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ANALYTICAL SOLUTIONS OF POLYMERIC GEL STRUCTURES UNDER BUCKLING AND WRINKLE

Z. S. LIU*,¶, S. SWADDIWUDHIPONG†, F. S. CUI*, W. HONG‡,
Z. SUO§ and Y. W. ZHANG*

*Institute of High Performance Computing
1 Fusionopolis Way, #16-16 Connexis, Singapore 138632

†Department of Civil and Environmental Engineering
National University of Singapore
E1A-07-03, 1 Engineering Drive 2, Singapore 117576

‡Department of Aerospace Engineering
Iowa State University, Ames, IA 50014, USA

§School of Engineering and Applied Sciences
Harvard University, Cambridge, MA 02138, USA
¶liuzs@ihpc.a-star.edu.sg

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One of the unique properties of polymeric gel is that the volume and shape of gel can dramatically change even at mild variation of external stimuli. Though a variety of instability patterns of slender and thin film gel structures due to swelling have been observed in various experimental studies, many are not well understood. This paper presents the analytical solutions of swelling-induced instability of various slender and thin film gel structures. We have adopted the well developed constitutive relation of inhomogeneous field theory of a polymeric network in equilibrium with a solvent and mechanical load or constraint with the incremental modulus concept for slender beam and thin film gel structures. The formulas of buckling and wrinkle conditions and critical stress values are derived for slender beam and thin film gel structures under swelling-induced instability using nonlinear buckling theories of beam and thin film structures. For slender beam structure, we construct the stability diagram with the distinct stable and unstable zones. The critical slenderness ratio and corresponding critical stresses are provided for different dimensionless material parameters. For thin film gel structures, we consider the thin film gel on an elastic foundation with different stiffness. The analytical solutions of critical stress and corresponding wrinkle wavelength, as well as buckling condition (or critical chemical potential) are given. These analytical solutions will provide a guideline for gel structure design used in polymeric gels MEMS and NEMS structures such as sensors and actuators. More importantly, the work provides a theoretical foundation of gel structure buckling and wrinkle, instability phenomena are different from normal engineering or material buckling.

Keywords: Buckling; gel; incremental modulus; instability; swelling; thin film gel; wrinkle buckling.

¶Corresponding author.

1. Introduction

Polymeric gels have recently attracted more attention, due to their unparalleled responsiveness to stimuli of various kinds, such as temperature, pH value, ionic strength, humidity, etc. [Hu *et al.*, 1995; Horkay and McKema, 2007; Sidorenko *et al.*, 2007; Beebe *et al.*, 2000; Dolbow *et al.*, 2005; Li *et al.*, 2007; Westbrook and Qi, 2007; Kim *et al.*, 2006]. For example, polymeric gels are capable of large and reversible deformation after being brought into equilibrium with a solvent. The volumetric ratio of some gels can reach up to 1000% under swelling. These unique properties make gels an attractive candidate material for certain applications such as sensors [Beebe *et al.*, 2000; Westbrook and Qi, 2000]. In addition to its capability of significantly changing shape and volume in response to stimuli, its biocompatibility and softness assure promising applications in the areas of bioengineering, drug delivery devices [Wichterle and Lim, 1960; Peppas *et al.*, 2006; Dong *et al.*, 2006] and tissue engineering [Lee and Mooney, 2001]. However, before we can go ahead and assimilate the gel materials into these devices, it is essential for us to understand the mechanics of gel structures, including their instability phenomena.

As new technology advances towards smaller, thinner and lighter devices, more stringent demands are imposed on the thin polymeric gel films such as diffusion barriers, dielectric coatings, electronic packaging etc. Therefore, it is imperative that we understand the mechanics of slender and thin polymer film structures. For proper applications of polymeric gels, one key issue is to have a reasonably short response time for gel device [Bassetti *et al.*, 2005] such as a sensor device. One way to achieve faster responses is to build miniaturized gel structures, such as gel beam and microgel beads [Klein *et al.*, 2007; Ladet *et al.*, 2008]. Sometimes, it is sufficient to have a structure that is thin in one or two directions, such as a gel film or a gel beam. When gel is immersed in solvent, the characteristic time for the swelling process of a gel film depends mainly on its thickness [Durning and Morman, 1993; Klein *et al.*, 2007]. Besides the rapid responses, a thin polymeric gel film can develop a great variety of off-plane deformation patterns during swelling or deswelling, while part of it is constrained [Cerda and Mahadevan, 2003; Sharon *et al.*, 2002; Klein *et al.*, 2007; Zhang *et al.*, 2008; Trujillo *et al.*, 2008; Brochard-Wyart and de Gennes, 2003; Southern and Thomas, 1965; Sidorenko *et al.*, 2007; Mullin *et al.*, 2007]. In this deformation process, not only the overall shape and morphology can be changed, but the curvature on each material point of the gel film can be modified on the fly [Klein *et al.*, 2007].

Among many thin-sheet natural and man-made structures, many can be considered as thin film gel. Some natural examples are flowers and leaves that can be shaped into a huge variety of diverse three-dimensional structures when grown. The opening and closing of a flower bud or a leaf sprout can be described as the swelling or deswelling of gel films [Gookin *et al.*, 2003; Doorn and Meeteren, 2003]. Indeed, many natural tissues of plants and animals are, to some extent, polymeric gels [Rinaudo, 2008]. Mixtures of macromolecular networks and solvents also constitute most tissues of plants and animals, where the networks retain the general shape and the solvents enable the transport of nutrients and wastes. The natural growth processes in some leaves and flowers could lead to a complex three-dimensional fractal shapes and complex patterns. How do we explain the mechanism, the morphogenesis and the natural growth of leaves, flowers and vesicles? The inhomogeneous gel deformation may be used to describe that phenomenon by studying buckling of gel structures [Liu *et al.*, 2010]. In summary, the wrinkling or buckling is indeed a common phenomenon that takes place in different slender and thin gel structures. Besides the analogy to growing tissues and the development of bio-mimic structures, the deformation pattern may also be used in the self-assembly of microscopic structures [Kofod *et al.*, 2007]. From mechanics point of view, all these off-plane deformation are attributed to the instability of thin and slender gel structures.

The study of buckling and wrinkle of thin film with deformable substrate have attracted many researchers' attention. Genzer and Groenewold [2006] reviewed the scientific aspects of wrinkling and the related phenomenon of buckling. They have specifically discussed how and why wrinkles/buckles form in various materials. For metal film vapor deposited on an elastomer, compressive residual stresses are generated in the film, leading to the wrinkling of the thin film. When the surface of elastomers is stiffened, the wrinkles may be hierarchical. Recent theoretical and experimental efforts have addressed the nonlinear post-buckling and herringbone patterns in metal capped elastomers [Chen and Hutchinson, 2004; Huang *et al.*, 2005; Song, 2010].

Experimental studies have shown that the appearance of a regular pattern on an originally smooth surface can be observed in a swelling polymer gel immersed in a solvent [Mora and Boudaoud, 2003, 2006]. This phenomenon was explained by a mechanical buckling instability of the soft surface gel layer under growing compressive stress [Chan *et al.*, 2009; Tanaka *et al.*, 2002; Volynskii *et al.*, 2000]. Sultan and Boudaoud [2008] explored experimentally the post-buckling of a thin film gel with strong residual stresses on a compliant substrate. More recently, Kang and Huang [2010a, 2010b, 2010c] investigated a swell-induced surface instability of a hydrogel layer on a rigid substrate. In their study, a linear perturbation analysis is performed to predict the critical condition for the onset of the surface instability. They showed through FE simulation, the swelling process, with the evolution of initial surface perturbations followed by the formation of crease-like surface patterns. Although a few numerical and analysis solutions have been proposed for thin film gel buckling and wrinkle problems, the gel buckling mechanism have not been well understood.

Based on a recently developed theoretical framework for neutral polymeric gels [Hong *et al.*, 2008, 2009], we investigate the buckling patterns induced by the constrained swelling or deswelling of slender polymeric gel rod/beam and polymeric gel film. In our analysis, an incremental modulus of gel concept is introduced and the analytical solutions of buckling and wrinkle of slender beam gel and thin film gel are presented. For slender beam gel, a stability diagram is constructed with two distinct regions for stable and unstable hydrogels depending on material parameters and geometrical parameters. For thin film gel, the analytical solutions of critical stress and wavelength of buckling under swelling are derived. These analytical solutions facilitate an elegant, efficient method for determining buckling conditions in a rapid and quantitative manner. The method exploits a buckling instability that occurs in thin film gel coated onto a relatively soft or stiffer thick substrate. Assuming highly periodic wrinkle modes, we calculate the film's critical stress and wavelength by applying well established nonlinear buckling mechanics and gel constitutive equations.

The paper is organized as follows. In Sec. 2, we present the thermodynamics of gel in equilibrium. The constitutive equations on the basis of a nonlinear field theory of swelling due to Gibbs [Gibbs, 1878; Hong *et al.*, 2009] are presented and an incremental modulus of gel concept is proposed in Sec. 3. Section 4 introduces the governing equations of thin film gel under buckling and the analytical solutions at buckling deformation of swollen gel films. Useful results that may be applied in gel structure design are demonstrated in this section. We conclude our presentation in the last section hoping that the presented analytical solutions be successfully applied to buckling and wrinkle gel problems facilitating the explanation of certain natural phenomena.

2. Thermodynamics of a Gel and Inhomogeneous Theory in Equilibrium

The inhomogeneous field theory of polymeric gel in equilibrium which was proposed by the Harvard research group [Hong *et al.*, 2008, 2009] is briefly introduced herein. We consider a network of polymers in contact with a solvent, subject to a mechanical load and geometric constraint, and held at a constant temperature. For the sake of simplicity, we take the stress-free dry network as the reference state, though in FE implementation, the reference status may be selected at a certain free-swelling state [Hong *et al.*, 2009]. Each small part of the network is described by its coordinate $\mathbf{X}$ in the reference state [Flory and Rehner, 1943; Hong *et al.*, 2008]. Let $dV(\mathbf{X})$ be an element of volume, $dA(\mathbf{X})$ be an element of area, and $N_K(\mathbf{X})$ be the unit vector normal to the element of area. When the network of polymers deform under chemical potential change and mechanical load, this part of the network moves to a new position with the coordinates $x_i(\mathbf{X})$. The deformation gradient of the network can be defined as

$$F_{iK} = \frac{\partial x_i(\mathbf{X})}{\partial X_K}. \tag{2.1}$$

In the deformed state, let $C(\mathbf{X})dV(\mathbf{X})$ be the number of solvent molecules in the element of volume. The field $x_i(\mathbf{X})$ describes the deformation of the network, while the field $C(\mathbf{X})$ describes the distribution of the solvent molecules in the polymeric gel system. In the inhomogeneous field theory of polymeric gel, the combination of these two fields describes the state of the gel system. The external solvent can be either a gas, or a pure liquid equilibrated with its own vapor. We may take the latter to be the reference state of the solvent, where the chemical potential is set to be zero. We also take the liquid solvent to be incompressible, and denote v as the volume per molecule, and p_0 as the vapor pressure. When the solvent is subjected to a pressure p greater than the vapor pressure, p_0, the chemical potential of the solvent molecules is $\mu = v(p - p_0)$. When the solvent is subjected to a pressure less than the vapor pressure, $p < p_0$, the solvent in equilibrium becomes a gas, which we assume to be an ideal gas, so that the chemical potential of the solvent molecules is $\mu = kT(p/p_0)$, where kT is the absolute temperature in the unit of energy, which is the product of the Boltzmann constant and the temperature. When the field of concentration in the gel changes by $\delta C(\mathbf{X})$, the external solvent does work $\mu \int \delta C dV$.

In a deformed state, let $B_i(\mathbf{X})dV(\mathbf{X})$ be the external mechanical force applied on the element of volume, and $T_i(\mathbf{X})dA(\mathbf{X})$ be the external mechanical force applied on the element of area. When the network deforms by a small amount, $\delta x_i(\mathbf{X})$, the field of mechanical load does work $\int B_i \delta x_i dV + \int T_i \delta x_i dA$. The integrals extend over the volume and the surface of the network in the reference state. In the study, we use chemical potential to represent the status of solvent environment. When the gel is in a state of equilibrium characterized by the two fields, $x_i(\mathbf{X})$ and $C(\mathbf{X})$, the total work done of gel system should be the work done by mechanical load and by the external solvent. We introduce $WdV(\mathbf{X})$ to be the Helmholtz free energy of the gel in the element of volume and assume that the free-energy density of the gel, W, is a function of the deformation gradient of the network, $\mathbf{F}$, and the concentration of the solvent in the gel, C. That is, $W(\mathbf{F}, C)$.

From thermodynamics, the change in the free energy of the gel should equal the sum of the work done by the external mechanical force and by the external solvent, namely,

$$\int \delta W dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA + \mu \int \delta C dV. \tag{2.2}$$

This equation holds for any small changes $\delta \mathbf{x}$ and δC from the state of equilibrium.

When the gel equilibrates with the solvent and the mechanical load, the chemical potential of the solvent molecules is homogeneous in the external solvent and in the gel, and the chemical potential can be expressed as:

$$\mu = \frac{\partial W(\mathbf{F}, C)}{\partial C}. \tag{2.3}$$

Introduce another free-energy function $\hat{W}$ by using a Legendre transformation:

$$\hat{W} = W - \mu C. \tag{2.4}$$

$\hat{W}$ is a function of the deformation gradient of the network and the chemical potential of the solvent molecules. That is $\hat{W}(\mathbf{F}, \mu)$.

A combination of Eqs. (2.2) and (2.4) gives

$$\int \delta\hat{W}dV = \int B_i\delta x_i dV + \int T_i\delta x_i dA. \tag{2.5}$$

When the gel is in a state of equilibrium, the chemical potential of the solvent molecules inside the gel is homogeneous and is equal to the chemical potential of the external solvent, μ. Indeed, the chemical potential plays a role analogous to that of the temperature. The equilibrium condition (2.5) takes the same form as that for a hyperelastic solid. Once the function $\hat{W}(\mathbf{F}, \mu)$ is prescribed, the boundary value problem is well established and can be solved as a normal solid mechanics problem. For complex problems, we can find solutions with finite element method. It is noted that the theory has no intrinsic length scale, so that the field depends only on lengths coming from the boundary conditions.

We have assumed that the free-energy density takes the functional form of $W(\mathbf{F}, C)$. Associated with a small change in the deformation gradient of the network, δF_{iK}, and a small variation in the concentration of the solvent molecules, δC, the free-energy density varies by

$$\delta W = \frac{\partial W(\mathbf{F}, C)}{\partial F_{iK}}\delta F_{iK} + \frac{\partial W(\mathbf{F}, C)}{\partial C}\delta C. \tag{2.6}$$

We can further define a nominal stress as the work conjugate to the deformation gradient, so that

$$s_{iK} = \frac{\partial W(\mathbf{F}, C)}{\partial F_{iK}}. \tag{2.7}$$

This nominal stress gives the same interpretation as the conditions for mechanical equilibrium in continuum mechanics. Using Eqs. (2.3) and (2.7), Eq. (2.6) becomes

$$\delta W = s_{iK}\delta F_{iK} + \mu\delta C. \tag{2.8}$$

From Eqs. (2.4) and (2.8), we get that

$$\delta\hat{W} = s_{iK}\delta F_{iK} - C\delta\mu, \tag{2.9}$$

so that

$$s_{iK} = \frac{\partial \hat{W}(\mathbf{F}, \mu)}{\partial F_{iK}}, \tag{2.10}$$

$$C = -\frac{\partial \hat{W}(\mathbf{F}, \mu)}{\partial \mu}. \tag{2.11}$$

The behavior of a gel is mainly entropic. As the solvent molecules mix with the long-chained polymers, the network swells, so that the configurational entropy of the network decreases, but the configurational entropy of mixture increases. The compromise of the two contributions to entropy equilibrates the network and the solvent. In this study, a particular form of the free-energy function $\hat{W}(\mathbf{F}, \mu)$ is taken as Flory–Rehner free-energy function [Flory and Rehner, 1943]. Thus, the free-energy form of a gel system consists of two components, the stretching free energy and the mixing free energy.

$$W = W_s + W_{sol}, \tag{2.12}$$

where

$$W_s(\mathbf{F}) = \frac{1}{2}NkT[F_{iK}F_{iK} - 3 - 2\log(\det \mathbf{F})], \tag{2.13}$$

$$W_{sol}(C) = -\frac{kT}{v}\left[vC\log\left(1+\frac{1}{vC}\right) + \frac{\chi}{1+vC}\right]. \tag{2.14}$$

Thus:

$$W = \frac{1}{2}NkT[F_{iK}F_{iK} - 3 - 2\log(\det \mathbf{F})] - \frac{kT}{v}\left[vC\log\left(1+\frac{1}{vC}\right) + \frac{\chi}{1+vC}\right], \tag{2.15}$$

where N is the number of polymeric chains per reference volume, χ is a dimensionless measure of the enthalpy of mixing with representative values $\chi = 0{\sim}1.2$. When $\chi > 0$, the solvent molecules like themselves better than they like the long-chained polymers. A representative value of the volume per molecule is $v = 10^{-28}\,\mathrm{m}^3$. At room temperature, $kT = 4 \times 10^{-21}\,\mathrm{J}$ and $kT/v = 4 \times 10^7\,\mathrm{Pa}$. In the absence of solvent molecules, the dry network has a shear modulus NkT under the small-strain conditions, with the representative value $NkT = 10^4{\sim}10^7\,\mathrm{N/m}^2$, which gives the range of $Nv = 10^{-4}{\sim}10^{-1}$.

As stated above, it is assumed that all molecules in a gel deformation are taken to be incompressible, so that the volume of the gel is the sum of the volume of the dry network and the volume of the pure liquid solvent. It means that there is no void in the gel when the gel system is in equilibrium with external mechanical force and solvent. Consequently, the concentration of the solvent in the gel relates to the deformation gradient of the network as Hong *et al.* [2008].

$$1 + vC = \det \mathbf{F}. \tag{2.16}$$

Substituting the above constraint into the Flory–Rehner free-energy function (2.12) to eliminate concentration C, the modified free-energy function for polymeric gel can be expressed as Hong *et al.* [2009].

$$\hat{W}(\mathbf{F},\mu) = \frac{1}{2}NkT(I - 3 - 2\log J) - \frac{kT}{v}\left[(J-1)\log\frac{J}{J-1} + \frac{\chi}{J}\right] - \frac{\mu}{v}(J-1), \tag{2.17}$$

where $I = F_{iK}F_{iK}$ and $J = \det \mathbf{F}$ are invariants of the deformation gradient. We use the deformation gradient of the network, $\mathbf{F}$, and the chemical potential of the solvent, μ, as the two independent variables. Consequently, the condition of molecular incompressibility is enforced without using the Lagrange multiplier, but is instead enforced by substituting constraint into the Flory–Rehner free-energy function to eliminate C. This is the advantage of the mono-phase inhomogeneous gel field theory of a polymeric gel.

Inserting Eq. (2.17) into Eq. (2.10), the constitutive equation of state of the gel can be obtained:

$$\frac{s_{iK}}{kT/v} = Nv(F_{iK} - H_{iK}) + \left[J\log\left(1 - \frac{1}{J}\right) + 1 + \frac{\chi}{J} - \frac{\mu}{kT}J\right]H_{iK}, \qquad (2.18)$$

where $F_{iK}H_{jK} = \delta_{ij}$.

In the above equation, we have normalized the chemical potential by kT, and the stress by kT/v. The above theory can be implemented in the finite element package, ABAQUS, by coding Eq. (2.18) into a user-defined subroutine for a hyperelastic material (UHYPER) or UMAT [Hong *et al.*, 2009; Liu *et al.*, 2010]. Having this constitutive equation, any complex boundary value problems can be solved by using FEM method.

It should be noted that in the implementation of the inhomogeneous field theory of a polymeric gel, the free energy (2.17) is singular when the network is solvent-free, $vC = 0$. To avoid this singularity, a reference state such that the network, under no mechanical load, equilibrates with a solvent of chemical potential $\mu_0(vC > 0)$, should be chosen. Relative to the dry network, the network in this state swells with isotropic stretches. We denote this free-swelling stretch by λ_0, which relates to the chemical potential μ_0 by setting stress (2.18) to be zero. Thus:

$$Nv\left(\lambda_0 - \frac{1}{\lambda_0}\right) + \left[\lambda_0^3\log\left(1 - \frac{1}{\lambda_0^3}\right) + 1 + \frac{\chi}{\lambda_0^3} - \frac{\mu_0}{kT}\lambda_0^3\right]\frac{1}{\lambda_0} = 0. \qquad (2.19)$$

This is a relationship of chemical potential and stretch in the case of freely swelling. It is emphasized that any gel structure deformation should satisfy the constitutive equation (2.18).

3. Analytical Solution of 1-D Beam Gel Buckling

3.1. *Incremental modulus of the gel*

This section and the next resume the main line of work of this paper, and prescribes a concept of incremental modulus of the gel structures. As the gel is hyperelastic and the values of modulus vary depending on the level of chemical potential and stretch, a reduced incremental modulus or tangent stiffness can thus be defined as $\tilde{E} = \partial s_1/\partial\varepsilon_1 = \partial s_1/\partial\lambda_1$ for gel deformation. For gel swelling or deswelling case, this definition is similar to a 1-D rod of a gel equilibrated in a solvent of chemical potential μ, and subjected to a uniaxial stress s_1 along the longitudinal direction. The state of deformation of gel rod can be characterized by the longitudinal stretch λ_1 with the remaining two transverse stretches $\lambda_2 = \lambda_3$. For other constraint swelling, the reduced incremental modulus can be similarly defined in a similar manner.

For a 1-D rod case, as the stresses in the transverse directions vanish, the constitutive equation (2.18) of the gel gives

$$N v\left(\lambda_2-\frac{1}{\lambda_2}\right)+\left[\lambda_1 \lambda_2^2 \log \left(1-\frac{1}{\lambda_1 \lambda_2^2}\right)+1+\frac{\chi}{\lambda_1 \lambda_2^2}-\frac{\mu}{k T} \lambda_1 \lambda_2^2\right] \frac{1}{\lambda_2}=0. \tag{3.1}$$

Equation (3.1) provides the relationship between longitudinal stretch λ_1 and the transverse stretch λ_2 at certain chemical potential. From gel constitutive equations, the longitudinal stress can be expressed as:

$$\frac{v s_1}{k T}=N v\left(\lambda_1-\frac{1}{\lambda_1}\right)+\left[\lambda_1 \lambda_2^2 \log \left(1-\frac{1}{\lambda_1 \lambda_2^2}\right)+1+\frac{\chi}{\lambda_1 \lambda_2^2}-\frac{\mu}{k T} \lambda_1 \lambda_2^2\right] \frac{1}{\lambda_1}. \tag{3.2}$$

Equations (3.1) and (3.2) give

$$\frac{v s_1}{k T}=N v\left(\lambda_1-\frac{\lambda_2^2}{\lambda_1}\right). \tag{3.3}$$

The reduced incremental modulus can be expressed as:

$$\frac{v}{k T} \tilde{E}=N v\left(1+\frac{\lambda_2^2}{\lambda_1^2}\right). \tag{3.4}$$

Equation (3.4) shows that the reduced incremental modulus $\tilde{E}$ of gel is a function of current deformation or stretch (current chemical potential).

For a typical gel, we assume that a representative value of the volume per molecule is $v = 10^{-28}\,\mathrm{m}^3$. At room temperature, $kT = 4 \times 10^{-21}$ J and $kT/v = 4 \times 10^7$ Pa. In the Flory–Rehner free-energy function, we take dimensionless material parameter Nv as 0.001 ($Nv = 10^{-3}$). Thus, the value of shear modulus of dry polymer network is $NkT = 4 \times 10^4$ Pa. For dimensionless material parameter χ which is a dimensionless measure of the enthalpy of mixing, the representative values are taken as 0 to 1.2 ($\chi = 0\sim1.2$). For ease of understanding and applications, the incremental modulus of gel, is usually normalized by NkT.

The variations of incremental modulus with stretch at different initial chemical potential and at dimensionless parameter of $\chi = 0.1$ are illustrated in Fig. 1. According to the present definition of incremental modulus of hydrogel, the incremental modulus are two times NkT under free-swelling condition. The free-swelling states are hence at the intersection points of the curves for different chemical potentials with the horizontal line of the value equalling to two. The values of the incremental modulus decrease and approach the limit values of NkT as the stretch values increase. When the gel is under compression, the incremental modulus can increase up to 20 times of NkT for zero chemical potential environment. The maximum incremental modulus under compression loading cases are about 15, 7.5, 3.4 and 2.3 times NkT for different initial chemical potential values of $\mu_0/kT = -0.001$, $\mu_0/kT = -0.01$, $\mu_0/kT = -0.1$ and $\mu_0/kT = -0.5$ respectively. While the gel is under tension, the incremental modulus decreases with the increase of stretch. Figure 2 shows the variation of the incremental modulus with stretch for different

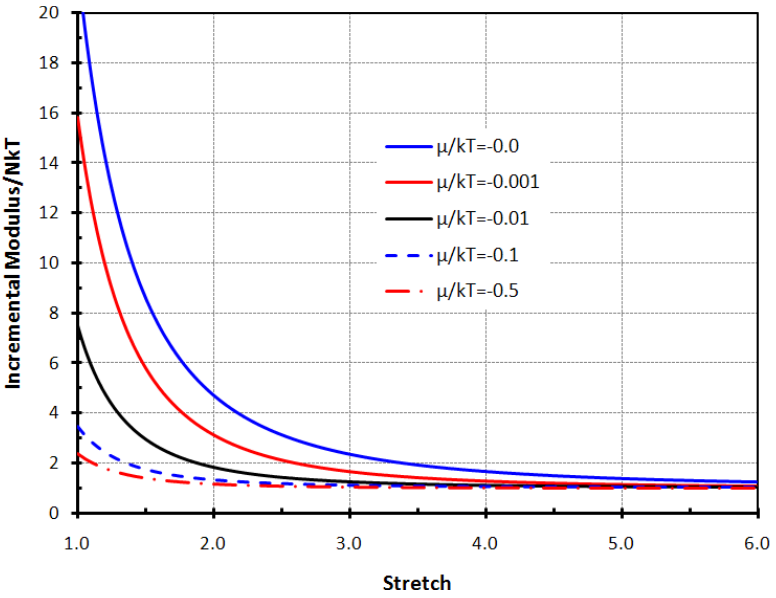


Fig. 1. Incremental modulus of gel varying with stretch for various initial chemical potentials ($kT = 4 \times 10^{-21}$ J, $kT/v = 4 \times 10^{7}$ Pa, $Nv = 10^{-3}$, $\chi = 0.1$).

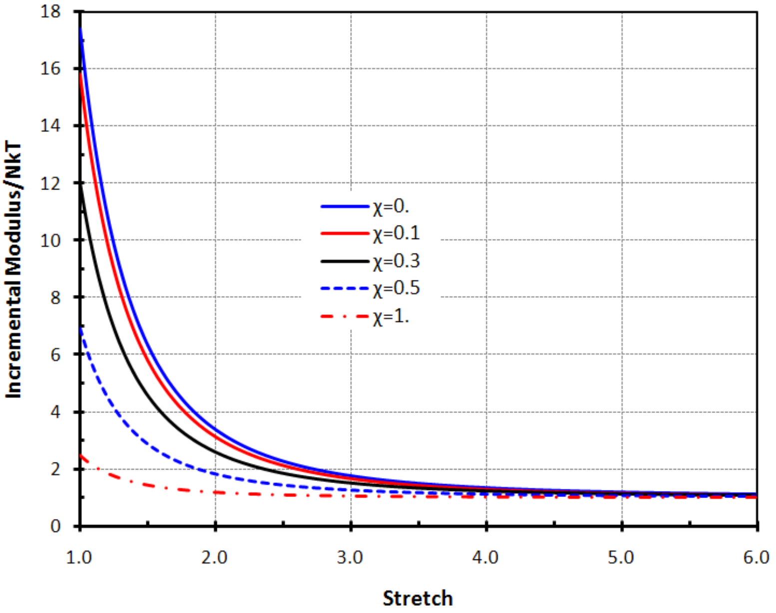


Fig. 2. Incremental modulus of gel varying with stretch for various dimensionless measures of the enthalpy of mixing ($kT = 4 \times 10^{-21}$ J, $kT/v = 4 \times 10^{7}$ Pa, $Nv = 10^{-3}$, $\mu/kT = -0.001$).

dimensionless measure of the enthalpy of mixing under the initial chemical potential of $\mu_0/kT = -0.001$. For a higher dimensionless measure of the enthalpy of mixing, the incremental modulus of gel is lower. For gel structures under compression, the incremental modulus abruptly increases with the decrease of dimensionless measure of the enthalpy of mixing. On the other hand, the variations are insignificantly less apparent in the case of tension loading. When $\chi = 0$, the maximum value of incremental modulus can reach up to 17 times of NkT, while achieving only 2.5 times of NkT for $\chi = 1.0$ under compression. In the large tension deformation, the minimum value of incremental modulus approaches that of the shear modulus of NkT (40 kPa). The values of incremental modulus for various cases can be used in the deformation analysis of gel structures. It should be noted that the values of incremental modulus defined in current study is higher than that of shear modulus as adopted by dry polymeric network. Indeed, the gel material under the coupling of chemical potential and mechanical load displays a property of auxetic materials in which its Poisson ratio is less than zero according to the normal Poisson ratio definition.

3.2. *Critical values of beam gel under buckling*

For example, let us consider a gel beam in contact with external solvent and subjected to central compressive load. It is assumed that the column has a certain initial curvature (which can be generated by compression force applied to column eccentrically). During deformation, the axial force increases simultaneously with lateral deflection. In such a case, the decrease of the stress on the convex side of the column during the initial stage of bending may be compensated by an increase of a compressive stress due to the continually increasing axial force. Thus, the actual deformation may proceed without any release of stress on the convex side of the column. According to Engesser–Karman inelastic buckling theory [Timoshenko and Gere, 1963], the critical stress of a column with hinged ends can be expressed as:

$$(s)_{cr} = \frac{\pi^2 \tilde{E}}{(l/r)^2}, \tag{3.5}$$

where l is the length of gel column, r is the radius of gyration of column and l/r is the slenderness ratio. Therefore, the critical stress of gel column buckling is dependent on incremental modulus of gel and gel column geometry.

For given slenderness ratio of a gel column, the buckling condition of the gel column can be determined by Eq. (3.5). For a column gel contacting with a solvent, it should satisfy the constitutive equation of gel (3.1) as well. Thus:

$$\begin{aligned}\frac{kT}{v}\left\{Nv\left(\lambda_1 - \frac{1}{\lambda_1}\right) + \left[\lambda_1\lambda_2^2 \log\left(1 - \frac{1}{\lambda_1\lambda_2^2}\right) + 1 + \frac{\chi}{\lambda_1\lambda_2^2} - \frac{\mu}{kT}\lambda_1\lambda_2^2\right]\frac{1}{\lambda_1}\right\}\\ = \frac{\pi^2 NkT}{(l/r)^2}\left(1 + \frac{\lambda_2^2}{\lambda_1^2}\right).\end{aligned} \tag{3.6}$$

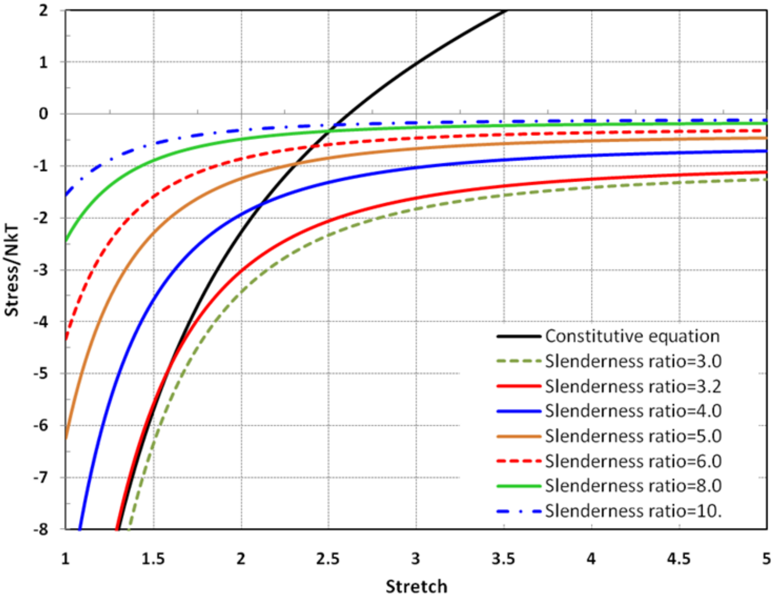


Fig. 3. Different stress curves varying with stretch ($kT = 4 \times 10^{-21}$ J, $kT/v = 4 \times 10^{7}$ Pa, $Nv = 10^{-3}$, $\mu/kT = -0.001, \chi = 0.1$).

According to Eq. (3.5), the stress curves of gel beams varying with stretch for different slenderness ratio are illustrated in Fig. 3. The constitutive stress curve of the gel structure varying with stretch is also displayed in Fig. 3. Stresses are normalized by NkT. The critical buckling stresses are those of the intersection points of constitutive stress curve and the stress curves from Eq. (3.5). According to Timoshenko inelastic buckling theory [Timoshenko and Gere, 1963], the column slenderness ratio should be greater than 4.0 for Eq. (3.5). In the case of column slenderness ratio being less than 4.0, there will be no global buckling taking place. The failure mode of structure will be local buckling or wrinkle along the edges. For the purpose of comparison, we still plot the cases of slenderness ratio of 3.0 and 3.2. No such intersection point is observed when the slenderness ratio is less than 3.2. This implies that even under compression, the gel column is globally stable when its slenderness ratio is less than 4. We can select the slenderness ratio of 4.0 as the critical slenderness ratio. At this critical slenderness ratio of 4.0, the corresponding normalized critical stress level is about 1.83. The higher the slenderness ratio of the gel column, the lower the critical stress values. For very higher slenderness ratio gel column ($l/r > 15$), the critical stress becomes very low.

Considering different initial chemical potential and gel column geometries, a stability diagram (as shown in Fig. 4) is constructed with two distinct regions for stable and unstable hydrogels beam/column. That is depending on dimensionless material parameters and geometric parameters of gel beam structure. Figure 4 shows

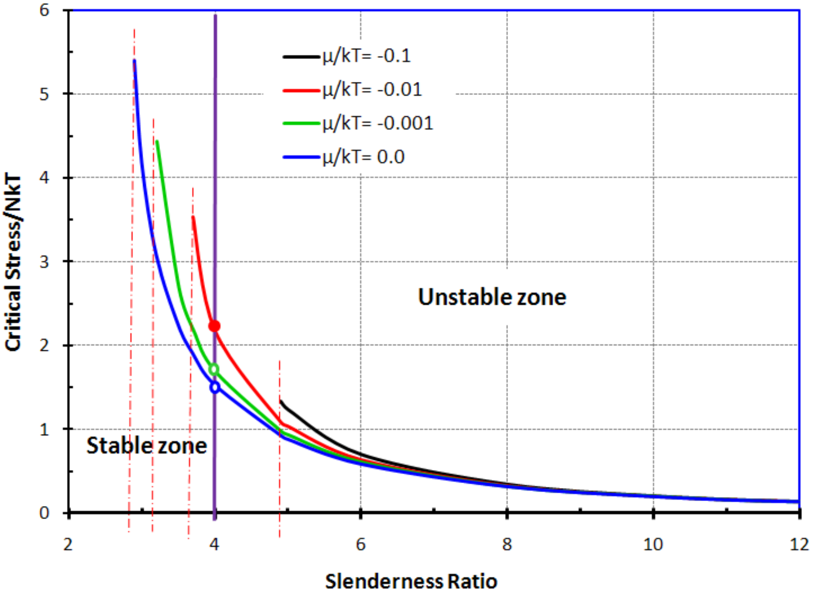


Fig. 4. Stability diagram showing normalized critical stress of gel beam varying with its slenderness ratio of beam for different chemical potentials ($kT = 4 \times 10^{-21}$ J, $kT/v = 4 \times 10^{7}$ Pa, $Nv = 10^{-3}, \chi = 0.1$).

the normalized critical stress varying with gel column slenderness ratio for different initial chemical potential. For initial chemical potential values of 0.0, −0.001 and −0.01, the intersection points to determine gel critical slenderness ratio only occur at the slenderness ratios to be less than 4.0. Thus we can define the critical slenderness ratios to be 4.0 for these initial chemical potential cases. It can also be observed that the critical slenderness ratio increases with the decrease of initial chemical potential. However the critical stress corresponding to the critical slenderness ratio are decreased. Considering the availability of Eq. (3.5), for zero, −0.001 and −0.01 initial chemical potential cases, the critical slenderness ratios are taken as 4.0 and corresponding critical normalized stresses are about 1.5, 1.7 and 2.2. For the initial chemical potential of −0.1, the critical slenderness ratio is 4.9 and corresponding critical stress is only about 1.3. This means that the gel beam will be stable if the slenderness ratios of beams are less than 4.0 and 4.9 for initial chemical potential of 0 and −0.1. The stability diagram will provide guidelines for column gel design. It should be noted that the buckling phenomena of gel column buckling are not the same as engineering material buckling phenomena. The critical conditions of gel column buckling are the functions of chemical potential, dimensionless material parameters and slenderness. In the present study, the critical slenderness ratios of gel beam or gel column are theoretically determined for different environmental conditions. At the same time, the critical stress corresponding to the slenderness ratio of gel beam for different chemical potential environment is provided.

4. Governing Equations of Thin Film Gel with One-Directional Wrinkle Mode

4.1. *In-plane incremental modulus of thin film gel*

For thin film gel with infinite in-plane dimensions as shown in Fig. 5, the in-plane stretches are depicted as λ_1 and λ_2, and the normal stretch as λ_3. When the film gel is first mounted on the substrate with initial chemical potential, the initial stretch is assumed to be λ_0. When the gel starts swelling with changing solvent environments, the stretches in three directions are $\lambda_1 = \lambda_2 = \lambda_0,\ \lambda_3 = \lambda_0\lambda$, where λ is stretch in the film normal, z direction and the value is relative to initial free-swelling state. Thus, the film gel is constrained in-plane but is freely swelling in the normal direction. When the generated in-plane compressive stresses reach the critical values, the gel film may buckle and wrinkle. These phenomena have been observed in many experiments [Kwon *et al.*, 2005]. Though these wrinkle patterns have certain dominant wavelengths, they often exhibit isotropic waveforms. From gel constitutive equation (2.18), we obtain

$$Nv\left(\lambda_3 - \frac{1}{\lambda_3}\right) + \left[\lambda_1\lambda_2\lambda_3 \log\left(1 - \frac{1}{\lambda_1\lambda_2\lambda_3}\right) + 1 + \frac{\chi}{\lambda_1\lambda_2\lambda_3} - \frac{\mu}{kT}\lambda_1\lambda_2\lambda_3\right]\frac{1}{\lambda_3} = 0. \tag{4.1}$$

Equation (4.1) provides the relationship between in-plane stretches λ_1, λ_2 and the transverse stretch λ_3.

The in-plane stresses in x and y directions can be expressed as:

$$\begin{aligned}\frac{vs_1}{kT} = Nv\left(\lambda_1 - \frac{1}{\lambda_1}\right) &+ \left[\lambda_1\lambda_2\lambda_3 \log\left(1 - \frac{1}{\lambda_1\lambda_2\lambda_3}\right) + 1\right.\\ &\left. + \frac{\chi}{\lambda_1\lambda_2\lambda_3} - \frac{\mu}{kT}\lambda_1\lambda_2\lambda_3\right]\frac{1}{\lambda_1},\end{aligned} \tag{4.2a}$$

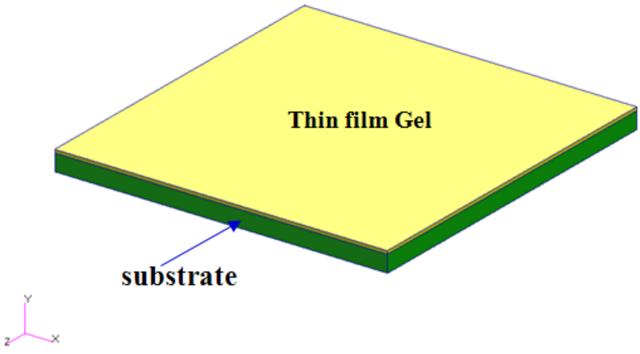


Fig. 5. Schematic model of thin film gel.

$$\frac{vs_2}{kT} = Nv\left(\lambda_2 - \frac{1}{\lambda_2}\right) + \left[\lambda_1\lambda_2\lambda_3 \log\left(1 - \frac{1}{\lambda_1\lambda_2\lambda_3}\right) + 1 + \frac{\chi}{\lambda_1\lambda_2\lambda_3} - \frac{\mu}{kT}\lambda_1\lambda_2\lambda_3\right]\frac{1}{\lambda_2}. \tag{4.2b}$$

Equations (4.1) and (4.2) give

$$\frac{vs_1}{kT} = Nv\left(\lambda_1 - \frac{\lambda_3^2}{\lambda_1}\right). \tag{4.3}$$

Adopting the same definition as incremental modulus of 1-D gel, the in-plane reduced incremental modulus of the film gel can be expressed as:

$$\frac{v}{kT}\tilde{E} = Nv\left(1 + \frac{\lambda_3^2}{\lambda_1^2}\right). \tag{4.4}$$

We assumed that the thin film gel starts swelling from an initial chemical potential λ_0. The incremental modulus thus becomes:

$$\frac{v}{kT}\tilde{E} = Nv(1 + \lambda^2). \tag{4.5}$$

This formula provides an in-plane incremental modulus of thin film gel under swelling or shrinking. This value which is the tangent modulus of a gel film is dependent on the gel material parameters and current deformation. Figure 6 shows the normalized in-plane incremental modulus of thin film gel varying with the chemical potentials for various initial chemical potential values, ($\mu_0/kT = -1$; $\mu_0/kT = -0.5$; $\mu_0/kT = -0.1$; $\mu_0/kT = -0.01$). It is observed that for lower initial chemical potential, the final incremental modulus in which the chemical potential approaches to zero, can reach up to 50 times of NkT. The larger the initial chemical potential, the lower the fully swelling incremental modulus. The initial incremental modulus is also about two times that of NkT for thin gel film. For all cases, the incremental modulus has a steep increase when chemical potential approaches zero. The incremental modulus for fully swelling are about 50.5, 41.7, 22.5, 8.0 and 3.4 times that of NkT for normalized initial chemical potential values of -1, -0.5, -0.1, -0.01 and -0.001 respectively. Figure 7 shows the in-plane incremental modulus of thin film gel varying with chemical potential for various dimensionless measures of the enthalpy of mixing under condition of initial chemical potential of $\mu_0/kT = -0.5$. It can be observed that the values of incremental modulus abruptly decrease with the increase of dimensionless measures of the enthalpy of mixing, χ. The variation of the incremental modulus with respect to the chemical potential is milder as the value of χ approaches 1.0, and the values of the normalized incremental modulus is about 2.5 times that of NkT at $\chi = 1.0$.

4.2. *The buckling stress and wavelength of thin film gel*

We consider an infinitely thin film gel of initial thickness h_0 attached to an elastic soft material substrate which extends to infinity in z direction. The film and

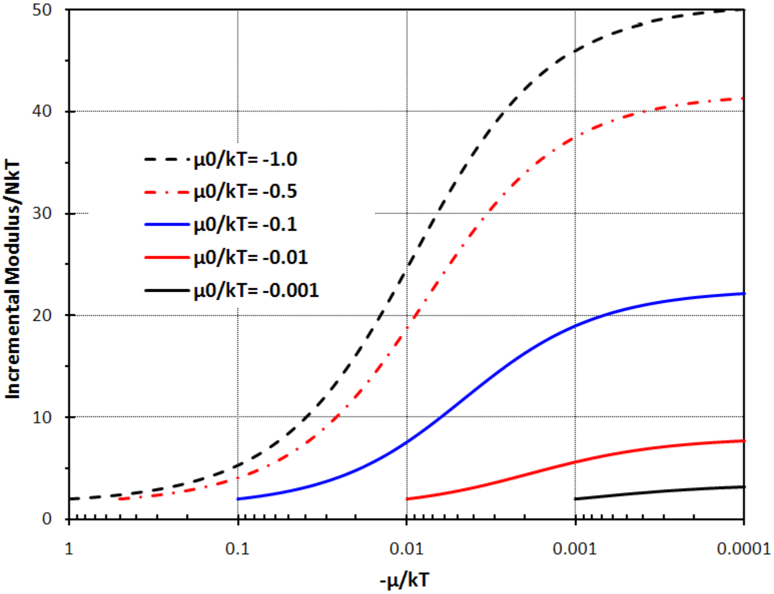


Fig. 6. In-plane incremental modulus of thin film gel varying with chemical potential for different initial chemical potentials ($kT = 4 \times 10^{-21}$ J, $kT/v = 4 \times 10^7$ Pa, $Nv = 10^{-3}$, $\chi = 0.1$).

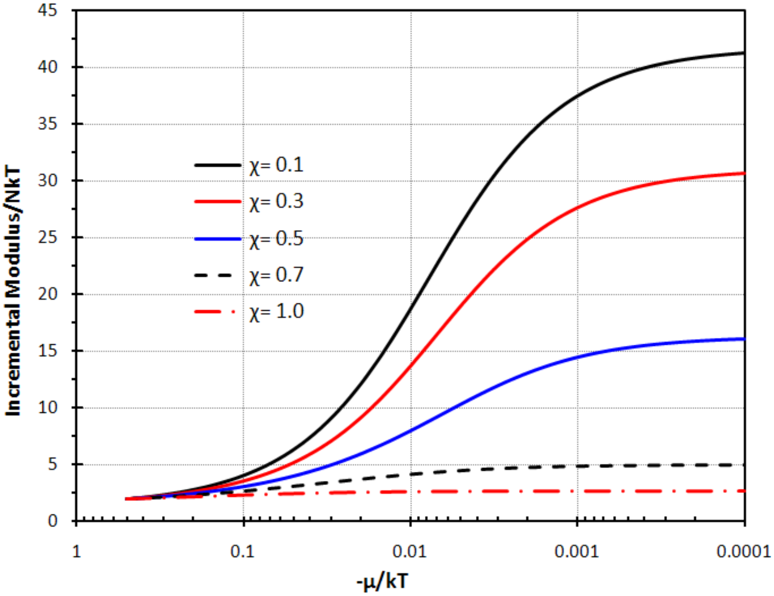
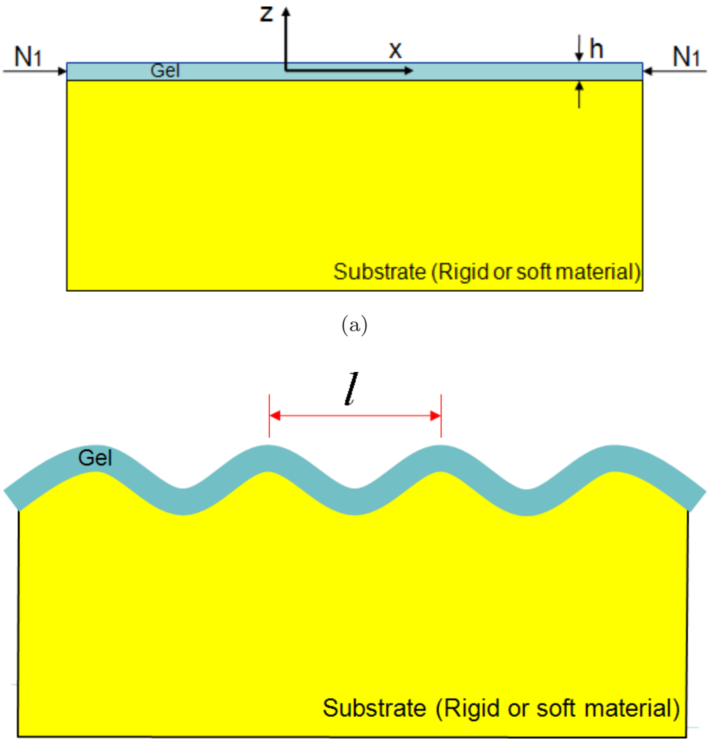


Fig. 7. In-plane incremental modulus of thin film gel varying with chemical potential for different dimensionless measures of the enthalpy of mixing ($\mu_0/kT = -0.5, kT = 4 \times 10^{-21}$ J, $kT/v = 4 \times 10^7$ Pa, $Nv = 10^{-3}$).



(a)

(b)

Fig. 8. Schematics of thin film gel before and after buckling.

substrate are of width b in y direction. For infinitely thin gel with the large b, the system of gel swelling can be regarded as a plane strain status. The gel film is flat as shown in Fig. 8(a) and subjected to a state of in-plane uniform compressive stresses when the gel film swells without buckling. Further swelling of the gel film may cause buckling or wrinkles to develop. We assume the thin film gel to buckle only along x direction with the same wave pattern along the y direction (Fig. 8(b)). The wavelength is normally much larger than its thickness when the gel film wrinkles, and the von Karman elastic nonlinear plate theory can be adopted to model the gel film [Landau and Lifshitz, 1959; Allen, 1969].

Upon wrinkling, let the deflection in z direction be w. The von Karman nonlinear equations, governing the deflection of the gel film are expressed as Allen [1969]

$$D\nabla^4 w - (N_1)\nabla^2 w = -bq, \tag{4.6}$$

where $D = \frac{\tilde{E}bh^3}{12}$, and q is the corresponding normal stress between the gel film and the substrate. $\tilde{E}$ is the incremental modulus of thin film gel as proposed in the preceding subsection. Following Chen and Hutchinson [2004] and Huang *et al.* [2005], we set the shear stress at gel film and soft/stiff gel film substrate to be zero.

Thus the in-plane equilibrium, Eq. (4.6), requires that the membrane forces N_1 ($N_1 = \sigma_1 b h_0$) be uniform in the gel film where σ_1 is the nominal stress of gel in x direction. The membrane strains are also uniform in the gel film. Suppose that the film gel buckles into sinusoidal waves of wavelength l, such that:

$$w = w_m \sin\frac{2\pi x}{l}. \tag{4.7}$$

The stress q corresponding to the buckling deformation may be written as:

$$q = \frac{2A}{l} w_m \sin\frac{2\pi x}{l} \tag{4.8}$$

where $A = \frac{2\pi E_s}{(3-\mu_s)(1+\mu_s)}$ and E_s, μ_s are Young's modulus and Poisson's ratio of the substrate material, respectively.

Substituting Eqs. (4.7) and (4.8) into Eq. (4.6), we can get the equation:

$$D\frac{8\pi^4}{l^4} - N_1\frac{2\pi^2}{l^2} = -\frac{bA}{l}. \tag{4.9}$$

The critical value of N_1 must exist to maintain the gel film in the buckling status and the value can be solved from Eq. (4.9). Since $N_1 = \sigma_1 b h_0$, thus:

$$\sigma_1 = \frac{4\pi^2 D}{b h_0^3}\left(\frac{h_0}{l}\right)^2 + \frac{A}{2\pi^2}\left(\frac{l}{h_0}\right) = \frac{4\pi^2 D}{b h_0^3}\left(\frac{1}{\phi}\right)^2 + \frac{A}{2\pi^2}\phi. \tag{4.10}$$

Equation (4.10) shows that the nominal stress in x direction of the thin film gel is a function of independent variables $\phi = (l/h_0)$ and gel material properties of incremental modulus of gel, which in turn is a function of stretch λ. To minimize σ_1 in Eq. (4.10) with respect to ϕ, we get:

$$\frac{\partial \sigma_1}{\partial \phi} = 0. \tag{4.11}$$

The critical value of wavelength and in-plane stress can be obtained from the above minimization.

$$\phi_{cr} = \left(\frac{l}{h_0}\right)_{cr} = \left(\frac{16\pi^4 D}{b h_0^3 A}\right)^{1/3} \tag{4.12}$$

$$\sigma_{1cr} = \frac{4\pi^2 D}{b h_0^3}\left(\frac{16\pi^4 D}{b h_0^3 A}\right)^{-2/3} + \frac{A}{2\pi^2}\left(\frac{16\pi^4 D}{b h_0^3 A}\right)^{1/3}. \tag{4.13}$$

Using the expression of incremental modulus of film gel, the current rigidity of thin film gel, D, can be expressed as $D = \frac{\tilde{E} b h^3}{12} = \frac{b h_0^3 NkT(1+\lambda^2)\lambda^3}{12}$.

Thus, the critical wavelength and critical nominal stress of buckling of gel film are:

$$\phi_{cr} = \left(\frac{l}{h_0}\right)_{cr} = \left(\frac{4\pi^4 NkT(1+\lambda^2)\lambda^3}{3A}\right)^{1/3} \tag{4.14}$$

$$\sigma_{1cr} = \frac{\pi^2 NkT(1+\lambda^2)\lambda^3}{3}\left(\frac{4\pi^4 NkT(1+\lambda^2)\lambda^3}{3A}\right)^{-2/3} + \frac{A}{2\pi^2}\left(\frac{4\pi^4 NkT(1+\lambda^2)\lambda^3}{3A}\right)^{1/3}. \tag{4.15}$$

It should be noted that the above critical status must also satisfy the thin film gel constitutive relation, Eq. (4.2). Solving Eqs. (4.2), (4.14) and (4.15) simultaneously, we can obtain the analytical solutions of the buckling critical wavelength and buckling critical stress.

For given expression for gel film and substrate stiffness factor NkT/E_s the critical stresses that vary with chemical potential according to Eq. (4.15) are displayed in Fig. 9. The normalized stress from constitutive relation of swelling thin film gel is also included in same figure. Buckling conditions occur at the intersection points of the stress curves from Eq. (4.15) and the constitutive equation curve. We can determine the critical stress values, the corresponding chemical potential under buckling and the critical wavelength for various gel substrate stiffness factors at these intersection points. Figure 10 shows the normalized critical stress, normalized buckling wavelength and buckling chemical potential varying with the gel substrate

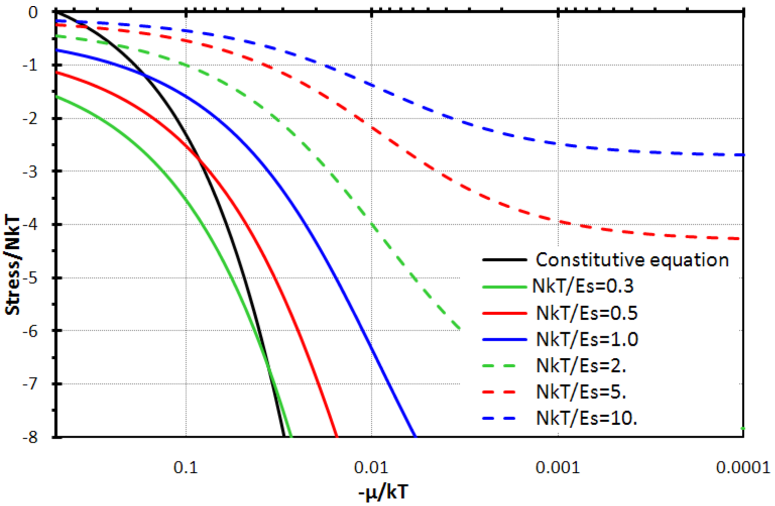


Fig. 9. Normalized stresses varying with chemical potential for different gel film and substrate stiffness factor of NkT/E_s ($\mu_0/kT = -0.5$, $kT = 4 \times 10^{-21}$ J, $kT/v = 4 \times 10^7$ Pa, $\chi = 0.1$, $Nv = 10^{-3}$).

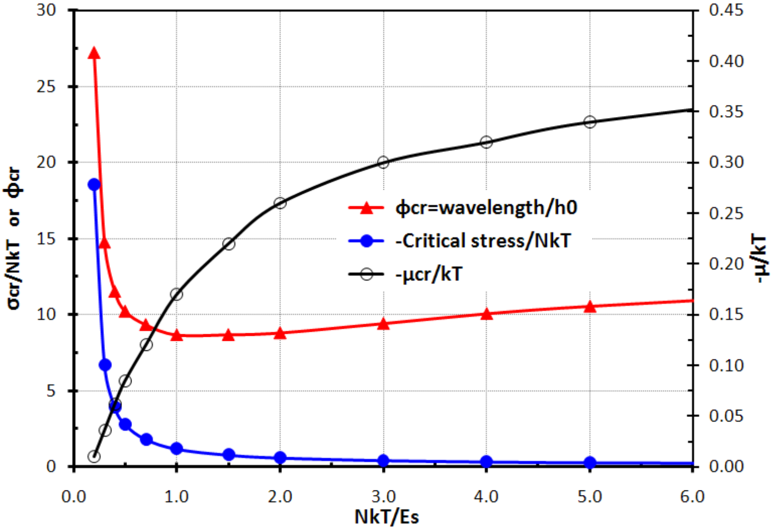


Fig. 10. Normalized critical stress, normalized wavelength and critical chemical potential of thin film gel varying with gel film and substrate stiffness factor of NkT/E_s ($\mu_0/kT = -0.5, kT = 4 \times 10^{-21}$ J, $kT/v = 4 \times 10^7$ Pa, $Nv = 10^{-3}$).

stiffness factors. It can be observed that both the critical chemical potential and the normalized critical stress decrease with the increase of stiffness factor, NkT/E_s. The minimum normalized buckling wavelength of the gel film occurs at about stiffness factor of $NkT/E_s = 1$. For relatively soft substrate, the wavelength ratio rise mildly when the substrate becomes softer. A steep rise is, however, observed as the substrate becoming stiffer for relatively stiff substrate. We can thus conclude that the buckling commences more easily for soft substrate thin film gel. For relatively stiffer substrate, the buckling of thin film gel starts at higher chemical potential (approaching to zero). This agrees with the trend observed in several experimental studies of the gel film buckling [Kwon *et al.*, 2005; Sultan and Boudaoud, 2008]. The stability diagram of the thin film gel as illustrated in Fig. 10 would be useful for gel thin film design.

5. Concluding Remarks

Researchers have observed a variety of instability patterns of slender beam and thin film gel structures due to swelling in various experimental studies. However, both of these have not been well understood. This paper presents analytical solutions of buckling and wrinkle deformation for slender beam and thin film gel structures. The inhomogeneous field theory in a swollen gel in equilibrium with a solvent and mechanical load is adopted to model the materials of gel beam and/or thin film gel structures. The concept of the incremental modulus of gel is proposed and the expressions are derived for the 1-D slender beam gel and thin film gel. The variation of the incremental modulus varies with stretch and/or chemical potential are displayed. The main contribution of the present work is providing analytical solutions for gel buckling and wrinkle. Analytical solutions and the stability diagram described in present study provide a systemic means for further detailed parametric and numerical solutions as the stability and instability regimes can be demarcated and the search become more deterministic. We hope that the problem formulation and the analytical solutions as presented herein will enable other researchers to be able to analyze complex phenomena in gels faster with significantly less computational time and efforts. Further study may be made in an attempt to explain and mimic the shape of a plant leaf from the swelling instability pattern of a gel.

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