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Constitutive equations for an elastic material with anisotropic rigid particles

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In this paper we have derived constitutive equations for an elastic material with anisotropic rigid particles. We have included a dependence on the Finger tensor **B** and the orientation tensor **Q** in the expression for the free energy of the system. With this expression for the free energy we have derived an expression for the stress tensor up to second order in both these variables. We have shown that the elastic modulus in this expression depends on **Q**, and this dependence leads to an *effective* elastic modulus that depends on the strain. We have calculated the explicit form of the equation for the stress tensor for a deformation in the xy plane with a strain equal to $-\gamma$. For fully isotropic materials with $\mathbf{Q}=\mathbf{0}$ this expression reduces to an equation containing only odd powers of γ. The inclusion of a non-zero value for the orientation tensor leads to an additional set of terms in the equation, all proportional to Q_{xy} (the xy component of the tensor **Q**), and all proportional to *even* powers of γ. We have qualitatively compared these expressions with Fourier transform (FT) rheological measurements of xanthan gels, at concentrations above and below the order-disorder transition. In FT rheometry an oscillatory deformation is applied in the nonlinear regime, and the resulting stress response is analyzed in Fourier space. In the 2% (w/w) xanthan system (disordered state) only odd harmonics were found in the stress response, whereas in the 4% (w/w) xanthan gel (ordered state) even harmonics could be detected. As predicted by our theory, the intensity of these even harmonics first increased with increasing γ, until a maximum value was reached. Beyond this maximum the intensity decreased continuously with increasing γ.

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I. INTRODUCTION

Many proteins and polysaccharides can self-assemble and form anisotropic colloidal particles, with a very long persistence length and high aspect ratio. For example, β-lactoglobulin, a globular whey protein, can form rigid particles with a persistence length of 600 nm, when heated for 10 h at 80 °C in an aqueous solution at pH 2 and an ionic strength of 13 mM. [1] These particles have a diameter equal to 2 nm, the diameter of a single globular molecule. Examples of polysaccharides that form long rigid particles are xanthan [2–7], cellulose [8], and cellulose derivatives like hydroxypropylcellulose [9].

Depending on their concentration and the strength of the interactions between them, these rodlike particles can form a viscous solution, an elastic gel, or a liquid crystalline phase. For this reason they are often used as thickening or structuring agents in foods. In the absence of external fields (electromagnetic, shear, etc.) the solutions and gels are usually isotropic from a macroscopic point of view, i.e., the orientation of the rodlike particles is completely random down to the scale of the individual particles. In contrast, liquid crystalline phases are aligned on a scale much larger than the scale of the individual particles.

Due to the highly anisotropic nature of the particles, the rheological behavior of these solutions, gels, and liquid crystalline phases is very complex and highly nonlinear. This behavior is the result of a change in the microstructure of the system caused by the applied deformation [10–12]. The anisotropic particles tend to align themselves with the direction of deformation. This coupling between (rate of) deformation and microstructure of the system is described very well on the microscopic level, for dilute, semidilute, and concentrated solutions of ideal rodlike particles [13]. Continuum theories have focused mainly on the description of liquid crystalline phases [14–19].

Little work has been done to derive a rigorous continuum theory based on nonequilibrium thermodynamics for the macroscopically isotropic solutions and gels. The shear viscosity of solutions containing anisotropic particles depends strongly on the shear rate $\dot{\gamma}$. However, classical nonequilibrium thermodynamics, as presented, for example, by de Groot and Mazur [20], does not allow such a dependence, since the shear rate is not a state variable. The dependence on the shear rate is in general incorporated by (semi)empirical closures, like, for example, the power-law model [21]. This model assumes that the viscosity is proportional to $\dot{\gamma}^n$, where n is an exponent determined from experiments. Recently, Bedeaux and Rubi [22] developed a theory for the viscosity of a solution of anisotropic particles, using the method of internal variables developed by Prigogine and Mazur [23]. They incorporated the orientation of the particles as an internal variable in the expression for the free energy. As the internal variable they chose the orientation tensor **Q**, defined by [19]

$$\mathbf{Q}(\mathbf{r},t)=\zeta\langle\overline{\overline{\mathbf{nn}}}\rangle, \tag{1}$$

where $\mathbf{n}(\mathbf{r})$ is a unit vector associated with the particles, with direction parallel to the long axis of the particles. The angular brackets $\langle\cdots\rangle$ denote a local average, and

$$\overline{\overline{\mathbf{nn}}}=\mathbf{nn}-\tfrac{1}{3}\mathbf{I} \tag{2}$$

is the traceless symmetric part of **nn**. The factor ζ is the order parameter, defined as

$$\zeta \equiv \sqrt{\frac{3}{2}}(\mathbf{Q}:\mathbf{Q})^{1/2}. \tag{3}$$

The orientation tensor is a traceless symmetric tensor, equal to zero when the material is isotropic on the macroscopic scale. In the presence of an aligning field (electromagnetic, shear, etc.) it will be nonzero. Bedeaux and Rubi showed that the incorporation of the orientation tensor in the expression for the free energy of the system leads to an expression for the traceless symmetric part of the stress tensor given by [24]

$$\boldsymbol{\sigma} = \eta \overline{\overline{\nabla \mathbf{v}}} + l\dot{\mathbf{Q}}, \tag{4}$$

where $\overline{\overline{\nabla \mathbf{v}}}$ is the traceless symmetric part of the velocity gradient, and η is the shear viscosity, a constant depending only on temperature and the concentration and orientation of the particles, but not on the shear rate. The term $\dot{\mathbf{Q}}$ denotes the material time derivative of $\mathbf{Q}$ [21]. The coefficient l has the dimension of a viscosity and is related to the rotational mobility of the particles. Bedeaux and Rubi showed that the inclusion of the second term in Eq. (4) leads to an expression for the *effective* viscosity with a dependence on the shear rate.

For liquid crystalline materials this is a well established result [19], [p. 219]. In simple shear flow of a shear-aligning nematic phase, with strong anchoring, a boundary layer develops close to the walls. Outside this boundary layer the particles are all aligned at a fixed angle with the direction of flow. Inside the layer the orientation of the particles changes progressively, as the wall is approached. The thickness of the boundary layer depends on the shear rate, and this shear dependence leads to an *effective* viscosity that depends on the shear rate. This effective viscosity can be calculated using Ericksen's law [25].

In this paper we will extend the approach outlined by Bedeaux and Rubi to gels with anisotropic particles. We will limit ourselves to purely elastic materials and neglect any viscous dissipation in the system. The more complex case of a nonlinear viscoelastic material will be treated in an upcoming paper. The constitutive equations derived here are valid for systems that are isotropic or nearly isotropic in the absence of shear, and valid for small deformations from the equilibrium state of the material. In Secs. II and III we briefly describe the material behavior of simple materials with internal structure and elastic materials without internal structure. In Sec. IV we then combine these descriptions to describe the behavior of an elastic material with internal structure. We incorporate a dependence on the Finger tensor $\mathbf{B}$ [26] and the orientation tensor $\mathbf{Q}$ in the expression for the free energy. Using this expression we derive an equation for the stress tensor up to second order in both these variables. We show that the elastic modulus in this expression depends on $\mathbf{Q}$, and this dependence leads to an *effective* elastic modulus that depends on the strain.

We calculate the explicit form of the equation for the stress tensor for a deformation in the xy plane with a strain equal to $-\gamma$. For fully isotropic materials with $\mathbf{Q}=\mathbf{0}$ this expression reduces to an equation containing only odd powers of γ. We show that the inclusion of the orientation tensor as an internal variable leads to an additional set of terms in the equation, all proportional to Q_{xy} (the xy component of the tensor $\mathbf{Q}$), and all proportional to *even* powers of γ. In Sec. V we qualitatively compare these expressions with Fourier transform (FT) rheological measurements of xanthan gels, at concentrations above and below the order-disorder transition [27]. In FT rheometry an oscillatory deformation is applied in the nonlinear regime, and the resulting stress response is analyzed in Fourier space [28,29].

II. SIMPLE MATERIAL WITH INTERNAL STRUCTURE

For a simple material with internal structure the free energy per unit mass $\hat{F}$ is given by

$$\hat{F} \equiv \hat{F}(T,\hat{V},\omega_f,\omega_s,\mathbf{Q}), \tag{5}$$

where T is the temperature, $\hat{V}$ the volume per unit mass, and ω_f and ω_s the mass fractions of fluid and particles. The absolute differential of $\hat{F}$ is given by

$$d\hat{F} = -\hat{S}dT - Pd\hat{V} + (\mu_f - \mu_s)d\omega_f + \mathbf{W}:d\mathbf{Q}, \tag{6}$$

where $\hat{S}$ is the entropy per unit mass, P the thermodynamic pressure, and μ_f and μ_s the chemical potential per unit mass of, respectively, the fluid and the particles. The second order tensor field $\mathbf{W}$ is defined as

$$\mathbf{W} \equiv \left(\frac{\partial \hat{F}}{\partial \mathbf{Q}}\right)_{T,\hat{V},\omega_f,\omega_s}. \tag{7}$$

We will now expand the free energy in terms of powers of $\mathbf{Q}$. Up to third order in $\mathbf{Q}$ the free energy is given by [19]

$$\begin{aligned} &\hat{F}(T,\hat{V},\omega_s,\omega_f,\mathbf{Q}) \\ &\quad = \hat{F}^0(T,\hat{V},\omega_s,\omega_f) + \tfrac{1}{2}\alpha(T,\hat{V},\omega_s,\omega_f)\mathbf{Q}:\mathbf{Q} \\ &\quad + \tfrac{1}{3}\beta(T,\hat{V},\omega_s,\omega_f)\mathrm{tr}(\mathbf{Q}\cdot\mathbf{Q}\cdot\mathbf{Q}) + O(\mathbf{Q}^4), \end{aligned} \tag{8}$$

where α and β are constants that depend only on temperature, $\hat{V}$, and the mass fractions of particles and fluid, but not on $\mathbf{Q}$. From Eqs. (7) and (8) we find that the tensor $\mathbf{W}$ is given by

$$\mathbf{W} = \alpha(T,\hat{V},\omega_s,\omega_f)\mathbf{Q} + \beta(T,\hat{V},\omega_s,\omega_f)\overline{\overline{\mathbf{Q}\cdot\mathbf{Q}}} + O(\mathbf{Q}^3), \tag{9}$$

where the double overbar again denotes the symmetric traceless part of a tensor.

III. ELASTIC MATERIAL WITHOUT INTERNAL STRUCTURE

The free energy of an elastic material depends on the state of deformation of the material. There are various measures to describe the state of deformation of a material. The simplest measures are the deformation gradient $\mathbf{F}$ and its inverse $\mathbf{E}$ defined by [26]

$$\mathbf{F} \equiv \frac{\partial \mathbf{r}}{\partial \overline{\mathbf{r}}}, \quad \mathbf{E} \equiv \frac{\partial \overline{\mathbf{r}}}{\partial \mathbf{r}}, \tag{10}$$

where $\overline{\mathbf{r}}$ denotes the position of a material particle in the reference configuration, and $\mathbf{r}$ is the position of that particle in the current configuration. Based on these two tensors we can define the right Cauchy-Green tensor $\mathbf{C}$ and the Finger tensor $\mathbf{B}$ as [26]

$$\mathbf{C} \equiv \mathbf{F}^T \cdot \mathbf{F}, \quad \mathbf{B} \equiv \mathbf{E} \cdot \mathbf{E}^T. \tag{11}$$

These tensors are symmetric positive definite, and reduce to the unit tensor when the deformation is a rigid body motion (translation plus rotation). For a purely elastic material without internal structure the free energy is assumed to be given by

$$\hat{F} \equiv \hat{F}(T, \hat{V}, \omega_f, \omega_s, \mathbf{B}). \tag{12}$$

We could have chosen any of the other strain measures without loss of generality. The predictions of the model will, however, vary with the choice of strain measure. Both $\mathbf{F}$ and $\mathbf{E}$ predict zero first and second normal stresses. $\mathbf{C}$ and $\mathbf{B}$ predict nonzero normal stresses and based on experimental evidence appear to be more plausible choices for the strain measure [26]. From Eq. (12) we find that the absolute differential of $\hat{F}$ is given by

$$d\hat{F} = -\hat{S}dT - Pd\hat{V} + (\mu_f - \mu_s)d\omega_f + \boldsymbol{\sigma}:d\mathbf{B}, \tag{13}$$

where the stress $\boldsymbol{\sigma}$ is defined as

$$\boldsymbol{\sigma} \equiv \left(\frac{\partial \hat{F}}{\partial \mathbf{B}} \right)_{T, \hat{V}, \omega_f, \omega_s}. \tag{14}$$

If we expand $\hat{F}$ in terms of $\mathbf{B}$, we find up to second order in $\mathbf{B}$

$$\begin{aligned} &\hat{F}(T, \hat{V}, \omega_s, \omega_f, \mathbf{B}) \\ &\quad = \hat{F}^0(T, \hat{V}, \omega_s, \omega_f) + \tfrac{1}{2}\mathbf{G}(T, \hat{V}, \omega_s, \omega_f) \odot^4 \mathbf{B}\mathbf{B} + O(\mathbf{B}^3). \end{aligned} \tag{15}$$

Note that there is no first order term in this expression. After differentiation with respect to $\mathbf{B}$ such a linear term would give a contribution to the stress equal to a constant times $\mathbf{I}$, the three-dimensional unit tensor. This term will be nonzero even if the deformation is zero, and constitutes a residual stress in the material. We will assume here that, in the absence of external fields and in the absence of any internal structure, all residual stresses in the material are zero. Hence terms linear in $\mathbf{B}$ must be identical to zero in the expression for $\hat{F}$. The symbol $\odot^4$ denotes a fourfold contraction. The fourth order tensor $\mathbf{G}$ is given by

$$\mathbf{G}(T, \hat{V}, \omega_s, \omega_f) \equiv \left(\frac{\partial^2 \hat{F}}{\partial \mathbf{B}^2} \right)_{T, \hat{V}, \omega_s, \omega_f}. \tag{16}$$

We see that $\mathbf{G}$ cannot depend directly on $\mathbf{B}$. For an isotropic medium we find that

$$\mathbf{G} \equiv 2G(T, \hat{V}, \omega_s, \omega_f)\boldsymbol{\Delta}_{ijkl}, \tag{17}$$

where G is the scalar elastic modulus of the material, and $\boldsymbol{\Delta}_{ijkl}$ is a fourth order symmetric traceless isotropic tensor given by [30]

$$\boldsymbol{\Delta}_{ijkl} \equiv \tfrac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - \tfrac{1}{3}\delta_{ij}\delta_{kl}. \tag{18}$$

Combining Eqs. (15), (17), and (18) we find that for an elastic material without internal structure $\hat{F}$ reduces to

$$\begin{aligned} \hat{F}(T, \hat{V}, \omega_s, \omega_f, \mathbf{B}) &= \hat{F}^0(T, \hat{V}, \omega_s, \omega_f) + G(T, \hat{V}, \omega_s, \omega_f)\mathbf{B}:\mathbf{B} \\ &\quad - \tfrac{1}{3}G(T, \hat{V}, \omega_s, \omega_f)(\operatorname{tr}\mathbf{B})^2 + O(\mathbf{B}^3). \end{aligned} \tag{19}$$

From Eqs. (14) and (19) we find that $\boldsymbol{\sigma}$ is given by

$$\boldsymbol{\sigma} = 2G\mathbf{B} - \tfrac{2}{3}G(\operatorname{tr}\mathbf{B})\mathbf{I} + O(\mathbf{B}^2). \tag{20}$$

If we specifically include a dependence on $\operatorname{tr}\mathbf{B}$ in the expression for $\hat{F}$ we get an additional term in this expression equal to $\frac{1}{2}K(\operatorname{tr}\mathbf{B})^2$, with $K(T, \hat{V}, \omega_s, \omega_f)$ the elastic compressibility modulus, and the equation for $\boldsymbol{\sigma}$ reduces to the familiar result [31]

$$\boldsymbol{\sigma} = 2G\mathbf{B} + (K - \tfrac{2}{3}G)(\operatorname{tr}\mathbf{B})\mathbf{I} + O(\mathbf{B}^2). \tag{21}$$

IV. ELASTIC MATERIAL WITH INTERNAL STRUCTURE

A. Material behavior

We will now combine the material descriptions presented in the previous two sections to describe the material behavior of an elastic material with anisotropic particles. We will assume that the free energy of such a material is given by

$$\hat{F} \equiv \hat{F}(T, \hat{V}, \omega_f, \omega_s, \mathbf{B}, \mathbf{Q}). \tag{22}$$

Using this expression we find that the absolute differential of $\hat{F}$ is given by

$$d\hat{F} = -\hat{S}dT - Pd\hat{V} + (\mu_f - \mu_s)d\omega_f + \boldsymbol{\sigma}:d\mathbf{B} + \mathbf{W}:\mathbf{Q}. \tag{23}$$

If we now make a combined expansion of $\hat{F}$ in terms of $\mathbf{B}$ and $\mathbf{Q}$ we find up to second order in $\mathbf{B}$ and $\mathbf{Q}$

$$\begin{aligned} &\hat{F}(T, \hat{V}, \omega_s, \omega_f, \mathbf{B}, \mathbf{Q}) \\ &\quad = \hat{F}^0(T, \hat{V}, \omega_s, \omega_f) + \tfrac{1}{2}K(\operatorname{tr}\mathbf{B})^2 + \tfrac{1}{2}\mathbf{G} \odot^4 \mathbf{B}\mathbf{B} \\ &\qquad + \tfrac{1}{2}\mathbf{L}_{BQ} \odot^4 (\mathbf{B}\mathbf{Q} + \mathbf{Q}\mathbf{B}) + \tfrac{1}{2}\alpha\mathbf{Q}:\mathbf{Q} + O(\mathbf{B}^3, \mathbf{Q}^3), \end{aligned} \tag{24}$$

where $\mathbf{L}_{BQ}$ is a fourth order tensor field defined by

$$\mathbf{L}_{BQ}(T, \hat{V}, \omega_s, \omega_f) = \left(\frac{\partial^2 \hat{F}}{\partial \mathbf{B} \partial \mathbf{Q}} \right)_{T, \hat{V}, \omega_s, \omega_f}. \tag{25}$$

For a nearly isotropic material and small deformations we may assume that $\mathbf{G}$ is still given by Eq. (17), with one important modification: the scalar elastic modulus G now depends on $\mathbf{Q}$, and is given by $G=G(T,\hat{V},\omega_s,\omega_f,\mathbf{Q})$. For nearly isotropic materials and small deformations $\mathbf{L}_{BQ}$ is given by

$$\mathbf{L}_{BQ}(T,\hat{V},\omega_s,\omega_f)=L_{BQ}(T,\hat{V},\omega_s,\omega_f)\boldsymbol{\Delta}_{ijkl}, \tag{26}$$

where L_{BQ} is a scalar, and $\boldsymbol{\Delta}_{ijkl}$ is again the fourth order tensor field defined by Eq. (18). For larger deformations, when $\mathbf{Q}$ is no longer small, $\mathbf{G}$ and $\mathbf{L}_{BQ}$ depend on the degree of alignment, and Eq. (17) has to be replaced by

$$\begin{aligned}\mathbf{G}=G_1\boldsymbol{\Delta}_{ijkl}+G_2(Q_{ij}\delta_{kl}+Q_{ik}\delta_{jl}+Q_{il}\delta_{jk}+Q_{jk}\delta_{il}+Q_{jl}\delta_{ik}\\ +Q_{kl}\delta_{ij})+G_3(Q_{ij}Q_{kl}+Q_{ik}Q_{jl}+Q_{il}Q_{jk}).\end{aligned} \tag{27}$$

The material is then characterized by three scalar elastic constants instead of one. A similar equation holds for the tensor $\mathbf{L}_{BQ}$. Here we will assume that $\mathbf{B}$ and $\mathbf{Q}$ are sufficiently small for Eqs. (17) and (26) to hold. Substituting these equations in the expression for $\hat{F}$, we find

$$\begin{aligned}\hat{F}(T,\hat{V},\omega_s,\omega_f,\mathbf{B},\mathbf{Q})=\hat{F}^0(T,\hat{V},\omega_s,\omega_f)+G\mathbf{B}:\mathbf{B}\\ +(\tfrac{1}{2}K-\tfrac{1}{3}G)(\operatorname{tr}\mathbf{B})^2+L_{BQ}\mathbf{B}:\mathbf{Q}\\ +\tfrac{1}{2}\alpha\mathbf{Q}:\mathbf{Q}+O(\mathbf{B}^3,\mathbf{Q}^3).\end{aligned} \tag{28}$$

Using Eqs. (7) and (14) we find that for an elastic material with anisotropic particles the tensors $\boldsymbol{\sigma}$ and $\mathbf{W}$ are given by (up to first order in $\mathbf{B}$ and $\mathbf{Q}$)

$$\boldsymbol{\sigma}=2G\mathbf{B}+(K-\tfrac{2}{3}G)(\operatorname{tr}\mathbf{B})\mathbf{I}+L_{BQ}\mathbf{Q}+O(\mathbf{Q}^2,\mathbf{B}^2), \tag{29}$$

$$\mathbf{W}=\alpha\mathbf{Q}+L_{BQ}\mathbf{B}+O(\mathbf{B}^2,\mathbf{Q}^2). \tag{30}$$

When comparing these equations to Eqs. (9) and (21) in Secs. II and III we see that in the expression for the stress tensor, apart form a linear dependence on $\mathbf{B}$, we now also have a linear dependence on $\mathbf{Q}$. The converse holds for the tensor $\mathbf{W}$. Note also the similarities between Eq. (29) and the expression for a viscous solution, given by Eq. (4). Using the expression for $\mathbf{G}$ given in Eq. (27) and setting $\mathbf{L}_{BQ}$ to zero would lead to a slightly more complicated expression for the stress tensor, which is basically the analog for elastic gels with anisotropic particles of Ericksen's transversely isotropic fluid model for a flowing nematic [14].

The inclusion of the linear dependence on $\mathbf{Q}$ in the expression for the stress leads to an effective elastic modulus that depends on the deformation. We will illustrate this for a simple shear deformation in the xy plane by $-\gamma$.

B. Simple shear with isotropy in *z* direction

For a simple shear deformation in the xy plane by $-\gamma$, in a system that is isotropic in the z direction, we find that the xy component of the stress tensor is given by (Appendix B)

$$\sigma_{xy}=2G\gamma+L_{BQ}Q_{xy}. \tag{31}$$

For the first and second normal stress differences we find

$$\sigma_{xx}-\sigma_{yy}=2G\gamma^2+L_{BQ}(Q_{xx}-Q_{yy}), \tag{32}$$

$$\sigma_{yy}-\sigma_{zz}=L_{BQ}(Q_{yy}+\tfrac{1}{3}). \tag{33}$$

We see that our model predicts nonzero first and second normal stress differences that depend on the orientation of the particles. We also see that the model predicts a positive second normal stress difference. In a strain controlled experiment we apply a strain γ to the sample and measure the resulting stress. From this we determine the effective elastic moduli by simply dividing the stress by the strain. Applying this procedure to our model, we find

$$G_{eff}\equiv\frac{\sigma_{xy}}{2\gamma}=G+\frac{L_{BQ}Q_{xy}}{2\gamma}, \tag{34}$$

$$G_{eff}^{\Psi_1}\equiv\frac{\sigma_{xx}-\sigma_{yy}}{2\gamma^2}=G+\frac{L_{BQ}(Q_{xx}-Q_{yy})}{2\gamma^2}, \tag{35}$$

$$G_{eff}^{\Psi_2}\equiv\frac{\sigma_{yy}-\sigma_{zz}}{2\gamma^2}=\frac{L_{BQ}(Q_{yy}+\frac{1}{3})}{2\gamma^2}. \tag{36}$$

We see that all the effective elastic moduli depend on γ through the dependence on the orientation tensor. We also see that the model predicts that for $\mathbf{Q}\neq\mathbf{0}$ the Lodge-Meissner rule $(G_{eff}/G_{eff}^{\Psi_1}=1)$ [32,33] will no longer hold.

C. Higher order terms

The expressions for $\boldsymbol{\sigma}$ and $\mathbf{W}$ derived in the preceding section were linear in $\mathbf{B}$ and $\mathbf{Q}$, and are (quasi)linear models (quasilinear since $\mathbf{B}$ contains terms proportional to γ^2 in its diagonal components). To investigate the non-linear behavior of these materials we will investigate the higher order contributions to the stress tensor. We find that the tensor $\boldsymbol{\sigma}$ is given up to second order in $\mathbf{B}$ and $\mathbf{Q}$ by (Appendix A)

$$\begin{aligned}\boldsymbol{\sigma}=2G\mathbf{B}+(K-\tfrac{2}{3}G)(\operatorname{tr}\mathbf{B})\mathbf{I}+L_{BQ}\mathbf{Q}\\ +L_{BBB}[\overline{\mathbf{B}\cdot\mathbf{B}}-\tfrac{1}{3}(\operatorname{tr}\mathbf{B})\mathbf{B}-\tfrac{1}{6}(\mathbf{B}:\mathbf{B})\mathbf{I}+\tfrac{1}{18}(\operatorname{tr}\mathbf{B})^2\mathbf{I}]\\ +\tfrac{1}{2}L_{BQQ}\overline{\mathbf{Q}\cdot\mathbf{Q}}+L_{BBQ}\overline{\mathbf{B}\cdot\mathbf{Q}}-\tfrac{1}{6}L_{BBQ}[(\operatorname{tr}\mathbf{B})\mathbf{Q}+(\mathbf{B}:\mathbf{Q})\mathbf{I}]\\ +\tfrac{1}{12}L_{BQQ}(\mathbf{Q}:\mathbf{Q})\mathbf{I}+O(\mathbf{Q}^3,\mathbf{B}^3),\end{aligned} \tag{37}$$

where the single overbar denotes the symmetric part of a tensor. From Eq. (9) we see that the tensor $\mathbf{W}$ is now given by

$$\begin{aligned}\mathbf{W}=(\alpha-\tfrac{1}{6}L_{BQQ}\operatorname{tr}\mathbf{B})\mathbf{Q}+\beta\overline{\overline{\mathbf{Q}\cdot\mathbf{Q}}}+L_{BQQ}\overline{\overline{\mathbf{Q}\cdot\mathbf{B}}}\\ +\tfrac{1}{2}L_{BBQ}(\overline{\overline{\mathbf{B}\cdot\mathbf{B}}}-\tfrac{1}{3}(\operatorname{tr}\mathbf{B})\overline{\overline{\mathbf{B}}}).\end{aligned} \tag{38}$$

For a simple shear deformation in the xy plane by $-\gamma$, in a system that is isotropic in the z direction, we find from Eqs. (37) and (B3)–(B5) that the xy component of the stress tensor is now given by

$$\sigma_{xy} = \sigma_{xy}^0 + (2G + L_{BBB} + \tfrac{1}{6}L_{BBQ})\gamma + \tfrac{2}{3}L_{BBB}\gamma^3 + \tfrac{1}{3}L_{BBQ}Q_{xy}\gamma^2, \tag{39}$$

where

$$\sigma_{xy}^0 \equiv (L_{BQ} + \tfrac{1}{2}L_{BBQ})Q_{xy} + \tfrac{1}{2}L_{BQQ}(\overline{\mathbf{Q}\cdot\mathbf{Q}})_{xy}. \tag{40}$$

For a fully isotropic system without internal structure $\mathbf{Q} = \mathbf{0}$, and this expression for the stress reduces to

$$\sigma_{xy} = (2G + L_{BBB})\gamma + \tfrac{2}{3}L_{BBB}\gamma^3. \tag{41}$$

We see that this expression contains only odd powers of γ. Adding higher order terms in $\mathbf{B}$ in the expression for $\hat{F}$ would result in additional terms proportional to $\gamma^5, \gamma^7, \ldots$. In an oscillatory deformation these odd powers of γ generate higher harmonics in the stress response. These harmonics can be studied with Fourier transform rheometry [28,29], where they appear in the frequency spectrum of the stress as multiples of the applied frequency. When the material behavior of a system is described by a constitutive equation containing only odd powers of γ, we should see only odd multiples of the applied frequency in the spectrum. However, in some FT experiments we sometimes also see small even harmonics in the frequency spectrum. The intensity of these harmonics is in general much lower than the intensity of the odd harmonics. In our equation for the stress tensor we see that for elastic systems with anisotropic particles the incorporation of a dependence on both $\mathbf{B}$ and $\mathbf{Q}$ in the expression for the free energy results in a term proportional to $\gamma^2 Q_{xy}$ in the expression for the stress tensor. Higher order corrections to the equations would result in the addition of (among others) a term proportional to $\overline{\mathbf{B}\cdot\mathbf{B}\cdot\mathbf{Q}}$. The xy component of this term is equal to

$$(\overline{\mathbf{B}\cdot\mathbf{B}\cdot\mathbf{Q}})_{xy} = \tfrac{1}{2}(2 + 4\gamma^2 + \gamma^4)Q_{xy} + \tfrac{1}{6}(\gamma^3 + 2\gamma). \tag{42}$$

We see that the mixed terms containing both $\mathbf{B}$ and $\mathbf{Q}$ generate terms in the equation for the stress tensor proportional to $\gamma^2 Q_{xy}, \gamma^4 Q_{xy}, \ldots$, i.e., all proportional to Q_{xy} and even powers of γ. In a FT rheometry experiment these terms would generate even harmonics in the stress response. The model presented in this paper therefore predicts the occurrence of small even harmonics in the stress response.

When the deformation is small the material will be nearly isotropic, and Q_{xy} will be small. Terms like $\gamma^2 Q_{xy}$ and $\gamma^4 Q_{xy}$ then amount to small even-power corrections to the odd-power behavior of the stress response. This implies that the even harmonics will have a lower intensity than the odd harmonics. When γ increases, Q_{xy} will first increase as a result of an increase of the alignment of the particles in the xy plane. After reaching a maximum value Q_{xy} will start to decrease with increasing γ, since the particles will align themselves more and more with the direction of the deformation (if the deformation is in the x direction, $n_x \to 1$ and $n_y \to 0$ as $\gamma \to \infty$, and therefore $Q_{xy} \to 0$ as $\gamma \to \infty$). So our model predicts that the intensity of the even harmonics should first increase with increasing γ, until a maximum intensity is reached. Beyond this maximum the intensity should decrease with increasing γ. This in contrast with the intensity of the odd harmonics, which increases continuously with increasing γ.

V. FT RHEOMETRY EXPERIMENTS ON XANTHAN GELS

To test some of the predictions of our constitutive model we have performed FT rheometry experiments on xanthan gels above and below the order-disorder transition [27]. Xanthan is an ultrahigh molecular weight anionic exopolysaccharide. It has a backbone consisting of β-1,4 linked glucose units with an anionic trisaccharide linked to every second glucose unit [34]. The trisaccharide contains pyruvate and acetate groups. Xanthan forms a double helix [2–5] with a persistence length of 120 nm [6,7]. For high molecular weight xanthan the contour length is larger than the persistence length and the xanthan helix can be considered a semiflexible polymer [27]. Depending on ionic strength, temperature, and xanthan concentration, the semiflexible polymers can self-assemble and form small liquid crystalline domains. In an aqueous solution with 0.1*M* NaCl, and at a temperature of 25 °C an order-disorder transition occurs at about 3% (w/w) xanthan [27]. Below this critical concentration the system is fully isotropic; above the critical concentration the system forms a solution of anisotropic crystalline particles in an isotropic continuous phase. At a concentration slightly above 8% a second transition occurs, from a solution of anisotropic particles to a nematic phase.

Our experiments were performed with solutions of 2% (w/w) and 4% (w/w) xanthan in an aqueous solution with 0.1*M* NaCl. The 2% solution is below the first order-disorder transition, and hence fully isotropic. For this case our theory predicts that we should not find any even harmonics in the Fourier spectrum of the stress response. The 4% solution is above the order-disorder transition and hence contains anisotropic colloidal particles. The frequency spectrum should contain both even and odd harmonics. The theory further predicts that the intensity of the even harmonics should be lower than the intensity of the odd harmonics. In addition the intensity of the even harmonics should first increase to a maximum as γ increases, and beyond this maximum decrease continuously with increasing γ.

The xanthan used in our experiments was a commercially purified product called Keltrol T (Batch CH008, Lot 68440) obtained from Danby Chemie BV (Danby Chemie B.V., Leidsestraat 106-108, 1017 PG Amsterdam, the Netherlands). The experiments were performed on an ARES (Rheometric Scientific) with parallel plate geometry. The diameter of the plates was 38 mm, the gap width was 0.5 mm, and the applied frequency was 1 Hz. Strains γ were applied with amplitudes of 0.1, 0.4, 0.7, 1.0, 1.5, 2.5, 5.0, and 10.0. The elastic modulus was determined after an equilibration time of 100 s. The stress signal was sent directly to a LT224 Waverunner 200 MHz digital oscilloscope (LeCroy), with four channels and fast Fourier transform (FFT) wave analyzer option. To obtain the FT spectrum of the stress response a discrete complex half-sided magnitude fast Fourier transform was applied to the real data set.

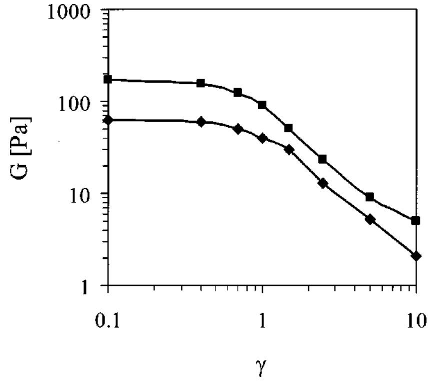

FIG. 1. Elastic modulus G as a function of strain amplitude γ for the 2% (w/w) xanthan sample (diamonds) and the 4% (w/w) xanthan sample (squares). The applied frequency was equal to 1 Hz.

Figure 1 shows the elastic modulus of both solutions. Up to an amplitude of about 0.4 the response of the material is linear. Beyond this amplitude the response is nonlinear, and the value of the elastic modulus has dropped by almost two orders of magnitude when an amplitude of 10 is reached. In Fig. 2 we see a spectrum of the stress response for the 4% (w/w) xanthan system at a strain amplitude of 1.0. Apart from the odd harmonics at 1, 3, 5, 7, and 9 Hz, we also see smaller even harmonics at 2, 4, 6, and 8 Hz. These even harmonics could not be detected in the 2% (w/w) xanthan sample. Figure 3 shows the normalized intensities for the odd harmonics at 3, 5, and 7 Hz. The normalized intensity is defined by I_n/I_1, were I_n is the intensity of the nth harmonic. We see that the normalized intensity of the odd harmonics increases continuously with increasing strain amplitude. Figure 4 shows the normalized intensity for the even harmonics at 2, 4, and 6 Hz. For the harmonics at 4 and 6 Hz we see that the normalized intensity first increases as γ increases, and reaches a maximum at strain amplitudes between 1.0 and 1.5. Beyond this value for the strain the intensity decreases continuously for increasing γ. This behavior is even more obvious when the intensity of the even harmonics is normalized by dividing by I_2, the intensity of the first even harmonic (Fig. 5). The curve for the harmonic at 2 Hz in Fig. 4 has a slightly different shape from those at 4 and 6 Hz. Apparently at a strain amplitude of 0.1 the second harmonic was already past its maximum value. The behavior of the even harmonics in Figs. 4 and 5 is exactly as predicted by our theory, and supports our assertion that the even harmonics are the result of a change in the structure of the material because of the alignment of the anisotropic colloidal particles in the system.

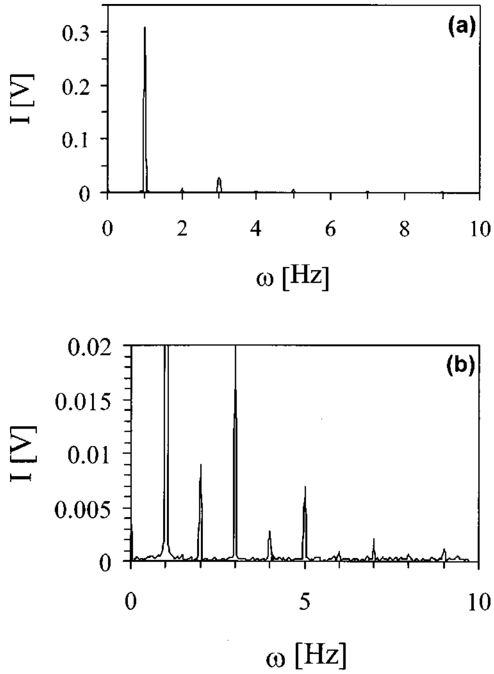

FIG. 2. (a) Frequency spectrum of the stress response of a 4% (w/w) xanthan sample at a strain amplitude of $\gamma = 1$, and an applied frequency of 1 Hz. (b) Magnification of (a).

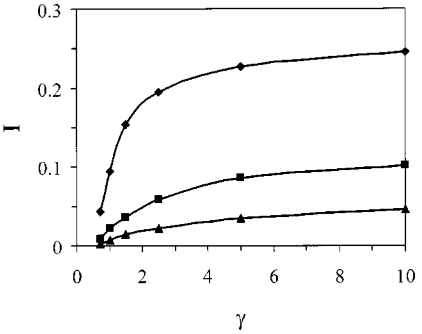

FIG. 3. Normalized intensities for the third (diamonds), fifth (squares), and seventh (triangles) harmonics for a 4% (w/w) xanthan sample as a function of strain amplitude γ.

VI. CONCLUSIONS

In the previous sections we derived a constitutive equation for the stress tensor of an elastic material with anisotropic rigid particles. We derived this expression by including a dependence on the Finger tensor **B** and the orientation tensor **Q** in the expression for the free energy of the system. The expression for the stress tensor is correct up to second order in both these variables. It is valid for systems that in the nondeformed state are (nearly) isotropic from a macro-

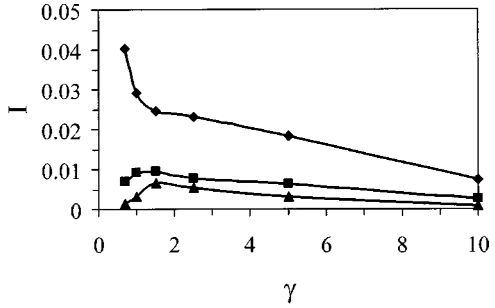

FIG. 4. Normalized intensities for the second (diamonds), fourth (squares), and sixth (triangles) harmonics for a 4% (w/w) xanthan sample as a function of strain amplitude γ. All even harmonics were normalized by I_1.

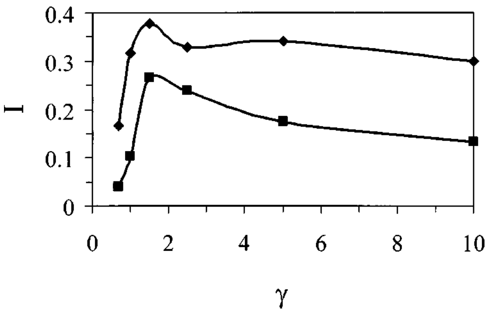

FIG. 5. Normalized intensities for the fourth (diamonds) and sixth (squares) harmonics for a 4% (w/w) xanthan sample as a function of strain amplitude γ. These harmonics were normalized by I_2.

scopic point of view, and valid for small deformations from equilibrium. We have shown that the elastic modulus in this expression depends on $\mathbf{Q}$, and this dependence leads to an effective elastic modulus that depends on the strain. We have calculated the explicit form of the equation for a deformation in the xy plane with a strain equal to $-\gamma$. For fully isotropic materials with $\mathbf{Q}=\mathbf{0}$ this expression reduces to an equation containing only odd powers of γ. The inclusion of a nonzero value for the orientation tensor leads to an additional set of terms in the equation, all proportional to Q_{xy} (the xy component of the tensor $\mathbf{Q}$), and all proportional to even powers of γ. We have qualitatively compared these expressions with Fourier transform rheological measurements of xanthan gels, at concentrations above and below the order-disorder transition. In the 2% (w/w) xanthan system (disordered state) only odd harmonics were found in the stress response, whereas in the 4% (w/w) xanthan gel (ordered state) even harmonics could be detected. As predicted by our theory the intensity of these even harmonics first increased with increasing γ, until a maximum value was reached. Beyond this maximum the intensity decreased continuously with increasing γ. These experiments support our assertion that the even harmonics in the stress response are the result of a change in the structure of the material because of the alignment of the anisotropic colloidal particles in the system.

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APPENDIX A: CALCULATION OF HIGHER ORDER TERMS

If we expand $\hat{F}$ up to third order in $\mathbf{B}$ and $\mathbf{Q}$ we find

$$\begin{aligned}\hat{F}(T,\hat{V},\omega_s,\omega_f,\mathbf{B},\mathbf{Q}) &= \hat{F}^0(T,\hat{V},\omega_s,\omega_f)+\tfrac{1}{2}K(\mathrm{tr}\,\mathbf{B})^2+\tfrac{1}{2}\mathbf{G}\odot^4\mathbf{BB}\\ &\quad+\tfrac{1}{2}\mathbf{L}_{BQ}\odot^4(\mathbf{BQ}+\mathbf{QB})+\tfrac{1}{3}\mathbf{L}_{BBB}\odot^6\mathbf{BBB}\\ &\quad+\tfrac{1}{6}\mathbf{L}_{BQQ}\odot^6(\mathbf{QBB}+\mathbf{BQB}+\mathbf{BBQ})\\ &\quad+\tfrac{1}{6}\mathbf{L}_{BBQ}\odot^6(\mathbf{QQB}+\mathbf{QBQ}+\mathbf{BQQ})\\ &\quad+\tfrac{1}{2}\alpha\mathbf{Q}:\mathbf{Q}+\tfrac{1}{3}\beta\,\mathrm{tr}(\mathbf{Q}\cdot\mathbf{Q}\cdot\mathbf{Q})+O(\mathbf{B}^4,\mathbf{Q}^4)\end{aligned} \tag{A1}$$

where $\odot^6$ denotes a sixfold contraction, and $\mathbf{L}_{BBB}$, $\mathbf{L}_{BQQ}$, and $\mathbf{L}_{BBQ}$ are sixth order tensor fields defined by

$$\mathbf{L}_{BBB}(T,\hat{V},\omega_s,\omega_f)=\left(\frac{\partial^3\hat{F}}{\partial\mathbf{B}^3}\right)_{T,\hat{V},\omega_s,\omega_f}, \tag{A2}$$

$$\mathbf{L}_{BQQ}(T,\hat{V},\omega_s,\omega_f)=\left(\frac{\partial^3\hat{F}}{\partial\mathbf{B}\partial\mathbf{Q}^2}\right)_{T,\hat{V},\omega_s,\omega_f}, \tag{A3}$$

$$\mathbf{L}_{BBQ}(T,\hat{V},\omega_s,\omega_f)=\left(\frac{\partial^3\hat{F}}{\partial\mathbf{B}^2\partial\mathbf{Q}}\right)_{T,\hat{V},\omega_s,\omega_f}. \tag{A4}$$

If we again assume that $\mathbf{B}$ and $\mathbf{Q}$ are sufficiently small, we may assume that these tensors are given by

$$\mathbf{L}_{BBB}(T,\hat{V},\omega_s,\omega_f)=L_{BBB}(T,\hat{V},\omega_s,\omega_f)\mathbf{\Delta}_{ijklmn}, \tag{A5}$$

$$\mathbf{L}_{BQQ}(T,\hat{V},\omega_s,\omega_f)=L_{BQQ}(T,\hat{V},\omega_s,\omega_f)\mathbf{\Delta}_{ijklmn}, \tag{A6}$$

$$\mathbf{L}_{BBQ}(T,\hat{V},\omega_s,\omega_f)=L_{BBQ}(T,\hat{V},\omega_s,\omega_f)\mathbf{\Delta}_{ijklmn}, \tag{A7}$$

where L_{BBB}, L_{BQQ}, and L_{BBQ} are all scalar fields, and $\mathbf{\Delta}_{ijklmn}$ is a sixth order symmetric traceless isotropic tensor field, given by

$$\begin{aligned}\mathbf{\Delta}_{ijklmn}\equiv\tfrac{1}{4}\big(&\tfrac{2}{9}\delta_{ij}\delta_{kl}\delta_{mn}-\tfrac{1}{3}\delta_{ij}\delta_{kn}\delta_{ml}-\tfrac{1}{3}\delta_{ij}\delta_{km}\delta_{nl}\\ &-\tfrac{1}{3}\delta_{ik}\delta_{jl}\delta_{mn}+\tfrac{1}{2}\delta_{ik}\delta_{jn}\delta_{ml}+\tfrac{1}{2}\delta_{ik}\delta_{jm}\delta_{ln}\\ &-\tfrac{1}{3}\delta_{il}\delta_{kj}\delta_{mn}+\tfrac{1}{2}\delta_{il}\delta_{km}\delta_{jn}+\tfrac{1}{2}\delta_{il}\delta_{kn}\delta_{jm}\\ &-\tfrac{1}{3}\delta_{im}\delta_{kl}\delta_{jn}+\tfrac{1}{2}\delta_{im}\delta_{kj}\delta_{ln}+\tfrac{1}{2}\delta_{im}\delta_{kn}\delta_{lj}\\ &-\tfrac{1}{3}\delta_{in}\delta_{kl}\delta_{mj}+\tfrac{1}{2}\delta_{in}\delta_{km}\delta_{lj}+\tfrac{1}{2}\delta_{in}\delta_{kj}\delta_{lm}\big).\end{aligned} \tag{A8}$$

Substituting Eqs. (A5) through (A8) in the expression for $\hat{F}$ we find that

$$\begin{aligned}\hat{F}(T,\hat{V},\omega_s,\omega_f,\mathbf{B},\mathbf{Q})\\ &=\hat{F}^0(T,\hat{V},\omega_s,\omega_f)+G\mathbf{B}{:}\mathbf{B}\\ &\quad+(\tfrac{1}{2}K-\tfrac{1}{3}G)(\operatorname{tr}\mathbf{B})^2+L_{BQ}\mathbf{B}{:}\mathbf{Q}\\ &\quad+\tfrac{1}{3}L_{BBB}[\operatorname{tr}(\mathbf{B}\cdot\mathbf{B}\cdot\mathbf{B})-\tfrac{1}{2}(\operatorname{tr}\mathbf{B})\mathbf{B}{:}\mathbf{B}+\tfrac{1}{18}(\operatorname{tr}\mathbf{B})^3]\\ &\quad+\tfrac{1}{6}L_{BQQ}[\operatorname{tr}(\mathbf{Q}\cdot\mathbf{Q}\cdot\mathbf{B})+\operatorname{tr}(\mathbf{Q}\cdot\mathbf{B}\cdot\mathbf{Q})+\operatorname{tr}(\mathbf{B}\cdot\mathbf{Q}\cdot\mathbf{Q})]\\ &\quad+\tfrac{1}{6}L_{BBQ}[\operatorname{tr}(\mathbf{B}\cdot\mathbf{B}\cdot\mathbf{Q})+\operatorname{tr}(\mathbf{B}\cdot\mathbf{Q}\cdot\mathbf{B})+\operatorname{tr}(\mathbf{Q}\cdot\mathbf{B}\cdot\mathbf{B})]\\ &\quad-\tfrac{1}{6}L_{BBQ}(\operatorname{tr}\mathbf{B})\mathbf{B}{:}\mathbf{Q}-\tfrac{1}{12}L_{BQQ}(\operatorname{tr}\mathbf{B})\mathbf{Q}{:}\mathbf{Q}+\tfrac{1}{2}\alpha\mathbf{Q}{:}\mathbf{Q}\\ &\quad+\tfrac{1}{3}\beta\operatorname{tr}(\mathbf{Q}\cdot\mathbf{Q}\cdot\mathbf{Q})+O(\mathbf{B}^4,\mathbf{Q}^4).\end{aligned}\qquad\text{(A9)}$$

Using Eq. (14), we find Eq. (37).

APPENDIX B: SIMPLE SHEAR

For a simple shear deformation in the xy plane by $-\gamma$ in a system that is isotropic in the z direction we find that the tensors **B** and **Q** are given by [19,26]

$$\mathbf{B}=\begin{pmatrix}1+\gamma^2 & \gamma & 0\\ \gamma & 1 & 0\\ 0 & 0 & 1\end{pmatrix},\qquad\text{(B1)}$$

$$\mathbf{Q}=\begin{pmatrix}Q_{xx} & Q_{xy} & 0\\ Q_{yx} & Q_{yy} & 0\\ 0 & 0 & -\frac{1}{3}\end{pmatrix}.\qquad\text{(B2)}$$

The terms in Eq. (37) are given by

$$\overline{\mathbf{B}\cdot\mathbf{B}}=\begin{pmatrix}\gamma^4+3\gamma^2+1 & \gamma^3+2\gamma & 0\\ \gamma^3+2\gamma & \gamma^2+1 & 0\\ 0 & 0 & 1\end{pmatrix},\qquad\text{(B3)}$$

$$(\operatorname{tr}\mathbf{B})\mathbf{B}=\begin{pmatrix}\gamma^4+4\gamma^2+3 & \gamma^3+3\gamma & 0\\ \gamma^3+3\gamma & \gamma^2+3 & 0\\ 0 & 0 & \gamma^2+3\end{pmatrix},\qquad\text{(B4)}$$

$$\overline{\mathbf{B}\cdot\mathbf{Q}}=\begin{pmatrix}(1+\gamma^2)Q_{xx}+\gamma Q_{xy} & \frac{1}{2}(2+\gamma^2)Q_{xy}+\frac{1}{6}\gamma & 0\\ \frac{1}{2}(2+\gamma^2)Q_{xy}+\frac{1}{6}\gamma & \gamma Q_{xy}+Q_{yy} & 0\\ 0 & 0 & -\frac{1}{3}\end{pmatrix}.\qquad\text{(B5)}$$

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