Ionically driven phase transitions in non-ideal systems

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We construct an explicitly solvable Landau mean-field theory for volume phase transitions of confined or fixed ions driven by relative concentrations of divalent and monovalent counterions. Such phase transitions have been widely studied in ionic gels, where the mechanism relies on self-attraction or elasticity of a network. We find here that non-ideal behavior of ions in aqueous solution can in theory drive phase transitions without a self-attracting or elastic network. We represent non-ideality by a Debye-Hückel-like power-law activity, or correlation free energy, and retain a mechanical self-repulsion to avoid runaway collapse due to the non-ideal term. Within this model we find a continuous line of gas-liquid-type critical points, connecting a purely monovalent, divalent-sensitive critical point at one extreme with a divalent, monovalent-sensitive critical point at the other. An alternative representation of the Landau functional handles the second case. We include a formula for electrical potential, which may be a convenient proxy for critically varying volume. Our relatively simple mean-field formulation may facilitate explorations of tunable critical sensitivity in areas such as ion detection technology and biological osmotic control.

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In charged polymer networks, phase transitions were observed and explained theoretically some time ago by Tanaka and co-workers [1–4]. In experiments, gels can exhibit ionically-driven collapse or expansion as the osmotic pressure responds to slight changes in external ion or composition. Volume phase transitions have long been discussed with an eye to applications [5, 6] and as candidate mechanisms for essential biophysical processes [7]. In previous models network self-attraction and restoring elasticity has played a crucial role, invoking specific elastic properties of polymer networks [8].

Here we seek to recast the theory of ionic phase transitions into a simple and mathematically solvable mean-field formulation, including (in simplified form) the non-ideality that is present in all ionic solutions. We find that in principle a self-attracting network is not necessary for a discontinuous phase transition in the presence of a simplified Debye-Hückel-type non-ideality, because non-ideality itself acts as an effective self-attraction that mediates an ionically driven phase transition of the gas-liquid type. Our model requires us, however, to attribute a self-repulsion to our fixed-ion system to avoid runaway collapse due to the non-ideal term.

Our simplified formulation of ionic transitions may, in practical terms, provide a tunable critical sensitivity to ion valence or concentration. This suggests, for example, a mechanism for biophysical cellular functions such as homeostasis. The theory may also lend itself to engineering applications involving ion detection. For these purposes electric potential $\Phi$, whose behavior is predicted, might often be a more convenient dependent parameter than volume in applications to ion detection or in biophysical roles for critical ionic sensitivity.

Consider a population of $N_0$ ions each of charge $q_0$ that may be bound to a mechanical structure, such as a polymer network, or otherwise confined within a volume permeable to counterions. These are the conditions for Donnan equilibrium [9] in which osmotic pressure of excess counterions goes hand-in-hand with an internal voltage $\Phi$, relative to outside, with the same sign as $q_0$. Even for $\Phi \neq 0$, neutrality holds to a good approximation whenever the voltage drop $\Phi$ occurs only at the boundary, or more generally if $N_0 \gg C\Phi/q_0$, where $C$ is the system capacitance.

The immobile ions, confined within a variable volume $V$, have concentration $c = N_0/V = 1/v$. Monovalent and divalent counterions with charges $q_a = -q_0$ and $q_b = -2q_0$ are introduced at external concentrations $a$ and $b$, and have within $V$ the concentrations $a' = N_a/V$ and $b' = N_b/V$. Their free diffusion in and out is controlled by the the electrical potential $\Phi$. We introduce nonideality of mobile ions by way of a Debye-Hückel interaction or correlation free energy [10]

$$F_{\text{DH}} = -v_b^{1/2} k_B T V \left( \sum_{\alpha} z_{\alpha} c_{\alpha} \right)^{3/2}$$

where $v_a = z_{\alpha} e$. The essential features of $F_{\text{DH}}$ are that it is negative and contains mobile-ion concentrations raised to the $3/2$ power. The constant $v_b$ is proportional to the cube of Bjerrum length. In standard aqueous conditions,

$$\frac{1}{v_b} = (12\pi)^2 \left( \frac{k_B T}{e^2} \right)^3 \approx 3.4 \text{ molar.}$$

To obtain closed-form solutions, we omit confined ions from the sum, and replace the factor $(a' + 4b')^{3/2}$ by $(a' + 2b')^{3/2}$, which will equal $c^{3/2}$ once neutrality is imposed. Thus we employ the Debye-Hückel-like interaction term

$$F_{\text{int}} = -v_b^{1/2} k_B T V (a' + 2b')^{3/2}.$$
With $a' = N_a/V$ and $b' = N_b/V$ and taking derivatives,
\[
\begin{align*}
-\partial F_{\text{int}}/\partial V &= P_{\text{int}} = -\frac{1}{2} v_a'^{1/2} k_n T (a' + 2b')^{3/2} \quad (4) \\
\partial F_{\text{int}}/\partial N_a &= k_n T \ln \gamma_a = -\frac{2}{3} k_n T v_{a'}^{1/2} (a' + 2b')^{1/2} \quad (5) \\
\partial F_{\text{int}}/\partial N_b &= k_n T \ln \gamma_b = -3 v_{b'}^{1/2} k_n T (a' + 2b')^{1/2} \quad (6)
\end{align*}
\]

Here $\gamma_a$ and $\gamma_b$ are activity coefficients [11] for the monovalent and divalent ions: $\mu_a = \mu_0^a + k_n T \ln \gamma_a a$. The proportionality of $\ln \gamma$ to the square root of ionic concentration represents Debye-Hückel behavior, a theory appropriate to low ionic strength [12]. The free energy, with $\Phi$ externally controlled, is
\[
F(N_a, N_b, V, \Phi) = F_{\text{int}}(N_a, N_b, V) + (N_0 - N_a - 2N_b) q_0 \Phi + F_0(V) = k_n T \left[ N_a \ln \frac{N_a}{c_0 e V} + N_b \ln \frac{N_b}{c_0 e V} \right] 
\]

(with $e$ the natural log base). Here $F_0(V)$ describes mechanical constraints on the immobile ions, such as a polymer network carrying the fixed ions or a membrane containing them. The logarithmic terms are the ideal free energy of the mobile ions, and the concentration scale $c_0$ will cancel out. The mechanical contribution to pressure is $-\partial F_{\text{int}}/\partial V = P_0$ (equivalently a function of $v$ or $c$) and the overall pressure and the chemical potentials $\mu_a = \partial F/\partial N_a$ and $\mu_b = \partial F/\partial N_b$ are
\[
\begin{align*}
P &= P_0(v) + (a' + b') k_n T + P_{\text{int}} \quad (8) \\
\mu_a &= -q_0 \Phi + k_n T \ln (\gamma a/c_0) \quad (9) \\
\mu_b &= -2 q_0 \Phi + k_n T \ln (\gamma b/c_0) \quad (10)
\end{align*}
\]

If we set $\mu_a = k_n T \ln (a/c_0)$ and $\mu_b = k_n T \ln (b/c_0)$, $a$ and $b$ become effective concentrations, referred to an ideal external solution. To fix $\Phi$, we impose neutrality, $c = a' + 2 b'$, and introduce a dimensionless potential $\phi = q_0 \Phi/k_n T$ which will always be positive (since $\Phi$ will always be of the same sign as $q_0$). We have altogether
\[
P = P_0(N_0/c) + \frac{1}{2} (a' + c) k_n T - \frac{1}{2} v_{a'}^{1/2} c^{1/2} k_n T \quad (11)
\]
\[
\phi = \ln (a'/a) - \frac{3}{2} v_{a'}^{1/2} c^{1/2} \quad (12)
\]
\[
2 \phi = \ln (b'/b) - 3 v_{b'}^{1/2} c^{1/2} \quad (13)
\]

which, together with $c = a' + 2 b' = N_0/v$, we will solve to find $P(v)$. Combining the equations involving $\phi$, putting $2b' + a' - c = 0$ for neutrality, and solving yields
\[
a' = (a'^2/4b') \left[ (1 + (8b/a^2)c)^{1/2} - 1 \right] \quad (14)
\]

We define the dimensionless divalent parameter
\[
\beta = \frac{8b}{v_{a'} a^2}. \quad (15)
\]

To motivate use of $\beta$, imagine $n$ divalent ions $B$ cooperatively exchanging with 2n monovalent ions $A$, according to $CA_{2n} + nB \Rightarrow CB_n + 2nA$. Equilibrium is then
\[
\frac{[CB_n]}{[CA_{2n}]} = K \left[ \frac{B^n}{A} \right]^{2n} \propto \left( \frac{b}{a'} \right)^n \quad (16)
\]

![FIG. 1: Coexistence diagram in dimensionless volume and pressure for a system tuned by repulsion $\alpha$ to the monovalent ($\lambda = 1$) critical point. The divalent parameter $\beta$ rises from zero upon addition of divalent ions, so that $\beta < 0$ is not possible. In similar coexistence diagrams for $0 < \lambda < 1$, the upper region will be accessible.](image)

For large $n$, the discontinuous transition $CB_n \rightarrow CA_{2n}$ occurs at a fixed value of $b/a^2$.

The dimensionless pressure $p(v) = P_{\text{int}}/k_n T$ is
\[
p_0(v) + \frac{1}{2} \frac{v_n}{v} + \frac{1}{\beta} \left[ (1 + (v_{n}/v)^{1/2} - 1 \right] - \frac{1}{2} \left( \frac{v_n}{v} \right)^{3/2} \quad (17)
\]

where $p_0 = P_0 v_n/k_n T$. If the system is to be stable against collapse to $v = 0$ due to the interaction term, we require that $p_0(v)$ include a repulsion diverging faster than $1/v^3/2$. We will use the minimal choice
\[
p_0(v) = + \alpha (v_n/v)^2 \quad (18)
\]

(with $\alpha$ dimensionless). The dimensionless electrical potential is
\[
\phi = \ln \frac{2}{\beta} \left[ (1 + (v_n/v)^{1/2} - 1 \right] - 3 \left( \frac{v_n}{v} \right)^{1/2} \ln (v_n a). \quad (19)
\]

From the Gibbs-Duhem relation (at constant $T$, or here $\beta$) we obtain the chemical potential, linking coexisting $v$ and $v'$ at specified $\beta$, as $\mu(v) = pv' - \int p(v) dv$, or
\[
\mu(v) = 2\alpha / v - \frac{3}{2} v^{-1/2} - \ln \left[ v + \sqrt{v(v+\beta)} \right] + \frac{1}{2}. \quad (20)
\]

Self-intersections of the curve $(p(v), \mu(v))$ yield phase boundaries as in Figs 1 and 2.
We solve our model in terms of the parameter
\[ x = \sqrt{v_\beta/v}. \] (21)
At a critical point the conditions \( p'(v) = p''(v) = 0 \) and \( p'(x) = p''(x) = 0 \) are equivalent. Regarding the critical value of \( p \) as a function of \( x \) and \( \beta \), and introducing the parameter \( \lambda = 1/\sqrt{1 + \beta_c x_c^2} \), we have the \( x \)-derivatives
\[ \tilde{p}_x = x_c [4\alpha x_c^2 - 3 x_c + 1 + \lambda] = 0 \] (22)
\[ \tilde{p}_{xx} = 12\alpha x_c^2 - 3 x_c + 1 + \lambda^3 = 0 \] (23)
Eliminating \( \alpha \) in favor of \( \lambda \) gives the line of critical points
\[ p_c = x_c^4 [\frac{1}{12} (1 - 6\lambda + \lambda^3) + \lambda/(1 + \lambda)] \] (24)
\[ x_c = \frac{3}{2} (2 + 3\lambda - \lambda^3) \] (25)
\[ \alpha_c = (1 + 2\lambda - \lambda^3)/4x_c^2 \] (26)
\[ \beta_c = 1/(x_c^2 \lambda^2) \] (27)
The interval \( 0 \leq \lambda \leq 1 \) corresponds to \( \infty \geq \beta \geq 0 \). Although we view \( \alpha(\lambda) \) as the mechanism by which ion critical points can be tuned, we can also view \( \alpha_c = \alpha(\lambda) \) as a critical value of the repulsion strength. With ionic conditions fixed, we could drive transitions by modulating \( \alpha \), analogous to transitions in ionic gels induced by variation of solvent composition \[ \text{[K]} \].

About each critical point, with \( \delta v = v - v_c \) and \( \delta \beta = \beta - \beta_c \), we construct a Landau expansion for the pressure,
\[ p(\beta, \epsilon) = p_c - A\delta \beta + B\delta \beta \epsilon - C \epsilon^3 \] (28)
where \( \epsilon = \delta v + \kappa \delta \beta \) is an order parameter linear in \( \delta v \) and \( \delta \beta \). In a potential application, we imagine tuning a system to a critical point, \( \beta = \beta_c \) and \( p = p_c \). Within mean-field theory, when the divalent ratio is changed by \( \delta \beta = \beta - \beta_c \) one predicts a singular expansion or contraction
\[ \epsilon \approx -(A/C)^{1/3} (\delta \beta)^{1/3} \] (29)
where the cube root is taken with the same sign as \( \delta \beta \). As discussed below, this singular behavior in volume might in practice be better monitored via the electric potential than the volume change \( \delta v \) or \( \epsilon \).

To evaluate the Landau coefficients, we expand the pressure around the critical point, to third order in \( \delta v = v - v_c \) and to first order in \( \delta \beta \), giving
\[ p(v, \beta) \approx p_c + \tilde{p}_\beta \delta \beta + \tilde{p}_{vv} \delta v \delta \beta + \frac{1}{6 \beta} \tilde{p}_{vvv} \epsilon^3 \] (30)
where \( \beta \) and \( v \) subscripts denote partial derivatives and \( \tilde{p}, \tilde{p}_\beta, \) etc. are critical values. We have chosen \( \kappa = \tilde{p}_{vvv}/\tilde{p}_{vvv} \) to eliminate an \( \epsilon^2 \) term. Evaluating the various derivatives, the Landau parameters along the critical line are
\[ A = \frac{1}{2} x_c^4 \lambda^3/(1 + \lambda)^2, \quad B = \frac{1}{4} x_c^6 \lambda^3 \] (31)
\[ C = \frac{1}{38} x_c^8 [2 + 12 \lambda - 7 \lambda^3 + 3 \lambda^5] \] (32)
\[ \kappa = (\lambda^3/x_c)^2/(8 \epsilon^2 \alpha_c - \beta_c \lambda^5) \] (33)
where \( x_c \) and \( \alpha_c \) are known functions of \( \lambda \) from Eqs (25) and (26). \( C \) has no zeros within \( 0 \leq \lambda \leq 1 \), while \( \kappa \) is zero only at \( \lambda = 0 \). At the monovalent critical point (\( \beta = 0 \), i.e. \( \lambda = 1 \)) Eqs (24) through (27) yield \( p_c = 32/27 \approx 1.185, \ x_c = 8/3 \approx 2.67, \ \alpha_c = 9/128 \approx 0.0703, \) the Landau coefficients are
\[ A = 2^9/3^4 \approx 6.321 \] (34)
\[ B = 2^{16}/3^6 \approx 89.90 \] (35)
\[ C = 5(2^{21}/3^8) \approx 1598.2 \] (36)
and the order parameter is \( \epsilon = \delta v + (1/2) \delta \beta \). Here the system enters coexistence for any value of \( \beta > 0 \), with \( \epsilon \approx -(0.158) \beta^{1/3} \). A system tuned to the monovalent critical point moves with infinite response towards a smaller volume with the introduction of any divalents. In the liquid-gas analogy, this path follows the critical isobar.

At the purely divalent critical point (\( \beta = \infty, \lambda = 0 \)) both \( A \) and \( B \) vanish, but we can here characterize the line of critical points by the alternative parameterization
\[ p(\beta, \epsilon) = p_c + A' \delta(\beta^{-1/2}) - B' \delta(\beta^{-1/2}) - C \epsilon^3 \] (37)
\[ A' = x_c(1 - \lambda)^{3/2}/(1 + \lambda)^2 \] (38)
\[ B' = \frac{1}{2} x_c^3 (1 - \lambda)^{3/2} \] (39)
The parameter \( \beta^{-1/2} \) is proportional to the monovalent concentration at fixed divalent concentration. The volume singularity (29) can be rewritten as
\[ \epsilon \approx +\left(\frac{A'}{C} \delta(\beta^{-1/2})\right)^{1/3} \] (40)
where again the cube root has the same sign as its argument. At the divalent critical point ($\beta = \infty$, $\lambda = 0$) Eqs (24) through (27) yield $p_c = 4/27 \approx 0.1481$, $x_c = 4/3$, $\alpha_c = 9/64 \approx 0.1406$, $A' = 4/3$, $B' = 32/27 \approx 1.185$ \( (41) \) $C = 2^{13}/3^9 \approx 0.4162$ \( (42) \)

For this divalent critical point at $\beta_c^{-1/2} = 0$, the order parameter is simply the volume, $\epsilon = \delta v$. A purely divalent system that is tuned to be critical moves with infinite response towards a larger volume with the introduction of any monovalents, as $\delta v \approx (1.214) \beta^{-1/6}$.

Returning to the dimensionless potential $\phi = q_0 \Phi / k_B T$ in Eq (19), along the critical line with a constant we find

$$\left[ \frac{\partial \phi}{\partial \nu} \right]_c = \frac{3}{4 \nu_B} \left[ \frac{1 + 2\lambda - \lambda^3}{2 + 3\lambda - \lambda^3} \right]$$ \( (43) \)

Since $\delta \phi \approx \phi'_c \delta v$, the potential will display the same power-law singularity as the volume.

Our simplified framework is intended to motivate investigation of ionic phase transitions in ever simpler systems. As a fascinating analogue of liquid-gas transitions, and in the context of ionic gels, such transitions have been a topic of discussion for many years. Possible roles in biological systems \[7\] and potential applications such as metal ion detection and electrical sensitivity \[5, 6\] should remain applicable to phase transitions as discussed here.

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