

Large network swelling and solvent redistribution are necessary for gels to show negative normal stress

Tetsuya Yamamoto,^{*,†} Yuichi Masubuchi,[†] and Masao Doi[‡]

National Composite Center, Nagoya University, Furocho, Chikusa-ku, Nagoya, 464-8603, Japan, and Center of Soft Matter Physics and its Application, School of Chemistry and Environment, Beihang University, Xueyuan Road 37, Beijing 100191, China

E-mail: tyamamoto@nuap.nagoya-u.ac.jp

Abstract

We use a statistical thermodynamic model to theoretically predict the normal stress of a polymer gel, which is twisted by a rotational rheometer in the parallel plate geometry. This theory predicts that the normal stress of the gel is positive at a short timescale. At longer time, the normal stress decreases significantly due to the redistribution of solvent, but is still positive when the polymer network is in the neo-Hookean regime. The normal stress becomes negative when the polymer network is greatly pre-stretched in the swelling process because large tension is generated by shearing already pre-stretched polymers. Our theory predicts the phase diagram with respect to the direction of normal stress as functions of the aspect ratio and swelling ratio of gels.

*To whom correspondence should be addressed

[†]NCC

[‡]Center of Soft Matter Physics and its Application, School of Chemistry and Environment, Beihang University, Xueyuan Road 37, Beijing 100191, China

Experimental tests on this prediction may advance our understanding of the physical mechanisms involved in the negative normal stress generated by polymer gels.

When shear strain is applied, polymeric materials generate stresses both in parallel and normal to the applied shear.¹ Many unusual rheological phenomena of polymeric materials result from the normal stress.¹ The normal stress does not depend on the direction of applied shear and thus is a non-linear effect. Most materials show ‘positive’ normal stress, with which materials expand.¹ Surprisingly, large negative normal stress has been experimentally measured from gels of biopolymers.² The rheological properties of biopolymer gels have been studied theoretically and experimentally to elucidate the physical mechanism involved in the negative normal stress of such gels.²⁻⁵ MacKintosh and coworkers theoretically predicted that the networks of semiflexible polymers generate negative normal stress because stiff polymers are compressed by smaller stresses than stretching it.^{2,3} Meng and Terentjev showed that gels of flexible polymers also generate negative normal stress when they are pre-stressed.⁴ This work also showed that this type of network theory predicts negative normal stress only when a specific network model is used. The forementioned theories²⁻⁴ highlight the roles played by the elasticity of polymers in the network and neglect the contributions of solvent. Recently, de Cagny and coworkers experimentally showed that even flexible polyacrylamide gels generate negative normal stress at a long timescale due to the redistribution of solvent.⁵ They used a phenomenological scaling theory to predict that *any* gels generate negative normal stress due to the solvent redistribution, however, this theory predicts that the direction of normal stress depends on the sign of phenomenological parameters. We thus use the statistical thermodynamic theory of polymer gels to theoretically predict the conditions with which gels show negative normal stress.

We treat cases in which a cylindrical gel is swollen in a solvent to the equilibrium by swelling ratio λ_{eq} and then it is twisted by angle $\delta\theta$ by using a rotational rheometer in the parallel plate geometry while the distance h_0 between the gel is fixed, see fig. 1. The top and bottom surfaces of the gel stick to the plates and thus the radius r_0 of the surface area

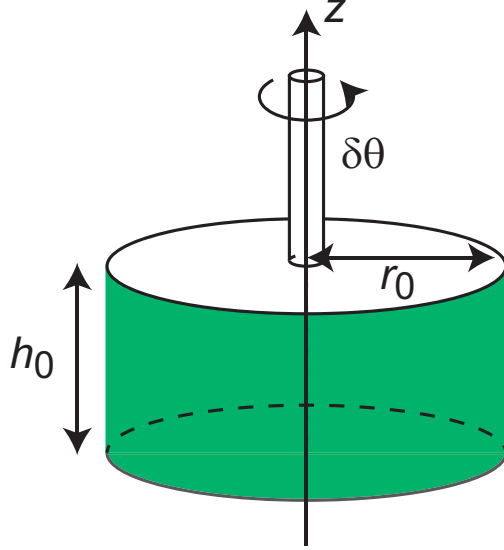


Figure 1: A polymer gel is twisted by angle $\delta\theta$ by using a rotational rheometer in the parallel plate geometry, fixing the height h_0 of the gel. The top and bottom surfaces of this gel are fixed to the parallel plates and the radius r_0 is constant; the total volume (the polymer network + the solvent) is fixed.

is constant. We use the cylindrical coordinate systems (r, θ, z) to represent the positions of the material points before the gel is swollen. After the swelling process, the positions of these material points change to (r_s, θ, z_s) , where $r_s = \lambda_{\text{eq}} r$ and $z_s = \lambda_{\text{eq}} z$. With the twist deformation, these material points further shift to (r', θ', z') , where $r' = \lambda_{\parallel}(z) \lambda_{\text{eq}} r$, $\theta' = \theta + \delta\theta z/h_0$, and $z' = \lambda_{\text{eq}} \int_0^z dz \lambda_{\perp}(z)$. The fixed distance h_0 between the plates is ensured by the condition

$$\frac{h_0}{\lambda_{\text{eq}}} = \int_0^{h_0/\lambda_{\text{eq}}} dz' \lambda_{\perp}(z'). \quad (1)$$

The magnitude of the shear strain is characterized by a parameter γ ($\equiv \delta\theta r_0/h_0$). We treat cases in which the thickness h_0 of the gel (in the swollen state) is smaller than the radius r_0 and derive the normal stress in the leading order with respect to the power of h_0/r_0 in the spirit of the lubrication approximation.⁶

The free energy density of a gel⁷ has the form

$$f_{\text{gel}} = f_{\text{ela}} + \frac{\phi_0}{\phi} f_{\text{sol}}, \quad (2)$$

where f_{ela} is the elastic energy of the polymer network and f_{sol} is the mixing free energy. ϕ is the volume fraction of polymer network and ϕ_0 is the volume fraction of the polymers when they are crosslinked.⁷ The neo-Hookean model assumes that the polymer network is composed of Gaussian chains and is widely used to treat polymer networks. With this model, the elastic energy f_{ela} has the form

$$f_{\text{ela}} = \frac{1}{2} G_0 J_1, \quad (3)$$

where G_0 is the shear modulus and $J_1 (\equiv g_{\alpha\alpha} - 3)$ is the first invariant. $g_{\alpha\alpha}$ is the trace of metric tensor $g_{\alpha\beta} (\equiv \frac{\partial x'_\gamma}{\partial x_\alpha} \frac{\partial x'_\gamma}{\partial x_\beta})$ (x_α is the position of a material point before the deformation and x'_γ is the position of the material point after the deformation). Henceforth, we use the indices α , β , and γ to collectively represent x , y , and z and use the Einstein convention, with which repeated indices in one term are summed over x , y , and z . We use prime ' to indicate material points after the deformation. The mixing free energy f_{sol} has the form $f_{\text{sol}} = \frac{k_B T}{v_c} [(1 - \phi) \log(1 - \phi) + \chi \phi(1 - \phi)]$, where k_B is the Boltzmann constant, T is the absolute temperature, v_c is the size of solvent, and χ is the interaction parameter.⁷ The volume fraction ϕ has a relationship $\phi = \phi_0 / \sqrt{g}$, where g is the determinant of the metric tensor $g_{\alpha\beta}$. The normal stress is derived by using the relationship

$$\sigma_\perp = -\frac{1}{\lambda_\parallel^2(z) \lambda_{\text{eq}}^3} \frac{\delta f_{\text{gel}}}{\delta \lambda_\perp(z)}. \quad (4)$$

Minimizing the free energy f_{gel} with respect to λ_{eq} (with $\lambda_\parallel(z) = \lambda_\perp(z) = 1$) leads to the force balance equation $\frac{G_0}{\lambda_{\text{eq}}} = \Pi_{\text{sol}}(\phi_{\text{eq}})$ in the swelling process, where $\Pi_{\text{sol}}(\phi) (= \phi^2 \frac{\partial}{\partial \phi} (\frac{f_{\text{sol}}(\phi)}{\phi}))$ is the osmotic pressure of the gel and $\phi_{\text{eq}} (\equiv \phi_0 / \lambda_{\text{eq}}^3)$ is the volume fraction of polymer

network in the swollen state.^{7,8} In the following, we use the swelling ratio λ_{eq} , which is derived by solving the force balance equation.

At the short timescale after the twist deformation is applied, the gel is treated as an incompressible material because the solvent has not been redistributed (to relax the hydrostatic pressure of solvent).⁸ With the incompressibility condition, $\lambda_{\parallel}^2 \lambda_{\perp} = 1$, the normal stress has the form

$$\bar{\sigma}_{\perp} = \frac{1}{4} \Pi_{\text{sol}}(\phi_{\text{eq}}) \gamma^2, \quad (5)$$

by the leading order terms with respect to the power expansion of γ ; the direction of the normal stress is independent of the sign of γ . Eq. (5) predicts that the normal stress is positive in this time scale as long as the system is stable, $\Pi_{\text{sol}}(\phi_{\text{eq}}) > 0$. This is because polymers are stretched in the θ -direction by the twist deformation and generate the hoop stress towards the rotation axis. This increases hydrostatic pressure (which is taken into account implicitly in the incompressibility condition) and thus generates normal stress in the positive direction.

At a long timescale, after the solvent is redistributed, the stretching ratios, $\lambda_{\parallel}(z)$ and $\lambda_{\perp}(z)$, are determined by minimizing the free energy f_{gel} with respect to $\lambda_{\parallel}(z)$ and $\lambda_{\perp}(z)$. Minimizing the free energy f_{gel} with respect to $\lambda_{\parallel}(z)$ leads to the force balance equation in the lateral direction

$$\frac{1}{2} G_0 \lambda_{\parallel}(z) \frac{\phi}{\phi_0} \left(2\lambda_{\parallel}(z) \lambda_{\text{eq}}^2 + \lambda_{\parallel}(z) \lambda_{\text{eq}}^4 \gamma^2 \frac{r^2}{r_0^2} - \lambda_{\parallel}''(z) \lambda_{\text{eq}}^2 r^2 \right) - \Pi_{\text{sol}}(\phi) = 0. \quad (6)$$

The first term in the round bracket of eq. (6) shows elastic forces due to the stretching of network in the radial direction, the second term is due to the hoop stress, and the third term is due to the shear elastic stress. These elastic forces are balanced by the osmotic pressure $\Pi_{\text{sol}}(\phi)$. We derive the solution of the force balance equation in the form $\lambda_{\parallel}(z) = 1 + \delta\lambda_{\parallel}(z)$ ($\delta\lambda_{\parallel}(z) \ll 1$) by the leading order terms with respect to the power expansion of h_0/r_0 and

shear strain γ . This leads to the form

$$\delta\lambda_{\parallel}(z) = \frac{\lambda_{\text{eq}}^2\gamma^2}{2r_0^2}z\left(z - \frac{h_0}{\lambda_{\text{eq}}}\right). \quad (7)$$

This is because the hoop stress towards the rotation axis deforms the network until it is balanced by the shear stress.

With eq. (7), the normal stress has the form

$$\bar{\sigma}_{\perp} = \frac{1}{6}(\phi_{\text{eq}}\Pi'_{\text{sol}}(\phi_{\text{eq}}) - \Pi_{\text{sol}}(\phi_{\text{eq}}))\frac{h_0^2}{r_0^2}\gamma^2 \quad (8)$$

by the leading order term with respect to h_0/r_0 . Eq. (8) predicts that the normal stress decreases considerably by the redistribution of solvent, but it is still positive for cases in which the gel is swollen in a good solvent, $\chi < 0$. This is because although the hydrostatic pressure is relaxed by the solvent redistribution, network polymers are attracted towards the rotation axis by the hoop stress and generate pressure due to the Poisson effect. This result is in contrast to the conclusions of the phenomenological theory by de Gagny *et al.*, which states that *any* gels generate negative normal stress at the long timescale.⁵ Our result implies that the direction of the normal stress at the equilibrium depends on the form of the elastic energy.

Motivated by the network theories,²⁻⁴ we take into account the finite extensibility of polymers in the gel in an extension of our theory. The Gent model is a simple model that takes into account the finite extensibility of polymers by using a phenomenological parameter J_m .⁹ With this model, the elastic energy f_{ela} of the network has the form

$$f_{\text{ela}} = -\frac{G_0}{2}J_m \log\left(1 - \frac{J_1}{J_m}\right). \quad (9)$$

Eq. (9) returns to the neo-Hookean model for $J_1 \ll J_m$. We use eq. (9), instead of eq. (3), for the elastic energy f_{ela} of the network (in eq. (2)) and derive the normal stress of the gel

in a similar manner to the cases of neo-Hookean model.

At the short timescale, the normal stress has the form of eq. (5) and is positive. In contrast, for the long timescale, the normal stress has the form

$$\bar{\sigma}_\perp = -\frac{1}{2} \frac{G_0 \lambda_{\text{eq}}}{J_m} \frac{1}{(1 - 3(\lambda_{\text{eq}}^2 - 1)/J_m)^2} \gamma^2 + \frac{1}{6} \frac{h_0^2}{r_0^2} (\phi_{\text{eq}} \Pi'_{\text{sol}}(\phi_{\text{eq}}) - \Pi_{\text{sol}}(\phi_{\text{eq}})) \gamma^2 \quad (10)$$

by the leading order term with respect to h_0/r_0 . The derivation of eq. (10) is shown in the ESI. Eq. (10) returns to eq. (8) for $J_m \rightarrow \infty$. Eq. (10) predicts that the normal stress decreases to a negative value for cases in which the polymers in the network are greatly stretched in the swelling process, $3(\lambda_{\text{eq}}^2 - 1)/J_m \sim 1$. This is due to the large tension generated by already pre-stretched polymers; although there are both stretched and compressed polymers by the twist deformation, the tensile forces generated by stretched polymers are larger than the contractile forces generated by compressed polymers because they are pre-stretched. This mechanism was proposed by Meng *et al.*, although their theory did not take into account solvent explicitly.⁴ Our theory predicts that both solvent redistribution and large pre-stretching of polymers are necessary for gels to generate negative normal stress. The polyacrylamide gels that were used in the experiments by de Cagny *et al.* might have been swollen beyond the neo-Hookean regime.

Eq. (10) predicts that the normal stress of gels at the long timescale decreases with increasing the swelling ratio λ_{eq} or decreasing the aspect ratio h_0/r_0 and eventually becomes negative for $\frac{h_0^2}{r_0^2} < \frac{3\lambda_{\text{eq}}^2/J_m}{1-3(\lambda_{\text{eq}}^2-1)/J_m}$ when the gels are swollen in a good solvent, see fig. 2. This prediction may be accessible by experiments that measure the normal stress of flexible polymer gels as a function of the swelling ratio λ_{eq} and/or the aspect ratio h_0/r_0 . One can systematically change the swelling ratio λ_{eq} of gels of polyelectrolytes by changing the concentration of added salt. However, one should be careful about the fact that the persistence length of polyelectrolytes also depends on salt concentration. Polyelectrolyte gels may also show volume phase transitions by changing temperature¹⁰ and our theory predicts that these

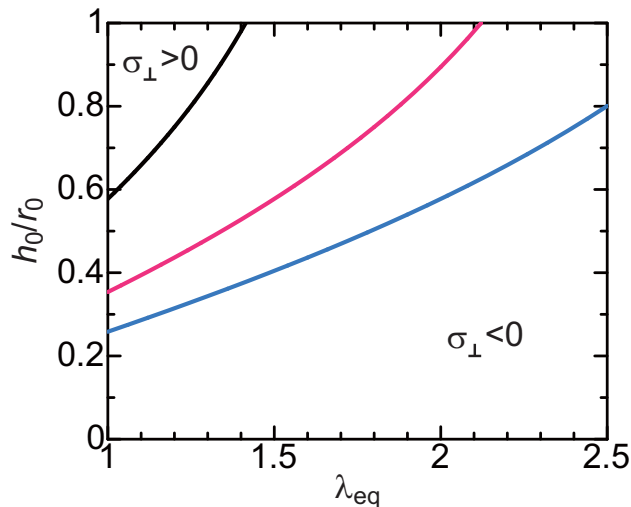


Figure 2: The maximum value of the aspect ratio h_0/r_0 , with which gels generate negative normal stress, is shown as a function of the swelling ratio λ_{eq} for $J_m = 9.0$ (black), 24.0 (magenta), 45.0 (cyan). This phase diagram is valid for small values of the volume fraction ϕ_{eq} of polymer network, see sec. S2 in ESI.

gels generate negative normal stress near the critical point (at which $\Pi'_{sol}(\phi_{eq}) \sim 0$), see the second term of eq. (10).

We used the neo-Hookean and Gent models to treat the elasticity of the polymer network. More elaborate forms of the elastic energy may be necessary to predict the normal stress in quantitative agreement with experiments.¹¹ Aside from such details, we believe that our theory captures the essential features of polymer gels – the solvent redistribution and the finite extensibility of polymer network. An experimental test of our theory may thus advance our understanding of the physical mechanisms involved in the negative normal stress of polymer gels.

Supporting Information Available

- Derivation of eq. (9).
- Derivation of fig. 2.

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

Acknowledgement

MD acknowledges the financial support of the National Natural Science of China (Grant number 21434001).

References

- (1) Bird, R.B.; Armstrong, R.C.; Hassager, O. *Dynamics of Polymeric Liquids*, 2nd ed.; Wiley-Interscience: New York, 1987; vol. 1.
- (2) Janmey, P.A.; McCormick, M.E.; Rammensee, S.; Leight, J.; Georges, P.C.; MacKintosh, F.C. Negative normal stress in semiflexible biopolymer gels. *Nature Materials* **2007**, *6*, 48-51.
- (3) Conti, E.; MacKintosh, F.C. Cross-Linked Networks of Stiff Filaments Exhibit Negative Normal Stress. *Phys. Rev. Lett.* **2009**, *102*, 088102.
- (4) Meng, F.; Terentjev, E. Nonlinear elasticity of semiflexible filament networks. *Soft Matter* **2016**, *12*, 6749-6756.
- (5) de Cagny, H.C.G.; Vos, B.E.; Vahabi, M.; Kurniawan, N.A.; Doi, M.; Koenderink, G.H.; MacKintosh, F.C.; Bonn, D. Porosity Governs Normal Stresses in Polymer Gels. *Phys. Rev. Lett.* **2016**, *117*, 217802.
- (6) de Gennes, P. G.; Brochard-Wyart, F.; Quéré, D. *Capillarity and Wetting Phenomena*. Springer-Verlag: 2004.
- (7) Doi, M. *Soft Matter*; Oxford University Press: Oxford, UK, 2013.
- (8) Doi, M. *Gel dynamics*. *J. Phys. Soc. Jpn*, **2009**, *78*, 052001.
- (9) Gent, A. N. A New Constitutive Relation for Rubber. *Rubber Chem. Technol.*, **1996**, *69*, 59-61.

- (10) Hirotsu, S. Softening of bulk modulus and negative Poisson's ratio near the volume phase transition of polymer gels. *J. Chem. Phys.* **1990**, *94*, 3949-3957.
- (11) Urayama, K. New aspects of nonlinear elasticity of polymer gels and elastomers revealed by stretching experiments in various geometries. *Poly. Int.*, **2017**, *66*, 195-206.