A Structural Reinterpretation of Linear Viscoelasticity: From Maxwell Modes to Molecular-State Distributions

Tommi Borg
TomCoat Oy, Kauppatie 5, 62500 Evijärvi, Finland
tommi.borg@tomcoat.com
ORCID ID 0009-0002-3168-6669

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Abstract

Linear viscoelasticity is conventionally characterized by modal decompositions of the relaxation modulus, most prominently through classical Maxwell-type models that represent macroscopic behavior as a superposition of discrete exponential modes. While these models effectively describe linear regime responses, they originate at the level of macroscopic relaxation behavior rather than molecular structure.

In this work, a control-theoretic (CT) [1–6] framework is presented in which viscoelastic response is derived from a continuous molecular-state representation. A rheologically effective distribution (RED), reflecting the underlying molecular fingerprint including molecular weight distribution and branching, forms the structural basis of the formulation. Elastic and viscous contributions emerge as differently weighted manifestations of the same distributed molecular state.

The generalized Maxwell model is shown to correspond to a finite-dimensional approximation of this distributed formulation. In this interpretation, classical relaxation spectra can be viewed as reduced representations of an underlying continuous molecular-state dynamics.

The work does not introduce a new constitutive model, but provides a structural interpretation and an explicit mathematical relation between distributed-state CT formulation and the generalized Maxwell model.

Linear viscoelasticity is conventionally characterized by modal decompositions of the relaxation modulus, notably through classical Maxwell-type models (CMM) that represent macroscopic behavior as a superposition of discrete exponential modes. While these models effectively capture linear regime responses in a reduced-order manner, they originate from macroscopic relaxation behavior and are not directly formulated in terms of molecular architecture.

This work introduces a control-theoretic (CT) framework wherein viscoelastic response is derived from a continuous distribution over molecular states. A rheologically effective distribution (RED), based on a comprehensive molecular fingerprint encompassing molecular weight distribution, long-chain branching, and architectural features, provides the model's structural basis. Elastic and viscous components are interpreted as distinct weighted outcomes of a unified distributed molecular-state, as opposed to being assigned to separate mechanical elements.

The structural hierarchy—Molecular fingerprint → RED → macroscopic response $\{G(t), G'(\omega), G''(\omega), \eta^*(\omega)\}$—enables direct calculation of observable viscoelastic properties from the underlying molecular-state distribution. It is demonstrated that the generalized Maxwell model is a finite-dimensional approximation of this continuum-based formulation, suggesting that classical modal spectra may be viewed as reduced representations of more fundamental molecular-state dynamics rather than stand-alone physical models.

This work does not introduce a new model, but provides a structural reinterpretation of linear viscoelasticity and establishes an explicit mathematical relation between distributed-state CT formulation and the generalized Maxwell model.

I. Generalized Maxwell Model

The classical Maxwell model (CMM), as described by Gross [7] and Ferry [8], represents linear viscoelastic behavior through discrete relaxation modes, each characterized by a modulus and a relaxation time. In its generalized form, the Maxwell spectrum approximates the relaxation modulus as a finite sum of exponential decays. In the present work, the generalized Maxwell model is not modified, but reinterpreted within a distributed-state framework.

For a single Maxwell element, the relaxation modulus is

$$G(t) = G_i e^{-t/\tau} \qquad (1)$$

The continuous representation in terms of the relaxation spectrum $h(\tau)$ (expressed per unit $d\ln\,\tau$) is

$$G(t) = \int_{-\infty}^{\infty} h(\tau)\, e^{-t/\tau}\, d\ln\,\tau \qquad (2)$$

Direct measurement of the relaxation modulus $G(t)$ is experimentally demanding. Therefore, oscillatory rheometers are commonly used. A periodic experiment at angular frequency ω is qualitatively related to transient behavior at time scale $t \sim 1/\omega$.

From the Maxwell element one obtains the complex dynamic shear modulus

$$G^*(\omega) = G'(\omega) + iG''(\omega) \qquad (3)$$

where $G'(\omega)$ is the storage modulus and $G''(\omega)$ is the loss modulus.

The elastic–dissipative balance is conveniently expressed through the loss tangent

$$\tan\,\delta(\omega) = \frac{G''(\omega)}{G'(\omega)} \qquad (4)$$

II. Control Theory (CT)

In the CT framework, the relaxation modulus is derived from a continuous molecular-state representation. The elastic (RED′) and viscous (RED″) rheologically effective distributions originate from the same underlying molecular fingerprint, incorporating molecular weight distribution (MWD), long-chain branching (LCB), and molecular architecture as shown in Fig. 1.

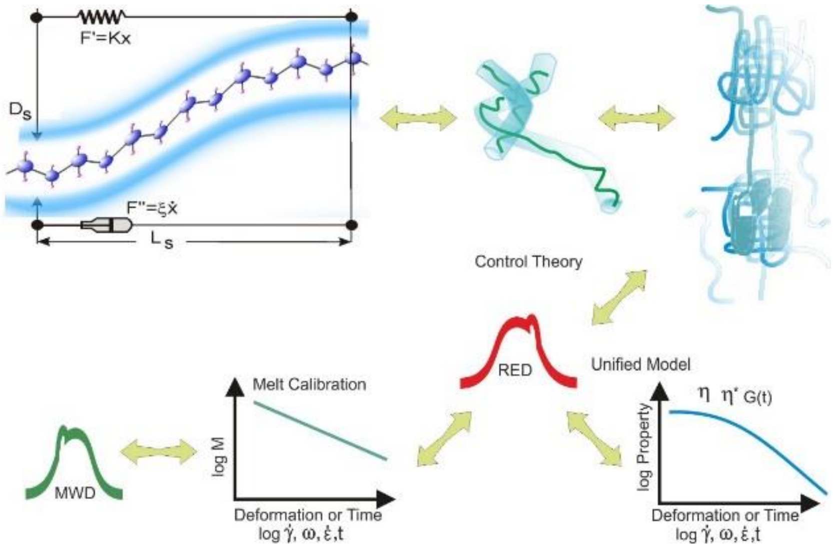

Figure 1 *Graphical demonstration of the system using Control Theory and the nanostructure model of a polymer melt. Relative diameters of the statistical tube for molecules of different sizes produce the accurate Rheologically Effective Distribution (RED), which is subsequently converted to the MWD through melt calibration. The signal bump is shown to observe and separate RED or MWD. Unified Model establishes accurate linear relation between REDs and different types of viscoelastic flows.*

Because CT in rheology is less familiar, we briefly outline its structural basis. Molecular rheology theories based on independent chain response (e.g., elastic dumbbell, Rouse, Zimm) or pseudo-independent chain response (e.g., unmodified Doi–Edwards) allow prediction of rheological behavior from molecular weight distribution, as described by Graessley [9]. For such systems,

$$G(t) = \sum_i w_i \, G_i(t) \qquad (5)$$

where w_i is the weight fraction of component i and $G_i(t)$ is the relaxation modulus of the corresponding monodisperse component.

We introduce the rheologically effective distribution (RED), denoted $w(t)$, and an impulse response $h(t)$. The relaxation modulus can then be written in convolution form:

$$G(t) = G_0 P' \int_{-\infty}^{t} w(\tau) h(t-\tau)\, d\tau \qquad (6)$$

where G_0 is a reference modulus and P' is a scaling factor.

Exciting the system by a small strain pulse at time t_0, the response is

$$y(t) = \int_{-\infty}^{t} w(\tau) h(t - \tau)\, d\tau \qquad (7)$$

In practice, RED′ and RED″ are defined in logarithmic time or rate coordinates and represent predominantly elastic and viscous effectiveness, respectively, over the observable range. This leads to the analytical relaxation expression

$$\log \frac{G(t)}{G_0} = -\int_{-\infty}^{\log t} \left(P' w'(\log \tau) + P'' w''(\log \tau/R)\right) \log \frac{t}{\tau}\, d\log \tau \qquad (8)$$

where $0 < P', P'' < 40$ represent effective entanglement and Rouse contributions, and R is a Rouse scaling parameter. These distributions $w'(\log \tau)$ and effective viscous $w''(\log \tau)$ are normalized before using Eq. (8).

Similar structural expressions are derived for $G^*(\omega)$ and steady shear viscosity $\eta(\dot{\gamma})$. The functional form of RED remains consistent across time, frequency, and shear-rate representations; only the abscissa scaling changes. We use a similar procedure as for shear viscosity to generate a unified formulation introduced by Borg [10]. In our earlier work [1–6], this formulation was termed the “Characteristic Model”. For complex viscosity $\eta^*(\omega)$ we have:

$$\log \frac{\eta^*(\omega)}{\eta_0^*} = -\log \frac{\omega}{\omega_\mathrm{c}} \int_{-\infty}^{\log \omega} \left(P' w'(\log \psi) + P'' w'' \left(\log \frac{\psi}{R} \right) \right) \mathrm{d} \log \psi \qquad (9)$$

RED originates from the same molecular fingerprint that determines MWD. Melt calibration allows conversion between RED and MWD. Comparison with GPC/SEC measurements provides additional information, particularly regarding long-chain branching.

Converting the normalized rheologically effective distribution RED $w(\log \omega)$ to molecular weight distribution MWD $\widetilde{w}(\log M)$ by formula, where the non-normalized distribution function $\tilde{w}(\log M)$ is indicated by a tilde. The transformation from RED to MWD is given by:

$$w(\log \omega) = \widetilde{w}(\log M)\Big|_{M = Mf\left(\frac{\omega}{\omega_1}\right)^{-\frac{1}{Hf}}} \qquad (10)$$

A. Summary of Structural Properties

Determination of MWD proceeds by fitting a segment of the complex viscosity curve $\eta^*(\omega)$, extending the distribution with appropriate boundary estimates, and iteratively adjusting P', P'', and R to minimize error between modelled and measured data. Measured and modelled dynamic data for storage G' and loss G'' moduli, for 1840H LDPE (a modern version of IUPAC A) shown in Fig 2.

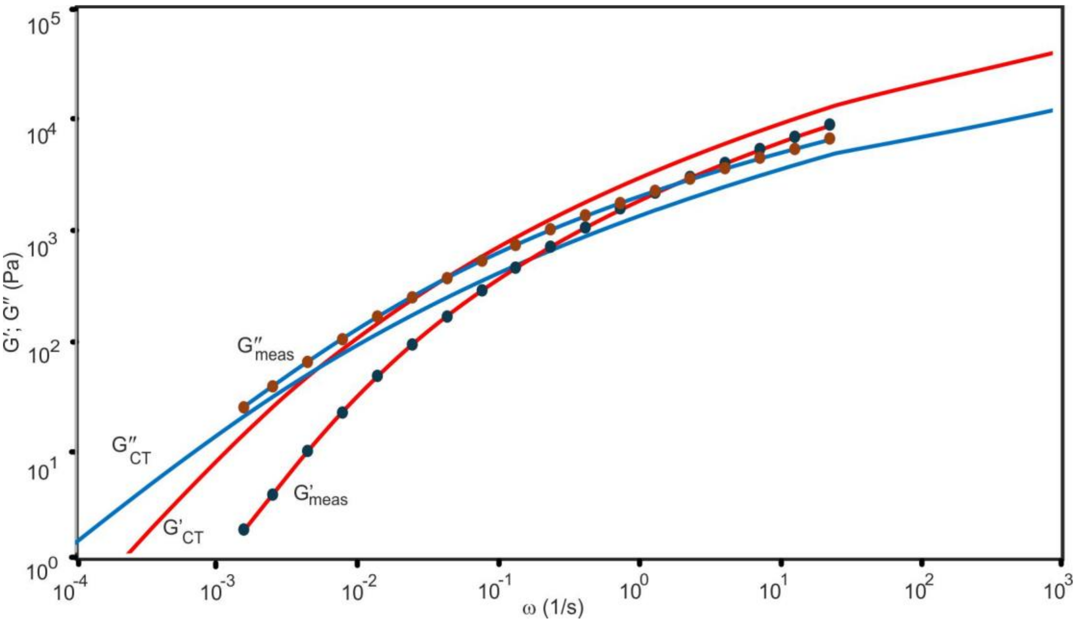

Figure 2. *Measured dynamic data (symbols) for the storage modulus G' and loss modulus G" of 1840H LDPE (a modern version of IUPAC A) at 190 °C. The corresponding CT/Unified Model predictions are shown as continuous lines. While deviations between measured and modeled G' and G" are observed in certain frequency ranges, the model provides an accurate representation of the complex viscosity η*(ω), as demonstrated in Fig. 3.*

Measured and modelled complex viscosity curve $\eta^*(\omega)$, the loss tangent tan $\delta(\omega)$ and computed RED, for 1840H LDPE (a modern version of IUPAC A) shown in Fig 3.

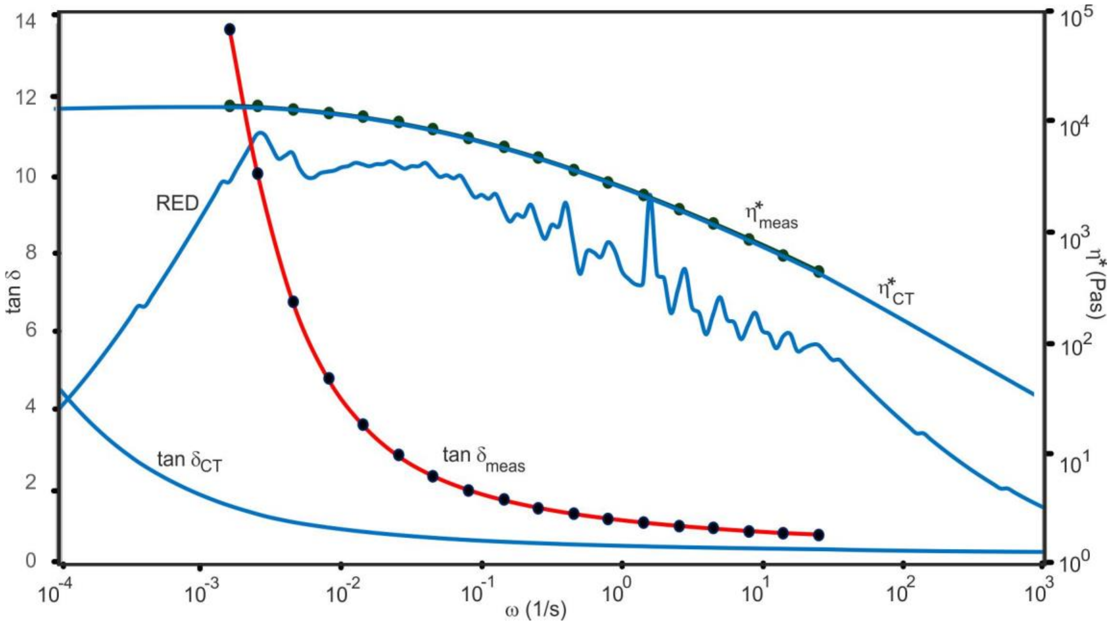

Figure 3. *Measured data (symbols) for complex viscosity and the loss tangent tan δ(ω) of 1840H LDPE (a modern version of IUPAC A) at 190 °C. The corresponding CT and Unified Model predictions for complex viscosity η*(ω) and tan δ(ω) are shown as continuous lines. The RED segment derived by CT is also indicated. The agreement with the measured η*(ω) is excellent within the experimental range, as local deviations between measured points and the modelled curve are accommodated by the detailed RED representation used for computing the flow curves. When RED is subsequently converted to MWD, slight smoothing of the distribution removes these local irregularities without affecting the viscosity fit.*

B. Distributed-State Representation of the CT Framework

In the CT formulation, macroscopic viscoelastic response is generated from a continuous molecular-state distribution rather than from discrete relaxation modes. Let $w(\xi)$ denote the rheologically effective distribution (RED) defined over a continuous molecular-state coordinate ξ. The relaxation modulus is obtained through an integral operator of convolution type,

$$G_{CT}(t) = \int_{-\infty}^{t} w(\xi)\, h(t-\xi)\, d\xi, \tag{11}$$

which may be written abstractly as $G_{CT} = \mathcal{F}[w]$.

The operator $\mathcal{F}$ is linear with respect to w. Thus, the CT framework represents a distributed-parameter system in which macroscopic response emerges from a continuous superposition of molecular contributions.

III. Relation to the Generalized Maxwell Model

The generalized Maxwell model expresses the relaxation modulus as a finite modal expansion,

$$G_M(t) = \sum_{i=1}^{N} G_i\, e^{-\frac{t}{\tau_i}}. \tag{12}$$

This representation can be interpreted as a finite-dimensional approximation of the distributed CT formulation. If the RED is approximated by a finite expansion,

$$w(\xi) \approx \sum_{i=1}^{N} a_i\, \phi_i(\xi), \tag{13}$$

then

$$G_{CT}(t) \approx \sum_{i=1}^{N} a_i\, \mathcal{F}[\phi_i](t). \tag{14}$$

Choosing basis functions that map under $\mathcal{F}$ to exponential kernels recovers the classical Maxwell form. In this sense, discrete relaxation modes correspond to modal projections of an underlying continuous molecular-state dynamics.

A simple illustration of the conceptual differences between the classical relaxation spectrum and the CT formulation is shown in Fig. 4. The relaxation spectrum $h(\tau)$, adapted from Honerkamp and Weese [11], is used to generate the relaxation modulus $G(t)$ according to Eq. (2). The same relaxation modulus is then reconstructed using the CT formulation of Eq. (8), starting from the rheologically effective distributions $w(t)$ (RED).

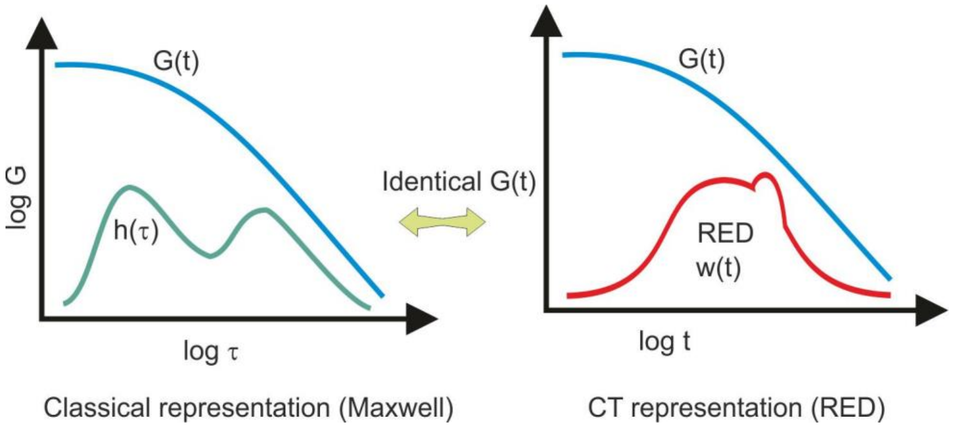

Figure 4 *Comparison of two alternative representations leading to the same relaxation modulus G(t). Left: classical relaxation spectrum h(τ) (Maxwell representation) used to compute G(t) via Eq. (2). Right: rheologically effective distribution w(t) (RED) used to reconstruct the identical G(t) via Eq. (8). The figure illustrates that different underlying representations can yield the same macroscopic viscoelastic response.*

IV. Philosophical Standpoint

The Maxwell model provides a phenomenological approach to describing polymer behavior, utilizing mechanical analogues such as springs and dashpots. In this conceptual framework, elastic and viscous effects are depicted as separate, formal elements, each making a distinct contribution to the overall viscoelastic properties observed in polymers. This separation allows for a clear representation of the different responses, with elasticity and viscosity treated independently within the model.

Polymer melts are commonly studied using rotational rheometers with cone–plate or parallel plate geometries. In cone–plate geometries, the shear rate is approximately constant across the radius, whereas in parallel plate geometries it varies with radial position. Consequently, measurements in parallel plate geometries inherently involve a distribution of shear rates, which must be considered when interpreting rheological data.

When oscillatory rheometers are used, an additional parameter—the oscillation frequency—is introduced. The complex viscosity or complex modulus determined during these experiments represents an averaged response, encompassing a spectrum of molecular states and deformation conditions. This averaging reflects the diversity of molecular environments encountered within the sample during oscillatory testing.

In contrast, the CT framework provides a structured representation of molecular-state contributions inferred from rheological observables.

Molecular fingerprint → RED → macroscopic response $\{G(t), G'(\omega), G''(\omega), \eta^*(\omega)\}$,

No relaxation spectrum is required at the structural level of the model. Within this hierarchy, observable relaxation behavior is derived from a unified molecular-state distribution. The scalar parameters P', P'', and R are determined through iterative fitting of the modeled viscosity data. From this fitted structure, the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ are obtained, while the complex modulus $G^*(\omega)$ follows directly.

From the CT viewpoint, steady shear viscosity measured with a sandwich rheometer (SSR) [12] may provide the most structurally consistent dataset for the Unified Model. Some high shear rate data are measured using a capillary tube, necessitating Bagley corrections.

This work does not introduce a new model, but provides a structural reinterpretation of linear viscoelasticity and establishes an explicit mathematical relation between the distributed-state CT formulation and the generalized Maxwell model.

V. Discussion Note

This work is intended as a structural interpretation rather than a replacement of existing models. The generalized Maxwell model remains an effective and widely used representation of linear viscoelasticity. The present formulation provides an alternative viewpoint, where such models arise naturally as reduced representations of a continuous molecular-state description.

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