Dynamic mechanical response of polymer networks

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Abstract

The dynamic-mechanical response of flexible polymer networks is studied in the framework of tube model, in the limit of small affine deformations, using the approach based on Rayleighian dissipation function. The dynamic complex modulus \(G^*(\omega)\) is calculated from the analysis of a network strand relaxation to the new equilibrium conformation around the distorted primitive path. Chain equilibration is achieved via a sliding motion of polymer segments along the tube, eliminating the inhomogeneity of the polymer density caused by the deformation. The characteristic relaxation time of this motion \(\tau_e\) separates the low-frequency limit of the complex modulus from the high-frequency one, where the main role is played by chain entanglements, analogous to the rubber plateau in melts. The dependence of storage and loss moduli, \(G'(\omega)\) and \(G''(\omega)\), on crosslink and entanglement densities gives an interpolation between polymer melts and crosslinked networks. We discuss the experimental implications of the rather short relaxation time and the slow square-root variation of the moduli and the loss factor \(\tan\delta(\omega)\) at higher frequencies.

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- 83.80.Dr Elastomeric polymers,
- 62.40.+i Anelasticity, internal friction, stress relaxation,
- 83.50.Fc Linear viscoelasticity

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1 Introduction

Viscoelastic properties of dense polymer melts have been successfully explained by the reptation model approach, where one examines the constrained motion of a chain within an effective tube formed by entanglements with other polymers [1, 2]. In this model, the effect of entanglements is to restrict the lateral motion of a chain and is modeled, in the first approximation, by a dynamic constraint in the form of a tube surrounding the thermally fluctuating polymer. The dynamics of the polymer is then described by the reptation motion within such a tube, essentially a diffusion of segments along the random primitive path, with an effective number of chain segments constrained by the tube a new dynamic variable. Accordingly, the characteristic disentanglement time for a chain is that required for all its length to diffuse out of the initial tube. On the other hand, the classical theory of rubber elasticity, see for example Treloar’s treatise [3] or [4], examines the response of a crosslinked polymer network to an affine deformation in the opposite limit of high dilution: Only the topologically quenched random crosslinks are affected by the strain, while the rest of the chain is assumed free to explore all its configurational space. Several penetrating attempts have been made over the years to improve this simple approach and address the issue of dense, entangled network [5, 6]. Although the disentanglement by reptation out of its tube is impossible in a permanently crosslinked network, the concept of a dynamic primitive path, around which the polymer segments are constrained to fluctuate, has been used to describe the static elastic properties of entangled networks. The slilink model [7], where the entanglements are treated as discrete overdamped but nevertheless mobile constraints, is also a variant of the tube approach.

The main success of reptation models in polymer melts has been the description of dynamic properties and viscoelastic relaxation rates. Analogous approaches to crosslinked networks are not well developed at the moment and, in fact, even the basic dynamics of stress relaxation in rubbers is not described theoretically. Much progress has been achieved in studies of secondary effects, such as the relaxation of free dangling ends attached to the network, leading to a slow power-law decay of stress [8, 9]. A significant contribution to understanding of the role of entanglements in rubber elasticity is made by computer simulation studies, e.g. [10]. However, on a basic level, one first needs to analytically describe the relaxation of an affinely deformed ideal network. In this paper we investigate the dynamic mechanical response (the linear complex modulus) of rubbery networks in the dense limit of high entanglement. One should note that, unlike in a case of free chains, the entanglements of networks strands ought to be understood in a more general sense. In particular, the knots of increasing complexity, described by corresponding topological invariants, e.g. [11], are not the only way to restrain the lateral motion of network strands: Even a simple loop,
both ends of which are held by crosslinks, will contribute to the formation of an effective reptation tube. Therefore, the traditional notion of minimal arc length required for a polymer to be entangled, cf. [2], should not be applied to networks – even relatively short strands could be highly constrained in a dense system. In such networks, one expects to find a storage modulus \( G' \) even at zero frequency of imposed deformation (the static modulus \( \mu_0 \), determined by the crosslink density in the classical rubber elasticity [3]), while at a finite frequency \( \omega \) the response should be increasingly controlled by chain entanglements in the similar way as the rubber plateau value of \( G' \) in a dense melt.

Let us consider a polymer chain with segments of Kuhn step length \( b \), of which both ends are crosslinked. The entanglement effect of other network strands is represented by a surrounding tube of diameter \( a \). The central line of such a tube, regarded as a sequence of taut paths between entanglement points, is given a name of primitive path and may be considered as a random walk of step length \( a \), with the end to end distance the same as that of the polymer chain. In the equilibrium state, the density of the polymer segments distributes uniformly along the primitive path. The linear viscoelasticity is then described by the response of chain segments to the instantaneous deformation. As a starting point, one may assume that the deformation of the primitive path is affine, in the sense that both the chain crosslinks and the entanglement points move in proportion to the macroscopic strain imposed on the body of rubber. Immediately after such a deformation, the density of polymer segments along the primitive path is inhomogeneous, because the deformed primitive path steps have different lengths depending on their directions and the chain cannot respond instantaneously to the change of its constraints. In time, the inhomogeneity of the polymer density relaxes through the sliding motion of the chain along the new primitive path.

In a network, the reptation motion of the chain is completely prohibited by the crosslinking. Therefore, this sliding motion of chain segments is considered to be more important for the dynamic properties of crosslinked networks than for corresponding melts, where the main effect is the reptation diffusion out of the deformed tube. In this paper, we clarify how the slip motion of polymer segments along the primitive path affects the dynamic modulus. The results are summarised in Fig. 1(b). We concentrate on relatively low frequencies, well below the glass region. One expects the linear static modulus \( \mu_0 = G'(\omega \rightarrow 0) \) to increase with the network crosslink density, but also with the density of entanglements. In the limit of higher frequency, \( \tau_\omega \gg 1 \), with the characteristic time \( \tau_\omega \) of diffusion along the primitive path, the storage modulus approaches the plateau value corresponding to the rubber plateau in a melt, where the role of entanglements is dominant. Our challenge is to develop a universal description that would also incorporate the limit of zero frequency, \( \mu_0 \), and the plateau modulus in a dense melt.
Figure 1: (a) The scheme of tube model and the relevant variables: the polymer conformation \( r(s,t) \) and the tube primitive path \( R(n,t) \), where the function \( n(s,t) \) specifies the position along the fixed-length path and \( s \) specifies the position along the chain. In a network, the chain is permanently crosslinked at both ends of the tube. (b) The “expected” behaviour of the dynamic storage modulus \( G'(\omega) \): For an uncrosslinked melt the static modulus is zero, but reaches a rubber plateau at a finite frequency due to entanglements. On increasing concentration of permanent crosslinks the static modulus \( G'|_{\omega=0} = \mu_0 \) increases; the plateau modulus has contributions from both crosslinks and entanglements. At a much higher frequency all curves should converge to the glass plateau, which is not the subject of this paper.

A classical theoretical description of polymer networks is based on the statistical-mechanical description of Gaussian chains with topologically quenched constraints of permanent crosslinks, in the simplest case, and entanglements on a more advanced level \[4, 7\]. The computation of a Gibbs partition function \( Z = \int e^{-\beta H} \) is insufficient because of the quenched distribution of crosslinks and the Replica method has been developed as an extension of classical statistical mechanics, as one of the ways to evaluate average macroscopic parameters, such as the free energy \( F_{\text{expt}} = \langle \log Z \rangle \) \[4, 12\]. However, in spite of many successes of the Replica method, it remains unsuitable for finding the dynamic properties, such as the complex modulus \( G^*(\omega) \) – a traditional parameter describing viscoelastic behaviour of polymers and rubbers \[13\]. One needs a dynamical, not static equilibrium solution. Here we utilise a method of solving the dynamical problem of rubber-elastic response by an extension of Boltzmann approach, based on Langevin and Fokker-Planck equations. One introduces the Rayleighian \( \mathcal{R} = L - F + \sum \lambda C \) to incorporate the chain equilibrium properties via its Lagrangian \( L \), the kinetic effects via the dissipative function \( F \) (not to be mixed with the free energy!) and all required constraints \( C \) with their corresponding Lagrange multipliers \( \lambda \).

The principles of Rayleigh’s dissipative function are described in some detail in textbooks on analytical dynamics, e.g. \[14, 15\]. Introduction of \( F = \sum \frac{1}{2} \gamma_{ik} v_i v_k \), with the velocities \( \mathbf{v} \equiv \dot{\mathbf{x}} \) and friction constants \( \gamma \), al-
allows the unified description of Lagrangian systems where the total energy is
dissipated at a rate \( \frac{d}{dt} E = -2F \), via the variational equations

\[
\frac{\delta}{\delta x} \int L \, dt - \frac{\delta}{\delta v} \int F \, dt = 0.
\]

For instance, for a damped one-dimensional motion, \( R = L - F = \frac{1}{2}m \ddot{x}^2 - U(x) - \frac{1}{2}\gamma v^2 \), and the variational equation correctly gives

\[
m \dddot{x} - \gamma \dot{x} + \partial U/\partial x = 0.
\]

This method has been proven to remain valid in problems involving an
arbitrary set of Lagrangian constraints \([16, 17]\) and promises a much greater
mileage in non-equilibrium statistical mechanics of random networks.

## 2 Tube model and equations of motion

In order to describe the sliding motion of a polymer segment along the prim-
itive path, we define the following variables, see Fig. 1(a). Let us consider a
polymer chain of the arc length \( L \). The arc distance from one end, \( s \in [0, L] \),
is used to specify a position along the chain. The conformation of the poly-
mer at time \( t \) is given, as a function of \( s \), by the segment coordinate \( r(s, t) \).
The chain is constrained within a tube of radius \( a \) – similarly, we take the
conformation of the primitive path, at time \( t \), given by the coordinate of
tube axis \( R(n, t) \), where \( n \in [0, Z] \) is used to specify a position along the
primitive path. Now, \( Za \) denotes the contour length of the primitive path
and \( na \) is the arc distance from one end along the tube axis (a variable anal-
ogous to \( s \) for the chain itself). An essential variable in the problem is the
number of chain segments \( s \) contained within one step of the primitive path
\( n \). The relation between the position \( s \) on the polymer and the correspond-
ning position \( n \) on the primitive path is then given by a function \( n = n(s, t) \).
Note that \( r(s, t) \) and \( n(s, t) \) are dynamical variables of the polymer chain,
while the tube conformation \( R(n, t) \) is given externally, by the surrounding
constraints.

In order to derive the over-damped equations of motion, we construct
the Rayleighian \( R \) as a functional of \( r \), \( \dot{r} \), \( R \) and \( \dot{R} \), omitting the inertial
effect of kinetic energy so that \( R = -U - F \). The potential energy term \( U \),
describing the Wiener random walk constrained around the path \( R(n, t) \) of
a fixed length, is given by

\[
U = \frac{3k_B T}{2b} \left[ \int_0^L \left( \frac{\partial r}{\partial s} \right)^2 ds + \frac{q_0^2}{b} \int_0^L (r - R)^2 ds \right] + \lambda \left[ \int_0^L \frac{\partial n}{\partial s} ds - Z \right]. \quad (1)
\]

Here, \( b \) is the step length of the polymer chain and \( k_B T \) is the Boltzmann
temperature energy scale. The potential term containing \( q_0^2 \) represents the
effect of confining the polymer segment $r(s)$ around the primitive path through a harmonic potential. The last term in the eq. (1) arises from the constraint on the primitive path, $n(L, t) - n(0, t) = Z$, with a Lagrange multiplier $\lambda$.

The dissipative function $F$ in the Rayleighian is determined by two relative velocities – the movement of a chain segment with respect to its environment

$$\left( \frac{dr}{dt} - \frac{dR}{dt} \right)_{s:fixed} = \left( v - \frac{\partial R}{\partial n} \right)_{t} v_{n} - \left( \frac{\partial R}{\partial t} \right)_{n}$$

and the slip motion of the chain segment equilibrium reference point along the primitive path

$$\left( \frac{dR}{dt} \right)_{s:fixed} = \left( \frac{\partial R}{\partial n} \right)_{t} v_{n},$$

where the local velocity of polymer segment and the rate of the primitive path evolution are given by, respectively,

$$v = \left. \frac{\partial r}{\partial t} \right|_{s} \quad \text{and} \quad v_{n} = \left. \frac{\partial n}{\partial t} \right|_{s}.$$

Two different friction constants are then introduced to describe the dissipation corresponding to these two relative velocities, eqs. (2) and (3), as they appear in the dissipative functional $F$:

$$F = \frac{1}{2} \zeta \int_{0}^{L} ds \left( v - \frac{\partial R}{\partial n} \right) v_{n} - \left( \frac{\partial R}{\partial t} \right)_{n} + \frac{1}{2} \nu \int_{0}^{L} ds \left( \frac{\partial R}{\partial n} \right) v_{n}^{2},$$

The equations of motion are obtained from the Rayleighian $R$ through the variational equations

$$- \delta F \delta v - \delta U \delta r = 0 \quad \text{and} \quad - \delta F \delta v_{n} - \delta U \delta n = 0.$$ 

The first of equations (5) gives, after evaluating the functional derivatives,

$$\zeta \left( \frac{\partial r}{\partial t} - \frac{\partial R}{\partial n} \frac{\partial n}{\partial t} - \frac{\partial R}{\partial t} \right) + \frac{3k_{B}T}{b} \left[ \frac{\partial^{2}r}{\partial s^{2}} + q_{0}^{2}(r - R) \right] = 0.$$ 

The second variational equation (5) gives

$$\nu \left( \frac{\partial R}{\partial n} \right) \frac{\partial n}{\partial t} + \frac{3k_{B}T}{b} \frac{\partial R}{\partial n} \cdot \left[ \frac{\partial^{2}r}{\partial s^{2}} \right] = 0.$$
with the help of eq. (6).

A natural dynamical variable in our problem is not the absolute chain segment position \( r(s, t) \) but the position relative to the primitive path, the fact we have already exploited in eq. (2) for the velocity. Accordingly, we introduce the transverse excursion

\[
\tilde{r}(s, t) \equiv r(s, t) - R[n(s, t), t].
\]

(9)

The reason for using of the relative-position variable \( \tilde{r}(s, t) \) is to separate the fast and slow contributions to the dynamic equations. In particular, examine the eq. (8) for evolution of the primitive path: the equation of motion for \( n(s, t) \). If we neglect the effect of fast transverse fluctuations around the primitive path, \( \tilde{r} \), this equation transforms to:

\[
\nu \left( \frac{\partial R}{\partial n} \right)^2 \frac{\partial n}{\partial t} + \frac{3 k_B T}{b} \frac{\partial R}{\partial n} \cdot \left[ -\frac{d^2 R}{ds^2} \right] = 0.
\]

(10)

After one identifies the full derivatives

\[
\frac{dR}{ds} = \frac{\partial R}{\partial n} \frac{\partial n}{\partial s} \quad \text{and} \quad \frac{d^2 R}{ds^2} = \frac{\partial^2 R}{\partial n^2} \left( \frac{\partial n}{\partial s} \right)^2 + \frac{\partial R}{\partial n} \frac{\partial^2 n}{\partial s^2}
\]

and makes the according substitution, the part of the dynamic equation (8) describing the slow evolution of the primitive path takes the form

\[
\frac{\partial n}{\partial t} + 3 \frac{k_B T}{b \nu} \left[ \frac{\partial R}{\partial n} \cdot \frac{\partial^2 R}{\partial n^2} \left( \frac{\partial R}{\partial n} \right)^2 \left( \frac{\partial n}{\partial s} \right)^2 - \frac{\partial^2 n}{\partial s^2} \right] = 0.
\]

(11)

Note that, because \( s \) is measured in units of length, the dimensionality of \( \nu \) (and \( \zeta \)) is such that the product \( (b \nu) \) is an ordinary friction constant measured, e.g., in \( \text{J s/m}^2 \). In equilibrium, when no external deformation is applied to the system, the primitive path \( R_0 \) is given by the static solution of the eq. (11)

\[
- \frac{\partial R_0}{\partial n} \cdot \frac{\partial^2 R_0}{\partial n^2} \left( \frac{\partial R_0}{\partial n} \right)^2 \left( \frac{\partial n_0}{\partial s} \right)^2 - \frac{\partial^2 n_0}{\partial s^2} = 0.
\]

(12)

Since the equilibrium step length of the primitive path \( a \) is assumed to be fixed, one finds

\[
\left| \frac{\partial R_0}{\partial n} \right| = a \quad \rightarrow \quad \frac{\partial R_0}{\partial n} \cdot \frac{\partial^2 R_0}{\partial n^2} = 0.
\]

(13)

With this orthogonality relation, the equilibrium condition (12) is simply

\[
\frac{\partial^2 n_0}{\partial s^2} = 0 \quad \rightarrow \quad n_0(s) = \frac{Z}{L} s,
\]

(14)
a homogeneous distribution satisfying the boundary conditions \( n_0(0) = 0 \) and \( n_0(L) = Z \). Let us note here, although a more extended discussion will follow later in the paper, that a limit of completely uncrosslinked system requires a non-trivial analysis. With respect to eq. (14) one simply needs to remember that \( Z \) and \( L \) are not independent parameters, in fact a direct proportionality \( Lb = Za^2 \) holds. Therefore, even for melt of uncrosslinked chains, or in the limit \( L \to \infty \), the constant ratio \( L/Z \) is always reflecting the average degree of entanglement, giving the arc distance between the constraints.

3 The linear response

We now consider the situation when an external deformation is suddenly applied to the network, and calculate the linear dynamic stress response. The principal feature of this analysis is the computation of non-equilibrium evolution of the tube surrounding the polymer chain. First, the primitive path trajectory, \( R(n, t) \), determined by local restrictions imposed by other chains in a dense system, is assumed to be deformed affinely with the whole body:

\[
R(n, t) = \tilde{E}(t) \cdot R_0(n)
\]

with \( \tilde{E}(t) \) the deformation gradient tensor. For example, in a fixed coordinate system, \( \tilde{E} \) is given by

\[
\tilde{E}_s = \begin{bmatrix} 1 & \lambda_{12} & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{and} \quad \tilde{E}_e = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix}
\]

for simple shear deformation and elongation, respectively. Since we shall be looking for the linear response, let us identify the small strain \( \varepsilon(t) \) through \( \varepsilon_{a\beta} = \delta_{a\beta} + \epsilon_{a\beta}(t) \) for the simple shear, only one component of strain tensor is present, \( \epsilon_{a\beta} = \varepsilon u_{a}g_{\beta} \), where \( u \) is the displacement direction, \( g \) is that of a gradient and the amplitude \( \varepsilon \ll 1 \). For the extension, one obtains \( \epsilon_{a\beta} = \varepsilon_{a} \delta_{a\beta} \). If the material is assumed fully incompressible, the imposed principle extension \( \varepsilon \equiv \varepsilon_3 \ll 1 \) results in the other two diagonal elements equal to each other by rotational symmetry and \( \varepsilon_1 = \varepsilon_2 = -\frac{1}{2} \varepsilon_3 \).

It is necessary to separate the small non-equilibrium correction to the primitive path coordinate, \( n_1 \), defined by \( n(s, t) = n_0(s) + n_1(s, t) \). Substituting the affine deformation condition (13) and using the fixed-step and orthogonality relations (13), the linearised dynamic equation (11) takes the form of one-dimensional diffusion equation for a scalar function \( n_1(s, t) \):

\[
\frac{b\nu}{3k_BT} \frac{\partial n_1}{\partial t} - \frac{\partial^2 n_1}{\partial s^2} = \Psi(s, t),
\]
with the external force

$$\Psi(s, t) = \left( \frac{Z}{aL} \right)^2 \frac{\partial R_0}{\partial n} \cdot (\vec{e} \cdot \tau + \vec{e}) \cdot \frac{\partial^2 R_0}{\partial n^2} \equiv \left( \frac{L}{a^2 Z} \right) \frac{d}{ds} \left[ \frac{dR_{0a}}{ds} \epsilon_{a\beta} \frac{dR_{0\beta}}{ds} \right].$$

(18)

The diffusion equation of motion for the primitive path, eq. (17), is similar to what one frequently finds in the statistical theory of polymers, cf. [2]. The diffusion constant of the homogeneous equation is $D_n = 3k_B T / b \nu$. In our case, since we shall be considering an oscillating imposed strain and looking for a response at a given frequency $\omega$, it is convenient to introduce the equilibrium Green’s function that satisfies

$$\left( i \omega \frac{b\nu}{3k_B T} - \frac{d^2}{ds^2} \right) G(s, s') = \delta(s - s')$$

(19)

and is explicitly given by

$$G(s, s') = \frac{1}{2\gamma} \left[ e^{-\gamma|s-s'|} - \frac{1}{\sinh \gamma L} \left\{ e^{-\gamma(L-s')} \sinh \gamma s + e^{-\gamma s'} \sinh \gamma (L-s) \right\} \right],$$

(20)

with the characteristic parameter, of the inverse-length dimensionality,

$$\gamma = \sqrt{\frac{i b\nu \omega}{3k_B T}}.$$  

(21)

This Green’s function satisfies the required chain reversal symmetry and the boundary conditions

$$G(s, s') = G(s', s); \quad G(s, 0) = G(s, L) = 0.$$  

The dynamical solution of the eq. (17) with the perturbation $\Psi(s, t)$ and the boundary conditions $n_1(0, t) = n_1(L, t) = 0$ is then given by the convolution

$$n_1(s, t) = \int_0^L ds' G(s, s') \Psi(s', t).$$  

(22)

The main dynamic equation (17), with the tensile force $\Psi(s, t)$ due to effective elongation of the primitive path under deformation, lead to a non-trivial relaxation behaviour – the key result of this paper.

Once the linear correction to the primitive path is obtained $[n_1(s, t)]$ generated by an imposed strain $\vec{e}(t)$, one can compute the dynamic stress response. In a first approximation, the macroscopic stress is calculated through the correlation function along the chain (cf. [2]),

$$\sigma_{\alpha\beta} = c_x \frac{3k_B T}{b} \int_0^L ds \left< \frac{\partial r_\alpha}{\partial s} \frac{\partial r_\beta}{\partial s} \right>,$$

(23)

where $c_x$ denotes the number density of polymer chains in the network (a quantity directly related to the crosslink density). In this equation, $r(s)$ is
the absolute position of chain segment given by \( r(s, t) = R[n(s, t), t] + \tilde{r}(s, t) \). By neglecting the small fast-fluctuating variable \( \tilde{r} \) we obtain

\[
\begin{align*}
  r(s) & \approx R_0[n_0(s)] + \tilde{\varepsilon}(t) \cdot R_0[n_0(s)] + \frac{\partial R_0[n_0(s)]}{\partial n_0} n_1(s, t),
\end{align*}
\]

up to the first order in \( \tilde{\varepsilon} \). Accordingly, one obtains three distinct contributions to the average stress tensor,

\[
\sigma_{\alpha\beta} = \sigma^{(0)}_{\alpha\beta} + \sigma^{(1)}_{\alpha\beta} + \sigma^{(2)}_{\alpha\beta},
\]

corresponding to the undistorted primitive path \( R_0 \) in the eq. (24), the equilibrium response to the imposed strain \( \tilde{\varepsilon} \) and the relaxation part determined by the sliding motion of polymer segments along the tube \( n_1(s, t) \), respectively:

\[
\begin{align*}
  \sigma^{(0)}_{\alpha\beta} & = \epsilon_x \frac{3k_BT}{b} \int_0^L ds \left\langle \frac{dR_{0\alpha}}{ds} \frac{dR_{0\beta}}{ds} \right\rangle, \\
  \sigma^{(1)}_{\alpha\beta} & = \epsilon_x \frac{3k_BT}{b} \int_0^L ds \left[ \left\langle \frac{dR_{0\alpha}}{ds} \frac{dR_{0\gamma}}{ds} \right\rangle \epsilon_{\beta\gamma} + \left\langle \frac{dR_{0\beta}}{ds} \frac{dR_{0\gamma}}{ds} \right\rangle \epsilon_{\alpha\gamma} \right], \\
  \sigma^{(2)}_{\alpha\beta} & = \epsilon_x \frac{3k_BT}{b} \left( \frac{L}{Z} \right) \int_0^L ds \left( \left\langle \frac{dR_{0\alpha}}{ds} \frac{dR_{0\beta}}{ds} \partial n_1(s, t) \right\rangle \right). 
\end{align*}
\]

The first term is the small correction to the isotropic hydrostatic pressure in the system, determined by thermodynamic conditions (see, e.g. [2]); we shall not discuss it any longer here. The second contribution, \( \sigma^{(1)} \), is the equilibrium entropic response of a chain confined to the primitive path random walk to an imposed strain; this is a time-independent effect. All leading-order effects of relaxation are concentrated in the third term, \( \sigma^{(2)} \), where the movement of chain segments is calculated with the help of equation (22).

### 4 The complex modulus \( G''(\omega) \)

We now turn to particular cases of imposed small deformation and, first, consider the oscillating simple shear of the sample, cf. \( \tilde{E}_s \) of eq. (16); the corresponding small strain tensor is \( \epsilon_{\alpha\beta} = \varepsilon u_\alpha g_{\beta} e^{i\omega t} \). In order to evaluate averages in equations (26) and (27) one needs to recognize that, for the equilibrium primitive path \( R_0(n_0) \) one has, for instance,

\[
\left\langle \frac{dR_{0\alpha}}{ds} \frac{dR_{0\beta}}{ds} \right\rangle = \left( \frac{Z}{L} \right)^2 \left\langle \frac{dR_{0\alpha}}{dn} \frac{dR_{0\beta}}{dn} \right\rangle = \left( \frac{Z}{L} \right)^2 \frac{1}{3}\delta^{\alpha\beta},
\]

the pair average of the primitive path tangent vector \( t = (dR_0/dn) \), which is assumed constant for all chain segments (labeled by \( s \)) belonging to the
same step \( n \). In this way, the contour integral over the chain segments is divided into a sum over steps of the primitive path:

\[
\int_0^L \, ds = \sum_{n=1}^{L} \int_{\frac{\mathcal{L}}{Z(n)}}^{\mathcal{L}(n)} ds.
\]

For the static stress \( \overrightarrow{\sigma}^{(1)} \) this division does not matter because the integrand in (29) is not a function of \( s \). One thus obtains

\[
\sigma^{(1)}_{\alpha\beta} = c_x \frac{3k_BT}{b} \frac{Z^2}{L^3} a^2 \varepsilon(t) \left[ u_{\alpha} g_{\beta} + u_{\beta} g_{\alpha} \right] = 2c_x Z L k_BT \epsilon^{(S)}_{\alpha\beta}, \tag{29}
\]

where \( \epsilon^{(S)} \) is the symmetric part of the imposed shear and the relation \( L_b = Z a^2 \) for the end to end distances of a chain and a primitive path is used. This equilibrium stress response is characterised by the effective rubber modulus \( \mu = 2c_x Z k_BT \), proportional to the total number of constraints for the average chain. Note that because the chain of length \( L \) is considered to have \( (Z - 1) \) entanglement points and one cross link, the product \( c_x Z \) can be written as \( c_x + c_e \), involving the density of entanglements \( c_e \).

Substituting the convolution relation (22) with the external force \( \Psi(s, t) \) given by the eq. (13) and integrating by parts to switch the s-derivative, we obtain for the relaxation part of stress:

\[
\sigma^{(2)}_{\alpha\beta} = -c_x \frac{3k_BT}{b} \left( \frac{L}{aZ} \right)^2 \int_0^L \int_0^L ds ds' \partial^2 G \frac{Z}{L} \left( \frac{dR_{0a}}{dn} \frac{dR_{0b}}{dn'} \right) \epsilon_{\alpha\beta}. \tag{30}
\]

For simple shear, with vectors \( \mathbf{u} \perp \mathbf{g} \), only the four-term average gives a non-zero result, \( \langle t_{\alpha\beta} t_{\gamma\delta} \rangle = \frac{1}{16} a^4 \left[ \delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma} \right] \) at \( n = n' \). One thus obtains, after replacing the integrals of full derivatives of the Green’s function \( G(s, s') \),

\[
\sigma^{(2)}_{\alpha\beta} = -c_x \frac{2k_BT}{5b} \left( \frac{aZ}{L} \right)^2 \epsilon_{\alpha\beta} \sum_{n=1}^{Z} G(s, s') \left| \frac{\mathcal{L}}{Z(n)} \right| \frac{\mathcal{L}(n)}{Z(n-1)} \tag{31}
\]

\[
= -c_x \frac{2k_BT}{5b} \left( \frac{aZ}{L} \right)^2 \frac{L}{\xi} f(\xi, Z) \epsilon_{\alpha\beta}(t),
\]

where

\[
f(\xi, Z) = 1 - e^{-\xi} - 2e^{-Z\xi} \mathrm{csch}(Z\xi) \sinh^2 \left( \frac{\xi}{2} \right) - \frac{1}{Z} \tanh \left( \frac{\xi}{2} \right) \tag{32}
\]

and

\[
\xi = \frac{L \gamma}{Z} \equiv \frac{L}{Z} \sqrt{\frac{ib\nu \omega}{3k_BT}}. \tag{33}
\]

For a simple fixed-frequency oscillating strain input, the linear complex modulus \( G_s^*(\omega) \) for shear deformation is defined by the combination of the two relevant contributions to the stress tensor:

\[
G_s^*(\omega) = 2c_x Z k_BT \left[ 1 - \frac{1}{5} f(\xi, Z) \right]. \tag{34}
\]
As should be expected for a classical rubber, one obtains exactly the same expression for the linear modulus in response to the imposed extension $\varepsilon_{\alpha\beta} = \varepsilon_\alpha \delta_{\alpha\beta} e^{i\omega t}$. That is, an explicit calculation gives $G^*_{\varepsilon}(\omega) = G^*_{\varepsilon}(\omega)$, where the latter is produced by the sum of two contributions to the normal stress,

$$\sigma^{(1)}_{\alpha\beta} = 2c_x Z k_B T \varepsilon_0 \delta_{\alpha\beta} \Re e^{i\omega t},$$

$$\sigma^{(2)}_{\alpha\beta} = -\frac{2}{5} c_x Z k_B T \varepsilon_0 \delta_{\alpha\beta} \Re e^{i\omega t},$$

where $c_x Z = (c_x + c_e)$ and the linear diagonal extensions are related by $\varepsilon_1 = \varepsilon_2 = -\frac{1}{2} \varepsilon_3$ if the fully incompressible case is considered.

5 Discussion

In eq. (34), the complex modulus $G^*_{\varepsilon}(\omega)$ is given as a function of the complex non-dimensional parameter $\xi$, which is defined in eq. (33). Since this parameter contains the frequency $\omega$, the rest of it represents a time scale. This characteristic time, which we denote $\tau_e$, is determined by the diffusion constant $D_n$ of the homogeneous equation of motion (17) for $n_1$. For $D_n = 3k_B T/b\nu$ we obtain

$$\tau_e = \frac{1}{2D_n} \left( \frac{L}{Z} \right)^2 = \frac{b\nu}{6k_B T} \left( \frac{a^2}{b} \right)^2,$$

which is the time for a density fluctuation $n_1$ to diffuse a distance $L/Z$, a step length of the primitive path or the arc length of the polymer between the entanglements. This time scale is also found in the theory of polymer melts, cf. [2], where it separates the regimes of free Rouse dynamics and that constrained by the tube. The relation to the Rouse time is established when one recognises the product $(b\nu)$ as the proper friction coefficient: $\tau_e \approx \tau_R/Z^2$.

The parameter $\xi$ can now be expressed as $\xi = (1 + i) \sqrt{\tau e \omega}$, which also means that $\tau_e$ is one of the characteristic time scales of the complex modulus $G^*_{\varepsilon}(\omega)$. Examining the eq. (35) one can identify the second characteristic time appearing in the non-dimensional exponent $Z\xi \sim \sqrt{\tau_R \omega}$, with $\tau_R = L^2/2D_n$, the time for the slip-motion to diffuse all of the chain contour length between the crosslinks.

The following limiting cases of non-dimensional function $f(\xi, Z)$ can be easily seen from the definition (32):

| $Z \to 1$ ($c_e/c_x \ll 1$) | $Z \to \infty$ | $\xi \to 0$ | $\xi \to \infty$ |
|-----------------------------|-----------------|-------------|-----------------|
| $f(\xi, Z) \to$            | $(Z-1) \frac{\xi \sinh(\xi)}{1+\cosh(\xi)}$ | $1 - e^{-\xi}$ | $\xi(1 - \frac{1}{Z})$ |

which leads to a number of important limiting cases for the storage and loss parts of the complex modulus $G^*_{\varepsilon}(\omega) = G' + iG'':$

$$G'(\omega) \quad G''(\omega)$$

(38)
\[ \tau_{e\omega} \ll 1 \quad \Rightarrow \quad \frac{2}{5} c_x k_B T \left[ \left( Z + \frac{1}{4} \right) + \frac{1}{30} (Z - 1) Z^3 (\tau_{e\omega})^2 \right] , \quad \frac{2}{15} (Z - 1) Z c_x k_B T \tau_{e\omega} \]
\[ \tau_{e\omega} \gg 1 \quad \Rightarrow \quad 2Z c_x k_B T - \frac{1}{5} (Z - 1) c_x k_B T (\tau_{e\omega})^{-1/2} , \quad \frac{1}{5} (Z - 1) c_x k_B T (\tau_{e\omega})^{-1/2} \]

Figure 2: (a) Plots of storage modulus \( G'(\omega) \), in absolute units, taking the value \( c_x k_B T = 10^5 \text{J/m}^3 \) (a typical rubber-elastic energy scale), against \( \tau_{e\omega} \) for \( Z = 1, 2, 3, 4 \) (increasing curves). The growth of the zero-frequency value \( \mu_0 \) and a difference between it and the plateau value at \( \tau_{e\omega} \gg 1 \) are in evidence. (b) Plots of loss modulus \( G''(\omega) \), for the same set of parameters and \( Zs \), show an increasing effect of relaxation for more entangled network strands.

The storage and loss moduli \( G' \) and \( G'' \) are plotted against the reduced frequency in Figs. 2(a,b), in absolute units: taking a typical for rubbers value \( c_x k_B T \sim 10^5 \text{Pa} \). An important relation between the storage modulus value at zero frequency, the static modulus \( \mu_0 \), and that in the high-frequency limit (the “rubber plateau” value at \( \tau_{e\omega} \gg 1 \)) is characterised by a universal ratio

\[ \frac{G'_{\tau_{e\omega} \gg 1}}{G'_{\omega \to 0}} = \frac{5Z}{4Z + 1} = \frac{1 + (c_e/c_x)}{1 + \left(\frac{c_e}{c_x}\right)^{1/5}}. \]

Figure 3(a) makes this point more explicit by plotting the non-dimensional reduced storage modulus \( G'/2c_x Z k_B T \), cf. eq. (34). At \( Z \to 1 \) there is no variation of \( G' \) with frequency. There is also no dissipation in this limit of high dilution, as shown by the plots of loss factor \( \tan \delta \) in Fig. 3(b). When entanglements dominate the rubber-elastic response, at \( Z \gg 1 \) (perhaps a more realistic case in typical rubber) one finds a 20% increase in the storage modulus for deformations on a time scale shorter than \( \tau_e \). There is a substantial dissipation effect in this limit of high entanglement, with the high-frequency tail of \( \tan \delta(\omega) \) decaying rather slowly, according to the square-root asymptotic dependence, cf. eqs. (38). Note that, the characteristic time of network strand relaxation is rather short: in the reptation theory of melt dynamics one obtains the hierarchy of time scales \( \tau_e \ll \tau_R \ll \tau_d \) (the disengagement time, not present in an ideal crosslinked network) with \( \tau_e \simeq \tau_R / Z^2 \) and \( \tau_d \simeq 3Z\tau_R \). Taking just a few recent cases [18], out a large
Figure 3: (a) Plots of reduced storage modulus $G'/2c_x Z k_B T$ (non-dimen-sional) for $Z = 1, 2, 3, 5$ and 100 (decreasing curves). (b) Plots of the loss factor $\tan \delta = G''/G'$, for the same set of $Z$s (increasing curves). Note a slow decay of $\tan \delta$ (and increase of $G'$) at $\tau_e \omega \gg 1$, which is due to the square-root approach to saturation values in eqs. (38).

Figure 4: Plots of the loss factor $\tan \delta$, for $\tau_e \omega \ll 1$ and the increasing values of $Z = 2, 4, 8$ and 100. At moderate $Z$ the linear regime is observed (the calculated slope is plotted as a dashed line for each $Z$). At large $Z \gg (\tau_e \omega)^{-1/4}$ one finds an apparent square-root scaling in a wide range of low frequencies.

As a result, in some experiments, it may be difficult to access the high-frequency end of the predicted relaxation behaviour. It is, therefore, interesting to examine the asymptotic low-frequency behaviour of the loss factor for the cases of $Z \geq 1$ and $Z \gg 1$, when the number of entanglements per network strand becomes large. Equations (38) indicate that at $\tau_e \omega \rightarrow 0$ the loss factor is linear: $\tan \delta \approx (Z - 1)Z/(12Z + 3)(\tau_e \omega)$. However, as $Z$ increases so that $Z \gg (\tau_e \omega)^{-1/4}$, a different regime becomes apparent – see Fig. 4. In fact, this intermediate regime $1 \gg \tau_e \omega \gg 1/Z^4$ is best fit by an effective power-law $\tan \delta \approx 0.09(\tau_e \omega)^{0.45}$, nearly another square-root.

The present calculation produces a static limit ($\omega \rightarrow 0$) which is exactly
equal to the result of Doi and Edwards [2], derived by assuming that the deformation of the primitive path is affine and that the tensile force is constant along the chain. Such a correspondence occurs because (i) the polymer density along the tube is uniform for $\omega = 0$ and (ii) in the presence of crosslinks at the both ends of the polymer there can neither be the contour length relaxation nor the disengagement relaxation.

Ball, Doi, Edwards and Warner (BDEW) [7] derived the formula for the elastic free energy within the slilink model for entangled polymer networks, which produced the following expression of the static modulus:

$$G' = 2k_B T \left[ N_c + N_s \frac{1}{(1 + \eta)^2} \right], \quad (39)$$

where, in the notation of [7], $N_c$ and $N_s$ denote the numbers of crosslinks and slip links, respectively. An additional parameter $\eta$ characterises the amount of chain which can slip through a slilink and, according to BDEW, is given by

$$\eta \sim \frac{4}{3} \left( \frac{(N_c + N_s)\Delta}{L} \right)^2. \quad (40)$$

Here, $L/(N_s + N_c)$ is the arc distance between two slipslinks, which is analogous to $L/Z$, the equilibrium step length of the primitive path, in the present paper, and $\Delta$ is the allowed slip arc length. By identifying that $c_x = N_c$ and $c_e = N_s$ for unit volume, we can see that the limits $G'(\tau_e \omega \gg 1)$ and $G'(\tau_e \omega \ll 1)$ of the present calculation correspond to the following values of $\Delta$ in the BDEW result (39): At $\omega \to \infty$ one obtains $\Delta = 0$ (no slipping past the constraint) and at $\omega \to 0$ the slipping occurs to the amount $\Delta \sim 0.3(L/Z)$.

One should note that a limiting case of zero crosslinking density, a corresponding entangled polymer melt, is not trivially achieved by setting $c_x \to 0$ in the consistent dynamical theory. At sufficiently short times, or frequency above $\tau_0 \omega \sim 1$, the dynamic mechanical response is controlled by the chain constraints which are assumed to have the fixed density $c_e \sim Z/Ld^2$ (for $c_x \sim 1/v_{\text{chain}} = 1/Ld^2$ with $d^2$ the cross-section). This, and a higher-frequency regime when $\tau_0 \omega \geq 1$, is where the present model of sliding motion along the tube finds its application. The regime of chain disentanglement in a corresponding melt could be achieved, in a simple way, by setting phenomenologically an effectively decreasing entanglement density $c_e^{\text{eff}} \sim \exp(-t/\tau_d)$, vanishing completely at $t \gg \tau_d$ due to reptation, see [2].

To conclude, we have developed a first-approximation description of polymer dynamics in an ideal permanently crosslinked network under small deformations. This results in a general expression for linear complex modulus $G'(\omega)$, which shows a characteristic single-relaxation time behaviour in its frequency variation. The low-frequency limits of storage and loss moduli have the classical dependence on frequency, square and linear, respectively.
We obtain a rather slow, square-root variation of $G'$ and $G''$ in the limit of high frequency, at $\tau_\omega \gg 1$. The relaxation time scale $\tau_e$, resulting from the description in terms of one-dimensional diffusion of chain segments along the distorted primitive path, is a quantity closely related to the characteristic entanglement (tube formation) time in a corresponding melt, although the topological sense (and, hence, the density of) entanglements changes when the chains are permanently crosslinked into a network.

One of the principal achievements of this work is its consistent use of Rayleighian dissipative function approach. This method is naturally adopted for the treatment of fluctuations, relaxation and constraints, and could be useful for many other problems of polymer dynamics.

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FIGURE 1. (a) The scheme of tube model and the relevant variables: the polymer conformation $r(s, t)$ and the tube primitive path $R(n, t)$, where the function $n(s, t)$ specifies the position along the fixed-length path and $s$ specifies the position along the chain. In a network, the chain is permanently crosslinked at both ends of the tube. (b) The “expected” behaviour of the dynamic storage modulus $G'(\omega)$: For an uncrosslinked melt the static modulus is zero, but reaches a rubber plateau at a finite frequency due to entanglements. On increasing concentration of permanent crosslinks the static modulus $G'|_{\omega=0} = \mu_0$ increases; the plateau modulus has contributions from both crosslinks and entanglements. At a much higher frequency all curves should converge to the glass plateau, which is not the subject of this paper.

FIGURE 2. (a) Plots of storage modulus $G'(\omega)$, in absolute units, taking the value $c_x k_B T = 10^5 J/m^3$ (a typical rubber-elastic energy scale), against $\tau e\omega$ for $Z = 1, 2, 3, 4$ (increasing curves). The growth of the zero-frequency value $\mu_0$ and a difference between it and the plateau value at $\tau e\omega \gg 1$ are in evidence. (b) Plots of loss modulus $G''(\omega)$, for the same set of parameters and $Z$s, show an increasing effect of relaxation for more entangled network strands.

FIGURE 3. (a) Plots of reduced storage modulus $G'/2c_x Z k_B T$ (non-dimensional) for $Z = 1, 2, 3, 5$ and 100 (decreasing curves). (b) Plots of the loss factor $\tan \delta = G''/G'$, for the same set of $Z$s (increasing curves). Note a slow decay of $\tan \delta$ (and increase of $G'$) at $\tau e\omega \gg 1$, which is due to the square-root approach to saturation values in eqs. (38).

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