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# On the solid-fluid transition in a yield stress shear thinning physical gel

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## Résumé:

*Ici est présentée une étude expérimentale de la transition solide-fluide dans un gel du type "fluide a seuil" (Carbopol 940) sous contrainte de cisaillement. Au cours d'une augmentation graduelle de la force externe, trois régimes de déformation distincts sont observés: un régime élastique quasi-solide (caractérisé par une dépendance contrainte-déformation linéaire), un régime de coexistence de phase solide et fluide (caractérisé par une compétition entre destruction et reformation du gel), et un régime purement visqueux (caractérisé par une dépendance déformation – contrainte de type puissance). La transition de comportement de solide à fluide montre une nette hystérésis avec des valeurs de la force externe croissante et décroissante; et la puissance correspondant à la région d'hystérésis s'étend linéairement avec le niveau auquel le milieu est contraint (le degré d'instationnarité de l'écoulement). À la limite asymptotique des petits niveaux de force, nos résultats s'accordent bien avec les précédentes études stationnaires de la transition de type seuil. Afin d'approfondir la transition solide-fluide, nos résultats expérimentaux sont accompagnés d'un modèle cinétique simple qui décrit qualitativement l'hystérésis structurelle observée dans nos expériences rhéologiques. Le modèle est clairement bien valide par rapport aux données d'écoulement oscillatoire.*

## Abstract:

*An experimental investigation of the solid–fluid transition in a yield stress shear thinning physical gel (Carbopol 940) under shear is presented. Upon a gradual increase of the external forcing, three distinct deformation regimes are observed: an elastic solid-like regime (characterized by a linear stress–strain dependence), a solid–fluid phase coexistence regime (characterized by a competition between destruction and reformation of the gel), and a purely viscous regime (characterized by a power law stress-rate of strain dependence). The transition from solid behaviour to fluid behaviour displays a clear hysteresis upon increasing and decreasing values of the external forcing and the power corresponding to the hysteresis region scales linearly with the rate at which the material is being forced (the degree of flow unsteadiness). In the asymptotic limit of small forcing rates, our results agree well with previous steady state investigations of the yielding transition. To get further insight into the solid–fluid transition, our experimental findings are complemented by a simple kinetic model that qualitatively describes the structural hysteresis observed in our rheological experiments. The model is fairly well validated against oscillatory flow data.*

**Keywords:** yield stress, hysteresis, Carbopol

## 1 Introduction

During the past several decades, physical gels have found an increasing number of applications in both industry (cosmetics, food processing, pharmaceuticals, etc.) and fundamental research (targeted drug delivery, biotechnology, etc.). More recently, injectable physical gels are used for medical implants, tissue regeneration, and non-invasive intervertebral disc repair [1]. From a rheological point of view, such gels are usually referred to as yield stress materials, that is they are able to sustain finite deformations prior to flowing. At the microscopic level, such materials are made of high- molecular-weight constituents (typically in the range of  $10^3 \div 10^7$  Da) that interact reciprocally forming complex mesoscopic structures. Although widely used, particularly in engineering and industrial contexts, the term yield stress has raised a strong controversy for over two decades; see [2] and [3]. One of the main debates triggered by the inherent inaccuracy of measuring arbitrarily small rates of strain relates to the very existence of a "yield stress." Indeed, according to Refs. [2] and [3], the yield stress might simply be an instrumental artefact due to the poor sensitivity of the measuring device in a range of vanishingly small deformations. During the past decade, the sensitivity and measuring range of commercial rheometers have significantly improved, and such a misinterpretation of the yield stress seems to be ruled out. However, yield stress materials remain quite

controversial and not fully understood. In spite of an increased resolution and accuracy of the modern rheometric equipment, measurements of the yield stress are still only partially reproducible. A detailed discussion of the technical issues that affect the yield stress measurements has been recently presented by Piau in Ref. [4].

A first class of possible reasons for the partial reproducibility of such measurements is related to the experimental protocols that different research groups use. This includes both chemical aspects of the solution preparation (such as a careful tuning of the ionic content or the pH of the solvents used) and the details of the solvation/homogenization protocol. A second sensitive issue is related to the choice of different types of rheological protocols employed in the yield stress: flow ramps (either in a controlled stress mode or a controlled rate of shear mode), creep tests, oscillatory sweeps. Although we do not underestimate the importance of these technical considerations, we want to suggest that part of the troubles with the yield stress measurements are actually a result of our poor physical understanding of the solid–fluid transition associated with the concept of yield stress. The present paper investigates the yielding of a physical gel with a particular focus on the nature and mechanism of the transition between solid and fluid states when the external forcing is gradually increased. Whereas most of the previous investigations of the yielding phenomenon we are aware of ([4-8] and many others) focused on steady state rheological measurements, this report aims to characterize the yielding process as a function of the degree of flow steadiness. Thus, the description of a steady state yielding process is not the primary goal of this work and can only be obtained via extrapolation of our results.

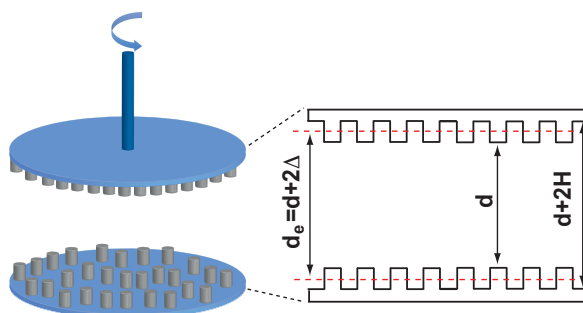
## 2 Experimental setup and methods

As working fluids, we used aqueous solutions of Carbopol-940 (from Noveon) with concentrations (by weight) ranging between 0.1% and 0.2%. The pH of the mixture (initially around 3) was brought to neutral values by the addition of about 140 parts per million of sodium hydroxide (NaOH). The final value of the pH was carefully monitored using a commercial pH meter. To homogenize the gelled mixture, the sample was stirred with a propeller mixer (at 400 rpm) for about 2 h and then allowed to rest for several more hours. Prior to each rheological test, the air bubbles entrapped in the gel during the stirring process were removed by placing the samples in a low-pressure chamber for 30 min.

The rheological properties of the solutions were investigated using a CVOR rheometer (from Malvern Instruments) equipped with a Peltier system able to control the temperature with an accuracy better than 0.1°C.

A first major concern for the rheological measurements was the occurrence of the wall slip phenomenon at the contact with the measuring geometry, which has been previously observed with Carbopol gels, [4]. To prevent this, a home-made parallel plate geometry with cleated surfaces has been used, Fig. 1.

The radius of the parallel plates is  $R = 40$  mm the gap measured by the rheometer (see the details in Fig. 1) is  $d = 1$  mm. The cleats have an equal height  $H = 600$   $\mu\text{m}$  and are disposed in a rectangular grid over each plate. Several advantages of cleated geometries over other methods of preventing the wall slip effect (such as using a sand blasted geometry or a vane tool) have been recently demonstrated experimentally, [9]. Among these advantages, the cleated geometry allows suppression of the wall slip effect even in the absence of significant normal forces and creates a well defined shear.



**Figure 1:** Schematic view of the cleat geometry. A magnified cross-sectional view is presented on the right side.

According to Ref. [9], the following stress correction needs to be applied to stress measurements obtained using the cleat geometry illustrated in Fig. 1:

$$\sigma = \sigma_m \frac{d + 2\Delta}{d} \quad (1)$$

where  $\sigma_m$  is the stress measured by the rheometer,  $d$  is the gap measured by the rheometer and  $\Delta$  is the flow penetration length through the cleats. By calibration measurements performed on a Silicon Oil with known viscosity, we have found  $\Delta \approx 600 \mu m$  which is consistent with values given in [9].

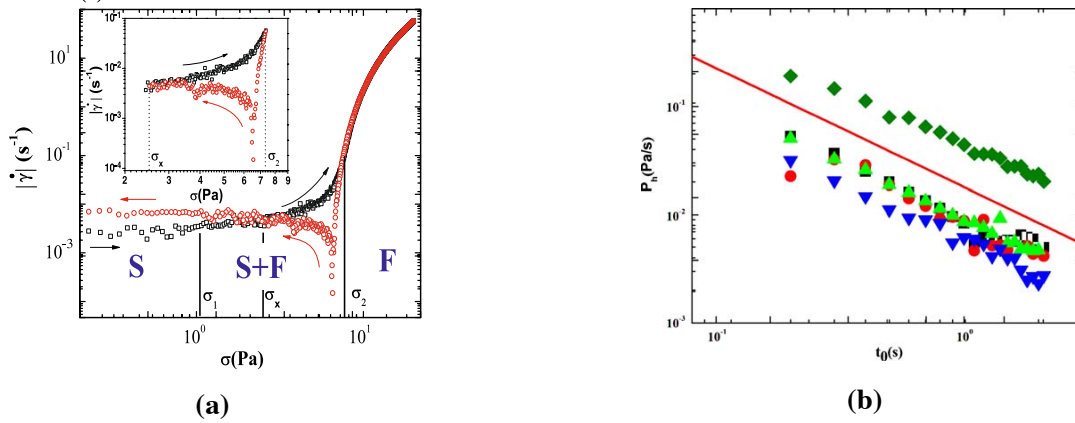
Two types of rheological tests have been performed: controlled stress linear ramps and controlled stress oscillatory sweeps at a fixed frequency. For each sample, we conducted controlled stress experiments for 19 different values of the total ramp time. Each constant stress rheological experiment started with an increasing stress ramp and ended with a decreasing stress ramp within the same range of stresses and the same stress step. The data averaging time per stress value,  $t_0$  (to be further referred as the characteristic time of forcing), has been varied between 0.2 and 2 s. For each up–down stress ramp, 1000 stress values have been explored ranging between 0.1 and 20 Pa. We emphasize here that a true steady state of deformation can only be inferred in the asymptotic limit  $t_0 \rightarrow \infty$ , unlike in previous studies concerning Carbopol gels, where a steady state was a priori set by deliberately choosing large values of  $t_0$  (an accurate description of such a procedure is presented, for example, [7]). Alternatively, the time-dependent response of the samples was tested via stress-controlled oscillatory experiments at several frequencies and in the same range of stresses.

### 3 Results

#### 3.1 The solid-fluid transition upon a increasing/decreasing stress ramp: the emergence of hysteresis

In order to characterize the solid-fluid transition in a Carbopol gel under shear, systematic measurements of flow curves in a controlled stress forcing regime have been performed. In Fig. 2(a), we display a typical flow curve for both increasing and decreasing stresses. The stress has been varied linearly in time and the characteristic measuring time per stress value was  $t_0 = 0.2$  s. Several features of the transition can be learned from Fig. 2(a). First, the transition from solid states (regime **S** in Fig. 2(a)) to fluid states (regime **F** in Fig. 2(a)) is not direct but intermediated by a third regime which can be interpreted as a coexistence regime between solid and fluid phases. Second, the solid-fluid transition is not reversible upon increasing/decreasing forcing. Indeed, it can be clearly seen in Fig. 2(a) that, upon decreasing stresses, a hysteresis of the deformation states emerges. Additionally, an elastic recoil effect can be observed in the form of a cusp on the decreasing stress branch. These experimental findings are at odds with the classical picture of yielding of a viscoplastic material according to which the solid-fluid transition occurs at a well-defined value of the applied stress (termed as the “yield stress”) and is reversible upon increasing/decreasing stresses. Hysteresis effects during the yielding of a Carbopol gel have been previously reported as either negligibly “small” or entirely absent, [8]. In the following, we quantify these effects by the power loss (per unit volume of material) associated to the hysteresis loop visible in Fig. 3,  $P_h = \oint_{loop} \dot{\gamma} d\sigma$ . Here the closed curvilinear integral is

calculated along the hysteresis loop. Quite remarkably, for the data presented in Fig. 2(a), the power loss corresponding to the hysteresis loop is nearly ten times larger than the power dissipated during the elastic solid deformation regime and, therefore, not negligible. The dependence of the hysteresis power loss  $P_h$  on the characteristic time of the forcing  $t_0$  is presented in Fig. 2(b). For each Carbopol concentration and each temperature, the hysteresis power loss scales algebraically with the characteristic forcing time,  $P_h \propto t_0^{-1}$ . The experimentally found scaling of the hysteresis losses allows a comparison of our flow curves with previous experimental results, which revealed no apparent hysteresis and time dependence, see Refs. [4-5]. Indeed, one can easily note that, corresponding to large values of  $t_0$  (“slow” forcing), the hysteresis area becomes vanishingly small and our flow curves reduce to the steady state data published by others. Thus, we conclude that there exists no apparent contradiction between the flow curves we have presented and the steady state measurements previously reported by others.



**Figure 2:** (a) Dependence of the absolute value of the rate of shear,  $|\dot{\gamma}|$  on the applied stress  $\sigma$  during a up/down stress ramp, Fig. 2. The inset presents a magnified view of the second flow regime,  $\sigma_x < \sigma < \sigma_2$ . The vertical dotted lines indicated the bounds of the relevant rheological regimes. The symbols are: squares, increasing stresses; circles, decreasing stresses. The experiment was conducted with a 0.1% Carbopol solution at  $T = 298$  K. The characteristic forcing time was  $t_0 = 0.2$  s. The labels **S** and **F** stand for the solid and fluid phases, respectively. (b) Dependence of the deformation power deficit on the characteristic forcing time  $t_0$  for several values of the Carbopol concentration and several temperatures: squares,  $c = 0.1\%$ ,  $T = 298$ K; circles,  $c = 0.1\%$ ,  $T = 308$ K; up triangles,  $T = 288$  K; down triangles,  $c = 0.12\%$ ,  $T = 288$  K; rhombs,  $c = 0.2\%$ ,  $T = 288$  K. The full line is a guide for the eye,  $P_h \sim t_0^{-1}$ .

### 3.2 A toy model for the solid-fluid transition

A detailed and direct experimental description of the Carbopol microstructure around the solid-fluid transition is still missing. This is mainly due to practical difficulties in visualizing the gel microstructure without altering it, [4]. A toy model using no explicit assumptions on the small-scale dynamics of the gel network under shear is presented in the following. We view the fluidization process of the gel under shear as a dissociation reaction,  $S \Leftrightarrow S + F$ , which can be modelled by the following kinetic equation:

$$\frac{d\phi}{dt} = R_d(\phi, t, \Gamma) + R_r(\phi, t, \Gamma) + \delta \quad (2)$$

where  $S$  and  $F$  denote the solid and fluid phases respectively,  $\phi = [S]$  is the concentration of the solid phase and  $\Gamma = \sigma / \sigma_2$  is a non dimensional forcing parameter;  $R_d$  is the destruction rate of the gel units,  $R_r$  their recombination rate and  $\delta$  a small thermal noise term. We assume that the destruction rate  $R_d$  is proportional to the applied forcing and the existing amount of solid, that is

$$R_d(\phi, t, \dot{\gamma}) = -K_r \Gamma \phi \quad (3)$$

The recombination rate  $R_r$  is assumed to be a smooth decreasing function of the applied stress proportional to both the amount of solid  $\phi$  and fluid  $1 - \phi$ :

$$R_r(\phi, t, \dot{\gamma}) = K_r [1 - \tanh(\Gamma / w)] \phi (1 - \phi) \quad (4)$$

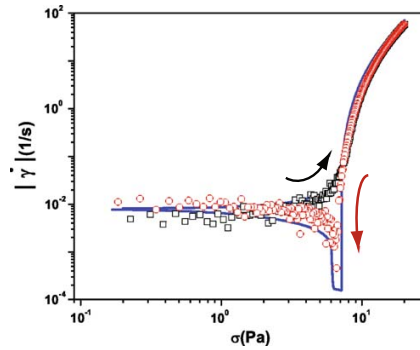
where  $K_r$  and  $w$  are constants.

Here, we have considered that recombination of the gel network takes place via binding of single polymer molecules to already existing solid blobs. As a constitutive equation, we use a thixo-elastic Maxwell-type

model previously employed by Quemada [10]:

$$\phi \frac{d\sigma}{dt} = \frac{G}{\sigma\eta} + \frac{G}{\sigma} \frac{d\dot{\gamma}}{dt} \quad (5)$$

where the viscosity is given by a regularized Herschel-Bulkley model,  $\eta = K \left( \varepsilon + \dot{\gamma} \right)^{m-1} + \sigma_2 / \left( \varepsilon + \dot{\gamma} \right)$ . Here  $K$  is the consistency,  $m$  the power law index,  $\sigma_2$  the yield stress and  $\varepsilon$  a small regularization parameter. The choice of this constitutive equation is motivated by the presence of elastic effects in the intermediate deformation regime (see the cusp in the decreasing stress branch in Fig. 2(a) and the corresponding discussion). It is easy to note that, in the limit  $\phi \rightarrow 1$ , Eq. 5 reduces to Hooke's law,  $G = \sigma \dot{\gamma}$ , and in the limit  $\phi \rightarrow 0$ , it reduces to a regularized Herschel-Bulkley model. A comparison of the prediction of the toy-model presented above with the rheological measurements is presented in Fig. 3.

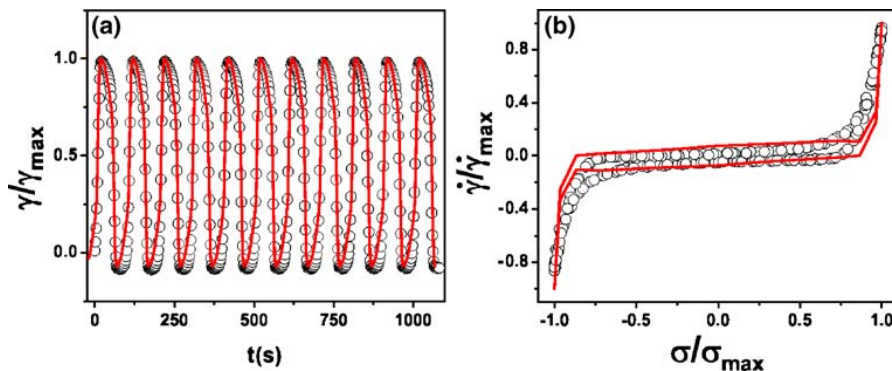


**Figure 3:** Linear (in time) stress ramp vs. model prediction: symbols, experiment; full lines, the prediction of the toy model. The squares/circles refer to increasing/decreasing stresses.

In spite of its simplicity, the toy-model is able to describe the two important features of the solid-fluid transition: the existence of an intermediate deformation regime and the irreversibility of the deformation states (the emergence of the hysteresis).

### 3.3 Validation of the toy model via oscillatory sweeps

In order to probe the time-dependent response of the material and the ability of our simplified model to capture for each of the three deformation regimes visible in Fig. 2(a), we now turn our attention to oscillatory flow measurements where a harmonic forcing  $\sigma = \sigma_0 \sin(2\pi f t)$  and the strain response  $\gamma = \gamma(t)$  is monitored. We focus here on the validation of both small-amplitude oscillatory shear and large-amplitude oscillatory shear measurements. In Fig. 4a, we display the response of the material corresponding to a stress amplitude  $\sigma_0$  close to the onset of the viscous regime, Fig. 2(a). The response of the material is clearly nonlinear, and



**Figure 4:** (a) Strain time series. (b) Lissajoux figure. The symbols are the experimental data and the full lines represent the prediction of the model using the same parameter values as in Figs. 3(a) and 4. The stress amplitude is  $\sigma_0 = 8$  Pa, and the forcing frequency is  $f = 0,01$  Hz. The data refer to a  $c = 0.1\%$  Carbopol solution at room temperature.

when the direction of the forcing is reversed, the material deformation is only partially recovered. Setting in the model the same parameter values used for the validation of controlled stress flow curves, (Fig. 3), one can describe very well the nonlinear oscillatory response illustrated in Fig. 4a. An implicit plot of the material response  $\gamma$  with respect to the time-dependent forcing  $\sigma$  defines a Lissajoux figure and provides a complex characterization of the time-dependent material response for a given forcing amplitude  $\sigma_0$  and frequency  $f$ . A comparison between an experimentally measured Lissajoux figure and the one predicted by our model is illustrated in Fig. 4b.

## 4 Conclusions

We have focused on the solid–fluid transition in a physical gel, an aqueous solution of Carbopol. Systematic measurements of controlled stress flow curves performed at both increasing and decreasing stresses revealed three deformation regimes: solid (corresponding to low values of the applied stress), fluid (corresponding to the largest values of the applied stress) and an intermediate regime characterized by a coexistence between solid and liquid behavior, Fig. 2(a). Associated with the phase coexistence deformation regime, a hysteresis of the deformation states is observed. The power deficit associated with the hysteresis effect scales algebraically with the characteristic forcing time,  $t_0$ . A simple model able to describe each of the experimentally observed deformation regimes and the hysteresis of the deformation states is presented. The model is validated against oscillatory measurements without any additional parametric adjustment.

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