Does Size Matter? Elasticity of Compressed Suspensions of Colloidal- and Granular-Scale Microgels

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Supplemental Information

Modeling the Osmotic Pressure of Microgel Suspensions

In a good solvent, interactions between solvent molecules and the monomeric units of a polymer are energetically favored against interactions between monomers or between solvent molecules alone. In addition with the entropic gain resulting from the mixing of the components, this drives the expansion of a polymer chain in solution. In the Flory–Rehner framework, this principle is expressed as:

$$\Pi_m = -\frac{N_a k_b T}{\upsilon_s}(\phi_p + \ln(1-\phi_p) + \chi\phi_p^2)$$

in which N_A is Avogadro's number, υ_s is the molar volume of the solvent, χ is the polymer–solvent interaction parameter, and ϕ_p is the volume fraction of polymer in the sample. The first two terms express the entropic gain associated with mixing, while the last one is an enthalpic term. In a good solvent, Π_m is positive, and polymers tend to maximize their interactions with the solvent. In a gel, however, cross-links between the polymer chains preclude their separation and complete dissolution. Upon swelling, polymer chains are stretched, which reduces their conformational degree of freedom and therefore generates a restoring, entropic force acting against swelling. This contribution is expressed in the same pressure units as the mixing term through the following equation

$$\Pi_e = \frac{\phi_{p,0}\rho_p N_A k_B T}{NM_n}\left[\frac{\phi_p}{2\phi_{p,0}} - \left(\frac{\phi_p}{\phi_{p,0}}\right)^{1/3}\right]$$

where V_0 and $\phi_{p,0}$ are the volume and the volume fraction of polymer in the reference state, ρ_p the polymer density, N the number of monomers between cross-links and M_n the molecular weight of the polymer.

This theory was developed to describe the behavior of a macroscopic gel; however, it has also been applied to individual microgel particles.[s1] At equilibrium, the osmotic pressure inside each particle, $\Pi = \Pi_m + \Pi_e$, equals that of the surrounding medium. At dilute conditions, where $\Pi \approx 0$, the Flory–Rehner equation gives the volume fraction of polymer in each particle. When the particle concentration increases, the external pressure arising from the particle's immediate neighbors increases, generating local rearrangements and/or compressing the particles; in both cases, the osmotic pressure inside the particles eventually equals that of their environment.

We use this approach to model the osmotic pressure of the compressed colloidal-scale microgel suspensions shown in Fig. 4. Since water is a good solvent for poly(NIPAAm-co-AAc) at low temperature, we use $\chi = 0$. To calculate the elastic term, we take an average monomer molecular weight of 111 g·mol^{-1}. The values of N can be estimated from the cross-linker/monomer stoichiometry used for the particle syntheses, however, due to both cross-linking heterogeneity[s2] and imperfect cross-linker efficiency, the real value might be significantly different. Thus, the values of N are determined experimentally from a linear fit of the elastic modulus scaling with polymer concentration at high packing fraction (see Fig. 6) we find $N = 11000$, 2200, and 250 for our soft, intermediate, and stiff particles, respectively.

The reference state is that in which the particles are synthesized: the volume fraction of the polymer, $\phi_{p,0}$, is estimated from the known voluminosity of the particles at 4 °C, and the ratio of its volume at 4 °C and 70 °C. We use 0.24, 0.86, and 0.97 for our soft, intermediate, and stiff particles, respectively.

This approach captures the fundamental physics that govern the swelling of a microgel suspension. However, previous studies have shown that the absolute values predicted by these expressions are about one order of magnitude higher than the experimental ones;[s3,s4] we find the same discrepancy here. Thus, we rescale the theoretical values to fit the experimental data.

A close look at the values of both components of the osmotic pressure, Π_m and Π_e, reveals that the elastic term, which is related to the polymer chain stretching inside the microgel particles, only plays a role at the lowest packing fractions, when particles are highly swollen, but becomes negligible at higher concentration, as shown in Fig. S1.

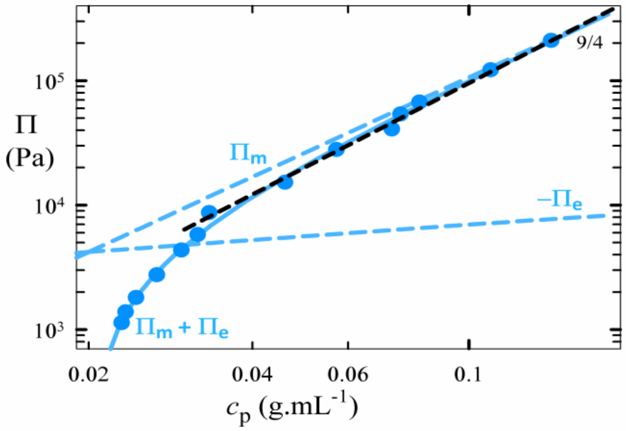

Figure S1 Osmotic pressure, Π, as a function of the polymer concentration, c_P, in a microgel suspension of densely packed colloidal-scale p(NIPAAm-*co*-AAc) microgel particles cross-linked with 1 wt.% BIS. The black dashed line represents a power law for $\Pi \sim c_p^{9/4}$. Dashed and continuous blue lines represent predictions from the Flory–Rehner theory for a macroscopic hydrogel, calculated as described above, while circles represent experimental data.

Supplemental References

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s3. A. Fernandez-Nieves, A. Fernandez-Barbero, B. Vincent and F. J. de las Nieves, *J. Chem. Phys.*, 2003, **119**, 10383-10388.

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