \varepsilon \) and changes in shape by the shear modulus \( G \). Power laws of the equilibrium dilational modulus \( \varepsilon_{eq} \) against concentration. Lines are fitted power laws, showing the well known scaling of this equilibrium property in the semi-dilute regime.

In polymer systems, different models are appropriate depending on the lengthscales and timescales that are being observed. The lengthscales \( q^{-1} \) probed with SQELS satisfy \( q \xi < 1 \), so the semidilute solution is expected to be in a “macroscopic” regime where it behaves like a gel \[17\]. The gel’s response is characterized by a rigidity modulus, \( \varepsilon' \), scaling like the number of contacts, hence proportional to the osmotic pressure, and by a viscous dissipation modulus \( \omega \varepsilon'' \) describing the friction involving the surface wave dispersion relation \( D(\omega) \) that relates the wave frequency to the wavelength has to be known:

\[
D(\omega) = \left[\varepsilon' q^2 + i \omega \eta(q + m)\right] \left[\gamma q^2 + i \omega \eta(q + m) - \frac{\rho \omega^2}{q}\right] + \left[i \omega \eta(m - q)\right]^2,
\]

where \( m = \sqrt{q^2 + \frac{i \omega \rho}{\eta}} \) and \( \text{Re}(m) > 0 \),

\[
\eta \text{ is the subphase Newtonian viscosity and } \rho \text{ is the subphase density. Buzza \[13\] recently proved that the model Eq. \[3\] which is commonly found in the literature \[7, 14\], is correct but that even under dynamical conditions the surface tension \( \gamma \) should be considered as a real quantity, equal to the equilibrium static surface tension \[23\]. As derived in ref. \[15\], the spectrum of light scattered by thermal roughness is given by:

\[
P_q(\omega) = \frac{k_B T}{\pi \omega} \text{Im} \left[ \frac{i \omega \eta(m + q) + \varepsilon q^2}{D(\omega)} \right].
\]

SQELS data is fitted with Eq. \[3\] and Eq. \[4\] with only three physical parameters to be determined. Details of our experimental methods, including calibration, data analysis and limits of the technique, are described in ref. \[16\].

FIG. 1: Surface pressure \( \Pi \) as a function of area. Data are representative of three systems studied in this Letter: (○) PVAc, (△) β-casein, (▽) β-lactoglobulin. Segments indicate the semi-dilute regime region where the equilibrium scaling exponents are determined. Inset: log plot of the equilibrium dilational modulus \( \varepsilon_{eq} \) against concentration. Lines are fitted power laws, showing the well known scaling of this equilibrium property in the semi-dilute regime.
the monomers and the solvent. This is well established in three dimensional solutions, where both a fast and a slow relaxation mode can be probed simultaneously, for example with dynamic light scattering. The fast relaxation can be described within the Rouse model and is related to a cooperative diffusion timescale \(\tau_{\text{coop}}\). This describes fluctuations that become faster as the concentration increases and the correlation length \(\xi\) decreases. The slow relaxation is related to the self diffusion coefficient for reptation and is determined by the time \(\tau_{\text{rept}}\) required for the chain to diffuse along its length. \(\tau_{\text{rept}}\) is an increasing function of the concentration. The approach of directly measuring the frequency spectrum of light scattered by concentration fluctuations is not possible in monolayers because there is insufficient optical contrast, and dynamics can be probed only by indirect methods such as SQELS.

Figure 3 shows the components of the monolayer viscoelastic moduli, measured with SQELS for different polymer monolayers. Both the elastic and viscoelastic components of \(\varepsilon^*\) exhibit a power law dependence on the concentration:

\[
\varepsilon' \sim \Gamma^{\nu_e'\gamma} \quad \text{and} \quad \varepsilon'' \sim \Gamma^{\nu_e''}\gamma
\]

A similar scaling behavior was recently reported by Monroy et al. but has not been explained. Results for all the systems considered in this work are summarized in Table I. Monolayers of very different compositions, comprising both synthetic polymers and proteins, have been studied, to cover the widest possible range of values of \(\nu\), the temperature, ionic strength and \(pH\) of the liquid subphase are all controlled, as they affect the chain configuration at the surface.

This data contains a wealth of information. Looking at Fig. 3 it can be clearly seen that for each monolayer the viscosity scales with a higher power than the elastic modulus. On general dimensionality terms, the viscosity can be regarded as the product of the modulus driving the relaxation and a characteristic time \(\tau\): \(\varepsilon'' \sim \varepsilon' \cdot \tau\). From this it immediately follows that the timescale \(\tau\) of these relaxations becomes longer the higher the concentration, hence a slow mode is being probed. The character of this mode can be read from Figure 4, where the power law exponents for \(\varepsilon^*\) defined in Eq. 5 are plotted against the concentrations. It is not surprising to find that \(y_{\varepsilon'} = y_{\varepsilon''}\), since the thermal fluctuations probed by SQELS fall within linear response theory. What is of interest is the apparently universally valid relation between the exponents for the elastic and the viscous components of \(\varepsilon^*\): \(y_{\varepsilon''} = 2y_{\varepsilon'}\). It finally follows that the timescale of these fluctuations, which we shall call \(\tau_{2d}\), scales like \(\tau_{2d} \sim \xi^{-2}\).

We are only able to speculate on the physical origin of this timescale. A simple explanation is that the slowing down of \(\tau_{2d}\) as the concentration increases is due to friction between the increased number of statistically independent blobs. The number of contacts in between blobs is proportional to \(\xi^{-2}\), giving:

\[
\varepsilon'' \sim \xi^{-4} \sim \Gamma^{2y_{\varepsilon'}}
\]

![FIG. 3: Log plot of the dilational elastic response modulus measured with SQELS as a function of the concentration, showing power-law scaling. Open symbols are the elastic (\(\varepsilon'\)) and filled symbols the viscous (\(\omega_{\varepsilon'}\)) components. Symbols are for different monolayers: (○) PVAc, (△) β-casein, (△) β-lactoglobulin, corresponding to data in Fig. 1. Standard deviations obtained from fitting repeated SQELS correlation functions (not shown on each data point for clarity) are used to weigh the power-law interpolation (lines). The exponents obtained from these fits are given in Table I and are plotted in Fig. 4. The correlation between the different exponents, highlighted in Fig. 4, represents the major result of this Letter.](image)

| Polymer | Conditions | Ref. | \(y_{\varepsilon'}\) | \(y_{\varepsilon''}\) |
|---------|------------|-----|----------------|-----------------|
| PVAc    | \(T=45^\circ\text{C}\) | 16  | 2.0            | 2.0             |
| PVAc    | \(T=25^\circ\text{C}\) | 16  | 2.4            | 5.9             |
| PVAc    | \(T=6^\circ\text{C}\)  | 16  | 2.4            | 5.5             |
| PVAc    | \(T=25^\circ\text{C}\) | 16  | 2.8            | 4.3             |
| β-casein| \(pH=5.3, 0.01M\) | 20  | 7.1            | 13.7            |
| β-casein| \(pH=7.2, 0.01M\)  | 20  | 6.0            | 11.9            |
| β-casein| \(pH=8.3, 0.01M\)  | 20  | 5.6            | 12.8            |
| β-casein| \(pH=7.6, 1.1M\)   | 20  | 4.6            | 9.3             |
| β-casein| \(pH=6.0, 0.02M\)  | 22  | 8.3            | 15.1            |
| β-casein| \(pH=8.3, 0.02M\)  | 22  | 5.3            | 13.3            |
| β-casein| \(pH=5.9, 0.1M\)   | 22  | 8.8            | 13.2            |
| P4HS    | \(pH=2, T=25^\circ\text{C}\) | 19  | 8.1            | 14.3            |
which describes the data of Fig. 3 very well. An analogy can be drawn between the diverging viscosity of the close-packed arrangement of blobs in the semi-dilute regime and the case of diverging viscosity of spheres at high packing density \( \phi \), both being determined by the number of contacts.

A question that arises is why this mode is not seen in 3\( d \). In bulk solutions in a good solvent a dynamical mode analogous to that just described for 2\( d \) would have a characteristic relaxation time scaling with the concentration \( \phi \) like \( \tau \sim \xi^{-3} \sim \phi^{9/4} \). This is a higher power of the concentration compared to reptation \( (\tau_{\text{rept}} \sim \phi^{1.5}) \), in agreement with the well known result that in 3\( d \) solutions the fluctuations relax via the self diffusion of the polymer chain and not the mechanism outlined above. In 2\( d \) relaxation by reptation is hindered by an effective confinement provided by neighboring chains.

In summary, it has been shown that the thermal concentration fluctuations in the semi-dilute regime of polymer monolayers reported in the present paper and in ref. \( [19] \) have a slow mode of decay with a timescale that had not been previously considered and that describes a specifically 2\( d \) process.

We thank E.M.Terentjev for very useful comments and discussions.

\[ \text{FIG. 4: The scaling exponents describing the power law dependence on the concentration of the dilational elasticity (open symbols) and viscosity (filled symbols) are plotted against the exponent for the equilibrium bulk modulus. (\( \bigcirc \)): PVAc, (\( \bigtriangledown \)): \( \beta \)-casein, (\( \bigtriangleup \)): \( \beta \)-lactoglobulin, (\( \blacksquare \)): data of Monroy et al. \( [19] \). This figure includes results from the data shown in Fig. 3 as well as the monolayers described in Table I. The lines have slopes of 1 and 2. It is clear from the data that the exponent for the viscosity is approximately twice the exponent of the elastic modulus. This result is different from analogous measurements on bulk polymer solutions, indicating a specific 2\( d \) dynamics.} \]