

# Theoretical Modulus of Gels

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## 1 Comments on Menut's paper: Does Size Matter?

In the second paragraph of section 3.2 of thier paper, Menut's et al. reported:

“For a macroscopic, continuous gel, the theory of rubber elasticity predicts  $G = \nu k_b T = C[N_a/M_m N]k_b T$ ,<sup>20</sup> with  $\nu$  the number density of elastically active chains,  $C$  the polymer concentration (in  $g\ m^{-3}$ ),  $N_a$  the Avogadro number,  $M_m$  the monomer molecular weight ( $g\ mol^{-1}$ ), and  $N$  the number of monomer units in each polymer chain between cross-links”

Here are my remarks on this:

- The wording “For a macroscopic, continuous gel, the theory of rubber elasticity predicts” is not accurate, for the cited equation is for an ideal rubber or a gel in the **unsowllen state**.
- In Flory's Principles of Polymer Chemistry (the reference they cited above) the shearing stress is given by equation 48 in chapter XI, page 470, as:

$$\tau_s = (RT\nu_e/V)\gamma \quad (1)$$

Where  $\tau_s$  is the shearing stress,  $\nu_e$  is the total number of effective chains (we call them segments, and for an ideal rubber  $\nu_e = \nu$ ),  $V$  is the total reference (or current) volume (constant volume is assumed), and  $\gamma$  is the shearing strain (defined as  $\alpha - 1/\alpha$  for an axial shearing where  $\alpha_x = \alpha$ ,  $\alpha_y = 1/\alpha$ ,  $\alpha_z = 1$ ). This equation, as clearly stated by Flory in the same section, applies only for ideal rubberlike materials (swelling is not allowed) as we will see in the following points.

- In Appendix B, chapter XI, page 492, Flory derived the equation of state of a swollen gel, but only for elongation. Here, I will present his derivation for the elongation case and, in a similar manner, derive the equation of shearing stress (to compare with equation 1 above): let  $v_2 = V_o/V$  where  $V_o$  is the reference unswollen, undeformed volume of the gel,  $V$  is the current volume. The volume is assumed to be fixed for the subsequent analysis. Let  $\alpha_x, \alpha_y, \alpha_z$  represent the change in dimensions between the reference state and the swollen, deformed state such that  $\alpha_x \alpha_y \alpha_z = 1/v_2$  is constant

during the deformation. Assume an elongation along the x-axis while keeping the volume fixed at  $V = V_{iso}$ , then we have

$$\alpha_x = \lambda L_{x,iso}/L_{x,o} = \lambda(V_{iso}/V_o)^{1/3} = \lambda/v_2^{1/3} \quad (2)$$

where  $L_{x,o}$  and  $L_{x,iso}$  are the length in x direction for the dry (unswollen, undeformed) state and the swollen, undeformed state, respectively. And since  $\alpha_x \alpha_y \alpha_z = 1/v_2^{-1}$  then

$$\alpha_y = \alpha_z = 1/(v_2 \alpha_x)^{1/2} = 1/(\lambda^{1/2} v_2^{1/3}) \quad (3)$$

The total change in entropy between the dry state and any arbitrarily deformed state is given by equation 41, chapter XI, page 468 as:

$$\Delta S = -(k\nu_e/2)[\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3 + \ln(\alpha_x \alpha_y \alpha_z)] \quad (4)$$

Now, substituting for the values of  $\alpha_x, \alpha_y, \alpha_z$  for the elongation case we obtain:

$$\Delta S = -k\nu_e/(2v_2^{2/3})[\lambda^2 + 2/\lambda - 3v_2^{2/3} + v_2^{2/3} \ln v_2] \quad (5)$$

Note that the  $v_2^{2/3}$  factor in the third and last terms in the square brackets is not in the original equation in Flory's (eq. B-3, page 492) but I think it should be there. However, it will not affect the final result as both terms vanish when we take the derivative of  $\Delta S$  with respect to  $\lambda$  in which  $v_2$  is constant.

The elastic retractive force for an ideal rubber is given in page 469 by equation 43 as:

$$f = -(T/L_o)(\partial S/\partial \lambda)_{T,V} \quad (6)$$

Application of eq. (5) in (6) with  $L_o$  replaced by  $L_{x,iso}$  and deviding by the transverse area of the swollen, unstretched state:

$$\tau = kT\nu_e/(v_2^{2/3}V)[\lambda - 1/\lambda^2] = (kT\nu_e/V_o)v_2^{1/3}[\lambda - 1/\lambda^2] \quad (7)$$

- Now we derive similar equations for axial shearing deformation. In this case we have:

$$\alpha_x = \lambda L_{x,iso}/L_{x,o} = \lambda(V_{iso}/V_o)^{1/3} = \lambda/v_2^{1/3} \quad (8)$$

$$\alpha_y = (1/\lambda)/v_2^{1/3} \quad (9)$$

$$\alpha_z = 1/v_2^{1/3} \quad (10)$$

And the change in entropy becomes:

$$\Delta S = -k\nu_e/(2v_2^{2/3})[\lambda^2 + 1/\lambda^2 - 3v_2^{2/3} + v_2^{2/3} \ln v_2] \quad (11)$$

Defining shearing strain  $\gamma = \lambda - 1/\lambda$  we obtain:

$$\Delta S = -k\nu_e/(2v_2^{2/3})[\gamma^2 + 2 - 3v_2^{2/3} + v_2^{2/3} \ln v_2] \quad (12)$$

The shear stress (treated as simple shear), in page 470, is given by:

$$\tau_s = -T[\partial(\Delta S/V)/\partial\gamma] \quad (13)$$

Application of equation 12 in 13 we obtain:

$$\tau_s = (kT\nu_e/V_o)v_2^{1/3}\gamma \quad (14)$$

- **The relation between our  $\phi$ , and  $v_2$ :**

As mentioned above, let  $V_o$  be the unswollen, undeformed volume of the gel network, and  $V$  is any arbitrarily deformed volume (generally is swollen and deformed). Equilibrium volume under **zero external forces** is of special interest in microgel suspensions, so let  $V_{eq}$  be the free swelling volume (swelling under zero surface tractions, or in the dilute state in suspensions). Let  $\lambda_x, \lambda_y, \lambda_z$  be the stretch ratios between x,y, and z dimensions, respectively, in any arbitrarily swollen and deformed state and the swollen, undeformed state. Then we have:

$$V_{eq} = (\lambda_x \lambda_y \lambda_z)_{eq} V_o = \lambda_{eq}^3 V_o = J_{eq} V_o \quad (15)$$

Since the swelling is isotropic. Where  $J = \det(\mathbf{F})$  is the volumetric ratio where  $\mathbf{F}$  is the deformation gradient tensor that maps vectors from the dry state to the current state. As defined above:

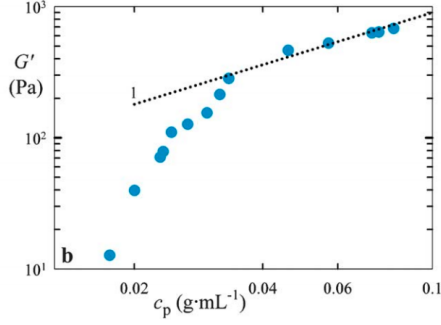
$$v_2 = \frac{V_o}{V} \quad (16)$$

We define our  $\phi$  as:

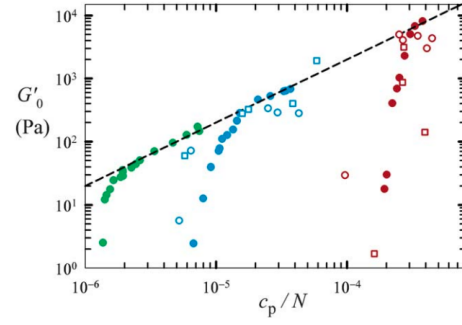
$$\phi = \frac{V_{eq}}{V} = \frac{J_{eq} V_o}{V} = v_2 J_{eq} \quad (17)$$

- From equation 14 we find that for gels, the shear modulus scales with  $v_2^{1/3}$  or, equivalently,  $\phi^{1/3}$ , unlike what is reported in Menut's paper, possibly erroneously. In both of figure 5 and 6 in the paper (shown below), Menut et al. plotted a dashed line that is, possibly, **numerically** represented by the equation for shear modulus of an ideal rubber  $G = RT\nu_e/V$  as given in equation (1) above, where, apparently, they simply substituted for the value of  $V$  as they compress. Their statement “**Data in the high concentration limit of each system follow the prediction from the theory of rubber elasticity**” is ambiguous, to say the least, in light of the

analysis presented above. The theory does not allow tampering with the dry volume of the rubber as you “compress it” to obtain the behavior at a different volume. In other words, the dashed line represents the behavior of different rubbers with different crosslinking densities, which could physically describe the behavior of highly confined microgels, in general, but in that case the prediction is not given by the theory for rubber elasticity in the sense that if you compress a monolithic piece of gel you would simply scale the modulus of the dry state with  $V$ .



**Fig. 5** Rheological behavior of a suspension of colloidal-scale p(NIPAAm-co-AAc) microgels cross-linked with 1 wt% BIS. (a) Selected frequency sweeps of the elastic ( $G'$ , full symbols) and viscous ( $G''$ , open symbols) part of the complex shear modulus at increasing particle compression, and hence, increasing polymer concentration (from bottom to top). The dashed line represents the power  $1/2$  scaling prediction. (b)  $G'$  ( $\omega = 1 \text{ rad s}^{-1}$ ) as a function of the polymer concentration in the microgel suspension,  $c_p$ . The dotted line represents a fit of the upper part of the dataset to the scaling prediction according to the theory of rubber elasticity,  $G \approx G' \sim (c_p/N) k_B T$ .<sup>20</sup>



**Fig. 6** Elastic shear modulus of compressed microgel suspensions,  $G'(\omega = 1 \text{ rad s}^{-1})$ , as a function of the polymer concentration,  $c_p$ , normalized by the average length of the elastically active network chains,  $N$ . Full symbols: colloidal-scale particles of p(NIPAAm-co-AAc) at cross-linker contents of 0.1 (green), 1 (blue), and 10 wt% (dark red). Empty symbols: granular-scale particles of p(NIPAAm-co-AAc) (circles) and pAAm (squares) at cross-linker contents of 1 (blue) and 10 wt% (dark red). Data in the high concentration limit of each system follow the prediction from the theory of rubber elasticity,  $G \approx G' \sim (c_p/N) k_B T$ ,<sup>20</sup> represented by the dashed line.