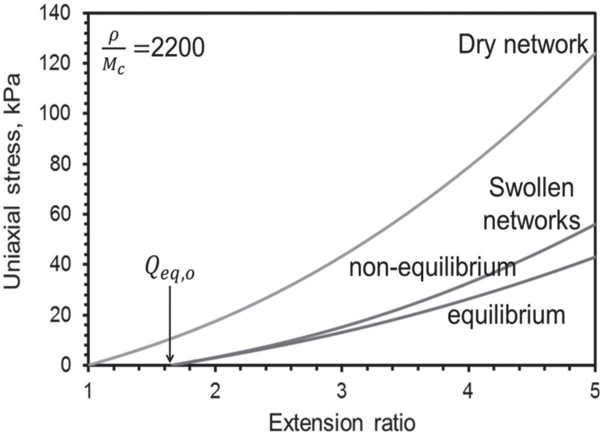

Fig. 5. Uniaxial tensile stress (true stress) as a function of extension ratio (referenced to undeformed dry network) for a polymer network in its dry state, and swollen state. For the swollen network, when the equilibrium swelling ratio is reached under no external force ($Q_{eq,o}$), the network can be subject to a fast uniaxial deformation (non-equilibrium) or a slow uniaxial deformation (equilibrium). In the former case, the swelling ratio remains unchanged during the test ($q = Q_{eq,o}$), while in the latter case at every single point of the experiment a new equilibrium swelling ratio is reached ($q = Q_{eq}$).

ratio can remain unchanged when a sudden mechanical deformation is inflicted to the network, e.g., when the tensile test is performed at high extension rates.

It is worth to note that, as the network is stretched (by swelling or mechanical deformation) the polymer chains are being extended as well. Eventually, the polymer chains are fully extended and no further deformation is possible. After this point, a sudden increase in the network's modulus is expected. Various treatments for this limited extensibility of the networks are available, such as by Gent (Gent 1996), but are not considered further here.

Mesh Size and Diffusion Coefficient

Transport properties of the hydrogels are also controlled directly by the network parameters. The rate of diffusion of small molecules through the network and the size of molecules that can pass through the network will depend on the crosslink density. These properties are important because in many hydrogel applications the polymer network is required to either swell/deswell in response to the environment or to uptake/release small molecules. Therefore, the rate of diffusion of small molecules through the network will determine the kinetics of swelling/deswelling and uptake/release. The diffusion of molecules through the polymer network takes place through the space available between polymer chains. The length scale of this space is called the mesh size. Depending on the structure of the polymer network, the mesh size can range from a few nanometers, for homogeneously crosslinked defectless networks, up to submicrons or even larger, for heterogeneous networks with structural defects. Also, because of the topological distribution of polymer chains, there is no single value for a network's mesh size. There are various definitions for the mesh size (Fig. 6), one of