Weierstraß-Institut

für Angewandte Analysis und Stochastik

im Forschungsverbund Berlin e.V.

Elementary Thermodynamic and Stochastic Arguments on Non-Newtonian Fluid

Ingo Müller

Technical University Berlin
10623 Berlin, Germany

Krzysztof Wilmański
Weierstrass Institute for Applied Analysis and Stochastics, Berlin
10117 Berlin, Germany

submitted:

Preprint No.

Berlin 1999

Abstract

A solution of dumbbell in a Newtonian solvent is a convenient molecular model for a non-Newtonian or visco-elastic fluid. The distribution of Hookean dumbbells obeys a continuity equation on which a hierarchy of moment equations may be erected. The closure of this hierarchy is effected by the observation that the dumbbell solution attempts to minimize its free energy, a combination of elastic energy, potential energy of the Stokes friction and entropy. The minimization provides an expression for the equilibrium distribution.

In this paper the hierarchy is closed after the second moment - the dumbbell stress tensor - by use of the equilibrium distribution. A rheological equation of state results from the closed system of equations. That rheological equation of state is simultaneously of "rate-type" and of "grade-type", in the jargon of continuum mechanics, and it satisfies all natural stability criteria.

If the rheological equation of state is forcefitted into an equation of grade-type the stability is lost. The conclusion from these considerations is that constitutive equations of grade-type do not represent viscoelastic properties of fluids well.

1 Introduction

Dunn & Fosdick [1] have made an important discovery in thermodynamics of rheological fluids. They were considering grade-type fluids when they found that thermodynamic stability required the wrong sign of the first normal stress coefficient, i.e. a sign that contradicted all rheological measurements. This result was not immediately fully appreciated by the community of mechanicians and thermodynamicists; indeed for some time it seemed that there was only one unattractive alternative: thermodynamics or rheology, one or the other had to be wrong. But then, as the dust settled, it became clear that both theories were right. What *was* wrong – as it so frequently is – was our intuition. Intuition had suggested that grade-type equations provided a good constitutive class for rheological fluids, but in reality they do not! Joseph [2] made that point most forcefully. Müller & Wilmanski [3], Wilmanski [4], and Müller [5] suggested that the constitutive equation for the stress should be replaced by a balance law, so that the rate of stress was involved. Thus they were able to get all the correct results: A minimum of the free energy and the correct sign of the first normal stress coefficient.

Actually in thermodynamics proper – the theory of heat and temperature – there exists a very similar problem with the Cattaneo equation [6] and its grade-type approximation. That problem presented itself as the so-called paradox of infinite speeds. In this field the problem has been fully resolved; and in the process the satisfactory rational structure of *extended thermodynamics* has been erected in which no infinite speed occurs and where stability is assured, see Müller & Ruggeri [7]. The latter reference also provides a discussion of the similarity between the Cattaneo paradox and Dunn & Fosdick's dilemma.

In both cases – rheology and thermodynamics – the view to the root of the matter was obstructed by the fact that ordinary thermodynamics does not easily accommodate "rate-type constitutive equations" in which the rates of stress or heat flux appear. Thermodynamics had the edge, however, in finding the solution, because it could develop along the lines laid down by the fully specific structure of the kinetic theory of gases.

Thus extended thermodynamics could be formulated as a rational theory and that theory has now progressed far beyond Cattaneo and the resolution of his paradox.

Now then, rheology also has a kinetic theory of sorts – rudimentary in comparison with gases, but nevertheless - and that theory is used in the present paper to explain the instability of grade-type constitutive equations and the stability of the corresponding rate-type ones. Basically we take the kinetic theory of rheological fluids from the review paper [8] by Bird, Warner & Evans, but we make some alterations for which those authors should not be held responsible. Those alterations result from long experience with statistical thermodynamics which permits us a shortcut at some places. We also refer the reader to Müller [9], who made a systematic study of the kinetic theory of dumbbells along the lines of Bird, Warner & Evans.

2 Motion of a dumbbell in solution

2.1 Equation of motion

A Hookean dumbbell consists of two masses $\frac{m}{2}$ with the distance vector $2R_i$ which are connected by a linearly elastic spring, so that the elastic force between the masses equals λR_i, see Fig. 1. $\frac{1}{2}\lambda > 0$ is the spring constant. The center of mass of the dumbbell lies at position r_i.

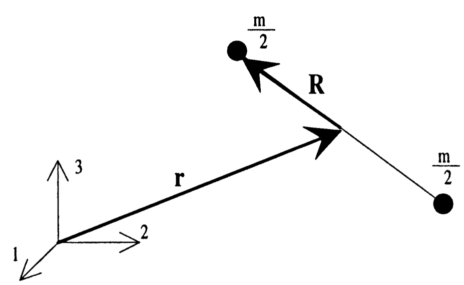

Fig. 1 Position of the masses of a dumbbell.

We assume that the dumbbell is immersed in a Newtonian fluid which flows past the masses $\frac{m}{2}$ with the velocity $\mathbf{u}(\mathbf{x})$ and exerts a Stokes drag force on them, proportional to the relative velocity. Therefore the equations of motion of the two masses read

$$\frac{m}{2}\left(\ddot{\mathbf{r}} \mp \ddot{\mathbf{R}}\right) = -\varsigma\left(\dot{\mathbf{r}} \mp \dot{\mathbf{R}} - \mathbf{u}(\mathbf{r} \mp \mathbf{R})\right) \pm \lambda \mathbf{R}. \tag{2.1}$$

$\varsigma > 0$ is the drag coefficient. Adding and subtracting these two equations we obtain equations for the motion of the center of mass and for the relative motion of the masses, viz.

$$\begin{aligned} m\ddot{r}_i &= -2\varsigma(\dot{r}_i - u_i(\mathbf{r})). \\ m\ddot{R}_i &= -2\varsigma\left(\dot{R}_i - \left.\frac{\partial u_i}{\partial x_j}\right|_{\mathbf{x}=\mathbf{r}} R_j\right) - 2\lambda R_i\ . \end{aligned} \tag{2.2}$$

$u(\mathbf{x})$ has been expanded about $\mathbf{x} = \mathbf{r}$ to within first order terms in $\mathbf{R}$. Hencewith $\left.\frac{\partial u_i}{\partial x_j}\right|_{\mathbf{x}=\mathbf{r}}$ will simply be written as $\frac{\partial u_i}{\partial x_j}$.

In rheology we may usually ignore the inertial terms $m\ddot{\mathbf{r}}$ and $m\ddot{\mathbf{R}}$. Thus we obtain [1]

$$\dot{r}_i = u_i(\mathbf{r}) \quad \text{and} \quad \overset{\triangle}{R_i} = -\frac{\lambda}{\varsigma} R_i + \frac{\partial u_{(i}}{\partial x_{j)}} R_j \ , \tag{2.3}$$

where $\overset{\triangle}{R_i} = \dot{R}_i - \frac{\partial u_{[i}}{\partial x_{j]}} R_j$ is the rate of change of R_i as seen by an observer who locally rotates with the angular velocity $\frac{\partial u_{[i}}{\partial x_{j]}}$ of the fluid.

We may rewrite (2.3) in the form

$$\overset{\triangle}{R_i} = -\frac{1}{\varsigma}\frac{\partial}{\partial R_i}\left(\frac{\lambda}{2}R^2 - \frac{1}{2}\varsigma \ R_p \frac{\partial u_{(p}}{\partial x_{q)}} \ R_q\right) , \tag{2.4}$$

which lends itself to the following interpretation: The rate of change $\overset{\triangle}{R_i}$ is proportional, but opposite to the gradient of the energy

$$E(\mathbf{R}) = \frac{\lambda}{2}R^2 - \frac{1}{2}\varsigma \ R_p \frac{\partial u_{(p}}{\partial x_{q)}} \ R_q \tag{2.5}$$

that consists of the elastic energy of the spring and the potential energy of the Stokes friction force.

Obviously the gradient vanishes at $\mathbf{R} = 0$ so that the dumbbell relaxes to that state of rest.

This would indeed be the case, were it not for the stochastic character of the Stokes forces. While these forces are given by the Stokes assumption *in the mean*, there is considerable fluctuation in them.

2.2 Stochasticity. Short Version[2]

The fluctuation of the Stokes forces keeps the masses of the dumbbell in permanent random motion and the best way to characterize that motion is by introducing an *ensemble* of N dumbbells in which $N_{\mathbf{R}}$ of them have the distance vector $\mathbf{R}$. $N_{\mathbf{R}}$ is called a distribution function. By common consent the ergodic hypothesis holds by which a mean value for the ensemble equals the expectation value for a single dumbbell.[3]

The thermodynamicists attends to the stochasticity by assuming that the energy $E = \sum_{\mathbf{R}} E(\mathbf{R}) N_{\mathbf{R}}$ of the ensemble must be supplemented by its entropy $S = k \ln N!/\prod_{\mathbf{R}} N_{\mathbf{R}}!$ Thus, by (2.5), he forms a free energy,

$$F = E - TS = \sum_{\mathbf{R}}\left(\frac{\lambda}{2}R^2 - \frac{1}{2}\varsigma \ R_p \frac{\partial u_{(p}}{\partial x_{q)}} \ R_q + kT \ln \frac{N_{\mathbf{R}}}{N}\right) N_{\mathbf{R}} \ , \tag{2.6}$$

[1] Round and square brackets indicate symmetric and antisymmetric tensors respectively.

[2] The longer – and perhaps more satisfactory – version is relegated to the appendix. It leads to the same results.

[3] The motion of the center of mass is also stochastic but we ignore this fact for simplicity and assume $(2.3)_1$ to hold for $\dot{\mathbf{r}}$.

where the Stirling formula has been used. The summation extends over all $\mathbf{R}$ from $-\infty$ to ∞ . Equation (2.6) suggests that

$$F(\mathbf{R}) = \frac{\lambda}{2} R^2 - \frac{1}{2} \varsigma \; R_p \frac{\partial u_{(p}}{\partial x_{q)}} \; R_q + kT \ln \frac{N_{\mathbf{R}}}{N} \tag{2.7}$$

is the free energy of a dumbbell with $\mathbf{R}$ and this quantity has to replace $E(\mathbf{R})$ in (2.5) in order to provide $\overset{\Delta}{R_i}$ under stochastic forces. We obtain

$$\overset{\Delta}{R_i} = -\frac{\lambda}{\varsigma} R_i + \frac{\partial u_{(i}}{\partial x_{j)}} R_j - \frac{kT}{\varsigma} \frac{1}{N_{\mathbf{R}}} \frac{\partial N_{\mathbf{R}}}{\partial R_i} \tag{2.8}$$

or with $\overset{\Delta}{R_i} = \dot{R}_i - \frac{\partial u_{[i}}{\partial x_{j]}} R_j$:

$$\dot{R}_i = -\frac{\lambda}{\varsigma} R_i + \frac{\partial u_i}{\partial x_j} R_j - \frac{kT}{\varsigma} \frac{1}{N_{\mathbf{R}}} \frac{\partial N_{\mathbf{R}}}{\partial R_i}. \tag{2.9}$$

2.3 Continuity equation and equation of transfer

The conservation of particles in the "R-space" requires a continuity equation to hold in the form

$$\frac{\partial N_{\mathbf{R}}}{\partial t} + \frac{\partial \dot{R}_i N_{\mathbf{R}}}{\partial R_i} = 0. \tag{2.10}$$

An alternative form of this equation results by elimination of $\dot{R}_i$ between (2.9) and (2.10). We obtain

$$\frac{\partial N_{\mathbf{R}}}{\partial t} + \frac{\partial}{\partial R_i} \left\{ -\frac{\lambda}{\varsigma} \; R_i N_{\mathbf{R}} + \frac{\partial u_i}{\partial x_j} \; R_j N_{\mathbf{R}} - \frac{kT}{\varsigma} \; \frac{\partial N_{\mathbf{R}}}{\partial R_i} \right\} = 0. \tag{2.11}$$

Multiplication of this continuity equation by a generic function $Q(\mathbf{R})$ and summation over $\mathbf{R}$ provides an equation of transfer for the mean value $\langle Q \rangle = \sum_{\mathbf{R}} Q(\mathbf{R}) \frac{N_{\mathbf{R}}}{N}$, viz.

$$\langle Q \rangle^{\bullet} + \left\langle \frac{\partial Q}{\partial R_i} \left(\frac{\lambda}{\varsigma} R_i \frac{\partial u_i}{\partial x_j} \; R_j \right) \right\rangle - \frac{kT}{\varsigma} \left\langle \frac{\partial^2 Q}{\partial R_i \partial R_i} \right\rangle = 0. \tag{2.12}$$

Two choices for Q are appropriate for us to consider: $Q = R_p$ and $Q = R_p R_q$. We obtain

$$\langle R_q \rangle^{\Delta} = -\frac{\lambda}{\varsigma} \langle R_q \rangle + \frac{\partial u_{(q}}{\partial x_{j)}} \; \langle R_j \rangle \qquad \text{and} \tag{2.13}$$

$$\langle R_p R_q \rangle^{\Delta} = -\frac{2\lambda}{\varsigma} \langle R_p R_q \rangle + \frac{\partial u_{(p}}{\partial x_{j)}} \; \langle R_q R_j \rangle + \frac{\partial u_{(q}}{\partial x_{j)}} \langle R_p R_j \rangle + \frac{2}{\varsigma} kT \delta_{pq} \;, \tag{2.14}$$

where $\langle R_p R_q \rangle^{\Delta} = \langle R_p R_q \rangle^{\bullet} - \frac{\partial u[p}{\partial x_{j]}} \; \langle R_q R_j \rangle - \frac{\partial u_{[q}}{\partial x_{j]}} \langle R_p R_j \rangle$ is the corotational derivative of the tensor $\langle R_p R_q \rangle$.

Comparison of (2.13) with $(2.3)_2$ shows that the two equations are essentially identical. $\overset{\Delta}{R}_i$ in (2.3), which does not account for stochasticity, obeys the same law as the mean value $\langle R_i \rangle^{\Delta}$ of the stochastic motion. This is as it should be, of course.

We shall be interested in incompressible solutions with incompressible solvents. In that case we have $\frac{\partial u_l}{\partial x_l} = 0$ and it will turn out that only the deviatioric part of (2.14) is of interest[4], viz.

$$\langle R_{<p} R_{q>} \rangle^{\Delta} = -\frac{2\lambda}{\varsigma} \langle R_{<p} R_{q>} \rangle + \frac{\partial u_{<<p}}{\partial x_{j>}} \left\langle R_{\langle q \rangle} R_{j>} \right\rangle + \frac{\partial u_{<<q}}{\partial x_{j>}} \left\langle R_{\langle p \rangle} R_{j>} \right\rangle + \\ + \frac{2}{3} \left\langle R^2 \right\rangle \frac{\partial u_{<p}}{\partial x_{q>}}. \tag{2.15}$$

We abbreviate that equation by introducing the Oldroyd derivative $\frac{\delta}{\delta t}$:

$$\frac{\delta}{\delta t} \langle R_{<p} R_{q>} \rangle = -2\frac{\lambda}{\varsigma} \langle R_{<p} R_{q>} \rangle + \frac{2}{3} \left\langle R^2 \right\rangle \frac{\partial u_{<p}}{\partial x_{q>}}. \tag{2.16}$$

2.4 Equilibrium distribution function

We refer back to the free energy F in (2.6). The free energy must assume a minimum in equilibrium and this requirement determines the form of the equilibrium distribution function $N_{\mathbf{R}}^E$. A short calculation provides

$$N_{\mathbf{R}}^E = N \frac{e^{-\frac{1}{kT}\left(\frac{\lambda}{2} R^2 - \frac{1}{2}\varsigma R_p \frac{\partial u_{<p}}{\partial x_{q>}} R_q\right)}}{\sum_{\mathbf{R}} e^{-\frac{1}{kT}\left(\frac{\lambda}{2} R^2 - \frac{1}{2}\varsigma R_p \frac{\partial u_{<p}}{\partial x_{q>}} R_q\right)}}. \tag{2.17}$$

We shall need this for the calculation of $\langle R^2 \rangle$, the expectation value of R^2.

$$\left\langle R^2 \right\rangle = \sum_{\mathbf{R}} R^2 \frac{N_{\mathbf{R}}}{N} = -2kT \frac{\partial}{\partial \lambda} \left(\ln \sum_{\mathbf{R}} e^{-\frac{1}{kT}\left(\frac{\lambda}{2} R^2 - \frac{1}{2}\varsigma R_p \frac{\partial u_{<p}}{\partial x_{q>}} R_q\right)} \right). \tag{2.18}$$

The result reads to within terms of second order in the shear rate $\frac{\partial \mathbf{u}}{\partial \mathbf{x}}$:

$$\left\langle R^2 \right\rangle = 5 \frac{kT}{\lambda}. \tag{2.19}$$

3 Rheological equation of state

3.1 Dumbbell contribution to stress

The Hookean dumbbells contribute to the stress of the solution, because of the "long-range", "non-local" force of the springs between the dumbbell masses. The contribution is well-known to rheologists and it has been derived in detail by Bird, Warner & Evans

[4] Angular brackets denote trace-less tensors.

[8]. (See also Müller [9].) We quote their results for the deviatoric dumbbell stress which reads

$$t^D_{\langle pq\rangle} = n \left\langle R_{<p} R_{q>} \right\rangle \ . \tag{3.1}$$

n is the number density of dumbbells.

Elimination of $\langle R_{<p} R_{q>} \rangle$ between (2.16) and (3.1) provides a rate-type constitutive equation for $\mathbf{t}^D$ in terms of the deviatoric velocity gradient, viz.

$$\left(1 + \frac{1}{2}\frac{\varsigma}{\lambda}\frac{\delta}{\delta t}\right) t^D_{\langle pq\rangle} = \frac{1}{3} n\varsigma \left\langle R^2 \right\rangle \frac{\partial u_{<p}}{\partial x_{q>}} \ , \tag{3.2}$$

or, with $\langle R^2 \rangle$ from (2.19)

$$\left(1 + \frac{1}{2}\frac{\varsigma}{\lambda}\frac{\delta}{\delta t}\right) t^D_{\langle pq\rangle} = \frac{5}{3} nkT \frac{\varsigma}{\lambda} \frac{\partial u_{<p}}{\partial x_{q>}} \ . \tag{3.3}$$

3.2 Total deviatoric stress

We denote the deviatoric stress of the solvent by $t^S_{\langle pq\rangle}$. It is given by the Navier-Stokes equation, so that we have

$$t^S_{\langle pq\rangle} = 2\eta_s \frac{\partial u_{<p}}{\partial x_{q>}} \ , \tag{3.4}$$

where η_s is the viscosity of the solvent. The total stress of the solution will be denoted by $\mathbf{t}$ and it is the sum of the stresses $\mathbf{t}^S$ and $\mathbf{t}^D$, i.e. we have

$$t_{\langle pq\rangle} = \mathbf{t}^D_{\langle pq\rangle} + t^S_{\langle pq\rangle} \ . \tag{3.5}$$

Between (3.3) through (3.5) we may eliminate $\mathbf{t}^D$ and $\mathbf{t}^S$ and obtain a *viscoelastic constitutive relation* for $t_{\langle pq\rangle}$, viz.

$$\left(1 + \frac{1}{2}\frac{\varsigma}{\lambda}\frac{\delta}{\delta t}\right) t_{\langle pq\rangle} = \eta_0 \left(1 + \frac{\eta_s}{\eta_0}\frac{1}{2}\frac{\varsigma}{\lambda}\frac{\delta}{\delta t}\right) \frac{\partial u_{<p}}{\partial x_{q>}} \ , \tag{3.6}$$

where $\eta_0 = \eta_s + \frac{5}{6} nkT \frac{\varsigma}{\lambda}$ has been introduced. η_0 plays the role of a quasistatic viscosity.

Equation (3.6) agrees formally with the result of Bird, Warner & Evans [8], even though we are not quite in agreement with all aspects of those author's argument about the dumbbell stress. In the present case of incompressibility our difference is reduced to a slight difference in the definition of η_0.

4 Consideration of Stability

4.1 Rheological equation of state

In the terminology of rheology equation (3.6) is called a rheological equation of state and that is how we shall refer to it. We investigate the stability of a solution that satisfies this equation and we proceed to do that in the simplest conceivable manner.

There are two simple criteria of stability.

i.) If the velocity gradient vanishes, we expect the deviatoric stress to relax to zero. Obviously by (3.6) this will be happen for

$$\frac{\varsigma}{\lambda} > 0. \tag{4.1}$$

ii.) If the deviatoric stress vanishes, we expect the deviatoric velocity gradient to relax to zero. This requires

$$\frac{\eta_s}{\eta_0}\frac{\varsigma}{\lambda} > 0. \tag{4.2}$$

It is clear that both conditions are satisfied, since ς, λ, η_s and η_0 are all positive.

4.2 Grade-type constitutive relation

In continuum mechanics and thermodynamics of rheological fluids it is common to assume constitutive functions of grade-type. Thus in a fluid of nth grade the stress is postulated to be a function of the velocity gradient and of up to n of its time derivatives[5]. It is clear that the rheological equation of state (3.6), which, after a fashion, is derived from first principles, – and is therefore more reliable than a mere postulate – does not support this postulate, since it contains the rate of the stress. We may say that our analysis has produced an equation that is simultaneously of rate-type and grade-type. However, equation (3.6) can be forcefitted into a grade-type form in the following manner.

Purely formally we invert the operator $\left(1+\frac{1}{2}\frac{\varsigma}{\lambda}\frac{\delta}{\delta t}\right)$ in (3.6) and "expand it" to give

$$\begin{aligned} t_{\langle pq\rangle} &= \eta_0\left(1+\frac{1}{2}\frac{\varsigma}{\lambda}\frac{\delta}{\delta t}\right)^{-1}\left(1+\frac{\eta_s}{\eta_0}\frac{1}{2}\frac{\varsigma}{\lambda}\frac{\delta}{\delta t}\right)\frac{\partial u_{<p}}{\partial x_{q>}} \\ &\approx \eta_0\left(1-\frac{1}{2}\frac{\varsigma}{\lambda}\frac{\delta}{\delta t}\right)\left(1+\frac{\eta_s}{\eta_0}\frac{1}{2}\frac{\varsigma}{\lambda}\frac{\delta}{\delta t}\right)\frac{\partial u_{<p}}{\partial x_{q>}} \\ &\approx \eta_0\left(1+\left(\frac{\eta_s}{\eta_0}-1\right)\frac{1}{2}\frac{\varsigma}{\lambda}\frac{\delta}{\delta t}\right)\frac{\partial u_{<p}}{\partial x_{q>}}\ . \end{aligned} \tag{4.3}$$

The two last steps neglect second order derivatives.

Thus we have obtained a rate-type constitutive equation for the stress. It is clear that the chain of equations leading to (4.3) is quite rough[6]. But it *has* produced an equation that exhibits unstable solutions just as the grade-type constitutive equation of continuum mechanics do, according to Dunn & Fosdick [1] and Joseph [2]. Let us consider:

If $t_{\langle pq\rangle}$ is zero, we should expect $\frac{\partial u_{<p}}{\partial x_{q>}}$ to relax to zero. For this to happen we must require

$$\left(\frac{\eta_s}{\eta_0}-1\right)\frac{1}{2}\frac{\varsigma}{\lambda} > 0\ . \tag{4.4}$$

[5]Such is the case in Rivlin-Ericksen fluids of grade 2.

[6]Incidentally this is equivalent to Cattaneo's argument on heat conduction. See Cattaneo [6] and Müller & Ruggeri [7], p. 12 ff and p. 367 ff for a discussion.

However, with $\eta_0 = \eta_s + \frac{5}{6} nkT \frac{\varsigma}{\lambda}$, the left-hand side of the inequality (4.4) reads

$$\left(\frac{\eta_s}{\eta_0} - 1\right) \frac{1}{2} \frac{\varsigma}{\lambda} = -\frac{5}{12} \frac{nkT}{\eta_0} \left(\frac{\varsigma}{\lambda}\right)^2 \tag{4.5}$$

so that the stability condition is violated.

5 Conclusion

We repeat that the arguments leading from the rheological equation of state (3.6) to the grade-type equation (4.3) are purely heuristic. On that ground they will most certainly be flatly rejected by people in rational mechanics. Such people are most careful about their analysis but, alas, they are often less than careful about physical motivation of assumptions.

In the present case, they have ignored the proper form of the rheological equation and assumed the stress as given by the history of the velocity gradient. This was not acceptable and has led to instability.

6 Appendix

In the appendix we provide a more careful derivation of the equation (2.11) for the benefit of those who may be unhappy with the arguments of Sections 2.2 and 2.3.

The distribution $N_{\mathbf{R}\dot{\mathbf{R}}}$ of the dumbbells with $\mathbf{R}$ and $\dot{\mathbf{R}}$ is a more detailed description of the ensemble that the previously used distribution $N_{\mathbf{R}}$. The new distribution satisfies a continuity equation in the $(\mathbf{R}, \dot{\mathbf{R}})$-space

$$\frac{\partial N_{\mathbf{R}\dot{\mathbf{R}}}}{\partial t} + \frac{\partial \dot{R}_i N_{\mathbf{R}\dot{\mathbf{R}}}}{\partial R_i} + \frac{\partial \ddot{R}_i N_{\mathbf{R}\dot{\mathbf{R}}}}{\partial \dot{R}_i} = 0 \ . \tag{6.1}$$

With R_i as given by $(2.2)_2$ we obtain

$$\frac{\partial N_{\mathbf{R}\dot{\mathbf{R}}}}{\partial t} + \frac{\partial \dot{R}_i N_{\mathbf{R}\dot{\mathbf{R}}}}{\partial R_i} - \frac{2\varsigma}{m} \frac{\partial}{\partial \dot{R}_i} \left(\left(\dot{R}_i - \frac{\partial u_i}{\partial x_j} R_j \right) N_{\mathbf{R}\dot{\mathbf{R}}} \right) - \frac{2\lambda}{m} R_i \frac{\partial N_{\mathbf{R}\dot{\mathbf{R}}}}{\partial \dot{R}_i} = 0 \ . \tag{6.2}$$

Multiplication of this equation by a generic function $g(\mathbf{R}, \dot{\mathbf{R}}, t)$ and summation over $\dot{\mathbf{R}}$ results in an equation of transfer of the form

$$\begin{gathered} \tfrac{\partial [g] N_{\mathbf{R}}}{\partial t} + \tfrac{\partial \left[g \dot{R}_i\right] N_{\mathbf{R}}}{\partial R_i} + \tfrac{2\varsigma}{m} \left[\left(\dot{R}_i - \tfrac{\partial u_i}{\partial x_j} R_j \right) \tfrac{\partial g}{\partial \dot{R}_i} \right] N_{\mathbf{R}} + \tfrac{2\lambda}{m} R_i \left[\tfrac{\partial g}{\partial \dot{R}_i} \right] N_{\mathbf{R}} - \\ - \left[\tfrac{\partial g}{\partial t} + \dot{R}_i \tfrac{\partial g}{\partial R_i} \right] N_{\mathbf{R}} = 0 \end{gathered} \tag{6.3}$$

where $[g]\, N_{\mathbf{R}}$ stands for $\sum_{\dot{R}_i} g N_{\mathbf{R}\dot{\mathbf{R}}}$, i.e. $[g]$ is the mean value of $g(\mathbf{R}\dot{\mathbf{R}})$ taken over all $\dot{\mathbf{R}}$.

For our purposes it is sufficient to choose $g = 1$ and $g = \dot{R}_p$. In the first case we obtain

$$\frac{\partial N_{\mathbf{R}}}{\partial t} + \frac{\partial \left[\dot{R}_i\right] N_{\mathbf{R}}}{\partial \mathbf{R}} = 0 \ . \tag{6.4}$$

and the second case provides the equation

$$\frac{\partial\left[\dot{R}_p\right]N_{\mathbf{R}}}{\partial t}+\frac{\partial\left[\dot{R}_p\dot{R}_i\right]N_{\mathbf{R}}}{\partial R_i}+2\frac{\lambda}{m}R_pN_{\mathbf{R}}=-2\frac{\varsigma}{m}\left[\dot{R}_p-\frac{\partial u_p}{\partial x_j}R_j\right]N_{\mathbf{R}}\ . \tag{6.5}$$

In order to convert (6.5) into an algebraic equation for $[\dot{R}_p]$ we use the first step of a formal iterative scheme that is known as the Maxwellian iteration in the kinetic theory[7]: In the present case the scheme reduces to a calculation of the mean values $[\dot{R}_p]$ and $[\dot{R}_p\dot{R}_i]$ on the left-hand side of (6.5) *in equilibrium* so as to obtain the first iterate $[\dot{R}_p]^1$ on the right-hand side. Equilibrium is characterized by the Maxwell distribution

$$N_{\mathbf{R}\dot{\mathbf{R}}}=N_{\mathbf{R}}\sqrt{\frac{m}{4\pi kT}}^{2}e^{-\frac{m}{4kT}\dot{R}^2}\ , \tag{6.6}$$

so that we obtain

$$\left[\dot{R}_p\right]^E=0,\qquad \left[\dot{R}_p\dot{R}_i\right]^E=\frac{2kT}{m}\delta_{pi}\ . \tag{6.7}$$

Insertion into (6.5) provides the equation

$$\left[\dot{R}_p\right]^1=-\frac{\lambda}{\varsigma}R_p+\frac{\partial u_p}{\partial x_j}R_j-\frac{kT}{\varsigma}\frac{\partial\ln N_{\mathbf{R}}}{\partial R_p}\ . \tag{6.8}$$

We may use this first iterate to eliminate $[\dot{\mathbf{R}}]$ from (6.4) and obtain

$$\frac{\partial N_{\mathbf{R}}}{\partial t}+\frac{\partial}{\partial R_i}\left\{-\frac{\lambda}{\varsigma}R_iN_{\mathbf{R}}+\frac{\partial u_i}{\partial x_j}R_jN_{\mathbf{R}}-\frac{kT}{\varsigma}\frac{\partial N_{\mathbf{R}}}{\partial R_i}\right\}=0\ , \tag{6.9}$$

which is identical with (2.11).

Actually the Mawellian iterative scheme may be used to determine refinements in the equation (6.9). However, it seems that there is not much interest in those in the field of rheology.

References

[1] E. Dunn, R. L. Fosdick; Thermodynamics, stability and boundedness of fluids of complexity 2 and fluids of second grade, *Arch. Rat. Mech. Anal.*, **56**, 1974, 191-252.

[2] D. D. Joseph; Instability of the rest state of fluids of arbitrary grade greater than one, *Arch. Rat. Mech. Anal.*, **75**, 1981, 251-256.

[3] I. Müller, K. Wilmanski; Extended thermodynamics of a non-newtonian fluid, *Rheologica Acta*, **22**, 1986, 335-349.

[4] K. Wilmanski; Thermodynamics of heat conducting maxwellian fluid, *Arch. Mech.*, **40**, 2-3, 1988, 217-232.

[7]The present case it too trivial to recognize the beauty of the scheme, particularly since we are content with the first iterate. For a more comprehensive view of the scheme we refer to Müller [9].

[5] I. Müller; Kinetic theory and extended thermodynamics, in: T. Ruggeri, I. Müller (eds.) *Kinetic Theory and Extended Thermodynamics*, Pitagora Editrice Bologna, 245-258, Bologna, 1987.

[6] C. Cattaneo; Sulla conduzione del calore, *Atti Sem. Mat. Fis. Univ. Modena*, **3**, 1948, 83-101.

[7] I. Müller, T. Ruggeri; *Rational Extended Thermodynamics*, Springer, N.Y.,1998.

[8] R. B. Bird, H. R. Warner jr., D. C. Evans; Kinetic theory of dumbbell suspensions with Brownian motion, *Adv of Polym. Sci.*, **8**, Springer, Heidelberg, 1971.

[9] I. Müller; Stress and heat flux in a dumbbell solution, *Arch. Mech.*, **31**, 2, 1979, 233-249.