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Nonaffine Transient Network Theory of Associating Polymer Solutions

Fumihiko Tanaka* and Tsuyoshi Koga

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan

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ABSTRACT: We studied the effect of nonaffine displacement of micellar junctions on the linear viscoelasticity of transient networks formed with telechelic associating polymers. For a junction of small aggregation number, the recoil motion is large when a hydrophobic end chain dissociates from it and, hence, leads to large nonaffine fluctuations. We show that diffusive motion around the mean position of the junction gives rise to nonsymmetric deviation of the loss modulus from that of Maxwell fluid with a single relaxation time. We calculate the high-frequency shoulder and the degree of low-frequency softening in the loss modulus as functions of the parameter $D\beta_0^{-1}/na^2$, the mean radius of fluctuations during the end-chain lifetime divided by the mean-square end-to-end distance of a bridge chain. The degree of softening in the storage modulus at low frequencies is also calculated. We find that nonlinearity in the tension-elongation curve of a chain significantly affects the linear viscoelasticity due to fluctuations of the end-to-end distance.

1. Introduction

Rheological properties of the transient networks formed with associating polymers have attracted much experimental and theoretical interest in recent years. Typical examples are networks in aqueous solutions of polymers with short hydrophobic chains attached at both chain ends (telechelic polymers) such as hydrophobic ethoxylated urethane (called HEUR),[1−4] hydrophobic poly(*N*-isopropylacrylamide),[5,6] poly(propylene oxide)−poly(ethylene oxide)−poly(propylene oxide) triblock copolymers,[7−9] etc. The rheological properties of the associating polymers are commonly studied by dynamic mechanical measurements. A simple theory of the transient networks in which network junctions can break and recombine by thermal motion of the polymers and/or under applied deformation was proposed by Green and Tobolsky[10] and later developed by Lodge[11] and Yamamoto.[12]

More recently, Tanaka and Edwards[13,14] (hereafter referred to as TE) refined their theory to establish a detailed molecular-theoretical picture for the Maxwellian behavior of the dynamic mechanical moduli and also to account for the observed shear-rate dependence of the nonlinear viscosity. The fundamental assumption of TE theory is the affine deformation of the network junctions as in the classical theory of rubber elasticity; the end-to-end vector of a bridge chain connecting the neighboring micellar junctions deforms affinely to the macroscopic deformation tensor. TE derived the master curve for the dynamic moduli with a well-characterized single relaxation time $\tau \simeq \beta_0^{-1}$, where β_0 is the disengagement rate of a bridge chain from the junction. (It is assumed at this stage to be independent of the chain extension. The effect of the tension along the chain on the disengagement rate will be discussed below in detail.) It was later experimentally confirmed that, in some ideal cases, the rheological time scale is governed by the disengagement rate β_0 given by the activation type

$$\beta_0 = \omega_0 \exp(-E/k_B T), \tag{1.1}$$

where E is the activation energy for the disengagement.[2]

The affiness assumption for the transient networks is the counterpart of the old Kuhn's theory[15,16] of rubber elasticity for the networks with permanent junctions. It is, however, now well-known that the fluctuations in the position of the network junctions significantly affects the elastic moduli of the rubber.[17,18] The phantom network theory proposed by James and Guth[19,20] (referred to as JG) had been the first attempt to study rubber elasticity without affiness assumption. They derived the free energy of deformation for the networks of Gaussian chains whose only action is to deliver tension (proportional to their end-to-end distance r) at the junctions to which they are attached. Without prior assumptions concerning the displacement of the junctions, JG derived that (JG1) the mean end-to-end vectors are affine in the strain, that (JG2) their fluctuations are Gaussian, and that (JG3) these fluctuations are independent of the strain. The fluctuations of the junctions were found to be substantial. The mean-squared magnitude of the fluctuations in the chain vectors caused by them is given by

$$\langle(\Delta r)^2\rangle = (2/\phi)\,\langle r^2\rangle_0 \tag{1.2}$$

where $\langle r^2\rangle_0 = na^2$ is the mean-square end-to-end distance of a chain consisting of n statistical units of the size a, and ϕ the average functionality of the junctions, i.e., the number of chain paths connected to one junction.[18]

The main purpose of this paper is to present our study of the effect of fluctuations in the position of network junctions on the dynamic mechanical moduli on the basis of nonaffine transient network theory. As in TE, we focus on the networks made up of telechelic polymers carrying associative groups at their chain ends. The network junctions are micelles formed by the aggregation of the associative groups. In our series of papers on thermoreversible gels,[21,22] the number of associative groups in a junction is referred to as multiplicity k. The functionality of the junction is therefore related to the multiplicity by $\phi = 2k$. (We neglect loops.) Because the associative groups can be extruded from a junction and recombine to another junction either by thermal motion or by the chain tension, the junctions can diffuse from one place to another

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* Corresponding author. E-mail: ftanaka@phys.polym.kyoto-u.ac.jp.

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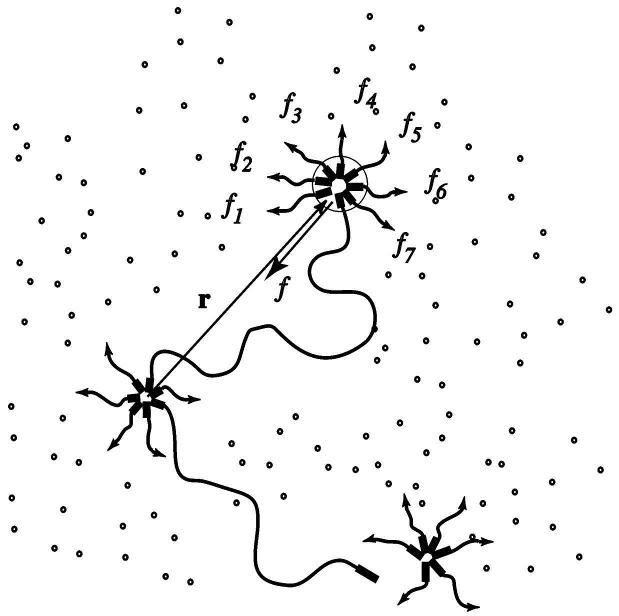

Figure 1. Bridge chain with the end-to-end vector **r**, and a dangling chain with one free end in the transient network made up of telechelic polymers. Micellar junctions make Brownian motion by the thermal force under tensions $\mathbf{f}_j$ given by the polymer chains whose ends are connected to them. The diffusion constant D of a junction depends on its aggregation number. The instantaneous vector **r** does not change affinely to the external deformation tensor.

through repetition of dissociation−association of the associative groups. Consider a bridge chain connecting two junctions. If the average diffusion constant of the network junctions is well defined and given by D, the mean square radius $\langle(\Delta r)^2\rangle$ of the displacement that a junction to which the bridge chain is attached makes before its end is dissociated is given by $D\beta_0^{-1}$. Let us compare this radius with the mean-square end-to-end distance $\langle r^2\rangle_0 = na^2$ of the bridge chain and introduce a very important dynamic parameter

$$\epsilon_D \equiv D\beta_0^{-1}/na^2 \tag{1.3}$$

If ϵ_D is small, the network is well described by the affine network of TE. But, to the contrary, if it is of the order of unity, the effect of fluctuations is large. The profile of the dynamic mechanical moduli deviates from that of Maxwell fluid with a single relaxation time. The storage modulus is softened at low frequencies, while the loss modulus loses its symmetric profile by forming a high-frequency tail. The diffusion constant D depends on the size of the junctions and, hence on their multiplicity, so that we can obtain molecular information on the aggregation number by rheological measurements. In particular, for small junctions, fluctuations are very large because there should be a large recoil at every moment when a chain end is extruded from them.

2. Theoretical Model of Nonaffine Transient Networks

Consider transient networks made up of telechelic polymers carrying short hydrophobic groups at their chain ends (Figure 1). Let ν be the number of chains in a unit volume, n the number of statistical units on a chain, and a the size of the statistical repeat unit. The total length of the chain is given by $l \equiv na$. (We neglect finiteness in the length of the end chains by assuming that they are negligibly short compared with the middle chain.) Typical polymers used in the experiments are poly(ethylene oxide) (PEO) of the molecular weight ranging from 6×10^3 to 35×10^3, carrying alkyl chains $-C_mH_{2m+1}$ ranging from $m = 12-22$,[23,24] and poly(N-isopropylacrylamide) (PNIPAm) of the molecular weight ranging from 7×10^3 to 5.9×10^4 with $m = 18$.[5,6]

There are fundamentally three kinds of chains in such networks: bridge chain (elastically effective chain), dangling chain, and loop chain. A bridge chain connects two different junctions, while a dangling chain has one free end. There may be many loops attached to the junctions, but we neglect them in this study for simplicity because their effect is only to reduce the number of chains in the network from the total number given by the polymer concentration to the effective number decided by the thermodynamic equilibrium condition.

We also neglect the free chains that are separated from the network and floating in the solution because their contribution to the viscoelasticity is small compared with that of the chains connected to the network.

Suppose the network is subjected under a time-dependent deformation described by the tensor $\hat{\lambda}(t)$. It can be a shear flow, an elongational flow, etc., but need not be specified at this stage. Let $\psi(\mathbf{r}, t)$ be the number of bridge chains per unit volume at time t whose end-to-end vector is given by **r**, and let $\phi(\mathbf{r}, t)$ be that of the dangling chain (see Figure 1). Consider a bridge chain with the end-to-end vector **r**, and let $\mathbf{f}(\mathbf{r})$ be the tension working on the micelle to which the bridge chain is connected. The tension is a function of the vector **r**. Similarly, let $\mathbf{f}_j$ (j = 1, 2, 3, ...) be the tensions given by the other chains connected to the same micelle. Then, the random motion of the micelle is described by the Langevin equation

$$m\frac{d\mathbf{v}}{dt} = -\zeta(\mathbf{v} - \bar{\mathbf{v}}(t)) + \mathbf{f} + \sum_j \mathbf{f}_j + \mathbf{R}(t) \tag{2.1}$$

where m is the mass of the micelle, ζ the friction coefficient it feels from the medium during its movements, **v** the instantaneous velocity vector of the micelle, $\bar{\mathbf{v}}(t)$ its average velocity vector, and $\mathbf{R}(t)$ the random force originating in the thermal motion of the medium. Throughout this paper, we neglect hydrodynamic interaction among the junctions caused by the local flow of the solvent medium. For the average movement of the micellar junction, we follow the assumption of JG1 described in the Introduction and assume an affine deformation

$$\bar{\mathbf{r}}(t + \Delta t; t) = \hat{\lambda}(t + \Delta t)\cdot\hat{\lambda}(t)^{-1}\mathbf{r}(t), \tag{2.2}$$

for a small time interval Δt. By taking the limit of $\Delta t \to 0$, we have

$$\bar{\mathbf{v}}(t) = \hat{\kappa}(t)\mathbf{r}(t) \tag{2.3}$$

for the average velocity,[13] where $\hat{\kappa}(t) \equiv d\hat{\lambda}(t)/dt\cdot\hat{\lambda}(t)^{-1}$. We also assume as in JG2 that the random force has Gaussian white noise

$$\langle R_\alpha(t)R_\beta(t')\rangle = 2\zeta k_B T\, \delta_{\alpha,\beta}\, \delta(t - t'), \tag{2.4}$$

where the value of ζ (friction coefficient) is independent of the deformation.

Similarly, the equation of motion of the free end of a dangling chain is given by

$$m_1\frac{d\mathbf{v}}{dt} = -\zeta_1\mathbf{v} + \mathbf{f} + \mathbf{R}_1(t) \tag{2.5}$$

where m_1 is the mass of the end group, **v** its velocity, and $\boldsymbol{R}_1(t)$ the random force acting on it. Because a dangling chain is free from macroscopic strain, the equation has no terms originating in the deformation. The mass m is related to m_1 through the multiplicity as $m = m_1(k + k')$, where k' is the number of end chains on the loops attached to the junction. As noticed above, however, we neglect the existence of loops in this study. The friction coefficient ζ of the micelle is also related to that of the end group ζ_1 through the multiplicity, but the relation depends on the structure of the micelle.

To study the time development of the two kinds of chains, let us next introduce their distribution functions. Let

$$\hat{\psi}(\mathbf{r}, t) \equiv \delta(\mathbf{r} - \hat{\mathbf{r}}(t)) \tag{2.6}$$

be the density operator for the chain vector of the bridge chains, and let

$$\hat{\phi}(\mathbf{r}, t) \equiv \delta(\mathbf{r} - \hat{\mathbf{r}}(t)) \tag{2.7}$$

be that for the dangling chains. (To show that the position vector is a dynamical variable, we indicate it by putting the hat symbol on $\mathbf{r}$.) These are operators (dynamical variables) at this stage, but eventually give their distribution functions $\psi(\mathbf{r}, t) = \langle \hat{\psi}(\mathbf{r}, t)\rangle$ and $\phi(\mathbf{r}, t) = \langle \hat{\phi}(\mathbf{r}, t)\rangle$ after the thermal average is taken. These operators obey the chain conservation law

$$\frac{\partial}{\partial t}\hat{\psi}(\mathbf{r}, t) + \nabla\cdot(\mathbf{v}(t)\hat{\psi}(\mathbf{r}, t)) = -\beta(\mathbf{r})\hat{\psi}(\mathbf{r}, t) + \alpha(\mathbf{r})\hat{\phi}(\mathbf{r}, t) \tag{2.8a}$$

$$\frac{\partial}{\partial t}\hat{\phi}(\mathbf{r}, t) + \nabla\cdot(\mathbf{v}(t)\hat{\phi}(\mathbf{r}, t)) = \beta(\mathbf{r})\hat{\psi}(\mathbf{r}, t) - \alpha(\mathbf{r})\hat{\phi}(\mathbf{r}, t) \tag{2.8b}$$

where $\beta(\mathbf{r})$ is the chain dissociation rate, i.e., the probability per unit time for an end chain to dissociate from the junction it is attached to, and $\alpha(\mathbf{r})$ is the chain recombination rate, i.e., the probability per unit time for a free end to catch a junction in the neighborhood at the position specified by the chain vector $\mathbf{r}$. (In TE, α was written as p and was assumed to be independent of the chain vector.)

We now neglect the inertial term (the acceleration term) in eq 2.1 as in the conventional treatment of the Brownian motion of polymer chains,[25,26] solve it in the form

$$\mathbf{v}(t) = \bar{\mathbf{v}}(t) + \zeta^{-1}[\mathbf{f} + \sum_j \mathbf{f}_j + \mathbf{R}(t)] \tag{2.9}$$

and substitute the result into eq 2.8a. After this procedure, we take the thermal average of the equation. The tensions $\mathbf{f}_j$ given by other members of the bridge chains connected to this junction are then averaged out and give the chemical affinity of the association−dissociation process. If the conversion from a bridge chain into a dangling chain, and vice versa, is regarded as a reversible chemical reaction, the equilibrium constant $K(\mathbf{r})$ is given by $K(\mathbf{r}) = \beta(\mathbf{r})/\alpha(\mathbf{r})$. Because the chemical affinity of the reaction is given by Gibbs's free energy $-k_BT \ln K(\mathbf{r})$, the average tension should be given by

$$\langle\sum_j \mathbf{f}_j\rangle = \nabla[k_BT \ln K(\mathbf{r})] \tag{2.10}$$

As for the random force due to thermal motion, we follow the conventional treatment of the Gaussian white noise,[27] leading to a diffusion term in the time-development equation of the distribution function. We then finally have the coupled equations for the chain distribution functions in the forms

$$\frac{\partial}{\partial t}\psi(\mathbf{r}, t) + \nabla\cdot(\bar{\mathbf{v}}(t)\psi(\mathbf{r}, t)) = D\nabla\cdot[\nabla + \mathbf{f}/k_BT + \ln K(\mathbf{r})]\psi(\mathbf{r}, t) - \beta(\mathbf{r})\psi(\mathbf{r}, t) + \alpha(\mathbf{r})\phi(\mathbf{r}, t) \tag{2.11a}$$

$$\frac{\partial}{\partial t}\phi(\mathbf{r}, t) = D_1\nabla\cdot[\nabla + \mathbf{f}/k_BT]\phi(\mathbf{r}, t) + \beta(\mathbf{r})\psi(\mathbf{r}, t) - \alpha(\mathbf{r})\phi(\mathbf{r}, t) \tag{2.11b}$$

where the diffusion constants are given by $D = k_BT/\zeta$ for a micelle, and $D_1 = k_BT/\zeta_1$ for an end chain. The characteristic time for diffusion is given by $\tau = l^2/D$ for the junctions, and $\tau_1 = l^2/D_1$ for the end chains. In these equations, we have changed the sign of the tension so that it agrees with the conventional definition. In the standard statistics of polymer chains, the elongation of a chain is expressed as a function of the force given at the chain end. In the present problem, therefore, the force given to the bridge chain from the junction must be taken as the positive direction, which is the opposite to the one we took in our equations of motion, eqs 2.1 and 2.5. In what follows, we adopt the conventional definition.

3. Solutions under No Deformation

Let us first find the solution of the coupled equations for ψ and ϕ under no deformation. Network junctions fluctuate around their average positions so that the mean velocity is zero ($\bar{\mathbf{v}}(t) = 0$). Because we have the situation of $D_1 \gg D$, the relaxation time of the free ends is much shorter than that of the micelles. We, therefore, assume, as in TE, that all the dangling chains instantaneously relax to equilibrium conformation and should fulfill the condition

$$(\nabla + \mathbf{f}/k_BT)\phi_0(\mathbf{r}, t) = \mathbf{0} \tag{3.1}$$

Hence, we find that their distribution function is given by

$$\phi_0(\mathbf{r}, t) = \nu_d(t)\Phi(\mathbf{r}) \tag{3.2}$$

where $\nu_d(t)$ is the number of dangling chains in a unit volume of the network at time t, and

$$\Phi(\mathbf{r}) \equiv C_n \exp[-\int_0^{\mathbf{r}} (\mathbf{f}/k_BT)\cdot d\mathbf{r}] \tag{3.3}$$

with C_n being the normalization constant, is the distribution function of the end-to-end vector. Such an assumption of complete relaxation for the dangling chains has recently been examined theoretically[28,29] and experimentally.[30] They found that, under a certain condition, a high-frequency tail in the loss modulus appears due to the incomplete relaxation of the dangling chains within the time interval between their dissociation and recombination. In this study, we assume the separability for the time scales τ_1 and τ due to the large size of the micellar junctions and neglect the effect of incomplete relaxation.

The tension along the chain depends on the nature of the polymer chain. If it is Gaussian, we have $\mathbf{f}/k_BT = 3\mathbf{r}/na^2$, and hence

$$\Phi(\mathbf{r}) = C_n \exp(-3r^2/2na^2) \equiv \Phi_0(\mathbf{r}) \tag{3.4}$$

where the normalization constant is given by $C_n \equiv (3/2\pi na^2)^{3/2}$ under the condition that the upper limit of the integral can be extended to infinity. If it is, for instance, a Langevin chain, we have

$$\Phi(\mathbf{r}) = C_n \exp[-\int_0^r L^{-1}(r/na)\, dr/a] \tag{3.5}$$

where $L(x) \equiv \coth x - 1/x$ is Langevin's function.[15]

Substituting the form eq 3.2 into eq 2.11b, and integrating the result over all possible values of **r**, we find

$$\mathrm{d}\nu_{\mathrm{d}}(t)/\mathrm{d}t = -\langle \alpha \rangle_0\, \nu_{\mathrm{d}}(t) + \int \beta(\mathbf{r})\psi(\mathbf{r}, t) \qquad (3.6)$$

where

$$\langle \alpha \rangle_0 \equiv \int \alpha(\mathbf{r})\Phi(\mathbf{r})\, \mathrm{d}\mathbf{r} \qquad (3.7)$$

is the average recombination rate of the free ends. The total number $\nu_{\mathrm{e}}(t)$ of the effective chains in a unit volume at time t is then given by

$$\nu_{\mathrm{e}}(t) = \nu - \nu_{\mathrm{d}}(t) \qquad (3.8)$$

due to the chain conservation law.

Consider next an aged system that has been kept quiescent for a long time so that all chains relax to the equilibrium state. We have $\phi_0(\mathbf{r}) = \nu_{\mathrm{d}}(\infty)\Phi(\mathbf{r})$, and from eq 2.11b, we find the equilibrium distribution of the effective chains in the form

$$\psi_0(\mathbf{r}) = \nu_{\mathrm{d}}(\infty)\alpha(\mathbf{r})\Phi(\mathbf{r})/\beta(\mathbf{r}) \qquad (3.9)$$

Because the ratio $\beta(\mathbf{r})/\alpha(\mathbf{r})$ is the equilibrium constant $K(\mathbf{r})$ of the "chemical reaction" between effective and dangling state, the above equation is transformed to

$$\psi_0(\mathbf{r}) = \nu_{\mathrm{d}}(\infty)C_n \exp[-\int_0^{\mathbf{r}} (\mathbf{f}/k_{\mathrm{B}}T + \nabla \ln K(\mathbf{r}))\cdot \mathrm{d}\mathbf{r}] \qquad (3.10)$$

Here, we can explicitly see that an effective chain experiences, in addition to the direct tension **f** along its contour, the chemical affinity $\nabla \ln K(\mathbf{r})$ originating in the tensions from other end chains connected to the same junction. Thus, the total force working on the end of an effective chain is given by

$$\mathbf{F}(\mathbf{r}) \equiv \mathbf{f}/k_{\mathrm{B}}T + \nabla \ln K(\mathbf{r}) \qquad (3.11)$$

Finally, by integrating eq 3.9 over all **r**, we find

$$\nu_{\mathrm{e}}(\infty)/\nu_{\mathrm{d}}(\infty) = \int \alpha(\mathbf{r})\Phi(\mathbf{r})/\beta(\mathbf{r})\, \mathrm{d}\mathbf{r} \equiv \langle \alpha\beta^{-1} \rangle_0 \qquad (3.12)$$

and hence we have

$$\nu_{\mathrm{d}}(\infty) = \nu/(1 + \langle \alpha\beta^{-1} \rangle_0) \qquad (3.13)$$

4. Linear Viscoelasticity

Consider a small oscillatory shear flow given by the deformation tensor

$$\hat{\lambda}(t) = \begin{pmatrix} 1 & \epsilon \sin(\omega t) & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad (4.1)$$

with a small amplitude ϵ. The velocity tensor is then given by

$$\hat{\kappa}(t) = \begin{pmatrix} 0 & \epsilon\omega \cos(\omega t) & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (4.2)$$

so that the average velocity of the junction is

$$\bar{\mathbf{v}}(t) = \begin{pmatrix} \epsilon\omega y \cos(\omega t) \\ 0 \\ 0 \end{pmatrix} \qquad (4.3)$$

The amplitude ϵ is assumed to be sufficiently small, and hence we can expand the chain distribution functions in powers of ϵ. Let us find the solution within the linear terms. We then have

$$\psi(\mathbf{r}, t) = \psi_0(\mathbf{r}) + \epsilon\psi_1(\mathbf{r}, t) \qquad (4.4)$$

and

$$\phi(\mathbf{r}, t) = \phi_0(\mathbf{r}) \qquad (4.5)$$

(The linear term in ϕ is zero as was shown by TE.) Substituting into eq 2.11a, we find

$$\frac{\partial \psi_1}{\partial t} + \omega y \cos(\omega t) \frac{\partial \psi_0}{\partial x} = D\nabla\cdot[\nabla + \mathbf{F}(\mathbf{r})]\psi_1 - \beta(\mathbf{r})\psi_1 \qquad (4.6)$$

for the linear term in ϵ. To solve this equation, we introduce two amplitudes A and B by assuming the form

$$\psi_1(\mathbf{r}, t) = [A(\mathbf{r}, \omega) \sin(\omega t) + B(\mathbf{r}, \omega) \cos(\omega t)]\psi_0(\mathbf{r}) \qquad (4.7)$$

for the stationary oscillatory state. Upon substitution into the above equation, we find these amplitudes should satisfy the coupled equations

$$\omega\left[A(\mathbf{r}, \omega) + y \frac{\partial \ln \psi_0}{\partial x}\right] = (D\hat{Q} - \beta(\mathbf{r}))B(\mathbf{r}, \omega) \qquad (4.8a)$$

$$-\omega B(\mathbf{r}, \omega) = (D\hat{Q} - \beta(\mathbf{r}))A(\mathbf{r}, \omega) \qquad (4.8b)$$

where the operator $\hat{Q} \equiv \nabla^2 - \mathbf{F}\cdot\nabla$ has been introduced to simplify the result. Eliminating one amplitude B from these equations, we find that A should satisfy the equation

$$[\omega^2 + (\beta(\mathbf{r}) - D\hat{Q})^2]A(\mathbf{r}, \omega) = \omega^2 y F_x \qquad (4.9)$$

To simplify the result still further, we assume the network is homogeneous. As in TE, we consider a constant recombination rate α and isotropic dissociation rate $\beta(\mathbf{r}) = \beta(r)$. The direction of the total force working on the chain end is then parallel to the end vector $\mathbf{F}(\mathbf{r}) = F(r)\mathbf{e}_r$, so that the operator $\hat{Q}$ takes the form

$$\hat{Q} = \nabla^2 - F(r)\frac{\partial}{\partial r} \qquad (4.10)$$

where $F(r) = f(r)/k_{\mathrm{B}}T + \mathrm{d} \ln \beta(r)/\mathrm{d}r$

The formal solution of eq 4.9 is given by

$$A(\mathbf{r}, \omega) = \frac{\omega^2}{\omega^2 + (\beta(r) - D\hat{Q})^2}\left(\frac{xy}{r}F(r)\right) \qquad (4.11)$$

From eq 4.8b, we then find

$$B(\mathbf{r}, \omega) = (\beta(r) - D\hat{Q})\frac{\omega}{\omega^2 + (\beta(r) - D\hat{Q})^2}\left(\frac{xy}{r}F(r)\right) \qquad (4.12)$$

5. Dynamic Mechanical Moduli

Following TE, the shear stress can be calculated by the relation

$$\sigma_{x,y}a^3 = \epsilon \int \mathrm{d}\mathbf{r}\, \frac{xy}{r} f(r)\psi_1(\mathbf{r}, t) \qquad (5.1)$$

Upon substitution of the above solution for ψ_1, we find

$$\sigma_{x,y}a^3 = \epsilon[G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t)] \qquad (5.2)$$

where

$$G'(\omega) = \int \mathrm{d}\mathbf{r}\, \frac{xy}{r} f(r)\, A(\mathbf{r}, \omega)\psi_0(\mathbf{r}) \tag{5.3a}$$

$$G''(\omega) = \int \mathrm{d}\mathbf{r}\, \frac{xy}{r} f(r)\, B(\mathbf{r}, \omega)\psi_0(\mathbf{r}) \tag{5.3b}$$

are storage and loss modulus. From the amplitude obtained above, we finally find the formal solutions for the dynamic mechanical moduli in the form

$$G'(\omega) = \int \mathrm{d}\mathbf{r}\psi_0(\mathbf{r})\left(\frac{xy}{r} f(r)\right) \frac{\omega^2}{\omega^2 + (\beta(r) - D\hat{Q})^2} \left(\frac{xy}{r} F(r)\right) \tag{5.4a}$$

$$G''(\omega) = \int \mathrm{d}\mathbf{r}\psi_0(\mathbf{r})\left(\frac{xy}{r} f(r)\right) \times (\beta(r) - D\hat{Q}) \frac{\omega}{\omega^2 + (\beta(r) - D\hat{Q})^2} \left(\frac{xy}{r} F(r)\right) \tag{5.4b}$$

Now, let us see the effect of nonaffine displacement of the junctions. At sufficiently high frequencies where $\beta \ll \omega$ holds, there is no effect on the plateau value of the storage modulus, but the loss modulus is changed to

$$G''(\omega) \simeq \frac{1}{\omega} \int \mathrm{d}\mathbf{r}\psi_0(\mathbf{r})\left(\frac{xy}{r} f(r)\right)(\beta(r) - D\hat{Q})\left(\frac{xy}{r} F(r)\right) \tag{5.5}$$

In what follows, we show the correction due to the diffusion is positive at high frequencies; nonaffine diffusion of the junction position leads to the appearance of the high-frequency shoulder in the loss modulus.

To see how the modulus is modified over all frequency ranges, let us next expand it in powers of the diffusion constant. Up to the first order, the storage and loss moduli take the form

$$G'(\omega) = G'_0(\omega) + DG'_1(\omega) + ... \tag{5.6a}$$

$$G''(\omega) = G''_0(\omega) + DG''_1(\omega) + ... \tag{5.6b}$$

where

$$G'_0(\omega) = \int \mathrm{d}\mathbf{r}\psi_0(\mathbf{r})\left(\frac{xy}{r} f(r)\right) \frac{\omega^2}{\beta(r)^2 + \omega^2} \left(\frac{xy}{r} F(r)\right) \tag{5.7a}$$

$$G''_0(\omega) = \int \mathrm{d}\mathbf{r}\psi_0(\mathbf{r})\left(\frac{xy}{r} f(r)\right) \frac{\beta(r)\omega}{\beta(r)^2 + \omega^2} \left(\frac{xy}{r} F(r)\right) \tag{5.7b}$$

are those given by the affine network theory studied by TE, and

$$G'_1(\omega) = \int \mathrm{d}\mathbf{r}\psi_0(\mathbf{r})\left(\frac{xy}{r} f(r)\right) \frac{\omega^2}{(\beta(r)^2 - \omega^2)^2} \hat{Q}_1 \left(\frac{xy}{r} F(r)\right) \tag{5.8a}$$

$$G''_1(\omega) = \omega \int \mathrm{d}\mathbf{r}\psi_0(\mathbf{r})\left(\frac{xy}{r} f(r)\right) \times \left\{-\hat{Q} \frac{1}{\beta(r)^2 + \omega^2} + \frac{\beta(r)}{(\beta(r)^2 + \omega^2)^2}\hat{Q}_1\right\} \left(\frac{xy}{r} F(r)\right) \tag{5.8b}$$

are the first-order corrections. Here, the new operator

$$\hat{Q}_1 \equiv \beta(r)\hat{Q} + \hat{Q}\beta(r) \tag{5.9}$$

has been introduced.

In Appendix A, we show detailed treatment of the operators $\hat{Q}$ and $\hat{Q}_1$. After lengthy calculation, we find that the specific forms of the moduli are given by

$$G'(\omega) = c_2 a_0 \tag{5.10a}$$

$$G''(\omega) = \frac{c_2 a_1}{\omega}[1 + D\delta_1] \tag{5.10b}$$

for high-frequency limit, and

$$G'(\omega) = c_2 \omega^2 d_0(\omega)[1 - D\delta_2(\omega)] \tag{5.11a}$$

$$G''(\omega) = c_2 \omega b_0(\omega)[1 - D\delta_3(\omega)] \tag{5.11b}$$

up to the first order of the diffusion constant over the whole range of the frequency, where

$$\delta_1 \equiv (a_2 + \lambda a_3)/a_1 \tag{5.12a}$$

$$\delta_2(\omega) \equiv [d_1(\omega) + \lambda d_2(\omega)]/d_0(\omega) \tag{5.12b}$$

$$\delta_3(\omega) \equiv [b_1(\omega) + \lambda b_2(\omega)]/b_0(\omega) \tag{5.12c}$$

are given in terms of the radial integrals in Appendix A, together with the ratio $\lambda \equiv c_{1,1}/c_2$. The numerical coefficients c_2 and $c_{1,1}$ come from the directional integral of the end-to-end vector. They are defined in Appendix A. Other coefficients from a_0 to a_3, and functions $b_i(\omega)$, $d_i(\omega)$ come from the radial integration over all possible elongations of the bridge chain ranging from 0 to l of full stretching. They are explicitly given in Appendix A. All results reduce to the affine network theory of TE when D is set to zero.

6. Numerical Results and Comparison with Experiments

For numerical calculation, we first scale all lengths by using the chain contour length $l = na$ as a unit. We then specify the dimensionless tension $\tilde{f}(\tilde{r}) \equiv f(r)a/k_BT$ as a function of the scaled end-to-end distance $\tilde{r} \equiv r/l$. Let us, as in Indei et al.,[31] assume the form

$$\tilde{f}(\tilde{r}) = 3\tilde{r}\left(1 + \frac{2}{3}A\frac{\tilde{r}^2}{1 - \tilde{r}^2}\right) \tag{6.1}$$

for the profile. The numerical amplitude A shows the effect of nonlinear stretching. If $A = 0$, the chain reduces to Gaussian. If $A = 1$, this profile agrees with that of a Langevin chain within a very high accuracy. The nonlinearity increases with the amplitude A. Hence, we can see the effect of nonlinear elongation of the bridge chains on the rheological properties of the networks by changing A.

As for the dissociation rate of the chain ends, it must be an even function of the tension by symmetry. We propose the form

$$\beta(r) = \beta_0(T)[1 + g\tilde{f}(\tilde{r})^2], \tag{6.2}$$

where $\beta_0(T)$ is the thermal dissociation rate, and g the coupling constant between the dissociation rate and the chain tension.[31] This form can be derived by applying the conventional Kramers's method[32] to calculate the first passage time required for a trapped Brownian particle to overcome the barrier height of the force potential. The coupling constant g provides a measure for how easily the end chains are extruded from the micelles they are attached to. In the work by Green and Tobolsky,[10] the dissociation rate was assumed to be independent of the end-to-end vector, and hence of the chain tension. We therefore go back to their theory by fixing $g = 0$ (referred to as GT limit). The thermal dissociation rate β_0 depends only on the temperature. In what follows, we use β_0^{-1} as a unit of time so that we may replace $\beta(r) = 1 + g\tilde{f}(\tilde{r})^2$ in the following

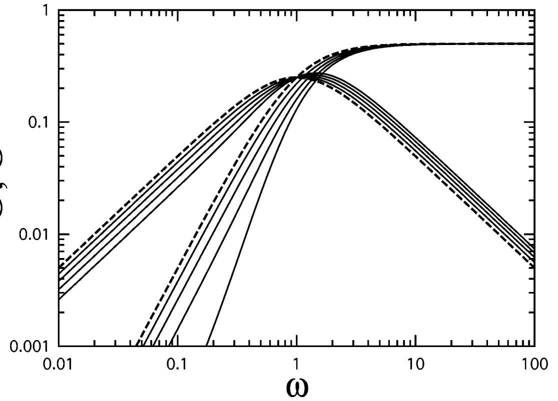

Figure 2. Complex moduli for the Gaussian chains in the GT limit. The diffusion parameter ϵ_D is changed from curve to curve ranging from 0 to 0.08 by the step 0.02.

integrals. The characteristic time for diffusion turns to $\tau = l^2/D\beta_0^{-1}$ for the junctions, and $\tau_1 = l^2/D_1\beta_0^{-1}$ for the end chains.

Looking into the n dependence of the equilibrium chain distribution function, we find $a_2/a_1 \sim a_3/a_1 \sim 1/na^2$, $b_1(\omega)/b_0(\omega) \sim b_2(\omega)/b_0(\omega) \sim 1/na^2$, and $d_1(\omega)/d_0(\omega) \sim d_2(\omega)/d_0(\omega) \sim 1/na^2$. We therefore easily confirm that the series expansions with respect to D given above are in fact the series expansion in powers of the dimensionless parameter

$$\epsilon_D \equiv D{\beta_0}^{-1}/na^2 \tag{6.3}$$

i.e., the average displacement of a junction during the lifetime of a bridge chain divided by the mean-square end-to-end distance of a free chain.

Let us first study the GT limit of $g = 0$. The dissociation rate remains constant even under the high tension. Although we study small oscillatory deformation, the effect of chain stretching is significant under such conditions. For Gaussian chains, we have explicitly

$$G'(\omega) = \nu_e(\infty)k_BT\frac{\omega^2}{1+\omega^2}\left[1 - 12\epsilon_D\frac{1}{1+\omega^2}\right] \tag{6.4a}$$

$$G''(\omega) = \nu_e(\infty)k_BT\frac{\omega}{1+\omega^2}\left[1 + 6\epsilon_D\frac{\omega^2-1}{1+\omega^2}\right] \tag{6.4b}$$

under the condition that the upper limit of the radial integrals can be extended to infinity.

In the following numerical calculation, we fix $n = 20$. (The effect of chain length is examined by changing from $n = 20$ to $n = 100$, and we found only minor differences.) We also assumed a constant recombination rate for α and fixed at $\alpha/\beta_0 = 1$. Figure 2 shows the storage and loss moduli plotted as functions of the frequency for Gaussian chains ($A = 0$). The moduli are scaled by the common factor νk_BT. The broken line shows the modulus of an affine network ($\epsilon_D = 0$). Solid lines show those for the parameter ϵ_D ranging from 0.02 to 0.08 by the step 0.02. At frequencies lower than the thermal dissociation rate, significant softening of the storage moduli due to the junction fluctuations can be seen. This is analogous to the fact that the JG phantom network theory gives lower elasticity than the affine network theory in the study of rubber elasticity.[18] In contrast, the effect of fluctuations on the loss moduli depends on the frequency. They are enhanced in the frequency region higher than the thermal dissociation rate, while they shift down in the low-frequency region. The power expansion with respect to ϵ_D breaks down when the parameter exceeds $1/12 = 0.083$ because the storage modulus becomes negative. We need calculate the second-order correction or numerically solve eqs 4.8a and b. In the high-frequency limit, however, the asymptotic form (eq 5.10b) remains valid irrespective of the value of ϵ_D.

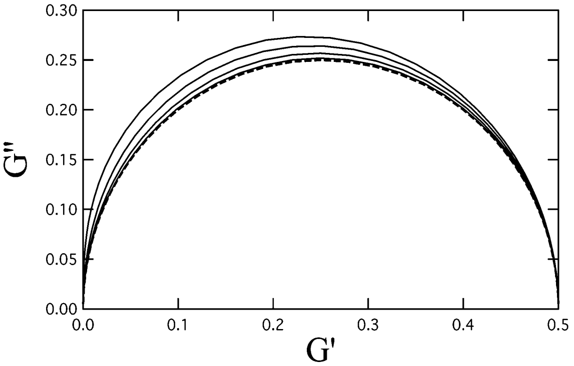

Figure 3. Cole−Cole plot of the complex moduli. There are significant upward deviations at low frequencies with the diffusion parameter.

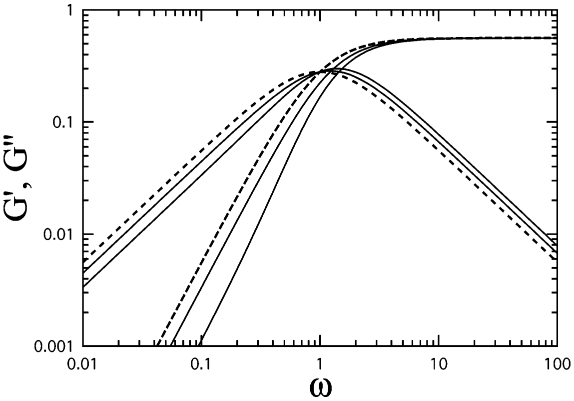

Figure 4. Complex moduli for the nonlinear chains with $A = 10$ in the GT limit. The diffusion parameter ϵ_D is changed from curve to curve, ranging from 0 to 0.04.

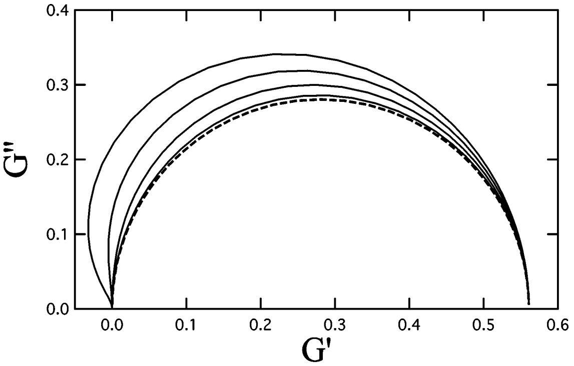

Figure 5. Cole−Cole plot of the complex moduli for $\epsilon_D = 0-0.08$. There are significant upward deviations at low frequencies with increase in the diffusion constant.

Figure 3 shows the Cole−Cole plot of the complex moduli. We can see an upward shift at low frequencies (shift of the maximum to lower frequency) from Debye's semicircle law[33] to Davidson−Cole's lemniscate law[34] with increase of ϵ_D.

Figure 4 shows more about the GT limit, but for a highly nonlinear chain with $A = 10$. Although we are studying linear viscoelasticity, the effect of nonlinear stretching of the main chain turns out to be significant. We can see a large shift of the maximum point in the low-frequency region in the Cole−Cole plot, as shown in Figure 5. This is because there are many chances for the bridge chains to be highly stretched if the fluctuations in the positions of the junctions are large.

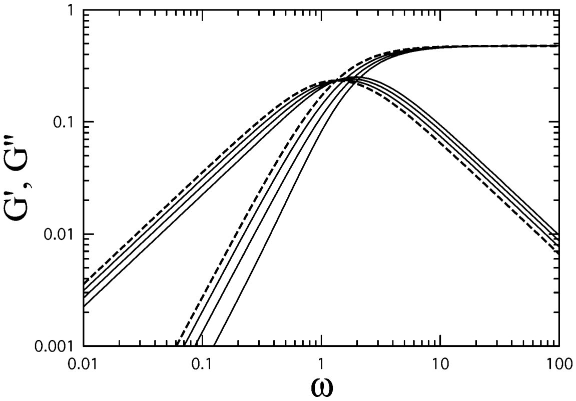

Figure 6. Complex moduli for the nonlinear chains with $A = 10$ with the coupling constant $g = 0.2$. The diffusion parameter ϵ_D is changed from curve to curve, ranging from 0 to 0.06.

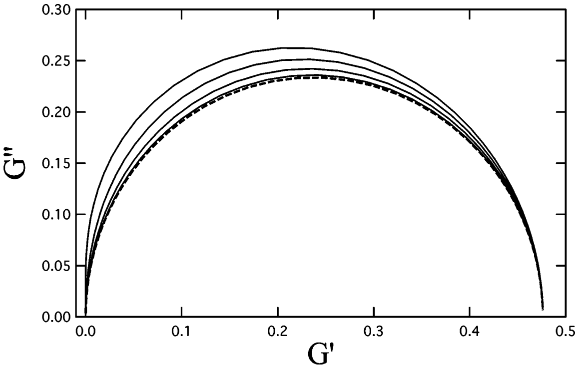

Figure 7. Cole−Cole plot of the complex moduli for a nonlinear chain. Similar upward shifts at low frequencies as in the GT limit can be seen.

Figure 6 shows the moduli for a nonlinear chain with the value $g = 0.2$ of the tension-dissociation coupling. In our previous study,[31] we calculated the initial slope of the nonlinear stationary viscosity as a function of the shear rate (referred to as "nonlinear intrinsic viscosity") and showed that $g = 0.2$ is the marginal case where the viscosity reveals shear thickening for the chains with amplitude A higher than a certain critical value around 10. Shear thinning phenomena for the chains with small A change to shear thickening as A increases above this critical value. If the coupling constant g is large, the end chains are so easily extruded from the micellar junction by the tension that the network always reveals shear thinning. In the GT limit of $g = 0$, to the contrary, chains with small A may show thickening because they can fully stretched until their ends are extruded by the shear force. Figure 7 for the chains with $A = 10$ falls on the thickening category. We find larger deviations from Maxwell's form both in storage and loss moduli with increase in the diffusion constant. The Cole−Cole plot, however, turns out to retain almost the same shape as before as in the previous cases.

7. Conclusions and Discussion

In this paper, we have eliminated the affiness assumption in the TE transient network theory and studied linear viscoelasticity of polymer networks formed with telechelic associating polymers. It was found that there is significant softening in the complex moduli at low frequencies by the fluctuations of junctions. The loss moduli show asymmetric profile with low-frequency softening and a high-frequency shoulder. The amplitudes of such shifts give a measure of nonaffine deformation in the relative positions of the network junctions. From the detailed measurements of the complex moduli, we can estimate the degree $\epsilon_D = D\beta_0^{-1}/na^2$ of the average displacement of a junction during the lifetime of a bridge chain connected to it.

We neglected the effect of loops throughout this paper. They may reduce the amplitude of the complex moduli from $\nu_e(\infty) = \nu - \nu_d(\infty)$ to $\nu_e(\infty) = \nu - \nu_d(\infty) - \nu_l(\infty)$, where $\nu_l(t)$ is the number of loops at time t. More importantly, they reduce the diffusion constant D of a micellar junction because its mass, as well as the friction with the solvent, increases with the number of loops attached to it. Information on the structure of the network junctions can therefore be obtained from detailed examination of the complex moduli.

In our recent study of shear thickening in model-associating polymer solutions,[35] we studied nonlinear stationary viscosity by the nonequilibrium molecular dynamics simulation. We found that the viscosity shows a maximum at a certain value of the shear rate where bridge chains are oriented in a direction of a fixed angle from the direction of shear and fully stretched. By three-dimensional visualization, we also observed that there are large fluctuations in the position of the junctions around the average one for all values of the shear rate. The fluctuations are particularly evident under a small shear rate where there is only small displacement of the average position. Application of the present theory to nonlinear viscosity and shear thickening is straightforward and will be reported in our forthcoming paper.

Appendix A. Derivation of the Radial and Angular Integrals

To separate the angular integral from the radial one, let us first move to the polar coordinates. The Cartesian coordinates are expressed by $x = r \sin\theta \cos\phi$, $y = r \sin\theta \sin\phi$, $z = r \cos\theta$ as usual. The $\hat{Q}$ operator is then split into

$$\hat{Q} = \hat{R} + r^{-2}\hat{\Lambda}, \tag{A.1}$$

where

$$\hat{R} \equiv \frac{\partial^2}{\partial r^2} - \left(F(r) - \frac{2}{r}\right)\frac{\partial}{\partial r} \tag{A.2}$$

is an operator acting only on functions of r, and

$$\hat{\Lambda} \equiv \frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\sin\theta\,\frac{\partial}{\partial\theta} + \frac{1}{\sin\theta}\,\frac{\partial^2}{\partial\phi^2}\right) \tag{A.3}$$

is the angular part of the Laplacian. Similarly, we have

$$\hat{Q}_1 \equiv \hat{R}_1 + \frac{2\beta(r)}{r^2}\,\hat{\Lambda} \tag{A.4}$$

for $\hat{Q}_1$ with

$$\hat{R}_1 \equiv \beta(r)\hat{R} + \hat{R}\beta(r). \tag{A.5}$$

Because we have $xy = r^2\Theta$ with $\Theta \equiv \sin^2\theta \sin\phi \cos\phi$, the angular parts in the integrals can be separated from the radial parts and easily be carried out. For instance, we have a relation

$$\hat{Q}\left(\frac{xy}{r}F(r)\right) = \Theta\hat{R}(rF(r)) + \frac{F(r)}{r}\,\hat{\Lambda}\Theta \tag{A.6}$$

Upon such decomposition, we are led to the two types of angular integrals defined by

$$c_m \equiv \int \sin\theta \, d\theta \, d\phi \, \Theta^m \tag{A.7a}$$

$$c_{l,m} \equiv (-)^m \int \sin\theta \, d\theta \, d\phi \, \Theta^l \hat{\Lambda}\Theta^m \tag{A.7b}$$

(The sign $(-)^m$ is included so that $c_{l,m}$ takes positive values.) In particular, we have $c_2 = 4\pi/15$. By noticing that Θ is an eigenfunction (d-orbit) of the operator $\hat{\Lambda}$ satisfying $\hat{\Lambda}\Theta = (-6)\Theta$, we have $\lambda = 6$.

After carrying out all angular integrals, we are left with the radial integrals. The necessary and sufficient ones to describe the dynamic mechanical moduli up to the first order of the diffusion constant are listed below:

$$a_0 = \int_0^l \mathrm{d}r\psi_0(r)(r^4 f(r)F(r)) \tag{A.8a}$$

$$a_1 = \int_0^l \mathrm{d}r\psi_0(r)(r^4\beta(r) f(r)F(r)) \tag{A.8b}$$

$$a_2 = \int_0^l \mathrm{d}r\psi_0(r)(r^4 f(r)F(r))\left(\frac{f'(r)}{f(r)} + \frac{1}{r}\right)\left(\frac{F'(r)}{F(r)} + \frac{1}{r}\right) \tag{A.8c}$$

$$a_3 = \int_0^l \mathrm{d}r\psi_0(r)(r^2 f(r)F(r)) \tag{A.8d}$$

$$b_0(\omega) = \int_0^l \mathrm{d}r\psi_0(r)\left(\frac{r^4\beta(r) f(r)F(r)}{\beta(r)^2 + \omega^2}\right) \tag{A.9a}$$

$$b_1(\omega) = \int_0^l \mathrm{d}r\psi_0(r)\left(\frac{r^4\beta(r)^2 f(r)F(r)}{[\beta(r)^2 + \omega^2]^2}\right) \times \left\{\left(1 - \frac{\omega^2}{\beta(r)^2}\right) \times \left(\frac{f'(r)}{f(r)} + \frac{1}{r}\right)\left(\frac{F'(r)}{F(r)} + \frac{1}{r}\right) + \left[\left(3 - \frac{8\beta(r)^2}{\beta(r)^2 + \omega^2}\right)\left(\frac{F'(r)}{F(r)} + \frac{1}{r}\right) + \frac{3f'(r)}{f(r)} + \frac{3}{r}\right]\left(\frac{\beta'(r)}{\beta(r)}\right) + \left(1 - \frac{4\beta(r)^2}{\beta(r)^2 + \omega^2}\right)\left(\frac{\beta'(r)}{\beta(r)}\right)^2\right\} \tag{A.9b}$$

$$b_2(\omega) = \int_0^l \mathrm{d}r\psi_0(r)(r^2 f(r)F(r))\frac{\beta(r)^2 - \omega^2}{[\beta(r)^2 + \omega^2]^2} \tag{A.9c}$$

$$d_0(\omega) = \int_0^l \mathrm{d}r\psi_0(r)\frac{r^4 f(r)F(r)}{\beta(r)^2 + \omega^2} \tag{A.10a}$$

$$d_1(\omega) = \int_0^l \mathrm{d}r\psi_0(r)\frac{r^4\beta(r) f(r)F(r)}{[\beta(r)^2 + \omega^2]^2} \times \left\{2\left(\frac{f'(r)}{f(r)} + \frac{1}{r}\right)\left(\frac{F'(r)}{F(r)} + \frac{1}{r}\right) + \left[\left(1 - \frac{8\beta(r)^2}{\beta(r)^2 + \omega^2}\right)\left(\frac{F'(r)}{F(r)} + \frac{1}{r}\right) + \frac{f'(r)}{f(r)} + \frac{1}{r}\right]\left(\frac{\beta'(r)}{\beta(r)}\right) - \frac{4\beta(r)^2}{\beta(r)^2 + \omega^2}\left(\frac{\beta'(r)^2}{\beta(r)}\right)^2\right\} \tag{A.10b}$$

$$d_2(\omega) = \int_0^l \mathrm{d}r\psi_0(r)\,\frac{2r^2\beta(r) f(r)F(r)}{[\beta(r)^2 + \omega^2]^2} \tag{A.10c}$$

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