

Shear induced formation of lubrication layers of negative normal stress gels

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

Department of Materials Physics, Nagoya University, Furocho, Chikusa-ku, Nagoya, 464-8603, Japan, and Center of Soft Matter Physics and its Application, Beihang University, Xueyuan Road 37, Beijing 100191, China

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

Abstract

Many biopolymer gels generate negative normal stress, with which the polymer networks shrink in the normal of applied shear. Here we theoretically predict the sliding velocity of such a gel on a solid surface when a constant shear stress is applied to the gel. Our theory predicts that the negative normal stress drives the flows of the solvent in the gel and this produces a solvent layer between the gel and the surface. The sliding velocity of the gel is proportional to the thickness of the solvent layer and is a cubic function of the applied shear stress. With constant applied normal and shear stresses, the thickness of the solvent layer is a non-monotonic function of time with a maximum because the solvent flow from the gel to the solvent layer is dominant in the short time scale and the solvent flow from the solvent layer to the outside is dominant in a longer time scale. The maximum layer thickness depends on the ratio of the time scales of the solvent flows in the gel and in the solvent layer.

*To whom correspondence should be addressed

[†]NCC

[‡]Beihang

1 Introduction

The tribology of hydrogels of synthetic polymers has been studied as models of connective tissues at animal joints, which show remarkably low friction constant.^{1,2} These materials have possible application to implants and lubricants.¹ Many of these researches treat the kinetic friction of a gel which is directly in contact with a solid surface. In these cases, the kinetic friction constant depends on the interfacial energy between the gel and the surface^{1,3} and the roughness of both surfaces.^{4,5}

In contrast, researches that treat cases in which there is a solvent layer between a gel and a solid surface are relatively few. A solvent layer between the gel and the solid surface may act as a lubrication layer and thus greatly reduces the kinetic friction constant. Indeed, recent experiments have shown that the kinetic friction constant is greatly reduced by a droplet of solvent which is accidentally entrapped between the gel and the surface.⁶ A polymer gel contains a large quantity of solvent in the polymer network and the solvent flows out from the gel by applied stress.^{7,8} It is thus of interest to design a polymer gel which drives the solvent out to deliberately form a solvent layer between the gel and the surface by applied stress. Indeed, recent experiments suggest that a similar mechanism may operate in the friction between a banana peel and a solid surface.⁹ With the solvent layer, the kinetic friction constant is determined by the thickness of the layer and the viscosity of the solvent, rather than the microscopic details of the gel and the surface.

At a first glance, one may think that a solvent layer is produced by simply applying a compressive stress to a gel. However, the theory of gel dynamics predicts that it is not the case because no forces are applied to the free ends of the polymer network, at least for usual cases in which the linearized theory is applicable.^{7,8} When shear strain is applied to polymeric materials, these materials generate stress both parallel and normal to the applied strain.¹⁰ The direction of the normal stress does not depend on the direction of applied shear strain and thus it is mostly determined by the choice of material¹¹ (and also the geometry and the time scale¹²). Biopolymer gels generate negative normal stress, with which they shrink

by applied shear stress,^{11,12} in contrast to many other materials.¹⁰ Our previous theory has predicted that even flexible polymer gels generate negative normal stress for cases in which the polymer network is greatly stretched in the swelling process.^{13,14} Applying shear stress to a negative normal stress gel may produce a solvent layer because the gel shrinks due to the negative normal stress and the solvent in the gel, in turn, flows to the interface between the gel and the surface.

In this paper, we use the theory of gel dynamics^{7,8} to theoretically predict that a negative normal stress gel produces a solvent layer due to applied shear stress and predict the kinetic friction of such a gel as a function of time when a constant shear stress is applied. The sliding velocity of a gel is proportional to the thickness of the solvent layer and thus is a cubic function of applied shear stress. Our theory also predicts that when both constant shear and normal stresses are applied at $t = 0$, the sliding velocity is a non-monotonic function of time with a maximum because the solvent flows from the gel to the solvent layer is dominant in the short time scale and the solvent flows from the solvent layer to the outside is dominant in a longer time scale.

2 Model

2.1 Gel dynamics

We treat a slab of gel which is swollen in a solvent to the equilibrium, see fig. 1. At the swollen state, the gel has the thickness h_0 and length L and these two dimensions are much smaller than the width. We use the Cartesian coordinate system, in which the z -axis is normal to the surface and the x -axis is parallel to the edge of length L . The top surface of the gel is fixed to a plate through which the solvent does not permeate. The gel is placed on a flat solid surface and the normal stress $\sigma_{0\perp}^{\text{app}}$ is applied to the gel to the equilibrium; the thickness of the gel is then h'_0 . We represent the positions (x, z) of the material points of the gel by treating this state as the reference state. For simplicity, we neglect the interfacial

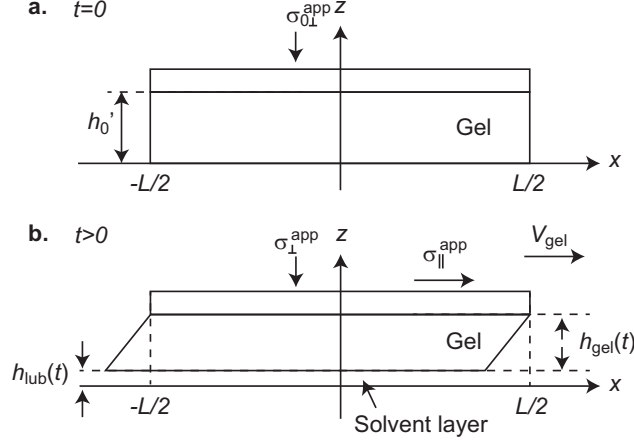


Figure 1: Continuum model of the friction of a gel on a solid surface. **a.** A slab of gel is swollen in a solvent to the equilibrium and then it is set on a solid surface. Before the gel is slid along the surface, a normal stress $\sigma_{0\perp}^{\text{app}}$ is applied to the gel to the equilibrium. The thickness and length of the gel are then h'_0 and L , respectively. **b.** Constant shear and normal stresses, $\sigma_{\parallel}^{\text{app}}$ and $\sigma_{\perp}^{\text{app}}$, are applied to the gel at $t = 0$. The gel then slides along the surface with velocity $V_{\text{gel}}(t)$. The gel produces a solvent layer of thickness $h_{\text{lub}}(t)$. The thickness of the gel is $h_{\text{gel}}(t)$. We use the Cartesian coordinate system (x, y, z) , where the z -axis is normal to the solid surface and the x -direction is parallel to the edge of the length L .

energy between the bottom surface of the gel and the solid surface. Experiments in such a geometry was performed by Baumberger and coworkers.³ In this paper, we theoretically predict the sliding velocity $V_{\text{gel}}(t)$ of the gel on a flat solid surface when a shear stress, $\sigma_{\parallel}^{\text{app}}$, is applied to the gel at $t = 0$ with a fixed gap distance in sec. 3.1 and with a constant applied normal stress, $\sigma_{\perp}^{\text{app}}$, in sec. 3.2.

The interstitial space between the polymers of a gel is occupied by a solvent and thus the deformation of the network drives the solvent flows. A continuum theory treats the dynamics of a gel by using the force balance equation and the law of mass conservation.^{7,8} The force balance equation has the form

$$-\sigma_{\perp}(x, t) = \sigma_{zz}^{\text{gel}}(x, z, t) - p(x, z, t), \quad (1)$$

in the gel region. **Eq. (1)** represents the balance of the local applied stress $\sigma_{\perp}(x, t)$, the elastic stress $\sigma_{zz}^{\text{gel}}(x, z, t)$ of the gel (which includes the contributions of the

osmotic pressure of the gel and the elastic stress of the polymer network), and the hydrostatic pressure $p(x, z, t)$. We neglect other forces, such as gravitational forces, to highlight the roles played by the negative normal stress in the formation of a solvent layer. Experimentally, the drainage of solvent is suppressed by using the polymers and the solvent which have similar densities. Following the treatment in refs.,^{7,8} we neglect the viscous stress of the solvent in the gel (this omits the penetration of shear flows into the gel by the hydrodynamic screening length). The local applied normal stress has a relationship

$$\sigma_{\perp}^{\text{app}} = \frac{1}{L} \int dx \sigma_{\perp}(x, t) \quad (2)$$

with the average applied normal stress $\sigma_{\perp}^{\text{app}}$.

The constitutive equation provides the relationship between the elastic stress tensor $\sigma_{zz}^{\text{gel}}(x, z, t)$ and the deformation of the gel. The deformation of the gel is represented by the displacement vector $\mathbf{u}(x, z, t) = \mathbf{r}' - \mathbf{r} = (u_x, u_y, u_z)$, where \mathbf{r}' is the material coordinate after the deformation and \mathbf{r} is the material coordinate before the deformation. The strain tensor $\epsilon_{\alpha\beta}$ is defined by the form

$$\epsilon_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_{\alpha}}{\partial x_{\beta}} + \frac{\partial u_{\beta}}{\partial x_{\alpha}} \right) + \frac{1}{2} \frac{\partial u_{\alpha}}{\partial x_{\gamma}} \frac{\partial u_{\alpha}}{\partial x_{\gamma}}. \quad (3)$$

Henceforth, we use the indices $\alpha, \beta, \gamma, \mu, \nu$ to collectively represent x, y , and z and the Einstein convention, in which repeated indices in the same term are summed over x, y , and z . **For simplicity, we here treat an isotropic gel, where the orientations of the polymer chain segments are random.** The elastic stress tensor of the gel has the form

$$\sigma_{\alpha\beta}^{\text{gel}} = K w \delta_{\alpha\beta} + 2G \left(\epsilon_{\alpha\beta} - \frac{1}{3} w \delta_{\alpha\beta} \right) + \Lambda_1 \epsilon_{\alpha\gamma} \epsilon_{\gamma\beta} + \Lambda_2 \epsilon_{\mu\nu} \epsilon_{\mu\nu} \delta_{\alpha\beta} + 2\Lambda_2 w \epsilon_{\alpha\beta} + \Lambda_3 w^2 \delta_{\alpha\beta} \quad (4)$$

by the second order terms with respect to the strain tensor $\epsilon_{\alpha\beta}$.¹³ w is the trace of the strain

tensor $\epsilon_{\alpha\beta}$. Eq. (4) is a general form as long as the gel is isotropic. K and G are the osmotic modulus and shear modulus of the gel, respectively. Λ_1 , Λ_2 , and Λ_3 are the elastic moduli for the non-linear stress terms. **Eq. (4) includes both of the contributions of the osmotic pressure of the gel and the elastic stress of the polymer network. Indeed, the expressions of the elastic moduli are derived by the systematic expansion of the free energy of a statistical thermodynamic model of gels with respect to the strain.**¹³

In the geometry of fig. 1b, the deformation of the gel due to the applied normal and shear stresses, $\sigma_{\perp}^{\text{app}}$ and $\sigma_{\parallel}^{\text{app}}$, is represented by a displacement vector $\mathbf{u} = (u_x, 0, u_z)$, where u_x and u_z have the form

$$u_x = \int_0^t dt' V_{\text{gel}}(t') + \gamma z \quad (5)$$

$$u_z = \epsilon z. \quad (6)$$

By substituting these forms into eqs. (3) and (4), the stress tensor components, σ_{zz}^{gel} and σ_{xz}^{gel} , are derived in the forms

$$\sigma_{zz}^{\text{gel}} = (K + 4G/3)\epsilon + \Lambda\gamma^2 \quad (7)$$

$$\sigma_{xz}^{\text{gel}} = G\gamma \quad (8)$$

in the leading order terms of an expansion with respect to h'_0/L , where we introduced a parameter $\Lambda = \frac{1}{2}K + \frac{2}{3}G + \frac{1}{4}\Lambda_1 + \frac{1}{2}\Lambda_2$ for simplicity.

The law of mass conservation has the form

$$\frac{\partial}{\partial z}(\phi\dot{u}_z(x, z, t) + (1 - \phi)v_{\text{sol}}(x, z, t)) = 0, \quad (9)$$

where ϕ is the volume fraction of the polymer network and $v_{\text{sol}}(x, z, t)$ is the z -component of the velocity field of the solvent. The dot above $u_z(x, z, t)$ indicates the time derivative. The

velocity $v_{\text{sol}}(x, z, t)$ of the solvent in the gel is given by the Darcy's law that has the form

$$(1 - \phi)(v_{\text{sol}}(x, z, t) - \dot{u}_z(x, z, t)) = -\kappa \frac{\partial}{\partial z} p(x, z, t), \quad (10)$$

where κ is the Darcy's constant.

We derive the forms of $p(x, z, t)$, $v_{\text{sol}}(x, z, t)$, $u_z(x, z, t)$ by using eqs. (1) - (10). The boundary conditions to solve these equations are a) the impermeability of the solvent at the top surface, $\dot{u}_z(x, h_0, t) = v_{\text{sol}}(x, h_0, t)$, b) the continuity of the hydrostatic pressure at the boundary between the gel and the solvent layer, $p(x, 0, t) = p_0(x)$ ($p_0(x)$ is the hydrostatic pressure in the solvent layer), c) the continuity of the total stress at the boundary

$$\sigma_{zz}^{\text{gel}}(x, 0, t) - p(x, 0, t) = -p_0(x) = -\sigma_{\perp}(x). \quad (11)$$

The initial condition is $u_z(x, z, 0) = 0$. The boundary conditions b) and c) imply that the external forces are not applied to the free end of the polymer network, $\sigma_{zz}^{\text{gel}}(x, 0, t) = 0$. The thickness $h_{\text{lub}}(t)$ of the solvent layer thus does not depend on the position x . **This is in contrast to the case of a sliding elastomer on a lubricated surface, where the hydrostatic pressure is not continuous at the interface between the elastomer and the lubrication layer.**¹⁵ Mathematically, this problem is equivalent to the dynamics of a gel on an impermeable surface when the temperature is changed, see sec. 4.1.1 in ref.⁸ The thickness of the gel $h_{\text{gel}}(t)$ ($= h_0^l + u(x, h_0, t) - u(x, 0, t)$) is derived in the form

$$\frac{h_{\text{gel}}(t)}{h_0^l} = 1 - \frac{\Lambda\gamma^2 - \sigma_{0\perp}^{\text{app}}}{K + 4G/3} + \frac{\Lambda\gamma^2 - \sigma_{0\perp}^{\text{app}}}{K + 4G/3} \sum_{n=0}^{\infty} \frac{8}{\pi^2(2n+1)^2} e^{-\pi^2(2n+1)^2 t / (4\tau_{\text{gel}})}, \quad (12)$$

where the time scale τ_{gel} of the solvent flows in the gel has the form

$$\tau_{\text{gel}} \equiv \frac{h_0^l{}^2}{\kappa(K + 4G/3)}, \quad (13)$$

see also eqs. (92) and (94) in ref.⁸ With the factor $\Lambda\gamma^2 - \sigma_{0\perp}^{\text{app}}$ in eq. (12), we take into account the fact that the normal stress $\sigma_{\perp}^{\text{app}}$ is applied to the gel when the gel is in contact with the solid surface, but it is not applied after it separates from the surface, see the boundary condition c).

2.2 Solvent layer

For cases in which the gap distance is constant, the thickness of the solvent layer is derived by using the form

$$h_{\text{lub}}(t) = h'_0 - h_{\text{gel}}(t). \quad (14)$$

In contrast, for cases in which the applied normal stress $\sigma_{\perp}^{\text{app}}$ is constant, the thickness of the solvent layer is determined by the dynamics of the solvent in the gel and the solvent layer. The velocity fields $v_{\text{lub}}(x, z, t)$ of solvent in the solvent layer are derived by using the Stokes equation that has the form

$$-\frac{\partial}{\partial x} p_0(x, t) + \eta_{\text{sol}} \frac{\partial^2}{\partial z^2} v_{\text{lub}}(x, z, t) = 0. \quad (15)$$

Eq. (15) is effective for cases in which the thickness $h_{\text{lub}}(t)$ of the solvent layer is smaller than the length L . η_{sol} is the viscosity of the solvent. $p_0(x, t)$ is the hydrostatic pressure in the solvent layer, see above eq. (11). We use the coordinate system after the deformation (so-called the actual coordinate system) to represent the positions (x, z) in the solvent layer. For simplicity, we use the same notation as the reference coordinate system, which we no longer use in this and following sections.

We derive the solution of eq. (15) with the incompressibility condition

$$\frac{d}{dt}(h_{\text{lub}}(t) + h_{\text{gel}}(t)) = -\frac{\partial}{\partial x} \int_0^{h_{\text{lub}}(t)} dz v_{\text{lub}}(x, z, t). \quad (16)$$

The boundary conditions to solve eqs. (15) and (16) are i) the non-slipping boundary conditions, $v_{\text{lub}}(x, 0, t) = 0$ and $v_{\text{lub}}(x, h_{\text{lub}}, t) = V_{\text{gel}}(t)$, ii) the continuity of the total stress, $p_0(x, t) = \sigma_{\perp}(x)$, and iii) the continuity of the hydrostatic pressure at the side $x = \pm L/2$ of the solvent layer, $p_0(\pm L/2) = 0$. Without changing the physics, we assume that the hydrostatic pressure of the external solution is zero.

With the boundary condition i), the velocity field $v_{\text{lub}}(x, z, t)$ is derived by using eq. (15) in the form

$$v_{\text{lub}}(x, z, t) = \frac{V_{\text{gel}}(t)}{h_{\text{lub}}}z - \frac{1}{2\eta_{\text{sol}}}\frac{\partial p_0(x, t)}{\partial x}z(h_{\text{lub}} - z). \quad (17)$$

Substituting eq. (17) into eq. (16) leads to the fact that $\frac{\partial^2}{\partial x^2}p_0(x, t)$ does not depend on the position x . The hydrostatic pressure is thus derived in the form

$$p_0(x, t) = \frac{6}{L^2}\sigma_{\perp}^{\text{app}}\left(\frac{L^2}{4} - x^2\right) \quad (18)$$

by using the boundary conditions ii) and iii). Substituting eqs. (12), (17), and (18) into eq. (16) leads to the form

$$\frac{d}{dt}h_{\text{lub}}(t) = \frac{2\kappa\Lambda\gamma^2}{h_0}\sum_{n=0}^{\infty}e^{-\pi^2(2n+1)^2t/(4\tau_{\text{gel}})} - \frac{\sigma_{\perp}^{\text{app}}}{\eta_{\text{sol}}L^2}h_{\text{lub}}^3(t). \quad (19)$$

We use eq. (19) to derive the thickness $h_{\text{lub}}(t)$ as a function of time t for constant applied normal stress $\sigma_{\perp}^{\text{app}}$. The sliding velocity $V_{\text{gel}}(t)$ of the gel is derived by using the relationship

$$V_{\text{gel}}(t) = \frac{\sigma_{\parallel}^{\text{app}}}{\eta_{\text{sol}}}h_{\text{lub}}(t). \quad (20)$$

3 Results

3.1 Constant gap distance

We first treat a simple case in which the normal stress $\sigma_{0\perp}^{\text{app}}$ is applied until the thickness of the gel becomes the equilibrium thickness $h'_0 = (1 - \sigma_{0\perp}^{\text{app}}/(K + 4G/3))h_0$ and then the shear stress $\sigma_{\parallel}^{\text{app}}$ is applied at $t = 0$ in the fixed gap distance (between the top plate and the solid surface). We predict the sliding velocity of the gel in a steady state as a function of applied shear stress $\sigma_{\parallel}^{\text{app}}$.

Substituting eq. (12) into eq. (14) leads to the thickness $h_{\text{lub}}(t)$ of the solvent layer. In a steady state, the thickness h_{lub}^* of the solvent layer has the form

$$h_{\text{lub}}^* = \frac{\Lambda\gamma^2 - \sigma_{0\perp}^{\text{app}}}{K + 4G/3} h'_0. \quad (21)$$

for $\Lambda\gamma^2 > \sigma_{0\perp}^{\text{app}}$ and $h_{\text{lub}}^* = 0$ for $\Lambda\gamma^2 < \sigma_{0\perp}^{\text{app}}$. The sliding velocity thus has the form

$$V_{\text{gel}}^* = \frac{\sigma_{\parallel}^{\text{app}}}{\eta_{\text{sol}}} h_{\text{gel}}^*, \quad (22)$$

see also eq. (20).

Our theory predicts that when the normal stress is not applied in advance, $\sigma_{0\perp}^{\text{app}} = 0$, the sliding velocity V_{gel}^* of the gel is proportional to the cubic of the applied shear stress $\sigma_{\parallel}^{\text{app}}$, see the black curve in fig. 2. This is because the solvent layer is produced by the negative normal stress, which is proportional to the square of the applied shear stress $\sigma_{\parallel}^{\text{app}}$ for a small applied shear stress, see eq. (21). When the normal stress $\sigma_{0\perp}^{\text{app}}$ is applied in advance, the sliding velocity V_{gel}^* is zero for $\sigma_{\parallel}^{\text{app}} < G\sqrt{\sigma_{0\perp}^{\text{app}}/\Lambda}$, see the magenta curve in fig. 2. This is because the normal stress $\sigma_{0\perp}^{\text{app}}$ is not applied to the free ends of the gel once these ends separate from the solid surface, see the boundary condition c) above eq. (12); the generated negative normal stress $\Lambda\gamma^2$ thus must be larger than the applied normal stress $\sigma_{\perp}^{\text{app}}$ to form the solvent layer. The sliding velocity V_{gel}^* increases monotonically with increasing

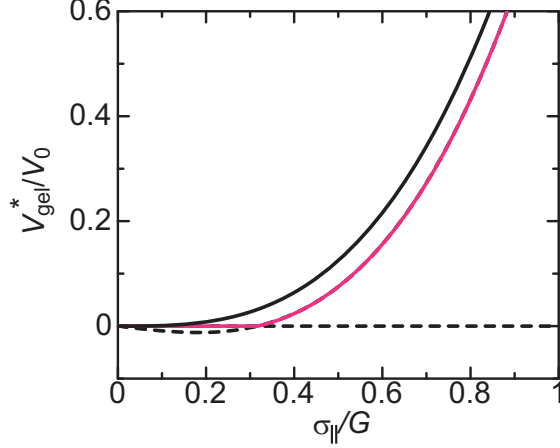


Figure 2: The sliding velocity V_{gel}^*/V_0 of a gel in a steady state (defined by eq. (22)) is shown as a function of the shear stress σ_{\parallel}/G in the constant gap distance condition for cases in which the gel is swollen in the zero-stress condition (black) and with the normal stress $\sigma_{0\perp}^{\text{app}}/\Lambda = 0.1$ is applied to the equilibrium in advance (magenta). The rescaling factor is defined by $V_0 = \eta_{\text{sol}}\Gamma Gh'_0/(K + 4G/3)$. V_{gel}^* is also the scale of the sliding velocity of the gel in the constant applied normal stress condition, see sec. 3.2.

the applied shear stress for $\sigma_{\parallel}^{\text{app}} > G\sqrt{\sigma_{0\perp}^{\text{app}}/\Lambda}$. The threshold value of the applied shear stress is proportional to the square root of the applied normal stress $\sigma_{0\perp}^{\text{app}}$.

3.2 Constant applied normal stress

Now we treat cases in which constant shear and normal stresses, $\sigma_{\parallel}^{\text{app}}$ and $\sigma_{\perp}^{\text{app}}$, are applied to the gel at $t = 0$. Before these stresses are applied, the prestress $\sigma_{0\perp}^{\text{app}}$ may or may not be applied to the gel to the equilibrium. We predict the sliding velocity $V_{\text{gel}}(t)$ of the gel as a function of time t .

Our theory predicts that the sliding velocity $V_{\text{gel}}(t)$ of the gel scales as V_{gel}^* , see eq. (22), and the thickness $h_{\text{lub}}(t)$ of the lubrication layer scales as h_{lub}^* , see eq. (21). The sliding velocity $V_{\text{gel}}(t)$ of the gel is a non-monotonic function of time, see fig. 3. For a short time scale, the sliding velocity $V_{\text{gel}}(t)$ increases with time. This is because the gel generates the negative normal stress to shrink the polymer network and the solvent in the gel, in turn, flows to increase the thickness $h_{\text{lub}}(t)$ of the solvent layer, see the first term of eq. (19). The sliding velocity $V_{\text{gel}}(t)$ shows a maximum at time $t = t_{\text{max}}$ and then decreases with time for

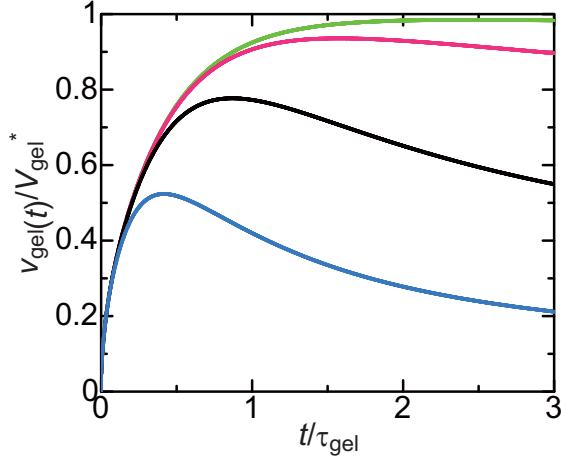


Figure 3: The sliding velocity $V_{\text{gel}}(t)/V_{\text{gel}}^*$ of the gel is shown as a function of time t/τ_{gel} for $\tau_{\text{lub}}/\tau_{\text{gel}} = 0.1$ (cyan), 1.0 (black), 10.0 (magenta), and 100.0 (light green), where τ_{gel} and τ_{lub} are time scales of the solvent flows in the gel and the solvent layer, respectively. The rescaling factor V_{gel}^* is defined by eq. (22).

a longer time scale. This is because the solvent flows out from the solvent layer due to the applied normal stress, see the second term of eq. (19), and thus the thickness $h_{\text{lub}}(t)$ of the solvent layer decreases. The solvent flows from the gel to the solvent layer in a time scale τ_{gel} , see eq. (13), and the solvent flows out from the solvent layer in a time scale τ_{lub} , which is defined by the form

$$\tau_{\text{lub}} \equiv \frac{\eta_{\text{sol}} L^2}{2\sigma_{\perp}^{\text{app}} h_{\text{lub}}^{*2}}. \quad (23)$$

At a first glance, one may think that the gel does not show a solvent layer for $\tau_{\text{gel}} > \tau_{\text{lub}}$. However, our theory predicts that the gel still stabilizes the solvent layer, see the cyan curve in fig. 3, due to the strong non-linearity of the solvent flows in the solvent layer, see the second term of eq. (19).

More quantitatively, for a short time scale, the thickness of the solvent layer has an asymptotic form

$$h_{\text{lub}}(t) = \frac{2}{\sqrt{\pi}} h_{\text{lub}}^* \sqrt{\frac{t}{\tau_{\text{gel}}}}. \quad (24)$$

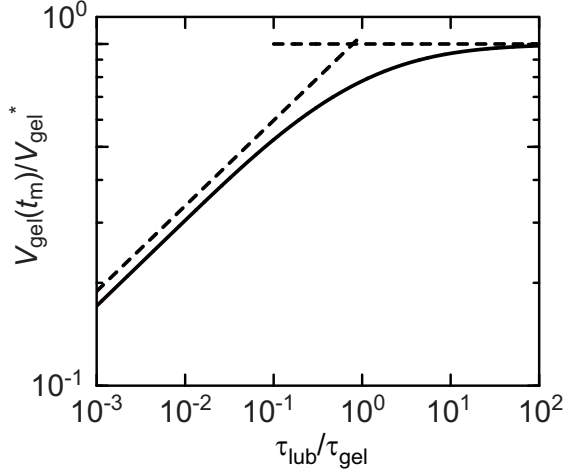


Figure 4: The sliding velocity $V_{\text{gel}}(t_{\text{max}})/V_{\text{gel}}^*$ of the gel is shown as a function of the ratio $\tau_{\text{lub}}/\tau_{\text{gel}}$ of time scales (solid curve). The broken curves are calculated by using the asymptotic expressions for small and large values of the ratio $\tau_{\text{lub}}/\tau_{\text{gel}}$, see eq. (26). The rescaling factor V_{gel}^* is defined by eq. (22).

In a longer time scale $t > t_{\text{max}}$, the thickness $h_{\text{lub}}(t)$ has an asymptotic form

$$h_{\text{lub}}(t) = \frac{h_{\text{lub}}^*}{\sqrt{1 + t/\tau_{\text{lub}}}}. \quad (25)$$

The sliding velocity of the gel in each time regime is derived by using eq. (20).

The maximum sliding velocity of the solvent layer increases as the ratio $\tau_{\text{lub}}/\tau_{\text{gel}}$ of time scales increases, see the solid curves in fig. 4. This is simply because the thickness of the gel decreases more before the solvent flows out from the solvent layer become significant. The maximum thickness has an approximate form

$$h_{\text{lub}}(t_{\text{max}}) \simeq h_{\text{lub}}^* \left(\frac{4\tau_{\text{lub}}}{\pi\tau_{\text{gel}}} \right)^{1/4} \quad (26)$$

for small values of the ratio $\tau_{\text{lub}}/\tau_{\text{gel}}$ and asymptotically approaches to unity for large values of the ratio $\tau_{\text{lub}}/\tau_{\text{gel}}$, see the broken curves in fig. 4. The maximum sliding velocity thus depends on the applied normal stress (only for cases in which the gel is not prestressed, $\sigma_{0\perp}^{\text{app}} = 0$) and the aspect ratio h'_0/L of the gel.

4 Discussion

Many biopolymer gels generate negative normal stress.^{11,12} In our previous theory, we predicted that even flexible polymer gels generate negative normal stress for cases in which the polymer network is greatly stretched in the swelling process.^{13,14} Our theory predicts that when shear stress is applied to such a gel, the gel forms a solvent layer because the polymer network of the gel shrinks due to the negative normal stress. The thickness of the layer is thus proportional to $\Lambda\gamma^2$, where the coefficient Λ is derived from the free energy of a statistical thermodynamic model of polymer gels¹³ and/or can be also measured by using a rotational rheometer.^{11,12} In a typical experiment, the thickness h_{lub}^* of the solvent layer is in the order of $\sim 5 \mu\text{m}$ for $\Lambda\gamma^2 \sim 50 \text{ Pa}$,¹¹ $h_0 \sim 1 \text{ mm}$, and $K + 4G/3 \sim 10^4 \text{ Pa}$,¹⁶ for cases in which the normal stress $\sigma_{0\perp}^{\text{app}}$ is not applied for $t < 0$. With the solvent layer of micrometer thickness, the interfacial energy and roughness of the gel and the solid surface will not play a significant role in the kinetic friction. This prediction is ideally tested by experiments, in which a gel is slid in a linear geometry, see fig. 1, and the normal stress $\sigma_{0\perp}^{\text{app}}$ is not applied before the shear stress is applied.

Our theory also predicts that **for cases in which the applied normal stress is constant**, the thickness $h_{\text{lub}}(t)$ of the solvent layer is a non-monotonic function of time and has a maximum because the solvent in the gel flows to the solvent layer in the short time scale and it flows out from the solvent layer in the longer time scale. We derived the asymptotic forms of the thickness $h_{\text{lub}}(t)$ of the solvent layer for short and long time scales and the approximate forms of the maximum value $h_{\text{lub}}(t_{\text{max}})$ of the layer thickness. The maximum thickness $h_{\text{lub}}(t_{\text{max}})$ is a function of the ratio of time scales $\tau_{\text{lub}}/\tau_{\text{gel}}$, see fig. 4. The time scale τ_{lub} of the solvent flow in the solvent layer is in the order of 100 s (for $\eta_{\text{sol}} = 8.0 \times 10^{-3} \text{ Pa s}$, $\sigma_{\perp}^{\text{app}} \sim 1 \text{ kPa}$, $h_{\text{lub}}^* \sim 2 \mu\text{m}$, and $L \sim 1 \text{ cm}$) in a typical experiment. The time scale τ_{gel} of the solvent flow in a gel ranges 1 s to 10 h, depending on the porosity of the gel.¹² These predictions may be experimentally accessible by quantitatively measuring the sliding velocity of biopolymer gels or greatly stretched flexible polymer gels as a function of time.

The main component of connective tissues is an extracellular matrix, which is a hydrogel of biofilaments connected by adherent cells. **Indeed, a hydrogel of collagen fibers, one of the main components of articular cartilages,² generates negative normal stress.¹¹** Our theory may thus provide insight in the physical mechanisms involved in the low friction constants of these connective tissues. **For a detailed treatment, one can change the forms of the elastic stress, eq. (4), and the Darcy constant κ to take into account the anisotropy of articular cartilages (however, our theory treats only the gel deformation and the solvent flows in the z -direction and thus may be enough for the first approximation).** The orientational ordering of fibers may enhance the negative normal stress generated by gels. We envisage a theory to predict the roles played by the orientational ordering in the negative normal stress of gels. Experimentally measuring the normal stress generated by articular cartilages (see, for example, ref.¹⁷) may be helpful to answer the intriguing questions involved in the tribology of articular cartilages.

Acknowledgement

MD acknowledges the financial support of the National Natural Science of China (Grant number 21434001). This work is supported in part by Grant-in-Aid for Scientific Research (A) (17H01152) from JSPS. We are grateful to Dr. Yoshifumi Amamoto (Nagoya University) for a critical reading of this manuscript.

References

- (1) J. P. Gong, Friction and lubrication of hydrogels – its richness and complexity. *Soft Matter*, 2006, **7**, 544-552.
- (2) G. A. Ateshian, The role of interstitial fluid pressurization in articular cartilage lubrication. *J. Biomech.*, 2009, **42**, 1163-1176.

- (3) T. Bamberger, C. Caroli, and O. Ronsin, Self-healing slip pulses and the friction of gelatin gels. *Eur. Phys. J. E.* 2003, **11**, 85-93.
- (4) S. Yashima, N. Takase, T. Kurokawa, and J. P. Gong, Friction of hydrogels with controlled surface roughness on solid flat substrates. *Soft Matter*, 2014, **10**, 3192-3199.
- (5) T. Tominaga, T. Kurokawa, H. Furukawa, Y. Osada, and J. P. Gong, Friction of a soft hydrogel on rough solid substrates. *Soft Matter*, 2008, **4**, 1645-1652.
- (6) T. Yamamoto, T. Kurokawa, J. Ahmed, G. Kamita, S. Yashima, Y. Furukawa, Y. Ota, H. Furukawa, and J. P. Gong, *In situ* observation of a hydrogel-glass interface during sliding friction. *Soft Matter*, 2014, **10**, 5589-5596.
- (7) M. Doi, *Soft Matter Physics*, Oxford University Press, Oxford, 2013.
- (8) M. Doi, Gel Dynamics. *J. Phys. Soc. Jpn.*, 2009, **78**, 052001.
- (9) K. Mabuchi, K. Tanaka, D. Uchijima, and R. Sakai, Frictional Coefficient under Banana Skin. *Tribology Online*, 2012, **7**, 147-151.
- (10) R. Byron Bird, R. C. Armstrong, and O. Hassager, *Dynamics of polymeric liquids, vol. 1*, Wiley-Interscience, New York, 1987.
- (11) P. A. Janmey, M. E. McCormick, S. Rammensee, J. L. Leight, P. C. Georges, and F. C. MacKintosh, Negative normal stress in semiflexible biopolymer gels. *Nat. Mater.*, 2007, **6**, 48-51.
- (12) H. C. G. de Cagny, B. E. Vos, M. Vahabi, N. A. Kurniawan, M. Doi, G. H. Koenderink, F. C. MacKintosh, and D. Bonn, Porosity Governs Normal Stresses in Polymer Gels. *Phys. Rev. Lett.*, 2016, **117**, 217802.
- (13) T. Yamamoto, Y. Masubuchi, and M. Doi, Relaxation dynamics of the normal stress of polymer gels. *Macromolecules*, 2017, **50**, 5208-5213.

- (14) T. Yamamoto, Y. Masubuchi, and M. Doi, Large network swelling and solvent redistribution are necessary for polymer gels to show negative normal stress. *ACS Macro Lett.*, 2017, **6**, 512-514.
- (15) W. Hutt and B. N. J. Persson, Soft matter dynamics: Accelerated fluid squeeze-out during slip. *J. Phys. Chem.*, 2016, **144**, 124903.
- (16) S. Hirotsu, Softening of bulk modulus and negative Poisson's ratio near the volume phase transition of polymer gels. *J. Chem. Phys.*, 1991, **94**, 3949-3957.
- (17) H. Wang and G. A. Ateshian, The normal stress effect and equilibrium friction coefficient of articular cartilage under steady frictional shear. *J. Biomech.*, **30**, 771-776 (1997).