Counterion-Induced Swelling of Ionic Microgels

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I. INTRODUCTION

Ionic microgel particles, when dispersed in a solvent, swell to equilibrium sizes that are governed by a balance between electrostatic and elastic forces. Tuning of particle size by varying external stimuli, such as pH, salt concentration, and temperature, has relevance for drug delivery, microfluidics, and filtration. To model swelling of ionic microgels, we derive a statistical mechanical theorem, which proves exact within the cell model, for the electrostatic contribution to the osmotic pressure inside a permeable colloidal macroion. Applying the theorem, we demonstrate how the distribution of counterions within an ionic microgel determines the internal osmotic pressure. By combining the electrostatic pressure, which we compute via both Poisson-Boltzmann theory and molecular dynamics simulation, with the elastic pressure, modeled via the Flory-Rehner theory of swollen polymer networks, we show how deswelling of ionic microgels with increasing concentration of particles can result from a redistribution of counterions that reduces electrostatic pressure. A linearized approximation for the electrostatic pressure, which proves remarkably accurate, provides physical insight and greatly eases numerical calculations for practical applications. Comparing with experiments, we explain why soft particles in deionized suspensions deswell upon increasing concentration and why this effect may be suppressed at higher ionic strength. The failure of the uniform ideal-gas approximation to adequately account for counterion-induced deswelling below close packing of microgels is attributed to neglect of spatial variation of the counterion density profile and the electrostatic pressure of incompletely neutralized macroions.

While numerous experimental studies have explored the effect of salt concentration on swelling of ionic microgels, relatively few have examined the influence of particle concentration. Borrega et al. [4] and Tan et al. [5] deduced particle sizes from viscosity measurements and demonstrated that free counterions in solution can induce osmotic deswelling of microgels in dense suspensions. Cloitre et al. [6] used dynamic light scattering (DLS) to quantify variations in hydrodynamic radius with cross-linker density and degree of ionization of polyelectrolyte microgels, synthesized from ethyl acrylate and methacrylic acid monomers, and proposed that free counterions may induce deswelling at microgel concentrations approaching close packing. Pelaez-Fernandez et al. [7] measured the osmotic pressure of suspensions of cross-linked poly-vinylpyridine microgels via osmometry and dialysis. Over a range of concentrations, from dilute to near hard-sphere freezing, they obtained pressures in excess of what could be reasonably attributed to the microgel particles alone. They explained their results...
by hypothesizing a dominant influence of free counterions in solution. Like Cloitre et al., they observed significant deswelling only at concentrations near close packing. Romeo et al. [8], using DLS to measure the hydrodynamic radius of relatively stiff PNIPAM particles over a range of concentrations, concluded that any counterion-induced shrinkage is negligible. In contrast, Holmqvist et al. [10] observed much stronger deswelling of loosely cross-linked PNIPAM-co-PAA particles in deionized suspensions.

Measurements of ionic microgel particle sizes are commonly interpreted in the dilute regime via scaling theories, originally developed for macroscopic gels [72–78], which assume strict electroneutrality and total confinement of counterions to the gel, or via phenomenological models [2–8], which allow local deviations from electroneutrality and partial release of counterions. Both approaches, by approximating the counterions as a uniformly distributed ideal gas, neglect continuous variation in the counterion density, which can be important for accurately modeling swelling of microscopically sized gel particles. To our knowledge, no previous studies have realistically modeled the direct relationship between the counterion density profile, osmotic pressure, and swelling of ionic microgels.

In this paper, we present a rigorous analysis of the dependence of ionic microgel size on counterion distribution and on the bulk concentration of particles. By coupling elasticity theory of cross-linked gel networks with a new statistical mechanical theorem for the electrostatic contribution to the internal osmotic pressure, we demonstrate how the counterion distribution determines the equilibrium size of ionic microgels. Through a combination of theory and simulation, we explain experimentally observed density-dependent deswelling and identify system parameters for which such effects can be enhanced. Thus, we predict that sufficiently soft and ionized microgels can penetrate apertures considerably narrower than their dilute size at concentrations below close-packing, with potentially important implications for drug delivery, microfluidics, and filtration.

II. MODELS

A. Microgel Suspension

We consider a suspension of soft, charged colloidal particles (macroions), permeable to water and microions. Common examples are polyelectrolyte microgels and capsules dispersed in an aqueous electrolyte. Within the primitive model of polyelectrolytes, the solvent is reduced to a dielectric continuum of dielectric constant $\epsilon$. For simplicity, we assume $\epsilon$ to be the same inside and outside of the macroion. This assumption can be easily relaxed to allow for nonuniform dielectric constant. We further assume spherical macroions, of dry (collapsed) radius $a_0$, swollen radius $a$, and charge number (valence) $Z$ associated with a fixed charge distribution, $n_f(r)$, which varies only with radial distance $r$ from the center. The fixed charge comes from dissociation of $Z$ counterions, which can contribute to the osmotic pressure by virtue of their freedom to move throughout the system. Any counterions that may be immobilized by condensation onto polyelectrolyte chains [83] are excluded from this count. It is important to note that this bare charge number can be substantially higher than the effective charge number associated with interparticle pair interactions, as is deduced from light scattering experiments [10]. The counterions and salt ions (microions) are modeled as point charges, of valence $\pm z$, that can freely penetrate the macroions. In equilibrium, the microions distribute themselves so as to equalize the chemical potential throughout the system.

In Donnan equilibrium, microions can exchange with a salt reservoir, of bulk microion pair concentration $n_0$, through an immovable, semipermeable membrane, which is impermeable to macroions, but permeable to both microions and solvent. Equality of chemical potentials entails a nonuniform distribution of ions between the suspension and reservoir and a corresponding osmotic pressure, i.e., a difference in bulk pressure between the suspension and the reservoir, which is sustained by a countering force exerted by the externally fixed membrane.

Within the suspension, microions can also exchange between the interior and exterior macroion regions. The periphery of a macroion thus acts analogously to a semipermeable membrane, allowing microions to penetrate, but holding the fixed charge within the macroion. In this internal Donnan equilibrium, the fixed charge on the polyelectrolyte chains creates a nonuniform distribution of microions that equalizes the chemical potential. The interior microion gas and the self-repulsion of the fixed charge within the macroion combine to generate an outward electrostatic pressure that swells the macroion. Swelling is limited by the inward elastic restoring forces exerted by the cross-linked gel. In equilibrium, a balance between these opposing pressures determines the average macroion size. As will become apparent below, the electrostatic contributions to the pressure inside and outside a microgel differ.
B. Cell Model

The cell model \[84\] centers a single macroion in a spherical cell along with \(N\) mobile microions (see Fig. 1). The Hamiltonian of the system, \(H = H_e + H_g\), decouples naturally into an electrostatic component \(H_e\), which incorporates all Coulomb interactions in the cell, and a gel component \(H_g\), which describes the elastic and mixing degrees of freedom for a polymer network. The electrostatic component can be further decomposed as follows:

\[
H_e = U_m(a) + U_{mp}(\{r\}; a) + U_{\mu \mu}(\{r\}) ,
\]

where \(U_m(a)\) is the macroion self-energy and \(U_{mp}(\{r\}; a)\) and \(U_{\mu \mu}(\{r\})\) are the macroion-microion and microion-microion interaction energies, respectively, which depend on the ion coordinates, \(\{r_1, \ldots, r_N\} \equiv \{r\}\). Note that only the first two terms in Eq. (1) depend on the macroion radius. The macroion-microion interaction may be expressed as

\[
U_{mp}(\{r\}; a) = \sum_{i=1}^{N} v_{mp}(r_i; a) ,
\]

where \(v_{mp}(r; a)\) is the macroion-microion pair potential. Although the cell model completely neglects macroion-macroion correlations, the relative contribution of such interparticle correlations to osmotic pressure is known to be weakest in the low-salt limit \[84, 86\], thus resulting in quite an accurate representation of deionized microgel suspensions \[60, 62\]. Furthermore, independent simulations of many microgel particles, interacting via a repulsive Hertz pair potential and fluctuating in size, reveal that for the same elastic parameters as considered here, macroion-macroion correlations and steric interactions begin to significantly affect swelling only at average volume fractions approaching close packing \[85\].

III. THEORY

A suspension that is free to exchange microions with a salt reservoir through a semipermeable membrane is best represented in the semi-grand canonical ensemble. Decoupling of the electrostatic and gel components of the Hamiltonian implies a factorization of the semi-grand canonical partition function, \(\Xi = \Xi_e \Xi_g\), into an electrostatic grand canonical partition function \(\Xi_e\) and a gel canonical partition function \(\Xi_g\). Correspondingly, the semi-grand potential, \(\Omega = -k_B T \ln \Xi = \Omega_e + F_g\), separates conveniently into an electrostatic grand potential, \(\Omega_e = -k_B T \ln \Xi_e\), and a gel Helmholtz free energy, \(F_g = -k_B T \ln \Xi_g\). We focus first on the electrostatic grand canonical partition function, in a spherical cell of fixed radius \(R\), which can be expressed as

\[
\Xi_e(\mu_0, a, R, T) \propto \sum_{N=0}^{\infty} \frac{e^{\mu_0 N}}{N!} \prod_{i=1}^{N} \int_0^R dr_i r_i^2 e^{-\beta H_e} ,
\]

with \(\beta \equiv 1/(k_B T)\) at temperature \(T\) and \(\mu_0 = k_B T \ln n_0\) the microion chemical potential in the reservoir.

The bulk osmotic pressure – the pressure in the suspension relative to the pressure in the reservoir – is defined via the derivative of the grand potential with respect to the system volume, \(V = 4\pi R^3/3\):

\[
\pi_b = -\frac{\partial \Omega}{\partial V}_{\mu_0, a, T} = \frac{k_B T}{4\pi a^2} \frac{\partial}{\partial a} \ln \Xi_e(\mu_0, a, R, T) ,
\]

where on the right side we have used the fact that \(\Xi_g\) is independent of \(R\) in the cell model. Substituting for \(\Xi_e(\mu_0, a, R, T)\) from Eqs. (1)-(3) yields

\[
\beta \pi_b = \langle n_+(R) \rangle + \langle n_-(R) \rangle ,
\]

where \(n_+(R)\) are the microion densities at the cell boundary and \(\langle \rangle\) denotes an ensemble average over microion coordinates. This classic theorem for the bulk osmotic pressure was first derived within PB theory \[84\], but proves exact within the cell model \[88\].

Similarly, the internal osmotic pressure – the pressure inside the microions relative to the bulk osmotic pressure – can be defined via a derivative of \(\Omega\) with respect to the single-macroion volume, \(v = 4\pi a^3/3\):

\[
\pi_i = -\frac{\partial \Omega}{\partial v}_{\mu_0, a, R, T} = \frac{k_B T}{4\pi a^2} \frac{\partial}{\partial a} \ln \Xi_e(\mu_0, a, R, T) .
\]

More explicitly, \(\pi_i\) is the excess of the osmotic pressure inside a macroion over the osmotic pressure \(\pi_b\) outside, within the suspension. In equilibrium, the electrostatic pressure is balanced by the elastic pressure of the polymer gel, resulting in \(\pi_i = 0\). Upon substituting \(\Omega = \Omega_e + F_g\) into Eq. (3), the internal osmotic pressure separates into electrostatic and gel contributions: \(\pi_i = \pi_e + \pi_g\). From Eqs. (1)-(3), the electrostatic contribution to the internal osmotic pressure may be expressed as

\[
\pi_e = -\frac{1}{4\pi a^2} \left( \frac{\partial}{\partial a} U_m(a) + \left< \frac{\partial}{\partial a} U_{mp}(a) \right> \right) .
\]

For the gel contribution, we invoke the Flory-Rehner theory of gel elasticity \[13, 72\], which combines mixing entropy, polymer-solvent interactions, and elastic network energy to predict a gel free energy

\[
\beta F_g = N_m \left[ (\alpha^3 - 1) \ln (1 - \alpha^{-3}) + \chi (1 - \alpha^{-3}) \right]
\]

\[
+ \frac{3}{2} N_{ch} (\alpha^2 - \ln \alpha - 1) ,
\]

where \(\alpha \equiv a/a_0\) is the particle swelling ratio, \(N_m\) and \(N_{ch}\) are the numbers of monomers and chains per microgel, and \(\chi\) is the Flory solvency parameter. The corresponding gel pressure is given by

\[
\beta \pi_g v = -N_m \left[ \alpha^3 \ln (1 - \alpha^{-3}) + \chi \alpha^{-3} + 1 \right]
\]

\[
- N_{ch} (\alpha^2 - 1/2) .
\]
At equilibrium swelling, the semi-grand potential is a minimum with respect to variation of \( \alpha \), which is equivalent to vanishing of the total internal osmotic pressure: \( \pi_{in}(\alpha) = \pi_+ (\alpha) + \pi_- (\alpha) = 0 \). From this stability criterion, we explore equilibrium swelling as a function of particle concentration in Sec. IV.

Our theorem for the electrostatic pressure difference across the surface of a permeable macroion [Eq. (21)] is exact within the cell model. Practical implementation now requires a model for the fixed charge distribution within a macroion. To illustrate, we proceed with the simplest model of a uniformly charged microgel of fixed charge number density \( n_f(r) = Z/e \) \( (r \leq a) \). In this case, the energy of interaction between a macroion and a microion of valence \( z \) is given by

\[
\beta v_{m\mu}(r) = -\frac{Zz\lambda_B}{2a} (3 - r^2/a^2), \quad r \leq a ,
\]

and the macroion self-energy is

\[
\beta U_m = \frac{3}{5} Z^2 \lambda_B^2 \frac{\alpha}{a} ,
\]

where \( \lambda_B \equiv e^2/(\kappa e_B T) \) is the Bjerrum length. From Eq. (10), it follows that

\[
\beta \left[ \frac{\partial}{\partial a} U_m(a) \right] = -\frac{Z\lambda_B}{2} \left( \frac{3}{a^2} - \sum_{i=1}^{N} z_i \left( 3 - \frac{r_i^2}{a^2} \right) \right),
\]

with \( z_i = \pm z \) denoting the valence of microion \( i \). Now substituting Eq. (12) into Eq. (7) yields

\[
\beta \pi_v = \frac{Z\lambda_B}{2a} \left( \frac{2}{5} Z - \langle N_+ \rangle + \langle N_- \rangle + \frac{\langle r^2 \rangle_+ - \langle r^2 \rangle_-}{a^2} \right),
\]

where, for given radial number density profiles \( n_{\pm}(r) \),

\[
\langle N_{\pm} \rangle = 4\pi \int_{0}^{a} dr \int_{0}^{a} r n_{\pm}(r)
\]

are the mean numbers of interior counterions/coions and

\[
\langle r^2 \rangle_{\pm} = 4\pi \int_{0}^{a} dr \int_{0}^{a} r^4 n_{\pm}(r)
\]

are second moments of the interior microion density profiles. Equation (13) provides an explicit formula — exact within the spherical cell model — for the electrostatic contribution to the internal osmotic pressure of an ionic microgel modeled as a uniformly charged sphere. This result may be easily generalized to other macroion architectures, such as core-shell microgels and polyelectrolyte capsules. Implementing Eq. (13) requires the microion density profiles inside of the macroion, which may be obtained from either theory or simulation. In the next section, we discuss computational methods for computing microion densities and osmotic pressure.

### IV. COMPUTATIONAL METHODS

#### A. Nonlinear Poisson-Boltzmann Theory

To explicitly compute the electrostatic contribution to the osmotic pressure internal to ionic microgel particles, we implemented Poisson-Boltzmann (PB) theory within the spherical cell model \([84, 88, 89]\). The Poisson equation for the electrostatic potential \( \psi(r) \) (in \( k_B T/e \) units),

\[
\nabla^2 \psi(r) = -4\pi \lambda_B [n_+(r) - n_-(r) - n_f(r)] ,
\]

combined with the mean-field Boltzmann approximation for the equilibrium microion densities,

\[
n_{\pm}(r) = n_0 \exp[\mp \psi(r)] ,
\]

yields the nonlinear PB equation,

\[
\psi''(r) + \frac{2}{r} \psi'(r) = \begin{cases} \frac{\kappa_0}{a} \sinh \psi(r) + \frac{3Z\lambda_B}{a^3}, & 0 < r \leq a \\ \frac{\kappa_0}{a} \sinh \psi(r), & a < r \leq R \end{cases}
\]

where \( \kappa_0 = \sqrt{8\pi \lambda_B \eta_0} \) is the Debye screening constant in the electrolyte reservoir. Solving Eq. (18), with boundary conditions \( \psi'(0) = \psi'(R) = 0 \), yields \( \psi(r) \) and thus \( n_{\pm}(r) \), from which we compute the electrostatic pressure via Eqs. (13)-(15). The electrostatic pressure may also be computed from the electrostatic grand potential,

\[
\beta \Omega_e = 4\pi \int_{0}^{R} dr \int_{0}^{R} \sum_{i=\pm} n_i(r) \ln \left( \frac{n_i(r)}{n_0} \right) - 1
\]

\[
+ \frac{1}{2\lambda_B} \int_{0}^{R} dr \int_{0}^{R} r |\psi'(r)|^2 ,
\]

by taking a derivative with respect to \( a \):

\[
\pi_e = -\frac{1}{4\pi a^2} \left( \frac{\partial}{\partial a} \Omega_e(\mu_0, a, R, T) \right)_{\mu_0, R, T} .
\]

#### B. Linearized Approximation

For comparison with the nonlinear PB theory, we also consider a linearized approximation that provides convenient analytical expressions. For a suspension of spherical, uniformly charged microgels with average microion densities \( n_{\pm} \), linear response theory \([56, 60]\) predicts microion density profiles (to within a constant)

\[
n_{\pm}(r) = \frac{Z n_{\pm}}{\mu} \left\{ \begin{array}{ll}
1 - \frac{1}{1+x} e^{-x} & \frac{\alpha}{a} \sinh \left( \frac{x}{a} \right), \quad r \leq a \\
(\cosh x - \sinh x) & \frac{\alpha}{a} e^{-x/r}, \quad r > a ,
\end{array} \right.
\]

where \( n_{\mu} = n_+ + n_- \) is the total average microion density, \( x = \kappa a \), and \( \kappa = \sqrt{4\pi \lambda_B n_\mu} \) is the screening constant in the suspension (cf. \( \kappa_0 \) in the reservoir). For a suspension
of average microgel and salt densities \( n_m \) and \( n_s \), respectively, electroneutrality dictates \( n_\mu = Zn_m + 2n_s \). Substituting Eq. (21) into Eqs. (14) and (15) yields (to within a constant) the mean numbers of interior microions,

\[
\langle N_\pm \rangle = \pm Z n_\mu \left[ 1 - 3 \frac{1 + x}{x^3} e^{-x} (x \cosh x - \sinh x) \right],
\]

and second moments of interior microion density profiles,

\[
\langle r^2 \rangle_\pm = \pm \frac{3}{5} Z a n_\mu \left[ 1 - 5 \frac{1 + x}{x^4} e^{-x} \right. \\
\left. \times \left[ x (x^2 + 6) \cosh x - 3(x^2 + 2) \sinh x \right] \right].
\]

Finally, combining Eqs. (22), (23), and (13) yields

\[
\beta \pi_e v = 3Z^2 \frac{\lambda_B}{a} \frac{1 + x}{x^4} e^{-x} \left( \frac{1 + x^2}{x} \sinh x - 3 \cosh x \right).
\]

This analytical approximation, which proves to be quite accurate, greatly eases calculations and facilitates comparisons with experiments (see Sec. V).

C. Molecular Dynamics Simulations

In addition to applying PB theory, we also performed molecular dynamics (MD) simulations within the spherical cell model. Using the LAMMPS molecular simulator [91, 91], we confined a fixed number of monovalent point counterions – interacting via Coulomb pair potentials – to a spherical cell of fixed radius by a repulsive Lennard-Jones wall force. We modeled the influence of the macroion on the counterions by imposing an “external” electric field equal to the negative gradient of Eq. (10) and maintained a constant average temperature via a Nose-Hoover thermostat. The canonical (constant-NVT) ensemble proves more practical here than the grand canonical ensemble and yields the same microion distributions for the same system salt concentration [61, 62, 88]. Following equilibration for 10<sup>6</sup> steps, we computed thermodynamic quantities by averaging over particle trajectories for 10<sup>7</sup> time steps. From the resulting histogram of the counterion density, we computed \( \langle N_+ \rangle \) and \( \langle r^2 \rangle_+ \), and then \( \pi_e \) from Eq. (13).

V. RESULTS AND DISCUSSION

A. Illustrative Example

As noted above, the interior pressure theorem [Eq. (7)] can be applied to predict the electrostatic contribution to the osmotic pressure within macroions of any architecture, including those with nonuniform cross-linker density, such as core-shell [3, 8, 10, 18, 51, 92] or hollow [93] microgels. To illustrate the implementation of the theorem, we present numerical results, in the spherical cell model, for a uniformly charged microgel of dry radius \( a_0 = 10 \text{ nm} \), swollen radius \( a = 25 \text{ nm} \), and valence \( Z = 1000 \) in a salt-free aqueous solution at room temperature \( T = 293 \text{ K} \) (\( \lambda_B = 0.714 \text{ nm} \)). Figure 2(a) shows radial profiles of monovalent counterion density for dry particle volume fractions \( \phi_0 \equiv (a_0/R)^3 = 0.01, 0.02, 0.03 \), corresponding to swollen particle volume fractions \( \phi \equiv (a/R)^3 = \alpha^3 \phi_0 \) = 0.156, 0.313, 0.469. The counterion density profiles are relatively flat near the microgel center, where the electric field is weak, and fall off toward the periphery over a distance comparable to the screening length, \( \kappa^{-1} \) in the salt-free limit [see Eq. (21)]. Close agreement between simulation and theory validates the PB approximation. Also shown in Fig. 2(a) is the linearized approximation for \( \phi_0 = 0.03 \), which proves quite
by solving the nonlinear PB equation \[ Eq. (18) \] for \( n \) and substituting theories (free vs. cell boundary conditions) \[56, 60\].

at lower volume fractions stem from nonlinear screening \( \pi \) proves to be accurate for results from the linearized approximation \[ Eq. (22) \], which monotonically and roughly linearly. A similar trend re-
average fraction of interior counterions is seen to increase

motional pressure, which promotes mi-
tract the osmotic pressure also from simulations, which

to the grand potential \[ Eqs. (7) and (13) \] can be used to ex-

sion limits swelling. For illustration, we present results of our calculations for particles characterized by \( \alpha_0 = 10 \) nm, \( Z = 1000, N_m = 2 \times 10^5 \) monomers, \( N_{ch} = 100 \) chains, and \( \chi = 0.5 \) in deionized solutions of dry particle volume fractions \( \phi_0 = 0.01 \) \( - \) 0.04 (right to left). To ease comparison, the

accurate, aside from slight deviations near the particle periphery. For comparison, Fig. 2(b) shows the counterion density profile assumed by the uniform ideal-gas approximation (see Sec. V).

From the simulations, we also extracted the average fraction of interior mobile counterions, \( f_{in} = (N_+) / Z \). Integrating the PB counterion density profile over the microgel volume gave nearly identical results. The in-
set of Fig. 2 shows that 20-30\% of the counterions reside outside of the macroion, confirming that bulk theories of polyelectrolyte gels, which assume total counterion con-
finement, are not applicable here. Over this range of volume fractions (\( \phi_0 = 0.01 \) \( - \) 0.04, \( \phi = 0.156 \) \( - \) 0.625), the average fraction of interior counterions is seen to increase monotonically and roughly linearly. A similar trend results from the linearized approximation \[ Eq. (22) \], which proves to be accurate for \( \phi_0 > 0.02 \) (\( \phi > 0.3 \)). Deviations at lower volume fractions stem from nonlinear screening and differences in boundary conditions between the two theories (free vs. cell boundary conditions) \[56, 60\].

Proceeding to the osmotic pressure, we computed \( \pi_e \) by solving the nonlinear PB equation \[ Eq. (18) \] for \( n_\pm (r) \) and substituting \( \langle N_\pm \rangle \) and \( \langle r^2 \rangle_\pm \) into Eq. \[13\]. As a consistency check, we also computed \( \pi_e \) numerically from Eq. \[20\], using the PB solution for the counterion density profile, and obtained results identical to those from Eq. \[13\]. We emphasize, however, that Eq. \[20\], because it relies on knowledge of the grand potential, is in prac-
tice limited to PB theory \[27\]. In contrast, our internal pressure theorem \[ Eqs. (11) and (13) \] can be used to ex-
trace the osmotic pressure also from simulations, which naturally include correlations between microions.

To explore the equilibrium particle size, we com-

FIG. 3. Semi-grand potential \( \Omega \) vs. particle swelling ratio \( \alpha \) of ionic microgels with valence \( Z = 1000 \), dry particle radius \( \alpha_0 = 10 \) nm, \( N_m = 2 \times 10^5 \) monomers, \( N_{ch} = 100 \) chains, and \( \chi = 0.5 \) in deionized solutions of dry particle volume fractions \( \phi_0 = 0.01 \) \( - \) 0.04 (right to left). To ease comparison, the

the most probable size then corresponding to the min-
imum of \( F_g (\alpha) \). In the case of ionic microgels, mobile counterions generate an internal electrostatic pressure that modifies this size distribution and enhances swelling.

Results for the semi-grand potential \[ from Eqs. \[5\] and \[19\] \] are shown in Fig. 3 over a range of dry particle vol-
ume fractions. To facilitate comparison, the minimum values of \( \Omega \) are shifted to zero. For these system pa-

hers, the electrostatic pressure evidently produces significant swelling, while at the same time broadening the particle size distribution by shifting the minimum of \( \Omega (\alpha) \) out to a range of \( \alpha \) with weaker curvature. With increasing particle concentration, however, swelling is re-
duced and the size polydispersity narrows. As the dry particle volume fraction increases from 0.01 to 0.04, the swollen particle volume fraction increases as well, despite deswelling, although more gradually, from 0.28 to 0.73. Nevertheless, it is essential to realize that the particle deswelling and narrowing polydispersity predicted here are driven only by a redistribution of counterions, not by correlations between microgels, which are neglected in the cell model. At sufficiently high concentrations of microgels, electrostatic and steric interactions between particles will eventually affect the size distribution.

In Fig. 3(a), we plot the electrostatic contribution to the internal osmotic pressure (relative to the suspension) vs. swelling ratio, as calculated from both theory and sim-

ulation. For comparison, the osmotic pressure in the sus-
pension (relative to the reservoir) is also plotted. These results were computed via Eqs. \[5\] and \[13\], using coun-

Variation of the Flory-Rehner free energy \[ Eq. \[5\] \] with swelling ratio implies thermally excited fluctuations in particle size, i.e., dynamical polydispersity. An isolated nonionic microgel has an equilibrium size that fluctuates according to a probability distribution,

\[
P(\alpha) \propto \exp[-\beta F_g (\alpha)],
\]

(25)
dry particle radius

\[
\pi \equiv \beta \pi_{id} \equiv \beta \left( f_{in} - (1 - f_{in}) \frac{\phi}{1 - \phi} \right),
\]

which is commonly used as an estimate of \( \pi_e \) when interpreting experimental data [2–10]. For these parameters, this approximation is seen to significantly underestimate the magnitude of the electrostatic contribution to the internal osmotic pressure. This disparity is perhaps not surprising, given that such a relatively small microgel is far from electroneutral. In qualitative terms, a physical explanation for the differing predictions of the two approaches is that the uniform ideal-gas approximation neglects, not only the spatial variation of the counterion density profile, as illustrated in Fig. 2(b), but also the outward electrostatic pressure of the incompletely neutralized macroion.

The electrostatic and elastic contributions to the internal osmotic pressure are juxtaposed in Fig. 5(a) over a range of dry volume fractions. We computed the elastic contribution from Eq. (9) and the electrostatic contribution from Eq. (13), using the counterion distributions determined from both PB theory [Eq. (15)] and MD simulation. Close agreement between theory and simulation again provides a consistency check on our calculations. With increasing dry volume fraction, the electrostatic pressure monotonically decreases, consistent with the shift in the semi-grand potential minimum. This decrease in outward pressure, again arising from a redistribution of counterions, drives a corresponding reduction in equilibrium particle size. Figure 5(b) shows the equilibrium swelling ratio \( \alpha \), computed as the root of the equation, \( \pi_e(\alpha) + \pi_g(\alpha) = 0 \), where \( \pi_e(\alpha) \) and \( \pi_g(\alpha) \) are obtained from Eqs. (13)–(17) and Eq. (9). For these parameters, the equilibrium swelling ratio drops by more than 10% from dilute to concentrated suspensions.

As a test, we also applied the linearized approximation, computing \( \pi_e \) from Eq. (24). As seen in Fig. 5(b), this approximation proves remarkably accurate. It is important to note that, despite the excellent agreement between PB theory and simulation in the present case of monovalent counterions, deviations can be expected for more strongly correlated multivalent counterions. In such cases, where PB theory fails, the new internal osmotic pressure theorem may prove especially valuable. Our predictions are consistent with experimental observations of weak concentration dependence of deswelling of relatively rigid particles [3], but a stronger effect for softer particles [10]. Next, we compare more directly with experiments.

### B. Comparisons with Experiments

To illustrate the practical utility of our approach to modeling internal osmotic pressure, we first compare our predictions of deswelling with experimental data of Holmqvist et al. [10], who combined static and dynamic...
light scattering with integral-equation theory and an effective pair potential model to determine the size and effective charge of PNIPAM-co-PAA core-shell particles as a function of concentration in deionized, pH-neutral solutions. We choose system parameters for maximum consistency with experiments and use corrected microgel concentrations [10] (Erratum). Following the prescribed limit on the number of dissociable groups [10, 47], we take $Z = 3.5 \times 10^4$. In a deionized solution, we set the salt concentration to zero ($n_s = 0$). For the collapsed radius, we use the measured value of $a_0 = 50$ nm. Consistent with particles of this size, comprised of close-packed monomers of radius $0.3$ nm, we choose the number of monomers as $N_m = 3 \times 10^6$. Again, $Z/N_m \ll 1$ precludes counterion condensation. To best fit the shape of the distribution, we set the Flory solvency parameter at $\chi = 0.53$, consistent with swollen polymers in water at $T = 20$ °C, and neglect any slight concentration dependence [8]. Lacking direct knowledge of the cross-linker density in the shell region, we treat $N_{ch}$ as a fitting parameter.

For particles of this size and charge, the nonlinear PB equation becomes so numerically stiff that our computational method fails to converge to a solution. More
sophisticated iterative methods are then effective \[27\]. However, in this parameter regime, in which most of the counterions are confined to the nearly electroneutral interior of the macroion, the linear response theory should be reasonably accurate. Thus, we apply the linearized approximation to model the electrostatic contribution to the internal osmotic pressure. As seen in Fig. 6, we obtain a close fit to the experimental data, over a wide range of particle densities, with chain fraction \( x \equiv N_{\text{ch}}/N_m = 0.002 \), which is consistent with the loosely cross-linked microgel particles in the experiments. To illustrate sensitivity to variation of parameters, we also show the prediction for \( x = 0.004 \) and \( \chi = 0.2 \). In general, the equilibrium swelling ratio decreases as \( x \) and \( \chi \) increase, i.e., as the particles become stiffer and the solvent poorer.

For comparison, Fig. 6 also shows the prediction of the uniform ideal-gas approximation, computed as the root of \( \pi_{\text{id}} + \pi_{\text{id}} \) with respect to \( \alpha \), using Eq. (22) for the fraction of interior counterions. Attempts to fit the data with this approximation yielded lower equilibrium radii and qualitatively different density dependence (dotted black curve in Fig. 6), attributable again to neglect of the macroion electrostatic pressure and to the relatively weak variation of \( \pi_{\text{id}} \) with \( \alpha \) and \( \phi \) [see Eq. (26)]. However, we find that the uniform ideal-gas approximation may be substantially improved by simply adding the electrostatic pressure associated with the self-energy of a macroion of uniformly distributed net charge \( Z_{\text{net}} \equiv Z (1 - f_{\text{in}}) \):

\[
\beta \pi_{\text{id}} = Z \left( f_{\text{in}} - (1 - f_{\text{in}}) \frac{\phi}{1 - \phi} \right) + \frac{Z_{\text{net}}^2 \lambda_B}{5a}. \tag{27}
\]

For comparison, predictions of Eq. (27) are also plotted in Fig. 6 (dashed black curve). While this heuristic adjustment may prove practical for some purposes, our theory is more accurate and clearly more physically consistent. Despite some potential mismatch between our model of uniformly charged macroions and the core-shell particles studied in ref. [10], and some uncertainty in the variation of local \( pH \) inside the microgels and solvency parameter with particle size and concentration, the level of agreement between our theory and experiment is encouraging and should motivate future comparisons.

While Holmqvist et al. [10] focused on deionized suspensions by working with microgels that fully ionize at neutral \( pH \) and flame-sealing their samples together with an ion exchange resin, other experiments were performed at higher ionic strengths. For example, Borrega et al. [4] studied suspensions containing substantial concentrations of sodium chloride (0.01-0.1 M), and Fernández-Nieves et al. [6, 7] studied poly-vinylpyridine microgels that fully ionize only at \( pH=3 \) (ionic strength \( \sim 1 \text{ mM} \)), achieved by adding sodium hydroxide. (Note that addition of NaOH to a sample adjusts \( pH \) by promoting acid group ionization, but does not otherwise contribute to the background ion concentration.)

To explore the interrelated effects of varying both particle and salt concentrations, we computed the equilibrium swelling ratio over a range of salt concentrations for parameters roughly consistent with the microgels studied in refs. [6] and [7]. We did so by including salt concentration \( n_s \) in the Debye screening constant \( \kappa \) and thus in the electrostatic contribution to the internal osmotic pressure \( \pi_c \) [Eq. (24)]. At ionic strengths sufficiently high that background salt ions outnumber counterions dissociated from the particles \((2n_s > Zn_m)\), \( \kappa \) and \( \pi_c \) become relatively insensitive to changes in particle concentration. As a consequence, with increasing salt concentration, not only is the degree of swelling reduced, but also the variation of swelling with particle density is weakened, as Fig. 7 illustrates. For reference, the salt-dominated regimes \((2n_s > Zn_m)\) are to the left of the dotted curves for respective salt concentrations. By comparison, the uniform ideal-gas approximation [Eq. (26)] predicts \( \alpha \approx 3.6 \), independent of \( \phi \) and \( c_s \) over these parameter ranges. Our calculations indicate that high background ion concentrations may suppress counterion-induced effects and forestall deswelling until near close packing, where steric interactions between particles become significant. Drawing conclusions about the swelling behavior observed in refs. [4, 5] is complicated, however, by the pronounced core-shell structure of the relatively large microgels studied in these experiments – 2-3 times larger than in refs. [4, 5, 9, 10]. Implementing our theory for a core-shell model of microgels may help to clarify the origins of microgel swelling and deswelling for inhomogeneously structured microgels.

VI. CONCLUSIONS

Based on an exact theorem for the electrostatic contribution to the osmotic pressure inside a permeable macroion, we presented the first rigorous analysis of connections between counterion distribution, osmotic pressure, and particle swelling. As an illustrative example, we applied the new theorem to ionic microgels, explaining observed deswelling of particles with increasing concentration and identifying conditions under which deswelling and narrowing of size polydispersity can be enhanced via redistribution of counterions. This electrostatically-driven phenomenon may be important for tuning rheological properties and facilitating microgel transport through narrow pores in applications ranging from drug delivery to microfluidics to filtration. We validated our results by comparing calculations from non-linear Poisson-Boltzmann theory with data from molecular dynamics simulations in the spherical cell model. In comparison, theories of macroscopic polyelectrolyte gels, which neglect both spatial variation of the counterion density and the electrostatic pressure of the incompletely neutralized macroion, fail to accurately predict swelling of ionic microgels.

For practical purposes, we also derived a linearized approximation, which provides a convenient analytical expression for the internal electrostatic pressure. By com-
paring predictions with experimental measurements of loosely cross-linked particles in deionized solutions, we demonstrated the ability of our theory to explain and interpret observations of particle swelling in real microgel systems. Our analysis demonstrates, in particular, that soft ionic microgels, when increasingly concentrated, can deswell due to a redistribution of counterions, and confirms that this unusual response can be amplified by increasing particle charge and softness and by minimizing ionic strength. Moreover, we demonstrated that sensitivity of swelling to variations in particle density diminishes with increasing concentration of background ions.

Further comparisons with experiments are possible for well-characterized suspensions of soft, ionic particles. For consistency, however, implementation of our theory should be augmented to incorporate the influence of interparticle interactions between macroions [60], which can be important at concentrations approaching close-packing. Work along these lines is in progress.

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[1] D. Vlassopoulos and M. Cloitre, Curr. Opin. Colloid Interface Sci. 19, 561 (2014).
[2] A. Fernández-Nieves, A. Fernández-Barbero, B. Vincent, and F. J. de las Nieves, J. Chem. Phys. 119, 10383 (2003).
[3] J. J. Liétor-Santos, B. Sierra-Martín, U. Gasser, and A. Fernández-Nieves, Soft Matter 7, 6370 (2011).
[4] R. Borrega, M. Cloitre, I. Bietremieux, B. Ernst, and L. Leibler, Euro. Phys. Lett. 47, 729 (1999).
[5] M. Cloitre, R. Borrega, F. Monti, and L. Leibler, C. R. Physique 4, 221 (2003).
[6] A. Fernández-Nieves, A. Fernández-Barbero, B. Vincent, and F. J. de las Nieves, Macromol. 33, 2114 (2000).
[7] M. Pelaez-Fernandez, A. Souslov, L. A. Lyon, P. M. Goldbart, and A. Fernández-Nieves, Phys. Rev. Lett. 114, 098303 (2015).
[8] G. Romeo, L. Imperialis, J.-W. Kim, A. Fernández-Nieves, and D. A. Weitz, J. Chem. Phys. 136, 124905 (2012).
[9] B. H. Tan, K. C. Tum, Y. C. Lam, and C. B. Tan, J. Rheol. 48, 915 (2004).
[10] P. Holmqvist, P. S. Mohanty, G. Nägele, P. Schurtenberger, and M. Heinen, Phys. Rev. Lett. 109, 048302 (2012), Erratum, in press (2016).
[11] J. J. Liétor-Santos, B. Sierra-Martín, R. Vavrin, Z. Hu, U. Gasser, and A. Fernández-Nieves, Macromol. 42, 6225 (2009).
[12] S. M. Hashmi and E. R. Dufresne, Soft Matter 5, 3682 (2009).
[13] Y. Hertle, M. Zeiser, C. Hasenöhrl, P. Busch, and T. Hellweg, Colloid Polym. Sci. 288, 1047 (2010).
[14] J. J. Liétor-Santos, B. Sierra-Martín, and A. Fernández-Nieves, Phys. Rev. E 84, 060402(R) (2011).
[15] B. Sierra-Martín, Y. Laporte, A. B. South, L. A. Lyon, and A. Fernández-Nieves, Phys. Rev. E 84, 011406 (2011).
[16] B. Sierra-Martín and A. Fernández-Nieves, Soft Matter 8, 4141 (2012).
[17] P. Menut, S. Seiffert, J. Sprakel, and D. A. Weitz, Soft Matter 8, 156 (2012).
[18] G. Romeo and M. P. Ciamarra, Soft Matter 9, 5401 (2013).
[19] T. G. Mason, J. Bibette, and D. A. Weitz, Phys. Rev. Lett. 75, 2051 (1995).
[20] F. Gröhn and M. Antonietti, Macromol. 33, 5938 (2000).
[21] Y. Levin, Phys. Rev. E 65, 036143 (2002).
[22] A. Fernández-Nieves and M. Márquez, J. Chem. Phys. 122, 084702 (2005).
[23] S. P. Singh, D. A. Fedosov, A. Chatterji, R. G. Winkler, and G. Gompper, J. Phys.: Condens. Matter 24, 464103 (2012).
[24] R. G. Winkler, D. A. Fedosov, and G. Gompper, Curr. Opin. Colloid Interface Sci. 19, 594 (2014).
[25] X. Li, L. E. Sánchez-Díaz, B. Wu, W. A. Hamilton, P. Falus, L. Porcar, Y. Liu, C. Do, A. Faraone, G. S. Smith, T. Egami, and W.-R. Chen, ACS Macro Lett. 3, 1271 (2014).
[26] S. A. Egorov, J. Paturej, C. N. Likos, and A. Milchev, Macromol. 46, 3648 (2013).
[27] T. Colla, C. N. Likos, and Y. Levin, J. Chem. Phys. 141, 234902 (2014).
[28] T. Colla and C. N. Likos, Mol. Phys. 113, 2496 (2015).
[29] S. Gupta, M. Camargo, J. Stellbrink, J. Allgaier, A. Radulescu, P. Lindner, E. Zaccarelli, C. N. Likos, and Richter, Nanoscale 7, 13924 (2015).
[30] S. Gupta, J. Stellbrink, E. Zaccarelli, C. N. Likos, M. Camargo, P. Holmqvist, J. Allgaier, L. Willner, and D. Richter, Phys. Rev. Lett. 115, 128302 (2015).
[31] L. A. Lyon and M. J. Serpe, eds., Hydrogel Micro and Nanoparticles (Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2012).
[32] A. Fernández-Nieves, H. Wyss, J. Mattsson, and D. A. Weitz, eds., Microgel Suspensions: Fundamentals and Applications (Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2011).
[33] L. A. Lyon and A. Fernández-Nieves, Annu. Rev. Phys. Chem. 63, 25 (2012).
[34] P. J. Yunker, K. Chen, E. Zaccarelli, G. S. Smith, T. Egami, and D. Richter, Phys. Rev. Lett. 115, 128302 (2015).
[35] L. A. Lyon and M. J. Serpe, eds., Hydrogel Micro and Nanoparticles (Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2012).
[36] R. Stepto, Adv. Colloid Interface Sci. 77, 247 (1998).
