# Phase diagram for jammed systems

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**Abstract**

Jammed systems such as colloidal pastes, gels, granular materials, etc. undergo a viscosity bifurcation at a critical stress: depending on the stress level, the steady-state viscosity is either finite and low, or (almost) infinite. This implies that below a critical shear rate, the flows are unstable. Under controlled flow rate this leads to a coexistence of 'solid' and 'liquid' phases, i.e., phases with infinite and finite viscosity. It follows that the stress-shear rate diagram for jammed systems is analogous to the Van der Waals phase diagram determining phase coexistence for simple substances in thermodynamic equilibrium, showing that the 'jamming transition' in these systems is analogous to the phase separation associated with a first-order phase transition. This makes a direct connection to the glass transition difficult.

Systems consisting of a more or less close packing of elements of mesoscopic size (colloidal particles, grains, bubbles, droplets) are frequently encountered in everyday life: in foodstuffs, cosmetic and pharmaceutical products, but also in civil engineering and natural flows; specific examples are mayonnaise, creams, concrete, clayey soils, shaving foams etc. Recently, an attempt was made to describe such 'jammed' systems in a single conceptual scheme [1], extending a previous proposal for the analogy between glasses and granular matter [2]: jammed systems do not flow and are consequently 'glassy' whereas unjammed systems are 'liquid'. The analogy with the glass transition comes from the identification of the blocked or jammed configurations with local minima of the free energy in a complicated energy landscape with many metastable states. Given a distribution of local energy minima [3], the response to an external forcing can be worked out explicitly [4]. This proposal implicitly assumes a similarity between the glass transition (as a function of temperature) and the mechanical transition between jammed and unjammed states (as a function of the applied load) [1,2]. Subsequent calculations for specific model glasses subjected to an external forcing indeed provided some evidence for this [5]: under an external forcing, the glass transition is shifted to lower temperatures, but its nature does not change.

We will show here however that, contrary to what is found for the glass transition, under forcing, coexistence between jammed and unjammed material is observed, underlining the *discontinuous* nature of the transition between jammed and unjammed configurations. In addition, we show that the analog of a phase diagram in the (load/deformation rate) plane can be drawn, in which the coexistence region shrinks to disappear at a 'critical point', beyond which the discontinuity disappears. This bears a strong analogy to equilibrium phase transitions, the coexistence region corresponding to the phase separation associated with a 'van der Waals' loop. The dynamical phase diagram we obtain can provide a unified description of the very different materials mentioned above on the basis of their very similar mechanical properties. In addition, we find that the (flow, temperature) history of these systems are crucial in determining for instance the location of the 'critical point', showing that time is an additional factor that needs to be taken into account (being absent from the 'jamming phase diagram' of [1]).

Jamming and unjamming are related to evolution of the configuration of the mesoscopic elements constituting the material, which interact via various forces that are system-specific. Here we consider systems made of an ensemble of elements (solid particles, liquid droplets, bubbles, or polymer chains) which interact, e.g. by colloidal forces, direct contact forces, entanglements or crosslinks between polymer chains, leading to a continuous network of forces throughout the sample. The result of these interactions is that at a macroscopic level the material responds elastically to a small stress applied to it: the system is said to exhibit a yield stress.

When submitted to a shear stress, the response of a perfect yield stress fluid is a slow flow provided the stress is slightly beyond the yield point: its viscosity diverges in a continuous fashion when the yield stress is approached from above. In practice, however, when submitted to flow, the microstructure of the material is partly destroyed, generally observed as a viscosity that decreases in time ('thixotropy'). On the other hand, at rest the microstructure reforms or evolves spontaneously: the systems are said to *age*. Experimentally, this is reported as an increase of an apparent yield stress with time [6]. The mechanical behavior of these systems consequently results from the competition between aging and rejuvenation by the shear flow.

We have shown recently that the direct consequence of this competition is that a bifurcation in the rheological behavior occurs: for a given load, the fluid either stops flowing, or fluidifies [7]. Applying different stresses to a sample and following the viscosity in time, it was found that for stresses smaller than a critical stress $\sigma_c$, the aging wins over the thixotropy (which can be looked upon as a shear rejuvenation [7]), i.e. the viscosity increases in time until the flow is halted altogether: the steady-state viscosity is infinite. On the other hand, for a stress only slightly above $\sigma_c$, the rejuvenation 'wins' over the aging. As a consequence, the viscosity decreases in time; for long times it reaches a (low) steady state value $\eta_0$. This implies that at the critical stress, the steady-state viscosity jumps *discontinuously* from infinity to a finite and low value at $\sigma_c$. This bifurcation was observed for colloidal gels and glasses, polymer gels and more recently also foams, emulsion and granular matter [7], and is therefore believed to be general for 'yield stress' or 'jammed' fluids. A direct consequence of the bifurcation is that, in steady-state, a whole range of shear rates is inaccessible to the system [7].

In this Letter we ask what happens within the fluid when such an inaccessible shear rate is imposed on the system. We find that the consequences on the flow characteristics in terms of the apparent shear rate can be described in a 'phase diagram' in the stress/shear rate ($\tau, \dot{\gamma}$) plane (Fig.1). As a particular example we consider here a colloidal gel, a solution of Bentonite which is a weakly flocculated clay suspension; the results are believed to be general also for the other systems. For this system, a viscosity bifurcation has been observed [7]. The rheometrical tests were done with a Bohlin C-VOR controlled stress rheometer equipped with a (roughened) cone and plate geometry (4°). A logarithmically increasing stress was applied to the materials starting from a low value. The detailed observations are that:

1)  for sufficiently small shear stresses, corresponding to small shear rates, the material does not flow appreciably: the critical deformation at which the network breaks has not been reached and as a result in this range the material is entirely in a 'solid' phase; the viscosity is very

large. The corresponding critical shear rate for the onset of measurable flow sensitively depends on the flow history, both because of intrinsic material structuration in time and because most likely there exists in fact a critical deformation rather than a critical shear rate;

**2)** at a critical stress there is a 'coexistence' plateau (see below) associated to a wide range of (apparent) shear rates; in our experiments the shear rate extremely rapidly increases at this critical stress;

3) beyond a critical shear rate $\dot{\gamma}_c$ the material is entirely liquid and the stress increases as a function of the apparent shear rate.

Upon increasing the particle concentration, in Fig.1(a) it is shown that one passes from a continuously increasing flow curve for the lowest concentration to one with a plateau. The same observations are made if we consider different initial degrees of jamming, i.e., different ages of the same system (Fig.1(b)): "Young", fluid systems do not exhibit coexistence, but older, more jammed systems do.

The main question is then what happens at the stress plateau; such a plateau is unphysical since it implies that for a given stress several shear rates are possible, and that consequently the system has several viscosities at this stress. We therefore measure the velocity profile of the sheared fluid in the stress plateau; these results are obtained in steady state with a cone-and-plate rheometer inserted in a magnetic resonance imager (MRI) (see details in [8]). The key observation is that for shear rates smaller than a critical one, we observe a *coexistence* between sheared and unsheared material, as can be observed directly from the determination of the velocity profiles (Fig.2). Although in a cone-plate geometry the shear stress is constant, the velocity profiles are composed of two regions: in the first region (close to the bottom) there is no apparent shear while in the second region the fluid is sheared at a large rate. It is worth noting that the effective rate of shear observed in MRI tests in the sheared region is about $50\,\mathrm{s}^{-1}$, which approximately corresponds to the critical shear rate at which the stress starts again increasing with shear rate in the phase diagram (for $\phi = 6\%$); thus our MRI tests effectively prove that no coexistence occurs beyond this apparent shear rate.

The stress plateau then signals a dynamic coexistence of unsheared (jammed) and sheared (unjammed) material, in analogy with the plateau in the equilibrium pressure-volume phase diagram for simple fluids. The observed coexistence of a sheared and an unsheared part of the material is likely to be a general property of these jammed systems. Indeed, measurements of the velocity profile for instance in slowly sheared foams and granular systems typically show a strong localization of the strain in a small band close to the moving wall, the rest of the material being

essentially undisturbed [9]. Similar observations were made in pastes, as was shown in cone and plate flows of silica suspensions [10] and the colloidal glass of Laponite [11]. However, besides the observation of localization, no quantitative study was made; the width of the sheared region, for instance, was often believed to be a material property.

The MRI observations show that for our system something very different happens: upon increasing the rotation velocity of the cone *the width of the sheared region increases* (Fig.2). This means that the macroscopically observed 'viscosity' in fact reflects the shear rate distribution rather than some intrinsic viscosity of the sample. The macroscopic shear rate calculated from the relative velocity ($V$) of the solid boundaries; is $\dot{\gamma} = V/H$ where $H$ is the sample thickness. In the cone-plate geometry, the stress is homogeneous. However there is always some slight deformation of the peripheral free surface, which may induce a slight heterogeneity of the stress distribution. Probably due to these slight variations in stress, we observe that the viscosity bifurcation can take place *within* the sample. We observe that the material is sheared at a rate $\dot{\gamma}_1$ in a layer of thickness $\xi H$ and at a rate $\dot{\gamma}_2 \approx 0$ in a layer of thickness $(1-\xi)H$. This is *a priori* always possible when the apparent shear rate is imposed at the boundary, the only condition being that: $\xi\dot{\gamma}_1 + (1-\xi)\dot{\gamma}_2 = \dot{\gamma}$.

We recently introduced a model that accounts for the viscosity bifurcation [7], and show here that a simple modification of this model provides a qualitative description of the results obtained here also. As before, we assume that the 'degree of jamming' can be described by a single parameter $\lambda$. For the colloidal gel considered here, $\lambda$ could for instance represent the number of attachments between particles per unit volume. This makes it a measurable quantity: the Young's modulus of gels is on the order of $k_BT$ divided by the number of cross-links per unit volume [12]. The new –and physically important ingredient- is that for the type of system we consider here, which have a very large but finite viscosity in the "solid" phase, the degree of jamming has a large but finite equilibrium value. We implement the aging by assuming that in the absence of shear, $\lambda$ relaxes to its equilibrium value, $\lambda_{eq}$, with a characteristic relaxation rate $1/\tau$. As before [7], we suppose that the rate of decrease of $\lambda$ under shear (the shear rejuvenation) is proportional to the shear rate $\dot{\gamma}$, since the number of elements pushed out of their potential wells is simply proportional to the total strain [4]: $\Delta\lambda \propto \dot{\gamma}\Delta t$. If we further suppose that the two processes (aging and shear rejuvenation) are independent, the rate of variation of $\lambda$ can be written as:

$$d\lambda/dt = 1/\tau \, (\lambda_{eq} - \lambda) - \alpha\dot{\gamma}\,\lambda \qquad\qquad\qquad (1)$$

where $\alpha$ is a material parameter. We further assume, as previously, that the viscosity of the material is a simple, power-law function of $\lambda$ :

$$\eta=\eta_0(1+\lambda^n) \tag{2}$$

In steady state, $\lambda = \lambda_{eq} / \alpha\dot{\gamma}\tau$ so that the shear stress becomes: $\sigma/\eta_0 = \dot{\gamma}\,(1+\lambda_{eq}{}^n/(1+\alpha\dot{\gamma}\tau)^n)$. Fig.3 shows the shear stress-shear rate curves predicted by the model: it gives a nearly Newtonian behavior for small shear rates, with $\sigma \approx \dot{\gamma}\,(1+\lambda_{eq}{}^n)$. For higher shear rates the stress-shear rate curve has a negative slope when n is sufficiently large. A simple linear stability analysis [13] shows that flows are necessarily unstable in the regions with a negative slope. This negative slope is the hallmark of a shear banding transition, for which localization of the shear in part of the sample occurs. We have shown here that this shear banding takes the form of a 'phase coexistence' in which the width of the sheared region increases upon increasing the macrosopically imposed shear rate. The unstable negative slope for the shear stress-shear rate curve in this region is then the equivalent of the "van der Waals" loop for equilibrium systems. Consequently, there is a clear transition between jammed and fluid systems, at the equivalent of a critical point in the phase diagram $(1/p, v)$ of simple matter at different temperatures. Here the 'critical point' is encountered as a function of the power n which measures the relative weight of the 'background' solvent viscosity $\eta_0$ to the non-Newtonian effects discussed here. It then follows naturally that upon increasing the non-Newtonian effects (i.e., n), these start to dominate the flow behavior. The behavior of the model for increasing n (cf. Fig.3) is analogous to that found experimentally in Fig.1(a) for increasing densities: the extent of the coexistence region decreases for decreasing n values (for a fixed value of $\lambda_{eq}$) and disappears at the critical point corresponding to $n_c = (\lambda_{eq}^{1+\frac{1}{n}}+1)/(\lambda_{eq}^{1+\frac{1}{n}}-1)$. Although phenomenological in nature, this model does well in reproducing the experimental observations; it shows in any case that only minimal ingredients are necessary to reproduce the 'critical point' that is observed in the experiments.

In conclusion, the effect of shear on jammed systems is likely to be more complicated than was hitherto assumed. Models borrowed from studies of the glass transition show that an external forcing leads to a decrease of the longest relaxation time that depends in a continuous way on the forcing. As it is this relaxation time that diverges at the glass transition (and its divergence is also believed to lead to jamming), this simply means that the main effect of the forcing will be that the transition is displaced in the phase diagram [1,2,4]. We show here however that the nature of the transition changes. Contrary to what is found for the glass transition, under forcing a *coexistence*

between jammed and unjammed material is observed, underlining the discontinuous nature of the transition between jammed and unjammed configurations. We have also shown that the observation (or not) of coexistence depends on the previous flow history of the material [8]. This is in fact a very peculiar observation since it implies that the system 'remembers' its entire flow history indefinitely: the viscosity in steady state is found to be different for the same system subjected to the same stress. This underlines that if a generalized 'phase diagram' for jammed systems can be constructed, time is probably an important variable that has been overlooked so far.

**Captions**

Figure 1: Shear stress-shear rate curves during increasing stress ramps imposed after a preshear ($500s^{-1}$ during 20s) followed by a certain time of rest, for Bentonite suspensions at different densities (a) (time of rest: 20s) or after different times of rest (b) ($\phi = 3.6\%$). The dotted lines indicate the probable position of the "phase" boundary.

Figure 2: MRI velocity profiles for a Bentonite suspension ($\phi = 6\%$): height in the sample at 4.6cm from the center as a function of the tangential velocity, during cone-and-plate (angle=8°, diameter=13cm) rheometrical tests at different rotation velocities of the cone.

Figure 3: Dimensionless shear stress $\sigma\alpha\tau/\eta_0\lambda_{eq}$ as a function of imposed dimensionless shear rate $\dot{\gamma}\alpha\tau/\lambda_{eq}$ from the phenomenological model given by Eqs. (1) and (2) for various values of the exponent n, n=1,1.25, 1.5...3 and $\lambda_{eq}$=6.6. For imposed stress, the range where the slope of the stress-shear relation is negative will be dynamically unstable. As a result, the range of shear where the slope is negative marks the region where homogeneously sheared solutions can not be obtained experimentally for imposed stress.

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"Solid"   "Solid" + "Liquid"   "Liquid"

Shear stress (Pa)

*Density*

Shear rate (1/s)

Solid fraction:
- □ 9%
- ★ 6.3%
- ○ 4.4%
- ■ 3.6%

100

10

1

0.1

1E-4  1E-3  0.01  0.1  1  10  100  1000  10000

10