Phase coexistence in temperature–driven volume transition in hydrogels and interface localization

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Abstract

We propose a detailed analysis of the so–called volume transition phenomenon in hydrogels establishing the ranges of both temperature and traction which allow for the coexistence of two different phases, the swollen and the shrunk one. Within the framework of continuum mechanics and considering in particular a one dimensional problem we show that assuming different models for the Flory parameter delivers different conclusions, in terms of admissible coexisting equilibria of the system. At the end, we study the position of the interface between the coexisting phases considering an augmented free energy which depends not only on the volume change but also on its gradient. The connection profile between the phases is captured numerically by implementing a proper finite element code.

Keywords: thermally–driven volume transition, swelling, gels

1. Introduction

Soft active materials have been largely employed to realize actuators in which deformations and displacements are triggered through a wide range of external stimuli (electric field, pH, temperature and solvent absorption). Interestingly, in several polymer gels changes in external stimuli can induce drastic changes in the volume of the gel. Under some conditions, swelling or shrinking can be discontinuous, so that a minute change in the external stimuli can cause a large change in volume. This feature can be interpreted as a phase transition in the system made of cross–linked polymer network and solvent, being the two swollen and shrunk phases characterized by a different network density. In addition to the scientific importance of completely understanding the relationship between the structural properties and the macroscopic behavior of hydrogels, improving the knowledge of volume transition can enhance the application of gel technology towards switches, sensors, memories, display units, and mechano–chemical transducers.

Temperature–induced discontinuous phase transitions were firstly reported in prolacrylamide gels in the ’80 (Tanaka, 1978, 1980), where the differences between a nearly continuous transition...
and a discrete transition due to the curing time of the polymer were observed. A behavior in con-
trast to the ionized acrylamide gels, which are swollen at high temperatures, was later observed
in nonionic N–isopropylacrilamide (NIPA) gels, where a discontinuous volume transition in water
was observed only by changing the temperature (Hirokawa and Tanaka, 1984). The mechanism
was attributed to a change in the balance between hydrophilic and hydrophobic interactions,
as a matter of fact in a collapsed state the polymer chains of NIPA, which have hydrophobic
properties, are hydrophobic, while in a swollen state they are hydrophilic. The phenomenon was
further studied in (Hirose et al., 1987), where it was identified as a phase transition universal to
all gels and similar to the gas–liquid phase transition, hence as a phenomenon depending on the
environmental conditions such as temperature and pressure.

Volume transition in NIPA was also investigated in (Hirotu, 1987); therein, the results of the
experiments were analyzed on the basis of the Flory–Rehner thermodynamic theory, in which
assigns the interactions between polymer and solvent are accounted for by a scalar parameter,
denoted Flory parameter or polymer–solvent interaction parameter (Flory and Rehner I, 1943;
Flory and Rehner II, 1943; Doi, 1996, 2009; Luantonio et al., 2013). The Flory parameter is
dimensionless and temperature–dependent and it represents the dis–affinity between the polymer
and the solvent; if it increases, solvent molecules are expelled from the gel and the gel shrinks,
while if it decreases, the gel swells (Doi, 2009). The Flory parameter has a primary role in
the analysis of temperature–dependent volume phase transition as it dictates the way in which
temperature influences free energy. In (Hirotu, 1987), the Flory parameter was considered as
consisting of an enthalpic and an entropic contribution, and it is expressed as a linear function
of inverse absolute temperature, and quantitatively characterized for different solvents. It was
also shown as the Flory parameter in NIPA/ethanol, NIPA/methanol, and NIPA/n–propanol is
almost independent on temperature, whereas it depends on temperature, in NIPA/water, and
changes abruptly at the transition.

In the same years, the influence of uniaxial tension on volume phase transition in poly–
N–isopropylacrilamide (PNIPAM)/water gels was investigated in (Hirotu and Homuki, 1989),
through a setup which overcame the difficulties related to impose a homogeneous uniaxial tension
on gels which are fragile whereas undergoing volume phase transition. An extensive experimental
research on the phase transition behaviors of NIPA gels under mechanical constraint and load
was carried out in (Suzuki and Kojima, 1994; Suzuki et al., 1997), in presence of small and
large elongation ratios. Therein, it was shown that the elastic response, especially in the case
of small deformations, was quite successfully described by the phenomenological model based
on the Flory–Rehner free energy as the deformation was small enough to not disturb the as-
sumption of Gaussian behavior of polymer networks. In (Suzuki et al., 1999), an investigation
on phase coexistence in NIPA gels with and without mechanical constraint was discussed. The
investigation was performed on cylindrical gels of sub-millimeter diameter; it was found that,
under a macroscopic mechanical constraint (isometric) the phase transition takes place at higher
temperatures, and the ratio of the swollen to the collapsed phase can be controlled by uniax-
ial stress. Moreover, it was also noted that phase coexistence in neutral polymer gels, that is,
coexistence of a locally collapsed and a swollen state, is in general stable and experimentally
observable when the gel suffers a mechanical constraint.

In spite of the large amount of data on temperature–dependent volume transition in gels avail-
able since ’80s, multiphysics–based models of thermally–driven volume transition in hydrogels
have only been recently proposed (Ji et al., 2006; Birgessson et al., 2008; Cai and Suo, 2011; Ding
et al., 2013; Drozdov, 2014). We wish to make some progress towards addressing this question.

Our approach is based on the Flory–Rehner theory which assigns a free energy comprehensive
of an elastic and a mixing component to the hydrogel. A key element of the model is the Flory
parameter, which is assumed temperature–dependent. As discussed in (Drozdov, 2014), different
models have been proposed in the Literature to account for the temperature–depending pattern of the Flory parameter. Here, we consider two different patterns: the first was proposed in (Hirotsu and Honuki, 1989) for NIPA hydrogels; the second, also used in (Cai and Suo, 2011; Ding et al., 2013), was proposed in (Afroze et al., 2000) for aqueous solutions of uncrosslinked PNIPAM. In both models, the Flory parameter depends linearly on the volume fraction of polymer within the gel; on the contrary, the dependence on temperature is different: whereas the first is based on a linear dependence of the Flory parameter on the inverse of the absolute temperature, the second considers a linear dependence on the temperature itself. Moreover, also the presence of a traction acting on the hydrogel is energetically taken into account. We propose a detailed analysis aimed to establish the ranges of both temperature and traction which allow for the coexistence of two different phases (swollen and shrunk). We show as assuming different models for the Flory parameter delivers different conclusions.

A distinguishing part of this study is the setup of a gradient theory which is used to localize the position of the interface between the two coexisting phases differing in the degree of swelling. As a main tool the Landau energy functional is considered with a term accounting for the interface energy. The degree of swelling profile, connecting the two phases0 on a one–dimensional sample, is obtained as the solution of the corresponding Euler–Lagrange equation endowed with Dirichlet boundary conditions, determined numerically by implementing a proper finite element code. By means of the methods developed in (Cirillo et al., 2012) we predict the position of the interface in the sample, by considering the limit for the stiffness parameter which tends to zero, and verify how this prediction is consistent with the results of the numerical calculations. We find that the interface position between the coexisting phases depends on the temperature so that the relative portion of the sample occupied by the shrunk and the swollen phase change with temperature as well.

The paper is organized as follows. We first introduce the equilibrium theory of gels in Section 2. In Section 3 we discuss the conditions of phase coexistence in hydrogels, depending on temperature and external pressure, distinguishing in particular two cases: the interaction parameter depending on the sole temperature and the same parameter depending on both temperature and polymer volume fraction. In Section 4 we consider temperature driven phase transitions in PNIPAM gels corresponding to two different models for the interaction parameter. At the end, in Section 5 we discuss through the gradient theory the location of the interface when pressure and temperature assume values which allow for phases coexistence.

2. Equilibrium theory of gels

Hydrogels are made of long-chain polymers which are crosslinked into a three–dimensional network and permeated by a solvent. From the point of view of continuum mechanics, they can be viewed as soft elastic materials consisting of an elastic matrix swollen with a fluid, and can be thermodynamically characterized through the choice of a free–energy. Let $T$ and $V$ be the temperature and the volume of the hydrogel, and $V_0 < V$ the volume of the dry polymer.

The solvent–polymer mixture is treated as a single homogenized continuum body allowing for a mass flux of the solvent and characterized by a dry reference configuration $\mathcal{B}$. The state of $\mathcal{B}$ is described by the motion $f$ and the polymer fraction field $\phi$ which is, locally, the fraction of volume occupied by the polymer. The motion is a smooth function that assigns to each material point $X \in \mathcal{B}$ and time $\tau \in \mathcal{I}$ a place $x \in \mathcal{E}$, in the space of positions, say $x = f(X, \tau) \in \mathcal{E}$. The region of space $\mathcal{B}_\tau = f(\mathcal{B}, \tau)$ occupied by the body at $\tau$ represents the current configuration of $\mathcal{B}$ at time $\tau$. Given a motion, each $f(\cdot, \tau)$ is a deformation of $\mathcal{B}$, with the deformation gradient $F(X, \tau) = \nabla f(X, \tau)$ at $X$ a linear map from the translation space $\mathcal{V}$ of $\mathcal{E}$ to $\mathcal{V}$; the corresponding
Jacobian determinant is denoted by \( J = \det \mathbf{F} \). Thus, the reference volume element \( dV \) is related to its current counterpart by: \( dv = J dV \).

The free energy density, per unit current volume, depends on the polymer fraction \( \phi \), on \( J \), and on \( T \) as follows (Flory and Rehner I, 1943; Flory and Rehner II, 1943; Doi, 2009):

\[
A_{T,P}(\phi, J) = A_{el,T}(J) + A_{mix,T}(\phi) + A_{ext,P}(J),
\]

(2.1)

being \( A_{el,T} \), \( A_{mix,T} \), \( A_{ext,P} \) the elastic, mixing, and external contribution, respectively. The elastic component is

\[
A_{el,T}(J) = \frac{d k_b T}{2 w} N_x x_1 J\left(\frac{J^2}{d} - 1\right)
\]

(2.2)

where \( k_b = 1.38 \times 10^{-23} \text{ JK}^{-1} \) is the Boltzmann constant, \( w > 0 \) denotes the volume of a segment of the polymer, \( N_x \) the number of segments in a polymeric chain (the Gaussian statistical mechanics which is behind the derivation of the representation form (2.2) holds for \( N_x \) very large), and \( d \) accounts for the dimension of the environment under consideration. We note that, in the three-dimensional context (\( d = 3 \)), once introduced the shear modulus \( G = k_b T \nu_c \) of the polymer, with \( \nu_c \) the number of partial polymeric chains per unit volume, the elastic free energy density, per unit dry volume, say \( A_{el,T} \), results equal to \( 3G((J^{1/3})^2 - 1)/2 \), which is the well-known neo-Hookean elastic energy of the three-dimensional elasticity.

The mixing component comes from the Flory–Huggins theory of polymer mixtures\(^1\) and is given by

\[
A_{mix,T}(\phi) = \frac{k_b T}{w} (1 - \phi) \log(1 - \phi) + \chi \phi,
\]

(2.3)

where, as explained in Doi (2009), “\( \chi \) is a temperature-dependent dimensionless parameter (called the chi parameter), which represents the dis-affinity between the polymer and the solvent. If \( \chi \) is increased, solvent molecules are expelled from the gel and the gel shrinks, while if \( \chi \) is decreased, the gel swells.” The \( \chi \) parameter will be also called the polymer–solvent interaction parameter. The representation form of the mixing contribution is based also on the assumption that the volume of a solvent molecule is equal to the volume of a polymer segment (as in the lattice model at the basis of the Flory–Huggins theory, there is no difference between sites occupied by segments and by solvent molecules).

The external term in the free energy density is due to the coupling between the system and an external force acting on the solid component. We shall thus write

\[
A_{ext,P}(J) = P \left(\frac{J - 1}{J}\right)
\]

(2.4)

and consider both positive (pressure) and negative (tension) values of \( P \).

Up to now, the two fields \( J \) and \( \phi \) have been considered mutually independent. From now on, we assume that both the volume of the solid and liquid component of the hydrogel do not change separately, and the change in volume of the system is a consequence of the variation of the

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\(^1\)Note that the “complete” Flory–Huggins expression of the free energy density has the extra additive term, see (Doi, 1996, equation (2.15)), \((1/N) \phi \log \phi\), with \( N \) the number of segments in a polymer. Note that \( N \) differs from \( N_x \) introduced above. This term is neglected in the gel case, since it is assumed that \( N \) is very large, see (Doi, 1996, equation (3.68)) and the remark just above this equation. This term is rather important in the discussion of polymer mixtures indeed, with such a term a double well structure of the free energy is seen (Doi, 1996, Section 2.1.3). On the other hand it seems, see also the discussion in the sequel of these notes, that in the gel case no such a double well structure can be observed.
fluid mass content, only. Under this assumption (usually known as *molecular incompressibility* assumption), we have that

\[ J = \frac{1}{\phi}, \quad (2.5) \]

and the total free energy of the system only depends on the field \( J \), i.e., \( A_{T,P}(\phi, J) \equiv A_{T,P}(J) \). As a consequence, the free energy density per unit reference volume can be finally written as

\[ J A_{T,P}(J) = \frac{RT}{\Omega} \left[ \frac{d}{2N_x} (J^{2/d} - 1) + (J - 1) \log \frac{J - 1}{J} + \chi \frac{J - 1}{J} \right] + P(J - 1) \quad (2.6) \]

where we have introduced the gas constant \( R = k_B N_A = 8.314 \text{JK}^{-1}\text{mol}^{-1} \), with \( N_A = 6.022 \times 10^{23} \text{mol}^{-1} \) the Avogadro number, and the solvent molar volume \( \Omega = w N_A \).

3. Phase coexistence in hydrogels

In this section we discuss the possibility of phase coexistence, (see also Šolc et al. (1985)) for a hydrogel described by the energy density (2.6). We identify a homogeneous phase of the system with a constant field \( J \) which is a global minimum of the energy density (2.6), and ask if there exist choices of the parameters \( T, \chi, \) and \( P \) of the model such that the system is in phase coexistence regime, that is to say, the energy density (2.6) has multiple isolated local minima.

For mathematical purposes, it will be very useful to consider also the relative change in volume between the dry and the current state, i.e., \( S = J - 1 \) and note that \( S > 0 \) as the reference configuration corresponds to the dry state of polymer gel. In terms of \( S \), the total free energy density (2.6) of the system becomes

\[ G_{T,P}(S) = \frac{RT}{\Omega} \left[ \log \frac{S}{S + 1} + \frac{1}{N_x} (S + 1)^{2/d} - 1 \right] + S \log \frac{S}{S + 1} + \chi \frac{S}{S + 1} \] + PS. \quad (3.7) \]

In order to study the homogeneous phases of the system we have to discuss the nature of the solutions of the equation

\[ \frac{\partial}{\partial S} G_{T,P}(S) = 0. \quad (3.8) \]

We study this equation in two cases: interaction parameter \( \chi \) depending on the sole temperature and interaction parameter \( \chi \) depending on both the temperature \( T \) and the volume fraction \( \phi \).

We approach the problem for \( d = 1, 2, 3 \), but, in view of the application to the interface location problem, we will give a thorough study in dimension \( d = 1 \).

We show that for \( \chi \) depending on the sole temperature, the existence of multiple coexisting phases is possible only in dimension one; whereas for \( \chi \) depending on \( T \) and \( \phi \), it will turn out that coexistence is possible at any dimension.

### 3.1. Interaction parameter depending on the sole temperature

We assume the interaction parameter \( \chi \) does not depend on the volume fraction. We then write \( \chi = \chi_T \) and the equation (3.8) as

\[ \frac{RT}{\Omega} \left[ \log \frac{S}{S + 1} + \frac{1}{N_x} (S + 1)^{2/d} - 1 + \frac{1}{S + 1} + \chi_T \frac{1}{(S + 1)^2} \right] = -P \quad (3.9) \]

We denote with \( L_T(S) \) the function on the left hand side in (3.9) and note that

\[
\lim_{S \to 0} L_T(S) = -\infty \quad \text{and} \quad \lim_{S \to \infty} L_T(S) = \begin{cases} 
\infty & \text{for} \quad d = 1 \\
(1/N_x)(RT/\Omega) & \text{for} \quad d = 2, 3 
\end{cases}
\]
Moreover, we have that the equation $\partial L_T(S)/\partial S = 0$ for the stationary points of $L_T$ reads

$$-1 + (2\chi_T - 1)S = \frac{1}{N_x} \left( \frac{2}{d} - 1 \right) S (S + 1)^{2/d+1}. \tag{3.10}$$

A graphical study of the above equation yields the following (see figure 1): for $d = 3$ the function $L_T$ has a single stationary point; for $d = 2$ the function $L_T$ has a single stationary point for $\chi_T > 1/2$ and no stationary point otherwise; for $d = 1$ there exists a real number$^2$ $\chi(N_x)$ (depending only on $N_x$) such that the function $L_T$ has two stationary points for $\chi_T > \chi(N_x)$, one stationary point for $\chi_T = \chi(N_x)$, and no stationary point otherwise.

Figure 1: Qualitative study of equation (3.10). Dotted and solid lines are respectively the graphs of the functions on the left and right hand sides of the equation. From the left to the right the cases $d = 3, 2, 1$ are depicted.

Figure 2: Possible qualitative graphs of the function $L_T(S)$ defined below (3.9). From left to the right: $d = 3$, $d = 2$ and $\chi_T \leq 1/2$, $d = 2$ and $\chi_T > 1/2$, $d = 1$ and $\chi_T < \chi(N_x)$, $d = 1$ and $\chi_T > \chi(N_x)$. Note that in the case $d = 1$ and $\chi_T = \chi(N_x)$ an horizontal inflection point is present.

From these remarks, it follows that the possible qualitative behavior of the function $L_T$ are those depicted in figure 2; thus, the structure of the equation (3.9) suggests that it can have three solutions only for $d = 1$ and $\chi_T > \chi(N_x)$. Hence, the free energy function can have a double well structure only in such a case; since for $d = 1$ the free energy $G_{T,P}(S)$ tends to $0$ and to $+\infty$ for $S \to 0$ and $S \to \infty$, respectively, it follows, from the standard Maxwell equal

$^2$It is possible to give a nice estimate of the number $\chi(N_x)$. Indeed, for $d = 1$ the equation (3.10) can be rewritten as

$$\frac{1}{N_x} S^4 + \frac{3}{N_x} S^3 + \frac{3}{N_x} S^2 + \left[ - (2\chi_T - 1) + \frac{1}{N_x} \right] S + 1 = 0.$$

Since, the signs of the coefficient of the above polynomial can exhibit at most two variations, the number of its positive roots is at most equal to two. The condition for having two variations is $\chi_T > 1/2 + 1/(2N_x)$. Hence we have that $\chi(N_x) > 1/2 + 1/(2N_x)$. 

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area construction, that it is possible to find a value of the pressure/traction $P$ such that the free energy is characterized by two equally deep wells.

In conclusion, in the case studied in this section, namely, for the interaction parameter $\chi_T$ not depending on the volume fraction $\phi$, the hydrogel described by the free energy (2.6) can exhibit coexisting homogeneous swelling states only in the one–dimensional case. This possibility is ruled out at larger dimensions.

3.2. Free swelling state

In the setup of the above Section 3.1, namely, under the assumption that the interaction parameter $\chi_T$ only depends on $T$, we quickly recall the properties of the equilibrium state under free swelling conditions, i.e., $P = 0$ (see also the discussion in (Doi, 1996, Section 3.4)). From the result in the previous section, it is immediate that phase coexistence is not possible in the cases $d = 2, 3$. We prove, here, that even for $d = 1$ the phase is unique. For $d = 1$ equation (3.9) reads

$$(S + 1)^2 \log \frac{S + 1}{S} - \frac{1}{N_x}(S + 1)^3 - (S + 1) = \chi_T.$$ (3.11)

We denote by $g(S)$ the function at the left hand side of the above equation and note that $g(S) \to +\infty$ for $S \to 0$, $g(S) \to -\infty$ for $S \to \infty$, and

$$\frac{\partial}{\partial S} g(S) = 2(S + 1) \log \frac{S + 1}{S} - \frac{S + 1}{S} - 1 - \frac{3}{N_x}(S + 1)^2.$$ 

Since the sum of the first two terms is smaller than or equal to 1, we have that $\partial g/\partial S \leq 0$ for any $S$. In conclusion, $g$ is a function decreasing monotonically from $+\infty$ to $-\infty$ in the interval for $S \in [0, +\infty)$; hence, the equation (3.11) has a unique not trivial solution whatever the value of $\chi_T$ is.

In the free swelling case, the free energy (3.7) is such that $G_{T,0}(S) \to 0$ for $S \to 0$ and $G_{T,0}(S) \to +\infty$ for $S \to +\infty$. Hence, the unique stationary point of $G_{T,0}(S)$ is a minimum. In conclusion in the free swelling case, for any value of $\chi_T$, namely, for any temperature, the system has a unique not trivial homogeneous phase. This result is in agreement with the discussion in
Figure 4: Graph of the dimensionless free energy \( \frac{\Omega}{RT} \) \( G_{T,P}(S) \) for \( N_x = 10^3, \chi_{0,T} = -0.3582, \chi_{1,T} = 1.988, \) and \( P = 0.0835 \) in dimension \( d = 3. \)

(Doi, 1996, Section 3.4). Therein, it is also said that under free swelling conditions, it is sometimes used the expression “volume transition in gel” to refer to the fact that the equilibrium polymer fraction changes abruptly from 0 to 1 when the parameter \( \chi_T \) is close to \( 1/2. \) This remark is illustrated in figure 3.

3.3. Interaction parameter depending on both the volume fraction and the temperature

In this section we assume that the interaction parameters depends on the volume fraction \( \phi \) linearly. The choice is rather common in the literature and can be thought as the first order Taylor expansion of an unknown function of \( \chi \). We shall then write

\[ \chi = \chi_{0,T} + \chi_{1,T} \phi \]

so that

\[ G_{T,P}(S) = \frac{RT}{\Omega} \left[ \frac{d}{2N_x} ((S+1)^{2/d} - 1) + S \log \frac{S}{S+1} + \left( \chi_{0,T} + \chi_{1,T} \right) \frac{1}{S+1} \right] + PS. \] (3.13)

We set the following problem: are there any values of the thermodynamic parameters \( T \) and \( P \) which determine two different swelling states of the system? In other terms, we look for values of \( T \) and \( P \) such that the free energy \( G_{T,P}(S) \) has a double well graph with equally deep wells. For \( d = 2,3 \), it is possible to get a double well free energy (as it is shown in figure 4 where the double well graph of the three–dimensional free energy function corresponding to \( N_x = 10^3, \chi_{0,T} = -0.3582, \chi_{1,T} = 1.988, \) and \( P = 0.0835 \) is shown). However, our aim is to address the problem for \( d = 1 \), being dimension one more suitable for setting and solving the interface location problem, through a technique already proposed in different contexts by some of the Authors (Cirillo et al., 2009, 2010, 2011, 2012). Then, from now on, we consider the case \( d = 1. \)

Firstly, we note that \( S > 0 \) and

\[ \lim_{S \to 0} G_{T,P}(S) = 0 \quad \text{and} \quad \lim_{S \to \infty} G_{T,P}(S) = +\infty. \]

Then, as the number of stationary points of the free energy is determined by its first partial derivative computed with respect to \( S \), we evaluate

\[ \frac{\partial}{\partial S} G_{T,P}(S) = \frac{RT}{\Omega} \left[ \frac{1}{N_x} (S+1) + \chi_{0,T} \frac{1}{(S+1)^2} + \chi_{1,T} \frac{1-S}{(S+1)^3} + \log \frac{S}{S+1} + \frac{1}{S+1} \right] + P. \] (3.14)
The equation determining the stationary points \( \partial G_{T,P}(S) / \partial S = 0 \) can be rewritten as

\[
L_T(S) = -P,
\]

where

\[
L_T(S) = \frac{RT}{\Omega} \left\{ \frac{1}{N_x} S + 1 + \chi_{0,T} \frac{1}{(S+1)^2} + \chi_{1,T} \frac{1 - S}{(S+1)^3} + \log \frac{S}{S+1} + \frac{1}{S+1} \right\},
\]

defines the traction exerted on the hydrogel. In order to establish the number of solution of the equation (3.15), we look at the graph of the function \( L_T(S) \). To do it, we note that

\[
\lim_{S \to 0} L_T(S) = -\infty \quad \text{and} \quad \lim_{S \to \infty} L_T(S) = +\infty
\]

The numerator of \( \partial L_T / \partial S \) is a fifth order polynomial and its number of positive zeros can be estimated by means of the Descartes rule: first note that four of the six coefficients are positive and the two remaining coefficients are consecutive. We then have that, assuming that all the coefficients of the polynomial are different from zero, their sign can exhibit either zero or two variations. This implies that \( \partial L_T / \partial S \) has either zero or two positive real zeros.

Hence, recalling (3.17), the graph of the function \( L_T(S) \) can be either monotonic (figure 5 (left)) or kinky (figure 5 (right)). The first case corresponds to absence of coexisting phases, whereas the second to the existence of two different phases. It is worth noting that the presence of two coexisting phase is possible only if the pressure is chosen properly via the Maxwell equal area rule.

Now the natural question is: for what values of \( \chi_{0,T} \) and \( \chi_{1,T} \) is the graph kinky? This question is not easy to answer, since studying the possibility of a quintic polynomial to have real roots is not trivial; we propose a nice estimate. With simple algebra we can write the derivative of the function \( L_T(S) \) as

\[
\frac{\partial}{\partial S} L_T(S) = \frac{RT}{\Omega} \left( \frac{1}{N_x} + \frac{1}{S(S+1)} \right) \left\{ \frac{S^2(1 - 2\chi_{0,T} + 2\chi_{1,T}) + 2S(1 - \chi_{0,T} - 2\chi_{1,T}) + 1}{S^4 - 2\chi_{0,T} - 2\chi_{1,T}} \right\},
\]
Figure 6: The light gray region is a graphical representation of the solutions of the inequality (3.20). The dark gray region is a graphical representation of the solutions of the inequality (3.21). Note that the results depicted in this figure are consistent with those discussed in Section 3.1: indeed, for $\chi_1,T = 0$ the interaction parameter does not depend on the volume fraction, and the graph above is consistent with the fact that the system admits coexisting phases provided $\chi_{0,T}$ is sufficiently large.

and note that, a sufficient condition for $\partial L_T/\partial S$ to be strictly positive is that the discriminant of the second order polynomial appearing in the above equation is negative. Indeed, in such a case it would be also ensured that the first coefficient $1 - 2\chi_{0,T} + 2\chi_{1,T}$ is positive, so that the second degree polynomial is positive defined. Hence, we find the sufficient condition

$$\begin{bmatrix}
(1 - \chi_{0,T} - 2\chi_{1,T})^2 - (1 - 2\chi_{0,T} + 2\chi_{1,T}) < 0, \\
1 - \chi_{0,T} - 2\chi_{1,T} > 0 \\
1 - 2\chi_{0,T} + 2\chi_{1,T} > 0
\end{bmatrix}\quad (3.20)$$

which has the nice geometrical interpretation on the plane $\chi_{0,T} - \chi_{1,T}$ depicted in figure 6 (light gray region).

Another condition ensuring the derivative $\partial L_T/\partial S$ to be positive for $S > 0$ is that the discriminant is positive but both the coefficient of $S^2$ and $S$ are positive too. Indeed, in such a case, by the Descartes’rule, it follows immediately that the two roots of the second order polynomial are both negative. Thus, we have the inequalities

$$\begin{bmatrix}
(1 - \chi_{0,T} - 2\chi_{1,T})^2 - (1 - 2\chi_{0,T} + 2\chi_{1,T}) > 0 \\
1 - \chi_{0,T} - 2\chi_{1,T} > 0 \\
1 - 2\chi_{0,T} + 2\chi_{1,T} > 0
\end{bmatrix}\quad (3.21)$$

which has the nice geometrical interpretation on the plane $\chi_{0,T} - \chi_{1,T}$ depicted in figure 6 dark gray region).

We remark that the conditions we found are sufficient, but not necessary, to rule out the existence of coexisting phases. Indeed, even if the second order polynomial in (3.19) were negative for some values of $S$, it could happen that, due to the $1/N_x$ additive term, the derivative $\partial L_T/\partial S$ is positive for any $S$. Hence, the region with absence of multiple coexisting phases could be larger than the one depicted in figure 6. We also note that such a condition becomes sharper and sharper when $N_x$ is chosen larger and larger.
Figure 7: Graphs of the traction $L_T(S)$ (3.16) on the left and the dimensionless free energy $G(S, T)/(\Omega/RT)$ (3.13) on the right with Flory parameter temperature dependence as in (4.22). From the top to the bottom $T = 283, 300, 311$ K and $P = 33.79, 15.00, -2.93$ MPa.
4. Temperature driven phase transition in PNIPAM

In this section we study the possibility of a temperature driven phase transition in PNIPAM in the framework of the one–dimensional model discussed in Section 3.3. We then assume that the interaction parameter depends on the volume fraction as in (3.12). Moreover, for the dependence on the temperature we assume

\[ \chi_{0,T} = A_0 + B_0 T \quad \text{and} \quad \chi_{1,T} = A_1 + B_1 T \]  

(4.22)

with \( A_0, B_0, A_1, B_1 \) reals. This is a common choice in the literature, which has been demonstrated experimentally to be valid for PNIPAM hydrogels with \( A_0 = -12.947, B_0 = 0.04496 \) K\(^{-1}\), \( A_1 = 17.92 \), and \( B_1 = -0.0569 \) K\(^{-1}\) (Cai and Suo, 2011).

Under this assumption condition (3.20) reads

\[
(B_0 + 2B_1)^2T^2 + 2[(A_0 + 2A_1)(B_0 + 2B_1) - 3B_1]T + (A_0 + 2A_1)^2 - 6A_1 < 0
\]  

(4.23)

whereas conditions (3.21) can be rephrased as follows

\[
\begin{align*}
\begin{cases}
(B_0 + 2B_1)^2T^2 + 2[(A_0 + 2A_1)(B_0 + 2B_1) - 3B_1]T + (A_0 + 2A_1)^2 - 6A_1 > 0 \\
1 - (A_0 + 2A_1) - (B_0 + 2B_1)T > 0 \\
1 - 2(A_0 + A_1) + 2(B_0 + B_1)T > 0
\end{cases}
\end{align*}
\]  

(4.24)

In the PNIPAM case (Cai and Suo, 2011), we have that (4.23) is satisfied for \( 291.198 \text{K} < T < 301.868 \text{K} \) while (4.24) is never satisfied. This means that the system can exhibit (depending on the pressure) two coexisting phases for \( T < T_{\text{low}} < 291.198 \text{K} \) and \( T > T_{\text{high}} > 301.868 \text{K} \). We recall that the numerical estimate for \( T_{\text{low}} \) and \( T_{\text{high}} \) are sharper and sharper provided \( N_x \) is larger and larger.

This behavior is illustrated in figure 7, where the traction is depicted in the left column and the free energy in the right one. In the traction graphs the Maxwell construction is illustrated at \( T = 283 \text{K} \) and \( T = 311 \text{K} \) in order to find the value of the coexisting pressure, namely, the pressure such that the two gray areas in figure 7 or analogously the two local minima of the free energy are equal. The corresponding free energy (3.13) is then plotted. Conversely at \( T = 300 \text{K} \) the free energy has a single minimum, for any value of the pressure, so that a unique phase is observed.

It is very interesting to mention that in the past, see Hirotsu and Homuki (1989), a different choice for the interaction \( \chi_T \) parameter has been done for PNIPAM hydrogels. More precisely,
in this paper the author suggested to parameterize the dependence on the volume fraction of the interaction parameter as in (3.12), but the two functions of the temperature $\chi_{0,T}$ and $\chi_{1,T}$ are chose as follows:

$$
\chi_{0,T} = A_0 + \frac{B_0}{T} \quad \text{and} \quad \chi_{1,T} = A_1
$$

with $A_0 = 2.68294$, $A_1 = 0.305$, and $B_0 = -589.348$ K. Under this assumption condition (3.20) reads

$$
\left[-1 + 2A_0 - 2A_1 + (-1 + A_0 + 2A_1)^2\right]T^2 + 2B_0(A_0 + 2A_1)T + B_0^2 < 0 \quad (4.26)
$$

whereas conditions (3.21) read

$$
\begin{cases}
[-1 + 2A_0 - 2A_1 + (-1 + A_0 + 2A_1)^2]T^2 + 2B_0(A_0 + 2A_1)T + B_0^2 > 0 \\
-B_0 + (1 - A_0 - 2A_1)T > 0 \\
-2B_0 + (1 - 2A_0 + 2A_1)T > 0
\end{cases} \quad (4.27)
$$

We have that (4.26) is satisfied for $126.869 < T < 303.825$ K while (4.27) is satisfied for $T < 126.869$. This means that the system can exhibit (depending on the pressure) two coexisting phases for $T > T_{\text{high}} > 303.825$ K. We recall that the numerical estimate for $T_{\text{high}}$ is sharper and sharper provided $N_x$ is larger and larger. This behavior is illustrated in figure 8; the traction is depicted in the left column and the free energy in the right one. In the traction graph the Maxwell construction is illustrated at $T = 315$ K and the coexistence pressure is found.

We remark that the estimate for the $T_{\text{high}}$ coexistence temperature is very similar in the two theories. The main difference is in the fact that with the choice (4.22) phase coexistence is possible even at low temperature ($T < T_{\text{low}}$), while with the choice (4.25) coexistence is possible only at high temperatures.

In the following we discuss the physical properties of the system in presence of two coexistence phases. We remind that the shrunk and the swollen phase indicate the admissible equilibria with lower and higher volume change, respectively.

In figure 9 we plot the coexistence pressure versus the temperature. On the left we consider the model (4.22) at $T < T_{\text{low}}$ and note that the coexistence between the two phases occurs under compression. In this regime the shrunk and the swollen phases are indeed quite similar, see e.g., the top right picture in figure 7. To the best of our knowledge the possibility of attaining coexistence in such regime has never been discussed in the related literature. On the right we consider both model (4.22) and (4.25) at $T > T_{\text{high}}$, where we stress that the two models differ in the value of $T_{\text{high}}$ (see the discussion below (4.24) and (4.27)). The coexistence between the

![Figure 9: Coexistence pressures vs. temperature. On the left results in the case (4.22) at $T < T_{\text{low}}$ are plotted. On the right results in the cases (4.22) (black) and (4.25) (gray) at $T > T_{\text{high}}$ are plotted.](image-url)
two phases occurs here under tension for almost all the considered values of temperature, but for the model (4.24) at temperatures close to $T_{\text{high}}$, where coexistence occurs under compression. It is worth to notice that in the $T-P$ plane there exist a region, the one between the two curves, where the two models predict different phases for the system.

In figure 10 we plot the coexisting phases versus the temperature. Again on the left we consider the model (4.22) at $T < T_{\text{low}}$ and on the right both model (4.22) and (4.25) at $T > T_{\text{high}}$. It is worth to notice that the volume changes associated to the shrunk and the swollen phase are quite similar when $T < T_{\text{low}}$, while they significantly differ one from the other at $T > T_{\text{high}}$. Increasing the absolute difference between the current and the limit temperature, both $T_{\text{low}}$ or $T_{\text{high}}$, the shrunk and the swollen phase tend to separate from each other.

5. Interface location

Gradient theories are suitable to be developed for modeling stress/strain concentration due, for instance, to the presence of geometrical singularities (crack propagation in fracture mechanics) or phase transitions as in the case of wetting. Whereas gradient poromechanics has been recently formulated (Sciarra et al., 2007, 2008) extending the standard arguments of the Biot theory (Biot, 1941), to the best of our knowledge, gradient theories have rarely been formulated to infer interface location when temperature–driven volume transition occurs in hydrogels.

More precisely, within the one–dimensional framework introduced above, the gradient theory will be used here as a tool to capture the position of the interface between two coexisting phases differing in the degree of swelling (shrunk and swollen phases).

We consider the finite interval $[0, 1]$ and introduce the Landau energy functional

$$\mathcal{F}[S] = \int_0^1 \left[ G_{T,P}(S) + \frac{\kappa}{2} (S')^2 \right] \, dx$$

with the standard free–energy component $G_{T,P}(S)$, defined as in the equation (3.13), and $\kappa > 0$ an appropriate stiffness; the prime denotes the derivative with respect to the space variable. We look for the equilibrium profile $S(x)$ by performing a standard variational computation and assuming either Dirichlet or homogeneous Neumann boundary conditions. We therefore get the following Euler–Lagrange equation

$$\kappa S'' = \frac{\partial G_{T,P}}{\partial S}.$$
We consider now Dirichlet boundary conditions corresponding to the shrunk \((S_{sh})\) and the swollen \((S_{sw})\) phases for the values of \(P\) and \(T\) ensuring coexistence. In other words we solve the problem (5.29) with the boundary conditions

\[ S(0) = S_{sh} \quad \text{and} \quad S(1) = S_{sw} . \]  

(5.30)

By exploiting the one–dimensionality of the model a phase space analysis proves that the problem (5.29) endowed with the above mentioned boundary conditions has a unique solution implicitly given by the integral

\[ \int_{S_{sh}}^{S_{sw}} \sqrt{\kappa} \, ds \sqrt{2[E_\kappa + G_{T,P}(s)]} = x \]  

(5.31)

where for any \(\kappa > 0\) we have defined implicitly \(E_\kappa\) by the equation

\[ \int_{S_{sh}}^{S_{sw}} \sqrt{\kappa} \, ds \sqrt{2[E_\kappa + G_{T,P}(s)]} = 1 \]  

(5.32)

namely, the integral in (5.31) with \(S = S_{sw}\) and \(x = 1\).

The profile given by (5.31) is a connection between the two phases and, in the limit \(\kappa \to 0\), presents a flat interface localized at

\[ x_I = \frac{\sqrt{\partial^2 G_{T,P}(S_{sw})/\partial S^2}}{\sqrt{\partial^2 G_{T,P}(S_{sh})/\partial S^2} + \sqrt{\partial^2 G_{T,P}(S_{sw})/\partial S^2}} \]  

(5.33)

see (Cirillo et al., 2012, Theorem 2). We note that, if the free energy \(G_{T,P}\) had equal second derivatives at the phases, the interface would fall in the middle point of the interval. We underline that in our case the free energy (3.7) is not symmetric and therefore the interface position will change depending on the temperature \(T\).

In figures 11 and 12 we show that the interface tends to a sharp kink when the stiffness is chosen smaller and smaller. We introduce a physically more relevant parameter, the characteristic length \(\ell\) defined as

\[ \ell^2 = \frac{\Omega}{RT\kappa} \]  

(5.34)

We plot the solution of the equation (5.29) with Dirichlet boundary conditions (5.30) for different values of the characteristic length \(\ell\) at given temperature and pressure ensuring coexistence. The
Figure 12: Profile (5.33) for the model (4.25) with $T = 308$ K and $P = -0.70$ MPa. The characteristic length $\ell$ (5.34) as been chosen as in the pictures.

Figure 13: Interface position (5.33) as a function of temperature at coexisting pressure. On the left results in the case (4.22) at $T < T_{\text{low}}$ are plotted. On the right results in the cases (4.22) (black) and (4.25) (gray) at $T > T_{\text{high}}$ are plotted.

plots show that the interface tends to localize in the small stiffness limit. In figure 11 we solved the problem for the model (4.22), whereas in figure 12 the case (4.25) was considered.

We remark that the boundary value problem (5.29)–(5.30) has been numerically solved by means of a properly implemented finite element code.

It is worth noting that, as already remarked above, due to the fact that even at coexistence the free energy $G_{T,P}$ is not symmetric with respect to the central local minimum (see, for instances, figures 7 and 8), the position of the interface depends on the temperature. From the physical point of view, this means that at different temperatures the relative portions of the sample occupied by the shrunk and the swollen phases change.

It is interesting to compare the graphs on the right in figure 11 and those in figure 12. At temperature $T = 308$ K, the model (4.22) predicts that the interface position is close to the end with the shrunk phase boundary condition, this means that the sample is mostly occupied by the swollen phase. On the other hand, at the same temperature, the model (4.25) predictions are slightly different, indeed the interface position is close to 0.3 so that a not negligible part of the system is occupied by the shrunk phase.

In figure 13 the interface position is plotted as a function of the temperature for both models. The difference between the (4.22) and (4.25) model predictions is pointed out in the picture on the right. From both pictures we conclude that at temperatures far from the limiting values

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$T_{\text{low}}$ and $T_{\text{high}}$, the interface position is close to zero so that the sample is mostly occupied by the swollen phase. Conversely, the interface moves towards the center of the sample when the temperature gets closer to its limiting values. This effect is much more important in the (4.25) case.

We remark that our result goes in the opposite direction with respect to that illustrated in (Cai and Suo, 2011, Fig. 14d). There, indeed, it is stated that at large temperature the shrunk phase tends to fill up the whole sample. We have to notice that the problems considered in our paper and in (Cai and Suo, 2011) are similar, but not equivalent, indeed, the setup in that paper is fully three–dimensional, whereas our discussion is limited to dimension one.

Conclusions

We addressed the modeling of thermally–driven volume transition in hydrogels, within the Flory–Rehner thermodynamic setting; precisely, accounting for the temperature–depending pattern of the interaction parameter determined in (Hirotu and Honuki, 1989) for NIPA hydrogels, and in (Afroze et al., 2000) for aqueous solutions of uncrosslinked PNIPAM. In both models, the Flory parameter depends linearly on the volume fraction of polymer within the gel; on the contrary, the dependence on temperature is different. We proposed a detailed analysis aimed to establish the ranges of both temperature and traction which allow for the coexistence of two different phases (swollen and shrunk) in the hydrogel. With specific reference to a one–dimensional problem, we showed as different models for the interaction parameter deliver different conclusions.

Finally, for the values of temperature and traction ensuring phase coexistence, we presented a gradient model, appropriately extending the Flory–Rehner free energy, and localize the interface position between the shrunk and the swollen phase, on one hand by means of a phase space analysis, previously developed by some of the Authors, on the other developing proper finite element numerical calculations.

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