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Article

Lyogel Equilibria with Helmholtz Equations of State. Part I: A Robust Second-Order Framework

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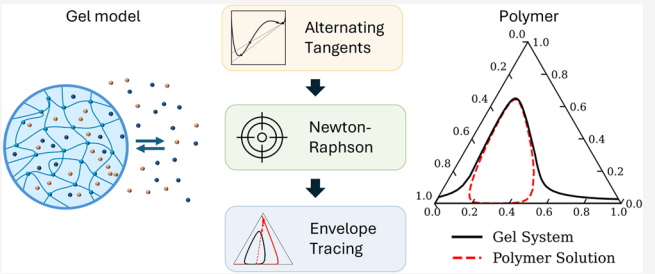
ABSTRACT: The thermodynamic calculation of gel phase equilibria is numerically challenging because of the strong asymmetry of polymer−solvent systems and the coupling of mixing and elastic contributions. In this work, a framework for gel phase equilibria is developed using the PC-SAFT equation of state. Building on strategies for polymer−solution liquid−liquid equilibria, the method is extended to gel systems by incorporating the elastic contribution of the polymer network through a Poynting-like correction. To improve numerical stability, the framework combines a second-order Newton−Raphson scheme with homotopy-based phase-envelope tracing and alternating-tangent initialization. The method is applicable to multicomponent systems and allows continuation in composition and temperature space. Its performance is demonstrated for pNIPAM−water and pNIPAM−water−ethanol systems. The results show that continuation strategies established for conventional polymer−solution phase equilibria can be transferred consistently to gel equilibria without repeated reinitialization.



INTRODUCTION AND MOTIVATION

Smart materials have attracted increasing interest in process engineering because they combine sensing and actuation within a single material platform. Among these, stimuli-responsive polymers, capable of undergoing reversible, large-scale structural changes in response to temperature,[1−3] solvent composition,[1−5] or pH,[6] are particularly promising for the development of autonomous, self-adjusting reactor systems. While the potential of these materials in medical[7] and industrial applications[8] is well-recognized, their successful deployment in adaptive reactor technology (e.g., Smart reactors)[9] is fundamentally contingent upon a reliable thermodynamic description.

Despite the extensive literature regarding the thermodynamic foundations of polymer and gel systems,[10−13] a critical gap remains: the availability of numerical methods capable of computing these equilibria with the robustness and speed required for engineering design. Current equilibrium calculations inherit the substantial numerical challenges of polymer−solution thermodynamics,[14−17] characterized by strong molecular asymmetry and the complex coupling of mixing and elastic contributions. These factors often lead to slow convergence and a high sensitivity to initialization, rendering standard algorithms insufficient for real-time process design, optimization, and control. For stimuli-responsive gels to function as active components in smart reactors, the underlying equilibrium problems must be solved with a reliability that matches the demands of practical use.

In this work, we address this bottleneck by extending the robust equilibrium algorithms originally developed for polymer solutions by Lindvig et al.,[18] von Solms et al.,[19] and Michelsen and Møllerup[20] to the specific requirements of gel systems. While these foundational works established efficient solvers for liquid−liquid and polymer−solvent equilibria, the modeling of gels introduces additional complexities, most notably the rigorous coupling of chemical potentials with the elastic energy of the polymer network. We address these requirements by integrating a second-order solution strategy with homotopy-based phase-envelope tracing, adapted specifically to handle the swelling behavior and mechanical constraints inherent to responsive gels. The methodology is implemented using the PC-SAFT equation of state,[21,22] which has proven success in capturing the complexities of polymer solutions,[23,24] associating polymers[25] and gel-containing mixtures.[26,27] By providing executable code[28] alongside this framework, we aim to

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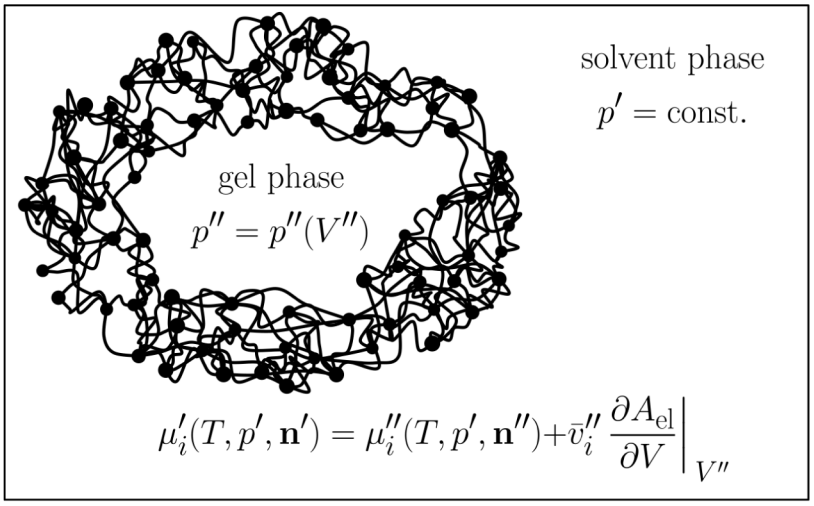

Figure 1. Simplified schematic of the pseudophase representation used for gel thermodynamics. The gel phase is treated as a homogeneous phase in equilibrium with an external solvent phase. This is a conceptual representation of the elastic constraint of the cross-linked polymer network and the resulting gel-phase pressure, not an explicit description of the porous gel structure or confinement effects.

establish a transparent and reproducible standard for the thermodynamic modeling of responsive materials, enabling the direct integration of these complex physics into the design of adaptive chemical processes.

Thermodynamic Modeling of Gels

The thermodynamic modeling of gels has been addressed in numerous studies.[1,11,26,27,29−33] Despite differences in formulation, most approaches share a common set of principles. First, the swelling behavior of a gel is described using a pseudophase approximation, in which the gel is treated as a distinct thermodynamic phase containing both the cross-linked polymer network and the solvent species. In this representation, the gel is modeled as a homogeneous pseudophase and its internal porous microstructure is not described explicitly. Accordingly, local confinement effects, pore-scale inhomogeneities, and other structural details of the network are not resolved. Instead, their thermodynamic effect is incorporated only in a lumped manner through the elastic contribution to the gel-phase pressure. This gel phase is assumed to be in equilibrium with an external solvent phase. Second, the polymer network is confined to the gel phase and does not exchange with the surrounding solvent. Third, the presence of the cross-linked polymer network gives rise to a pressure within the gel phase that differs from the ambient pressure of the surrounding solvent phase.

The system considered in this work is schematically illustrated in Figure 1. Two phases are present and in thermodynamic equilibrium, with the gel phase experiencing an internal pressure p'' that generally differs from the pressure of the solvent phase. The internal gel pressure depends on the current gel volume V''. Solvent molecules are free to exchange between the two phases, whereas the network-forming polymer is restricted to the gel phase. The schematic should therefore be understood as a simplified thermodynamic representation of the system rather than a structural model of the gel morphology.

Network Contribution in the Pseudo−Phase Approximation. The pressure difference between the gel phase and the surrounding solvent phase can be treated in several ways. In this work, the approach proposed by Maurer and Prausnitz[11] is adopted. It is based on evaluating the Gibbs free energy of the gel phase at the ambient pressure and applying a Poynting-type correction to obtain the Gibbs free energy at the gel pressure. This yields

$$G''(T,\ p'',\ \boldsymbol{n}'') = G''(T,\ p',\ \boldsymbol{n}'') + V''(p'' - p') \tag{1}$$

where $\boldsymbol{n}$ denotes the vector of mole numbers of each component in the respective phases. The elastic free energy A_{el} describes the pressure difference between the ambient pressure p', corresponding to a polymer solution without a network, and the pressure p'' generated by the cross-linked network. Following the notation of Maurer and Prausnitz[11] the relation is expressed as

$$\mathrm{d}A_{\text{el}} = -(p' - p'')\mathrm{d}V'' \tag{2}$$

Based on this expression, a modified equilibrium condition for component i can be formulated as

$$\mu_i'(T,\ p',\ \boldsymbol{n}') = \mu_i''(T,\ p',\ \boldsymbol{n}'') + \overline{v}_i'' \left.\frac{\partial A_{\text{el}}}{\partial V}\right|_{V''} \tag{3}$$

which enables a direct evaluation of the chemical potentials at the ambient pressure p'. This formulation implicitly assumes that the partial molar volumes $\overline{v}_i''$ remain constant over the pressure range between p' and p'' for the solvent molecules in the gel phase.

Several alternative treatments reformulate the elastic free energy contribution of the network as an effective additive contribution to the Helmholtz free energy.[26,27,34,35] While this distinction is mostly one of representation, we argue that incorporating elasticity directly into the Equation of State (EOS) framework could lead to a redundant accounting of the network's influence. In the present work, the network contribution is thus kept explicit to maintain thermodynamic clarity and is treated as a Poynting-type correction rather than an internal EOS contribution.

This approach is motivated by the fact that the elastic response fundamentally dictates the internal pressure of the gel phase, creating a direct coupling between the chemical potential and the mechanical pressure balance. Framing the elasticity as a contribution in the EOS can result in an inconsistent treatment of both the pressure and chemical

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potential balances and could lead to a double counting of the elastic contribution.

In equilibrium calculations, the primary quantity derived from network models is the elastic pressure, $-(\partial A_{el}/\partial V)_{T,N}$. An experimental gel specimen contains a fixed amount of polymer and thus has a well-defined reference volume V_{ref}. In a thermodynamic formulation based on the pseudo−phase approximation, $A(N, V, T)$, this constraint is not built in. The polymer content is not fixed by construction, and V_{ref} therefore remains ambiguous unless a reference state is introduced explicitly. One convenient choice is the dry polymer state, in which V_{ref} is determined by the density of the pure polymer.[26,27] A more general treatment follows Maurer and Prausnitz[11] by using the polymer volume fraction ϕ_{poly}, allowing the reference state to coincide with the network-formation state even in the presence of solvent. In this way, the pseudo−phase description can be related consistently to the experimentally accessible gel volume V.

$$\frac{\phi_{poly}^{ref}}{\phi_{poly}} = \frac{\overline{v}_{poly}^{ref}\, n_{poly}}{V_{ref}} \frac{V}{\overline{v}_{poly}\, n_{poly}} \approx \frac{V}{V_{ref}} \tag{4}$$

While the number of polymer molecules n_{poly} is constant by definition, the partial molar volume of the polymer $\overline{v}_{poly}$ may, in principle, differ between the reference and the current state. In agreement with Maurer and Prausnitz[11] this difference is neglected as an approximation.

Second-Order Numerical Approach

The solution of liquid−liquid equilibria (LLE) in polymer solutions poses significant numerical challenges due to the pronounced asymmetry in size between solvent molecules and polymer chains. This asymmetry is particularly relevant when Helmholtz-energy equations of state are used, since these models are formulated in terms of mole numbers, volume, and temperature. This variable basis is advantageous because it preserves the molecular-mechanical structure of models such as PC-SAFT, but it also requires the equilibrium calculation to resolve very small polymer mole fractions that may nevertheless correspond to substantial mass, segment, or volume fractions. Classical polymer−solution theories, most notably Flory−Huggins theory, avoid part of this numerical difficulty by using volume fractions as the natural composition descriptor. However, such formulations are typically more phenomenological and do not provide the same molecular Helmholtz-energy framework used here. This motivates the present second-order methodology. At the same time, transformed composition variables, such as mass fractions, segment fractions, volume fractions, or logarithmic mappings, can be useful during initialization and search procedures because they may provide a smoother and better-scaled representation of the composition space. Standard approaches for calculating the LLE behavior for low molecular mass solvents based on successive substitution and the Rachford-Rice equation have been described as unreliable,[14] not applicable[16] and unstable[36] for polymer solutions. This issue has been extensively studied in the literature, with proposed solution strategies ranging from damped successive-substitution algorithms,[36,37] to generalized gradient-free optimization methods,[27,38] and second-order approaches.[14,39] For complex equations of state, such as SAFT-type models, the explicit evaluation of second-order derivatives has traditionally been avoided. However, with the increasing availability of automatic differentiation techniques based on dual and hyper-dual numbers,[40] as well as open-source implementations,[41] Newton-type methods exploiting second-order information have become a promising and attractive alternative to gradient-free solvers such as Powell's method or the Nelder−Mead algorithm. This work follows the Newton−Raphson scheme proposed by Lindvig et al.,[18] with subsequent extensions introduced to account for gel equilibria. While each of these elements has been studied individually, their consistent integration into a second-order continuation framework for gel equilibria has not been reported previously.

Formulation of the Newton−Raphson Scheme. Following Lindvig et al.[18] the solution vector $\boldsymbol{y}$ for a system consisting of two phases in equilibrium is defined as

$$y_i = \ln x_i' \tag{5}$$

$$y_{NC+i} = \ln x_i'' \tag{6}$$

$$y_{2NC+i} = \ln K_i \tag{7}$$

$$y_{3NC+1} = \ln T \tag{8}$$

where x_i' and x_i'' denote the mole fractions of component i in the solvent phase and the gel phase, respectively. The partition coefficients K_i and the temperature T are included as independent variables. The solution vector therefore has $3NC + 1$ entries with NC being the number of components in the system. The system of equilibrium equations is then given by

$$f_i = \ln K_i - (\ln \hat{\phi}_i'' - \ln \hat{\phi}_i') = 0 \tag{9}$$

$$f_{NC+i} = \ln K_i - (\ln x_i' - \ln x_i'') = 0 \tag{10}$$

$$f_{2NC+1} = \sum_{i=1}^{NC} x_i' - 1 = 0 \tag{11}$$

$$f_{2NC+2} = \sum_{i=1}^{NC} x_i'' - 1 = 0 \tag{12}$$

$$f_{2NC+2+j} = y_{s,j} - S_j = 0 \tag{13}$$

Equations 9 and 10 represent the standard isofugacity conditions for liquid−liquid equilibrium. It is noted that the composition variables x_i are treated as independent variables. The closure conditions for the phase compositions are enforced through eqs 11 and 12. Since the isofugacity criterion alone generally admits multiple solutions, particularly when considering variable temperature or multicomponent systems, additional constraints are required to identify a unique tie line. This is accomplished through the set of eq 13, with S_j serving as the value of the respective constraint j. For binary systems, specification of the temperature is sufficient, whereas for ternary and higher-order systems additional composition constraints must be imposed. This finally leads to $NC - 1$ constraints, with $j = NC - 1$ and $y_{s,j}$ being the constraint element of $\boldsymbol{y}$, required to reach the value S_j. A detailed discussion of this formulation is provided by Lindvig et al.[18] and Michelsen and Møllerup.[20]

Modification for Gel Equilibria. In the present model, it is assumed that the polymer is excluded from the solvent phase. Consequently, the polymer mole fraction in the solvent

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phase is zero, $x'_{poly} = 0$, and the corresponding partition coefficient is $K_{poly} = 0$. These quantities are fixed and are therefore not updated within the Newton−Raphson iterations.

For gel equilibria, however, the partition coefficients K_i of the solvent components behave differently. Due to the modified equilibrium condition given by eq 3, the elastic contribution of the network alters the equilibrium relations. To account for this effect, an adjusted partition coefficient $\tilde{K}_i$ is formally introduced as

$$\tilde{K}_i = \frac{x_i'}{x_i''} \neq \frac{\hat{\phi}_i''}{\hat{\phi}_i'} \tag{14}$$

with both fugacity coefficients $\hat{\phi}$ evaluated at the ambient pressure p'. This modification leads to a revised form of eq 9,

$$f_i = \ln \tilde{K}_i - \left(\ln \hat{\phi}_i'' - \ln \hat{\phi}_i'\right) - \frac{\bar{\mathbf{v}}_i''}{RT}\frac{\partial A_{el}}{\partial V}\bigg|_{V''} = 0 \tag{15}$$

while the structure of the solution vector $\boldsymbol{y}$ remains unchanged, with $\tilde{K}_i$ replacing K_i in eq 7.

The partial molar volume $\bar{v}_i$ is evaluated using second-order derivatives of the Helmholtz free energy, yielding

$$\bar{v}_i = \frac{\partial V}{\partial n_i}\bigg|_{T,p} = -\frac{\partial^2 A^{EOS}}{\partial n_i \partial V}\left[\frac{\partial^2 A^{EOS}}{\partial V^2}\right]^{-1} \tag{16}$$

As a consequence of this formulation, the evaluation of the Jacobian matrix requires third-order derivatives of the Helmholtz free energy.

Tracing of the Solution. All solvers discussed above are local optimization methods and therefore require an initial guess sufficiently close to the final solution. To address this limitation, a homotopy-based approach is employed in this work, in which the initial guess for a new equilibrium calculation is estimated from previously converged solutions. This approach is commonly referred to as envelope tracing.[18,20] It enables the systematic continuation of liquid−liquid equilibria from simple systems, such as binaries, to multicomponent mixtures.

During tracing, two numerical steps have to be distinguished. First, the Newton−Raphson method is used to converge an individual coexistence point from a given initial guess. Second, the continuation step size determines how far the algorithm advances along the equilibrium curve before the next Newton solve is initialized. The latter step size must be adjusted because the local sensitivity of the solution with respect to the continuation variable can vary strongly along the binodal. In regions where a small change in the traced variable leads to a large change in the solution vector, for example near turning points or critical regions, smaller continuation steps or a change of the tracing variable might be beneficial. This is explained in detail in the literature.[18,20]

In the present implementation, the step size is adapted based on the convergence behavior of the Newton−Raphson correction, in particular the number of iterations required to converge the new coexistence point. This provides a simple and robust practical indicator of the local difficulty of the continuation step. More elaborate sensitivity-based criteria can also be incorporated into the tracing procedure and may improve stability and efficiency for higher-dimensional multicomponent systems or near critical regions. Such extensions are compatible with the present framework but were not required for the examples considered here. A detailed description of the implemented step-size-control procedure is provided in the Supporting Information.

Alternating Tangents for the Initial Guess. Since no reliable initial guess is available for the first equilibrium calculation, the method of alternating tangents proposed by von Solms et al.[19] is employed. The alternating tangent method has been successfully applied to binary polymer solutions.[18,19] A detailed explanation can be found in the Supporting Information. To stabilize the subsequent Newton−Raphson calculations, the iterations were originally formulated using logarithmic composition variables. In the present work, numerical stability is improved by reformulating the composition variable through the logit function, thereby constraining it to the physically admissible range $0 < x < 1$. It requires only a minor adjustment of the derivatives, given by

$$\frac{\partial f}{\partial \mathrm{logit}(x)} = \frac{\partial \ln(x)}{\partial \mathrm{logit}(x)}\frac{\partial f}{\partial \ln(x)} = (1-x)\frac{\partial f}{\partial \ln(x)} \tag{17}$$

As demonstrated by Lindvig et al.[18] this binary solution provides an ideal starting point for second-order continuation. The alternating tangent method is therefore used here only for binary initialization, while multicomponent envelopes are traced from accessible lower-dimensional solutions by continuation in composition or temperature. If no miscibility gap is present on the binary edges, or if the phase split is disconnected from such starting points, alternative initialization strategies may be required, including spinodal analysis, tangent-plane-distance stability analysis,[42] composition-space scanning, or convex-hull-based methods.[43,44] An example of such a case is discussed below, where the phase split is not located on the binary edges at the target conditions but can still be accessed by first generating an initial guess with the alternating tangent method at a suitable temperature and subsequently continuing the solution in temperature.

Thermodynamic Model

The methodology presented in this work is independent of the underlying thermodynamic model but is specifically designed to address numerical challenges encountered when applying Helmholtz-energy-based equations of state (EOS) to polymer solutions. These challenges arise primarily from the mole-number-based formulation of Helmholtz EOS, which leads to pronounced asymmetry in polymer−solvent systems.[14,36,37,45]

In the present study, the perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state[22] is employed due to its proven reliability in describing the thermodynamic behavior of polymer solutions.[23,24] In this framework, molecules are modeled as chains of spherical segments that interact through various additive repulsive and attractive forces. A major advantage of this strong physical basis is that it not only ensures accurate modeling but also aids in interpreting the underlying molecular mechanisms, providing insight into why these systems exhibit complex macroscopic behaviors.

PC-SAFT expresses the total Helmholtz free energy as a sum of physically meaningful contributions: the ideal-gas term A_{id}, the short-range hard-sphere contribution A_{hs}, the hard-chain contribution A_{hc}, the long-range dispersion contribution A_{disp}, and the directional association (hydrogen-bonding) contribution A_{assoc}. The free energy is therefore given by

$$A^{PC\text{-}SAFT} = A_{id} + A_{hs} + A_{hc} + A_{disp} + A_{assoc} \tag{18}$$

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The model requires five pure-component parameters for associating fluids: the segment number m, the segment diameter σ, the dispersion energy parameter ε, the association energy ε^{AB}, and the association volume κ^{AB}. The number of association sites, n^A and n^B, is assigned based on the component's molecular structure. For mixtures, the cross-dispersion interaction may be adjusted through the binary interaction parameter k_{ij}, defined by

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}(1 - k_{ij}) \tag{19}$$

Setting $k_{ij} = 0$ recovers the standard mixing rule without any additional correction. The formulation applied in this work follows the original PC-SAFT framework proposed by Gross and Sadowski[22] with the chain and association contributions following Chapman et al.[21] Once the Helmholtz free energy is evaluated, all thermodynamic properties and derivatives required in this work follow from standard thermodynamic relations.

METHODS

To illustrate the method, pure-component parameters for pNIPAM, water, and ethanol were sourced from literature,[26,46,47] and are summarized in Table 1, following the work of Arndt and Sadowski[26] The corresponding binary interaction parameters k_{ij} used for the mixture calculations are provided in Table 2.

Table 1. PC-SAFT Parameters for pNIPAM, Water, and Ethanol (EtOH)

Parameter	Unit	pNIPAM[26]	Water[46]	EtOH[47]
M	g mol^{-1}	$m{\cdot}M_{monomer}$	18.015	46.069
m	–	eq 22	1.20466	2.38267
σ	Å	5.38	See note[a]	3.17706
ε	K	297.343	353.9449	198.237
$n^A = n^B$	–	$2m$	2	2
$\varepsilon^{A_iB_i}$	K	175	2425.67	2653.39
$\kappa^{A_iB_i}$	–	0.045	0.04509	0.03238
Φ	–	2.24/2.65	–	–

[a] σ_{H_2O} = 2.7927 + 10.11 exp(−0.01775 T/K) − 1.417 exp(−0.01146 T/K).

Table 2. Binary Interaction Parameters k_{ij} Used in This Work

Binary pair (i/j)	k_{ij}
Water/Ethanol	−0.185
Water/pNIPAM	−0.17 + 0.0013 × (T/K − 298.15)
Ethanol/pNIPAM	0.0

The segment number per chain, m_{chain}, is estimated based on the relative cross-linker content y, which is experimentally accessible. It is defined as

$$y = \frac{n_{linker}}{n_{linker} + n_{monomer}} \tag{20}$$

where n_{linker} and $n_{monomer}$ denote the amounts of substance of linker and monomer used during gel preparation. Most network theories introduce a network functionality Φ as a descriptor of the connectivity of strands within the network. This parameter is generally assumed to be characteristic of a given gel preparation and to remain invariant during swelling. Assuming an ideal tetrahedral network, the network functionality Φ takes the value $\Phi = 4$, which allows the number of chains n_{chain} between the nodes to be approximated as

$$n_{chain} \approx \frac{\Phi}{2} n_{linker} \tag{21}$$

The resulting chain length is then determined by

$$m_{chain} \approx m_{monomer} \frac{n_{monomer}}{n_{chain}} = m_{monomer} \frac{2}{\Phi} \frac{1 - y}{y} \tag{22}$$

The framework is designed to be modular, allowing for the exchangeable selection of the elastic contribution. In this study, the network elasticity is described by the Flory–Rehner[48] affine model:

$$\frac{A_{el}^{aff}}{k_B T} = n_{chain} \frac{\Phi - 2}{\Phi} \left[\frac{3}{2} \left(\left(\frac{V}{V_{ref}} \right)^{2/3} - 1 \right) - \ln\left(\frac{V}{V_{ref}} \right) \right] \tag{23}$$

While the original parameters from Arndt and Sadowski[26] utilized a functionality of Φ = 2.24, this work employs a slightly adjusted value of Φ = 2.65 to better represent experimental data. This adjustment stems from a difference in the treatment of the elastic term. Arndt and Sadowski incorporated the elastic contribution into both the pressure and the chemical equilibrium calculations. In contrast, this work follows the approach of Maurer and Prausnitz, where the elastic contribution is treated as a Poynting-like correction.

The double consideration of the elastic contribution in the previous literature gave rise to an apparent increase in network stiffness; by adopting the current method, a higher functionality is required to match the observed swelling behavior. Accordingly, the adjusted value of Φ does not represent a free recalibration introduced to recover the swelling behavior, but follows from the revised thermodynamic treatment in which the elastic contribution is handled explicitly.

Because the purpose of the present work is to demonstrate the proposed equilibrium framework, the selected value of Φ = 2.65 is used as a representative model parameter for the illustrative calculations. A systematic analysis of different network models, the physical interpretation of the associated network parameters, and their influence on the predicted gel behavior is beyond the scope of this methodological contribution. These aspects are discussed in detail in the companion publication,[49] where the focus is placed on system parametrization, parameter identification, and the sensitivity of the predicted swelling behavior to the selected network-model parameters.

TRACING OF THE PHASE ENVELOPE

The following examples illustrate the applicability of the proposed tracing method to both polymer–solution and gel equilibria. In particular, they show that the method can be applied to binary and ternary systems, can be continued in both composition and temperature, and can be transferred from conventional liquid–liquid equilibrium calculations to pseudophase descriptions of gels.

Figure 2 presents the pNIPAM–water system. This case is used to illustrate both the phase behavior of the un-cross-linked polymer solution (red dashed curve) and the corresponding swelling behavior of the gel (black solid curve). Experimental swelling data are included for comparison. The comparison is intended as an illustrative comparison of the order of magnitude and qualitative behavior rather than as a complete parameter-identification study. The interpretation of swelling data requires care because experimental data may be represented either in terms of the degree of swelling or, after conversion, in terms of the gel-phase composition used in the pseudophase description. These different representations can affect the apparent weighting of individual data points during parameter fitting. Moreover, the combination of associating PC-SAFT with an elastic contribution provides a rich parameter space, whereas experimental data for such gel systems are often scarce. Consequently, fitted parameters may

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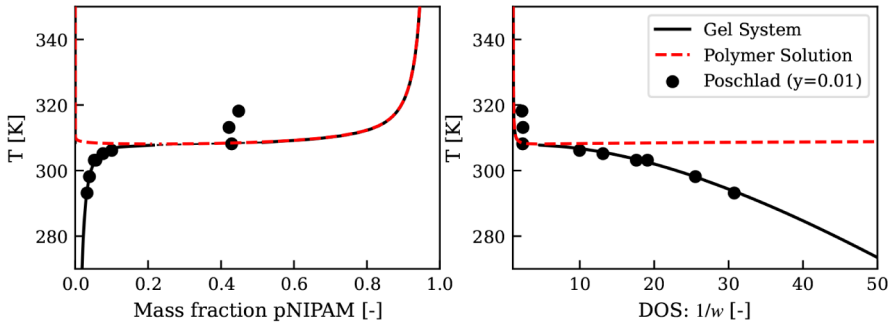

Figure 2. Effect of the network-model on the calculated swelling behavior. The elastic contribution was evaluated using a modified network functionality. Two different representations are shown: swelling expressed in terms of mass fractions, consistent with the pseudophase approximation, and swelling expressed in terms of the degree of swelling, which is closer to the experimental representation. Experimental swelling data from Poschlad et al.[1] are also shown. The solid black curve shows results for the cross-linked polymer and the red dashed curve shows phase behavior for the polymer solution with no cross-linking.

reproduce the swelling behavior without being uniquely interpretable. The implications of this parameter richness and possible strategies for parameter identification are discussed in detail in the companion publication.[49]

Starting from the high-temperature regime, the phase envelope is traced toward lower temperatures.

From a thermodynamic perspective, the equation of state describes polymer−solvent mixing. In the absence of cross-linking, the polymer is completely miscible below approximately 307 K. Cross-linking introduces elastic constraints that prevent macroscopic dissolution and thereby establishes a phase boundary between the gel and the surrounding solvent. Conversely, if the underlying polymer−solvent system exhibits a miscibility gap, only limited swelling is expected because the thermodynamic driving force for mixing is reduced. An overlap between the polymer solution phase boundary and the gel swelling curve can be observed. The equilibrium degree of swelling therefore results from the balance between the thermodynamic driving force for mixing and the elastic restoring force of the network.

In this context, it is important to emphasize that the macroscopic degree of swelling, which is readily accessible experimentally, can contain different levels of information when interpreted within a pseudophase-equilibrium framework. The gravimetric degree of swelling, *DOS*, is defined as

$$\mathrm{DOS} = \frac{m_{\text{swollen gel}}}{m_{\text{dry gel}}} = \frac{1}{w^{\text{gel}}_{\text{polymer}}} \tag{24}$$

where $w^{\text{gel}}_{\text{polymer}}$ denotes the polymer mass fraction in the swollen gel, $m_{\text{swollen gel}}$ the mass of the swollen gel including the solvent, and $m_{\text{dry gel}}$ the mass of the dry gel, that is, the polymer mass. This relationship highlights the strongly nonlinear mapping between *DOS* and composition. For example, $DOS = 1$ corresponds to $w^{\text{gel}}_{\text{polymer}} = 1$, whereas $DOS = 3$ already implies $w^{\text{gel}}_{\text{polymer}} \approx 0.33$. Differences of this magnitude may still lie within typical experimental uncertainties, particularly at low *DOS*. Consequently, small swelling degrees provide only limited quantitative information on network elasticity or on the underlying thermodynamic description, although they remain useful for qualitatively distinguishing between swollen and collapsed states. In contrast, large swelling degrees observed in formally miscible regions of the polymer−solution phase behavior provide much stronger constraints and are therefore more informative for assessing the elastic response of the network.

Figure 3 illustrates the tracing procedure for a ternary solution of pNIPAM, water, and ethanol. In this example, the

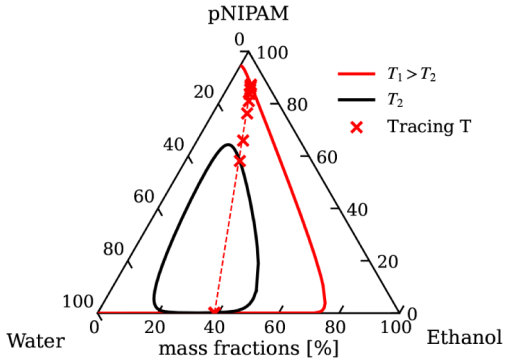

Figure 3. Illustration of phase-envelope tracing for a ternary pNIPAM−water−ethanol solution. Starting from a binary pNIPAM−water equilibrium point obtained by the alternating tangent method at temperature T_1, the solution is continued first into ternary composition space and subsequently in temperature until the target temperature T_2 is reached. The example demonstrates the tracing of the envelope across both composition and temperature space.

desired phase envelope is to be obtained at the target temperature T_2. For the system considered, the binary system of polymer and water exhibits lower critical solution temperature (LCST) behavior, as shown in Figure 2, resulting in a miscibility gap on the binary axis at the higher temperature T_1. This provides an initial starting point for the ternary system, which is calculated using the method of alternating tangents. The phase envelope at T_1 is first traced into the ternary composition space. Subsequently, the temperature is adjusted incrementally from T_1 to the target temperature T_2. Once T_2 is reached, tracing is continued to determine the complete phase envelope. This example demonstrates that the method is not restricted to a single binary cut, but can be continued systematically across both composition and temperature dimensions.

Critical points pose a particular challenge for continuation methods. Steps taken normal to the curvature of the phase envelope may lead to much larger changes in the solution vector than steps taken tangentially along the envelope. In such cases, a change of the traced specification variable is often

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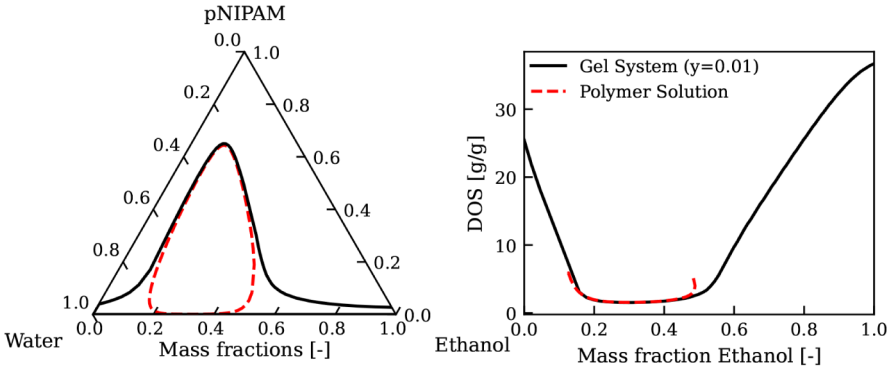

Figure 4. Calculated ternary LLE of the pNIPAM−water−ethanol system, shown both in the pseudophase representation and in terms of the degree of swelling, for the polymer solution (red dashed) and the gel (solid black). The results demonstrate that the tracing method can be applied successfully to ternary gel equilibria.

required. In the present work, however, this complication does not arise for gel equilibria. Within the present pseudophase formulation, miscibility gaps are enforced by the modeling assumptions, so critical points do not occur in the gel calculations. As a result, envelope tracing for gel systems is considerably simpler than for polymer−solution equilibria.

Figure 4 shows the results for the pNIPAM−water−ethanol mixture. Using the parameters reported by Arndt and Sadowski,[26] the model predicts pronounced cononsolvency. The tracing algorithm again successfully reproduces the corresponding equilibrium manifold.

It is noteworthy that, within the present contribution based modeling approach, the polymer−solution LLE behavior largely determines the extent to which the gel shrinks or swells. This observation deserves further attention. The current results suggest that the temperature-triggered swelling response is governed primarily by the LCST behavior, while the cononsolvency effect in the water−ethanol mixture is represented through two critical regions in the polymer−solution LLE. Within the model, these features are then directly reflected in the pronounced swelling behavior of the gel. Since this constitutes a modeling assumption, it should be examined more critically in future work. In particular, a clearer separation between elastic effects and the underlying polymer−solution thermodynamics would be desirable. The additive treatment of mixing and elastic contributions follows the classical Flory−Rehner-type framework, in which swelling is described as a balance between polymer−solvent mixing and the elastic penalty of network deformation.[10,50] This separation is physically plausible, for example because the LCST of linear pNIPAM solutions is close to the transition temperature of cross-linked pNIPAM gels[1] but the independence of elastic and chemical effects is not generally proven. The resulting parameter interpretation, especially regarding molar-mass effects and network parameters, is discussed in the companion publication.[49]

Overall, the presented examples show that the tracing approach can be transferred consistently from binary polymer−solution equilibria to ternary systems and to gel pseudophase equilibria. In particular, the method enables the systematic continuation of an existing equilibrium solution across changes in composition, temperature, and network constraints. This makes it possible to construct phase diagrams and swelling equilibria in a unified manner, without reinitializing the phase-equilibrium calculation at each state point.

CONCLUSION

This work addresses a central challenge in the thermodynamic modeling of stimuli-responsive gels: the development of a robust numerical framework for equilibrium calculations in systems with strong molecular asymmetry and coupled mixing-elastic effects. By extending second-order solution strategies and homotopy-based phase-envelope tracing to gel pseudophase equilibria, a computational approach was established that can be applied consistently across binary, ternary, and cross-linked polymer systems.

Within the PC-SAFT framework, the methodology was shown to provide a systematic route for following equilibrium states over changes in composition and temperature. Its main practical benefit lies in the combination of second-order convergence and continuation-based tracing, which reduces the need for repeated manual initialization and facilitates the generation of complete equilibrium manifolds. This is particularly relevant for future embedding of such calculations into process-modeling workflows, for example in flowsheeting, optimization, or adaptive reactor models.

Beyond the numerical aspects, the present work also clarifies the thermodynamic treatment of gel elasticity in an EOS-based NPT framework. In particular, the explicit pseudophase formulation and the interpretation of the elastic contribution as a Poynting-like correction provide a transparent and thermodynamically consistent basis for describing gel swelling equilibria. At the same time, the present results also highlight that the predicted swelling behavior remains strongly linked to the underlying polymer−solution phase behavior, so a clearer separation between elastic effects and polymer−solution thermodynamics remains an important task for future work.

Although PC-SAFT was chosen here because of its physical foundation and proven suitability for polymer systems, the proposed framework is modular and can, in principle, be transferred to other Helmholtz-energy-based thermodynamic models. The essential requirement is that the chosen model provides thermodynamically consistent residual Helmholtz energies and the corresponding first- and second-order derivatives needed for the Newton and continuation calculations. Therefore, other SAFT variants, CPA-type equations of state, or related models may also be suitable within the same numerical framework. Together with the provision of executable code,[28] this work therefore contributes a transparent and reproducible basis for further studies on

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responsive materials and their integration into adaptive process concepts such as smart reactors.

■ ASSOCIATED CONTENT

Data Availability Statement

The data and source code required to fully reproduce the figures presented in this paper are publicly available at 10.15480/882.16926.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.6c01490.

Additional numerical details and the nomenclature (PDF)

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Notes

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