

# Relaxation dynamics of the normal stress of polymer gels

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## Abstract

We use the two-fluid model to theoretically predict the relaxation dynamics of the normal stress of a gel, which is twisted by a rotational rheometer in the parallel plate geometry. We derive the equations of motion of solvent and polymer network by using an expansion of the free energy of the statistical thermodynamic model of polymer gels by the leading order non-linear terms and solve these equations in the spirit of the lubrication approximation. Our theory predicts that the normal stress of the gel decreases exponentially with time due to the redistribution of solvent. The time scale of the normal stress relaxation scales with the square of the distance between the plates because the solvent redistribution results in the parabolic distribution of network displacements between the plates.

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# Introduction

When shear strains are applied, polymeric materials generate stresses both parallel and normal to the applied strain.<sup>1</sup> The direction of normal stress does not depend on the sign of the applied shear and it is thus a non-linear effect. Many materials generate normal stress in the positive direction, with which the materials expand.<sup>1</sup> In contrast, many biopolymer gels generate normal stress in the negative direction.<sup>2</sup>

The rheological properties of biopolymer gels have been studied to elucidate the physical mechanisms involved in the negative normal stress of these gels.<sup>2-6</sup> MacKintosh and coworkers theoretically predicted that the network of semiflexible polymers generates negative normal stress because semiflexible polymers are compressed with smaller stress than stretching it.<sup>2,3</sup> Meng and Terentjev theoretically predicted a phase diagram with respect to the direction of normal stress as a function of the parameters involved in the stiffness and tension of polymers in the network.<sup>4</sup> This theory also predicted that the network of flexible polymers also generates negative normal stress when they are sufficiently pre-stressed. These theories highlight the roles played by the elasticity of biopolymers in the network and do not take into account the solvent explicitly.

Recently, de Cagny and coworkers have experimentally shown that even flexible polyacrylamide gels show negative normal stress in a long time scale.<sup>5</sup> They used a phenomenological theory to predict that the normal stress of a polymer gel decreases with time to negative due to the redistribution of solvent. However, this theory did not show the relationship between the phenomenological parameters used in this theory and the free energy of a polymer gel. Indeed, in our recent theory, we have predicted that the sign of the normal stress at the equilibrium depends on the form of the elastic energy of the polymer network by using the free energy, in which the contributions of the solvent are taken into account explicitly.<sup>6</sup> In this paper, we predict the relaxation dynamics of the normal stress of a polymer gel in an extension of our previous theory.

With small applied shear strain, the normal stress of gels is proportional to the square of

the shear strain. We thus expand the stress tensor by the second order terms with respect to the magnitude of applied strain and take into account this stress tensor in an extension of the two-fluid model of gel dynamics.<sup>7,8</sup> By solving the mass conservation equation and the force balance equation in the spirit of the lubrication approximation,<sup>9</sup> we predict the normal stress of a polymer gel *as a function of time* when the gel is twisted by using rotational rheometer in the parallel plate geometry with fixed plate distance. Our theory predicts that the twisted gel generates large positive normal stress in the short time scale because the hoop stress, which is generated by twisted polymer network, increases the hydrostatic pressure of the solvent. In the long time scale, the hydrostatic pressure is relaxed due to the redistribution of the solvent and the polymer network is displaced towards the rotation axis so that the hoop stress is balanced by the shear stress. The time scale of the solvent redistribution scales with the gel thickness and the shear modulus. These results are in agreement with our previous theory<sup>6</sup> and the phenomenological theory by de Cagny *et al.*<sup>5</sup> We also show that our approach is useful to treat the reciprocal problem, with which the thickness of a twisted gel is predicted *as a function of time* when a constant normal stress is applied to the gel. The expansion of the stress tensor and the lubrication approximation greatly simplify the formalism. It is relatively easy to extend this approach to cases, in which the elastic energy of the polymer network has different form.

## Non-linear dynamics of polymer gels

### Free energy of polymer gels

The deformation of polymer gels is represented by the positional vector  $\mathbf{r}'$  of material points after the deformation (the actual coordinate), which is a function of the material points  $\mathbf{r}$  before the deformation (the reference coordinate). The displacement of each material point by the deformation is represented by the displacement vector  $\mathbf{u}(\mathbf{r}) = \mathbf{r}' - \mathbf{r}$ . Because uniform translations do not change the distance between material points, the elastic energy is a

function of the gradient of the displacement vector  $\mathbf{u}(\mathbf{r})$ . A vector  $\delta\mathbf{r} = \delta x \mathbf{e}_x + \delta y \mathbf{e}_y + \delta z \mathbf{e}_z$  connecting two material points changes to  $\delta\mathbf{r}' = \delta x \mathbf{e}'_x + \delta y \mathbf{e}'_y + \delta z \mathbf{e}'_z$  by the deformation, where  $\mathbf{e}_x$ ,  $\mathbf{e}_y$ , and  $\mathbf{e}_z$  are the unit vector to the  $x$ ,  $y$ , and  $z$  directions and  $\mathbf{e}'_x$ ,  $\mathbf{e}'_y$ , and  $\mathbf{e}'_z$  are the curvilinear coordinate that has the form

$$\mathbf{e}'_\alpha = \mathbf{e}_\alpha + \frac{\partial}{\partial x_\alpha} \mathbf{u}(\mathbf{r}). \quad (1)$$

Henceforth, we use indices  $\alpha$  and  $\beta$  to collectively represent  $x$ ,  $y$ , and  $z$  and use Einstein convention, with which repeated indices in each term are summed over  $x$ ,  $y$ , and  $z$ . The distance  $\delta\mathbf{r}'^2 = g_{\alpha\beta} \delta x_\alpha \delta x_\beta$  between the two material points in the actual coordinate is thus determined by the metric tensor  $g_{\alpha\beta}(\mathbf{r}) = \mathbf{e}'_\alpha \cdot \mathbf{e}'_\beta$ . The metric tensor has three invariants;  $J_1 = g_{\alpha\alpha} - 3$ ,  $J_2 = g_{yy}g_{zz} + g_{zz}g_{xx} + g_{xx}g_{yy}$ , and  $J_3 = g$ , where  $g_{\alpha\alpha}$  is the trace of the metric tensor and  $g$  is the determinant of the metric tensor. The elastic energy of an isotropic gel is a functional of these invariants.

The free energy density of a gel has the form

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

where  $f_{\text{ela}}$  is the elastic energy of the polymer network and  $f_{\text{sol}}$  is the mixing free energy. Following the convention, the state, at which the polymers are cross-linked (without solvent), as the reference state of eq. (2).<sup>7</sup>  $\phi$  is the volume fraction of the polymer network after the deformation and  $\phi_0$  is the volume fraction in the reference state. The volume fraction has a relationship  $\phi = \phi_0/\sqrt{g}$ .

The neo-Hookean model assumes that the network is composed of cross-linked Gaussian chains and is widely used to treat the elasticity of polymer network.<sup>7</sup> This model thus does not take into account the finite extensibility of polymers in the network. We have shown that the gels of polymer network in the neo-Hookean regime do not generate negative normal stress.<sup>6</sup> Gent model takes into account the finite extensibility of polymers in the network in

an extension of the neo-Hookean model.<sup>10</sup> With this model, the elastic energy has the form

$$f_{\text{ela}} = -\frac{G_0}{2} J_m \log \left( 1 - \frac{J_1}{J_m} \right), \quad (3)$$

where  $G_0$  is the shear modulus and  $J_m$  is the phenomenological parameter that accounts for the finite extensibility of polymers in the network. This elastic energy returns to the elastic energy of neo-Hookean model,  $f_{\text{ela}} = \frac{G_0}{2} J_1$ , in the limit of  $J_m \rightarrow \infty$ . It is relatively easy to extend our theory to cases in which the elastic energy has a different form. The mixing free energy  $f_{\text{sol}}$  has the form

$$f_{\text{sol}} = \frac{k_B T}{v_c} [(1 - \phi) \log(1 - \phi) + \chi \phi(1 - \phi)], \quad (4)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $v_c$  is the size of solvent, and  $\chi$  is the interaction parameter.

## Stress tensor of polymer gels

We think of a two-step process, with which i) a polymer network is swollen in a solvent to the equilibrium, without applying forces, and then ii) the swollen gel is set to rheometer to apply twist deformation, see fig. 1. Our theory treats cases in which the gel is twisted only by a small angle and thus the finite extensibility of polymers, represented by eq. (3), is involved only in the swelling process.

During the swelling process, the gel is swollen isotropically by the swelling ratio  $\lambda_{\text{eq}}$  that is determined by the force balance equation

$$\frac{G_0}{\lambda_{\text{eq}}} \frac{1}{1 - 3(\lambda_{\text{eq}}^2 - 1)/J_m} = \Pi_{\text{sol}}(\phi_{\text{eq}}), \quad (5)$$

where  $\phi_{\text{eq}}$  ( $\equiv \phi_0/\lambda_{\text{eq}}^3$ ) is the volume fraction of polymer network after the swelling process and  $\Pi_{\text{sol}}(\phi)$  ( $\equiv \phi^2 \frac{\partial}{\partial \phi} \left( \frac{f_{\text{gel}}}{\phi} \right)$ ) is the osmotic pressure of the gel. Eq. (5) is derived by minimizing

the free energy, eq. (2), with respect to the swelling ratio  $\lambda_{\text{eq}}$  by using the fact that the first invariant has the form  $J_1 = 3(\lambda_{\text{eq}}^2 - 1)$ . Henceforth, the swelling ratio  $\lambda_{\text{eq}}$  is the solution of eq. (5).

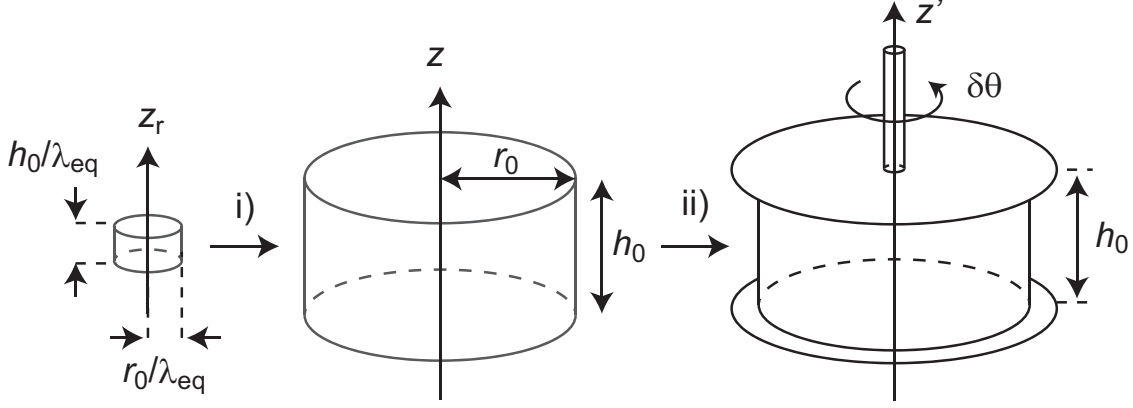


Figure 1: We treat a cylindrical polymer network of radius  $r_0/\lambda_{\text{eq}}$  and thickness  $h_0/\lambda_{\text{eq}}$ . This network is swollen in a solvent, without applying forces – process i). The gel is then twisted by angle  $\delta\theta$  by using a rotational rheometer in the parallel plate geometry – process ii).

We then apply the twist deformation to the swollen gel. For cases in which the applied strain is small, the free energy density of the gel has the form

$$\tilde{f}_{\text{gel}} = \frac{1}{2}Kw^2 + G \left( \epsilon_{\alpha\beta} - \frac{1}{3}w\delta_{\alpha\beta} \right)^2 + \frac{1}{3}\Lambda_1\epsilon_{\alpha\beta}\epsilon_{\beta\gamma}\epsilon_{\gamma\alpha} + \Lambda_2w\epsilon_{\alpha\beta}\epsilon_{\alpha\beta} + \frac{1}{3}\Lambda_3w^3. \quad (6)$$

The reference state of eq. (6) is the swollen state, after the swelling process. The strain tensor  $\epsilon_{\alpha\beta}$  has the form

$$\epsilon_{\alpha\beta} = \frac{1}{2} \left( \frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) + \frac{1}{2} \frac{\partial u_\gamma}{\partial x_\alpha} \frac{\partial u_\gamma}{\partial x_\beta}. \quad (7)$$

The trace  $w (\equiv \epsilon_{\alpha\alpha})$  of the strain tensor is the ratio of volume change. The non-linearity arising from the finite displacement is taken into account in the second term of eq. (7).  $K$  is the osmotic modulus and  $G$  is the shear modulus. The moduli  $\Lambda_1$ ,  $\Lambda_2$ , and  $\Lambda_3$  account for the non-linearity of the free energy by the leading order term with respect to the strain tensor. The form of eq. (6) is solely determined by the symmetry of the gel, however, the

expressions of the moduli  $K$ ,  $G$ ,  $\Lambda_1$ ,  $\Lambda_2$ ,  $\Lambda_3$  depend on the form of the elastic energy of the polymer network. The functional derivative  $\delta \tilde{f}_{\text{gel}}/\delta \epsilon_{\alpha\beta}$  of eq. (6) with respect to the strain tensor  $\epsilon_{\alpha\beta}$  leads to the stress tensor

$$\begin{aligned} \sigma_{\alpha\beta} = & Kw\delta_{\alpha\beta} + 2G \left( \epsilon_{\alpha\beta} - \frac{1}{3}w\delta_{\alpha\beta} \right) + \Lambda_1 \epsilon_{\alpha\gamma} \epsilon_{\gamma\beta} \\ & + \Lambda_2 \epsilon_{\mu\nu} \epsilon_{\mu\nu} \delta_{\alpha\beta} + 2\Lambda_2 w \epsilon_{\alpha\beta} + \Lambda_3 w^2 \delta_{\alpha\beta}. \end{aligned} \quad (8)$$

The expressions of the moduli  $K$ ,  $G$ ,  $\Lambda_1$ ,  $\Lambda_2$ ,  $\Lambda_3$  are derived by a systematic expansion of the free energy of a statistical thermodynamic model of the gel in the power of the strain tensor  $\epsilon_{\alpha\beta}$ . For cases in which the elastic energy has the form of eq. (3), these moduli have the form

$$K = -\frac{1}{3}\Pi_{\text{sol}}(\phi_{\text{eq}}) + \phi_{\text{eq}}\Pi'_{\text{sol}}(\phi_{\text{eq}}) + \frac{G_0}{\lambda_{\text{eq}}} \frac{2\lambda_{\text{eq}}^2/J_{\text{m}}}{(1 - 3(\lambda_{\text{eq}}^2 - 1)/J_{\text{m}})^2} \quad (9)$$

$$G = \Pi_{\text{sol}}(\phi_{\text{eq}}) \quad (10)$$

$$\Lambda_1 = -4\Pi_{\text{sol}}(\phi_{\text{eq}}) \quad (11)$$

$$\Lambda_2 = \Pi_{\text{sol}}(\phi_{\text{eq}}) - \phi_{\text{eq}}\Pi'_{\text{sol}}(\phi_{\text{eq}}), \quad (12)$$

where we used the fact that eq. (6) is the free energy per unit volume in the swollen state (the state right after the swelling process). The derivation of eqs. (9) - (12) and the expression of  $\Lambda_3$  is shown in eq. (S1) in the Electronic Supplementary Information (ESI).

## Dynamics of polymer gels

Because the space between the polymer network is filled with solvent, the deformation of the network drives the flows of the solvent. The coupling between the network deformation and solvent flows is treated by using the force balance equation and the equation of mass

conservation. The force balance equation has the form

$$-\nabla p(\mathbf{r}, t) + \frac{\partial}{\partial x_\beta}(\mathbf{e}'_\alpha \sigma_{\alpha\beta}) = 0, \quad (13)$$

where  $\nabla$  is the gradient operator. We use the bases  $\mathbf{e}'_\alpha$  of the curvilinear coordinate to take into account the non-linearity arising from the finite displacement,<sup>11</sup> see eq. (1). The pressure  $p(\mathbf{r})$  ensures that the space is filled with the network or solvent. This condition has the form

$$\nabla \cdot (\phi \dot{\mathbf{u}}(\mathbf{r}, t) + (1 - \phi) \mathbf{v}_{\text{sol}}(\mathbf{r}, t)) = 0, \quad (14)$$

The dots in  $\dot{\mathbf{u}}(\mathbf{r}, t)$  indicate the time derivative. The local velocity  $\mathbf{v}_{\text{sol}}(\mathbf{r}, t)$  of solvent is determined by the Darcy's law

$$(1 - \phi)(\mathbf{v}_{\text{sol}}(\mathbf{r}, t) - \dot{\mathbf{u}}(\mathbf{r}, t)) = -\kappa \nabla p(\mathbf{r}, t), \quad (15)$$

where  $\kappa$  is the Darcy's constant. Substituting eq. (15) into eq. (14) leads to the form

$$\kappa \nabla^2 p(\mathbf{r}, t) = \dot{w}(\mathbf{r}, t). \quad (16)$$

We derive the form of the displacement vector  $\mathbf{u}(\mathbf{r}, t)$  and pressure  $p(\mathbf{r}, t)$  by solving eqs. (13) and (16) with the boundary conditions and initial conditions for a given problem.

## Normal stress of twisted gels

We treat the dynamics of a cylindrical polymer network, which is swollen in a solvent to the equilibrium and it is then twisted by an angle  $\delta\theta$  by using a rotational rheometer in the parallel plate geometry, see fig. 1. During the twist deformation, the top and bottom surfaces of the gel are fixed to the plates and the distance between the plates is fixed to  $h_0$ . We use



the cylindrical coordinate system  $(r, \theta, z)$  to represent the positions of material points in the swollen state, before the gel is twisted. The displacement vector due to the deformation has the form  $\mathbf{u}(\mathbf{r}, t) = u_r(r, z, t)\mathbf{e}_r + u_\theta(r, z, t)\mathbf{e}_\theta + u_z(r, z, t)\mathbf{e}_z$  with  $u_\theta(r, z, t) = \delta\theta rz/h_0$ . The magnitude of the shear strain is characterized by a parameter  $\gamma$  ( $\equiv \delta\theta r_0/h_0$ ). We treat cases in which the thickness of the gel is smaller than its radius and derive the normal stress by the leading order terms with respect to  $h_0/r_0$  in the spirit of the lubrication approximation.<sup>9</sup> With this approximation, the hydrostatic pressure  $p(\mathbf{r}, t)$  does not depend on the distance  $z$  from the bottom plate.

The components of the curvilinear coordinate  $\mathbf{e}'_\alpha$ , the strain tensor  $\epsilon_{\alpha\beta}$ , the stress tensor  $\sigma_{\alpha\beta}$  are derived by using eqs. (1), (7), and (8) (see sec. S2.1 in the ESI). Substituting these forms into eq. (13) leads to the force balance equation

$$-\frac{\partial}{\partial r}p(r, t) + \frac{1}{r}\frac{\partial}{\partial r}(r\sigma_{rr}) - \frac{\sigma_{\theta\theta}}{r} + \frac{\partial}{\partial z}\sigma_{rz} - \frac{2\sigma_{z\theta}}{r}\frac{\partial u_\theta}{\partial z} = 0 \quad (17)$$

$$-\frac{\partial}{\partial z}p(r, t) + \frac{\partial}{\partial z}\sigma_{zz} = 0 \quad (18)$$

in the  $r$ - and  $z$ -directions. The derivation of eqs. (17) and (18) are shown in sec. S2.2 in the ESI. The polymers in the network are stretched towards the  $\theta$ -direction due to the twist deformation and generate hoop stress towards the rotation axis, see the third term of eq. (17). The hoop stress is balanced by the hydrostatic pressure, see the first term of eq. (17), and the forces due to the shear stress  $\sigma_{rz}$ , see the fourth term of eq. (17). The fifth term is due to the non-linearity arising from the finite displacement; the direction of the forces due to the shear stress  $\sigma_{\theta z}$  changes by the finite displacement arising from the twist deformation. This term and the second term of eq. (17) are significant, but do not depend on time.

We derive the form of the hydrostatic pressure  $p(r, t)$  and the displacement vector,  $u_r(r, z, t)$  and  $u_z(r, z, t)$  by using eqs. (16), (17), and (18). The boundary conditions to solve these equations are a) the gel is fixed to the plate,  $u_r(r, h_0) = u_r(r, 0) = 0$ , b) the distance between the plates is fixed,  $u_z(r, h_0) - u_z(r, 0) = 0$ , c) the plates do not permeate

the solvent,  $\partial p(r, t)/\partial z = 0$  at  $z = 0$  and  $h_0$ , d) total forces are continuous at the side of the gel,  $-p(r_0, t) + \sigma_{rr}(r_0, z, t) = 0$ . The initial condition is  $\mathbf{u}(\mathbf{r}, 0) = 0$ .

By using eq. (17), the displacement vector  $u_r(r, z, t)$  is derived in the form

$$u_r(r, z, t) = -\frac{1}{2G} f_r(r, t) z(z - h_0), \quad (19)$$

where we used the boundary condition a) to derive this equation. The forces  $f_r(r, t)$  in the  $r$ -direction (other than the forces due to the shear stress  $\sigma_{rz}$ ) have the form

$$f_r(r, t) = -\frac{\partial}{\partial r} p(r, t) + \frac{1}{r} \frac{\partial}{\partial r} (r \sigma_{rr}) - \frac{\sigma_{\theta\theta}}{r} - \frac{2\sigma_{z\theta}}{r} \frac{\partial u_\theta}{\partial z}. \quad (20)$$

The expression of  $f_r(r, t)$  is determined later by using the boundary condition and the initial condition. We substitute eq. (19) into eq. (16) and integrate both sides of eq. (16) with respect to  $z$  from  $z = 0$  to  $h_0$ . Eq. (16) is rewritten in the form

$$\frac{\partial}{\partial t} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} p(r, t) \right) \right] = -\frac{1}{\tau_\perp} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} p(r, t) \right), \quad (21)$$

where we used the boundary condition b) and c) to derive this equation (see sec. S2.3 for the derivation). We used the fact that the terms of stress tensor components, which are proportional to  $\partial u_z/\partial z$ , are eliminated in eq. (20) for cases in which  $u_z$  does not depend on  $r$ . The time scale  $\tau_\perp$  of the relaxation of hydrostatic pressure has the form

$$\tau_\perp = \frac{h_0^2}{12\kappa G}. \quad (22)$$

The hydrostatic pressure is thus derived by using eq. (21) in the form

$$p(r, t) = p_0(r) e^{-t/\tau_\perp}, \quad (23)$$

where  $p_0(r)$  is the hydrostatic pressure at  $t = 0$ . The initial condition  $u_r(r, z, 0) = 0$  leads

to the fact that  $f_r(r, t) = 0$  at  $t = 0$ , see eq. (19). By using the boundary condition d), the hydrostatic pressure  $p_0(r)$  is derived in the form

$$p_0(r) = \Lambda_{rr} \frac{r^2}{r_0^2} \gamma^2 + \frac{1}{2} \left( \frac{1}{4} \Lambda_1 + 2G \right) \left( 1 - \frac{r^2}{r_0^2} \right) \gamma^2, \quad (24)$$

where we introduced a parameter  $\Lambda_{rr} = \frac{1}{2}K - \frac{1}{3}G + \frac{1}{2}\Lambda_2$  to simplify the form. The first term of eq. (24) is indeed equal to the stress  $\sigma_{rr}$ ; this is because forces are not applied to the sides,  $r = r_0$ , of the gel, see the boundary condition d). Eq. (24) suggests that the hoop stress (and the stresses  $\sigma_{rr}$  and  $\sigma_{\theta z}$ ) is balanced by the hydrostatic pressure in the short time scale. The forces  $f_r(r, t)$  are derived by substituting eq. (23) into eq. (20) in the form

$$f_r(r, t) = \left( 2\Lambda_{rr} - \frac{1}{4}\Lambda_1 - 2G \right) \frac{r}{r_0^2} \gamma^2 \left( 1 - e^{-t/\tau_\perp} \right). \quad (25)$$

Integrating eq. (18) with respect to  $z$  leads to the form

$$-\sigma_\perp(r, t) = -p(r, t) + \sigma_{zz}. \quad (26)$$

The normal stress is thus generated by the hydrostatic pressure and the stress  $\sigma_{zz}$ . We first integrate both sides of eq. (26) over the (top or bottom) surface of the gel and derive the average normal stress  $\bar{\sigma}_\perp = \frac{1}{\pi r_0^2} \int_0^{r_0} dr 2\pi r \sigma_\perp(r, t)$  in the form

$$\begin{aligned} \bar{\sigma}_\perp = & \frac{1}{2} \left( \Lambda_{rr} + \frac{1}{8}\Lambda_1 + G \right) \gamma^2 e^{-t/\tau_\perp} - \frac{1}{2} \Lambda_{zz} \gamma^2 \\ & - \left( K - \frac{2}{3}G \right) \frac{2}{r_0} u_r(r_0, z, t) - \left( K + \frac{2}{3}G \right) \frac{\partial u_z}{\partial z}. \end{aligned} \quad (27)$$

The average normal stress  $\bar{\sigma}_\perp$  does not depend on  $z$ , see also eq. (18). The average normal stress  $\bar{\sigma}_\perp$  is derived by integrating both sides of eq. (27) with respect to  $z$  from  $z = 0$  to  $h_0$ .

The normal stress thus has the form

$$\frac{2\bar{\sigma}_\perp(t)}{\gamma^2} = \Lambda_\infty + (\Lambda_0 - \Lambda_\infty)e^{-t/\tau_\perp}, \quad (28)$$

where  $\Lambda_0 = -\Lambda_1/8$  and  $\Lambda_\infty = -K/2 - 2G/3 - \Lambda_1/4 - \Lambda_2/2$  by the leading order term with respect to  $h_0/r_0$ . The derivation of eq. (28) is shown in sec. S2.4 in the ESI.

The Gent model predicts that the normal stress is positive,  $2\bar{\sigma}_\perp/\gamma^2 = \Pi_{\text{sol}}(\phi_{\text{eq}})/2$ , for the short time scale,  $t < \tau_\perp$ . This is because the polymers in the network are stretched in the  $\theta$ -direction by the applied shear strain and thus generate hoop stress towards the rotation axis of the gel, see the third term of eq. (17). The hoop stress is balanced by the hydrostatic pressure  $p(r, t)$  (see the first term of eq. (17)) because the solvent has not been redistributed in this time scale and this generates large positive normal stress. The normal stress decreases with time because the hydrostatic pressure is relaxed by the solvent redistribution. The hoop stress drives the displacement of the polymer network towards the rotation axis and the flows of solvent towards the side of the gel. Because the top and bottom surfaces of the gel are fixed to the plates, the displacement  $u_r(r, z, t)$  of the polymer network is a parabolic function of the distance  $z$  from the bottom plate, see eq. (19). The hoop stress is now balanced by the shear forces  $\partial\sigma_{rz}/\partial z$ , which are generated by the curvature  $\partial^2 u_r/\partial z^2$  of the polymer network (see the fourth term of eq. (17)). The time scale  $\tau_\perp$  of the relaxation of the normal stress is thus scales with the shear modulus  $G$  (rather than the osmotic modulus) and the height  $h_0$  (rather than the radius). These results agree with our previous results by using the free energy minimization<sup>6</sup> and the results of the phenomenological theory by de Cagny *et al.*<sup>5</sup>

For the long time scale,  $t > \tau_\perp$ , the normal stress has the form

$$\frac{2\bar{\sigma}_\perp}{\gamma^2} = -\frac{G_0 \lambda_{\text{eq}}}{J_m} \frac{1}{(1 - 3(\lambda_{\text{eq}}^2 - 1)/J_m)^2} + \frac{1}{3}(\phi_{\text{eq}} \Pi'_{\text{sol}}(\phi_{\text{eq}}) - \Pi_{\text{sol}}(\phi_{\text{eq}})) \frac{h_0^2}{r_0^2}. \quad (29)$$

In the limit of  $J_m \rightarrow \infty$ , the first term of eq. (29) is zero and the equation returns to the

normal stress of the neo-Hookean model. In this case, the normal stress is positive when the polymer network is swollen in a good solvent,  $\chi < 0$ . The positive normal stress is generated by the Poisson effect of the polymer network that is attracted to the rotational axis. The parameter  $J_m$  represents the finite extensibility of polymers in the network. The first term of eq. (29) becomes larger than the second term as the swelling ratio  $\lambda_{\text{eq}}$  approaches to the maximum extension  $\sqrt{1 + J_m/3}$ . The normal stress thus becomes negative for cases in which the polymer network is largely swollen in the swelling process. This is because large tension is generated by already pre-stretched polymers although there are both stretched and compressed polymers in the network by the twist deformation. This mechanism is first proposed by Meng and Terentjev.<sup>4</sup> Eq. (29) agrees with the results of our previous work.<sup>6</sup> The relaxation dynamics of the normal stress is thus predicted in a relatively simple manner by using the expansion of the free energy and the lubrication approximation.

## Time dependence of the thickness of twisted gel under constant load

In the previous section, we predicted the relaxation dynamics of the normal stress generated by a twisted gel for cases in which the distance between the plates is fixed. We here treat a reciprocal problem, which predicts the thickness  $h_{\text{gel}}(t)$  of a twisted gel when a constant (average) normal stress  $\bar{\sigma}_{\parallel}$  is applied to the gel. This problem is treated by using eqs. (16), (17), and (18) with the appropriate boundary conditions and the initial condition  $\mathbf{u}(\mathbf{r}, 0) = 0$ . The boundary conditions a), c), d) (see the third paragraph of the previous section) are effective and b) should be replaced to

$$h_{\text{gel}}(t) - h_0 = u_z(r, h_0, 0) - u_z(r, 0, 0). \quad (30)$$

The force balance equation in the  $r$ -direction, eq. (17), predicts that the displacement

of the polymer network has the form of eq. (19) and is again a parabolic function of the distance  $z$  from the bottom plate. We substitute eq. (19) into eq. (16) and then integrate both sides of the equation with respect to  $z$  from  $z = 0$  to  $h_0$ . This leads to the form

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} p(r, t) \right) = -\frac{1}{\tau_{\perp}} \frac{\partial}{\partial t} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} p(r, t) \right) \right] + \frac{1}{\kappa} \frac{\dot{h}_{\text{gel}}(t)}{h_0}, \quad (31)$$

where we used eq. (30) and the boundary condition c) (see also the third paragraph of the previous section) to derive this equation. We also used the fact that the terms of stress tensor components, which are proportional to  $\partial u_z / \partial z$ , are eliminated in eq. (20) because  $u_z$  does not depend on  $r$ . The hydrostatic pressure is generated by both of the hoop stress (the first term in the right side of eq. (31)) and the applied normal stress (the second term in the right side of eq. (31)). The solution of eq. (31) has the form

$$p(r, t) = p_0(r) e^{-t/\tau_{\perp}} - \frac{1}{4} \frac{r_0^2}{\kappa \tau_{\perp}} \left( 1 - \frac{r^2}{r_0^2} \right) \int_0^t dt' \frac{\dot{h}_{\text{gel}}(t')}{h_0} e^{-(t-t')/\tau_{\perp}}, \quad (32)$$

where  $p_0(r)$  is the hydrostatic pressure at  $t = 0$  and is given by eq. (24). We used the boundary condition, with which the second term of eq. (32) is zero at  $r = r_0$ . This is because solvent flows out from the side of the gel in the time scale, at which the second term is relevant, and the gel is thus in contact with the solvent; the hydrostatic pressure is continuous at the boundary between the gel and the solvent.<sup>8</sup>

The balance of the applied normal stress and the internal stress generated by the gel has the form of eq. (26). We substitute eq. (32) in eq. (26) and integrate both sides of this equation over the (top or bottom) surface of the gel. This leads to the average normal stress in the form

$$\begin{aligned} \bar{\sigma}_{\perp} = & \frac{1}{2} \left( \Lambda_{rr} + \frac{1}{8} \Lambda_1 + G \right) \gamma^2 e^{-t/\tau_{\perp}} - \frac{1}{2} \Lambda_{zz} \gamma^2 \\ & - \frac{1}{8} \frac{r_0^2}{\kappa \tau_{\perp}} \int_0^t dt' \frac{\dot{h}_{\text{gel}}(t')}{h_0} e^{-(t-t')/\tau_{\perp}} - \left( K + \frac{4}{3} G \right) \frac{\partial u_z}{\partial z}. \end{aligned} \quad (33)$$

The average normal stress  $\bar{\sigma}_\perp$  does not depend on  $z$ , see also eq. (18). Integrating both sides of eq. (33) with respect to  $z$  from  $z = 0$  to  $h_0$  leads to an integro-differential equation only of  $h_{\text{gel}}(t)$ . We multiply  $e^{t/\tau_\perp}$  to both sides of the equation and then take derivative with respect to  $t$ ; this leads to the differential equation of  $h_{\text{gel}}(t)$  (see eq. (S67) in the ESI). The thickness  $h_{\text{gel}}(t)$  of the gel is derived by solving this equation (see sec. S2.4 in the ESI for the derivation) in the form

$$h_{\text{gel}}(t) = h_0 + h_0 \epsilon^* (1 - e^{-t/\tau_\parallel}), \quad (34)$$

where the time scale  $\tau_\parallel$  and the strain  $\epsilon^*$  at the equilibrium state have the forms

$$\tau_\parallel = \frac{1}{8} \frac{r_0^2}{\kappa(K + 4G/3)} \quad (35)$$

$$\epsilon^* = -\frac{\bar{\sigma}_\perp + \Lambda_{zz}\gamma^2/2}{K + 4G/3}. \quad (36)$$

The thickness of the gel thus changes with a time scale  $\tau_\parallel$  that is different from the time scale  $\tau_\perp$  of the solvent redistribution.

Substituting eq. (34) into eq. (32) leads to the form

$$p(r, t) = p_0(r) e^{-t/\tau_\perp} - \frac{1}{4} \frac{r_0^2}{\kappa\tau_\parallel} \frac{\epsilon^*}{1 - \tau_\perp/\tau_\parallel} \left(1 - \frac{r^2}{r_0^2}\right) (e^{-t/\tau_\parallel} - e^{-t/\tau_\perp}). \quad (37)$$

Eq. (37) predicts that the dynamics of the gel proceeds with two steps. In the time scale  $\tau_\perp$ , the solvent is redistributed within the gel and the polymer network is displaced towards the rotation axis, by keeping the distance between the plates approximately constant, much like the situation of constant plate distance, see the first term of eq. (37). In the time scale  $\tau_\parallel$ , the distance between the plates decreases to the equilibrium gel thickness  $h_0(1 + \epsilon^*)$  and the solvent flows out from the gel, see the second term of eq. (37). Which process is earlier depends on the aspect ratio  $h_0/r_0$  of the gel and the ratio  $K/G$  of the elastic moduli, see eqs. (22) and (35). For cases in which the gel is swollen in a good solvent, the osmotic pressure is

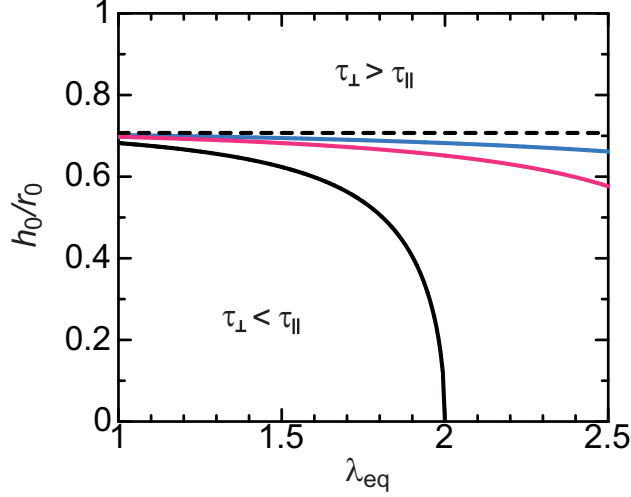


Figure 2: The phase diagram with respect to the time scales,  $\tau_{\perp}$  and  $\tau_{\parallel}$  (defined by eqs. (22) and (35)), is shown as a function of the aspect ratio  $h_0/r_0$  ( $h_0$  is the thickness of the gel and  $r_0$  is its radius) and the swelling ratio  $\lambda_{\text{eq}}$  of a gel for the several values of the phenomenological parameter  $J_m$  of the Gent model;  $J_m = 9.0$  (black solid),  $24.0$  (magenta), and  $45.0$  (cyan). The black broken curve ( $h_0/r_0 = 1/\sqrt{2}$ ) corresponds to the cases of neo-Hookean model.  $\tau_{\perp} < \tau_{\parallel}$  in the region below the curves and  $\tau_{\perp} > \tau_{\parallel}$  in the region above the curves. The log-log plot of this figure is shown in fig. S1 in the ESI.

approximated in the form  $\Pi_{\text{sol}}(\phi_{\text{eq}}) \simeq \frac{k_B T}{v_c} \left(\frac{1}{2} - \chi\right) \phi_{\text{eq}}^2$ . In this case, the Gent model predicts that the condition, with which the time scale  $\tau_{\perp}$  is smaller than the time scale  $\tau_{\parallel}$ , has the form

$$1 + \frac{2\lambda_{\text{eq}}^2/(3J_m)}{1 - 3(\lambda_{\text{eq}}^2 - 1)/J_m} < \frac{1}{2} \frac{r_0^2}{h_0^2}, \quad (38)$$

where it is derived by using eqs. (9) and (10). The time scale  $\tau_{\perp}$  tends to be smaller than the time scale  $\tau_{\parallel}$  when the aspect ratio  $h_0/r_0$  of the gel is small and the swelling ratio  $\lambda_{\text{eq}}$  is small, see fig. 2. The aspect ratio  $h_0/r_0$  and the swelling ratio  $\lambda_{\text{eq}}$  are thus important parameters that determine the dynamics of twisted gels with constant applied normal stress.



## Discussion

We have predicted the relaxation dynamics of the normal stress of polymer gels for cases in which the gel is twisted by a rotational rheometer in the parallel plate geometry. Our theory predicts that the normal stress of a gel is positive at  $t = 0$  and then exponentially decreases with time to a smaller value due to the redistribution of the solvent. The systematic expansion of the free energy by the leading order non-linear terms with respect to the strain tensor and the lubrication approximation greatly simplify the formalism. Our theory predicts the generic forms of the normal stress as a function of time by using the elastic moduli,  $K$ ,  $G$ ,  $\Lambda_1$ , and  $\Lambda_2$ , and the forms of these elastic moduli are derived from the free energy of the statistical thermodynamic model of a polymer gel (see also sec. S1 in the ESI for the procedure). Once the forms of the elastic energy of a polymer gel is derived theoretically<sup>2,4</sup> or experimentally,<sup>12</sup> our theory predicts the relaxation dynamics of the normal stress of the gel. Our approach is thus applicable to treat the relaxation dynamics of the normal stress of biopolymer gels, where the persistence length is as long as the length of subchains in many cases.<sup>4,13</sup>

Our theory predicts a couple of experimentally accessible predictions: i) For the constant gap distance, the normal stress of a polymer gel decreases by a single exponential curve with time. This is in contrast to the phenomenological theory by de Cagny *et al.*, probably because they used the cone plate geometry. ii) For the constant applied normal stress, the gap distance decreases with a two-step process. The time scale of one process is determined by the gap distance  $h_0$  and the shear modulus  $G$  of the gel and the time scale of the other process is determined by the radius  $r_0$  of the gel and the modulus  $K + 4G/3$  of the gel. Eq. (38) predicts the crossover of these time scales. The fact that the characteristic time scales of the gel dynamics are sensitive to the boundary conditions has been shown experimentally.<sup>14,15</sup>

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## Supporting Information Available

The following items are available free of charge.

- Expansion of the free energy of gels.
- Gel dynamics.
- Figure S1: The log-log plot of fig. 2.

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

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