

the dry network dimensions, in Equation 19 the undeformed but swollen network is the reference state. The impact of swelling on the mechanical properties of a swollen gel is highlighted by the  $1/\lambda_s$  factor in Equation 19. While the modulus of the dry network is  $G_o = k_B T v / V_o$ , the swollen network has a reduced modulus of  $G = k_B T v / \lambda_s V_o$ . As  $\lambda_s$  is related to the swelling ratio of the network by  $\lambda_s = q^{1/3}$ , the two moduli are related to each other through the swelling ratio:

$$G = G_o / q^{1/3} \quad 20$$

The physical meaning of Equation 20 is that swelling only has a diluting effect on the stiffness of the network. Note that the swelling ratio in Equation 20 does not need to be the equilibrium swelling ratio,  $Q_{eq}$ . The swelling ratio will reach its equilibrium value when the overall free energy is at a minimum with respect to any change in the number of solvent molecules within the swollen network:

$$\partial \Delta F / \partial n_s = 0 \quad 21a$$

Equation 21a can be expanded using Equation 13 to obtain:

$$\partial \Delta F_{el} / \partial n_s + \partial \Delta F_m / \partial n_s = 0 \quad 21b$$

Recalling any of the statistical models presented in the previous section, the elastic free energy term in Equation 21b can be determined as a function of network deformation. When there is no external load applied, the extension ratios resulted from the equilibrium swelling of the network is  $\lambda_{s,o}$  which can be related to the free equilibrium swelling ratio of the network,  $Q_{eq,o}$  by:

$$\lambda_{s,o} = (Q_{eq,o})^{1/3} \quad 22$$

For an affine network, the elastic free energy as a function of equilibrium swelling extension ratio is:

$$\Delta F_{el} = (3V_o/2)(\rho RT/M_c)(\lambda_{s,o}^2 - 1) \quad 23$$

Separately, for any swelling ratio the following relationship exists between mole number of solvent molecules per unit volume of dry network,  $n_s/V_o$ , and the molar volume of the solvent molecules,  $v_s$ :

$$q = 1 + (n_s/V_o)v_s \quad 24$$

Equation 24 guarantees the molecular incompressibility of the system and is independent of the hypothesis presented in the form of Equation 13. At equilibrium under free swelling conditions  $q \rightarrow Q_{eq,o}$  in Equation 24. Now, by inserting Equation 22 in Equation 23, and using Equation 24 to establish a correlation between  $Q_{eq,o}$  and  $n_s$ , the equilibrium swelling ratio can be determined from Equation 21b and Equation 14 as:

$$\ln \left( 1 - \frac{1}{Q_{eq,o}} \right) + \frac{1}{Q_{eq,o}} + \frac{\chi}{Q_{eq,o}^2} + \frac{(\rho v_s / M_c)}{Q_{eq,o}^{1/3}} = 0 \quad 25$$

Solving Equation 25 for any given  $\chi$ ,  $v_s$  and  $\rho/M_c$  will give the equilibrium swelling ratio when no external stress is applied. For hydrogels swollen in water  $v_s$  is