

$$W_{af}(\lambda_i, \lambda_j, \lambda_k) = (k_B T v / 2 V_o) (\lambda_i^2 + \lambda_j^2 + \lambda_k^2 - 3) \quad 8$$

For compressible materials, the logarithmic term in Equation 2 appears in the free energy function of the affine model (Equation 8), with  $A$  taken to be  $-N_c/V_o$ . Again,  $v/V_o$  and  $N_c/V_o$  are network parameters determining the density of elastically active chains and degree of crosslinking.

While the phantom and affine models account for two extreme scenarios in which the crosslinking points are treated, other intermediate models have been developed to consider only partial constraints on the crosslinking points. Categorically, these models can be referred to as *the constrained junction affine* models. One widely used model in this category was proposed by Flory and Erman based on a phantom network in which the fluctuations of crosslinking points are spatially hindered by the adjacent chains (Flory 1977; Erman and Flory 1978; Flory 1979; Flory and Erman 1982). The strain energy density function in this case is the sum of two separate energy densities:

$$W = W_{ph} + W_c \quad 9a$$

where,

$$W_c = (k_B T \zeta / 2 V_o) \sum_n [(1 + g_n) B_n - \ln((B_n + 1)(g_n B_n + 1))] \quad 9b$$

$$g_n = \lambda_n^2 [\kappa^{-1} + \zeta (\lambda_n - 1)] \quad 9c$$

$$B_n = (\lambda_n - 1) (1 + \lambda_n - \zeta \lambda_n^2) (1 + g_n)^{-2} \quad 9d$$

The term  $W_c$  in Equation 9a is the free energy contribution of spatial constraints applied to the crosslinking points of a phantom network, while  $W_{ph}$  is the free energy function of that phantom network determined by Equation 6. In Equation 9c and 9d,  $\zeta$  determines the non-affine deformation of the constraint domains, and  $\kappa$  accounts for the extent of spatial restriction applied to the crosslinking points. Depending on how much restriction is applied on the fluctuation of these crosslinking points, the model spans from a phantom network (no restriction:  $\kappa \rightarrow 0$ ) to an affine network (full restriction:  $\kappa \rightarrow \infty$  and  $\zeta \rightarrow 0$ ). Note that the Flory-Erman model is a specific form of the Valanis-Landel strain energy density function. The Flory-Erman model was later modified by Erman and Monnerie to apply the constraints to the center of the mass of the polymer chains rather than their crosslinking points only (Erman and Monnerie 1989; 1992).

Other versions of constraint theories have also been developed in which the topological constraints restrict the fluctuation of all units of every polymer chains within the network. The impact of these restrictions on polymer chain movement can be imagined as an uncrossable tube around the polymer strand. The random movement of the polymer segments is limited to the boundaries of these imaginary tubes, and any crossover is penalized. One example of these tube models is the Gaylord-Douglas theory (Gaylord and Douglas 1987; 1990). Similar to the Flory-Erman model, in the Gaylord-Douglas theory the elastic free energy is the summation of two terms: (1) the free energy term originated from a phantom network and (2) a free energy term accounting for tube restriction:

$$W = (k_B T v / 4 V_o) (\lambda_i^2 + \lambda_j^2 + \lambda_k^2 - 3) + \gamma (\lambda_i + \lambda_j + \lambda_k - 3) \quad 10$$