negligible. Hence Eq. (29.2) is written in terms of the principal stress differences. In the case of a uniaxial deformation $\lambda = \lambda_1$ in the 1 direction Eq. (29.2) becomes:

$$\sigma_{11} - \sigma_{22} = \lambda_1\, w'(\lambda_1) - \lambda_2\, w'(\lambda_2) \qquad (29.3)$$

and because of the incompressibility condition that $\lambda_1\lambda_2\lambda_3 = 1$ we find that $\lambda_2 = \lambda_1^{-1/2}$ and Eq. (29.3) becomes:

$$\sigma_{11} - \sigma_{22} = \lambda\, w'(\lambda) - \lambda^{-1/2} w'(\lambda^{-1/2}), \qquad (29.4)$$

where $\lambda = \lambda_1$. For uniaxial extension $\lambda > 1$ while for uniaxial compression $\lambda < 1$.

From a practical viewpoint, Eq. (29.4) can be used to describe the stress–strain relation of a material if $w'(\lambda)$ is known. $w'(\lambda)$ can be obtained in the laboratory in various ways, such as pure shear experiments as described by Valanis and Landel [60], by torsional measurements as described by Kearsley and Zapas [62] and by a combination of tension and compression experiments as also described by Kearsley and Zapas [62]. Treloar and co-workers [63] have also shown that the VL function description of the mechanical response of rubber is a very good one. The reader is referred to the original literature for these methods.

Another point to keep in mind here is that, in most models, the description of rubber elasticity given from statistical mechanical models results in a Valanis–Landel form of strain energy density function. This will be important in the following developments. We now look at some common representations of the strain energy density function used to describe the stress–strain behavior of crosslinked rubber.

There are two common phenomenological strain energy functions that have been used to describe the stress–strain response of rubber [58,59,64]. These are referred to as the Neo-Hookean form and the Mooney–Rivlin form and both can be written as Valanis–Landel forms, although they represent truncated forms of more general strain energy density functions. The Neo-Hookean form is a special form of the Mooney–Rivlin form, so we will begin with the latter. For a Mooney–Rivlin material the strain energy density function is written as:

$$W(\lambda_1,\lambda_2,\lambda_3) = C_1(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + C_2(\lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2} - 3) \qquad (29.5)$$

and we see that the VL function for this is of the form $w(\lambda_i) = C_1\lambda_i^2 + C_2\lambda_i^{-2}$ and the VL derivative is given as:

$$w'(\lambda_i) = 2C_1\lambda_i - 2C_2\lambda_i^{-3}, \qquad (29.6)$$

where C_1 and C_2 are material constants, often referred to as the Mooney–Rivlin Coefficients.

For uniaxial deformations of magnitude λ one then writes Eq. (29.4) for the Mooney–Rivlin stress–strain response as:

$$\sigma_{11} - \sigma_{22} = (\lambda^2 - 1/\lambda)(2C_1 + 2C_2/\lambda). \qquad (29.7)$$

Equation (29.7) makes obvious the reasons for the representation of experimental data in the so-called Mooney–Rivlin plot. If the material has a Mooney–Rivlin strain energy density function then a plot of $(\sigma_{11} - \sigma_{22})/(\lambda^2 - 1/\lambda)$ vs. $1/\lambda$ results in a straight line with the slope and intercept at $\lambda = 1$ determining $2C_2$ and $(2C_1 + 2C_2)$, respectively.

For the Neo-Hookean material, the strain energy density function is the same as the Mooney–Rivlin material but with $C_2 = 0$:

$$W(\lambda_1,\lambda_2,\lambda_3) = C_1(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3). \qquad (29.8)$$

The VL derivative is:

$$w'(\lambda_i) = 2C_1\lambda_i. \qquad (29.9)$$

The corresponding reduced stress σ_R is:

$$\sigma_R = (\sigma_{11} - \sigma_{22})/(\lambda^2 - 1/\lambda) = 2C_1. \qquad (29.10)$$

Hence, in the Mooney–Rivlin plot, the stress–strain data are reduced to a line of slope zero.

A point worth noting here is that several of the molecular models that will be described in the subsequent sections are Neo-Hookean in form. Normally, dry rubbers do not exhibit Neo-Hookean behavior. As for the Mooney–Rivlin form of strain energy density function, rubbers may follow such behavior in extension, yet they do not behave as Mooney–Rivlin materials in compression. In Fig. 29.2, we depict typical experimental data for a polydimethylsiloxane network [39] and compare the response to Mooney–Rivlin and Neo-Hookean behaviors. The horizontal lines represent the affine and the phantom limits (see "Network Models" in Section 29.2.2). The straight line in the range $\lambda^{-1} < 1$ shows the fit of the Mooney–Rivlin equation to the experimental data points.

Statistical Theories

Structural Characteristics of Polymer Networks

In this section we discuss the most important structural parameters characteristic of an ideal polymer network. The structure of a real network always displays deviation from that of an ideal network. Network defects, such as unreacted functionalities, cyclic structures and entanglements, arise from the statistics of the crosslinking process. The crosslinking reaction, in general, results in a length distribution for the network chains. In addition to the molecular imperfections, real networks always contain inhomogeneities, i.e., regions in which the polymer concentration is permanently higher than the average concentration. The topological structure of any real network can be very complex and treatment of the topology is beyond the scope of the present work. (The reader is referred to [56,66–69] for discussions of this topic.) It is worthwhile, however, to define the structural parameters for a perfect network because it allows us to treat any real network by reference to these parameters.