

THE INTERACTION BETWEEN MECHANICS AND SWELLING ON THE CAVITATION OF ELASTOMERIC SOLIDS

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Abstract. *In this paper we present a finite-strain theory for the study of the interaction between mechanics and absorption of a swelling agent on the cavitation of elastomeric spheres. The swollen sphere is modeled as a two-component body composed of two incompressible components: the elastic solid and the swelling-agent. The initially dry sphere undergoes a spherically-symmetric deformation induced by mechanical loading, which comprises the ambient pressure and a normal Piola traction, and absorption of a swelling agent from the environment. We also consider that chemical equilibrium prevails at the solid-environment interface and that the chemical potential of the swelling agent in the environment is fixed.*

Keywords: *cavitation, swelling, mechanochemistry*

1. INTRODUCTION

Consider a rubber sphere undergoing a spherically-symmetric deformation induced by a combination of mechanical loading and the absorption of a swelling agent from the environment. In this work, building upon the framework of Duda et al. 2010, we investigate the problem of finding mechanochemical equilibrium states for which the sphere undergoes uniform expansion and uniform swelling. For a uniform equilibrium state, we also investigate the possibility of the existence of an associated cavitated state, with the same degree of swelling but in mechanical equilibrium only, involving a central traction-free spherical cavity. This corresponds to a sudden void formation or cavitation of an initially solid sphere.

More specifically, we suppose that the rubber sphere is subjected to a conservative loading defined in terms of a surface traction encompassing the ambient pressure and an extra normal Piola traction, and that the chemical potential of the swelling agent in the environment is fixed. The swollen rubber is modeled as a two-component body composed of a polymer network and swelling-agent molecules, as described by Treloar's (1975) theory for the swelling of rubber. Accordingly, volume changes undergone by the rubber are due solely to swelling, the degree of which is represented by the polymer volume fraction. Moreover, the free-energy density of the swollen rubber is given by the sum of an elastic contribution for a Gaussian network and a Flory–Huggins mixing contribution. Under these circumstances, we show that a uniform equilibrium state is obtained from the knowledge of the equilibrium polymer volume fraction which in turn is a critical point of the canonical free-energy of the swollen sphere. Furthermore, the corresponding cavitated state, which is obtained from the knowledge of the cavity radius, is a critical point of the total mechanical energy of the swollen sphere. In particular, we investigate the effects of the constitutive parameters entering the theory, namely the number of polymer chains per unit reference volume c_S , the volume v occupied by a swelling-agent molecule, and the Flory–Huggins interaction parameter χ , on the existence, stability and uniqueness of uniform equilibrium states as well as on the existence of cavitated states.

The following remark is in order. Pence & Tsai (2006) have extended the conventional treatment of cavitation in elastic and incompressible spheres (see Ball (1982)) to account for swelling-induced volumetric changes at a fixed degree of swelling. They concluded that a Treloar material always supports cavitation under uniform swelling provided that the load is sufficiently large. Here, however, rather than being given a priori, the degree of swelling is obtained by solving an equation imposing mechanochemical equilibrium. Consequently, the interaction between mechanics and chemistry plays a central role in determining the degree of swelling and the aforementioned conclusion does not hold for the case under consideration. In fact, we show that there is a critical value for the interaction parameter χ below which a Treloar material does not support cavitation regardless of the magnitude of the load. This critical value increases with the product $c_S v$ and is greater than $1/2$, whereby it follows that cavitation is impossible for a good solvent ($\chi \leq 1/2$).

2. PRELIMINARIES

We consider a body \mathcal{B} composed of a polymer network and the molecules of a swelling-agent (or solvent). For simplicity, we suppose that \mathcal{B} is identified with a fixed reference configuration free of solvent molecules (that is, with a dry polymer network). The fields \mathbf{y} , c_S , and c denote the deformation of the polymer network, the number of polymer chains per unit reference volume, and the number of solvent molecules per unit reference volume. The polymer network

is conserved and deforms elastically via two distinct processes, one mechanical and other chemical, or solvent induced, that is responsible for the swelling of \mathcal{B} .

We assume that \mathcal{B} can be described using Treloar's (1975) theory of swelling of rubbers. Accordingly, local volume changes of the solid are related to its composition via the constraint

$$\det \mathbf{F} = 1 + \nu c =: \phi^{-1}, \quad (1)$$

where $\mathbf{F} := \nabla \mathbf{y}$ is the deformation gradient, ν is the volume of one solvent molecule, and ϕ is the polymer volume fraction. In addition, the free-energy density is given by

$$\hat{\psi}(\mathbf{F}, \phi) = \hat{\psi}_e(\mathbf{F}) + \hat{\psi}_m(\phi) = \frac{\nu}{2}(|\mathbf{F}|^2 - 3) + \frac{k_B T}{\nu} \left(\frac{1 - \phi}{\phi} \right) (\ln(1 - \phi) + \chi \phi), \quad (2)$$

where $\hat{\psi}_e(\mathbf{F})$ is the elastic free-energy density and $\hat{\psi}_m(\phi)$ is the Flory–Huggins mixing energy. Here and throughout this paper, $\nu = c_S k_B T$ is the shear modulus, k_B is the Boltzman constant, T is the absolute temperature, and χ is the Flory–Huggins interaction parameter. The Flory–Huggins parameter characterizes the interaction between polymer and solvent molecules: if $\chi > 0$ ($\chi < 0$) then there is a net repulsion (attraction) between polymer and solvent molecules.

Suppose that \mathcal{B} is immersed in a special environment involving a conservative loading environment with potential energy \mathcal{L} and a chemical reservoir wherein the chemical potential of the swelling agent is equal to μ_a . In this case, the net potential-energy of \mathcal{B} is defined by

$$\mathcal{F}(\mathbf{y}, \phi) = \int_{\mathcal{B}} (\hat{\psi}(\mathbf{F}, \phi) - \mu_a c) dV - \mathcal{L}(\mathbf{y}). \quad (3)$$

Notice that, for a fixed composition, the net potential-energy of \mathcal{B} coincides, modulo a inconsequential constant, with its mechanical energy. Under the assumption that chemical equilibrium prevails at the body-environment interface, Duda et al. (2010) found that mechanochemical equilibrium states correspond to critical points of the net potential-energy functional subject to the constraint (1). In addition, on the basis of the energy criterion for stability, an equilibrium state is stable if it is a local minimum of \mathcal{F} and otherwise is unstable.

2.1 Geometry

We now suppose that \mathcal{B} is a spherical specimen of radius B subjected to a spherically-symmetric load applied on its boundary. Due to spherical symmetry the deformation \mathbf{y} is characterized by a scalar-valued radial mapping f such that $r = f(R)$, where r and R are the radial coordinates of a material point in the deformed and reference configuration, respectively.

The matrix $[\mathbf{F}]$ corresponding to deformation gradient \mathbf{F} in the spherical basis is given by

$$[\mathbf{F}] = \text{diag}\{\lambda_R, \lambda, \lambda\} \quad \text{where} \quad \lambda_R = f'(R), \quad \lambda = \frac{f(R)}{R}. \quad (4)$$

In this case, it follows from the constraint (1) that

$$\lambda_R(R) \lambda^2(R) = \frac{f^2(R) f'(R)}{R^2} = \frac{1}{\phi(R)} \quad (5)$$

which implies that ϕ depends only on R and, after integration, that

$$f^3(R) = r_c^3 + 3 \int_0^R \frac{x^2 dx}{\phi(x)}, \quad (6)$$

where $r_c := f(0)$. Therefore, it follows that λ is given by

$$\lambda(R) = \frac{1}{R} \left(r_c^3 + 3 \int_0^R \frac{x^2 dx}{\phi(x)} \right)^{\frac{1}{3}}. \quad (7)$$

In these simple circumstances, the elastic free-energy density (2) specializes to

$$\hat{\psi}_e(\mathbf{F}) = \frac{\nu}{2}(\lambda_R^2 + 2\lambda^2 - 3) = \frac{\nu}{2} \left(\frac{1}{\lambda^4 \phi^2} + 2\lambda^2 - 3 \right) =: \bar{\psi}_e(\lambda, \phi). \quad (8)$$

From now on we assume that the chemical environment corresponds to a pure and incompressible solvent at fixed pressure p_a . This implies that chemical potential (of the solvent) in the environment can be expressed as $\mu_a = \nu p_a$, where

p_a is the ambient pressure in the environment. In addition to the ambient pressure p_a , we consider a normal Piola traction σ , therefore, in view of (3), the corresponding net potential energy is given by

$$\mathcal{F}(r_c, \phi) = 4\pi \int_0^B (\bar{\psi}(\lambda(R), \phi(R)) - p_a \nu c(R)) R^2 dR - 4\pi B^3 \sigma (\lambda_B - 1) + \frac{4\pi B^3}{3} p_a (\lambda_B^3 - 1) \quad (9)$$

where $\lambda_B = \lambda(B)$, determined by (7) and, recalling the definitions (2) and (8) of $\hat{\psi}_m$ and $\bar{\psi}_e$, $\bar{\psi}$ is determined via $\bar{\psi}(\lambda, \phi) = \bar{\psi}_e(\lambda, \phi) + \hat{\psi}_m(\phi)$.

2.2 Uniform equilibrium states

We now seek equilibrium solutions for which $r_c = 0$, so that cavitation does not occur, and ϕ is uniform. In this case, the energy (9) reduce to the function \mathcal{F} of ϕ given by

$$\mathcal{F}(\phi) := \frac{4\pi B^3 \nu}{3} \left(h(\phi) - 3\bar{\sigma}(\phi^{-\frac{1}{3}} - 1) \right) \quad (10)$$

$$\text{with } \bar{\sigma} = \frac{\sigma}{\nu}, \quad h(\phi) = \frac{3}{2}(\phi^{-\frac{2}{3}} - 1) + \alpha \left(\frac{1-\phi}{\phi} \right) (\ln(1-\phi) + \chi\phi), \quad \alpha = \frac{1}{c_S \nu}, \quad (11)$$

where $\bar{\sigma}$ is dimensionless measures of applied Piola traction and α measures the relative importance of the elastic and mixing contributions of the free-energy density. Importantly, the higher the value of α , the lower (higher) is the relevance of the elastic (mixing) contribution. It is noteworthy that when the polymer volume-fraction ν is constant, the ambient pressure p_a that generally contributes to (10) cancels.

Our objective is to obtain the equilibrium values of ϕ for the prescribing Piola traction. This entails determining the critical points of \mathcal{F} . A detailed discussion of these issues follows.

From (10), the first and second derivatives of the function \mathcal{F} are given by

$$\mathcal{F}'(\phi) = -\frac{\nu\pi B^3}{3} \phi^{-\frac{4}{3}} (\hat{\sigma}(\phi) - \bar{\sigma}) \quad \text{and} \quad \mathcal{F}''(\phi) = \frac{\nu\pi B^3}{3} \left(\frac{4}{3} \phi^{-\frac{7}{3}} (\hat{\sigma}(\phi) - \bar{\sigma}) - \phi^{-\frac{4}{3}} \hat{\sigma}'(\phi) \right) \quad (12)$$

where $\hat{\sigma}$ is defined by

$$\hat{\sigma}(\phi) = \phi^{-\frac{2}{3}} \left(\phi^{\frac{1}{3}} + \alpha (\ln(1-\phi) + \phi + \chi\phi^2) \right). \quad (13)$$

To determine the equilibrium values of the polymer volume-fraction ϕ , we must solve the equation $\mathcal{F}'(\phi) = 0$, which, by (12)₁, is equivalent to solving the equation

$$\bar{\sigma} = \hat{\sigma}(\phi). \quad (14)$$

In addition, a solution ϕ to (14) is stable (that is, a local minimum of \mathcal{F}) whenever $\mathcal{F}''(\phi) \geq 0$ or, by (12)₂, whenever $\hat{\sigma}'(\phi) \leq 0$. It is worthwhile to recall that a solution of (14) defines the mechanochemical equilibrium state of a spherical body for which the degree of swelling is uniform and the corresponding deformation, with respect to an unswollen spherical body, is spherically symmetric and homogenous. Furthermore, observe that a two-phase equilibrium state of a spherical body, in which each phase is associated with one and only one solution of (14), is impossible since the corresponding deformation, homogenous and spherically symmetric in each phase, would not be continuous.

We begin by investigating the issue of existence of solutions to (14). We observe that $\hat{\sigma}$ is continuous on the interval $(0, 1)$

$$\lim_{\phi \rightarrow 0} \hat{\sigma}(\phi) = +\infty \quad \text{and} \quad \lim_{\phi \rightarrow 1} \hat{\sigma}(\phi) = -\infty.$$

Therefore, $\hat{\sigma}$ maps $(0, 1)$ onto the real line. This implies that (14) admits a solution ϕ_e for any choice of $\bar{\sigma}$. As discussed previously, such a solution is stable only if $\hat{\sigma}'(\phi_e) \leq 0$. Multiple solutions are possible whenever $\hat{\sigma}' > 0$ holds over a portion of $(0, 1)$. Hence, the behavior of $\hat{\sigma}$ is crucial for the analysis of both the stability and the uniqueness of solutions. In what follows we investigate how the behavior of $\hat{\sigma}'$ is affected by the parameters χ and α .

To investigate the influence of the parameters χ and α on the behavior of $\hat{\sigma}'$, we introduce the function

$$\hat{\chi}(\phi, \alpha) := \frac{3}{4(1-\phi)} + \frac{1}{2} \phi^{-2} (\ln(1-\phi) + \phi) + \frac{1}{4\alpha} \phi^{-\frac{5}{3}}. \quad (15)$$

A simple calculation using the definition of $\hat{\sigma}$ shows that, for a given α , $\hat{\sigma}'(\phi)$ and $(\chi - \hat{\chi}(\phi, \alpha))$ have the same sign. Moreover, for each α , the minimum of $\hat{\chi}$ is attained at a value ϕ_c of ϕ in $(0, 1)$, that is, $\chi_\alpha := \hat{\chi}(\phi_c, \alpha) \leq \hat{\chi}(\phi, \alpha)$. As a result, it follows that if $\chi \leq \chi_\alpha$, then $\hat{\sigma}'(\phi) \leq 0$ for all ϕ in $(0, 1)$, which implies that $\hat{\sigma}$ decreases monotonically.

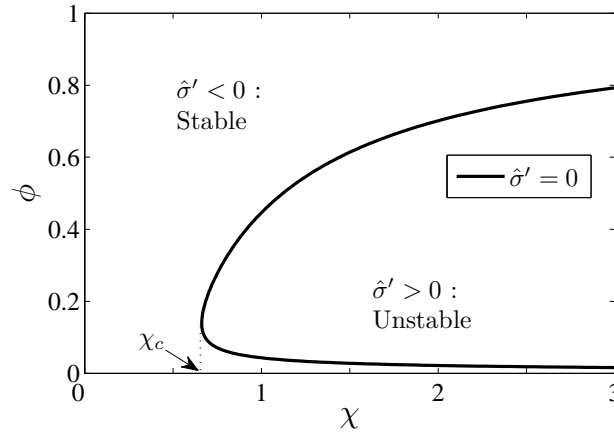


Figure 1: (ϕ, χ) -diagram at constant α , with the solid line separating unstable and stable regimes.

Otherwise, if $\chi > \chi_\alpha$, then, by continuity, $\hat{\sigma}'(\phi) \leq 0$ and $\hat{\sigma}'(\phi) > 0$ over two non-empty and complementary portions of $(0, 1)$, which implies that $\hat{\sigma}$ is nonmonotonic. These conclusions are depicted in Figure 1, which shows the behavior of $\hat{\sigma}'$ in the (ϕ, χ) -diagram for a fixed value of α . It contains two complementary regions in which $\hat{\sigma}' < 0$ (the stable regime) and $\hat{\sigma}' > 0$ (the unstable regime) separated by the set of points for which $\hat{\sigma}' = 0$. In addition, it shows that the condition $\chi < \chi_\alpha$ implies that $\hat{\sigma}' < 0$ and, consequently, that $\hat{\sigma}$ is monotonically decreasing and therefore (14) admits a unique and stable solution for a given $\bar{\sigma}$. On the other hand, for $\chi > \chi_\alpha$, the monotonicity of $\hat{\sigma}$ is lost, which indicates the possibility of multiple solutions. This fact is better illustrated in Figure 2, which depicts a typical (σ, λ) -diagram for $\chi > \chi_\alpha$, in which case ϕ_1 and ϕ_2 satisfy the conditions $\hat{\sigma}'(\phi) = 0$, $\sigma_1 = \hat{\sigma}(\phi_1)$, and $\sigma_2 = \hat{\sigma}(\phi_2)$. Using Figure 2, it follows that:

- If $\sigma < \sigma_1$ or $\sigma > \sigma_2$, (14) admits a unique and stable solution. Notice that $\sigma_1 > 0$ which implies that $\sigma \leq 0$ is sufficient for unique and stable solutions. In other words, the solution is unique for free swelling ($\sigma = 0$) and for compressive Piola traction ($\sigma < 0$);
- If $\sigma = \sigma_1$ or $\sigma = \sigma_2$, (14) admits two solutions, both of which stable;
- If $\sigma_1 < \sigma < \sigma_2$, (14) admits three solutions, two stable and one unstable.

Now we investigate how χ_α varies with α . As can be seen in Figure 3, χ_α decreases monotonically with α and obeys $\lim_{\alpha \rightarrow +\infty} \chi_\alpha = 1/2$. Recalling that ν can be written as $\nu = k_B T / \alpha v$ and considering T and v fixed, this implies that the softer the solid (that is, the lower the shear moduli ν), the lower is the threshold χ_α demarking the boundary between unique and multiple solutions to (14). Note that χ_α is bounded below by the value $1/2$ corresponding to the unattainable limit where the polymer network vanishes.

For a given set of environmental conditions, the existence of two distinct values for the polymer volume fraction associated with stable equilibrium states indicates the possibility of volume phase transition between swollen and shrunken phases, which are defined by the lower and higher values of the equilibrium polymer volume fraction, respectively. This type of phase transition has been the subject of many theoretical and experimental works since its theoretical prediction by Dusek & Patterson (1968) and experimental observation by Tanaka (1978). Consequently, there is a vast literature on the subject and the reader is referred to the survey articles by Onuki (1993), Hirotsu (1994), Shibayama & Tanaka (1993), Li & Tanaka (1992), and Doi (2009). However, it is worth noticing that the present theory, which is based on the Treloar's theory of swelling, precludes phase transition during free swelling, i.e., when $\sigma = 0$. The same occurs within the context of the Flory's theory of swelling, which differs from Treloar's theory via a logarithmic contribution to the elastic energy, unless the interaction parameter χ is concentration dependent (Erman & Flory, (1986)). On the other hand, Flory's theory of swelling of ionized gels predicts that volume phase transition is possible even if χ is concentration independent (see Hirotsu (1994)), which is due to the presence of counter ions. In this regard, the stress σ plays a role similar to the counter ions to bring about phase transition. Observe that the requirement of continuity of the deformation rules out the possibility of the coexistence of swollen and shrunken phases separated by a sharp phase boundary in a two-phase equilibrium state. However, the coexistence between these phases is possible provided that the phase boundary is diffuse across which the deformation is presence of inhomogeneous (see Sekimoto (1989), Hirotsu (1994), and Doi (2009)).

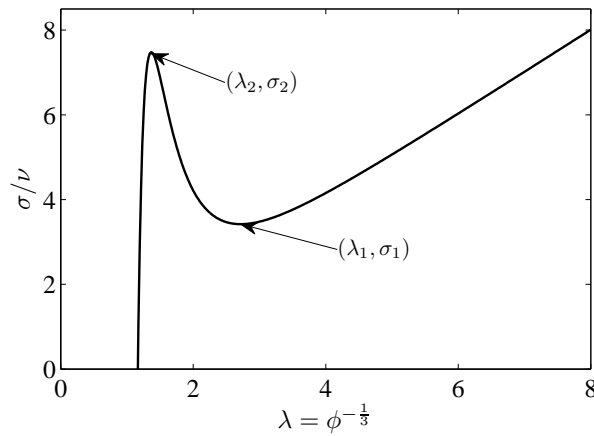


Figure 2: (σ, λ) -diagram at constant α . ϕ_1 and ϕ_2 are such that $\hat{\sigma}'(\phi) = 0$, $\sigma_1 = \nu \hat{\sigma}(\phi_1)$ and $\sigma_2 = \nu \hat{\sigma}(\phi_2)$.

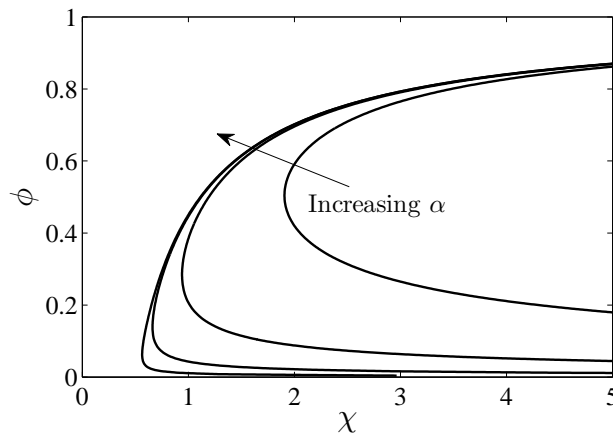


Figure 3: (ϕ, χ) -diagram for different values of α . The solid lines separate unstable and stable regimes for the corresponding value of α .

2.3 Cavitation analysis

Consider a spherical specimen in mechanochemical equilibrium as described above. We now investigate the possibility of the opening of a load-free cavity in the center of the specimen. We assume that the cavitation process is very so fast that there is insufficient time for mass redistribution to occur and that mechanical equilibrium is attained instantaneously. Under these circumstances, ϕ remains uniform and is determined by (14), whereas the cavity radius r_c is obtained by solving a purely the mechanical part of the problem.

Form ϕ uniform, it follows from (7) that

$$\lambda(R) = \frac{1}{R} \left(r_c^3 + \frac{R^3}{\phi} \right)^{\frac{1}{3}}. \tag{16}$$

In particular, evaluating (16) at the outer boundary $R = B$ of the sphere yields

$$\lambda_B := \lambda(B) = \left(\frac{r_c^3}{B^3} + \frac{1}{\phi} \right)^{\frac{1}{3}}. \tag{17}$$

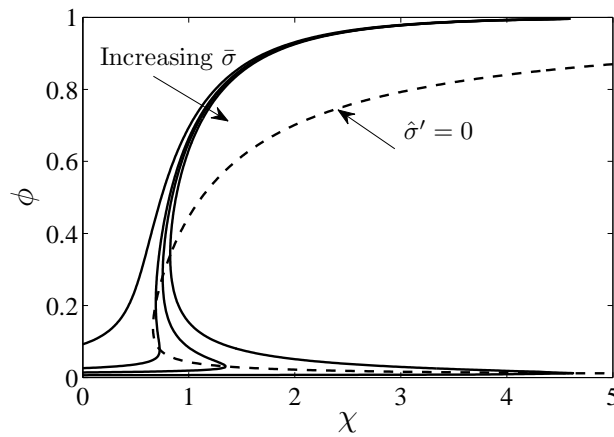


Figure 3: (ϕ, χ) -diagram for a given value of α . Each solid line represents the equilibrium values of ϕ for the corresponding $\bar{\sigma}$. The dashed line separates unstable and stable regimes.

On the other hand, since the cavity surface is assumed to be load free, we can base our analysis on the expression (9), which now is functions of r_c and, modulo inconsequential additive constants, can be written as

$$\mathcal{F}^c(r_c) = 4\pi \int_0^B \bar{\psi}_e(\lambda, \phi) R^2 dR - 4\pi b^3 \sigma (\lambda_B - 1) + \frac{4\pi B^3}{3} p_a (\lambda_B^3 - 1) \quad (18)$$

Notice that (18) represents the total energy of an elastic sphere undergoing a prescribed swelling and subjected to a normal surface traction defined in terms of the pressure p_a and an applied normal Piola traction σ . The cavitation analysis carried out here for a given environment therefore consists of obtaining the critical points of the corresponding total energy.

Following Ball (1982), we evaluate the integral in (18) after introducing a change of variables defined by (16). In fact, for $u(\lambda) = \bar{\psi}_e(\lambda, \phi)$, it can be showed that

$$\int_\epsilon^B u(\lambda) R^2 dR = -\phi^2 r_c^3 \int_{\lambda(\epsilon)}^{\lambda_B} u(\lambda) \frac{\lambda^2}{(1 - \phi \lambda^3)^2} d\lambda = -\frac{\phi r_c^3}{3} \left(\frac{u(\lambda)}{1 - \phi \lambda^3} \Big|_{\lambda(\epsilon)}^{\lambda_B} - \int_{\lambda(\epsilon)}^{\lambda_B} \frac{u'(\lambda)}{1 - \phi \lambda^3} d\lambda \right), \quad (19)$$

with $\epsilon > 0$. On using (8) and (16), it is immediate to conclude that $\lim_{\epsilon \rightarrow 0} \lambda(\epsilon) = \infty$ and $\lim_{\epsilon \rightarrow 0} u(\lambda(\epsilon)) / (\phi \lambda^3(\epsilon - 1)) = 0$. A single calculation shows that (19) is reduced to

$$\int_0^B u(\lambda) R^2 dR = \lim_{\epsilon \rightarrow 0} \int_\epsilon^B u(\lambda) R^2 dR = 4\pi B^3 \nu \left(\lambda_B^2 - \frac{1}{2\phi \lambda_B} - \frac{1}{2} \right). \quad (20)$$

It follows then that the energy \mathcal{F}^c can be written as

$$\frac{1}{4\pi B^3 \nu} \mathcal{F}^c(r_c) = \lambda_B^2 - \frac{1}{2\phi \lambda_B} - \frac{1}{2} - \bar{\sigma} (\lambda_B - 1) + \frac{1}{3} \bar{p}_a (\lambda_B^3 - 1) \quad \text{with} \quad \bar{\sigma} = \frac{\sigma}{\nu}, \quad \bar{p}_a = \frac{p_a}{\nu}. \quad (21)$$

For a given σ , the cavitation problem consists of finding a cavity radius $r_c > 0$ such that $d\mathcal{F}^c/dr_c = 0$. On using (21), this implies that

$$\bar{\sigma} = \hat{\sigma}_c(r_c, \phi) := \frac{1}{2\lambda_B^2 \phi} + 2\lambda_B + \bar{p}_a \lambda_B^2, \quad \text{with} \quad \bar{\sigma} = \frac{\sigma}{\nu}, \quad \bar{p}_a = \frac{p_a}{\nu}, \quad (22)$$

where λ_B is related with r_c through (17) and ϕ is solution of (14). We investigate the the issues of existence and uniqueness for this problem with an emphasis on how these issues are affected by the chemical parameters α and χ .

First we investigate the conditions under which nucleation occurs. For this, we recall that the normalized nucleation load $\bar{\sigma}_N$ is the value of the load $\bar{\sigma}$ for which $r_c = 0$. On using (17) and (22) we find that the normalized nucleation load is given by

$$\bar{\sigma}_N = \frac{5}{2} \phi^{-\frac{1}{3}} + \bar{p}_a \phi^{-\frac{2}{3}}. \quad (23)$$

Using equations (23) and (14), it follows that the nucleation is possible provided that ϕ satisfies the equation:

$$\alpha \underbrace{(\ln(1 - \phi) + \phi + \chi \phi^2)}_{g(\phi)} - \frac{3}{2} \phi^{\frac{1}{3}} - \bar{p}_a = 0. \quad (24)$$

Since g is strictly negative for $0 < \phi < 1$, (24) does not admit solution for a good solvent ($\chi \leq 1/2$). On the other hand, for a bad solvent ($\chi > 1/2$), we observe that:

$$g'(\phi) = 2\chi \frac{\phi}{1-\phi} (\phi_m - \phi), \quad \phi_m = \frac{2\chi - 1}{2\chi} \in (0, 1). \quad (25)$$

Therefore, it follows that ϕ_m is the only critical point of g . Furthermore, $g(\phi_m)$ corresponds to the maximum value of g . On using the properties of the functions involved in (24), it can be shown that a condition necessary and sufficient for the existence of a solution of (24) is

$$\alpha g(\phi_m) \geq \frac{3}{2} \phi_m^{\frac{1}{3}} + \bar{p}_a. \quad (26)$$

In particular, for a given α the equality (26) provides a special value of χ , say χ_α^N , below which nucleation is impossible. This is depicted in Figure 5, which also shows that for a given $\chi > \chi_\alpha^N$ equation (24) admits two solutions, where the largest (smallest) one corresponds to an stable (unstable) solution for the intact sphere. As indicated in Figure 6, the critical value χ_α^N decreases with α . Figure 7 illustrates the dependency of the nucleation load on both χ and α , corresponding to the solution giving the stable ϕ . Notice also that, for $\chi_\alpha < \chi < \chi_\alpha^N$, multiple uniform equilibrium solutions are possible, but that the nucleation of a cavity is impossible.

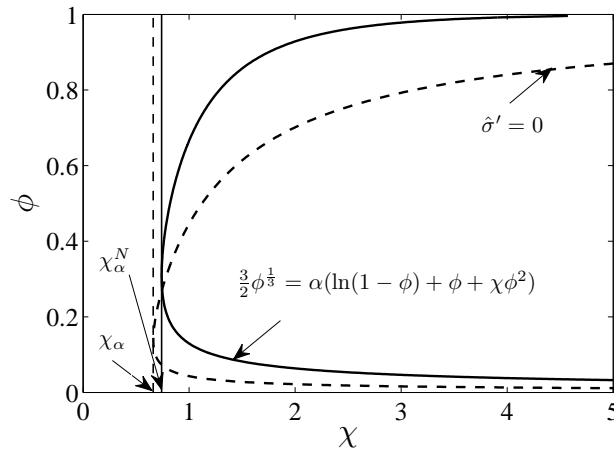


Figure 5: (ϕ, χ) -diagram for a fixed value of α . The solid line represents the solution of the nucleation condition; the dashed line separate stable and unstable regimes for the intact sphere.

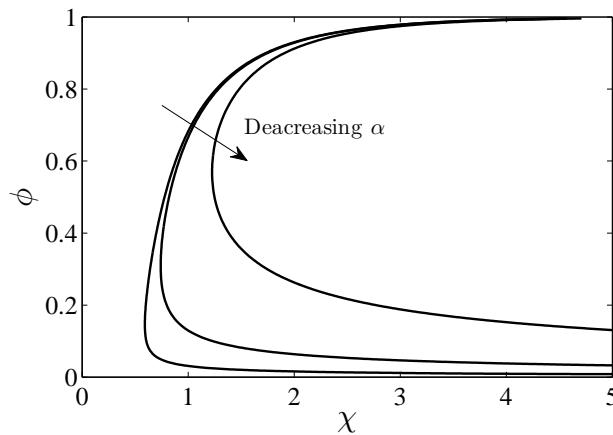


Figure 6: The solid lines represent solutions (24) in (ϕ, χ) -diagram for different values of α .

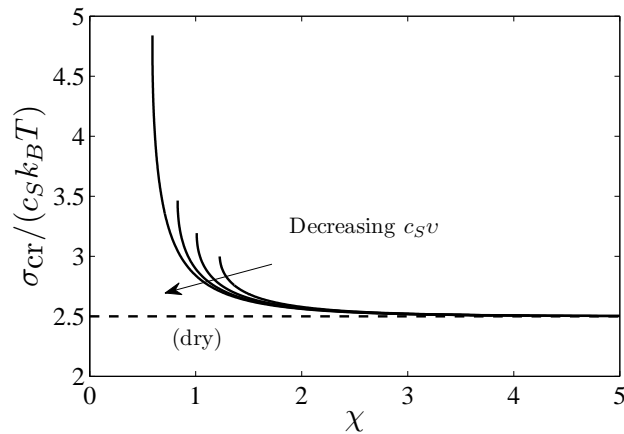


Figure 7: Influence of χ and α on the nucleation load $\bar{\sigma}_N$.

Now we investigate the cavitation problem for $r_c > 0$. Again, we appeal for the (ϕ, χ) -diagram for a given value of α represented in Figure 8. It shows solutions of (14) and (22) for different values of r_c . It is interesting to observe that, for a given $\chi > \chi_\alpha^N$, there is a maximum admissible value for r_c .

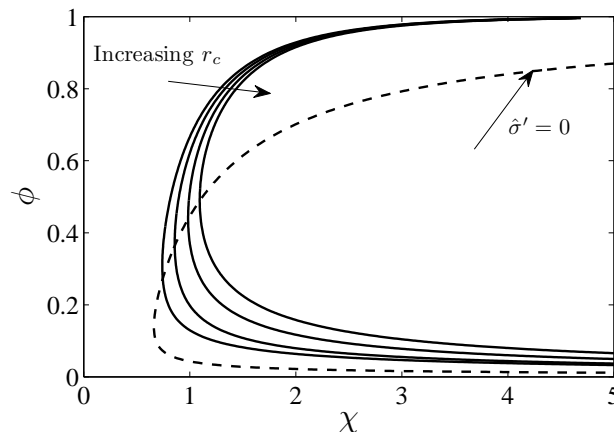


Figure 8: (ϕ, χ) -diagram for a fixed value of α . The solid lines represent the solutions for the cavitation problem for different values of r_c ; the dashed line separate stable and unstable regions for the intact sphere.

Additional understanding can be gained through the analysis of the $(\bar{\sigma}, \chi)$ -diagram in Figure 9. This diagram shows two set of curves corresponding to two set of equations: equation (14) for a fixed value of α and two values of χ ; equation (22) for different values of the normalized cavity radius r_c . The second of these shows that $\bar{\sigma}$ is an increasing function of r_c . Solutions for the cavitation problem correspond to the intersection of these two set of curves.

3. CONCLUSIONS

Following Duda et al. (2010), we present a theoretical framework for investigating the influence of the mutual interaction of mechanics and absorption of a swelling agent on the occurrence of multiphase equilibria and cavitation in elastic spheres. More specifically, we consider an initially dry and intact, i.e. not hollow, elastic sphere undergoing a spherically-symmetric deformation and swelling induced by the combined action of mechanical loads, defined in terms of the ambient pressure and a normal Piola traction, and absorption of a swelling agent. The swollen sphere is viewed as a two-component body composed of two incompressible components, the elastic solid and the swelling-agent. The state of the swollen sphere is, therefore, fully characterized by the distribution of the swelling agent and the radius of a central hole, which is zero if the swollen sphere remains intact. Under the conditions that the ambient chemical potential of the

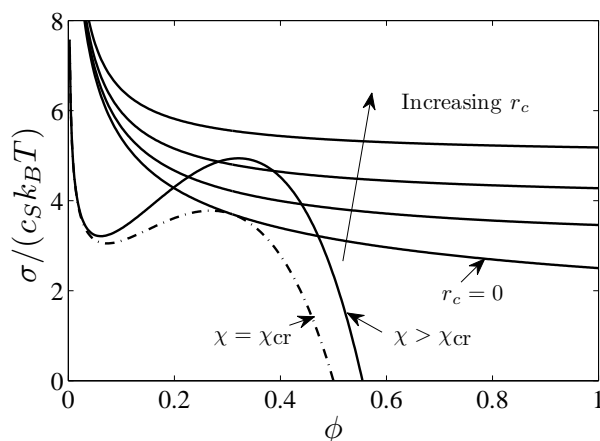


Figure 9: $(\bar{\sigma}, \chi)$ -diagram for a fixed value of α .

swelling agent is fixed and that chemical equilibrium prevails at the solid-environment interface, we describe the intact state, namely uniform equilibrium state. For this state, we also investigate the possibility of cavitation, i.e. the sudden appearance of a central traction-free cavity. Central for the analysis presented here is the notion of net-free energy potential, the definition of which requires the specification of the environment and the prescription for the constitutive equation for the free-energy density. In this paper, we extended the conventional treatment of cavitation in elastic and incompressible spheres introduced by Ball (1982) to account for the presence of a given degree of swelling. Our approach, however, differ in one crucial aspect: the degree of swelling is obtained rather than being given a priori. In fact, the degree of swelling is obtained by solving equations that account for the simultaneous interaction of mechanics and absorption. Therefore, this study may be of some relevance in regard to environment stress cracking in elastomers as well as failure in responsive polymeric gels, i.e. for gels that respond to changes in environment.

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