

$18.03 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ (at 25°C). The interaction between water molecules and network polymer chains determines the value of χ . The degree of crosslinking and the nature of polymer chains determine ρ/M_c . Figure 2 plots equilibrium free swelling ratio of a hydrogel network for various degrees of crosslinking.

From Fig. 2 and Equation 25 the effect of the degree of crosslinking of a network on its equilibrium swelling ratio is clear. Separately, Equation 12 suggests that there is a direct relationship between the degree of crosslinking and the dry modulus of a network. Therefore, it is possible to relate the dry network's modulus directly to the equilibrium swelling ratio of the swollen network. This relationship is power-law in the form of:

$$G_o \sim (Q_{eq,o})^\alpha \quad 26$$

where α depends on the polymer-solvent interaction. For a θ -solvent, in which polymer chains are inert to themselves and solvent molecules (monomer-monomer interactions are identical to the monomer-solvent interaction), α is $-8/3$. For an athermal solvent, a perfectly good solvent in which polymer chains are fully solvated, α is -1.75 (Rubinstein and Colby 2003).

It is important to remember that the free equilibrium swelling ratio, $Q_{eq,o}$, is different from the equilibrium swelling ratio of the same network subject to an external stress, Q_{eq} . Indeed, applied external stresses have a direct effect on the equilibrium swelling ratio of the network. Initially, Flory, Rehner and Gee looked at a simple tensile situation and concluded that the equilibrium swelling ratio of a polymer network under uniaxial tensile stress is higher than its free equilibrium swelling ratio: $Q_{eq,o} < Q_{eq}$ (see Flory and Rehner 1944; Gee 1946; Treloar 1950). A more general treatment of this problem was later presented by Treloar in which an homogeneous strain was assumed to act on a polymer network followed by network equilibrium in the solvent (Treloar 1975).

In general, the Flory-Rehner assumption for the total change in free energy of the network-solvent system (Equation 13) along with the molecular incompressibility assumption (Equation 24) are the starting points. In the Flory-Rehner hypothesis, the total change in free energy is the summation of network deformation (entropic)

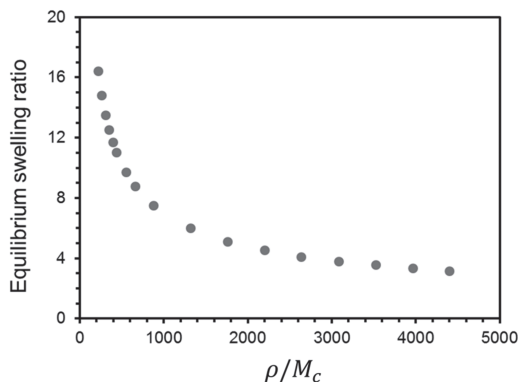


Fig. 2. Theoretical equilibrium free swelling ratio, $Q_{eq,o}$, as a function of ρ/M_c for a hydrogel network with $\chi = 0.1$.