

A new interpretation of internal-variable theory in finite thermo-viscoelasticity

HUANG ZhuPing^{1*}, DUI GuanSuo² & YANG ShengYou²

¹Department of Mechanics and Engineering Science, Peking University, Beijing 100871, China;

²Institute of Engineering Mechanics, Beijing Jiaotong University, Beijing 100044, China

Received August 28, 2012; accepted November 23, 2012

Based on the non-equilibrium thermodynamics, an internal- variable theory in thermo-viscoelasticity at finite deformation was proposed by Huang in 1999. In this theory, a modified stretch of the molecular chain was introduced, and hence the molecular network model in rubber elasticity was extended to take into account the viscous and thermal effects of the material. The viscous dissipation of the material can then be described by means of these internal variables, which appear in the expression of the modified stretch. In order to give a clearer explanation on the physical implication of the internal variables, a connection between the internal-variable theory and theoretical formulation based on the multiplicative decomposition of the deformation gradient in existing literature is presented in this paper, which allows the above internal-variable theory to be more systematic.

thermo-viscoelasticity, internal variables, finite deformation, multiplicative decomposition of the deformation gradient

PACS number(s): 46.05.+b, 46.35.+z

Citation: Huang Z P, Dui G S, Yang S Y. A new interpretation of internal-variable theory in finite thermo-viscoelasticity. *Sci China-Phys Mech Astron*, 2013, 56: 610–616, doi: 10.1007/s11433-013-5019-3

1 Introduction

It is well known that linear viscoelastic constitutive relations can be constructed according to the Boltzmann superposition principle. By means of the introduction of the internal variables (or hidden variables), ref. [1–3] proposed the internal-variable theory in linear viscoelasticity under isothermal conditions. This theory can be intuitively modeled by a combination of parallel and series connections of linear springs and linear dashpots. Therefore, the Helmholtz free energy $\psi = \psi(\theta, \mathbf{E}, \boldsymbol{\xi}_m)$ in this theory can be expressed as a quadratic expansion in terms of $\mathbf{E}$ and $\boldsymbol{\xi}_m$, where θ is the absolute temperature, $\mathbf{E}$ is the Lagrangian strain and $\boldsymbol{\xi}_m$ ($m=1, 2, \dots, M$) is a set of internal variables. In order to extend the above theory to the case of finite deformation to

consider the high deformability of polymers, several viscoelastic constitutive models have been developed in the past several years. For instance, in the framework of finite deformation, the free energy was assumed to be a quadratic expansion in terms of internal variables [4–6]. However, as pointed out by Huang [7], this quadratic expansion is only a linear approximation of the theory proposed.

It should be noted that the viscoelastic constitutive theory at finite deformation can also be formulated by means of the multiplicative decomposition of the deformation gradient (e.g., [8–11]). However, it seems that investigations of the connection between the internal-variable theory and the theory based on the multiplicative decomposition of the deformation gradient have not been reported in the literature.

The mechanical behaviors of high polymers exhibit strong dependence on both strain rates and temperature near the glass transition temperature. In order to describe these

*Corresponding author (email: huangzp@pku.edu.cn)

mechanical responses of polymeric materials, the following requirements are suggested to be satisfied in the formulation of the thermo-viscoelastic constitutive relations: firstly, it must be compatible with the second law of thermodynamics; secondly, under reasonable physical assumptions, it can be properly interpreted by micro- or meso- scopic deformation mechanisms; thirdly, it should be consistent with the classical theory of linear viscoelasticity when the deformation is infinitesimal; fourthly, material parameters (or material functions) should be as few as possible, and these parameters can be determined by experiments and have clear physical meaning; and lastly, during sufficiently slow (or fast) deformation process, the constitutive relation can reduce to the one in thermo-elasticity at finite deformation.

According to the above requirements, a set of internal variables is introduced in this paper, and hence the molecular network model in rubber elasticity is extended to include the viscous and thermal effects of the material. Furthermore, in order to give a more clear explanation on the physical implication of these internal variables, it is the first time that the connection between the internal-variable theory proposed by Huang [7] and the theory based on the multiplicative decomposition of the deformation gradient in the existing literature is discussed, which enables the above internal-variable theory to be more systematic.

2 Helmholtz free energy in rubber elasticity based on the molecular network model

It is well known that under small to moderate deformations the strain-energy function of incompressible rubbers can be derived on the basis of Gaussian statistical theory. At reference temperature θ_0 , this strain-energy function can be written as:

$$W^0 = \mu^0 \frac{1}{2} (I_1 - 3), \quad (1)$$

which is referred to as the neo-Hookean strain-energy function. In eq. (1), I_1 is the first invariant of the right Cauchy-Green tensor $\mathbf{C} = \mathbf{U}^2$, μ^0 is the ground-state shear modulus, which is a linear function of the absolute temperature θ . Eq. (1) can also be equivalently written as:

$$W^0 = \int_0^\pi d\varphi \int_0^{2\pi} h(\varphi, \omega) w^0(\theta_0, \lambda) \sin \varphi d\omega, \quad (2)$$

where $\lambda = (\mathbf{L}_0 \cdot \mathbf{C} \cdot \mathbf{L}_0)^{1/2}$ is the stretch of an individual chain directed along a unit vector $\mathbf{L}_0$ in the reference configuration, and this directional vector $\mathbf{L}_0$ may be expressed in the spherical polar coordinates (r, φ, ω) by (φ, ω) with the components being $(\sin \varphi \cos \omega, \sin \varphi \sin \omega, \cos \varphi)$ in the rectangular Cartesian coordinate system. $w^0(\theta_0, \lambda)$ is the strain energy stored in a single chain and is given by

$\frac{3}{2} \mu^0 (\lambda^2 - 1)$. $h(\varphi, \omega)$ is the initial orientation distribution function of the chains in the spherical polar coordinates, satisfying the normalized condition $\int_0^\pi d\varphi \int_0^{2\pi} h(\varphi, \omega) \sin \varphi d\omega = 1$. If the material is assumed to be isotropic relative to the reference configuration, that is, the chains are randomly oriented in the natural state, we have $h(\varphi, \omega) = \frac{1}{4\pi}$.

In the case of large deformation, the non-Gaussian statistical theory should be utilized. For instance, by means of the Langevin function $\mathcal{L}(\beta) = \coth \beta - 1/\beta$, the strain-energy function proposed by Arruda and Boyce [12] can be written as:

$$W_{(8)}^0 = \mu^0 n \left[\frac{\lambda_{(8)} \beta_{(8)}}{\sqrt{n}} + \ln \left(\frac{\beta_{(8)}}{\sinh \beta_{(8)}} \right) \right], \quad (3)$$

where $\lambda_{(8)} = \frac{1}{\sqrt{3}} (\lambda_1^2 + \lambda_2^2 + \lambda_3^2)^{1/2}$, $\beta_{(8)} = \mathcal{L}^{-1} \left(\frac{\lambda_{(8)}}{\sqrt{n}} \right)$ is

the inverse Langevin function and $\lambda_\alpha (\alpha = 1, 2, 3)$ are the principal stretches. The above constitutive model is referred to as the 8-chain model, which can capture the effect of the limiting extensibility of the chain stretch with the maximum extension ratio of molecular chains being $\sqrt{n}$. In the full-network model, the chains are assumed to be randomly distributed in space and to deform in an affine manner, and the strain-energy function suggested by Wu and Van der Giesen in ref. [13] is given by

$$W_{(full)}^0 = \mu^0 n \int_0^\pi d\varphi \int_0^{2\pi} \left[\frac{\lambda \beta}{\sqrt{n}} + \ln \left(\frac{\beta}{\sinh \beta} \right) \right] h(\varphi, \omega) \sin \varphi d\omega, \quad (4)$$

where $\lambda = (\mathbf{L}_0 \cdot \mathbf{C} \cdot \mathbf{L}_0)^{1/2}$ and $\beta = \mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{n}} \right)$.

Eqs. (1)–(4) are only applicable to incompressible rubbers. Although rubber materials are generally considered to be incompressible, in reality they are only nearly incompressible, and the most accurate constitutive models should include compressibility of the materials. In the following, the strain-energy function for incompressible materials will be extended to include compressibility and thermal effect. For instance, if the compressibility of the neo-Hookean material is considered, eq. (1) can be extended to be

$$W = \mu^0 \left[\frac{1}{2} (I_1 - 3) - \ln J - h(J) \right] + \lambda^0 U(J), \quad (5)$$

where $J = \det \mathbf{U}$, μ^0 and λ^0 are ground-state Lamé constants. In order to meet the third requirement in the introduction, material functions $h(J)$ and $U(J)$ should be chosen to satisfy the conditions $h(1) = h'(1) = 0$, $h''(1) = 0$ and

$U(1) = U'(1) = 0$, $U''(1) = 1$ at $J = 1$. It is noted that there are infinitely many functions satisfying the above conditions. Here the expression of $U(J)$ is given by considering the purely dilatational deformation, and is uniquely determined from the first term of the right hand side of eq. (5):

$$U(J) = \frac{9}{4} \left[J^{2/3} - 1 - \frac{2}{3} (\ln J + h(J)) \right], \quad (6)$$

Therefore only one fitting function $h(J)$ in eq. (5) is required, which can be determined by the experiments in the pressure-volume relations.

Next, the above expression will be extended to take into account the thermal effect. If the specific heat C_E is assumed to be a constant, the Helmholtz free energy can be written as [14]:

$$\begin{aligned} \psi(\theta, \mathbf{E}) \\ = \varepsilon_0 - \theta_0 \eta_0 + (C_E - \eta_0)(\theta - \theta_0) - C_E \theta \ln \frac{\theta}{\theta_0} + \frac{1}{\rho_0} \tilde{W}, \end{aligned} \quad (7)$$

where ρ_0 , ε_0 and η_0 are the mass density, internal energy and entropy at the reference temperature θ_0 , respectively, and $\tilde{W} / \rho_0 = \tilde{\varepsilon}(\theta_0, \mathbf{E}) - \theta_0 \tilde{\eta}(\theta_0, \mathbf{E})$ is a linear function of temperature. Therefore, the problem will be reduced to determine $\tilde{W}$. In particular, at the reference temperature θ_0 , the expression of $\tilde{W}$ for the neo-Hookean material should be equal to W given by eq. (5). The effects of temperature variation can be considered as follows: firstly, according to the statistical theory of incompressible rubber elasticity, the free energy is entirely entropic in origin, and the ground-state shear modulus is proportional to the temperature. Hence μ^0 in eq. (5) should be replaced by $\mu^0(\theta / \theta_0)$; secondly, the contribution of the dilatational deformation caused by thermal expansion should be included. Here we assume that the material is thermally isotropic and the linear thermal expansion coefficient α_0 is a constant. In such a case, eq. (5) can be modified with the following additional term:

$$-3k^0 \frac{dU}{dJ} J \alpha_0 (\theta - \theta_0) = -\omega_{(th)}(J)(\theta - \theta_0), \quad (8)$$

$$\text{where } \omega_{(th)}(J) = \frac{9}{2} k^0 \alpha_0 (J^{2/3} - 1) - \frac{9}{2} k^0 \alpha_0 J h'(J).$$

From eqs. (6) and (8), the explicit expression of $\tilde{W}$ in eq. (7) can be written as:

$$\begin{aligned} \tilde{W} = \mu^0 \left(\frac{\theta}{\theta_0} \right) & \left[\frac{1}{2} (I_1 - 3) - \ln J - h(J) \right] \\ & + \frac{9}{4} \lambda^0 \left[(J^{2/3} - 1) - \frac{2}{3} (\ln J + h(J)) \right] \end{aligned}$$

$$- \frac{9}{2} k^0 \alpha_0 \left[(J^{2/3} - 1) - J h'(J) \right] (\theta - \theta_0). \quad (9)$$

Thus the Helmholtz free energy corresponding to the neo-Hookean material is obtained.

3 Introduction of internal variables and the connection between internal-variable theory and the theory based on the multiplicative decomposition of the deformation gradient

Near the glass transition temperature the mechanical behavior of polymeric materials is known to be rate dependent due to the viscous dissipation. Based on the full-network model (eq. (4)), the viscoelastic behavior of incompressible polymers has been discussed in [15,16]. In this paper, thermo-viscoelastic constitutive relations of compressible polymers will be constructed through the modification of eq. (9).

A viscoelastic medium is thought of as a network consisting of $M+1$ ($m=0, 1, 2, \dots, M$) kinds of chains. Different kinds of chains have different relaxation times. The mechanical response of $m=0$ kind of chain is purely elastic. The viscous dissipation property of the m th ($m=1, 2, \dots, M$) kind of chain can be described by a second-rank symmetric tensor ξ_m called the m th internal variable [7]. Similar to eq. (2), for isotropic materials, the strain-energy function of the m th kind of chain can be written as:

$$W^{(m)} = \frac{X_m}{4\pi} \int_0^\pi d\varphi_0 \int_0^{2\pi} w^{(m)}(\theta, \lambda, J; \lambda_m, \tilde{\xi}_m) \sin \varphi_0 d\omega_0, \quad (10)$$

where $w^{(m)}(\theta, \lambda, J; \lambda_m, \tilde{\xi}_m)$ depends not only on the stretch λ of an individual chain directed along a unit vector $\mathbf{L}_0$ and the volume ratio J , but also on the effective stretch

$\lambda_m = (\mathbf{L}_0 \cdot (\mathbf{U} - \xi_m)^2 \cdot \mathbf{L}_0)^{1/2}$ and $\tilde{\xi}_m = (\mathbf{L}_0 \cdot \xi_m \cdot \mathbf{L}_0)$ for the m th kind of chains. Eq. (10) can be equivalently written as

$W^{(m)}(\theta, \mathbf{E}^{(\frac{1}{2})}; \mathbf{E}_m, \xi_m)$, where $\mathbf{E}^{(\frac{1}{2})} = \mathbf{U} - \mathbf{I}$ and $\mathbf{E}_m = \mathbf{U} - \xi_m - \mathbf{I}$, are defined as the “engineering strain” and the m th “effective engineering strain” respectively. Therefore, the effect of the viscous dissipation can be included if the expression of $\tilde{W}$ in eq. (7) is replaced by

$$\tilde{W}^{vis} = W^{(0)}(\theta, \mathbf{E}^{(\frac{1}{2})}) + \sum_{m=1}^M W^{(m)}(\theta, \mathbf{E}^{(\frac{1}{2})}; \mathbf{E}_m, \xi_m), \quad (11)$$

where $W^{(0)}$ and $W^{(m)}$ are the strain-energies of purely elastic chain and the m th kind of chain respectively. In the following, the expression of $W^{(m)}$ will be assumed to have the form:

$$W^{(m)} = W_v^{(m)}(\theta, J) + W_D^{(m)}(\theta, \mathbf{E}_m, \xi_m), \quad (12)$$

$$W_D^{(m)} = W_{D1}^{(m)}(\theta, \mathbf{E}_m) + W_{D2}^{(m)}(\theta, \boldsymbol{\xi}_m), \quad (13)$$

where $W_{D1}^{(m)}$ and $W_{D2}^{(m)}$ are isotropic functions of their variables. In addition, it is required that the stress derived from these functions must be rendered zero in the natural state.

The physical interpretation of eq. (12) will be given as follows. For simplicity, the subscript m in the symbol will be omitted.

Firstly, let us consider the polar decomposition of the deformation gradient $\mathbf{F}$ of the m th kind of chain, which is written as $\mathbf{F} = \mathbf{R} \cdot \mathbf{U}$. Then we have the following spectral decomposition $\mathbf{U} = \sum_{\alpha=1}^3 \lambda_{\alpha} \mathbf{L}_{\alpha} \otimes \mathbf{L}_{\alpha}$ and $\mathbf{R} = \sum_{\alpha=1}^3 \mathbf{l}_{\alpha} \otimes \mathbf{L}_{\alpha}$, where

λ_{α} ($\alpha=1,2,3$), $\mathbf{L}_{\alpha}$ and $\mathbf{l}_{\alpha}$ are the principal stretch, the Lagrangian principal direction and the Eulerian principal direction, respectively.

Secondly, we imagine that the m th kind of chain is infinitely fast unloaded from the current state with the deformation gradient $\mathbf{F}$ to the stress-free state, which corresponds to an intermediate configuration. This rapidly unloading process can be considered as a purely elastic response with a deformation gradient $\mathbf{F}_e^{-1}$. Hence, $\mathbf{F}$ can be multiplicatively decomposed into

$$\mathbf{F} = \mathbf{F}_e \cdot \mathbf{F}_i, \quad (14)$$

where $\mathbf{F}_i$ represents the deformation gradient of the m th kind of chain from the reference configuration to the stress-free intermediate configuration and $\mathbf{F}_e$ is the deformation gradient from the intermediate configuration to the current configuration. The polar decomposition of $\mathbf{F}_i$ and $\mathbf{F}_e$ can be respectively written as:

$$\mathbf{F}_i = \mathbf{R}_i \cdot \boldsymbol{\Phi}, \quad \mathbf{F}_e = \mathbf{R}_e \cdot \mathbf{U}_e, \quad (15)$$

where $\boldsymbol{\Phi}$ and $\mathbf{U}_e$ are symmetric positive-definite tensors, $\mathbf{R}_i$ and $\mathbf{R}_e$ are the rotation tensors from the reference configuration to the intermediate configuration and from the intermediate configuration to the current configuration, respectively. The spectral representation of $\mathbf{U}_e$ is

$$\mathbf{U}_e = \sum_{\beta=1}^3 \lambda_{\beta}^e \mathbf{r}_{\beta} \otimes \mathbf{r}_{\beta}, \quad (16)$$

where $\mathbf{r}_{\beta}$ is the unit principal direction of the right stretch tensor $\mathbf{U}_e$ corresponding the intermediate configuration.

Note that $\mathbf{R}$ can be written as:

$$\mathbf{R} = \mathbf{R}_e \cdot \mathbf{R}_i', \quad (17)$$

with

$$\mathbf{R}_e = \sum_{\delta=1}^3 \mathbf{l}_{\delta} \otimes \mathbf{r}_{\delta}, \quad \mathbf{R}_i' = \sum_{\beta=1}^3 \mathbf{r}_{\beta} \otimes \mathbf{L}_{\beta},$$

we have

$$\mathbf{F} = \mathbf{R}_e \cdot \mathbf{R}_i' \cdot \mathbf{U} = \mathbf{R}_e \cdot \mathbf{U}_e \cdot \mathbf{R}_i \cdot \boldsymbol{\Phi}$$

and

$$\mathbf{F}_i = \mathbf{R}_i \cdot \boldsymbol{\Phi} = \sum_{\alpha=1}^3 \left(\frac{\lambda_{\alpha}}{\lambda_{\alpha}^e} \right) \mathbf{r}_{\alpha} \otimes \mathbf{L}_{\alpha} = \mathbf{R}_i' \cdot \left[\sum_{\alpha=1}^3 \left(\frac{\lambda_{\alpha}}{\lambda_{\alpha}^e} \right) \mathbf{L}_{\alpha} \otimes \mathbf{L}_{\alpha} \right].$$

Hence from the uniqueness of the polar decomposition, we obtain

$$\mathbf{R}_i = \mathbf{R}_i' \text{ and } \boldsymbol{\Phi} = \sum_{\alpha=1}^3 \Phi_{\alpha} \mathbf{L}_{\alpha} \otimes \mathbf{L}_{\alpha} = \sum_{\alpha=1}^3 \left(\frac{\lambda_{\alpha}}{\lambda_{\alpha}^e} \right) \mathbf{L}_{\alpha} \otimes \mathbf{L}_{\alpha},$$

which indicate that $\boldsymbol{\Phi}$ and $\mathbf{U}$ have the same principal direction $\mathbf{L}_{\alpha}$. Thus, λ_{β}^e in eq. (16) can be written as:

$$\lambda_{\beta}^e = \left(\frac{\lambda_{\beta}}{\Phi_{\beta}} \right) \quad (\text{no summation over } \beta). \quad (18)$$

If the m th kind of molecule network is thought as a nonlinear spring arranged in series with a dashpot or a Kelvin-Voigt element, the right stretch tensor of the nonlinear spring defined on the intermediate configuration can be written as:

$$\mathbf{U}_e = \mathbf{R}_i \cdot \bar{\mathbf{U}}_e \cdot \mathbf{R}_i^T, \quad (19)$$

where

$$\bar{\mathbf{U}}_e = \sum_{\alpha=1}^3 \left(\frac{\lambda_{\alpha}}{\Phi_{\alpha}} \right) \mathbf{L}_{\alpha} \otimes \mathbf{L}_{\alpha} \quad (20)$$

is the right stretch tensor of the spring defined in the reference configuration.

Now let us consider a unit directional vector $\mathbf{L}_0$ in the reference configuration. The relationship between $\mathbf{L}_0$ and a unit vector $\mathbf{r}_0$ in the intermediate configuration is given by $\mathbf{r}_0 = \mathbf{R}_i \cdot \mathbf{L}_0$. Hence the effective stretch of the nonlinear spring of the m th kind of chain can be defined by

$$\lambda_e = (\mathbf{r}_0 \cdot \mathbf{U}_e^2 \cdot \mathbf{r}_0)^{\frac{1}{2}} = (\mathbf{L}_0 \cdot \bar{\mathbf{U}}_e^2 \cdot \mathbf{L}_0)^{\frac{1}{2}}. \quad (21)$$

Comparing eq. (21) with the definition of the effective stretch in terms of the internal variable in sect. 2, we have $\mathbf{U} - \boldsymbol{\xi} = \bar{\mathbf{U}}_e$. Therefore the internal variable $\boldsymbol{\xi}$ corresponding to the m th kind of chain can be expressed by

$$\boldsymbol{\xi} = \sum_{\alpha=1}^3 \xi_{\alpha} \mathbf{L}_{\alpha} \otimes \mathbf{L}_{\alpha}, \quad (22)$$

where $\xi_{\alpha} = \lambda_{\alpha} \left(1 - \frac{1}{\Phi_{\alpha}} \right)$, $\xi_{\alpha} = \lambda_{\alpha} (1 - \frac{1}{\Phi_{\alpha}})$ ($\alpha=1,2,3$; no

summation over α). This means the principal direction $\mathbf{L}_{\alpha}$ of the internal variable $\boldsymbol{\xi}$ in eq. (22) is identical to that of the right stretch tensor $\mathbf{U}$.

It is seen from the above discussion that the strain-energy function of the nonlinear spring can be expressed in terms

of U_e (or $\bar{U}_e$) or $U-\xi$ (or $E=U-\xi-I$). Therefore, apart from the contribution of the purely dilatational deformation, the strain-energy function of the m th kind of chain can be written as $W_D^{(m)}$ given on the right hand side of eq. (12). For a Maxwell element, that is, a nonlinear spring in series with a dashpot, the corresponding strain-energy function is $W_D^{(m)}=W_{D1}^{(m)}$; if the nonlinear spring is arranged in series with a Kelvin-Voigt element, the strain-energy of this Kelvin-Voigt element $W_{D2}^{(m)}$ given on the right hand side of eq. (13) should also be included in the expression of the total strain-energy function of the m th kind of chain.

4 A simple example of the thermo-viscoelastic constitutive theory

In the above discussion, the strain-energy function of a viscoelastic material is formally written in eq. (11). In this section, an illustrative example of the derivation of a thermo-viscoelastic constitutive relation for an isotropic material will be given as follows.

Firstly, in order that the strain-energy function of the material can be interpreted from the microscopic deformation mechanism, the Gaussian statistical theory or the non-Gaussian statistical theory should be employed. In the former case, the strain-energy function of the material can be given by the neo-Hookean strain-energy function in the rubbery state at relatively high temperature. If the material compressibility and thermal effects are considered, this strain-energy function can be replaced by the Helmholtz free energy given in eq. (9). In the following, we assume the strain-energy function of purely elastic molecular chain in the viscoelastic material has the similar form as that given in eq. (9). However, it should be noted that the elastic modulus of the materials near the glass transition temperature is much higher than that in the rubbery state and the dependence of the elastic modulus on the temperature also differs from that in the Gaussian statistical theory. In view of this consideration, $W^{(0)}$ in eq. (11) can be assumed to have the following form:

$$W^{(0)} = \mu_0(\theta) \left[\frac{1}{2}(I_1 - 3) - \ln J - h(J) \right] + W_v^{(0)}(\theta, J), \quad (23)$$

where

$$\begin{aligned} W_v^{(0)}(\theta, J) = & \frac{3}{4}(3k_0(\theta) - 2\mu_0(\theta)) [J^{2/3} - 1 - \frac{2}{3}(\ln J + h(J))] \\ & - \frac{9}{2}k_0^0\alpha_0 [(J^{2/3} - 1) - Jh'(J)](\theta - \theta_0). \end{aligned} \quad (24)$$

In the above equation, $\mu_0(\theta)$ and $k_0(\theta)$ are, respectively, the ground-state shear and bulk moduli of the $m=0$ kind of mo-

lecular chain without viscous dissipation. Both are linear functions of the temperature θ . In particular, at the reference temperature θ_0 , we have $\mu_0(\theta_0) = \mu_0^0$ and $k_0(\theta_0) = k_0^0$. α_0 in eq. (24) is the linear thermal expansion coefficient, $h(J)$ can be determined by the experimental pressure-volume data at the reference temperature θ_0 .

Secondly, we can assume the strain-energy function of the m th kind of molecular chain with viscous dissipation has the similar form as given in eq. (23) and $h(J)$ will approximately be taken as zero. We can further assume that the purely dilatational deformation and the thermal expansion do not cause any viscous dissipation. Hence $W_v^{(m)}$ and $W_D^{(m)}$ in eq. (12) can be written as:

$$\begin{aligned} W_v^{(m)}(\theta, J) = & \frac{3}{4}(3k_m(\theta) - 2\mu_m(\theta)) \left(J^{2/3} - 1 - \frac{2}{3}\ln J \right) \\ & - \frac{9}{2}k_m^0\alpha_0 (J^{2/3} - 1)(\theta - \theta_0), \end{aligned} \quad (25)$$

$$\begin{aligned} W_D^{(m)}(\theta, E_m) = & \mu_m(\theta) \left\{ \frac{1}{2}[(U - \xi_m) : (U - \xi_m) - 3] - \ln J_m \right\}, \end{aligned} \quad (26)$$

where $U - \xi_m = E_m + I$, $J_m = \det(U - \xi_m)$. In the above equations, $\mu_m(\theta)$ and $k_m(\theta)$ are linear functions of θ , with $\mu_m(\theta_0) = \mu_m^0$, $k_m(\theta_0) = k_m^0$.

Eq. (26) can be regarded as the strain energy stored in the nonlinear spring in a Maxwell element. It should be noted that in order the stress is zero in the natural state, a term $\ln J_m$ in eq. (26) is necessary even if the material is incompressible. Moreover, it can be seen from the following discussion that the evolution of the internal variable can only be adequately described if this additional term $\ln J_m$ is included in eq. (26) as pointed out in ref. [15]. From eqs. (11) and (23)–(26), the engineering stress which conjugates to the engineering strain can be written as:

$$T = \sum_{m=0}^M \frac{\partial W^{(m)}}{\partial E}. \quad (27)$$

The ground state shear and bulk moduli of the material are given by $\sum_{m=0}^M \mu_m(\theta)$ and $\sum_{m=0}^M k_m(\theta)$, respectively.

In order to complete the above constitutive formulation, the evolution equations of internal variables are needed. Here we assume the evolution equation of the m th internal variable ξ_m obeys the Onsager-Casimir reciprocal relation and can be written in an uncoupled form as:

$$\eta_m(\theta) \frac{\Delta}{\partial \xi_m} A^{(m)} = - \frac{\partial W^{(m)}}{\partial \xi_m} \quad (\text{no summation over } m), \quad (28)$$

where $m=1, 2, \dots, M$ and η_m is the m th viscous coefficient,

$$\dot{\xi}_m^\Delta = \dot{\xi}_m + \xi_m \cdot \Omega^L - \Omega^L \cdot \xi_m = \sum_{\alpha=1}^3 \dot{\xi}_\alpha^{(m)} L_\alpha \otimes L_\alpha \quad \text{and} \quad \Omega^L \text{ is}$$

the Lagrangian spin defined by eq. (2.144) in ref. [14]. From eq. (26), the above evolution equation can be written as:

$$\begin{cases} \eta_m(\theta) \dot{\xi}_m^\Delta = -\frac{\partial W_D^{(m)}}{\partial \xi_m} \\ \quad = \mu_m(\theta) [(U - \xi_m) - (U - \xi_m)^{-1}] \quad \text{or} \\ \xi_m^\Delta = \frac{1}{2\tau_{(m)}} [(U - \xi_m) - (U - \xi_m)^{-1}] \end{cases} \quad (29)$$

$$(m = 1, 2, \dots, M; \text{ no summation over } m),$$

where $\tau_{(m)}(\theta) = \frac{\eta_m(\theta)}{2\mu_m(\theta)} (> 0)$ is the m th relaxation time.

Thus the thermo-viscoelastic constitutive relations based on the Gaussian statistical model are obtained.

As an illustrative example, the mechanical response of a thermo-viscoelastic material (high-density polyethylene) under shear deformation with different strain rates will be discussed. The material parameters used in the simulation at room temperature (23°C) are as follows: the Young's modulus: 5.04×10^2 MPa, the Poisson's ratio: 0.41, the mass density: 0.953 g/cm^3 , the specific heat capacity: 1.256 J/(g K) , and the viscous coefficient: 10^{10} Pa [17,18]. For simplicity and without losing the key features of the viscoelastic properties of the material, we only consider the simplest case of $M=1$ in eq. (27). Namely, there are only two kinds of molecular chains used in the simulation, one is purely elastic and the other is viscoelastic corresponding to a Maxwell element. These two kinds of elements are connected in parallel. The shear moduli of the elastic one and the viscoelastic one are assumed to be $\mu_e = 0.05\mu(\theta)$ and $\mu_v = 0.95\mu(\theta)$, respectively, where $\mu(\theta)$ is the total shear modulus of the material. Moreover, it can be assumed that the material can expand freely under a purely thermal action and therefore the stress caused by thermal expansion can be ignored.

Now the material coordinates $\{X^A\}$ and the spatial coordinates $\{x^i\}$ are chosen to coincide with rectangular Cartesian coordinates with base vectors (e_1, e_2, e_3) . Consider a shear deformation $x = \chi(X)$ defined (in terms of the components in the Cartesian coordinates) by

$$x_1 = X_1 + d_0 X_2, \quad x_2 = X_2, \quad x_3 = X_3,$$

where d_0 is the shear strain. Detailed geometrical descriptions of this shear deformation can be referred to ref. [16].

The shear stress-shear strain curves corresponding to different strain rates in isothermal condition (the temperature of the material equals the ambient temperature) are shown in Figure 1. For simplicity, the viscous coefficient and the

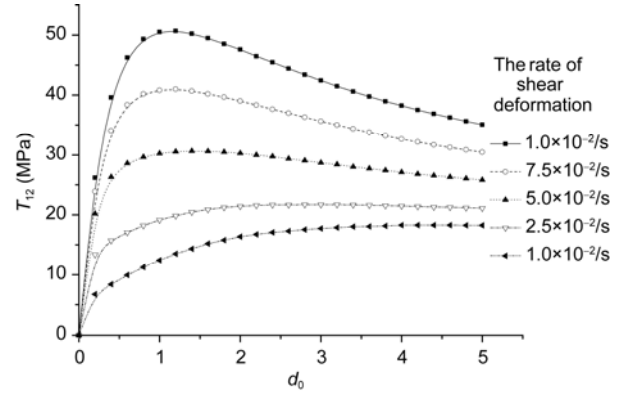


Figure 1 Shear stress T_{12} versus shear strain d_0 .

Young's modulus are assumed to be constants during the shear deformation. It can be seen that the present theory can be used to describe the strain rate effect of polymeric materials in the glass transition region to show the viscoelastic properties of the materials. In general, at low strain rate, the deformation can be considered as a quasi-static one so that there is enough time to exchange the heat energies with the ambient conditions. Therefore, this is nearly an isothermal process with the temperature of the material being the reference temperature. Conversely, in the case of high strain rates, the deformation can be considered as an adiabatic one, since there is not sufficient time to exchange heat energies with the ambient conditions. It should be noted that the temperature rise will significantly influence the mechanical response of the material because of the temperature dependence of the shear modulus and viscosity of the material (see WLF equation, [16]). Hence the temperature variation caused by energy dissipation has a major role in the rate-dependent mechanical behavior of the materials. To sum up, the thermo-mechanical coupling effect can be neglected at low strain rates but should be carefully investigated at high strain rates. A detailed discussion of the latter can be referred elsewhere [16].

4 Conclusion

Based on five requirements for constructing the viscoelastic constitutive relations, a new constitutive formulation in finite thermo-viscoelasticity is presented. The Gaussian statistical model is used as an example to show the effectiveness of the present formulation. The internal-variable theory in thermo-viscoelasticity at finite deformation proposed [7] is further developed. As pointed out by Huang [7], a quadratic expansion of the free energy in terms of internal variables (such as eq. (53), [6]) is only a linear approximation of the present theory. In order to give a more clear explanation on the physical implication of the internal variables, the relationship between the constitutive theory based on internal-variables and that based on the multiplicative decompo-

sition of the deformation gradient in existing literature is discussed. This allows the physical meaning of the internal variables to be rendered clearer. Moreover, only a few material parameters (functions) are needed in the present constitutive formulation, therefore the internal-variable theory given in this paper can be widely applied to many practical problems.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 11132003, 11172033, 11272007 and 10932001), and the National Basic Research Program of China (Grant No. 2010CB-7321004).

- 1 Biot M A. Theory of stress-strain relations in anisotropic viscoelasticity and relaxation phenomena. *J Appl Phys*, 1954, 25: 1385–1391
- 2 Biot M A. Variational principles in irreversible thermodynamics with application to viscoelasticity. *Phys Rev*, 1955, 97: 1463–1469
- 3 Fung Y C. *Foundations of Solid Mechanics*. London: Prentice-Hall, INC, 1965
- 4 Holzapfel G A, Simo J C. A new viscoelastic constitutive model for continuous media at finite thermomechanical changes. *Int J Solids Struct*, 1996, 33: 3019–3034
- 5 Holzapfel G A. *Nonlinear Solid Mechanics*. New York: John Wiley & Sons, Ltd, 2000
- 6 McBride A T, Javili A, Steinmann P, et al. Geometrically nonlinear continuum thermomechanics with surface energies coupled to diffusion. *J Mech Phys Solids*, 2011, 59: 2116–2133
- 7 Huang Z P. A constitutive theory in thermo-viscoelasticity at finite deformation. *Mech Res Comm*, 1999, 26: 679–686
- 8 Reese S, Govindjee S J. A theory of finite viscoelasticity and numerical aspects. *Int J Solids Struct*, 1998, 35: 3455–3482
- 9 Huber N, Tsakmakis C. Finite deformation viscoelasticity laws. *Mech Mater*, 2000, 32: 1–18
- 10 Reese S. A micromechanically motivated material model for the thermo-viscoelastic material behaviour of rubber-like polymers. *Int J Plast*, 2003, 19: 909–940
- 11 Hasanpour K, Ziaei-Rad S, Mahzoon M. A large deformation framework for compressible viscoelastic materials: Constitutive equations and finite element implementation. *Int J Plast*, 2009, 25: 1154–1176
- 12 Arruda E M, Boyce M C. A three-dimensional constitutive model for the large stretch behavior of rubber elastic materials. *J Mech Phys Solids*, 1993, 41: 389–412
- 13 Wu P D, van der Giessen E. On improved 3-D non-Gaussian network models for rubber elasticity. *Mech Res Comm*, 1992, 19: 427–433
- 14 Huang Z P. *Fundamentals of Continuum Mechanics*. Beijing: Higher Education Press, 2003
- 15 Zhang Y, Huang Z P. A model for the non-linear viscoelastic behavior of amorphous polymers. *Mech Res Comm*, 2004, 31: 195–202
- 16 Zhang Y, Huang Z P. Mechanical behavior of amorphous polymers in shear. *Appl Math Mech*, 2004, 25: 1089–1099
- 17 Mark J E. *Polymer Data Handbook*. Oxford: Oxford University Press, 1999
- 18 Drozdov A D, Christiansen J. Thermo-viscoelastic and viscoplastic behavior of high-density polyethylene. *Int J Solids Struct*, 2008, 45: 4274–4288