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The Structure of Convective Nonlinearities in Polymer Rheology

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We derive nonlinear hydrodynamic equations for visco-elastic media using the Eulerian description for all macroscopic quantities and *especially* for the strain tensor. The form of the convective nonlinearities is fixed by the requirement that in the appropriate limit the hydrodynamic equations for solids have to emerge. Differences to previous descriptions are discussed.

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I. INTRODUCTION

Visco-elastic fluids behave as Newtonian ones at low frequencies, and as solids at higher frequencies. A consistent hydrodynamic description needs to reflect this fact and must therefore contain, as special cases, both the hydrodynamic theory for simple liquids and for solids (elastic media). The liquid limit is well known (Navier-Stokes equations) and universally correctly implemented in the dynamic descriptions of visco-elasticity (Truesdell 1962, 1965, Noll 1958a, Larson 1988, Bird *et al.* 1977, Coleman and Noll 1961, Oldroyd 1950, Giesekus 1966). The solid limit is much more problematic, and compatibility especially in the nonlinear regime of large displacements and rotations (*e.g.* under the condition of strong flow in the case of visco-elastic fluids) has so far proven elusive, as we shall see. Thus, we will review the nonlinear hydrodynamic description of solids in the Appendix.

Hydrodynamics, the macroscopic description of condensed systems in the low frequency, long wavelength limit (Martin *et al.* 1972, Forster 1975), is a well-established, systematic approach in condensed matter physics. This method can be applied not only to simple fluids (Landau and Lifshitz 1959, Kadanoff and Martin 1963), to systems with broken symmetries, like liquid crystals (Forster *et al.* 1971, Martin *et al.* 1972, Pleiner and Brand 1996, Brand and Pleiner 1981, Liu 1981, Lubensky 1972) and superfluids (Khalatnikov 1965, Hohenberg and Martin 1965, Graham 1974, Graham and Pleiner 1975, Liu 1979, Brand *et al.* 1979), but also to complex fluids with slowly relaxing degrees of freedom. The transient elasticity of visco-elastic fluids is an example of the latter case (Brand *et al.* 1990).

Of the three major non-Newtonian features in polymer rheology (visco-elasticity, normal stress differences, and shear thinning or thickening) we will tackle particularly the first one (having of course implications for the second one), but we will neither deal with shear thinning or thickening nor with additional slowly relaxing mesoscopic features (Pleiner and Brand 1999) that *e.g.* add to normal stress differences. We concentrate on deriving a valid hydrodynamic description of visco-elasticity for arbitrarily large deformations, rotations and flow. Taking the solid limit correctly the structure of the equations will be determined completely. As a result we find i) that it is inevitable to use a Eulerian description, ii) that the stress tensor is not the correct relaxing quantity (at least for nonlinear equations) and iii) that only under rather special circumstances does the 'upper convected derivative' give the correct quadratic nonlinearities concerning flow. On the other hand, the relaxation of the strain field guarantees that the limit of simple fluids is taken correctly, too.

II. VISCO-ELASTICITY

Visco-elasticity is the phenomenon where complex fluids react elastically (solid-like) at higher frequencies (frequency $\omega \to \infty$), while at sufficiently low frequencies ($\omega \to 0$) the response is viscous (fluid-like). This can be described by replacing the (Newtonian) shear viscosity (in the Navier-Stokes equation for isotropic fluids) by a complex generalized viscosity

$$\nu \quad \to \quad \nu(\omega) = \nu + \frac{\tau C}{1 + i\omega\tau} \tag{1}$$

where τ is the characteristic (Maxwell) time that discriminates between the long- and short-time limit and C is the elastic modulus. Such a simple treatment may be sufficient for the linear theory of isotropic visco-elastic fluids, but its generalization to nonlinear descriptions of more complex fluids is impossible. First Eq. (1) is based on Fourier transformation, which is not a suitable tool for nonlinear equations and, second, it is not at all obvious how additional degrees of freedom (of complex fluids) can be incorporated into such a description. The natural thing to do is to establish additional dynamic equations for the visco-elastic degree of freedom. The questions are what variables to choose and what the additional equations then look like.

In the Appendix we discuss the correct nonlinear hydrodynamic description of elastic media (i.e. all media that sustain a static shear modulus). The requirement that any nonlinear visco-elastic description reduces to that of elastic media in the high frequency limit is sufficient to identify the correct variables and the form of their dynamic equations.

The central quantity describing deformations and orientations is $\nabla_i a_\alpha$ (cf. Appendix), which has to be added to the list of the other relevant variables. Here $a_\alpha(\vec{r})$ are three fields ($\alpha = 1, 2, 3$ as for any Greek index) describing displaced body points $\vec{r}$. These fields can be viewed as the symmetry variables according to the spontaneous broken translational symmetry (in 3 directions) in solids. In the Appendix it is discussed in detail how $\nabla_i a_\alpha$ is related to more familiar strain and rotation tensors. Taking into account gradients of the symmetry variables as well as the densities, ϵ, ρ, and $\vec{g}$, of the conserved quantities energy, mass, and linear momentum, respectively, the Gibbs relation takes the form

$$d\epsilon = T ds + \mu d\rho + v_i dg_i + \psi_{\alpha i} d\nabla_i a_\alpha + \psi_{\alpha ij} d\nabla_i \nabla_j a_\alpha \tag{2}$$

where the thermodynamic conjugate quantities, temperature T, chemical potential μ, velocity $\vec{v}$, $\psi_{\alpha i}$, and $\psi_{\alpha ij}$ are defined via Eq. (2); s is the entropy density. All fields are functions of the (laboratory) space $\vec{r}$ and time t, since we use consistently the Eulerian description. We have added second order gradients of a_α describing bending and inhomogeneous rotations. Although negligible for solids (and therefore disregarded in the Appendix) they are probably important for visco-elastic fluids like polymers.

The energy is invariant under infinitesimal rotations, if $\psi_{\alpha j} \nabla_i a_\alpha + (\psi_{\alpha ik} + \psi_{\alpha ki}) \nabla_j \nabla_k a_\alpha = \psi_{\alpha i} \nabla_j a_\alpha + (\psi_{\alpha jk} + \psi_{\alpha kj}) \nabla_i \nabla_k a_\alpha$, which acts as a constraint on $\psi_{\alpha i}$ and $\psi_{\alpha ik}$.

The dynamic equation for a_α in elastic media has been derived in the Appendix. Eq. (A.5) has to be taken over for visco-elastic fluids (in order to guarantee the high frequency limit) with the difference that the strains are not permanent but have to relax (in order to guarantee the correct low frequency limit). Without strain relaxation

$$\nabla_i \dot{a}_\alpha + (\nabla_i v_k)(\nabla_k a_\alpha) + v_k \nabla_k \nabla_i a_\alpha + \nabla_i Y_\alpha = 0 \tag{3}$$

The quantity Y_α is a phenomenological current containing diffusive effects (rather than relaxation) and reads (neglecting cross-couplings) $Y_\alpha = \mu_{\alpha\beta ij} \nabla_i \psi^{tot}_{\beta j}$ with $\psi^{tot}_{\beta j} = \psi_{\beta j} - \nabla_k \psi_{\beta jk}$. This diffusion is kept here for completeness, but does not play a crucial role in polymers.

In order to describe strain relaxation one has to disentangle the quantity $\nabla_i a_\alpha$ into strains and rotations. As discussed in the Appendix there are two appropriate strain tensors in the Eulerian description, the Eulerian strain tensor U_{ij} and the invariant strain tensor $\epsilon_{\alpha\beta}$. The former (being a second rank tensor in space) is not rotationally invariant, while the latter one is (like any scalar quantity in real space). In order to tie in closely with the existing literature, we will formulate the dynamics using the Eulerian strain. The popular Lagrangian strain tensor cannot be used within the Eulerian description necessary for a consistent treatment.

The price one has to pay for using strains and rotations separately is that the theory can no longer be given in full generality. The dynamic equations can be formulated in closed form only as a power expansion in the strains, as can be seen from Eqs. (A.2,A.4). There is no restriction to the magnitude of the rotations. From the definition Eq. (A.1) of U_{ij} and from the decomposition Eq. (A.2) $\nabla_i a_\alpha = R_{\alpha j} \Xi_{ij}$ the equation of motion Eq. (3) for $\nabla_i a_\alpha$ can be written in the implicit form ($d/dt \equiv \partial/\partial t + v_j \nabla_j$)

$$2\tfrac{\mathrm{d}}{\mathrm{dt}} U_{ij} = [\Xi_{jl} \Xi_{lk} \nabla_i v_k + R_{\alpha k} \Xi_{jk} \nabla_i Y_\alpha + i \leftrightarrow j] \tag{4}$$

$$0 = \Xi_{ij} R_{\alpha l} \tfrac{\mathrm{d}}{\mathrm{dt}} R_{\alpha j} + \Xi_{lj} \nabla_i v_j - R_{\alpha l} \nabla_i Y_\alpha + \tfrac{\mathrm{d}}{\mathrm{dt}} \Xi_{il} \tag{5}$$

$$0 = 2(\mathrm{d}/\mathrm{dt}) U_{ij} + \Xi_{ik} (\mathrm{d}/\mathrm{dt}) \Xi_{kj} + \Xi_{jk} (\mathrm{d}/\mathrm{dt}) \Xi_{ki} \tag{6}$$

Eqs. (4,5,6) can be solved iteratively using Eq. (A.4) by (i) taking U_{ij}, $\frac{\mathrm{d}}{\mathrm{dt}} R_{\alpha i}$, $(\nabla_i Y_\alpha)$, and $(\nabla_i v_j)$ as small quantities, and (ii) noting that U_{ij} and Ξ_{ij} are symmetric. To second order the result is

$$\tfrac{\mathrm{d}}{\mathrm{dt}} U_{ij} = A_{ij} + [\tfrac{1}{2} R_{\alpha i} \nabla_j Y_\alpha - U_{kj} \nabla_i v_k - (\tfrac{1}{2\tau})_{ijkl} \Psi^{tot}_{kl} + i \leftrightarrow j] \tag{7}$$

$$\tfrac{\mathrm{d}}{\mathrm{dt}} R_{\alpha i} = R_{\alpha j} \omega_{ij} + \frac{1}{2} R_{\alpha j} [R_{\beta i} \nabla_j Y_\beta + R_{\alpha j} U_{jk} A_{ik} - i \leftrightarrow j] \tag{8}$$

with $2A_{ij} \equiv \nabla_j v_i + \nabla_i v_j$ and $2\omega_{ij} \equiv \nabla_j v_i - \nabla_i v_j$. In Eq. (7) we have now inserted strain relaxation (the $1/\tau$ term) in order to describe correctly the simple fluid limit. We have switched to the new thermodynamic quantity $\Psi_{ij}^{tot} \equiv \Psi_{ij} - \nabla_k \Psi_{ijk}$ defined by the rewritten Gibbs relation

$$d\epsilon = Tds + \mu d\rho + v_i dg_i + \Psi_{ij} dU_{ij} + \Psi_{ijk} d\nabla_k U_{ij} + \chi_{\alpha i} dR_{\alpha i} + \chi_{\alpha ij} d\nabla_j R_{\alpha i} \tag{9}$$

with $\Psi_{ij} = \Psi_{ji}$, $\Psi_{ijk} = \Psi_{jik}$, $\chi_{\alpha i} R_{\alpha j} = -\chi_{\alpha j} R_{\alpha i}$ and $\chi_{\alpha ik} R_{\alpha j} = -\chi_{\alpha jk} R_{\alpha i}$.

The remaining equations of motion denote mass, momentum, and energy conservation

$$\begin{aligned} \dot\rho + \nabla_i \rho v_i &= 0 && (10)\\ \dot g_i + \nabla_j \sigma_{ij} &= 0 && (11)\\ \dot\epsilon + \nabla_i j_i^{(\epsilon)} &= 0 && (12) \end{aligned}$$

with σ_{ij} the stress tensor and $j_i^{(\epsilon)}$ the energy density current. The momentum density g_i is equal to the mass current ρv_i. The Gibbs relation Eq. (9) can be used to replace Eq. (12) by the entropy balance

$$\dot s + \nabla_i f_i = R/T \tag{13}$$

which is more convenient for nonlinear descriptions. The energy dissipation function R is positive (zero) for irreversible (reversible) processes. This leads to the following expressions for the currents

$$\begin{aligned} Y_\alpha &= \mu(R_{\alpha k} \nabla_j \Psi_{kj}^{tot} - \nabla_k \chi_{\alpha k}^{tot}) + \beta_{\alpha i} \nabla_i T && (14)\\ f_i &= s v_i - \kappa_{ij} \nabla_j T - \beta_{\alpha i}(R_{\alpha k} \nabla_j \Psi_{kj}^{tot} - \nabla_k \chi_{\alpha k}^{tot}) && (15)\\ \sigma_{ij} &= \delta_{ij} p + v_i g_j - \Psi_{ij}^{tot} + \chi_{\alpha j}^{tot} R_{\alpha i} - \nu_{ijkl} A_{kl} + 2\Psi_{ki}^{tot} U_{jk} + \tfrac{1}{2}\chi_{\alpha k}^{tot}(U_{ki} R_{\alpha j} + U_{kj} R_{\alpha i}) \\ &\quad + \Psi_{lkj} \nabla_i U_{lk} + \chi_{\alpha kj} \nabla_i R_{\alpha k} && (16) \end{aligned}$$

with $\chi_{\alpha i}^{tot} \equiv \chi_{\alpha i} - \nabla_j \chi_{\alpha ij}$. The result Eq. (16) for the stress tensor σ_{ij} is valid to second order of the expansion Eq. (A.4) in the strain, only. For completeness we also give the exact expression in terms of a_α

$$\sigma_{ij} = \delta_{ij} p + v_i g_j + \psi_{\alpha j} \nabla_i a_\alpha + \psi_{\alpha kj} \nabla_i \nabla_k a_\alpha - (\nabla_k \psi_{\alpha kj}) \nabla_i a_\alpha - \nu_{ijkl} A_{kl} \tag{17}$$

The entropy current f_i contains entropy transport, heat conduction, and the cross-coupling to elasticity. The stress tensor σ_{ij} comprises the hydrostatic pressure p, defined by the Gibbs-Duhem relation

$$p = -\epsilon + Ts + \mu\rho + v_i g_i \tag{18}$$

as well as momentum convection, three elastic and the viscous contributions.

The dynamic equations above are fully nonlinear in the symmetry- and thermodynamics-governed parts, but linear (in the sense of linear irreversible thermodynamics) in the phenomenological, irreversible parts (nonlinearities enter there implicitly through variable dependencies of the material parameters like temperature dependence of viscosities etc.). The dynamic equations are now set-up in terms of the conjugate quantities. In order to close the system one needs constitutive equations relating the conjugate quantities to the variables. These relations are completely static in nature, since any time (or frequency dependence) has been taken care of explicitly by equations of motion. We find

$$\begin{aligned} \delta T &= \frac{T}{C_V}\delta s + \frac{1}{\rho\alpha_s}\delta\rho + \lambda_{ij}^{(T)} U_{ij} && (19)\\ \delta\mu &= \frac{1}{\rho^2\kappa_s}\delta\rho + \frac{1}{\rho\alpha_s}\delta s + \lambda_{ij}^{(\mu)} U_{ij} && (20)\\ \Psi_{ij} &= c_{ijkl} U_{kl} + d_{ijklmn} \nabla_l \nabla_k U_{mn} + \lambda_{ij}^{(T)} \delta s + \lambda_{ij}^{(\mu)} \delta\rho && (21)\\ \Psi_{ijk} &= e_{ijklmn} \nabla_l U_{mn} && (22)\\ \chi_{\alpha i} &= f_{\alpha\beta ijkl} \nabla_j \nabla_k R_{\beta l} && (23)\\ \chi_{\alpha ij} &= g_{\alpha\beta ijkl} \nabla_k R_{\beta l} && (24) \end{aligned}$$

containing specific heat (C_V), compressibility (κ_s), heat expansion (α_s), elastic ($c_{\alpha\beta ij}$) and bending-elastic (d, e) moduli, as well as cross couplings of thermal and mechanical degrees of freedom with elasticity. These equations are linear in the deviations from equilibrium, but can be generalized into the nonlinear domain (e.g. nonlinear elasticity) if necessary. Implicit nonlinearities are given by state dependence of the static susceptibilities. In case one neglects inhomogeneous rotations $\chi_{\alpha i}$ and $\chi_{\alpha ij}$ are zero, which simplifies Eqs. (7-16) considerably.

Above we have established the general framework for the hydrodynamics of visco-elastic fluids starting with the fields $\nabla_i a_\alpha$ and switching to the Eulerian strain U_{ij} and rotations $R_{\alpha i}$. This was possible only within an expansion into powers of the strain and we gave explicit equations up to quadratic nonlinearities. We will now specify and simplify these equations for the case of isotropic polymers. First, the static and dynamic material tensors are of rather simple forms

$$\beta_{\alpha i} = \beta R_{\alpha i} \qquad \kappa_{ij} = \kappa\delta_{ij} \qquad \lambda_{ij}^{(\mu,T)} = \lambda^{(\mu,T)}\delta_{ij} \quad \text{and} \quad c_{ijkl} = c_\parallel \delta_{ij}\delta_{kl} + c_\perp \delta_{ik}\delta_{jl} \tag{25}$$

where the latter form is also valid for the other fourth rank tensors ν_{ijkl} and $(1/\tau)_{ijkl}$ involving shear and bulk viscosity $(\nu_\parallel, \nu_\perp)$ as well as transverse and longitudinal strain relaxation $(1/\tau_\perp, 1/\tau_\parallel)$. The sixth rank tensors d and e in Eqs. (21,22) contain four, while f and g in Eqs. (23,24) have two coefficients. The latter do not contain any $R_{\alpha i}$ factor (only $\delta_{\alpha\beta}$), because of the antisymmetry conditions on $R_{\alpha j}\chi_{\alpha i}$. As a consequence, the dynamic equation (8) for $R_{\alpha i}$ is not needed for isotropic systems.

In the case of the (additional) approximation of neglecting diffusion compared to relaxation (i.e. setting β, μ, d, e, f, and g to zero) the dynamic equations read

$$\begin{aligned}
(\frac{\partial}{\partial t} + v_k\nabla_k)U_{ij} &= A_{ij} - (U_{kj}\nabla_i v_k + U_{ki}\nabla_j v_k) && (26)\\
&\quad -\delta_{ij}\left((\frac{3c_\parallel + c_\perp}{\tau_\parallel} + \frac{c_\parallel}{\tau_\perp})U_{kk} + (\frac{3}{\tau_\parallel} + \frac{1}{\tau_\perp})(\lambda^{(T)}\delta s + \lambda^{(\mu)}\delta\rho) \right) - \frac{c_\perp}{\tau_\perp}U_{ij} &&\\
(\frac{\partial}{\partial t} + v_k\nabla_k)g_i &= -g_i\nabla_k v_k - \nabla_i(\tilde{p} - \nu_\parallel A_{kk}) + \nabla_j \Big(\nu_\perp A_{ij} + c_\perp U_{ij} && (27)\\
&\quad +2U_{ij}(c_\parallel U_{kk} + \lambda^{(T)}\delta s + \lambda^{(\mu)}\delta\rho) + 2c_\perp U_{ik}U_{jk} \Big) &&\\
(\frac{\partial}{\partial t} + v_k\nabla_k)s &= -s\nabla_k v_k + \nabla_j(\kappa\nabla_j(\frac{T}{C_V}\delta s + \frac{1}{\rho\alpha_s}\delta\rho + \lambda^{(T)}U_{kk})) + \frac{R}{T} && (28)\\
(\frac{\partial}{\partial t} + v_k\nabla_k)\rho &= -\rho\nabla_k v_k && (29)
\end{aligned}$$

For the hydrodynamic pressure $\tilde{p}$ we have $\nabla_i\tilde{p} = \nabla_i p - c_\parallel \nabla_i U_{kk} - \lambda^T\nabla_i s - \lambda^\mu \nabla_i \rho$ with p, the thermodynamic pressure defined in Eq. (18), while

$$R = R_0 + (\frac{1}{2\tau_\parallel} + \frac{3}{2\tau_\perp})\Psi_{kk}^2 + \frac{c_\perp}{\tau_\perp}\Psi_{kk}U_{kk} + \frac{c_\perp^2}{2\tau_\perp}U_{ij}U_{ij} \tag{30}$$

with $\Psi_{kk} = c_\parallel U_{kk} + \lambda^T\delta s + \lambda^\mu\delta\rho$ and R_0 the dissipation function of simple liquids.

Eqs. (26) and (27) are in a form that can be compared with the rheology literature. It turns out that Eq. (26) can be written as $\hat{D}(\underline{U}) = \underline{A}$, if the phenomenological currents are neglected, where $\hat{D}(*) = (\partial/\partial t + \vec{v}\cdot\vec{\nabla}) * + (\vec{\nabla}\vec{v})^T \cdot * + * \cdot (\vec{\nabla}\vec{v})$ is the upper convected derivative. For Eq. (27) no such simple form of the convective nonlinearities is found. It should be recalled, however, that the present formulation is restricted to quadratic nonlinearities in the strain (but see Note Added in Proof). We are therefore lead to the conclusion that previous descriptions (Truesdell 1962, Noll 1958b, Larson 1988, Bird *et al.* 1977, Oldroyd 1950, Giesekus 1966), which allowed upper and lower convected derivatives or the Jaumann derivative and others of U_{ij} or σ_{ij}, are not suitable to describe the nonlinear macroscopic behavior of non-Newtonian liquids such as polymer melts. Or to phrase it differently: if one is interested in a hydrodynamic approach to the nonlinear description of systems with slowly relaxing quantities, only Eq. (3) derived in the present manuscript can be used as a starting point. It should also be kept in mind that the convective-type nonlinearities are not the only ones possible and that for a realistic description of the rheological behavior of complex fluids additional slowly relaxing variables (other than strains and rotations) are necessary (Pleiner and Brand 1999).

In anisotropic fluids the material tensors – as measured in the laboratory frame – depend on the orientation of the material. It is therefore necessary to know the (time evolution of the) rotation matrix $R_{\alpha i}$ that transforms real space quantities into those of the reference space, since material properties are defined in reference space.

In addition, in an anisotropic visco-elastic fluid (like, e.g., liquid crystalline polymers) there are additional degrees of freedom related to the broken orientational symmetry (and others, cf. Pleiner and Brand 1991, 1992). The nature of such variables depends on the actual symmetry of the phase. Here we do not want to go into these details, but only mention that quantities like the stress tensor become even more complicated when the additional degrees of freedom are taken into account.

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III. APPENDIX: ELASTICITY

In this appendix we follow quite closely recent work on the nonlinear hydrodynamics of crystals (Temmen et al. 2000). A proper description relies on two coordinates: the actual spatial coordinate $\mathbf{r}$, specifying a point in an elastic body, and the coordinate $\mathbf{a}$ this point possesses in the absence of any stresses. More carefully, starting from a stress-free elastic body, we consider a point at the initial coordinate $\mathbf{a}$. As the body is displaced, rotated, compressed and sheared, the given point is displaced to $\mathbf{r}$, especially in soft matter generally rather different from $\mathbf{a}$. Since all points of the body have a unique pair of $\mathbf{a}$ and $\mathbf{r}$, the function $\mathbf{r}(\mathbf{a})$ is unique and invertible, the result of which we denote as $\mathbf{a}(\mathbf{r})$. For brevity, we shall refer to all $\mathbf{r}$ as the real space, and to all $\mathbf{a}$ as the reference space.

Despite its prevalence, the Lagrangian description is not the appropriate one when dealing with dynamics of strongly deformable systems. This is because we choose, even need, to express our physics in local terms. In particular, the state variables characterizing the elastic body (such as the temperature T and the chemical potential μ) must be taken as functions of the real space coordinates $\mathbf{r}$ rather than of the reference space coordinates $\mathbf{a}$. Consider for instance the diffusive heat current, which is clearly along $\nabla_k T(\mathbf{r})$ in an isotropic medium, and not along $\partial T(\mathbf{a})/\partial a_k$. Similarly, with $\boldsymbol{g}$ as the momentum density, the angular momentum density is $\mathbf{r}\times\boldsymbol{g}$ rather than $\mathbf{a}\times\boldsymbol{g}$.

Consistency also forces us to take a strain tensor that is a function of $\mathbf{r}$. Following Chaikin and Lubensky (1995), we therefore employ the (Eulerian) strain tensor, introduced via $\mathrm{d}r_i^2 - \mathrm{d}a_i^2(r) = 2U_{ik}\mathrm{d}r_i\mathrm{d}r_k$, where $U_{ik} = \frac{1}{2}[\nabla_k u_i + \nabla_i u_k - (\nabla_i u_j)(\nabla_k u_j)]$. Remarkably, we may skip the detour over the displacement vector $\mathbf{u}$, and write the proper strain tensor directly as

$$U_{ik} = \tfrac{1}{2}[\delta_{ik} - (\nabla_k a_\alpha)(\nabla_i a_\alpha)]. \tag{A.1}$$

The elastic energy is independent of the orientation of the unstressed body, and we are quite free to take an arbitrary rotation of the reference space with respect to the real space. Therefore, we must treat $\mathbf{a}$ and $\mathbf{r}$ as vectors of two different spaces, and a quantity such as $\nabla_i a_\alpha \equiv \partial a_\alpha/\partial r_i$ – instead of being a second rank tensor – is in fact a vector both in real and reference space. We shall emphasize this fact here by using Latin and Greek indices to denote the components in real and reference space, respectively. (So the displacement $r_i - a_\alpha$ is indeed an oxymoron. Similar problems are associated with the Lagrangian strain tensor, which is neither completely in real nor completely in reference space.)

It is useful to separate the two pieces of information contained in $\nabla_i a_\alpha$: the local strain and the local orientation. The polar decomposition theorem (Noll 1958b) states

$$\nabla_i a_\alpha = R_{\alpha j}\Xi_{ij}, \tag{A.2}$$

where $R_{\alpha j}$ is the rotation matrix that rotates the local preferred directions in real space back to the global ones in reference space, while the symmetric matrix Ξ_{ij} deviates from δ_{ij} only for finite strains. To understand this formula, first consider the strainless case $\Xi_{ij} = \delta_{ij}$. Because of $\mathrm{d}a_\alpha = (\nabla_i a_\alpha)\mathrm{d}r_i$ with $\mathrm{d}a_\alpha^2 = \mathrm{d}r_i^2$, the gradient $\nabla_i a_\alpha$ is indeed the rotation matrix $R_{\alpha j}$ characterized above (with $R_{\alpha j}R_{\alpha k} = \delta_{jk}$). For finite strains, Eq. (A.1) implies

$$\delta_{ij} - 2U_{ij} = (\nabla_i a_\alpha)(\nabla_j a_\alpha) = R_{\alpha k}\Xi_{ik}\, R_{\alpha l}\Xi_{lj} = \Xi_{ik}\Xi_{kj}, \tag{A.3}$$

and we deduce

$$\Xi_{ij} = \sqrt{\delta_{ij} - 2U_{ij}} \approx (\delta_{ij} - U_{ij} - \tfrac{1}{2}U_{ik}U_{kj}\ldots), \tag{A.4}$$

where the expansion is valid for small strains U_{ij}, but arbitrary $R_{\alpha j}$.

The equation of motion for a_α is

$$\dot{a}_\alpha + v_k\nabla_k a_\alpha + Y_\alpha = 0. \tag{A.5}$$

In equilibrium, $Y_\alpha = 0$ and the equation of motion $\frac{\mathrm{d}}{\mathrm{dt}}a_\alpha \equiv (\frac{\partial}{\partial t} + v_j\nabla_j)a_\alpha = 0$ states the simple fact that the (initial) coordinate a_α of a mass point does not change when one moves with it. Y_α contains in general dissipative as well as reversible contributions.

From the definition Eq. (A.1) the equation of motion for U_{ij} follows unambiguously

$$\tfrac{\mathrm{d}}{\mathrm{dt}}U_{ij} - A_{ij} = [\tfrac{1}{2}R_{\alpha i}\nabla_j Y_\alpha - U_{kj}\nabla_i v_k] + [i \leftrightarrow j] \tag{A.6}$$

which for finite $\nabla_j Y_\alpha$ is not independent of $R_{\alpha i}$.

Another useful notation for the strain (Temmen 1997) is $2\epsilon_{\alpha\beta} \equiv \delta_{\alpha\beta} - (\nabla_i a_\alpha)(\nabla_i a_\beta)$, or $\epsilon_{\alpha\beta} = R_{\alpha i} R_{\beta j} U_{ij}$. Being a tensor in the reference space, it is invariant under a real space rotation. Again one can split up $\nabla_i a_\alpha = R_{\beta i} \Sigma_{\alpha\beta}$ into rotations and a symmetric matrix $\Sigma_{\alpha\beta}$ describing strains. From

$$\delta_{\alpha\beta} - 2\epsilon_{\alpha\beta} = (\nabla_i a_\alpha)(\nabla_i a_\beta) = R_{\gamma i} \Sigma_{\alpha\gamma} R_{\delta i} \Sigma_{\beta\delta} = \Sigma_{\alpha\gamma} \Sigma_{\beta\gamma} \tag{A.7}$$

one gets the approximate expansion of $\Sigma_{\alpha\beta}$

$$\Sigma_{\alpha\beta} \approx \delta_{\alpha\beta} - \epsilon_{\alpha\beta} - \frac{1}{2}\epsilon_{\alpha\gamma}\epsilon_{\gamma\beta} + \ldots \tag{A.8}$$

in terms of the invariant strain tensor. For the latter the dynamic equation follows from Eq. (A.5)

$$\dot{\epsilon}_{\alpha\beta} + v_k \nabla_k \epsilon_{\alpha\beta} - A_{ik} (\nabla_i a_\beta)(\nabla_k a_\alpha) - \frac{1}{2}[(\nabla_i a_\beta)(\nabla_i Y_\alpha) + (\nabla_i a_\alpha)(\nabla_i Y_\beta)] = 0 \tag{A.9}$$

Clearly, the dynamics of the symmetric $\epsilon_{\alpha\beta}$ depends on the total, non-symmetric $\nabla_i a_\alpha$, reflecting the coupling between strains and rotations, especially in the nonlinear regime. In other words, the dynamic equation for $\epsilon_{\alpha\beta}$ (as well as for U_{ij}) is not closed, and one generally also needs the equation for $R_{\alpha i}$, to be distilled from Eq. (A.5).

Note Added in Proof: In Eq. (26) the upper convected form of the time derivative is valid to any order in the strain expansion.

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