Porosity governs normal stresses in polymer gels


DOI
10.1103/PhysRevLett.117.217802

Publication date
2016

Document Version
Final published version

Published in
Physical Review Letters

Citation for published version (APA):
The magnitude of the normal stress again increases with a controllable pore size as a model system, we show that the normal-stress response to an applied shear is positive at short times, but decreases to negative values with a characteristic time scale set by pore size.

Using a two-fluid model, we develop a quantitative theory that unifies the opposite behaviors encountered in synthetic and biopolymer gels. When sheared, most elastic solids including metals, rubbers, and polymer gels dilate perpendicularly to the shear plane. This behavior, known as the Poynting effect, is characterized by a positive normal stress. Surprisingly, fibrous biopolymer gels exhibit a negative normal stress under shear. Here we show that this anomalous behavior originates from the open-network structure of biopolymer gels. Using fibrin networks as a model system, the pore size of which can be tuned from nanometers to micrometers by simply changing the temperature, ionic strength, and pH during self-assembly [23]. This is demonstrated in Figs. 2(a) and 2(b), which show fluorescence microscopy images of two fibrin gels that are assembled at the same monomer concentration of 8 mg/mL but at different temperatures. Using quantitative measurements of the fiber mass-length ratio by light microscopy, we find that the normal-stress difference sensor to applied shear is largely determined by the porosity of the gel.

Here, we aim to understand the mechanistic basis of the fundamentally different response of synthetic and biopolymer gels and to develop a minimal model that can capture the behavior of both types of gels. In either case, the normal-stress response is fundamentally nonlinear, since its sign cannot reverse when the shear train γ is reversed. Thus, to lowest order, normal stress is expected to vary as \( \gamma^2 \), even while the shear stress remains linear in \( \gamma \). Although both gels in Fig. 1 are hydrogels containing over 90% interstitial water, there is structurally a profound difference in the pore size. While polyacrylamide gels have a pore size of order 10 nm [16], fibrin networks have pore sizes that can be in the micrometer range [17–19]. Fluid permeability can therefore play an important role in the mechanical response. For hydrogels with a small pore size, we expect a strong viscous coupling between the network and the solvent, which will suppress motion of the network relative to the solvent and effectively render the gel, as a whole, incompressible. By contrast, biopolymer gels can expel interstitial fluid to relax pressure gradients on long-enough time scales, allowing the network to contract upon shearing [7,20–22].

To study the role of porosity, we choose fibrin networks as a model system, the pore size of which can be tuned from nanometers to micrometers by simply changing the temperature, ionic strength, and \( p\text{H} \) during self-assembly [23].
To quantitatively model the effects of network poroelasticity in the shear rheology of polymer networks, we start from the two-fluid model [24-27] that describes a polymer gel as a biphasic system composed of a linear elastic network immersed in a viscous and incompressible liquid [9]. The two components are coupled by a force per unit volume, \( \Gamma (\vec{u} - \vec{v}) \), acting on the liquid and opposite to the force on the network. This dissipative force arises from the relative motion of the solvent, which moves with velocity \( \vec{v} \) and the network, with velocity \( \vec{u} \). For a network with pore size \( \xi \) and a fluid with viscosity \( \eta \), \( \Gamma \sim \eta \xi^2 \), since the Stokes drag force on a network strand of size \( \xi \) moving with relative velocity \( \sim v \) is \( \sim \eta \xi^2 \Delta v \) and this acts on a volume \( \sim \xi^3 \) [9]. Given the small polymer volume fraction \( \phi \) of most hydrogels and biopolymer networks (\( \phi \sim 10^{-3} \) for fibrin gels), the radial velocity component of the incompressible fluid effectively vanishes and the only radial motion is due to the network. This radial motion, \( \vec{u}_r \), generates a radial pressure gradient in the solvent given by

\[
\nabla_r P = \Gamma \vec{u}_r = -\frac{\sigma}{r} - (K/r^2)\vec{u}_r, \tag{1}
\n\]

scattering, we calculate average mesh sizes of 0.36 and 0.29 \( \mu \)m for these networks (see [9] for further details).

To test the influence of pore size on the normal-stress response, we subject each network to a constant shear stress and we monitor the normal stress as a function of time. Intriguingly, we find that in each case, the normal stress relaxes from an initially positive or close-to-zero value to a negative steady-state value with a rate that strongly varies with pore size. The characteristic relaxation time, \( \tau \), increases from just a few seconds to \( \sim 100 \) s as the pore size of fibrin decreases from 0.36 to 0.08 \( \mu \)m. For PAAm gels with a pore size \( \sim 10 \) nm [16], the relaxation time grows to over 15 hours [Fig. 2(c)]. These observations support our hypothesis that the sign of the normal stress is controlled by the time scale for solvent flow through the network. The data suggest that the normal stress is positive as long as the polymer network and the fluid remain viscously coupled, and switches sign to become negative when the fluid can move relative to the network. Importantly, the time scale separating these behaviors is unrelated to the time scales apparent in the linear viscoelastic response [see Fig. 2(c)].

To quantitatively model the effects of network poroelasticity in the shear rheology of polymer networks, we start from the two-fluid model [24-27] that describes a polymer gel as a biphasic system composed of a linear elastic network immersed in a viscous and incompressible liquid [9]. The two components are coupled by a force per unit volume, \( \Gamma (\vec{u} - \vec{v}) \), acting on the liquid and opposite to the force on the network. This dissipative force arises from the relative motion of the solvent, which moves with velocity \( \vec{v} \) and the network, with velocity \( \vec{u} \). For a network with pore size \( \xi \) and a fluid with viscosity \( \eta \), \( \Gamma \sim \eta \xi^2 \), since the Stokes drag force on a network strand of size \( \xi \) moving with relative velocity \( \sim v \) is \( \sim \eta \xi^2 \Delta v \) and this acts on a volume \( \sim \xi^3 \) [9]. Given the small polymer volume fraction \( \phi \) of most hydrogels and biopolymer networks (\( \phi \sim 10^{-3} \) for fibrin gels), the radial velocity component of the incompressible fluid effectively vanishes and the only radial motion is due to the network. This radial motion, \( \vec{u}_r \), generates a radial pressure gradient in the solvent given by

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\nabla_r P = \Gamma \vec{u}_r = -\frac{\sigma}{r} - (K/r^2)\vec{u}_r, \tag{1}
\n\]
for a cone-plate geometry. The net force on the network has two distinct elastic contributions. The first contribution comes from the hoop stress \( \sigma \), which tends to drive the network radially inward [Fig. 2(d)] [9]: hoop stresses generated by shearing tend to drive radial contraction of the network and expulsion of the solvent, much as a twisted sponge expels water by contracting radially. By symmetry, \( \sigma \sim \gamma^2 \) to lowest order, as noted above, although Eq. (1) is linear in \( u_r \). The second contribution to the net force on the network comes from a restoring force that balances the radial contraction on long time scales (i.e., as \( \dot{u}_r \to 0 \)). This restoring force originates from the gradient in the elastic shear stress \( \sim G \nabla u_r \) that results from the axial (\( z \)) variation of \( u \) [see Fig. 2(d)]. For a cone-plate rheometer with small gap size \( d \) and small cone angle \( \alpha \), the restoring force \( \sim G/d^2 u_r \). Thus, since \( d = \tan(\alpha) r, K \sim G/\tan(\alpha)^2 \) in Eq. (1). We thus predict a characteristic relaxation time \( t \sim \eta d^2/G \). Indeed, we experimentally observe a rapid decrease of the relaxation time with increasing pore size, consistent with the predicted scaling (see Fig. S1 in [9]).

We can consider two opposite limits of Eq. (1). In the limit of small pore size and \( \Gamma \to \infty \), the radial displacement \( u_r \to 0 \) (with finite \( \Gamma \dot{u}_r \)) and Eq. (1) reduces to \( \nabla P = -\sigma / r \). Shearing will thus increase the pressure toward the axis of the rheometer, which results in a positive contribution to the normal force. Dense hydrogels will therefore effectively behave as incompressible materials for which the normal force \( F \) is related to the normal-stress difference \( \sigma_{xx} - \sigma_{zz} \) by \( N_1 = 2F/\pi R^2 \), where \( R \) is the sample radius [28]. \( N_1 \) is positive for a rubberlike material, consistent with measurements on polyacrylamide gels [5]. In the opposite limit of networks with a large pore size, the pressure difference can relax by water efflux and in steady state the two terms on the right-hand side of Eq. (1) cancel.

A key prediction of the two-fluid model is that the response of the normal stress measured in a rheology experiment should depend on the experimental time scale relative to the characteristic relaxation time, \( t \sim \eta d^2/G \). To quantitatively test this prediction, we subject the fibrin gels to an oscillatory shear stress with frequencies between 0.001 and 5 Hz, allowing us to conveniently probe a range of time scales from 0.2 to 1000 s in a single experiment. We measure the normal stress response after the system has reached steady state (Fig. S2 in [9]). We focus on fibrin gels polymerized at 27°C, which have a relaxation time \( t \approx 12.5 \) s that lies in the middle of the experimentally accessible frequency range. In steady state, the observed normal stresses are indeed negative over the entire frequency range.

When we plot the time-dependent normal stress [Figs. 3(d)–(f)] as a function of shear stress, we obtain the Lissajous curves shown in Figs. 3(a)–3(c). Strikingly,
the Lissajous curves completely change with changing frequency. For oscillation periods longer than \( \tau \) [Fig. 3(a)], the normal stress decreases with increasing shear stress, demonstrating contractile behavior under shear. By contrast, for oscillation periods shorter than \( \tau \), the normal stress increases with increasing shear stress, demonstrating extensile behavior [Fig. 3(c)]. The transition occurs at an intermediate frequency that is of order \( 1/\tau \) [Fig. 3(b)].

This experiment unambiguously shows that the normal stress response of a polymer gel is governed by fluid flow, which is suppressed at higher frequencies. The normal stress response is therefore controlled by the network pore size, and is furthermore dependent on the shear modulus \( G \) and the gap size \( d \) between the cone and the plate (see Fig. S3 in [9]).

The two-fluid model allows us to perform an even more rigorous test of the mechanism governing the normal stress response of polymer gels, since we can calculate more rigorous test of the mechanism governing the normal stress response of polymer gels, since we can calculate

\[
\sigma = \frac{\gamma}{\gamma + \frac{1}{2} \omega \tau^2} + \frac{1}{2} \omega \tau^2.
\]

where

\[
\gamma = \frac{1}{8 \omega \tau} \log \left( 1 + 4 \omega^2 \tau^2 \right).
\]

with \( \gamma = A_1 - A_2 \) and \( \tau = \Gamma R^2 / K \sim \eta d^2 / G \xi^2 \). In the limit where \( \omega \tau \gg 1 \), Eq. (2) reduces to the well-known Mooney-Rivlin expression for incompressible materials, \( N_1 = G \gamma^2 \).

In the opposite limit where \( \omega \tau \ll 1 \), Eq. (2) instead reduces to

\[
N_1^{(\text{app})} = -2A_1 G \gamma^2 + \tilde{A} G \gamma^2 [A \cos(2\omega t) + B \sin(2\omega t)].
\]

where

\[
A = \frac{1}{8 \omega \tau} \left[ 2 \tan^{-1}(1 + 2 \sqrt{\omega \tau}) + 2 \tan^{-1}(1 - 2 \sqrt{\omega \tau}) - \pi + 4 \omega \tau \right],
\]

\[
B = \frac{1}{8 \omega \tau} \log \left( 1 + 4 \omega^2 \tau^2 \right),
\]

This work was supported by the Foundation for Fundamental Research on Matter (FOM), which is part of the Netherlands Organisation for Scientific Research (NWO).

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