Universal McMillan–Mayer van der Waals Langevin Gel

Gerald S. Manning

Department of Chemistry and Chemical Biology, Rutgers University, New Brunswick, New Jersey 08854, United States

ABSTRACT: We present a theory for a universal gel based on a McMillan–Mayer treatment of a solute–solvent fluid as a generalization of the universal van der Waals equation of state for a pure liquid/vapor system. The elastic resilience of the networked gel is modeled by a universal Langevin function. This combination of van der Waals interactions and nonlinear Langevin elasticity produces an abrupt onset of large-amplitude density fluctuations deep in the interior of the gel at a critical temperature. Then, at a second, lower, critical temperature, the entire swollen gel collapses to a high-density phase. The universal gel has an “upper” critical temperature behavior, meaning that the gel transition to high density occurs on decreasing the temperature. At the cost of loss of universality, the theory is generalized to predict lower critical temperature dependence, whereby an aqueous hydrophobic gel exhibits phase coexistence when the temperature is raised. The theory is consistent with the Gibbs phase rule, suitably generalized to coexisting phases that are not at the same pressure in equilibrium conditions.

1. INTRODUCTION

An equilibrated swollen gel as immersed in its solvent is a physically or chemically cross-linked polymer mesh infused to capacity with the solvent.1–3 At critical environmental conditions, an initially swollen gel can collapse discontinuously to a much smaller volume.4–7 The observation by scattered light of divergent density fluctuations at a critical temperature is a strong indicator of an actual phase transition.8,9 As the result of extensive observations on a wide variety of gels, both synthetic and as formed from naturally occurring biopolymers, Tanaka suggested that the possibility of a gel phase transition may be universal to all gels.5 Moreover, if one considers the complexity of polymeric materials, Tanaka’s great insight was that the universality of the gel transition supports an analogy to the universal liquid/vapor system. The elastic resilience of the networked gel and the attractive force that acts to shrink the network may be consistent with a partial analogy but the elastic resilience of the cross-links endows the gel with solid-like properties that are absent from a free fluid.10–12 Specifically, unlike a vapor that expands to fill its container, or a liquid confined only by the container walls, a swollen gel has a distinct shape and volume of its own, and a distinct boundary separates it from the solvent bath in which it is immersed. In conditions of coexistence, the gel is a three-phase system, swollen and collapsed polymer network, and a pure solvent.12

The van der Waals equation of state predicts a universal vapor–liquid phase separation for pure fluids.13–15 This classic 1873 insight into the properties of gases and liquids was so successful, wrote Uhlenbeck and Ford, that it “practically killed the subject for more than 50 years.”16 To clarify the partial analogy of fluid and gel phase transitions, we revisit the van der Waals equation as suitably generalized by McMillan–Mayer (MM) statistical mechanics to apply to a liquid solution with a solute (the gel particles) distinguished from a solvent.17,18 To model the limited expansion of the gel because of its phase that impedes entropic dispersal (by far the dominant effectively repulsive thermodynamic force). These same opposed tendencies must operate in a gel also, thus accounting for Tanaka’s analogy. The high density of gel material in the collapsed phase is stabilized by the dominance of attractive interactions that impede entropic dissolution into the solvent. However there is a qualitative difference that prevents outright identification of the two systems, gel and vapor/liquid. The gel “solute” is networked into a mesh. The presence of the network may be consistent with a partial analogy but the elastic resilience of the cross-links endows the gel with solid-like properties that are absent from a free fluid.19–21
networking, we impose a nonlinear restoring potential on the solute that allows calculation of gel density in a restricted volume. The famous van der Waals instability of a pure fluid below a critical temperature occurs also in our model for the gel but because of the potential energy of the network, in an augmented form that we think has not previously been explored. Moreover, the gel transition is universal in the same sense that the reduced van der Waals equation implies the universal law of corresponding states.15–18

It will be noticed that our analysis does not rely on traditional Flory-style polymer theory21–25 or its more modern elaborations.26 Relevant commentary on this point and on previous approaches to gel modeling are reserved for the Discussion section, where we also take up diverse topics such as the pressure inside the gel and the applicability of the Gibbs phase rule.

2. RESULTS AND DISCUSSION

2.1. Van der Waals Equation of State: A Review. The van der Waals equation suggests how the temperature, pressure, and volume (here, the density) of a one-component fluid at equilibrium may be related

\[(P + \alpha n^2)(1 - \beta n) = n k_B T\]  

(1)

where \(P\) is the pressure, \(T\) is the Kelvin temperature, and \(n\) is the number density \(N/V\), where \(N\) is the number of molecules, \(V\) is the volume. Boltzmann’s constant is designated by \(k_B\). The van der Waals constant \(\alpha\) characterizes the quadratic effect of attractive interactions between pairs of fluid molecules, and the constant \(\beta\) accounts collectively for the excluded volume of fluid molecules.

The van der Waals equation is cubic in the density \(n\). At low densities, the \((\alpha, \beta)\) corrections are small, and the equation is almost the same as for an ideal gas. Therefore, in the low density range, there is only one real root for \(n\) near its ideal value \(P/k_B T\) and two complex conjugate roots. Following Wall’s treatment,15 we note that for the existence of a critical isotherm at lower temperatures and higher densities, the cubic equation must collapse to the form \((n - n_c)^3 = 0\) at a unique critical point, where \(n_c\) the critical density, is a real root of multiplicity 3. The reason is that this form yields the necessary inflection point for criticality. Indeed, if we expand both forms of the equation and compare coefficients of the powers of \(n\), we find the well-known formulas for the critical (subscript \(c\)) temperature, pressure, and density in terms of the van der Waals constants, \(n_c = 1/3\beta\), \(P_c = \alpha/(27\beta^3)\), \(k_B T_c = 8\alpha/(27\beta)\). The next step in this classic analysis is to measure the state variables in units of their critical values. That is, reduced temperature, pressure, and density \((t, p, \rho)\) are defined by \(T = T_c t\), \(P = P_c p\), and \(n = n_c \rho\), and then the critical values of the reduced variables are all equal to unity. Substitution into the van der Waals eq 1 yields the universal reduced van der Waals equation

\[(p + 3\rho^2)(3 - \rho) = 8\rho t\]  

(2)

All quantities in this equation are dimension-free. It is a universal equation of state in that the van der Waals constants \(\alpha\) and \(\beta\), specific to fluid species, are absent.

For isotherms below critical but still nearby, a continuity argument requires that the equation have three distinct real roots, not far from the critical root, and this requirement is numerically confirmed in Figure 1 (which of course can be found in any physical chemistry textbook, usually with variable volume instead of density). For still more dense states at lower temperatures, a real root \(\rho\) near but less than 3 (closest packing) is evident from eq 2, as well as a pair of complex conjugate roots near \(\rho^2 = -(1/3)p\).

For our purposes, the most interesting aspect of the reduced van der Waals equation is the “wiggle” for intermediate densities seen in Figure 1.17 In this region the slope is negative, that is, the vapor pressure \(p\) is a decreasing function of density \(\rho\). But a general requirement for stable thermodynamic equilibrium for any system is that a higher pressure results in decreased volume (higher density).16 In this range of densities the van der Waals equation therefore describes an unstable fluid, which must split into two stable phases, a low-density vapor and a high-density liquid. Maxwell’s rule of equal areas,15 and the lever rule, are required to supplement the van der Waals equation in this region if the values of the densities and coexisting amounts of vapor and liquid are to be determined, but we have no need to pursue the analysis further.

2.2. MM Generalization of van der Waals. In this section, we consider a two-component liquid solution in which a solute species is distinguished from the solvent. The van der Waals equation for a one-component fluid has been generalized to fluid mixtures of any number of components, with the variables of state being pressure, temperature, volume, and composition.27 In our present application, we are not interested in the vapor pressure \(P\) of a mixture but instead focus on the osmotic pressure \(\Pi\) of our solute—solute solution. When this solution is separated from pure solvent by a membrane permeable only to solvent and not to the solute, the pressure at equilibrium of the solution is different from the pressure on the pure solvent side of the membrane. The quantity \(\Pi\), the osmotic pressure, is the pressure difference \(P(\text{solute}) - P(\text{pure solvent})\).

The McMillan–Mayer (MM) theory is an exact result of statistical mechanics.19,20 It states that there is a virial series for the osmotic pressure that is an exact replica of the virial series for the pressure of a real gas. The latter of course was the first fundamental advance over the van der Waals equation as applied to a real gas. It corrects the ideal gas not only for interactions between two gas molecules but sequentially for

![Figure 1. Representative isotherms (t is the reduced temperature) for the reduced van der Waals equation of state if the ordinate is the reduced pressure p or for the reduced MM van der Waals equation of state if the ordinate is the reduced osmotic pressure \(\pi\). The isotherms are plotted as functions of reduced number density \(\rho\) of a one-component van der Waals fluid or of the solute for an MM van der Waals solution.](image-url)
interactions among three, four, ... gas molecules. The coefficients of the series in powers of the gas density are exact, and depend on the vacuum potentials among two, three, ... gas molecules. The MM virial series for the osmotic pressure of a solute–solvent solution has exactly the same form as its counterpart for a gas. It is an infinite series in powers of the solute density. The expressions for the coefficients have exactly the same form, but with the vacuum potentials replaced by the potentials of mean force among solute molecules, as averaged over positions of the solvent molecules.

The van der Waals eq 1 is itself an approximation to the full virial series, but within that limitation, the replacement of $P$ in the van der Waals equation of state for a real gas by the osmotic pressure $\Pi$ of a solute–solvent solution can be said from MM theory to be an exact procedure

$$\Pi = n k_B T$$

The density $n$ is now the number density of solute molecules, whereas the van der Waals constants $\alpha$ and $\beta$ become MM van der Waals constants. The constant $\alpha$ reflects attractive interactions between two solute molecules as influenced by the solvent, and $\beta$ characterizes the excluded volume of solute, again as influenced by solvent molecules. We have to make an additional approximation beyond that inherent in the van der Waals equation itself. Because the MM van der Waals constants are influenced by the randomized configurations of solvent molecules, they must be dependent on temperature. We continue our development with the assumption that it applies to solutions for which this dependence is slight and may be neglected, if not for quantitative purposes, then at least for the qualitative considerations of interest here.

We can now apply exactly the same analysis as in the previous section to obtain a reduced universal MM van der Waals equation for the reduced osmotic pressure $\pi$ of a solute–solvent solution in terms of the reduced solute number density $\rho$ and reduced temperature $t$

$$\pi = n k_B T$$

The isotherms are exactly as in Figure 1, only with reduced osmotic pressure replacing reduced vapor pressure as the ordinate.

In Figure 1 for $p$ versus $\rho$, a negative slope in an isotherm indicates an unstable state, which must separate into vapor and liquid phases according to the discussion of the previous section. But if Figure 1 represents $\pi$ versus $\rho$ for a solute–solvent solution, what then is the meaning of a region of negative slope? It would say that the osmotic pressure decreases when the impermeable solute density increases, which intuition suggests might well be an unstable situation resolved by separation into two phases of low and high solute density, analogous to vapor–liquid coexistence. We give the proof in the next paragraph.

From the reduced MM van der Waals equation, we can extract the reduced form of van’t Hoff’s law $\pi = (8/3)p t$ for dilute solutions by letting $\rho \rightarrow 0$ in the terms on the left representing nonideal corrections. Then to represent the corrections in a formal way, we introduce the reduced osmotic coefficient $\varphi$ by $\pi = (8/3)\varphi \rho t$. The osmotic coefficient is a measure of the nonideality of the chemical potential of solvent, and the Gibbs–Duhem equation, $\rho \ln(\varphi \rho) = d(\varphi \rho)$, may be used to obtain the reduced solute activity coefficient $\gamma$ from it.

We want the slope of an isotherm on a $\pi$ versus $\rho$ plot, $d\pi/d\rho = (8t/3)(\varphi \rho)/d\rho = \rho d\ln(\varphi \rho)/d\rho = \rho d\mu/d\rho$, where $\mu$ is the chemical potential of solute. An absolute thermodynamic requirement for stable equilibrium is that the solute density dependence of the chemical potential of solute be monotonously increasing, which completes the proof.

We will need an explicit expression for the activity coefficient of solute. Substituting $(8/3)\varphi \rho t$ for $\pi$ in the MM van der Waals equation, and solving for the osmotic coefficient, we get

$$\varphi = \frac{3}{3 - \rho} - \frac{9\rho}{8t}$$

Note that $\varphi$ properly tends to unity (the solution becomes ideal dilute) as $\rho \rightarrow 0$. Next, by actually performing the integration of the Gibbs–Duhem differential equation of the previous paragraph, we find the solute activity coefficient $\gamma$

$$\ln \gamma = \frac{\rho}{3 - \rho} + \frac{3}{3 - \rho} - \frac{9\rho}{4t}$$

The activity coefficient also tends to unity as our universal solution becomes ideal dilute, $\rho \rightarrow 0$. In Figure 2, we show a plot of the function $\rho(d\mu/d\rho) = 1 + (\ln \gamma/d\ln \rho)$ for a supercritical temperature $t = 3$, the critical temperature $t = 1$, and a subcritical $t = 0.5$. The negative region for the latter marks instability, where the solute chemical potential increases with decreasing density. Considering that the range of $\rho$ is from zero only up to 3 (close packing of the excluded volume), we understand that universal solution instability occurs in a wide range of densities when the temperature is below critical.

2.3 Gel Model. Our goal in this paper is to illuminate the analogy between the universal gel volume transition (equilibrium coexistence of a swollen solvent-rich phase with a collapsed phase dense in gel material) and the universal vapor–liquid transition of a one-component fluid. The MM van der Waals solute–solvent liquid solution discussed in the previous section is not sufficient to this purpose. Certainly, the MM van der Waals solution illustrates the close connection between the vapor–liquid transition and phase separation in solution into solute-rich and solute-lean regions. However, an ordinary solution is not a gel. If solute molecules are initially confined to a small spatial region of solvent, then in time, the
solvent is good enough, the solute diffuses out until at
equilibrium it uniformly fills the container. In contrast, a
networked gel has been likened to a “giant molecule” with
internal constraints among its parts that prevent complete
dissolution even when invaded by good solvents. In this sense,
a gel—solvent system is more like a permeable solid than a
liquid solute—solvent solution, and indeed, its elastic moduli
are measurable. The problem for us then is to devise a gel
model that clearly illustrates the observationally close analogy
with a vapor—liquid transition while still being recognizable as
at least an abstracted representation of a real gel network.

We start with the solute in an ordinary solute—solvent liquid
solution. For the solute to represent the gel material, we
 impose a potential energy \( u \) on each solute unit. The potential
energy must meet some requirements if this minimal model is
to resemble a gel immersed in a solvent bath. To restrain the
solute from complete dissolution it must be suitably chosen to
reach infinite energy before the solute particles reach the walls
of the container. We note that the averaged resultant of the
constraining forces in a homogeneous and isotropically
distributed gel must be radially directed toward the center,
so we take \( u(r) \) as a function of radial distance \( r \). Here, we are
thinking of a gel with a spherical or long cylindrical shape, so
that \( r \) is the distance from the center of the sphere or radial
distance from the central axis of the cylinder. To take many
nodes of the gel mesh into account with no assumption of
rubber elasticity (see Discussion), we reason that the strength
of \( u(r) \) should be correlated with the number of nodes in a ball
or rod of gel material of radius \( r \). That is, in the equilibrated
gel, further outward diffusion of gel material at \( r \) has been
restrained by a positive net number of nodes behind it (the
nodes behind minus the nodes ahead). The implication is that
\( u(r) \) increases with the distance. Finally, we know that a gel has
measurable elastic moduli, therefore it is reasonable to assume
that \( u(r) \) reduces to Hooke’s law for small \( r \). In summary, \( u(r) \)
is a monotonically increasing function that reaches infinity at
some distance \( r_{\text{max}} \) short of the walls of the container, but that
acts like a linearly elastic spring for small \( r \).

Out of an infinite number of functions that meet these
minimal requirements, we choose the familiar. Consider the
statement

\[
\coth(3u) - \frac{1}{3u} = r^2
\]

(7)

where \( u \) must be a dimension-free quantity, and hence \( r \) also.
The series expansion of the hyperbolic cotangent shows that
where \( u \) is small, then to first order, \( u = r^2 \). Thus, if \( u(r) \)
represents a potential energy measured in units of \( k_B T \), and if \( r^2 \)
is defined by \( (1/2)(q/k_B T)R^2 \), where \( R \) is the radial distance
from the origin, and \( q \) is an elastic constant, then \( u(r) \) is a
nonlinear reduced generalization of Hooke’s law; it becomes
anharmonic as the distance from the origin increases. Because
\( \coth(3u) \) approaches unity when \( u \) tends to \( \infty \), we see also
from eq 7 that the reduced elastic energy \( u(r) \) becomes infinite
when \( r \) approaches unity. The function \( u(r) \) is therefore
consistent with what we are looking for; it restricts the density
of solute particles (the gel material) to a ball or rod of finite
(reduced) radius \( r = 1 \). Because \( u(r) \) cannot be given as an
explicit function of \( r \), we will be working with \( r \) as a function of
\( u \), as illustrated in Figure 3, showing \( r = 1 \) as the outer
boundary of the gel where \( u(r) \) becomes infinite and prevents
further swelling.

Of course, \( r(u) \) is the square root of the Langevin function,
and \( u(r) \), the inverse of \( r(u) \), is well known in the classical theory
of flexible polymers as describing a single chain stretched
beyond a Gaussian distribution. Oppermann in particular has
applied this function to individual chains in a gel to explore
its e effects on gel elasticity, remaining within the framework of
Flory theory. Here we use it in a related but different context.
The scale of the variable \( r \) is macroscopic. A concentric volume
element \( 4\pi r^2 \) \( dr \) contains a large number of polymer segments
and a large number of mesh nodes. Correspondingly, the
potential energy \( u(r) \) is not that of an individual polymer
segment or monomer at \( r \). Instead, we conceptualize a solute
“unit”, or “particle”, as including sufficiently many polymer
segments and nodes such that spatial correlation among units
is almost lost, and is therefore consistent with the MM van der
Waals equation of state. The chemical potential of the section
following is then the chemical potential of these coarse-grained
solute units.

2.4. MM van der Waals Analysis of the Universal Gel.
We begin by writing the chemical potential of gel solute in \( k_B T \)
units. On a macroscopic scale, it is a local quantity with individual
contributions dependent on \( r \)

\[
\mu(r) = \mu^0(r) + \ln \rho(r) + \ln \chi(r) + u(r)
\]

(8)

The first term on the right accounts for thermal free energy
of individual gel solute particles and interactions of a single
solute particle with surrounding solvent molecules. Its
dependence on \( r \) is only through a pressure that varies locally
(see Discussion). This dependence is negligible in any
condensed phase (except in an ultracentrifuge). The \( \ln \rho \)
term is the ideal entropy. The activity coefficient term accounts
for interactions among solute molecules; its dependence on \( r \)
is through \( \rho(r) \). Finally, the potential energy term \( u(r) \)
contributes to the energy component of the chemical potential.

A fundamental thermodynamic principle is that at
equilibrium the chemical potential is uniform, \( d\mu(r)/dr = 0 \).
Its individual contributions may depend on \( r \), but in such a way
that the total chemical potential does not

\[
1 + \frac{\ln \chi}{\ln \rho} \frac{d\ln \rho}{dr} + \frac{du}{dr} = 0
\]

(9)

With eq 6 for the activity coefficient, we get

\[
\left( \frac{1}{\rho} + \frac{(6 - \rho)}{(3 - \rho)^2} - \frac{9}{4T} \right) \rho = -du
\]

(10)
Integrating,
\[ \ln \left( \frac{\rho}{3 - \rho} \right) + \frac{3}{3 - \rho} - \frac{9\rho}{4t} = -u + \text{const} \] (11)

We know that \( u = 0 \) when \( r = 0 \), and at \( r = 0 \), we designate \( \rho(0) \) by \( \rho_0 \) so that the integration constant is just the left-hand side with \( \rho \) set equal to \( \rho_0 \). Then
\[ u = -\ln \left( \frac{\rho(3 - \rho_0)}{\rho_0(3 - \rho_0)} \right) - \frac{3(\rho - \rho_0)}{(3 - \rho)(3 - \rho_0)} + \frac{9(\rho - \rho_0)}{4t} \] (12)

This equation for \( u \) may be substituted into eq 7 to give \( r[u(\rho,t,\rho_0)] \), that is, location \( r \) as a function of density and temperature with “initial” density \( \rho_0 \) as the parameter. In other words, the density profiles \( \rho(r) \) have been determined as implicit functions, and we apply ourselves to some numerical work.

In van der Waals theory, \( t = 1 \) is a critical temperature above which coexisting liquid and vapor phases cannot exist. For our gel, also, \( t = 1 \) is critical in the same sense. Figure 4 shows gel density profiles, all at \( t = 1 \), as functions of location \( r \). The different curves correspond to different choices of reduced density at \( r = 0 \), \( \rho_0 = \{0.5, 1.0, 1.5, 2.0, 2.5\} \), covering a density range from low to high (recall the value 3 as the maximum density). All trajectories converge to \( \rho = 0 \) at the gel periphery \( r = 1 \). For each choice of \( \rho_0 \), there is only one stable gel; that is, the curves \( \rho(r) \) are single-valued. This feature is true for all \( t > 1 \) as well (not shown). For all choices of \( \rho_0 \), the gel density decreases as the periphery is approached. The density decrease is gentle for the relatively dilute gel; whereas the nearly closest packed gel remains uniformly dense almost up to the periphery, then abruptly falls to zero in a thin layer. The monotone decrease of density is easily understood as a consequence of increasing potential energy (Figure 3). The question is what universal significance might be attached to the negative value of \( d\mu/dr \), so we interrupt the numerical work for a brief return to analysis.

From eq 8 for the chemical potential, we have
\[ \frac{d\mu}{d\rho} = \frac{1}{\rho} \left( 1 + \frac{d\ln \gamma}{d\ln \rho} \right) + \frac{d\mu}{dr} \frac{dr}{d\rho} \] (13)

But \( d\mu/d\rho = (d\mu/dr)(dr/d\rho) \), and at equilibrium \( d\mu/dr = 0 \). So at equilibrium
\[ \frac{d\rho}{dr} = -\rho \left( 1 + \frac{d\ln \gamma}{d\ln \rho} \right)^{-1} \] (14)

The thermodynamic factor in brackets must be positive, \( d\mu/dr > 0 \), if the system is to return to uniform solute density, as it must, when the elasticity field \(-d\mu/dr\) is turned off. A stable positive density gradient, \( d\rho/dr > 0 \), is then consistent only with a negative elasticity gradient, \( d\mu/dr < 0 \). However, \( u(r) \) is given in our model as increasing with \( r \). Therefore, \( d\rho/dr < 0 \) is a universal requirement for stability of the gel.

To see clearly what happens at temperatures \( t \) less than unity, we construct the density profile \( \rho(r) \) in Figure 5 with \( t = 0.75 \). We have picked the free parameter, the density at the origin, as \( \rho_0 = 1 \). Despite this single choice \( \rho_0 = 1 \), two other values of \( \rho(0) \) appear near 0.19 and 2.07. The curve now has three branches, the low density branch (leftmost) corresponding to \( \rho(0) = 0.19 \), a high density branch (rightmost) for \( \rho(0) = 2.07 \), and a third branch for the intermediate density \( \rho(0) = \rho_0 = 1 \). The latter two branches coalesce at an asymmetric maximum at the point \((\rho, r) = (1.65, 0.56)\). In the gap, and for densities higher than 2.07, the values of \( r \) are imaginary. Because the graph has been generated from the equation \( d\mu/dr = 0 \), the chemical potential is equal along any continuous curve in the graph, but more than that, the chemical potential is equal at the three points on the three branches that are intersected by a horizontal line at any constant \( r \) (there are no discontinuities of chemical potential). The chemical potential is the same for all points on all three branches. These statements have been confirmed by direct numerical checking. All points represent coexisting equilibrium gel densities.

The low-density branch and the high-density branch (to the right of the maximum) behave properly; for both, \( d\rho/dr < 0 \), that is, density decreases with increasing \( r \) as the potential energy increases. These branches represent stable equilibrium gel states. The intermediate branch, to the left of the maximum, has density increasing as \( r \) becomes larger. This state of the gel is an equilibrium state, but it is unstable. At equilibrium, these densities coexist with the others. However...
such a state cannot exist for more than a practically infinitesimal length of time. The instant it comes into existence, the gel splits into stable, coexisting, low-, and high-density regions, while the unstable densities disappear. More specifically, in a given spherical shell (or, for a cylinder, an annular ring) at some fixed \( r \) (in Figure 5, visualize any horizontal line for constant \( r \) that intersects all three branches), regions of gel density corresponding to the leftmost and rightmost branches for that value of \( r \) will coexist (their chemical potentials have the same values). Any fixed volume element \( r^2 \sin \theta \, dr \, d\theta \, d\phi \) within the spherical shell will experience density fluctuations. Densities in a volume element at the origin will, for example, jump discontinuously back and forth between 0.19 and 2.07.

We also offer a concluding remark intended to be helpful in the physical interpretation of Figure 5. Multiple coexisting phases within a single macroscopic gel signify that at any instant of time some regions of the gel are dilute in the gel material, whereas other regions are dense, or, equivalently, a single region fluctuates in density between dilute and condensed. The same is true for ordinary liquid—vapor coexistence; in a gravity-free environment, liquid droplets are interspersed with vapor.

By skipping from \( t = 1 \) in Figure 4 to \( t = 0.75 \) in Figure 5, we have skirted the most interesting aspect of gel behavior, its criticality. For a closer look, we have generated Figure 6 for a range of temperatures. Here, the points represent the gel density at the origin \( \rho(0) \), plotted against temperature \( t \). Each point has been computed for the same choice of free parameter \( \rho_0 = 1 \). The red points in the range \( t \geq 1 \) show that only one stable gel (the fully swollen one) exists at each temperature in this range. For these points, \( \rho(0) = \rho_0 = 1 \). However at \( t = 1 \), there is an abrupt bifurcation. For any \( t < 1 \), there are two stable gels that coexist, one with relatively low density and small value of \( \rho(0) \), and one with relatively high density and large value of \( \rho(0) \). As \( t \) decreases, the low-density gel decreases in density, and the high-density gel increases in density.

The continuous bifurcation at \( t = 1 \) in Figure 6 is a special case, contingent on the choice of unity for \( \rho_0 \); both quantities in this case being the familiar critical values for an ordinary van der Waals fluid. In Figure 7, a different choice \( \rho_0 = 0.5 \) has been made for each point. Here, we see a discontinuity at \( t = 0.944 \). From the high to the low side of this temperature, the density \( \rho(0) \) jumps from the dilute swollen value 0.5 to a dense 1.30. To see intuitively why there is a discontinuity instead of a smooth bifurcation is not too easy because we are dealing with the numerical outcomes of nonlinear transcendental equations. However if there were not a discontinuity at any value of \( t < 1 \) when \( \rho_0 = 0.5 \) is also less than unity (as in Figure 7), then as the temperature decreases further the increasingly more dense phase would ultimately have a \( \rho(0) \) value increasing past unity (i.e., greater than 0.5). However we already know from Figure 6 that \( \rho(0) = 1 \) corresponds to \( t = 1 \). This contradiction shows why the discontinuity must occur.

Figure 8 shows gel density profiles proceeding outward from \( \rho_0 \). As in Figure 7, the free parameter \( \rho_0 \) is set to 0.5. Figure 8 shows stable density profiles for various temperatures (see caption) in the implicit function form \( r \) versus \( \rho(r) \). Unstable profiles are not shown. The figure is color coded, so that, for...
example, the pair of gray profiles represents the pair of coexisting phases, one dilute, the other much more dense, present at $t = 0.75$. From left to right in the subset of dense profiles (on the right), the values of $t$ decrease in the order $0.943 > 0.93 > 0.87 > 0.75 > 0.6$. The dense phase at $t = 0.943$ (black, at right), a value just lower than the critical value 0.944..., can barely be seen (it would not be present at all if $t$ were just greater than critical, say $t = 0.95$). In fact, note that only a dilute phase is present at $t = 1.1$ (red) because dense phases emerge only for lower temperatures, $t = 0.944...$. The collection of profiles in Figure 8 shows that the dense phase grows and becomes denser as the temperature decreases, whereas the amount of gel material in the coexisting dilute phase diminishes. The small amplitude dense profiles, for example at $t = 0.943$ and $t = 0.93$, illustrate the discontinuous emergence of high-density phases only near the gel center when the temperature decreases just below critical. Using $t = 0.943$ again as the example, its (barely visible) density is in the range $1.3 - 1.4$, discontinuously greater than the corresponding dilute phase density 0.5 at the center $r = 0$.

Although a same-color pair of density profiles in Figure 8 represents coexisting gels, it does not necessarily make full contact with typical laboratory experiments. Because the amount of gel material is correlated with the area under (i.e., to the left) of the density curves, it should be apparent that the high-density blue trajectory in Figure 8 represents a gel containing much more material than in the corresponding dilute gel. However in a typical phase-transition experiment, a single gel, initially fully swollen, transits to a shrunken state as the temperature decreases. Because the gel consists of an intact polymer network, the two gel states contain the same network and hence the same amount of gel material. We have not yet imposed a condition of invariant number of gel particles on our model, and we proceed to do so.

At the same temperature, the condition for particle number invariance in the present universal gel model is

$$\int_0^1 r^4 \rho(r) 4\pi r^2 \, dr = \int_0^r \rho_l(r) 4\pi r^2 \, dr$$

(substitute $2\pi r \, dr$ for the cylindrical case), where subscript $v$ evokes the swollen low-density "vapor" branches of the MM van der Waals $r$ versus $\rho$ trajectories, while $l$ for "liquid" stands for the high-density trajectories. We have recognized that all of the swollen gels, by construction, have periphery at $r = 1$ but the maximum values $\rho_l$ of the dense forms can be different (obvious from Figure 8). Integration by parts, using $\rho_4(1) = 0$ yields

$$\rho_l(1)^3 + \int_{\rho_l(1)}^{\rho_4(0)} r^3 \, d\rho_l = \int_0^{\rho_4(0)} r^3 \, d\rho_l$$

(16)

For any dilute/dense isothermal pair of density trajectories, all the parameters in this equation are numerically available; hence the integrations can be performed numerically. For example, $r_1$ is the value of $r$ corresponding to the root $\rho_l$ of $d\rho_l/\rho_l = 0$. In this way, we find for spherical symmetry that when $\rho_4$ is chosen to equal unity, density fluctuations in the swollen gel arise at $t = 1$ (Figure 6), whereas the entire swollen gel collapses to a dense gel with the same amount of gel material at $t = 0.84$. At this temperature, the swollen gel has density 0.31 at its center $r = 0$, and zero density at its periphery $r = 1$. The collapsed gel has a density of 1.85 at its center and 1.45 at its outer edge $r = 0.42$. The swollen/collapsed pair in this case is shown as the green density profiles in Figure 8.

2.5. Inverted Temperature Dependence of Hydrophobic Hydrogels. The universal gel analyzed in the previous section has an intuitively temperature dependence; the collapsed high density phase appears at subcritical temperatures. However, a commonly employed class of gels has the opposite dependence on temperature.5 With water as the solvent, the gel polymer backbone is partially hydrophobic, bearing groups such as N-isopropyl. The self-attraction of the gel material then strengthens at higher temperatures because of its entropic nature, and a swollen-to-collapsed transition is observed to occur above a critical temperature. We can capture this inverted temperature dependence with a slight modification of the present model, but only at the cost of the loss of universality.

In a van der Waals fluid, the pairwise and excluded volume interactions are in vacuum, and there is assumed to be no dependence of the two van der Waals parameters $\alpha$ and $\beta$ on temperature. In a MM solute–solvent system, the interactions are through solvent, and the corresponding parameters are potentials of mean force and thus, in general, are affected by temperature. For our "universal" gel, discussed in previous sections, we carried over the van der Waals assumption that the two parameters do not depend on temperature, or if they do, then slightly enough to be neglected. If we take the temperature dependence of $\alpha$ and $\beta$ into account, and repeat the mathematical analysis, the result corresponding to eq 12 is

$$\ln \frac{\rho(3 - \tilde{\beta} \rho)}{\rho_0(3 - \beta \rho)} + \frac{3\tilde{\beta}(\rho - \rho_0)}{(3 - \beta \rho)(3 - \beta \rho)} - \frac{\delta \alpha(\rho - \rho_0)}{4t}$$

where $\rho$, $t$, and $u$ are the same reduced density, temperature, and elastic potential energy of previous sections. The quantities $\tilde{\alpha}$ and $\tilde{\beta}$ are also reduced; $\tilde{\alpha} = \alpha(T)/\alpha(T_c)$, $\tilde{\beta} = \beta(T)/\beta(T_c)$. If there is no dependence on $T$, then $\tilde{\alpha} = \tilde{\beta} = 1$, and this equation reduces to the universal case.

For numerical work, we will assume that hydrophobicity does not affect excluded volume, $\tilde{\beta} = 1$. We do know, however, that hydrophobic attraction increases with temperature; $\tilde{\alpha} > 1$ if $T > T_c$, i.e., if $t > 1$. In fact, we gain qualitative capture of the experimentally observed behavior if $\tilde{\alpha}$ increases more strongly than $t$ itself; that is, if $\tilde{\alpha} = t^{\delta}$, $\delta > 0$. In Figure 9, we have set $\tilde{\alpha} = t^{1.5}$ for illustrative purposes. The red density profile is the single stable phase profile at $t = 1$. A second, dense, phase appears (gray curve) when $t$ is raised past 1.3, and increases in amplitude (black curve to right of maximum) as temperature is raised toward $t = 2$; the coexisting dilute phases (gray, black) change only slightly in this range.

2.6. Discussion. We have presented a model for a gel that brings into sharp relief an analogy between the gel phase transition from a solvent-rich swollen gel to a polymer-rich collapsed structure, and the vapor–liquid transition of a one-component fluid, whereby the rarified vapor condenses to a
closely packed, nearly incompressible liquid. Our MM van der Waals analysis of a solute—solvent system, proceeds in direct analogy with van der Waals’ equation of state, which historically provided the first clear understanding of the related physical properties of gases and liquids. However the analysis then goes beyond van der Waals in imposing a distance-dependent potential energy on the solute (gel particles) to mimic gel networking, thereby restricting the gel to a discrete volume, like a solid. The analysis is thrown into a reduced form, freeing it from dependence on parameters specific to the gel material. In this way, we find a universal equation of state for a gel in the form of a temperature- and location-dependent density.

The central feature of the universal gel is an unstable density profile, \( \frac{d\rho}{dr} > 0 \), for intermediate densities at subcritical temperatures, as illustrated in Figure 5. This density distribution is unstable because the elastic potential energy is higher near the periphery than in the interior. The instability is resolved by discrete internal density fluctuations between low and high values that set in abruptly at a critical temperature. At a second, lower, critical temperature, the entire swollen gel collapses to a dense structure. These predictions of the theory are consistent with laboratory observations of critical gel behavior.5,9

What is the scope of the “universal” equation of state? Certainly it does not describe the behavior of hydrophobic hydrogels, which possess an opposite temperature dependence because of the water-organizing properties of the hydrophobic groups.3 However at the cost of a loss of universality, we find a simple extension of the model sufficient to capture this behavior, allowing as well the quasi-universal characterization of such “inverted” gels as those with reduced van der Waals attractive interactions that strengthen with temperature like \( t^a \), \( a > 1 \).

With this exception, the universal gel may be regarded as applicable to neutral gels, such as unhydrolyzed polyacrylamide. However, we believe it is also consistent with ionized gels. For that, we accept the generally held assessment that the colligative properties of ionized macroscopic gels are usually dominated by the numerous counterions. Then the reduced number density \( \rho \) refers to the counterion density. However because electroneutrality holds throughout the interior of a macroscopic gel, and because the number density is a reduced quantity (a dimensionless ratio of densities), \( \rho \) equally well refers to the density of gel polymer material. Then, the excluded volume factor in the MM van der Waals equation presents no conceptual problem; however, the quadratic term could represent counterion-mediated gel particle attraction in these relatively dense systems.28–31

The model and theoretical analysis offered here contains features in common with previous treatments but also differs from them. The possibility of a gel phase transition was theoretically predicted by Dusék and Patterson,32 a decade before the phenomenon was observed in the laboratory with polyacrylamide gels.4 These authors also noted a theoretical similarity to the condensation of a van der Waals gas but their calculations were based on Flory’s polymer theories and did not make the use of the van der Waals equation of state. Subsequently, Shibayama and Tanaka6 presented a related Flory-type theory, employing the van der Waals equation only as introductory material, enabling the derivation of a formula for the \( \theta \)-temperature of a free polymer solution. More importantly, neither of these analyses went beyond our Figure 1, in effect identifying a gel with a free fluid. However, a gel is not a free fluid; the gel material is networked, endowing the gel with a discrete volume that does not disperse to fill its container. Despite inclusion in these early theories of Flory-type terms purporting to represent the effect of the network, a distinctive gel behavior does not appear to have been captured.

The improved theory of Khokhlov33 and subsequent elaborations34 require a third virial coefficient and so cannot be directly compared with a van der Waals based theory. The van der Waals equation of state may be formally expanded into an infinite series in powers of fluid density but the resulting virial coefficients of order three and higher are of no physical significance because all of them stem from the excluded volume factor, whereas the complete van der Waals equation of state contains attractive interactions of the molecules only in pairs, and not in triples or higher order clusters.

The description of the polymer network of a gel is most often based on Flory’s entropic model for gel swelling. In turn, Flory argued “by analogy with the deformation of rubber”.35,41 However we know that, in contrast to most materials, rubber shrinks when heated; most materials expand. Most gel types also expand when heated. Hydrophobic gels are the cardinal exception but they shrink when heated because of their hydrophobicity, not because they are like rubber. Hirotsu10–12 has measured Poisson’s ratio \( \sigma \) for a gel, that is, the negative of the ratio of transverse to longitudinal strains. All common materials have positive Poisson’s ratio, signifying that they become thinner when stretched, thicker when compressed. The value for rubber is very close to a perfect (no volume change) \( \sigma = 0.5 \). The measured value of \( \sigma \) for the collapsed gel was indeed close to 0.5 but \( \sigma \) for the swollen gel was about half this value, closely corresponding to Poisson ratios of common hard solids such as steel, copper, glass, carbon fiber, and so forth.

To our awareness, simulated data have thus far been restricted to gels on the nanometer size scale.13–18 The thermodynamic framework of present considerations requires a macroscopic gel for its subject, so that direct comparison is difficult. Even when transitions are reported on the nanoscale, the simulations have not addressed experimentally observed indicators of gel phase transitions, such as divergence of critical fluctuations in scattered light,4,9 critical anomalous behavior of measured elastic moduli,10–12,14 or perhaps most fundamen-

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Figure 9. Inverted temperature dependence of hydrophobic gels. The red curve is the single stable phase at \( t = 1 \). A second, dense, phase appears when \( t > 1.3 \), coexisting with the dilute phase (gray curves). The dense phase is more prominent at \( t = 2 \) (black curves).
tally, the stable equilibrium coexistence of visually observable distinct phases.12

A feature of some previous theories and simulations of the gel phase transition is an emphasis on negative pressure, vanishing or negative osmotic pressure, or applied tension.6,32,35,38 Our Figure 1 in fact does exhibit a subcritical isotherm at \( t = 0.75 \) that falls into negative values but it is important to understand that Figure 1 pertains only to free one-component fluids or free solute—solvent solutions. Looking at Figure 1, we see the van der Waals interpretation of the negative pressure region of the \( t = 0.75 \) isotherm as an absence of coexistence of a stable vapor phase because the attractive interactions in the liquid overwhelm the temperature. Analogously, if Figure 1 represents the osmotic pressure of a semi-permeable solute—solvent system, a negative osmotic pressure is possible at low temperatures. It would mean that at equilibrium the pressure of the pure solvent compartment is higher than the pressure of the solution with its impermeable solute. If the two pressures were maintained as equal, the solvent would flow from the solution side to the pure solvent side, ultimately leaving behind only dry solute.

We do not believe that the understanding of gel behavior requires invocation of such extreme conditions. In fact, the pressure inside our universal gel is always positive, and always greater than the pressure of the pure solvent in which it is immersed. To explain, we recall the basic equation of hydrostatic balance, where forces imposed on the contents of a volume element are balanced by the pressure gradient across that element. In the present case, with reduced quantities, this equation reads

\[
\frac{dp}{dr} = -\frac{8}{3}\rho \frac{du}{dr}
\]

Since \( du/dr \) is positive (potential energy of network increases toward the periphery), the pressure gradient inside the gel is negative. If the pressure of the bathing solvent is, say, 1 atm, then the pressure inside the gel increases from 1 atm at the gel periphery to higher values toward the center.

There has been discussion of the applicability of the Gibbs phase rule to gel systems.12,39 This rule for any thermodynamic system at equilibrium15,16 states that \( NDF = NC - NP + 2 \), where \( NC \) is the number of components; \( NP \) is the number of phases; and \( NDF \) is the number of degrees of freedom (intensive variables) necessary and sufficient for description of the equilibrated system. For example, a homogeneous pure liquid or gas has two degrees of freedom according to the rule (\( NC = NP = 1 \)), and they may be chosen as temperature and pressure; whereas a single phase solute—solvent liquid solution has three degrees of freedom (\( NC = 2, NP = 1 \)), corresponding to temperature, pressure, and solute concentration. An apparent “breakdown” for gels of this thermodynamically rigorous theorem has led to suggestions that of the two coexisting gel phases, one must be metastable (with solvent and solute chemical potentials not the same as in the other). We agree with Hirotsu that this suggestion is unfounded,12 and proceed to show consistency with the Gibbs theorem as suitably modified to cover osmotic systems such as gels.

For a conventional osmotic system (two compartments separated by a membrane permeable only to solvent, one compartment containing pure solvent, the other a solute—solvent solution), the Gibbs phase rule predicts 2 degrees of freedom (\( NC = 2, NP = 2 \)). However there are three; we are free to choose the temperature of the system, the pressure of the pure solvent compartment, and the solute concentration of the solution, all of them consistent with osmotic equilibrium. The reason for “breakdown” of the phase rule is simply that its derivation does not apply to this system; specifically, the pressure at equilibrium is not uniform across both compartments, nor is the solute chemical potential. An applicable derivation provides the correct answer. For the system in general nonequilibrium conditions, there are two temperatures and two pressures, one of each for each phase (compartment), and one composition variable (the concentration of solute), for a total of five. At equilibrium, there are two constraints: the two temperatures are equal, and the chemical potential of the solvent is the same in both phases. Five minus two equals three. (Note that the equilibrium pressure in the solution compartment is determined by the equality of solvent chemical potentials at equilibrium; it is not an independent constraint).

For a gel system containing three coexisting phases, two stable gels (swollen and collapsed) in a pure solvent bath, \( NP = 3, NC = 2 \) (solvent plus gel material), so the Gibbs phase rule predicts a single degree of freedom at equilibrium. However again there are three; we are free to choose the temperature (in the range of phase coexistence), the pressure of the solvent reservoir, and the density of pregelation material. Again, the reason for the breakdown of the phase rule is that its derivation does not apply to the system in question; specifically, the equilibrated pressures in the three phases are not equal, and the chemical potential of gel material is absent from the pure solvent phase. Again, an applicable modification of the derivation provides the correct answer. In general nonequilibrium conditions, there are three temperatures and three pressures, one of each for each of the three phases, and two gel densities, one for the swollen gel and one for the coexisting collapsed gel, for a total of 8. At equilibrium, there are five constraints: all three temperatures are equal (two constraints), the solvent chemical potential is equal in all three phases (two constraints), and the solute chemical potential is equal in the two gel phases (one constraint), for a total of five constraints. Eight minus five equals three.

Our universal gel is consistent with this analysis. We have seen that for a choice of subcritical temperature, and, implicitly, a pressure for the solvent bath, a single free choice of \( \rho_0 \) determines the other two values of \( \rho(0) \). Once again, reference to extreme conditions or states of matter, such as metastability, may not be necessary to understand gel behavior.

### AUTHOR INFORMATION

**Corresponding Author**

*E-mail: jerrymanning@rcn.com.*

**ORCID**

Gerald S. Manning: 0000-0002-6210-4353

**Notes**

The author declares no competing financial interest.

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