

This is the accepted manuscript made available via CHORUS. The article has been published as:

Influence of the standard free energy on swelling kinetics of gels

James P. Keener, Sarthok Sircar, and Aaron L. Fogelson

Phys. Rev. E **83**, 041802 — Published 8 April 2011

DOI: [10.1103/PhysRevE.83.041802](https://doi.org/10.1103/PhysRevE.83.041802)

The Influence of the Standard Free Energy on Swelling Kinetics of Gels

James P. Keener*, Sarthok Sircar and Aaron L. Fogelson*
 Departments of Mathematics and Bioengineering*
 University of Utah
 Salt Lake City, UT 84112

In this paper we present a model for the swelling kinetics of gels that incorporates the free energy in a novel way. We provide a complete analysis of how the swelling kinetics and stable states and sizes of the swelled gel depends on the free energy parameters, specifically the free energy of the pure phases, i.e., the polymer standard free energy. Classical theories of gel swelling employ the mixing free energy. Such theories do not include effects of the polymer standard free energy, and as we show, cannot correctly describe equilibrium states or the swelling kinetics.

Acknowledgment: This research was supported in part by NSF grant DMS-0540779 and NIGMS grant R01-GM090203.

PACS 82.35.Lr, 82.70.Gg, 83.80.Kn, 47.57.Ng

I. INTRODUCTION

The theory to understand the swelling and deswelling of gels has a long history beginning with the classical work of Flory [1–3] and Katchalsky [4]. (See also [5, 6].) In this theory, the free energy is used to make predictions about the thermodynamical equilibrium configurations of polymer gels and their dependence on environmental parameters such as temperature or ion solvent concentrations.

An important problem is to understand how the kinetics (and not simply the equilibria) of swelling and deswelling is governed. An early answer was given by Tanaka and colleagues [7, 8] who developed a kinetic theory of swelling gels viewing a gel as a linear elastic solid immersed in a viscous fluid.

This early work gave rise to the concept of gel diffusivity as a way to characterize the kinetics of swelling. The gel diffusivity is defined as $D = \frac{aL^2}{\tau}$ where L is the equilibrium size (length or radius) of a gel and τ is the time constant of exponential swelling toward the equilibrium size. The dimensionless scale factor a is related to the geometry of the gel. They found that expansion of the gel was governed approximately by a diffusion equation with diffusion coefficient D . However, how the diffusivity of the gel, or more generally the kinetics of swelling, is affected by the free energy is less well understood.

There are numerous studies of the kinetics of gel swelling [9–15] and numerous applications of these theories to study, for example, cartilage mechanics [16–19], the contraction of actin-myosin networks [20, 21], the propulsion of myxobacteria via swelling of slime [22, 23] and biofilm formation [24–26].

A feature of all of these works is that at some point there is use or invocation or extension of the Flory-Huggins theory of polymer gels. In most, if not all, of these works, something akin to the mixing free energy is used.

The main point of this paper is that to get a correct understanding of the kinetics of swelling gels, it is not sufficient to consider the mixing free energy; one must include in the free energy the standard free energy of the pure polymer state and the solvent state.

II. DESCRIPTION OF THE MODEL EQUATIONS

We view a polymer gel as a two phase fluid, consisting of polymer network phase with volume fraction θ and solvent phase with volume fraction $1 - \theta$. These two phases move with velocity \mathbf{v}_p and \mathbf{v}_s respectively, and since both are conserved quantities (there is no interconversion between polymer and solvent),

$$\frac{\partial \theta}{\partial t} + \nabla \cdot (\mathbf{v}_p \theta) = 0, \quad \nabla \cdot (\mathbf{v}_p \theta + \mathbf{v}_s (1 - \theta)) = 0. \quad (1)$$

Force balance equations are also assumed to hold in each of the two phases

$$\nabla \cdot (\theta \sigma_p) - \xi \theta (1 - \theta) (\mathbf{v}_p - \mathbf{v}_s) - \theta \nabla \mu_p - \theta \nabla P = 0, \quad (2)$$

and

$$\nabla \cdot ((1 - \theta)\sigma_s) - \xi\theta(1 - \theta)(\mathbf{v}_s - \mathbf{v}_p) - (1 - \theta)\nabla\mu_s - (1 - \theta)\nabla P = 0. \quad (3)$$

Here σ_j , $j = p, s$, are the stress tensors, ξ measures the drag between solvent and network, and μ_p and μ_s are the network and solvent chemical potentials, respectively. Finally, P is the pressure, required to maintain overall incompressibility.

The solvent stress tensor σ_s is taken to be that for a Newtonian fluid. The polymer stress tensor σ_p can include viscous, elastic or visco-elastic contributions, arising, for example, from permanent bonds between polymer strands or the effect of entanglements amongst polymer strands. For this paper, we consider a polymer with no permanent cross-linking bonds (hence no elastic stresses). This assumption is appropriate for many biological gels, such as mucus. While entanglements are important in such gels, they do not change substantially the analysis presented here, and so are not considered. Hence, the stress tensors have the form $\sigma_j = \frac{1}{2}\eta_j(\nabla\mathbf{v}_j + \nabla\mathbf{v}_j^T) + \lambda_j\mathbf{I}\nabla \cdot \mathbf{v}_j$, $j = p, s$, with viscosities η_j and λ_j . To insure that the system is dissipative, it must be that $\eta_j > 0$ and $\eta_j + 3\lambda_j > 0$.

Typically, a gel is immersed in a bath of pure solvent, where $\theta = 0$. Thus, between the region with gel and no gel, there is an edge, i.e., a discontinuity in θ , which may move when the gel is swelling or deswelling. For a radially symmetric gel, the condition at the interface is [27]

$$\frac{\partial}{\partial r} \left(\frac{\eta_e v_p}{(1 - \theta)} \right) = \mu_p - \mu_s, \quad (4)$$

where $\eta_e = \eta_p(1 - \theta) + \eta_s\theta$, and v_p is the radial component of the network velocity. A derivation of these governing equations is given in the Appendix.

The chemical potentials are defined in the usual way [28] as

$$\mu_p = F + (1 - \theta)\frac{\partial F}{\partial \theta}, \quad \mu_s = F - \theta\frac{\partial F}{\partial \theta}. \quad (5)$$

where F is the free energy density. With these definitions, it is immediate that

$$\mu_p - \mu_s = \frac{\partial F}{\partial \theta}, \quad \theta\mu_p + (1 - \theta)\mu_s = F. \quad (6)$$

The second of these is also known as the *Gibbs-Duhem relationship*. Another important identity is that

$$\theta\nabla\mu_p + (1 - \theta)\nabla\mu_s = 0, \quad (7)$$

implying that the force that the network exerts on the solvent is equal and opposite to the force of the solvent acting on the network.

Classical theories of polymer mixtures begin with a free energy density $F(\theta)$ of the form

$$\nu_m \frac{F(\theta)}{k_B T_0} = f(\theta) = \frac{k_B T}{k_B T_0} \left(\frac{\theta}{N} \log(\theta) + (1 - \theta) \log(1 - \theta) \right) + \chi\theta(1 - \theta) + \underline{\mu^0\theta + \mu_s^0}, \quad (8)$$

where N is the number of monomers per polymer, ν_m is the monomer volume, k_B is the Boltzmann constant, T is absolute temperature, T_0 is some reference temperature, χ is the Flory interaction parameter, and $\mu^0 \equiv \mu_p^0 - \mu_s^0$, where $k_B T_0 \mu_p^0$ and $k_B T_0 \mu_s^0$ are the standard free energies of polymer and solvent, respectively. Note that μ_p^0 and μ_s^0 are non-dimensional numbers.

In most (if not all) of the literature on the kinetics of gel swelling [1–3, 6, 14, 24–26, 28–32] the mixing free energy is used rather than the total free energy. The difference between these two is that the mixing free energy does not include the standard free energies, i.e, takes $\mu^0 \equiv \mu_p^0 - \mu_s^0 = 0$ and $\mu_s^0 = 0$, thus ignoring the underlined terms in (8). Because energies are always relative quantities, one can take $\mu_s^0 = 0$ without loss of generality, however, in general, the difference $\mu_p^0 - \mu_s^0$ is not zero and should not be ignored.

The standard free energies $k_B T_0 \mu_p^0$ and $k_B T_0 \mu_s^0$ are also known as the cohesive energies or the latent heat of vaporization (ΔE) for pure polymer and solvent, respectively. These are the energy of all the interactions between the molecule and its neighbors in a pure state that have to be disrupted to remove the molecule from the pure state [33] pg. 141–144. These can be determined from the Hildebrand solubility parameters $\delta_{j,HI}$ via

$$-k_B T_0 \mu_j^0 = \nu_m \Delta E_j / V_j = \nu_m \delta_{j,HI}^2 \quad (9)$$

with $j = p, s$, where V_p, V_s are the molar volume of the polymer and the solvent, respectively. The negative sign indicates that $k_B T_0 \mu_p^0, k_B T_0 \mu_s^0 < 0$ (since they are the interaction energies) while the latent heats are positive. The value of these solubility parameters for some hydrogels can be found in a standard handbook of solubility parameters [34]. For example, $\delta_{p,HI}$ for Poly(N-Butyl Acrylamide) at $T_0 = 298\text{K}$ is $17.6 \text{ MPa}^{1/2}$ giving the cohesive energy density as $\Delta E_p/V_p = \delta_{p,HI}^2 = 309.76 \text{ MPa}$.

Similarly, the cohesive energy density for a common solvent, e.g. water, at the same temperature is $\Delta E_s/V_s = 552.25 \text{ MPa}$ ($\delta_{water,HI} = 23.5 \text{ MPa}^{1/2}$) [35]. With $\nu_m = 2 \times 10^{-29} \text{ m}^3$ as the monomeric volume, the values of the non-dimensional parameters μ_p^0 and μ_s^0 for the above mentioned polymer and solvent are

$$\begin{aligned}\mu_p^0 &= -\nu_m \delta_{p,HI}^2 / (k_B T_0) = -1.51, \\ \mu_s^0 &= -\nu_m \delta_{s,HI}^2 / (k_B T_0) = -2.68,\end{aligned}$$

so that for this polymer-solvent mixture, $\mu^0 = \mu_p^0 - \mu_s^0 = 1.17$.

The eqns.(1-4) are derived and studied in [27]. A significant result of that study is a determination of how the free energy affects both the equilibrium size and volume fraction of the gel as well as the time constant for expansion (or contraction) to equilibrium. It follows from the interface condition (4) and (6) that for the model presented here, the equilibria for volume fraction of the gel are extremal values of the free energy, i.e., values of θ for which $\frac{\partial f}{\partial \theta} = 0$.

According to classical theory, the swelling of a gel is well approximated by a first order process characterized by the diffusivity

$$D = \frac{\alpha L^2}{\tau}, \quad (10)$$

where τ is the time constant (or inverse decay rate) for equilibration, L is the equilibrium radius of the gel and α is a geometrical factor. This definition of gel diffusivity comes from early work of Tanaka and Fillmore [7] who derived a diffusion equation to describe the return of an elastic network to its equilibrium size, subject to drag with the surrounding fluid. According to that study, the diffusivity D is a constant.

Our analysis of the model equations [27] provides more detail for how the time constant for gel expansion depends on the rheological parameters of the gel and on the free energy. In particular, it is found that the decay rate (inverse time constant) is given by

$$k_d = \frac{1}{\tau} = k_B T \frac{\theta^*(1 - \theta^*) f''(\theta^*)}{\eta_e^* + \frac{\xi L^2}{\omega^2}} = \frac{k_B T k_0}{\eta_e^* + \frac{\xi L^2}{\omega^2}}, \quad (11)$$

where θ^* is the equilibrium volume fraction, $\eta_e^* = (\eta_p + \lambda_e)(1 - \theta^*) + (\eta_s + \lambda_s)\theta^*$, L is its size, and ω is a geometric factor, which for a one-dimensional gel is $\frac{\pi}{2}$, and $k_0 = \theta^*(1 - \theta^*) f''(\theta^*)$. Thus, we have explicit formulas for how the equilibrium volume fraction θ^* and the time constant of gel swelling depend on the free energy density. Specifically, for the free energy function (8),

$$k_0 = k_B T \left(\frac{1 - \theta}{N} + \theta \right) - 2\chi\theta(1 - \theta). \quad (12)$$

The main purpose of this paper is to examine in more detail the effect of the polymer standard free energy on the equilibria and the diffusivity of a gel, and to show that this effect is significant.

III. MAIN RESULTS

The equilibrium volume fraction of a gel is at a critical point of the free energy. For the free energy function (8) there are only two cases to consider. For this free energy, $f'(\theta) \rightarrow -\infty$ as $\theta \rightarrow 0$, while $f'(\theta) \rightarrow \infty$ as $\theta \rightarrow 1$. Thus, there is always at least one critical point between 0 and 1. If the Flory interaction parameter is negative, $\chi < 0$, then $f''(\theta) > 0$ and the critical point is a unique minimum. However, if $\chi > 0$ then it is possible that there are two interior minima separated by a maximum.

Since μ^0 appears as an additive constant in $f'(\theta)$, increases in μ^0 shift the location of a minimum to the left, and the location of a maximum to the right. The physical consequence of this is that increasing μ^0 causes a gel to swell or hydrate, while decreasing μ^0 causes the gel to dehydrate.

This is illustrated in Fig. 1 where we show free energy curves with $T = T_0$ and $\chi = -1$, for three different values of μ^0 . When the free energy density of the pure polymer phase is substantially larger than the pure solvent phase ($\mu^0 = 3.0$), the pure polymer phase is thermodynamically unfavourable and hence the gel dissolves (equilibrium volume fraction $\theta^* \rightarrow \approx 0$). Conversely, a value of the pure polymer phase free energy density much lower than the pure solvent free-energy density ($\mu^0 = -3.0$), causes the gel to dehydrate ($\theta^* \rightarrow \approx 1$). When the pure phase free energy densities are equal ($\mu^0 = 0.0$), the sol-gel mixture phase equilibrates to a value near but not exactly the equal phase mixture ($\theta^* = 0.5$), since the free energy density is not a symmetric function of θ .

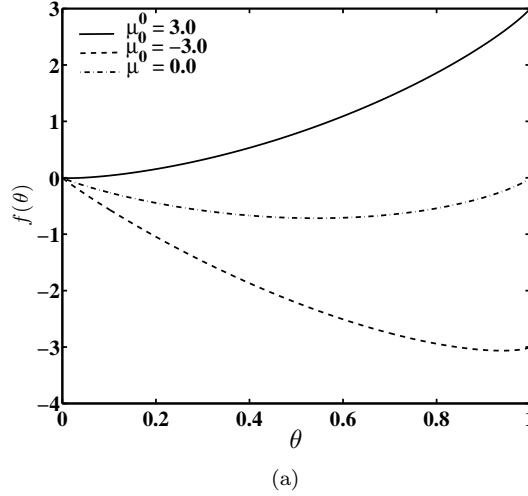


FIG. 1: Swelling free energy density (Eqn. 8) for Flory interaction parameter $\chi = -1.0$ and $\mu^0 = (3.0, 0.0, -3.0)$. The number of monomers in one polymer chain is fixed at $N = 3$, and $T = T_0$.

In Fig. 2, θ^* is shown plotted as a function of μ^0 for several values of χ , N , and T/T_0 . Here we see illustrated the fact that the unique equilibrium value is always a decreasing function of μ^0 , with θ^* close to 1 if μ^0 is sufficiently negative and close to zero if μ^0 is sufficiently positive.

The decay rate for return to equilibrium is also affected by μ^0 . This is illustrated in Fig. 3, where $k_0 = \theta^*(1 - \theta^*)f''(\theta^*)$ is plotted as a function of μ^0 . Note that, from (12), k_0 is a monotone function of θ if χ is sufficiently small in magnitude. Hence, k_0 is also a monotone decreasing function of μ^0 when χ is sufficiently small in magnitude.

In Fig. 4(a,b,c), θ^* is shown plotted as a function of T/T_0 for several values of μ^0 and $\chi < 0$. The important observation here is that when $\mu^0 = 0$, θ^* is an increasing function of T , so that decreasing temperature causes the gel to hydrate or swell. This remains true for positive values of μ^0 . However, for sufficiently large negative values of μ^0 , decreasing T causes the gel to dehydrate rather than hydrate. In fact, one can easily show that there is a negative number μ^* for which if $\mu^0 > \mu^*$ then decreasing temperature causes hydration whereas if $\mu^0 < \mu^*$, then decreasing T causes dehydration.

In Fig. 4(d) are shown the scaled decay rates k_0 corresponding to the case (b). For all other cases, k_0 is quite similar. Because θ^* asymptotes to a fixed value for large T , these curves are, not surprisingly (see Eqn. 12), approximately linear in T . Notice that k_0 is always positive if χ is negative, indicating that the steady solution is always stable if χ is negative.

In the case that $\chi > 0$, for appropriate values of T and μ^0 , the free energy function can have two minima. However, for T and $|\mu^0|$ sufficiently large, the free energy function can have only a single minimum. This is illustrated in Fig. 5 where free energy curves with $T_0 = T$ and $\chi = 1.9$, for three different values of μ^0 , are shown.

For each value of χ , the T - μ^0 phase space can be divided into two regions, one in which there is a unique equilibrium and another in which there are two stable equilibria. Examples of the phase diagrams are shown in Fig. 6.

Plots of the equilibrium values θ^* as function of μ^0 and T/T_0 are shown in Fig. 7 and 8 respectively. Since these correspond to slices of the phase diagram, Fig. 7 a μ^0 ‘slice’ holding T fixed, and Fig. 8 a T ‘slice’ holding μ^0 fixed, we expect these curves to exhibit bistability and hysteresis, as indeed they do.

We make several observations about these curves. First, the bistability seen in Fig. 7 is reversible, whereas in Fig. 8 it is not. That is, increasing μ^0 always leads to swelling and decreasing μ^0 always to deswelling, through a discontinuous jump if there is bistability, or continuously if not. However, a cycle in which μ^0 is first increased and

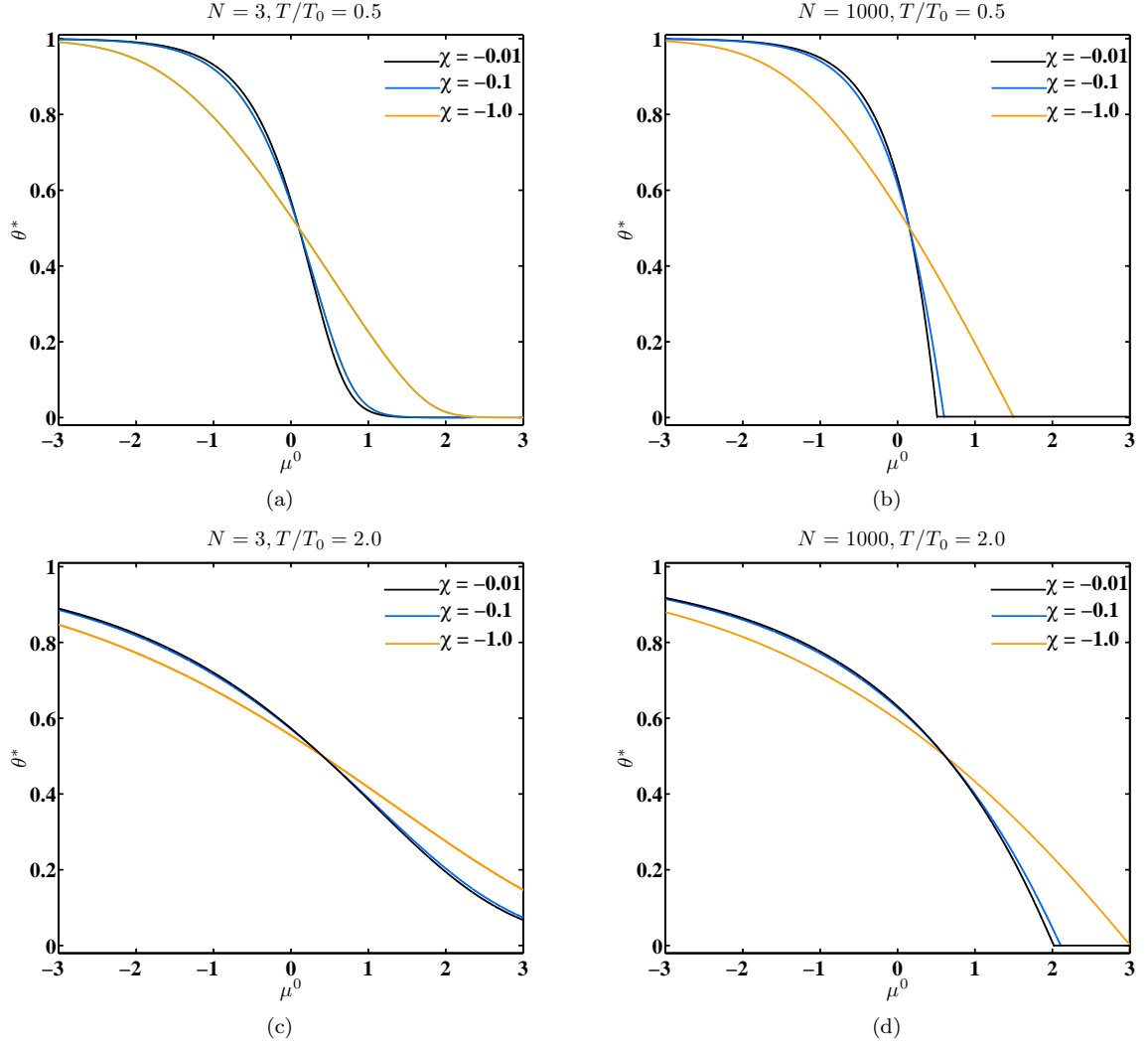


FIG. 2: (Color Online) Equilibrium solution θ^* plotted as a function of μ^0 for different negative values of χ and at the indicated values of N and T/T_0 .

then decreased can bring the gel back to the state from which it started.

Such is not the case with temperature variation. In this case there is a solution branch which exists for all temperatures and a second branch which exists only for small temperatures. Furthermore it is possible to leave the second branch by increasing T , but it is not possible to leave the first branch. Thus, if one starts on the second branch and increases temperature, thereby experiencing a phase transition to the first branch, it is not possible by decreasing the temperature to reverse this transition.

The second interesting feature of the curves in Fig. 8 is that, similar to the case when $\chi < 0$, here increases in temperature lead to swelling if μ^0 is zero or negative, but increases in temperature lead to deswelling if μ^0 is sufficiently positive.

The scaled decay rates k_0 for these are shown in Figs. 9 and 8(b, d, f). In Fig. 9 there is a single curve for each value of χ corresponding to the fact that the equilibrium solutions lie on a single curve. The transition at which k_0 changes sign corresponds to the change of stability and saddle-node bifurcation. In contrast, in Fig. 8(b, d, f) there are two curves for each value of χ , one for the branch which exists for all temperatures and one for the branch which exists only for small values of temperature. As expected, k_0 is asymptotically linear for large values of T , but in contrast to the earlier case, there are significant deviations from linearity when T is small. Nonetheless, k_0 is always positive on this branch, indicating that these solutions are always linearly stable.

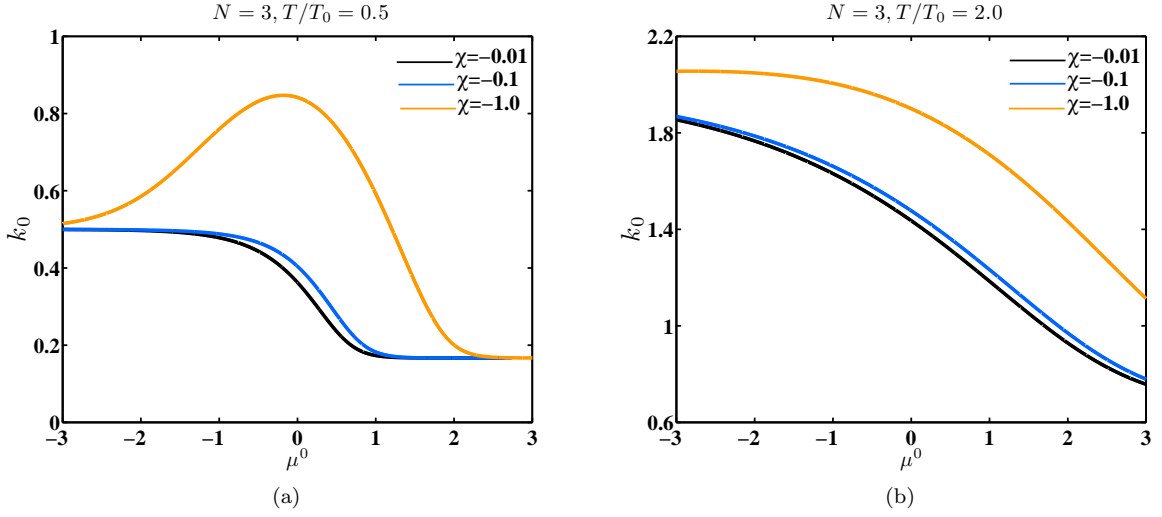


FIG. 3: (Color Online) The decay rate k_0 vs μ^0 for $N = 3$ and negative χ .

IV. DISCUSSION AND CONCLUSION

As described here, the equilibrium states and the swelling kinetics of a gel are significantly affected by the standard free energy of the pure polymer state relative to the standard free energy of pure solvent, $k_B T \mu^0 \equiv k_B T (\mu_p^0 - \mu_s^0)$. Thus, theories that do not include this term in the free energy, using instead the mixing free energy, are certain to miss important features of gel swelling kinetics.

One of the more striking observations is that increasing temperature causes swelling if μ^0 is sufficiently large whereas increasing temperature causes deswelling if μ^0 is sufficiently small (i.e. less than a certain positive number).

Including the standard free energy is particularly important for chemically reactive polymers, or polyelectrolyte gels, where the concentration of different ion species can influence the free energy of the pure state. For example, mucins, which are negatively charged polymers, can have their charges shielded by monovalent (sodium) or divalent (calcium) ions, and the relative concentrations of these ions can have a significant impact on how the gel swells. Furthermore, changes in the affinities of the mucin for these ions, as may happen in disease states such as cystic fibrosis, can also affect the swelling kinetics and equilibrium states of the gel.

A detailed exploration of how the balance of monovalent and divalent ions affects the standard free energy of the pure polymer state, and thus the swelling and deswelling of polyelectrolyte gels, is the topic of a separate publication [36].

The model we described here is not appropriate for gels for which there are permanent chemical bonds. Such a situation was studied by Hirotsu [37], who included a rubber elasticity term in the free energy. Hirotsu found that, in order to have multiple equilibria (i.e., a double well energy function) it was necessary to allow the Flory interaction parameter to be a function of volume fraction. (A similar volume fraction dependence was also included in [14].)

While the inclusion of standard free energy as described here does not resolve the issues raised by Hirotsu, the standard free energy does have a significant effect on the nature of equilibria for these other free energy functions, as well.

V. APPENDIX

Here, we derive Eqs. (1-4) using the notation θ_p and θ_s for the polymer and solvent volume fractions. We suppose that Ω is a fixed domain inside of which there is polymer and solvent, and on the boundary of which the velocities specified. Let Γ denote an interface across which θ_p is discontinuous. We extremize the total energy dissipation rate

$$\begin{aligned}
 E_T \equiv & \int_{\Omega} \left\{ \frac{1}{2} \eta_p \theta_p \epsilon(\mathbf{V}_p) : \epsilon(\mathbf{V}_p) + \frac{1}{2} \eta_s \theta_s \epsilon(\mathbf{V}_s) : \epsilon(\mathbf{V}_s) + \frac{1}{2} \xi \theta_p \theta_s (\mathbf{V}_p - \mathbf{V}_s)^2 \right. \\
 & \left. - \mu_p \nabla \cdot (\theta_p \mathbf{V}_p) - \mu_s \nabla \cdot (\theta_s \mathbf{V}_s) \right\} dV,
 \end{aligned} \tag{13}$$

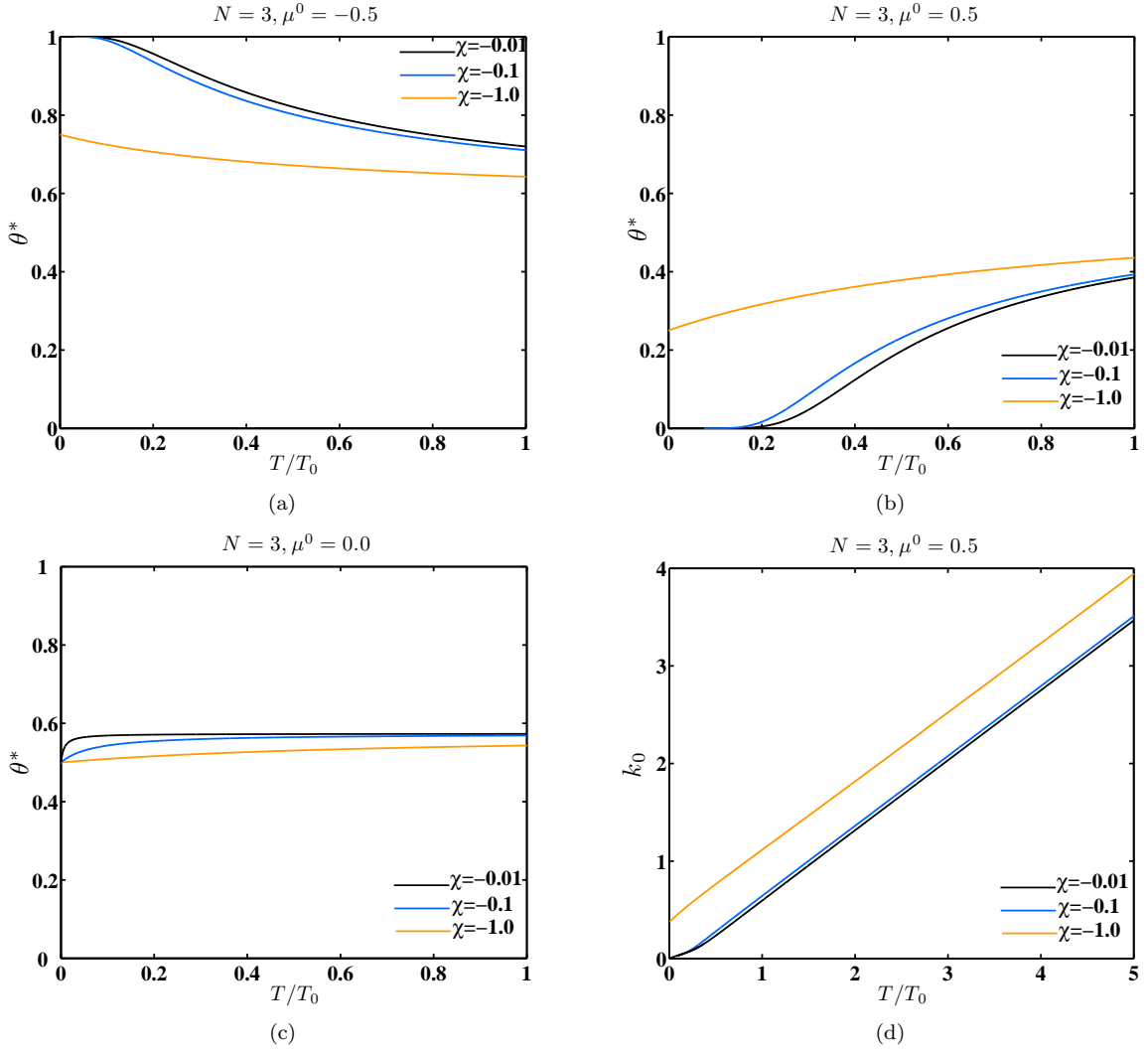


FIG. 4: (Color Online) (a, b, c) Equilibrium value θ^* plotted as a function of T/T_0 at the indicated values of the parameters and (d) the decay rate k_0 corresponding to (b).

subject to the incompressibility constraint

$$\nabla \cdot (\theta_p \mathbf{V}_p + \theta_s \mathbf{V}_s) = 0, \quad (14)$$

That is, we extremize the functional

$$\begin{aligned} F_T \equiv \int_{\Omega} \left\{ \frac{1}{2} \eta_p \theta_p \epsilon(\mathbf{V}_p) : \epsilon(\mathbf{V}_p) + \frac{1}{2} \eta_s \theta_s \epsilon(\mathbf{V}_s) : \epsilon(\mathbf{V}_s) + \frac{1}{2} \xi \theta_p \theta_s (\mathbf{V}_p - \mathbf{V}_s)^2 \right. \\ \left. - \mu_p \nabla \cdot (\theta_p \mathbf{V}_p) - \mu_s \nabla \cdot (\theta_s \mathbf{V}_s) - P \nabla \cdot (\theta_p \mathbf{V}_p + \theta_s \mathbf{V}_s) \right\} dV, \end{aligned} \quad (15)$$

over all admissible $(\mathbf{V}_p, \mathbf{V}_s, P)$. In Eq. 15, the first three terms represent dissipation of energy by viscosity and drag, the terms $\mu_p \nabla \cdot (\theta_p \mathbf{V}_p)$ and $\mu_s \nabla \cdot (\theta_s \mathbf{V}_s)$ represent the work required to compress the network and solvent, respectively, and P is the Lagrange multiplier used to enforce the incompressibility constraint Eq. 14. Functions \mathbf{V}_p and \mathbf{V}_s are admissible if they are differentiable and specified on the boundary of Ω and if $\nabla \cdot (\theta_p \mathbf{V}_p + \theta_s \mathbf{V}_s)$ is well defined.

The Euler-Lagrange equations are calculated in the standard way. We let $(\mathbf{V}_p + \epsilon \mathbf{v}_p, \mathbf{V}_s + \epsilon \mathbf{v}_s)$ be a perturbation, and set to zero the derivative of F_T with respect to ϵ at $\epsilon = 0$. After applying the divergence theorem to the result,

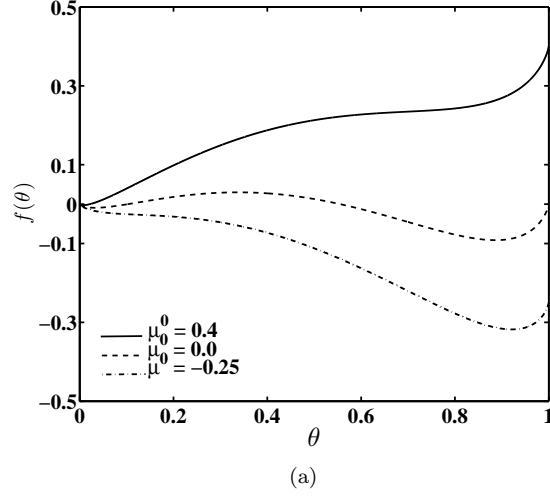


FIG. 5: Free energy density (equation 8) for Flory interaction parameter $\chi = 1.9$, $T = T_0$ and $\mu^0 = (0.4, 0.0, -0.25)$. The number of monomers in one polymer chain is fixed at $N = 3$.

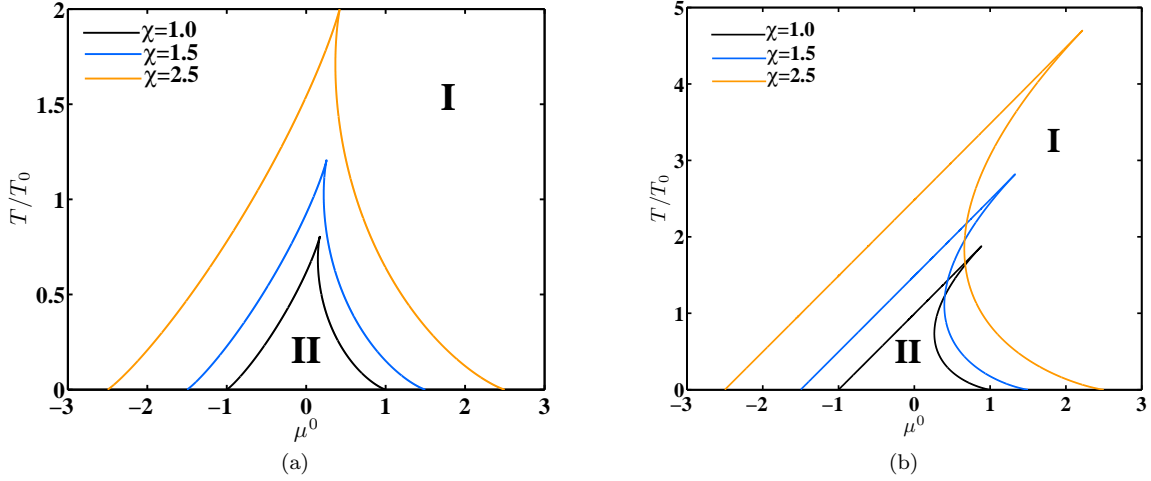


FIG. 6: (Color Online) Phase diagram T/T_0 vs μ^0 for different values of χ and (a) $N = 3$, (b) $N = 1000$. In region I (the exterior domain) there is a unique equilibrium, while in region II (the interior domain) there are two minima and hence two stable equilibria.

we obtain

$$\begin{aligned}
 0 = & \int_{\Omega} \left\{ -\nabla \cdot (\eta_p \theta_p \epsilon(\mathbf{V}_p) + \xi \theta_p \theta_s (\mathbf{V}_p - \mathbf{V}_s) + \theta_p \nabla \mu_p + \theta_p \nabla P) \right\} \cdot \mathbf{v}_p \, dV \\
 & + \int_{\Omega} \left\{ -\nabla \cdot (\eta_s \theta_s \epsilon(\mathbf{V}_s) + \xi \theta_p \theta_s (\mathbf{V}_s - \mathbf{V}_p) + \theta_s \nabla \mu_s + \theta_s \nabla P) \right\} \cdot \mathbf{v}_s \, dV \\
 & + \int_{\Gamma} [\theta_p \mathbf{e}_p \mathbf{v}_p + \theta_s \mathbf{e}_s \mathbf{v}_s] \, dS.
 \end{aligned} \tag{16}$$

Here, $\mathbf{e}_p \mathbf{v}_p = \eta_p \epsilon(\mathbf{V}_p) : (\mathbf{n} \mathbf{v}_p) - P \mathbf{v}_p \cdot \mathbf{n} - \mu_p \mathbf{v}_p \cdot \mathbf{n}$, and $\mathbf{e}_s \mathbf{v}_s$ is defined analogously, \mathbf{n} is the unit outward normal along Γ , and $[g]$ denotes a jump in the quantity g across Γ . Treating \mathbf{v}_p and \mathbf{v}_s on the interior as arbitrary, we obtain the force balance equations Eqs. 1-4, and we are left with the integral over Γ in Eq. 16 required to be zero. The individual velocities need *not* be continuous across the interface, but $\theta_p \mathbf{V}_p + \theta_s \mathbf{V}_s$ must be because of conservation of mass, and

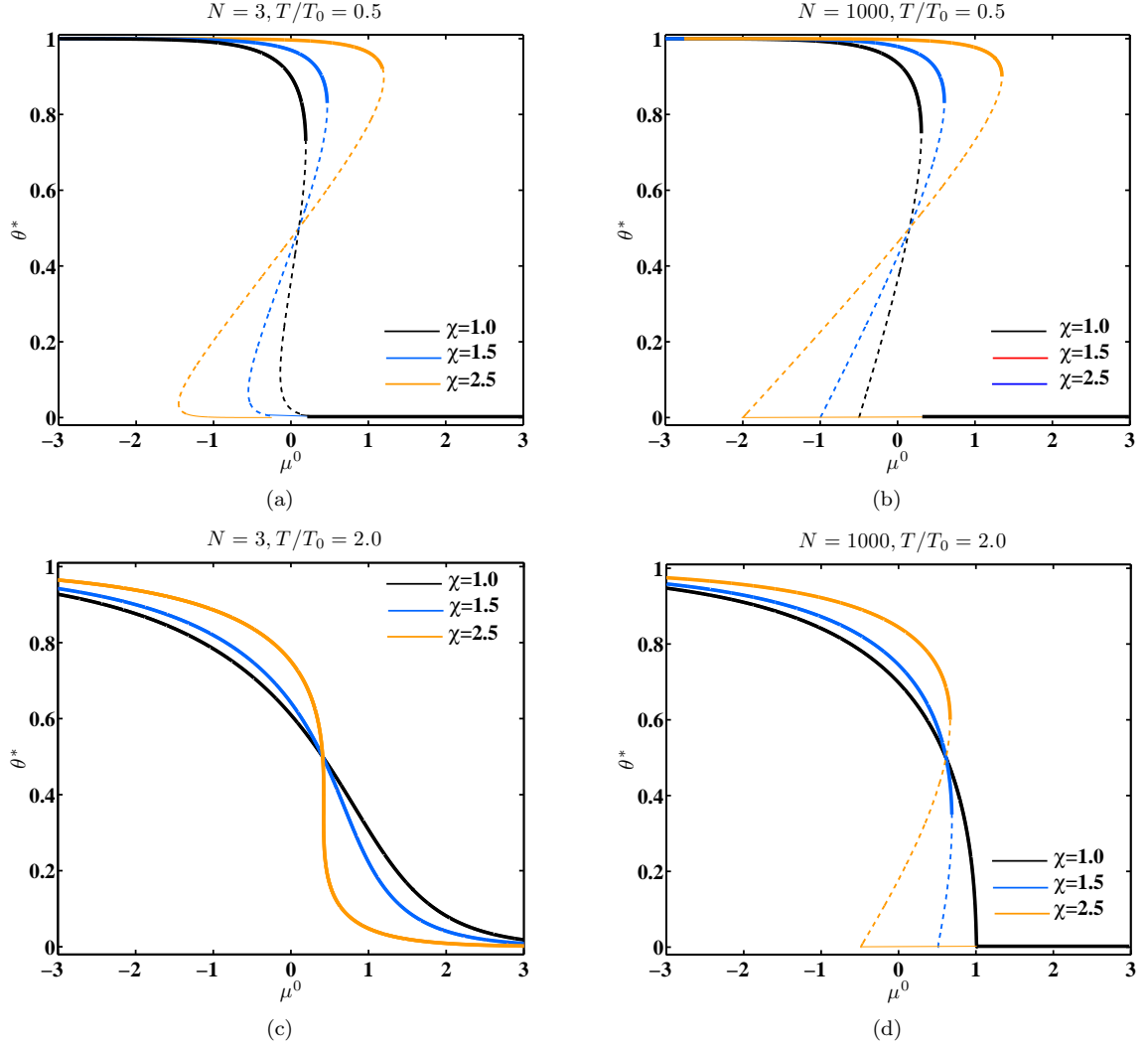


FIG. 7: (Color Online) Equilibrium values θ^* plotted vs μ^0 for different positive values of χ and at the indicated values of N , T/T_0 .

so the variation must satisfy $0 = [\theta_p \mathbf{v}_p + \theta_s \mathbf{v}_s]$ on Γ . This implies that three independent variations $(\mathbf{v}_p^-, \mathbf{v}_s^-, \mathbf{v}_p^+)$ are possible and that

$$0 = \{\mathbf{e}_p^- - \mathbf{e}_s^+\} \theta_p^- \mathbf{v}_p^- + \{\mathbf{e}_s^- - \mathbf{e}_s^+\} \theta_s^- \mathbf{v}_s^- - \{\mathbf{e}_p^+ - \mathbf{e}_s^+\} \theta_p^+ \mathbf{v}_p^+. \quad (17)$$

Since $\theta_p^- \neq 0$ and $\theta_s^- \neq 0$, we must have that $\mathbf{e}_p^- = \mathbf{e}_s^+$ and $\mathbf{e}_s^- = \mathbf{e}_s^+$ (and $\mathbf{e}_p^+ = \mathbf{e}_s^+$ if $\theta_p^+ \neq 0$). In this paper, $\theta_p^+ = 0$ and the interface conditions reduce to

$$\sigma_p^- \mathbf{n} - \sigma_s^- \mathbf{n} = (\mu_p^- - \mu_s^-) \mathbf{n}, \quad (18)$$

where $\sigma_p = \eta_p \epsilon_p$ and $\sigma_s = \eta_s \epsilon_s$ are the viscous stress tensors for polymer and solvent, respectively. In the case of a radially symmetric gel, the radial component of this equation is

$$\eta_p \frac{\partial v_p^-}{\partial r} - \eta_s \frac{\partial v_s^-}{\partial r} = (\mu_p^- - \mu_s^-), \quad (19)$$

where v_p^- and v_s^- are the radial components of the polymer and solvent velocities. Since the free energy $f(\theta)$ satisfies

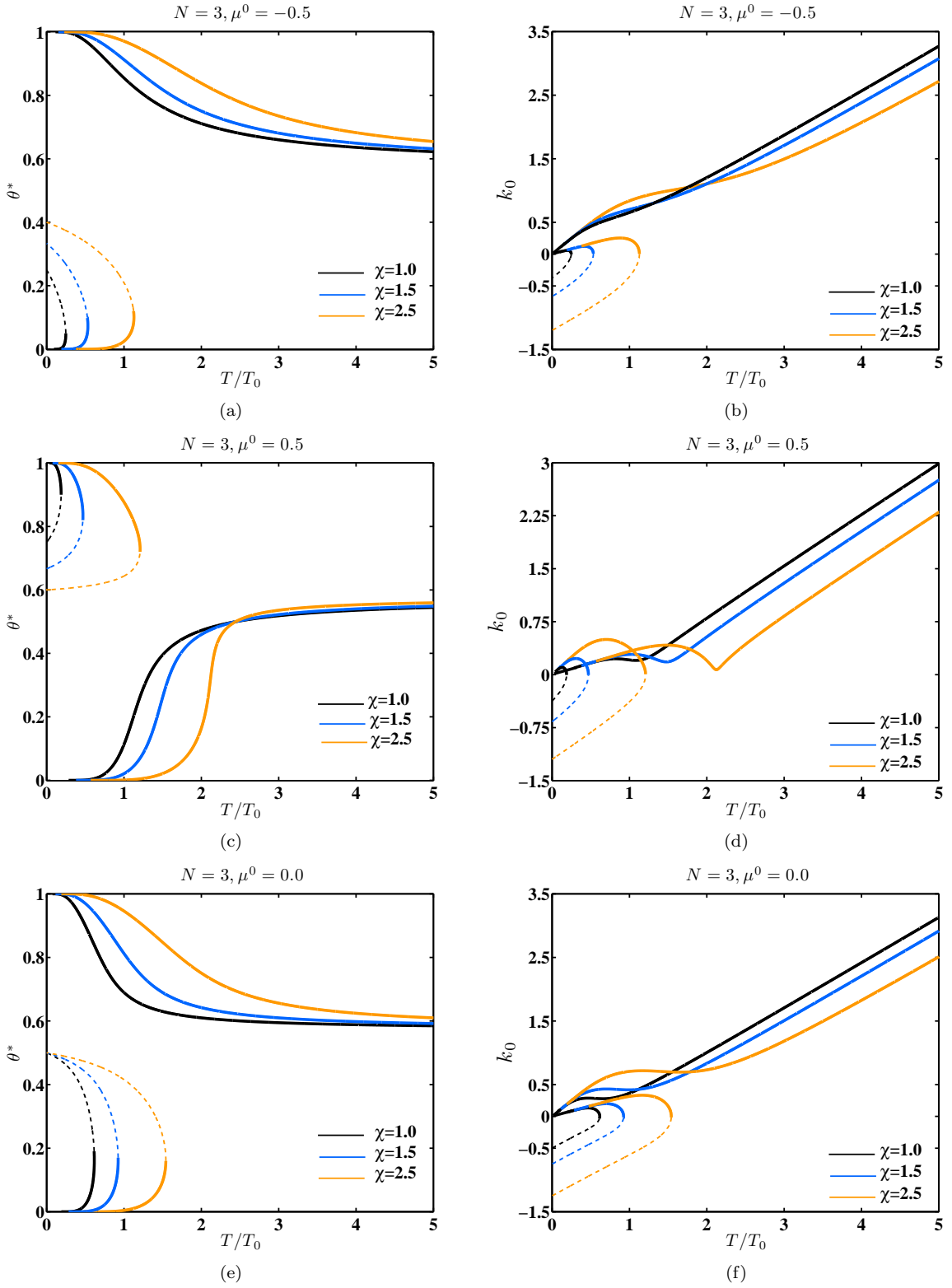


FIG. 8: (Color Online) (a,c,e) Equilibrium value θ^* vs T/T_0 at the indicated values of the parameters and (b,d,f) the corresponding decay rate k_0 .

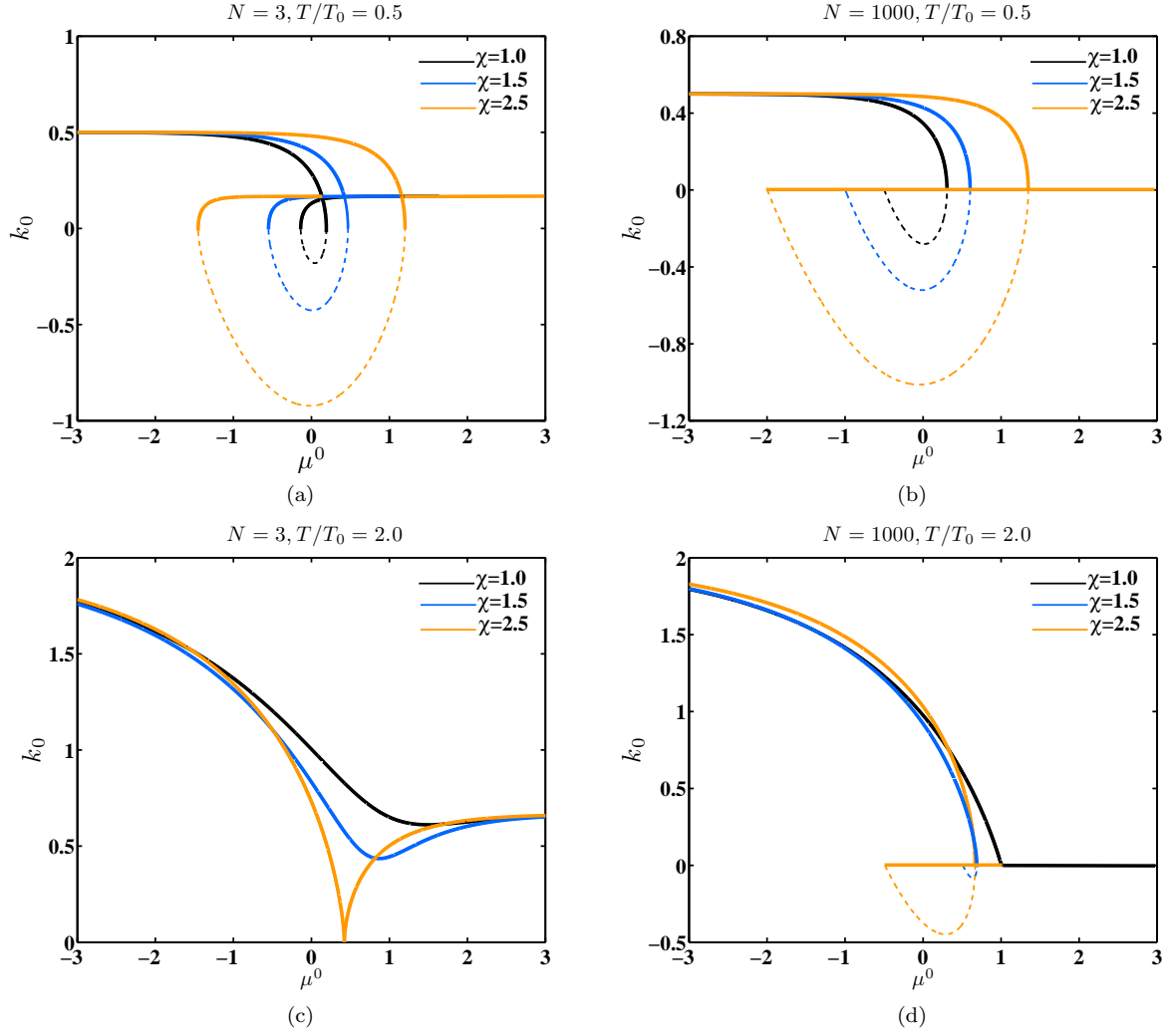


FIG. 9: (Color Online) The decay rate k_0 vs μ^0 for indicated values of $N = 3$ and T/T_0 and with positive χ .

$f' = \mu_p^- - \mu_s^-$, and because $\theta_p v_p + \theta_s v_s = 0$, Eq. 19 reduces to

$$\frac{\partial}{\partial r} \left(\eta_p v_p + \eta_s \frac{\theta_p}{1 - \theta_p} v_p \right) = f', \quad (20)$$

which is equivalent to Eq. 4.

-
- [1] P. J. Flory. *Principles of Polymer Chemistry*. Cornell University Press, Ithaca, NY, 1953.
 - [2] P. J. Flory and J. Rehner Jr. Statistical mechanics of crosslinked polymer networks I. rubberlike elasticity. *Journal of Chemical Physics*, 11:512, 1943.
 - [3] P. J. Flory and J. Rehner Jr. Statistical mechanics of crosslinked polymer networks II. swelling. *Journal of Chemical Physics*, 11(11):521, 1943.
 - [4] A. Katchalsky and I. Michaeli. Polyelectrolyte gels in salt solutions. *J Polym Sci*, 15:69–86, 1955.
 - [5] M. Doi and S. F. Edwards. *Theory of Polymer Dynamics*. Clarendon Press, Oxford, England, 1986.
 - [6] P. J. Flory. Statistical thermodynamics of random networks. *Proc. R. Soc. Lond. A.*, 351:351–380, 1976.
 - [7] T. Tanaka and D. J. Fillmore. Kinetics of swelling in gels. *J Chem Phys*, 70:1214–1218, 1979.

- [8] T. Tanaka, D. Filmore, S. T. Sun, I. Nishio, G. Swislow, and A. Saha. Phase transition in ionic gels. *Phys. Rev. Lett.*, 45(20):1636, 1980.
- [9] C. J. Durning and K. N. Morman. Nonlinear swelling of polymer gels. *J Chem Phys*, 98:4275–4293, 1993.
- [10] J. Maskawa, T. Takeuchi, K. Maki, K. Tsuijii, and T. Tanaka. Theory and numerical calculation of pattern formation in shrinking gels. *J. Chem Phys*, 110:10993–10999, 1999.
- [11] A. Onuki. Theory of pattern formation in gels: surface folding in highly compressible elastic bodies. *Phys. Rev. A*, 39:5932–5948, 1989.
- [12] K. Sekimoto, N. Suematsu, and K. Kawasaki. Spongelike domain structure in a two-dimensional model gel undergoing volume-phase transition. *Phys. Rev. A*, 39:4912–4914, 1989.
- [13] C. Wang, Y. Li, and Z. Hu. Swelling kinetics of polymer gels. *Macromolecules*, 30:4727–4732, 1997.
- [14] C. Wolgemuth, A. Mogilner, and G. Oster. The hydration dynamics of polyelectrolyte gels with applications to cell motility and drug delivery. *Eur. Biophys. J.*, 33:146–158, 2004.
- [15] T. Yamaue, T. Taniguchi, and M. Doi. Shrinking process of gels by stress-diffusion coupled dynamics. *Prog. Theor. Phys. Supp.*, 138:416–417, 2000.
- [16] W. Y. Gu, W. M. Lai, and V.C. Mow. A mixture theory for charged-hydrated soft tissues containing multi-electrolytes: Passive transport and swelling behaviors. *Trans ASME J. Biomech. Eng.*, 120:169–180, 1998.
- [17] J. S. Hou, M. H. Holmes, W. M. Lai, and V. C. Mow. Boundary conditions at the cartilage-synovial fluid interface for joint lubrication and theoretical verifications. *J Biomech Eng*, 111(1):78–87, 1989.
- [18] W. M. Lai, J. S. Hou, and V. C. Mow. A triphasic theory for the swelling and deformation behaviors of articular cartilage. *J. Biomech. Eng.*, 113(245-258), 1991.
- [19] Y. Lanir. Plausibility of structural constitutive equations for swelling tissues-implications of the c-n and s-e conditions. *Trans ASME J. Biomech. Eng.*, 118(10-16), 1996.
- [20] X. He and M. Dembo. On the mechanics of the first cleavage division of the sea urchin egg. *Exp. Cell Res.*, 233:252–273, 1997.
- [21] G. F. Oster and G. M. Odell. The mechanochemistry of cytogels. *Physica D*, 12:333–350, 1984.
- [22] C. Wolgemuth, E. Hoiczyk, D. Kaiser, and G. Oster. How myxobacteria glide. *Current Biology*, 12(5):369–377, March 2002.
- [23] C. W. Wolgemuth, E. Hoiczyk, and G. Oster. How gliding bacteria glide. *Biophysical Journal*, 82(1):1956, January 2002.
- [24] N. Cogan and J. P. Keener. The role of the biofilm matrix in structural development. *Mathematical Medicine and Biology*, 21, 2004.
- [25] T. Zhang, N. Cogan, and Q. Wang. Phase field models for biofilms. I. theory and one-dimensional simulations. *SIAM J. Appl. Math.*, 69(3):641–669, 2008.
- [26] T. Zhang, N. Cogan, and Q. Wang. Phase field models for biofilms. II. 2-D numerical simulations of biofilm-flow interaction. *Comm. Comp. Phys.*, 4(1):72–101, 2008.
- [27] J. P. Keener, S. Sircar, and A. L. Fogelson. Kinetics of swelling gels. *SIAM J. Appl. Math.*, submitted, 2010.
- [28] M. Doi. *Introduction to Polymer Dynamics*. Oxford University Press, Oxford, England, 1996.
- [29] N. Cogan and J. P. Keener. Channel formation in gels. *SIAM J. Appl. Math.*, 69:1839–1854, 2005.
- [30] M. Doi. Gel dynamics. *Journal of Physical Society of Japan*, 78(5):052001–1–19, 2009.
- [31] P. J. Flory. Phase equilibria in solutions of rod-like particles. *Proc Royal Soc Lond, Ser A*, 234:60–73, 1956.
- [32] P. J. Flory. *Statistical Mechanics of Chain Molecules*. Hanser Publishers, Cincinnati, 1988.
- [33] M. Rubenstein and R. H. Colby. *Polymer Physics*. Oxford University Press, 2004.
- [34] A.F.M. Barton. *Handbook of polymer-liquid interaction parameters and solubility parameters*. CRC press, 1990.
- [35] C.M. Hansen. The three dimensional solubility parameters - key to paint component affinities. *Journal of Paint Technology*, 39:505, 1967.
- [36] S. Sircar, J. P. Keener, and A. L. Fogelson. The effect of counter-ion valence on the swelling kinetics of a polyelectrolyte gel. in preparation, 2010.
- [37] S. Hirotsu. Softening of bulk modulus and negative poisson’s ratio near the volume phase transition of polymer gels. *J .Chem. Phys.*1991,94, 94(3939-3957), 1991.