



Fig. 4. Theoretical equilibrium swelling ratio, Q_{eq} , as a function of linear extension ratio for a swollen hydrogel subject to a uniaxial stress. The curves are obtained from Equation 31a for $\chi = 0.1$. The dotted line represents $\lambda = 1$ and the filled circles show the equilibrium state when no external stress is applied: $Q_{eq} = Q_{eq,o}$.

increasing the magnitude of applied stress, λ goes further away from 1. Clearly, when $\lambda = 1$ there is no external force applied to the network and $Q_{eq} = Q_{eq,o}$. The dotted line in Fig. 4 represents $\lambda = 1$ and separates the tensile and compression regions. The black circles obtained at the interception of $\lambda = 1$ line with each curve show $Q_{eq,o}$ for networks with different degree of crosslinking. Here, ρ/M_c is a network parameter and is proportional to the degree of crosslinking. When an external stress is applied to a network, the equilibrium swelling ratio begins to deviate from $Q_{eq,o}$, following the curve that corresponds to that network's ρ/M_c value. Depending on whether the stress is tensile or compression, the equilibrium swelling ratio will shift to, respectively, right or left side of the curve. Also, for highly crosslinked networks, the equilibrium swelling ratio is less sensitive to the network deformation than in the case of loosely crosslinked networks.

To illustrate the impact of swelling ratio on the mechanical behaviour of swollen polymer networks, Fig. 5 presents a series of stress-extension curves for a network subject to uniaxial stresses. Three different conditions are considered here: (1) a uniaxial extension is applied to a dry network, (2) the same network is brought to contact with a swelling agent until equilibrium is reached, followed by tensile extension at a constant swelling ratio, such as can occur during fast stretching, (3) similarly, the tensile extension is performed slowly on the swollen network so that enough time is allowed to reach the new equilibrium points during the execution of the tensile test. The behaviour of the dry network under a uniaxial stress can be captured by any of the relevant equations in section two of this chapter. For the swollen network, however, the swelling ratio can vary with network deformation, as shown in Fig. 5. In reality this can happen when the mechanical deformation takes place over an extended period of time, e.g., when a very slow tensile test is undertaken. On the other hand, the swelling