

## The Use of Statistical Mechanics to Explore the Structure of the Fully-Coupled Thermo-Mechanical Free-Energy Function

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The mechanical behavior of polymers is strongly influenced by thermal effects. Temperature influences this behavior by affecting the viscosity of the materials as well influencing the elasticity of the underlying materials. For finite deformation systems the two predominant underlying elastic modeling frameworks are due to Lu and Pister(1975); Chadwick (1974) and Chadwick and Creasy (1984). Lu and Pister set up a modeling framework based upon a multiplicative split of the deformation gradient  $\mathbf{F}$  into a thermal and mechanical portion  $\mathbf{F} = \mathbf{F}_m \mathbf{F}_\theta$ , where the thermal portion is taken to be isotropic. The material response is assumed to be characterized by a free energy function of the form  $\Psi(\mathbf{F} \mathbf{F}_\theta^{-1}, \theta) + h(\theta)$ . In the Chadwick and Chadwick and Creasy framework, the basic free energy structure is developed from the concept of a free energy function at a fixed reference temperature in the form  $\Psi_0(F) \frac{\theta}{\theta_0} - U_0(F) \left( \frac{\theta}{\theta_0} - 1 \right) - \int_{\theta_0}^{\theta} \left( \frac{\theta}{\theta_0} - 1 \right) c(F, \theta') d\theta'$  where the subscript o indicates fixed temperature state functions and c is the heat capacity. This functional form involves *no* assumptions beyond an acceptance of basic thermo-mechanical notions. The two functional forms can provide the same material response if desired but they can also provide strongly disparate responses with appropriate choices for the state functions. Each also has its natural advantages and disadvantages.

In this presentation we re-examine the underlying assumptions of both of these modeling frameworks to highlight their similarities and differences. We then examine the micro-mechanical origins of the state functions from a statistical mechanical viewpoint. In particular we look beyond the classical freely-jointed random walk model for polymeric structure and look in detail at the effects of internal energy terms into a polymer chain's Hamiltonian function. By adopting a stress ensemble (Gibbs-like) version of the Chadwick theory, we are able to effectively compute partition functions for single chains and idealized networks. This allows us to compute thermo-mechanical response functions which leads to a testable simple hypothesis on the nature of the dominant non-linear thermo-mechanical coupling terms for such materials.