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Scaling of dynamics in 2d semi-dilute polymer solutions

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Abstract. – We consider the dynamics of thermal concentration fluctuations in polymer Langmuir monolayers, probed with surface light scattering. We present data on the proteins β-lactoglobulin and β-casein and on the synthetic polymers Poly(vinyl acetate) and Poly(4-hydroxystyrene). We show that for all these systems, in the semi-dilute concentration regime, there is a power law dependency of both the elastic and viscous components of the dilational modulus on the concentration. We find that for all the systems considered, the viscosity scales with a power that is double that of the elasticity. A simple explanation for this universal dynamical behavior in semidilute polymer monolayers is suggested.

Introduction. – Polymers are flexible long chain molecules, of outstanding importance in diverse fields from processing of materials to biological activity. It is possible to effectively confine some polymers to two dimensions, for example by anchoring each monomer to the interface between immiscible fluids [1, 2]. Despite there being important examples both in the life sciences and in technology where polymer molecules are confined to a plane, polymer dynamics in two dimensions (2d) has remained relatively unexplored compared to bulk solutions.

While the equilibrium properties of polymer monolayers are well understood, despite a few decades of experiments very little is known about the physical nature of the divergence of the viscosity and elasticity as the concentration increases. These dynamical properties are important as they control processes like foam drainage [3] and stabilization and flow in emulsions [4] when polymers are used as surfactants. The theoretical framework to describe complex non-Newtonian flow and the dynamics of chains is well developed in 3d [5, 6], but cannot be applied straightforwardly in 2d. We present experimental results on the dynamics of thermal concentration fluctuations, obtained from measurements of surface dynamic light scattering (SQELS) [7]. A direct probe of concentration fluctuations is not currently feasible in monolayers, because there is insufficient optical contrast, so dynamics can be measured only by indirect methods such as SQELS. SQELS is sensitive to surface roughness fluctuations, which are coupled to in-plane concentration fluctuations.

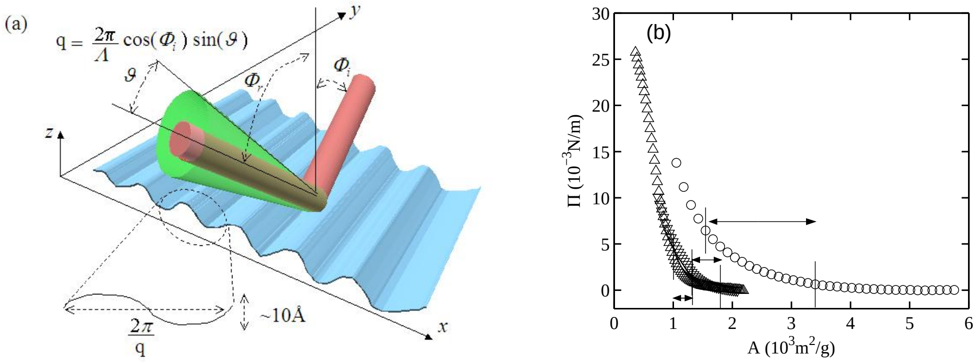

Fig. 1. – (a) Geometry of scattering from thermal surface roughness fluctuations (SQELS). Typical values of the scattering vector q are of the order of 400cm^{-1}, corresponding to capillary wave frequencies ω of order 10^5Hz. Λ is the wave length of the laser light. See [7] for a review of this technique. Details of our apparatus and methods are given in ref. [14]. (b) Surface pressure Π as a function of area. Data are representative of three systems studied in this Letter: (○) PVAc, (▽) β-casein, (△) β-lactoglobulin. See Table 1 for detailed monolayer conditions. Arrows indicate the semi-dilute regime region where the equilibrium scaling exponents are determined.

A surface layer can exert a lateral osmotic pressure $\Pi = \gamma_0 - \gamma$, which is the amount by which the surface tension γ is reduced compared to the free interface tension γ_0 [2]. For polymer layers this pressure becomes significant above the overlap of single chains, where a power-law dependence of Π on the concentration has been known for some time [8]. For sufficiently long chains the semi-dilute regime covers a wide range of concentrations. Polymer chains are statistically described by the Flory exponent ν, relating the number of monomers N to the radius of gyration: $R_g \sim N^\nu$. The equilibrium properties of polymers in the semi-dilute regime regime are given by scaling laws, with exponents related to ν. In particular, fluctuations of the density of monomers are correlated over a length ξ, defining a region known as a "blob" [9]. In 2d ξ scales with the concentration Γ as:

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

decreasing from a value of the order of R_g at the overlap concentration down to the monomer size at high concentration. The osmotic pressure in a monolayer scales like:

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

as was first shown experimentally in ref. [8].

The response to a deformation in an isotropic 2d material is characterized in general by two elastic moduli: changes in area are controlled by the dilation modulus ε and changes in shape by the shear modulus G [10]. Polymer monolayers in the semi-dilute regime are fluid-like and the shear modulus is negligible, at least at low frequencies [11]. In these conditions the equilibrium dilational modulus ε_{eq} can be determined from measurements of pressure as a function of area:

$$\varepsilon_{eq} = d\Pi/d\ln A. \tag{3}$$

By definition, the modulus ε_{eq} has the same scaling properties as the osmotic pressure, Eq. 2. The dilational modulus can also be measured dynamically. In the SQELS technique, the

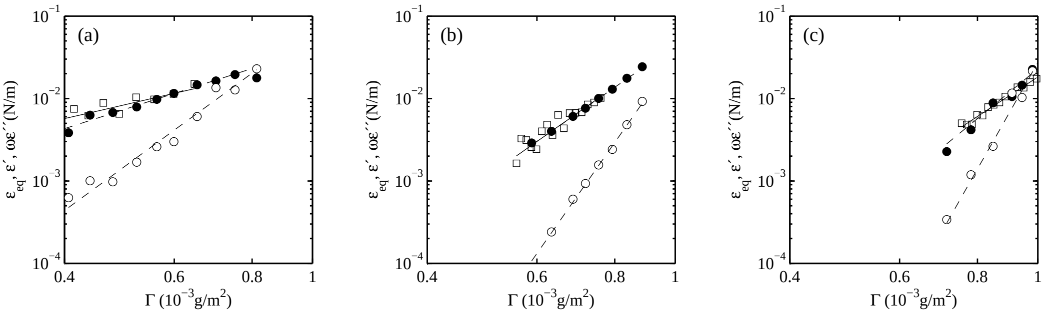

Fig. 2. – Log plots of the elastic response moduli as a function of the concentration, for three of the systems studied in this letter: (a) PVAc, (b) β-casein, (c) β-lactoglobulin. (□) is the equilibrium dilational modulus, obtained from surface pressure isotherms (data in Fig. 1b), showing the well known scaling (the exponent y_{eq}) of this equilibrium property in the semi-dilute regime. (●) are the elastic (ε') and (○) the viscous ($\omega\varepsilon''$) components of the elastic response, measured with SQELS. This dynamical response data also shows clear power-law scaling, and the power law exponents are $y_{\varepsilon'}$ and $y_{\varepsilon''}$ respectively. Lines are fits to power laws. The correlation between these scaling exponents is highlighted in Fig. 3 and represents the major result of this work.

capillary waves cause the surface area to oscillate in time with a frequency ω. This motion is a uniaxial compression, and it can be shown in this case that the response is given by the sum of the dilation and shear moduli [12]. The dynamic complex modulus

$$\varepsilon^* = \varepsilon' + i\omega\varepsilon'' \tag{4}$$

is probed. This notation, where ε' is the elastic component of the response modulus and ε'' is a viscosity, is the usual convention for 2d rheology and it differs from the usual notation in 3d. In the regime studied here, ε' is dominated by dilation, however ε'' contains the sum of dilational and shear viscosities, both of which may be finite.

This letter discusses in a unified manner a range of results on polymer monolayers. Experiments on β-lactoglobulin are presented here for the first time. We also analyze further previous data from our own group on β-casein [13] and Poly(vinyl acetate) (PVAc) [14]. Finally we also consider the viscoelasticity data by Monroy et al. [15]. We analyze all of this data to a further level than was done previously, to show that all systems exhibit scaling behavior in the semi-dilute regime, and that there are very interesting relations between the scaling properties of different physical parameters. Studying this wide range of monolayers enables us to consider the widest possible range of values of ν. For each given system the chain configuration at the surface can be affected by temperature, ionic strength and pH of the liquid subphase, so these parameters are systematically varied and controlled. We will show that the confinement to the surface affects the dynamics of these systems in a general way.

Experimental Methods. – The proteins β–casein and β–lactoglobulin (Sigma, 90% pure) have been used as supplied. 1mg/ml solutions in deionised water are prepared from the dried, powdered protein, stored in a refrigerator and used within 5 days. Buffer solutions are made up using deionised (Elgastat UHQ, Elga, U.K.) water. Phosphate buffer is used to control pH and NaCl to control ionic strength. Quoted ionic strengths also include the contribution of the buffer salts. PVAc (Acros, Mw = 170,000) has been used as received. It is dissolved in tetrahydrofurane (0.12 mg/ml) and spread on a deionised water subphase at different temperatures. Surface pressure is measured using a Langmuir trough with a filter paper Wilhelmy plate sensor (Nima Technology, U.K.) mounted on an active anti-vibration table (Halycion, Germany), both of which are enclosed in a draft proof enclosure. Monolayer material is spread on the liquid/air interface by careful dropwise ($\simeq 2\mu l$) addition of the spreading solution. In all of the experiments discussed in this paper, polymers are spread in dilute conditions. After spreading, the concentration can be increased by reducing the available surface area within a Langmuir trough [1]. The systems we consider form stable monolayers, where chains cannot submerge and re-surface. Under these conditions polymer chains are unable to cross each other. The reversibility and reproducibility in the isotherms and the absence of aging have been checked for all the systems reported here, within the semi-dilute regime. For clarity, it should be remarked that at higher concentrations, or for absorbed layers, much more complex behavior is well known in protein surface layers.

Surface viscoelasticity can be measured by surface dynamic light scattering. This technique is only briefly summarized here, as it is thoroughly reviewed by Langevin [7] and our own setup is described in detail elsewhere [13, 14]. SQELS measures the time correlation function of light scattered from thermal surface roughness acting as a phase grating, as sketched in Fig. 1a. These out of plane fluctuations are underdamped waves with a frequency ω, and their motion is affected by the presence of a surface film [16]. By choosing the scattering angle θ, a particular surface roughness mode q is selected. The typical range of this technique corresponds to fluctuation frequencies between 10^4 and 10^5 Hz. In [14] we recently studied the conditions under which surface viscoelasticity can be reliably recovered. Details of calibration, data analysis and limits of the SQELS technique are described in detail in [14]. Various groups have studied polymer monolayers with SQELS [17], however some very important issues concerning the data analysis have been resolved only very recently [12, 14].

Results. – Figure 1b presents equilibrium data obtained from compression isotherms, for some of the systems studied in this work. The surface pressure increases continuously as the area per polymer decreases. For all the systems we find a range of concentrations, corresponding to pressures of a few mN/m, where the surface pressure and the dilational modulus ε_{eq} both have a power law scaling behavior as a function of concentration, as clearly shown in Figure 2.

It is remarkable that proteins (at least some) can effectively be approximated as a polymer (or polyampholyte) chain at the interface. This was the subject of our previous study [13]. We believe that the reason why this simple approximation is effective for these proteins lies with the loss of much secondary structure by unfolding at the interface [18].

The data in Figure 2 illustrates well known limiting regimes for chain conformation in 2d: $y_{eq} = 3$ in a "good solvent" where the chain behaves as a self-avoiding random walk, and $y_{eq} = 8$ at "θ conditions" where the effects of excluded volume balance the monomer-monomer preferential attraction [19].

Figure 2 shows the viscoelastic moduli measured with SQELS, for the same monolayers considered in Figure 1b. It can be seen that both the elastic and viscous components of ε^* exhibit a power law dependence on the concentration. We define the exponents $y_{\varepsilon'}$ and $y_{\varepsilon''}$:

$$\varepsilon' \sim \Gamma^{y_{\varepsilon'}} \text{ and } \varepsilon'' \sim \Gamma^{y_{\varepsilon''}}. \tag{5}$$

The experimental error on each of the data points in Figure 2 is known from the standard deviation obtained from fitting repeated SQELS correlation functions. This is not shown on each point for clarity, but is used as an appropriate weight to obtain the power-law interpolations (lines). The exponents $y_{\varepsilon'}$ and $y_{\varepsilon''}$ obtained from these fits are given in Table I. They are plotted in Figure 3 for various different monolayer systems, to highlight the relation

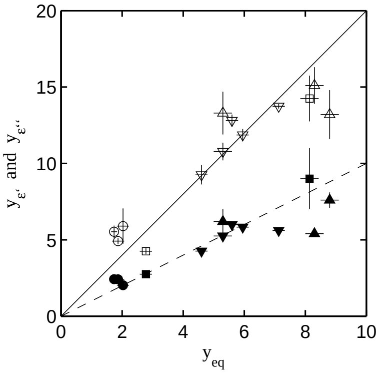

Fig. 3. – The scaling exponents describing the power law dependence on the concentration of the elasticity (filled symbols) and viscosity (open symbols) are plotted against the exponent for the equilibrium bulk modulus. (●): PVAc, (▼): β-casein, (▲): β-lactoglobulin, (■): data of Monroy *et al.* [15]. This figure includes results from the data shown in Fig. 2 as well as the monolayers described in Table I. The lines have slopes of 1 and 2, showing that the exponent for the viscosity is close to twice the exponent of the elastic modulus.

that exists between different exponents. This relation is the major finding presented in this work, and is discussed in the following section.

Discussion. – The lengthscales q^{-1} probed with SQELS are much larger than the polymer size and clearly also satisfy $q\xi < 1$, so the semidilute solution is expected to be in a "macroscopic" regime [20]. For a fluid system with a single relaxation time τ, the frequency dependence of the response modulus is [6]:

$$\varepsilon' = \varepsilon_{eq} + \varepsilon_o \frac{\omega^2\tau^2}{1+\omega^2\tau^2} \text{ and } \varepsilon'' = \varepsilon_o \frac{\tau}{1+\omega^2\tau^2}. \tag{6}$$

From the fact that the equilibrium and dynamic elastic components of the real modulus are the same, see Figure 2, it is clear that we are in the low frequency limit, where Eq. 6 becomes

$$\varepsilon' \simeq \varepsilon_{eq} \text{ and } \varepsilon'' \simeq \varepsilon_o \cdot \tau. \tag{7}$$

We do not have access to the full frequency dependence of the response, which would enable us to measure ε_o and thus extract the absolute value of τ from Eq. 6. However in the semidilute regime the concentration dependence of all the elastic response moduli (Π, ε_{eq}, ε' and ε_o) is expected to be the same. Hence we obtain from Eq. 7 a relation that can be used to extract the concentration dependence of τ:

$$\varepsilon'' \sim \varepsilon' \cdot \tau. \tag{8}$$

Looking at Fig. 2, it can be clearly seen that for each monolayer the viscosity (open symbols) scales with a higher power than the elastic modulus (closed symbols). From this it immediately follows that the timescale τ of these relaxations becomes longer the higher the concentration, hence a slow mode is being probed.

To gain more information on the character of this mode, we consider the results from the complete set of available experiments: In Figure 3 the power law exponents for ε^*, defined

Monolayer	q (cm^{-1})	y_{eq}	$y_{\varepsilon'}$	$y_{\varepsilon''}$
PVAc, T=45^{o}C	306	2.0	2.0	5.9
PVAc, T=25^{o}C (*)	306	1.9	2.4	5.5
PVAc, T=6^{o}C	306	1.7	2.4	5.5
PVAc, T=25^{o}C, [15]	344	2.8	2.8	4.3
β-casein, pH=5.2, 0.01M	426	7.1	5.6	13.7
β-casein, pH=7.2, 0.01M	508	6.0	5.8	11.9
β-casein, pH=8.3, 0.001M	507	5.6	6.0	12.8
β-casein, pH=8.3, 0.01M (*)	426	5.3	5.3	10.8
β-casein, pH=7.6, 1.1M	498	4.6	4.3	9.3
β-lg, pH=6.0, 0.02M	303	8.3	5.4	15.1
β-lg, pH=8.3, 0.02M (*)	307	5.3	6.2	13.3
β-lg, pH=5.9, 0.1M	367	8.8	7.6	13.2
P4HS, pH=2, T=25^{o}C, [15]	344	8.1	9.0	14.3

Table I. – *Static and dynamic scaling exponents for monolayers studied in this work. Values of y_{eq} are obtained from measurements of the equilibrium surface pressure with Langmuir trough methods, while values of $y_{\varepsilon'}$ and $y_{\varepsilon''}$ are obtained from SQELS data. The SQELS data of Cicuta and Hopkinson have all been fitted following the method described in ref. [14]. (*) mark the data presented in Figure 1b and Figure 2.*

in Eq. 5, are plotted against the equilibrium exponent. As discussed above, it is not surprising to find that $y_{\varepsilon'} = y_{eq}$. What is of interest is the relation between the exponents for the elastic and the viscous components of ε^*. It is clear that there is a strong correlation, and we find that $y_{\varepsilon''} \simeq 2y_{\varepsilon'}$ describes the data to a good approximation. It will be important to test this result further in the future, especially with additional data at high values of y_{eq}.

From the experimental observation that $y_{\varepsilon''} = 2y_{\varepsilon'}$, it finally follows using Eq. 8 that the timescale of these fluctuations, which we shall call τ_{2d}, scales like $\tau_{2d} \sim \xi^{-2}$. Monroy *et al.* recently reported data on synthetic polymer monolayers showing scaling behavior of ε^* [15]. It should be noted that the argument by Monroy *et al.*, attempting to describe the observed behavior within the Rouse model predictions for τ_{coop} [20], is fundamentally flawed and gives a dimensionally wrong result for the viscosity.

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

$$\varepsilon'' \sim \xi^{-4} \sim \Gamma^{2y_{\varepsilon'}}. \tag{9}$$

Taking into account that experimentally the measurements are most difficult at the higher values of y, as reflected in the larger error bounds in Fig. 3, it is clear that Eq. 9 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 [21], both being determined by a proportionality to the number of contacts.

A question that naturally arises is why the slow mode described here is not seen in 3d bulk solutions. In bulk solutions in a good solvent the Flory exponent is $\nu_{3d} = 3/5$ and the osmotic pressure scales with the concentration ϕ like $\Pi_{3d} \sim \phi^{9/4}$. By analogy with the arguments above, a dynamical mode that like τ_{2d} were determined by the number of contacts would have in 3d a characteristic relaxation time scaling with the concentration like $\tau_{3d} \sim \xi^{-3} \sim \phi^{9/4}$. This is a higher power of the concentration compared to reptation ($\tau_{rept} \sim \phi^{1.5}$)[9], in agreement with the well known result that in 3d solutions the fluctuations relax via the self diffusion of the polymer chain and not the mechanism outlined above. In 2d relaxation by reptation is hindered by an effective "cage-like" confinement provided by neighboring chains.

Conclusions. – We have considered the behavior of various polymer and protein monolayers in the semidilute regime, reviewing our own data from previous publications as well as data from another group and results on a new system. By looking at this wide set of experimental results we have seen that the scaling properties of all these monolayers obey a universal relation. Based on this experimental finding, we have proposed that thermal concentration fluctuations in this regime have a slow mode of decay with a timescale that had not been previously considered and that is specific to the two dimensional relaxation process.

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