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Wide frequency rheological modeling of crosslinked polyacrylamide gels

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Abstract

Gels are known to behave as viscoelastic materials but only a small amount of data is usually provided in the glassy transition. Results concerning the dynamic moduli G' and G'' are presented here using AFM in contact oscillatory mode and show good agreement with classical rheological data. Different gels are studied with increasing polymer concentration. G_N^0 , the plateau modulus, is measured at low frequencies, but interestingly another one, G^1 , is found at high frequencies. A model based on fractional derivatives is proposed, covering the whole frequency range. The relaxation spectrum is recovered, and the physical parameters contain interesting information about the local dynamics of crosslinks.

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Polymers are known to exhibit a wide range of material patterns since they can successively behave as liquids, elastic materials showing a rubbery plateau, then undergo a glassy transition before reaching the solid domain [1], all these processes occurring respectively as frequency increases (or as temperature decreases). They are widely used in a large variety of industrial applications and are present in biological processes as well. It has often been difficult to characterize their material properties, as the range of frequencies involved covers several decades [2, 3]. Thus various experiments are required to help understanding their complex behaviors such as rheometry, DLS and DWS [4] or ultrasound [5, 6]. When it comes to probing the linear viscoelastic behavior (LVE), one often uses the time-temperature superposition principle, by shifting results obtained at various temperatures onto a reference temperature master curve [3]. Different models providing relaxation spectra have been proposed, ranging from multiple Maxwell models to continuous relaxation spectra [2], involving both liquid and glassy modes. The concept of soft glassy rheology [7, 8] appeared most recently and provides an interesting alternative and seems well suited for many systems. Indeed it is based on the idea that sub-elements in the microstructure are linked via weak interactions, and are in a disordered metastable state. Based on this concept, many complex fluids can be described thanks to this model, in particular packed colloidal suspensions, the cell cytoskeleton [9] as well as foams or slurries.

Polymeric gels may share similar properties [7], however the modeling part of the matter is still an open question. However they can be easily characterized using modern microrheology techniques [10, 11], as applied in particular for actin networks [12, 13]. The behavior of classical gels is in fact similar in the glassy transition domain, but no modelling attempt has been made to characterize the entire frequency domain covered by recent instruments. Therefore, it is important to characterize a wide domain of frequency for various polymeric gels, and develop a model for such behavior. This is the main purpose of the work presented here. In addition, a new AFM-based microrheology method [14, 15] will be used allowing to investigate the high frequency regime.

Polyacrylamide gels were prepared using acrylamide at four different volume concentrations (5–7.5–10–15%), and bis-acrylamide (fixed concentration 0.03%) in deionized water, in other words they were slightly crosslinked. Polymerization was initiated by incorporating N,N,N,N-tetramethylethylenediamine (TEMED, Sigma) and ammonium persulfate 10% solution (APS), as described in [16]. These gels are known to exhibit a viscoelastic behavior,

with an almost constant elastic modulus G' , and a frequency-dependent viscous modulus G'' , usually one decade below in the classical rheology domain [0.01 Hz – 10 Hz] [17]. This elastic modulus (G_N^0) has been investigated and increases with acrylamide concentration [18]. Gels were 70 μm in height and prepared at the bottom of a pre-treated glass Petri dish for a better gel adhesion [16]. Gels were always kept in PBS (Phosphate-Buffered Saline), so that they are swelled and in equilibrium. They were set onto an AFM (JPK Instruments, Berlin) equipped with an inverted microscope (Zeiss, model D1, Berlin) for visualization. The AFM chips (Bruker, MLCT, pyramid shape, tip half-angle $\theta = 20^\circ$) were mounted onto the AFM glass block and calibrated using the thermal fluctuations method. Then an initial indentation δ_0 of the sample was made under a prescribed force F_0 given by:

$$F_0 = \frac{3 E \tan \theta}{4 (1 - \nu^2)} \delta_0^2 \quad (1)$$

where E is Young's modulus, ν is the Poisson ratio (usually assumed to be close to 0.5 for such gels [19]) and θ as defined above. δ_0 is chosen so that the tip penetration depth into the sample is large enough to have a sufficient contact area and not too large to remain within the linear elasticity assumptions corresponding to the Hertz model. In order to carry out microrheology measurements, a small perturbation (frequency f from 1 Hz to 8 kHz, and $\omega = 2\pi f$ is the angular frequency) was superposed to the initial indentation. The perturbation being small, Eq. (1) can be linearized around the equilibrium. By the correspondence principle of LVE, in the ω -domain, one operates with complex quantities. Let δ^* , F^* be the complex indentation and force. The complex shear modulus $G^*(\omega)$ is given by:

$$G^*(\omega) = \frac{1 - \nu}{3 \delta_0 \tan \theta} \frac{F^*(\omega)}{\delta^*(\omega)} \quad (2)$$

Note that we subtracted the hydrodynamic drag [14] which induces a decrease in the imaginary part of the modulus, but the drag was found to be negligible here, due to the relative values of the loss modulus G'' for these gels.

Rheometry measurements were carried out on a controlled stress rheometer (Malvern, Gemini 150) at low frequencies [0.001 Hz – 10 Hz] in the linear regime (deformation of 1%). Interestingly an overlapping region was found between these measurements and the AFM microrheology experiments [1 Hz – 8 kHz]. The results of these experiments performed at 25°C show very good agreement for the 7.5% concentration gel, as seen in Fig. 1.

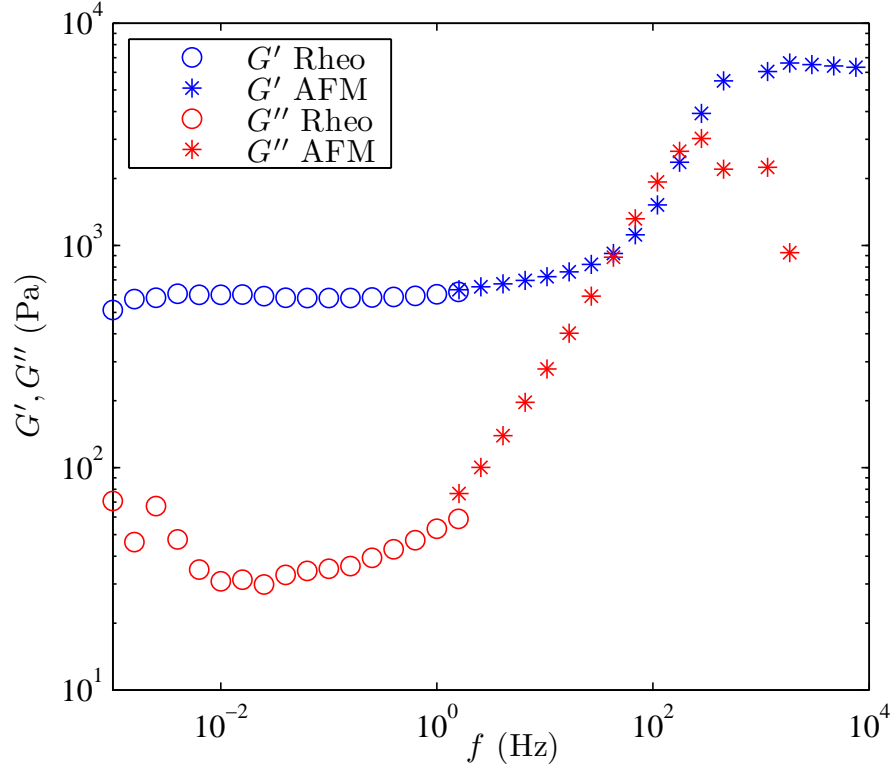


FIG. 1: Superposition of rheometric and AFM microrheology. Acrylamide content is 7.5% in this case. Typical error bars (not shown) are around 10%.

The variation of the dynamic moduli (Fig. 1) shows a constant elastic plateau modulus (G_N^0) at low frequencies ($G_N^0 \simeq 700$ Pa in the case in Fig. 1). The gel undergoes a glassy transition in the higher frequency regime as the AFM measurements do show. The slopes of the moduli G' and G'' are similar at these intermediate frequencies [30 – 300 Hz] for both moduli. Surprisingly, at higher frequencies ($> 10^3$ Hz), another plateau modulus G^1 is found ($G^1 \simeq 6000$ Pa here) and G'' decreases. The existence of such a plateau modulus for G' has never been reported before experimentally, although it was postulated earlier [20]. It was found to occur everytime experiments were repeated, with a good reproducibility. This is the signature of a critical frequency (~ 300 Hz) above which single macromolecule segments are sollicitated by such vibrations. Note that other studies using DWS, dynamic light scattering and microrheology [4] did not report similar behavior at such frequencies, but rather a simple power law increase for G' and G'' vs. frequency, or a rather constant behavior using AFM [21]. This could be due to the fact that the ratio between crosslinker and polymer was much higher (0.1 instead of 0.002 – 0.006 here).

To predict the observed behavior, it is suggested to use a rheological model. Due to the high frequencies reported, it was found more adequate to combine two models, one relevant to the flow regime at low frequencies, together with a special form of the Maxwell model including fractional derivatives [3, 22] for the glassy state. The complex modulus $G^*(\omega)$ can be related to a relaxation function $H(\lambda)$ using the general formalism [2] :

$$G^*(\omega) = \int_0^\infty H(\lambda) \frac{i\omega\lambda}{1 + i\omega\lambda} \frac{d\lambda}{\lambda} \quad (3)$$

$H(\lambda)$ is the continuous relaxation spectrum, the expression of which is shown in this work to model the LVE response from flow to glassy state. In particular, it is suggested here to describe the flow regime with the corresponding function $H_f(\lambda)$:

$$H_f(\lambda) = \begin{cases} n_f G_N^0 \left(\frac{\lambda}{\lambda_{\max}} \right)^{n_f} & \text{if } \lambda \leq \lambda_{\max} \\ 0 & \text{if } \lambda > \lambda_{\max} \end{cases} \quad (4)$$

This power law behavior will then describe the continuous relaxation time distribution required to model the plateau regime observed in Fig. 1 at low frequencies. This model is unsuitable to describe the high frequency state and the second plateau observed at high frequencies. Therefore a fractional derivative model [22] is coupled to the previous one, to account for this behavior. The corresponding solution for the dynamic complex modulus $G_g^*(\omega)$ is simply given by :

$$G_g^*(\omega) = G^1 \frac{(i\omega\lambda_1)^b}{1 + (i\omega\lambda_1)^a} \quad (5)$$

where a and b are the orders of fractional derivatives [22]. Thermodynamical related principles require $0 < a \leq b$ [3]. This type of model accounts for possible α -relaxation as observed for polymeric materials. Note that, in the formalism of Eq. 4, there exists an analytical relaxation function $H_g(\lambda)$ [3]. The coupling of the two linear models is insured by the simple relationship $G^*(\omega) = G_f^*(\omega) + G_g^*(\omega)$, to account for the whole frequency spectrum. The parameters of this global model are G_N^0 , λ_{\max} , n_f , G^1 , λ_1 , a and b as described in Fig. 2. G_N^0 and G^1 appear naturally as the two plateaux at intermediate and high frequencies. λ_{\max} is a transition time (i.e. the maximum relaxation time) corresponding to the flow domain. In the case of gels, this typical time is out of reach since gels do not actually flow but exhibit a plateau even at very low frequencies [20]. $-n_f$ is the slope of G'' at low frequencies, in log-log axes and is found in the typical range $[-0.4, -0.1]$. b represents the slopes of G' and

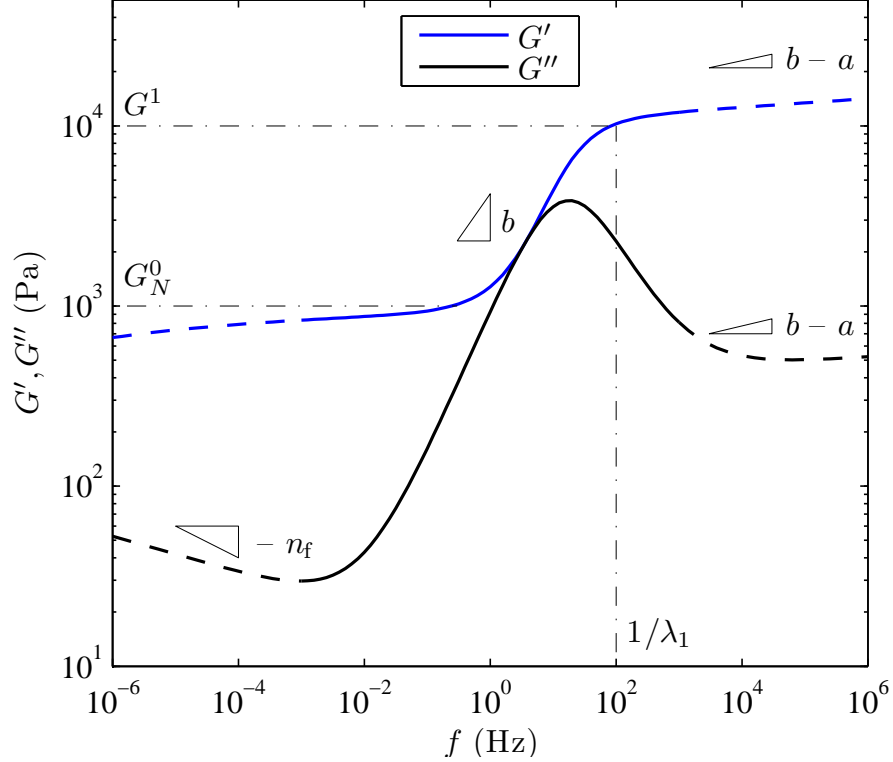


FIG. 2: Significance of the model parameters G_N^0 , n_f , G^1 , λ_1 , a and b . λ_{\max} is not shown but should appear at lower frequencies at the intersection of G' and G'' occurring for $\omega \sim 1/\lambda_{\max}$. This does not occur in such gels since the flow region is not reached at low frequencies.

G'' in the glass transition regime and could be linked to the parameter $x - 1$ in the Sollich model [7]. Finally $b - a$ is the limiting slope of G' and G'' moduli at the highest frequencies, possibly shown by the small increase of G' at high frequencies in the experiments.

Fitting of the data was carried out for the four different gels characterized both in rheometry and AFM microrheology. The best-fitting values of the parameters were determined by minimizing the weighted sum of squared residuals. The weights have been chosen from the data. The thermodynamic constraint required a special attention. The parameter b was written as $b = a + \varepsilon$ with $\varepsilon > 0$ and the minimization was achieved by combining two methods [23]: the standard one-dimensional Brent method related to ε and the Levenberg–Marquardt method to determine the other parameters for each value of the ε generated by the first method. The initial guesses followed the discussion on the role of each single parameter (see Fig. 2). The best-fitting values of the parameters are reported in Table I

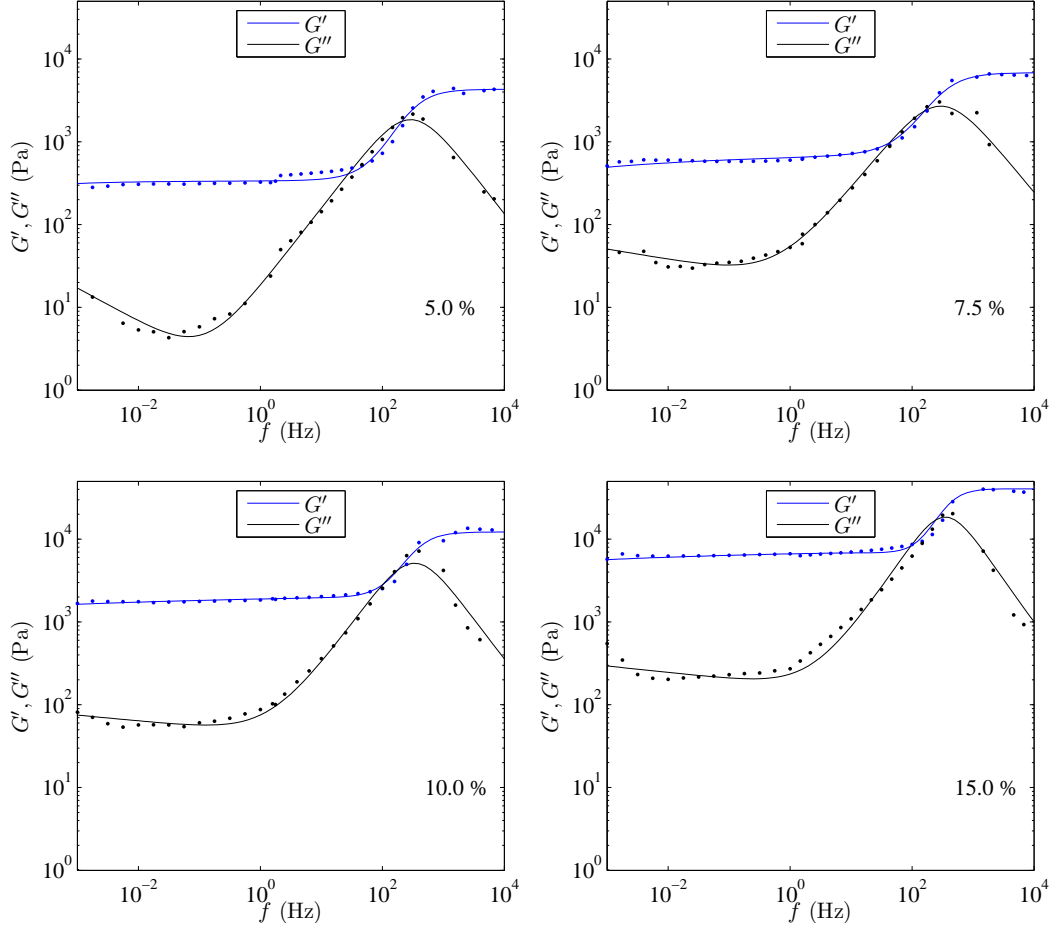


FIG. 3: Gel rheology: 5%, 7.5%, 10% and 15% acrylamide concentrations. Solid lines: best-fit parametric curves, dotted lines: experimental data.

TABLE I: Best-fitting values of parameters used in the model.

Gel	G_N^0 (Pa)	λ_{\max} (s)	n_f	G^1 (Pa)	λ_1 (s)	a	b
5%	337	1.3×10^5	0.41	3987	5.5×10^{-4}	0.95	0.95
7.5%	747	9.0×10^5	0.13	6146	5.4×10^{-4}	0.92	0.92
10%	2307	6.0×10^9	0.07	10131	4.7×10^{-4}	1.00	1.00
15%	8064	1.0×10^9	0.08	33109	4.5×10^{-4}	1.07	1.07

and the associated curves are presented below in Figs 3. Excellent agreement is obtained.

Note that, as expected, the plateau modulus G_N^0 increases with c , the acrylamide concentration, and interestingly the second plateau G^1 as well. These values are shown in Fig. 4 and the slopes can be compared to other available data from the literature. For the lower

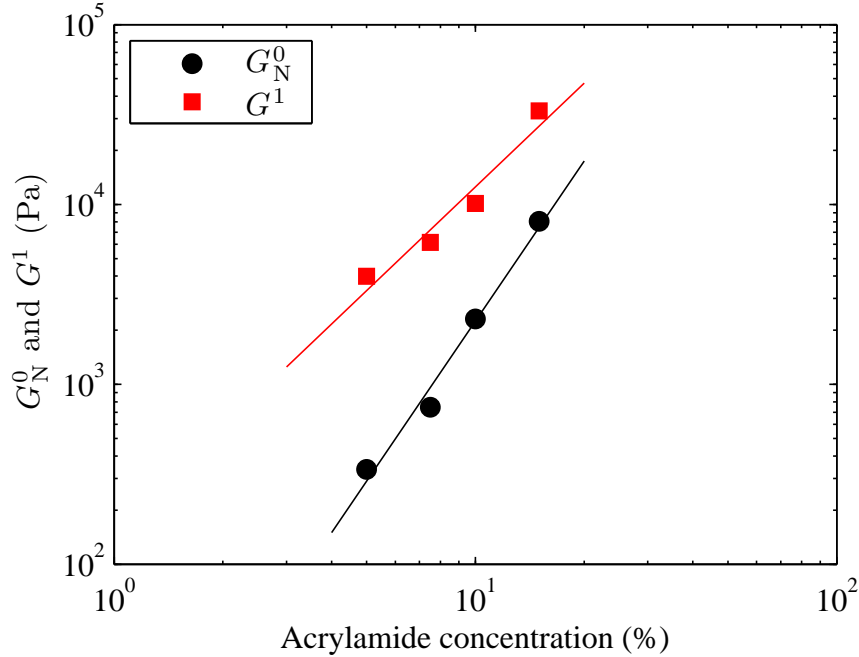


FIG. 4: Evolution of gel moduli G_N^0 and G^1 vs. concentration. The slopes of the power law exponent correspond respectively to 3.0 ± 0.3 and 1.9 ± 0.3

frequency plateau, the relationship is of the kind $G_N^0 \sim c^{3.0}$ whereas $G^1 \sim c^{1.9}$. Previous observations using combined light scattering and mechanical tests [18] were reported, showing an exponent 2.55 using dynamic mechanical measurements (and 2.35 using dynamic light scattering) as compared to the theory of de Gennes giving 2.25 for good solvents [24]. The value of the exponent for G_N^0 is also close to the exponent 2.55, found for collagen gels [25, 26] but is larger than the typical exponent of 1.4 obtained for entangled actin solutions [27]. With regard to the secondary plateau G^1 , the existence of such a solid modulus is most likely due to the fact that few crosslinkers are available here, therefore a rigid behavior (existence of G^1) is obtained at such frequencies, as compared to the increase of G' and G'' when more crosslinks are used [4].

The longest relaxation time λ_{\max} does not seem to play a significant role, because it is related to a possible crossover of the G' and G'' moduli at low frequencies which does not occur for such gels since they do not flow at low frequencies. Furthermore, the initial slope of G'' , i.e. $-n_f$ is an important parameter here, and decreases as gel concentration increases. This further emphasizes the fact that high concentration gels exhibit moduli which

have almost flat G' and G'' moduli (see in particular Figs 3 at 10% and 15% acrylamide concentration) and do not cross at low frequencies. Note that values of G' and G'' at low frequencies (0.001 Hz) using the classical rheometry setup are difficult to obtain, due to the long experimental times required, therefore a larger uncertainty is unavoidable for n_f . For the four gels, λ_1 was found to be slightly decreasing with increasing c , revealing a difference in the relaxation mode as the acrylamide concentration increases. Possibly, since there is a small amount of crosslinks, these are used in different amounts for linking the polymeric chains. As the acrylamide concentration increases, the network structure becomes looser, as less crosslinks can be used because of the larger number of chains, so the relaxation mode λ_1 should be smaller, and this is indeed obtained in table I. This short time relaxation process is close to a single Maxwellian mode with values of a and b close to 1, but not quite equal to 1, ranging between 0.92 and 1.07. In most cases, the optimal value of $b - a$ was found to be 0, so $a = b$ (see table I). The values of a (or b) are directly related to the use of the fractional derivative model.

Further extensions of the model may be considered for other physical (or chemical) gels, as well as the study of biological gels, involving cytoskeleton filaments such as actin, tubulin, fibrin, and finally living cells [14]. Thus this model, coupled with the use of high frequency AFM measurements, allows to investigate different types of filamentous networks in order to determine their behavior in a large range of frequencies.

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