# Bulk modulus of poly(N-isopropylacrylamide) microgels through the swelling transition

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# Bulk modulus of pNIPAM microgels through the swelling transition

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We report measurements of the bulk modulus of individual poly($N$-isopropylacrylamide) microgels along their swelling transition. The modulus is determined by measuring the volume-deformation of the microgel as a function of osmotic pressure using dextran solutions. We find that the modulus softens through the transition, displaying a non-monotonous behavior with temperature. This feature is correctly reproduced by the theory of Flory for polymer gels, once the concentration dependence of the solvency parameter is properly incorporated.

## I. INTRODUCTION

Microgels are cross-linked polymer networks in the colloidal-size domain that are able to swell and de-swell in response to changes in external stimuli [1, 2]. They are isotropic elastic materials. As a result, they can be characterized with two elastic moduli. Of particular relevance are the bulk and shear moduli, as they both play an important role in microgel applications [3] and affect the particle swelling kinetics [4] and determine its response to external osmotic and shear stresses [5–8]. In addition, single-particle elasticity affects the suspension non-equilibrium [9] and mechanical behavior [10, 11]. Among most microgels, those based on the thermosensitive polymer poly($N$-isopropylacrylamide) (pNIPAM) have received most attention [12, 13]. Particles based on pNIPAM appreciably deswell at a lower critical solution temperature (LCST) of $\sim$ 305K; it is the change in solubility around this temperature which is responsible for this behavior.

Interestingly, recent measurements of the Young's modulus of individual microgel particles reveal a significant softening around the LCST [14]. While the shear modulus, $G$, of the particles can only undergo a continuous increase with temperature, since $G$ is mainly determined by the cross-link density, which progressively increases as the particle size decreases, the bulk modulus, $K$, of the particles can exhibit a non-monotonous behavior, as has been observed for macroscopic hydrogels [15]. However, direct measurements of $K$ for pNIPAM microgels through the deswelling transition are non-existent, reflecting the difficulties in performing these experiments. A major problem is that pNIPAM microgels aggregate and eventually gel [16] at temperatures above the LCST; the change in solubility responsible for particle deswelling also induces the required interparticle attraction for the suspension to become colloidally unstable. As a result, methods relying on measuring the size change of microgel particles in suspension are inapplicable. A solution to this problem relies in directly probing an individual isolated particle. This has been very beautifully achieved recently using a microfluidics-based method consisting of pushing a microgel particle through a tapered capillary and quantifying its deformation as a function of applied pressure [7]. However, the method uses optical imaging and is limited to microgels with diameter $\gtrsim 2\mu$m; this excludes the important size range below the micron. Atomic force microscopy is an alternative, but up to date, only measurements of the microgel Young's modulus have been reported [14].

In this paper, we report measurements of the bulk modulus of pNIPAM microgels co-polymerized with poly(ethylene glycol) diacrylate (PEG), which acts as cross-linker, through the thermal swelling transition. By incorporating PEG units into the microgels, we maintain a repulsive interaction between particles at all temperatures [17], avoiding aggregation and gelation around and above the LCST. We find that along the temperature-induced, monotonic deswelling transition, the bulk modulus exhibits a softening behavior around the LCST. As a result, $K$ displays a non-monotonic behavior with temperature. We further use the theory of Flory for polymer gels [18] to describe our observations. Remarkably, the values of the parameters needed to describe this particular behavior agree with those obtained from a description of the swelling transition. Our results are the first experimental evidence that $K$ softens around the LCST for pNIPAM-based microgels supporting the interpretation that the softening of the particle Young's modulus resulted from the behavior of the bulk modulus. This clearly suggests that rich and unexpected suspension behavior could happen in the vicinity of the LCST.

## II. EXPERIMENTAL METHODS

Microgels are synthesized using aqueous free radical precipitation polymerization using a total monomer concentration of 70 mM with a molar composition of 98% NIPAM and 2% PEG with molecular weight 700 g/mol. Surfactant SDS is used at a concentration of 1 mM. The aqueous monomer+surfactant solution is magnetically stirred in a three-neck round bottom flask and purged with $N_2$ for approximately 1 hour while the solution was heated to 70 $^o$C. The initiator APS (1 mM final concentration) was dissolved in 1 mL of deionized water and added to initiate the polymerization. The reaction was allowed to proceed for 4 hours at 70 $^o$C under a blanket of $N_2$. Microgels of this composition have been shown previously to resist aggregation and non-specific protein adsorption at temperatures above the pNIPAM LCST [17]. The inferred hydrophilicity of the particles at elevated temperatures has been ascribed to surface-segregation of PEG segments; this has been confirmed by variable tem-

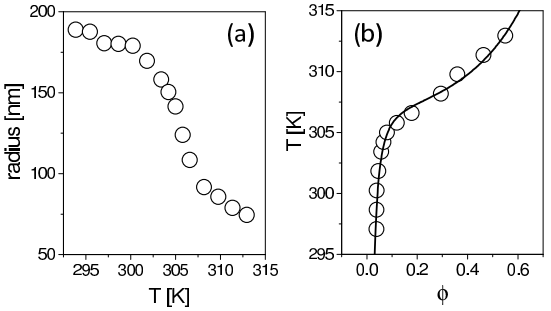


FIG. 1: (a) Swelling transition of pNIPAM-PEG microgels as a function of temperature. (b) Fit to the theory of Flory for polymer gels, considering a first-order concentration dependence for $\chi$. The deswollen size is taken as the high temperature size, $a_0$=74.5 nm.

perature $^1H$ NMR measurements [17].

We determine the particle size using dynamic light scattering. We use a 3D-DLS set-up from LS Instruments equipped with a He-Ne laser ($\lambda$=632.8nm, 25mW) that is split into two parallel beams, which are forced to cross inside the sample. The scattered light from these two beams is collected in two avalanche photodiodes looking at the same scattering volume and their signals are cross-correlated to obtain the intensity correlation function, $g_2(\tau)$, with $\tau$ being the correlation time. Operated in this way, this function is only sensitive to single scattering events [19]. The electric field correlation function, $g_1(\tau)$, is obtained using the Siegert relation, $g_2(\tau) = g_1(\tau) + \Omega g_1^2(\tau)$, with $\Omega$ being the coherence factor. For dilute microgel suspensions, $g_1(\tau)$ is well described by a single exponential function, as expected for diffusion processes. As a result, $g_1(\tau) = e^{-Dq^2\tau}$, where $D$ is the diffusion coefficient of the microgel particle and $q = (\frac{4\pi n}{\lambda})\sin(\frac{\theta}{2})$ is the modulus of the scattering wave vector, with $n$ the refractive index of the sample and $\theta$ the scattering angle. From $D$, we obtain the microgel radius, $a$, using the Stokes-Einstein relation, $D = (\frac{k_B T}{6\pi\eta a})$, with $k_B$ the Boltzmann constant and $\eta$ the solvent viscosity. The temperature dependence of the microgel size is reminiscent of that of the more typical pNIPAM microgels cross-linked with N,N'-methylene(bisacrylamide) (BIS) [12, 13], as shown in Fig. 1(a). At room temperature the microgel particle is highly swollen with a radius $a$=188 nm and gradually deswells as temperature rises. We note the transition temperature, defined as the temperature corresponding to the largest size-T slope, is slightly shifted by $\sim$ 2K with respect to the usual 305K of pNIPAM-BIS microgels; this probably results from the increased hydrophilicity of the particles due to the presence of PEG, which slightly shifts the hydrophobic collapse of the polymer network [20].

## III. TEMPERATURE-INDUCED DESWELLING

To account for these results, we consider that at equilibrium, the total osmotic pressure is equal to zero: $\Pi_{total}$=0. For non-ionic microgels, this condition implies a balance between the osmotic pressure resulting from the polymer-solvent mixing, $\Pi_{mix}$, and an elastic osmotic pressure, $\Pi_e$. Both contributions are described in the theory of Flory for polymer gels [21]:

$$\Pi_{mix} = \frac{N_A k_B T}{\nu_s}[\phi + ln(1-\phi) + \chi\phi^2] \qquad (1)$$

$$\Pi_e = \frac{N_c k_B T}{V_0}[(\frac{\phi}{2\phi_0}) - (\frac{\phi}{\phi_0})^{1/3}] \qquad (2)$$

where $N_A$ is Avogadro's number, $\nu_s$ is the molar volume of the solvent, $\chi$ is the solvency parameter, $N_c/V_0$ is the number of chains per unit volume in the deswollen state, and $\phi$ is the polymer volume fraction within the microgel. The key parameter in this balance is $\chi$; it reflects the free energy change when a solvent-polymer contact is replaced by a solvent-solvent contact [18]: $\chi = \frac{\Delta H - T\Delta S}{k_B T} = \frac{1}{2} - A(1 - \frac{\Theta}{T})$ where $\Theta = \frac{2\Delta H}{2\Delta S + k_B}$ is the $\Theta$-temperature of the polymer in the solvent and $A = \frac{2\Delta S + k_B}{2k_B}$, with $\Delta H$ and $\Delta S$ being the enthalpy and entropy changes in the process, respectively. Despite the inherent temperature-dependence of the solvency parameter, the theory does not succesfully account for the swelling behavior unless a concentration-dependence is introduced [22, 23]. This is done by expanding $\chi$ as a power series of $\phi$: $\chi = \chi_0 + \chi_1\phi + \chi_2\phi^2 + ..$ [24], where $\chi_0$ is the solvency parameter defined above, and $\chi_i$ are empirical coefficients. By considering that at equilibrium $\Pi_{mix} + \Pi_e = 0$ and using eqs. (1) and (2), together with the concentration dependence of $\chi$, we obtain the equation of state of the system:

$$T_{\Pi=0} = \frac{A\phi^2\Theta}{\frac{\nu_s N_c}{N_A V_0}[(\frac{\phi}{2\phi_0}) - (\frac{\phi}{\phi_0})^{1/3}] - \phi - ln(1-\phi)} + \frac{A\phi^2\Theta}{(A-\frac{1}{2})\phi^2 - (\chi_1\phi + \chi_2\phi^2 + ..)\phi^2} \qquad (3)$$

This equation relates the microgel size to the temperature after considering that for isotropic swelling, $\frac{\phi}{\phi_0} = (\frac{a_0}{a})^3$, where the zero subscript refers to the deswollen state of the system [18]. As the parameter $\phi_0$ is unknown, we perform different fits of the T-$\phi$ curve for different values of $\phi_0$, leaving $N_c$, $A$, $\Theta$, $\chi_0$, $\chi_1$ and $\chi_2$ as free parameters. For a given value of $\phi_0$, the best fits are always obtained for $\chi_2$=0 [25]. We pick $\phi_0$ by comparing the values of the parameters that result from the fit with the expected values from the microgel synthesis and observed microgel swelling, provided the quality of the fit, which we quantify using the statistical measure $\chi^2$, remains the same. From the synthesis, we know that $N_c/V_0 = 7 \cdot 10^{25} m^{-3}$. From Fig. 1(a), we know that the transition temperature, and thus the $\Theta$ temperature, is 307K. In addition, the values of $A$ and $\Theta$ should lead to

TABLE I: Fitting parameters describing the swelling behavior

| $\phi_0$ | A | $\Theta$(K) | $N_c/V_0(m^{-3})$ | $\chi_1$ | $\Delta S(J/K)$ | $\Delta H(J)$ |
|---|---|---|---|---|---|---|
| 0.55 | -8.15 | 307.1 | $3.05{\cdot}10^{25}$ | 0.30 | $-11.9{\cdot}10^{-23}$ | $-3.67{\cdot}10^{-20}$ |

a range of values for $\chi_0$(T) between 0 and 1 [24, 25]. The result from all these consideration is $\phi_0$=0.55 and the set of parameters is given in Table 1, where we also quote the resulting values for $\Delta H$ and $\Delta S$; they are both negative and consistent with what has been reported for pNIPAM microgels [25, 26], and macrogels [23]. The corresponding fit is shown in Fig. 1(b). We note that $\phi_0$=0.55 is below the more usual value of 0.8 reported for pNIPAM-BIS microgels [25–27]; the presence of hydrophilic PEG inside the particles leads to a more hydrated de-swollen state.

## IV. SOFTENING OF THE BULK MODULUS

The microgel compressibility studies are performed using dextrans as the stressing polymer; these have a molecular weight of 150000 g/mol and exert a known osmotic pressure at a given concentration [28, 29]. The experiments consist in measuring $g_2(\tau)$ for microgel-dextran suspensions in the range of dextran concentration $c$=[0, 10] %, where depletion-induced flocculation is absent [6]. At low $c$, $g_2(\tau)$ is characterized by a single decay due to the microgel diffusion, whilst at larger $c$ there are two decays in $g_2(\tau)$; a short time decay reflecting the fast dynamics of the dextran solution and a longer time decay related to diffusion of the microgel particles. By carefully considering all contributions to $g_2(\tau)$, we can extract the microgel size [28]. We do this for different dextran concentrations and different temperatures, as shown in Fig. 2(a), where we have already converted the dextran concentration into the corresponding osmotic pressure, $\Pi_{ext}$. We observe that for low $\Pi_{ext}$, the microgel size remains essentially constant indicating that in this region the external osmotic pressure is smaller than the particle bulk modulus and deswelling does not occur. For larger $\Pi_{ext}$, the particles begin to de-swell; this occurs when $\Pi_{ext}$ is comparable to $K$ [30]. To determine $K$, we first plot the data in terms of the microgel volume, as shown in Fig. 2(b) for the case of T=298 K. From the $\Pi_{ext}$-V slope, we obtain the bulk modulus, $K = -V(\frac{d\Pi_{ext}}{dV})$. We do so for two different swelling states, $V$=0.85$V_s$ and $V$=0.7$V_s$, corresponding to particle compressions of 15 % and 30 %, respectively, with $V_s$ the volume of the swollen particle.

Remarkably, we obtain an appreciable softening of the bulk modulus through the swelling transition; as the microgel monotonically deswells with temperature, the modulus decreases, reaches a marked minimum around the LCST, and recovers again, as shown in Fig. 3(a). This behavior is seen irrespective of where we evaluate $K$ in the swelling curve. The presence of the minimum in $K$ reflects the larger compressibility of the microgels around the transition temperature, where a small change

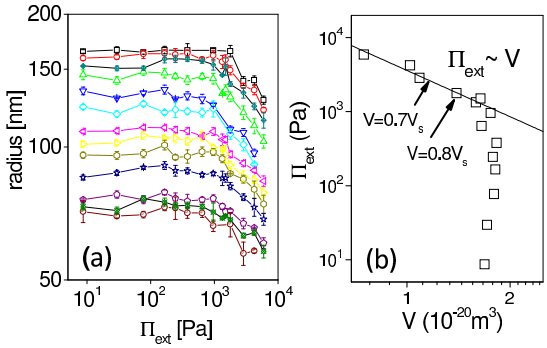


FIG. 2: (Color online). (a) Radius of the pNIPAM-PEG microgels versus osmotic pressure. The temperature increases from top to bottom in the range [298-311] K. (b) Log-log plot of the osmotic pressure versus the particle volume. From the slope in the region where the microgel is deswelling, we determine de bulk modulus. We pick to states in this region to illustrate that our results do not strongly depend on where you estimate $K$.

in temperature induces large changes in size. As a result, the equilibrium state of the microgel can be unbalanced at smaller external osmotic pressures around this point. We emphasize here that the bulk modulus of water is $\sim 10^4$ times higher than that of the microgel. As a result, the rigidity of the water does not contribute to the bulk modulus of the microgel. To describe the behavior of $K$ around the transition temperature, we consider Flory's theory again. Within this theory, using $\Pi_{total}$ and the definition of the bulk modulus, we obtain [18]:

$$K = \frac{k_B T}{\nu_s}\{\frac{N_c}{V_0}\nu_s[\frac{\phi}{2\phi_0} - (\frac{\phi}{2\phi_0})^{1/3}] + \frac{\phi^2}{1-\phi} - 2\chi\phi^2\} \quad (4)$$

We see that $K$ depends on the density of chains and on $\chi$, which in turn depends on temperature and polymer volume fraction. We use this equation and perform a fit of $K/T$ versus temperature, using the size-temperature relation of Fig.1(a) and considering the swelling is isotropic. We further fix the value of $\chi_0$ to the value at the transition temperature obtained from the theoretical description of the swelling curve and perform fits at different $\phi_0$, leaving $N_c/V_0$, $\chi_1$ and $\chi_2$ as free parameters. Interestingly, we are unable to describe the experimental results if the concentration dependence of $\chi$ is truncated in the first order approximation. Only after considering the power expansion in $\phi$ up to $\phi^2$ we are able to capture the experimental behavior. This suggests that around the transition temperature, where concentration fluctuations are expected to be the largest [31, 32], many body interactions are most important. In this situation, the best fits are obtained for $\phi_0$=0.55, consistent with what we found before. In addition, the value of $N_c/V_0$ agrees reasonably well with what we obtained from the swelling behavior, as shown in Table 2. The theory thus correctly captures quantitatively the softening behavior of $K$ near the transition temperature; the best fits to the

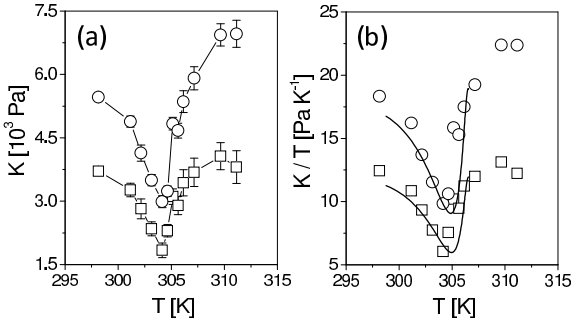


FIG. 3: (a) Bulk modulus of pNIPAM-PEG microgels as a function of temperature. We show the results obtained for $V$=0.85$V_s$ (□) and $V$=0.7$V_s$ (○), which correspond to particle compressions of 15 % and 30 %, respectively. The solid lines are guides to the eye. (b) $K/T$ versus $T$ and fits of the data around the LCST using Flory's theory.

TABLE II: Parameters used to model the softening of the bulk modulus around the LCST

| | $\phi_0$ | $N_c/V_0(m^{-3})$ | $\chi_0$ | $\chi_1$ | $\chi_2$ |
|---|---|---|---|---|---|
| V=0.85$V_s$ | 0.55 | $12 \cdot 10^{25}$ | 0.55 | 0.03 | 1.00 |
| V=0.70$V_s$ | 0.55 | $8 \cdot 10^{25}$ | 0.53 | 0.13 | 0.78 |

data are shown in Fig. 3(b). However, we note that the difference in $K$ for high and low temperature is small compared to the theoretical expectation. Furthermore, for pNIPAM microgels [14] and macrogels [15], a difference of about an order of magnitude is observed. We think this discrepancy results from the presence of PEG, which maintains a flexible, hydrated state well above the transition temperature [20], thus reducing the expected particle stiffness. In addition, PEG is expected to be more inhomogeneously distributed inside the particles, particularly at high temperature where it is the main responsible for providing the required repulsion between the particles to guarantee the colloidal stability of the suspension [17].

## V. CONCLUSIONS

We have measured the bulk modulus of pNIPAM-PEG microgels as a function of temperature by monitoring the particle size as a function of external osmotic pressure. We find that whereas the microgel monotonically deswells with temperature, the corresponding bulk modulus shows a significant softening through the swelling transition. This feature is well reproduced on the basis of Flory's theory for polymer gels, after considering a strong concentration dependence of the solvency parameter. Our findings directly support the interpretation that the softening of the Young's modulus of other pNIPAM microgels [14] results from the behavior of $K$. In addition, the observed softening can have important implications over the mechanical behavior of packed suspensions of pNIPAM microgels, as recently suggested [16]. We also emphasize that the observed softening, if sufficiently large, can result in a negative Poisson ratio. In this case, a microgel will expand in all directions after being stretched. The implications of this peculiar behavior over the suspension mechanical behavior have never been explored and can result in novel material behaviors.

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