

# Variational bounds for the relaxation times of swelling gels

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Variational bounds are found for the relaxation times of a gel of general shape swelling in a solvent based on the stress-diffusion coupling model. It is shown that in the case of free swelling, the longest relaxation time is inversely proportional to the osmotic modulus  $K$  in the limit of  $K \rightarrow 0$  and  $K \rightarrow \infty$ . This indicates that the relaxation time diverges at the point of  $K=0$ . The divergence, however, disappears if a part of the gel is mechanically constrained.

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## I. INTRODUCTION

A gel placed in a solvent absorbs or desorbs solvent and eventually takes an equilibrium shape [1]. The dynamics of this process was first studied by Tanaka and Fillmore (TF) [2], who proposed a basic equation describing the swelling dynamics and analyzed their experimental results for the swelling of spherical gels. This work initiated the study of the kinetics of gel swelling and their equation (the TF equation) has been regarded as the basic equation describing the swelling and deformation of gels.

Later studies, however, showed that the TF equation is valid only in the very special case (such as the swelling of spherical gels) in which the motion of polymer network and the motion of solvent are always parallel (or antiparallel) to each other. Extensions of the Tanaka-Fillmore theory have been done by various authors [3–6]. These studies clarified that it is necessary to take into account of the solvent velocity (or other velocity which involves the solvent velocity) other than the polymer network velocity. We shall call the new set of equations the stress-diffusion coupling model.

Although a consensus seems to have been established in the physics of the stress-diffusion coupling model, a precise mathematical formulation for the model has not been done until recently [7]. This is, in our view, due to the strange character of the basic equations of the model and due to the unawareness of the important role of the solvent pressure  $p$ . As a result, many of the earlier works, although they captured the essence of the physics, are not mathematically consistent. An example is seen in the history of the study of the swelling kinetics of rodlike gels [8]. For small degrees of swelling, the stress-diffusion coupling model gives a set of linear partial differential equations, but the equations have not been set up in proper mathematical form, and it is only recently [8] that a complete solution was obtained after many earlier works [3,5,9,10].

In general, the computation of the longest relaxation time based on the stress-diffusion coupling model is not a trivial problem as the problem involves the coupling of the elastic deformation of polymer network and the permeation of solvent. Rigorous results are known only for three cases: sphere, rod, and slab. In this paper, we derive a variational formula which is useful to calculate the longest relaxation time of the swelling gel of general shape.

The present study was motivated by the following observation. Tanaka *et al.* [11] argued that the relaxation time  $\tau$  of

the spherical gel goes to infinity at the critical point where the osmotic modulus  $K$  goes to zero. Their argument, however, has a flaw as it is based on an approximation which is valid only for the case of  $K \gg G$ , where  $G$  is the shear modulus which always remains positive. Onuki [5] solved the Tanaka-Fillmore equation rigorously and showed that the relaxation time indeed diverges as  $K \rightarrow 0$ . The divergence is by no means obvious since the swelling kinetics of gels involves the shear modulus which is always positive. Onuki [5] also examined other cases such as the swelling of rods and disks and found that the relaxation time also diverges as  $K \rightarrow 0$  for these cases as well. This strongly suggests that the relaxation time diverges as  $K$  goes to zero for any shape of the gel, but there is no mathematical proof for that.

In the following we shall prove that this conjecture is correct using a variational formula derived from the stress-diffusion coupling model. The formula is useful not only for proving the theorem, but also for evaluating the relaxation time of a gel of general shape as it gives a bound very close to the rigorous result.

The present theory is based on the linearized continuum equation for gel dynamics and does not take into account any nonlinear effects. Especially, the nonlinear mode coupling effect associated with the critical dynamics is ignored.

## II. VARIATIONAL FORM FOR THE RELAXATION RATE

The basic equations for the stress-diffusion coupling model is given in Ref. [7]. In this model, a gel is considered to consist of a polymer network and solvent. The gel as a whole is assumed to be incompressible: therefore the gel can swell only by absorbing solvent from the surrounding. To describe the swelling and associated deformation of the gel, we consider a certain stress-free isotropic state and call this the reference state. Let  $\mathbf{u}(\mathbf{x}, t)$  be the displacement of a point of polymer network which was located at  $\mathbf{x}$  in the reference state. The local volume strain of the gel is expressed by

$$f(\mathbf{x}, t) = \partial_i u_i, \quad (1)$$

where  $\partial_i$  stands for  $\partial/\partial x_i$  and the summation convention is used.

The thermodynamic property of the gel is entirely characterized by the constitutive equation for the stress  $\sigma_{ij}$  for the polymer network:

$$\sigma_{ij} = K(\partial_k u_k) \delta_{ij} + G \left[ \partial_j u_i + \partial_i u_j - \frac{2}{3} \delta_{ij} \partial_k u_k \right], \quad (2)$$

where  $K$  and  $G$  are the osmotic modulus and the shear modulus, respectively. The osmotic modulus  $K$  stands for the thermodynamic force which resists when the gels takes excessive amount of water and becomes zero at the critical point.

The basic equation for gel dynamics consists of two parts: the force balance equation and the Darcy's law. The first is written as

$$\partial_j (\sigma_{ij} - p \delta_{ij}) = 0, \quad (3)$$

where  $p$  is the pressure which was introduced to satisfy the incompressible condition [4]. Equations (2) and (3) give

$$\left( K + \frac{G}{3} \right) \partial_i \partial_j u_j + G \partial_j^2 u_i = \partial_i p. \quad (4)$$

On the other hand, Darcy's law and the incompressible condition give the following equation [7]:

$$\partial_i \dot{u}_i = \kappa \partial_i^2 p, \quad (5)$$

where  $\dot{u}_i$  stands for  $\partial u_i / \partial t$  and  $\kappa$  is the material constant called the Darcy constant.

The above set of equations have to be supplemented by the boundary conditions at the gel surface. There are two kinds of boundary conditions: one stands for the mechanical condition and the other stands for the solvent permeation condition. In the case of free swelling, there is no force acting on the surface of gel and the solvent can permeate freely. In such a case, the boundary conditions are written as

$$\sigma_{ij} n_j = 0, \quad (6)$$

$$p = 0, \quad (7)$$

where  $\mathbf{n}$  is the unit vector normal to the gel surface.

The set of equations (3)–(7) is composed of the basic equations of the stress-diffusion coupling model for free swelling. Notice the peculiar mathematical structure of the equation: the time derivative  $\dot{u}_i$  is appearing in the spatial differential equation [see Eq. (5)]. The dynamics described by the above set of equations has aspects not seen in the usual diffusion-type equations [7]. Therefore it is interesting to set up a variational form for calculating the longest relaxation time  $\tau$ .

Now, let  $\Omega$  be the smallest relaxation rate—i.e.,  $\Omega = 1/\tau$ . Determination of  $\Omega$  is an eigenvalue problem and can be obtained by finding the nonzero solution for  $(\mathbf{u}, p)$  which satisfies Eq. (4) and the eigenvalue equation

$$-\Omega \partial_i \dot{u}_i = \kappa \partial_i^2 p \quad (8)$$

together with the boundary conditions (6) and (7).

To solve the set of equations, we define the Green function  $\mathcal{G}(\mathbf{x}, \mathbf{x}')$  which is the solution of

$$\nabla^2 \mathcal{G}(\mathbf{x}, \mathbf{x}') = -\delta(\mathbf{x} - \mathbf{x}') \quad (9)$$

satisfying the boundary condition

$$\mathcal{G}(\mathbf{x}, \mathbf{x}') = 0 \quad (10)$$

on the surface of the gel. Equations (8) and (4) then give the following eigenvalue equation for  $\mathbf{u}(\mathbf{x})$ :

$$\kappa \left[ \left( K + \frac{G}{3} \right) \partial_i \partial_j u_j + G \partial_j^2 u_i \right] = \Omega \int d\mathbf{x}' \partial_i \mathcal{G}(\mathbf{x}, \mathbf{x}') \partial_j' u_j(\mathbf{x}'). \quad (11)$$

This can be furthermore transformed to the following variational form. Let  $\Omega_{\text{exact}}$  be the correct smallest eigenvalue; then, for an arbitrary choice of  $\mathbf{u}$ , the following inequality holds:

$$\Omega_{\text{exact}} \leq \frac{A[\mathbf{u}]}{N[\mathbf{u}]}, \quad (12)$$

where  $A[\mathbf{u}]$  is the elastic energy of the system,

$$A[\mathbf{u}] = \int d\mathbf{x} \left[ \frac{1}{2} K (\partial_i u_i)^2 + \frac{1}{4} G \left( \partial_i u_j + \partial_j u_i - \frac{2}{3} \delta_{ij} \partial_k u_k \right)^2 \right], \quad (13)$$

and  $N[\mathbf{u}]$  is defined by

$$N[\mathbf{u}] = \frac{1}{2\kappa} \int d\mathbf{x} d\mathbf{x}' G(\mathbf{x}, \mathbf{x}') \partial_i u_i(\mathbf{x}) \partial_j u_j(\mathbf{x}'). \quad (14)$$

It should be noted that for the free-swelling case, no conditions are imposed for  $\mathbf{u}$  since the boundary condition for  $\mathbf{u}$  [Eq. (6)] is a natural boundary condition.

### III. UPPER BOUND FOR THE RELAXATION RATE

#### A. Limit of $K/G \gg 1$

In the case of  $K/G \gg 1$ , the minimum value of the functional  $A[\mathbf{u}]/N[\mathbf{u}]$  can be easily obtained. In this case, the energy of shear deformation may be ignored and the functional to be minimized is

$$\mathcal{I}[\mathbf{u}] = \frac{K \kappa \int d\mathbf{x} f^2(\mathbf{x})}{\int d\mathbf{x} d\mathbf{x}' \mathcal{G}(\mathbf{x}, \mathbf{x}') f(\mathbf{x}) f(\mathbf{x}')} \quad (15)$$

The functional  $\mathcal{I}[\mathbf{u}]$  can be minimized by the function  $f(\mathbf{x})$  which satisfies

$$\int d\mathbf{x}' \mathcal{G}(\mathbf{x}, \mathbf{x}') f(\mathbf{x}') = \frac{1}{\lambda_1} f(\mathbf{x}) \quad (16)$$

or, by Eq. (9),

$$\nabla^2 f = -\lambda_1 f. \quad (17)$$

Thus  $\lambda_1$  is the smallest eigenvalue of the Laplacian with the boundary condition

$$f = 0 \quad \text{on the surface of the gel.} \quad (18)$$

$\Omega_{\text{exact}}$  is then given by

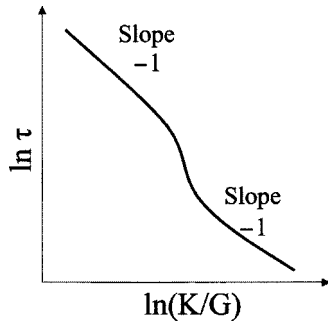


FIG. 1. The general shape of the curve of the longest relaxation time of a free-swelling gel plotted against the ratio between the osmotic modulus  $K$  and the shear modulus  $G$ .

$$\Omega_{exact} = \kappa K \lambda_1 \quad \text{for } K/G \gg 1. \quad (19)$$

Notice that  $\lambda_1$  is a parameter having dimension of length<sup>-2</sup> and is determined by the shape of the gel.

The above result can also be obtained easily from the differential form of the stress-diffusion coupling model.

### B. Limit of $K/G \ll 1$

The exact minimum for the variational problem can also be found for the case of  $K/G \ll 1$ . In this case, in order to minimize the functional  $I[\mathbf{u}]$ , we need to put the shear energy term equal to zero. This gives the following shear-free condition for the trial function  $\mathbf{u}(\mathbf{x})$ :

$$\partial_i u_j + \partial_j u_i = 2f(\mathbf{x}) \delta_{ij}. \quad (20)$$

If we can find such function  $\mathbf{u}(\mathbf{x})$ , the minimum value of  $I[\mathbf{u}]$  becomes independent of  $G$  and proportional to  $K$ . In fact, the function satisfying Eq. (20) does exist: the simplest example is the isotropic expansion

$$\mathbf{u}(\mathbf{x}) = \alpha \mathbf{x}, \quad (21)$$

where  $\alpha$  is a certain scalar. In the Appendix, we show that Eq. (20) and the stress-free boundary condition (6) essentially limit the functional form of  $\mathbf{u}(\mathbf{x})$  to this simple form.

Therefore, the bound given by the trial function (21) is the exact minimum. Equations (12) and (21) then give

$$\Omega_{exact} = \kappa K \lambda_2 \quad \text{for } K/G \ll 1, \quad (22)$$

where  $\lambda_2$  is given by

$$\frac{1}{\lambda_2} = \frac{1}{V} \int d\mathbf{x}' d\mathbf{x}'' \mathcal{G}(\mathbf{x}, \mathbf{x}') \quad (23)$$

and  $V$  is the volume of the gel.

In the general case, the variational principle indicates that

$$\Omega_{exact} \leq \kappa K \lambda_2. \quad (24)$$

From Eqs. (19), (22), and (24), one can conclude that if we plot the relaxation time as a function of  $K/G$ , the curve must look as shown in Fig. 1: the slope of the two asymptotic lines are equal to  $-1$ , and the line for  $K/G \gg 1$  comes above the line for  $K/G \ll 1$ . Especially, the relaxation time always diverges as  $K \rightarrow 0$ .

### C. Application of the variational form

To demonstrate the usefulness of the variational principle, we calculated the relaxation time of a cylindrical gel using the variational principle. We consider a long cylindrical gel of radius  $a$ . We choose the following trial function written in the cylindrical coordinate  $(r, \theta, z)$ :

$$u_r(r) = r + \beta r^3, \quad u_\theta = 0, \quad u_z = \epsilon z, \quad (25)$$

where  $\beta$  and  $\epsilon$  are the variational parameter to be determined. The functional is then evaluated as

$$\frac{\Omega}{\kappa} = \frac{K[1 + A + (1/3)A^2] + G[(4/3)B^2 + (1/9)A^2]}{1 + (2/3)A + (1/8)A^2}, \quad (26)$$

where  $A = (2 + \epsilon)/4\beta$  and  $B = \epsilon - 1 - \beta$ . It is clear that the minimum is obtained for  $B = 0$ , which shows that the apparent aspect ratio  $(a/L)(1 + u_r(a)/a - \epsilon)$  remains constant during the swelling process. Figure 2 shows the comparison between the exact relaxation time [8] and the result of the variational calculation. It is seen that the variational calculation

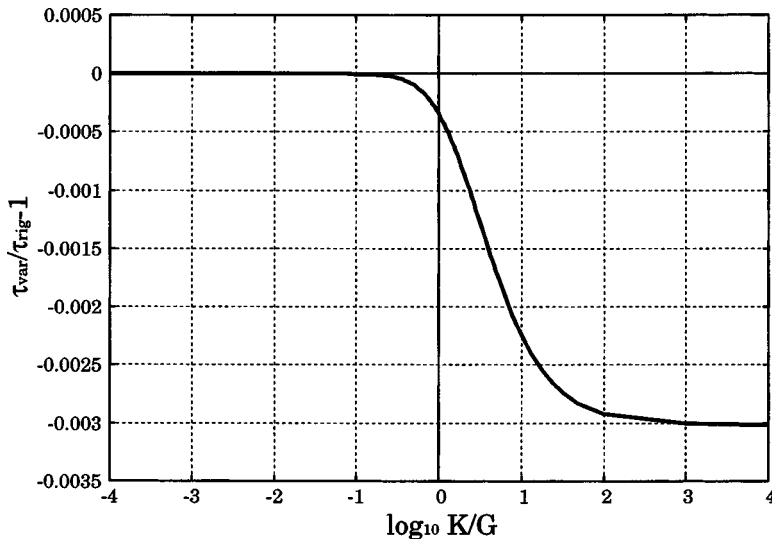


FIG. 2. The error of the variational calculation for the relaxation time of long rodlike gel is plotted against  $K/G$

tion gives results amazingly close to the rigorous results: the variational calculation gives rigorous results for  $K/G \ll 1$ , and the deviation starts as  $K/G$  increases, but the error is less than 0.3% in the entire range of  $K/G$ .

#### IV. CONCLUSION

We have shown that the smallest relaxation rate  $\Omega$  of free-swelling gel can be written as  $\kappa K \lambda$  in the two limiting cases of  $K/G \ll 1$  and  $K/G \gg 1$ . Therefore the shear modulus  $G$  plays a minor role in the case of free swelling over the entire region of  $K/G$ .

It should be noted that this conclusion is true only for the free-swelling case specified by the boundary conditions (6) and (7). For the other boundary conditions the results are different.

It is easy to formulate the variational principle for other boundary conditions. If solvent is not allowed to permeate on some part of the gel surface, the boundary condition for  $p$  becomes  $\mathbf{n} \cdot \nabla p = 0$  for such surface. Accordingly, the boundary condition for the Green function  $\mathcal{G}(\mathbf{x}, \mathbf{x}')$  becomes

$$\mathbf{n} \cdot \nabla \mathcal{G}(\mathbf{x}, \mathbf{x}') = 0 \quad \text{for nonpermeable membrane.} \quad (27)$$

If part of the gel is constrained mechanically—e.g., fixed to rigid wall or constrained by slippery wall—the trial function  $\mathbf{u}(\mathbf{x})$  has to satisfy such a condition. Apart from that, the same inequality as (12) holds. However, the inequality (24) cannot be used since the trial function (21) does not satisfy the imposed boundary condition.

It is interesting to note that the behavior shown in Fig. 1 is also true even if solvent permeation is partially prevented: the relaxation time diverges as  $K \rightarrow 0$  as long as the gel is not constrained mechanically. For example, suppose that some part of the gel surface is coated by a liquid film which prevents solvent permeation. This will slow down the permeation of the swelling process, but the  $K$  dependence will be the same as it is shown in Fig. 1 since the condition for the solvent permeation only changes the form for the Green function  $\mathcal{G}(\mathbf{x}, \mathbf{x}')$ , but does not change the  $K$  dependence of the asymptotic behavior.

On the other hand, if the gel is mechanically constrained, the relaxation time will not diverge in the limit of  $K \rightarrow 0$ . In this case the trial function of the isotropic swelling does not satisfy the boundary condition, and the inequality (24) is not valid anymore. In such a case, as  $K$  goes to zero, the relaxation time will approach a certain limiting value determined by the shear modulus  $G$ . Examples of such cases can be seen in our previous works [7].

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#### APPENDIX

Here we prove that the deformation which satisfies the shear-free condition

$$\partial_i u_j + \partial_j u_i = 2f(\mathbf{x}) \delta_{ij} \quad (A1)$$

and the stress-free boundary condition is the rotation of uniform dilation,

$$\partial_i u_j(\mathbf{x}) = \alpha \delta_{ij} + e_{ijk} \omega_k, \quad (A2)$$

where  $\alpha$  and  $\omega$  are constants independent of  $\mathbf{x}$ .

In general, the deformation gradient  $\partial_i u_j$  satisfying Eq. (A1) can be written as

$$\partial_i u_j(\mathbf{x}) = f(\mathbf{x}) \delta_{ij} + e_{ijk} g_k(\mathbf{x}), \quad (A3)$$

where  $\mathbf{g}(\mathbf{x})$  is a vectorial function of  $\mathbf{x}$ . Equation (A3) can be explicitly written as

$$\begin{aligned} \partial_1 u_1 &= \partial_2 u_2 = \partial_3 u_3 = f, \\ \partial_1 u_2 &= -\partial_2 u_1 = g_3, \\ \partial_2 u_3 &= -\partial_3 u_2 = g_1, \\ \partial_3 u_1 &= -\partial_1 u_3 = g_2. \end{aligned} \quad (A4)$$

From this set of equations, we can show

$$\begin{aligned} \partial_1 g_1 &= \partial_2 g_2 = \partial_3 g_3 = 0, \\ \partial_2 g_3 &= -\partial_3 g_2 = \partial_1 f, \\ \partial_3 g_1 &= -\partial_1 g_3 = \partial_2 f, \\ \partial_1 g_2 &= -\partial_2 g_1 = \partial_3 f. \end{aligned} \quad (A5)$$

For example,  $\partial_2 g_3 = \partial_2 \partial_1 u_2 = \partial_1 \partial_2 u_2 = \partial_1 f$ . One can then prove

$$\partial_i \partial_j f = 0. \quad (A6)$$

This equation, together with the stress-free boundary condition, imposes the constraint that  $f$  be constant. Furthermore, from Eq. (A5),  $\mathbf{g}$  is shown to be a constant vector. This proves our theorem.

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