

## Quasilinear thermodynamics and relation between material functions

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### Summary

With the help of quasilinear irreversible thermodynamics, a relation between the shear viscosity and the primary normal-stress coefficient can be derived. A similar relation has been proposed by Bird, Hassager and Abdel-Khalik [1] for the first term of the Goddard expansion [2]. Here, we show that by incorporating the Carreau viscosity equation [3] with the irreversible thermodynamics the primary normal-stress coefficient can be expressed in closed form.

### 1. Introduction

The knowledge of material functions other than the non-Newtonian viscosity ( $\eta$ ) is necessary for the understanding and the optimal design of process equipment, involving the transport of viscoelastic materials such as polymer solutions and melts. The viscosity function can be measured by a variety of relatively inexpensive methods, but the measurements of normal-stress differences are currently much more involved. Consequently, it is very useful to predict interrelations amongst a variety of material functions. A simple relation between the primary normal-stress coefficient ( $\psi_1$ ) and the viscosity ( $\eta$ ) derived via the theory of fluctuations is discussed in this contribution and represents a powerful example of the prediction of one material function ( $\psi_1$ ) in terms of a more easily measured quantity ( $\eta$ ).

### 2. Theory

Onsager's linear thermodynamics of irreversible processes [4] has been generalized by Vodak and Stastna [5,6]. The quasilinear theory incorporating the theory of relaxation phenomena is based on the following hypotheses [6]:

(a) The relation between fluxes ( $J_i$ ) and forces ( $X_i$ ) is given by the following equations:

$$J_i + \lambda_i \frac{dJ_i}{dt} = \sum_{k=1}^n L_{ik} \left( X_k + \lambda_k^* \frac{dX_k}{dt} \right). \quad (1)$$

(b) The phenomenological coefficients satisfy the Onsager relations [4]

$$L_{ik} = L_{ki}, \quad (2)$$

i.e. they are symmetric.

(c) The entropy production  $\sigma$ , the fluxes  $J_i$  and the forces  $X_i$  are related through

$$\sigma = \sum_{i=1}^n J_i X_i \geq 0. \quad (3)$$

According to the nature of the fluxes and the thermodynamic forces, irreversible processes can be divided into three groups: (i) vector processes, associated with the transport of energy and matter, (ii) tensor processes, associated with the transport of momentum, and (iii) scalar processes, describing volume changes. Material functions associated with these three types are: thermal conductivity, shear viscosity and bulk viscosity, respectively [4].

Only the tensor process is considered in this contribution. For an isotropic medium, the relations between forces and fluxes can be simplified if we take into account that, according to Curie's theorem [4], fluxes and thermodynamic forces of different tensor dimensions cannot be connected. As a result of assumptions (1–3) the quasilinear theory is restricted to slow processes. Using Eqn. (3) to represent the entropy production, in terms of linear contributions only, one avoids the problems raised by Woods [8] with respect to nonlinear irreversible processes violating the Clausius-Duhem inequality.

Equation (1) can be written in co-rotational form using the Jauman time derivative and solved with the help of the Laplace-Jauman transform technique developed by Goddard and Miller [7].

Another procedure, using the Fourier transform technique, can be applied. Such a technique is used in statistical physics to study fluctuations [9]. Applying the Fourier transform to Eqn. (1) yields the following relation between the fluxes and thermodynamic forces:

$$J_i(t) = \sum_{k=1}^n \int_{-\infty}^{\infty} \tilde{L}_{ik}(s) X_k(t-s) ds. \quad (4)$$

$\tilde{L}_{ik}(s)$  are coefficients obtained from Eqn. (1) with the help of the Fourier transform, i.e.,

$$\tilde{L}_{ik}(s) = h(s) L_{ik} \frac{\lambda_i - \lambda_k^*}{\lambda_i^2} e^{-s/\lambda_i} \quad (5)$$

where  $h(s)$  is the unit step function.

As noted earlier, we will consider only tensor processes. Then, one can write

$$J(t) = \int_{-\infty}^{\infty} \tilde{L}(s) X(t-s) ds, \quad (6)$$

and this equation describes the response of the system to an external mechanical perturbation (the quantities  $J$  and  $X$  are now second-order tensors). If the thermodynamic force  $X$  can be represented by its Fourier integral, i.e.,

$$X(t-s) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \Phi[X] e^{i\dot{\gamma}(t-s)} d\dot{\gamma} \quad (7)$$

where  $\Phi[X]$  is the Fourier transform of  $X$ , then one obtains the following linear relation

$$J(t) = a(\dot{\gamma}) X(t). \quad (8)$$

Here the notations  $\dot{\gamma}$  is used to be consistent with the rheological literature [1,2].

The function  $a$ , which might be called the generalized response function, is computed from

$$a(\dot{\gamma}) = \int_0^{\infty} \tilde{L}(s) e^{-i\dot{\gamma}s} ds \quad (9)$$

where we have used the causality principle. The function  $a$  is a complex function of the real variable  $\dot{\gamma}$ , i.e.  $a(\dot{\gamma}) = a'(\dot{\gamma}) + ia''(\dot{\gamma})$  and from the definition of  $a(\dot{\gamma})$  it follows that: i)  $a(-\dot{\gamma}) = \overline{a(\dot{\gamma})}$ , ii)  $a'(-\dot{\gamma}) = a'(\dot{\gamma})$  and iii)  $a''(-\dot{\gamma}) = -a''(\dot{\gamma})$ . One can apply the complex Eqn. (8) to the steady shear flow of an incompressible viscoelastic fluid. In such a case Eqn. (8) must be time averaged, i.e.  $\langle J(t) \rangle = a(\dot{\gamma}) \langle X(t) \rangle$  where  $\langle \rangle$  represents a time average. In this case  $\langle J(t) \rangle$  will represent the extra stress tensor and since the constitutive equation must be materially invariant the “deformation function”  $\langle X \rangle$  is an isotropic function of the first two Rivlin-Ericksen tensors [10]. A generalized second-order fluid model can be obtained for the following “complex deformation function”:

$$\langle X \rangle = \alpha A_1^2 + \beta A_2 - i\dot{\gamma} A_1 \quad (10)$$

where  $A_1$  and  $A_2$  are the first two Rivlin-Ericksen tensors,  $\alpha$  and  $\beta$  are real constants and  $i$  is the imaginary unit. A real constitutive equation can now be written as

$$\begin{aligned} \tau &= \text{Re} \left[ a(\dot{\gamma}) (\alpha A_1^2 + \beta A_2 - i\dot{\gamma} A_1) \right] \\ &= a'(\dot{\gamma}) [\alpha A_1^2 + \beta A_2] + \dot{\gamma} a''(\dot{\gamma}) A_1. \end{aligned} \quad (11)$$

Evaluating Eqn. (11) for a steady shear-flow process one realises that the shear viscosity  $\eta(\dot{\gamma})$  is equal to  $\dot{\gamma} a''(\dot{\gamma})$ :

$$\eta(\dot{\gamma}) = \dot{\gamma} a''(\dot{\gamma}). \quad (12)$$

The primary normal-stress coefficient  $\psi_1(\dot{\gamma}) = (\tau_{11} - \tau_{22})/\dot{\gamma}^2$  and the secondary normal-stress coefficient  $\psi_2(\dot{\gamma}) = (\tau_{22} - \tau_{33})/\dot{\gamma}^2$  are related to  $a'(\dot{\gamma})$  as follows:

$$\psi_1(\dot{\gamma}) = -2\beta a'(\dot{\gamma}), \quad \psi_2(\dot{\gamma}) = (\alpha + 2\beta) a'(\dot{\gamma}). \quad (13)$$

It is now accepted that  $\psi_1$  is positive and  $\psi_2$  (of smaller magnitude than  $\psi_1$ ) is negative. The real and imaginary parts of the generalized response  $a(\dot{\gamma})$  are related through the Kramers-Kronig relations [4]

$$\begin{aligned} a''(\dot{\gamma}) &= -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{a'(x) dx}{x - \dot{\gamma}}, \\ a'(\dot{\gamma}) &= \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{a''(x)}{x - \dot{\gamma}} dx \end{aligned} \quad (14)$$

where  $P$  refers to the principal value of the integral. Since the imaginary part of the function  $a(\dot{\gamma})$  is an odd function one can write

$$a'(\dot{\gamma}) = \frac{2}{\pi} P \int_0^{\infty} \frac{x a''(x)}{x^2 - \dot{\gamma}^2} dx. \quad (15)$$

With the help of (12) and (13) this equation can be written as the following relation between the viscometric functions  $\psi_1(\dot{\gamma})$  and  $\eta(\dot{\gamma})$ :

$$\psi_1(\dot{\gamma}) = \frac{4}{\pi} \beta P \int_0^{\infty} \frac{\eta(x)}{\dot{\gamma}^2 - x^2} dx \quad (16)$$

Which can be written in the form given by Bird et al. [1],

$$\psi_1(\dot{\gamma}) = \frac{4}{\pi} \beta \int_0^{\infty} \frac{\eta(\dot{\gamma}) - \eta(x)}{x^2 - \dot{\gamma}^2} dx. \quad (17)$$

This relation has been derived in [1] with the help of the Goddard expansion [2].

### 3. Example

Let us assume that the viscosity function can be fitted by the Carreau viscosity equation [3]

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{(1 + (\lambda' \dot{\gamma})^2)^N}, \quad N \in \langle 0, \frac{1}{2} \rangle \quad (18)$$

where  $\lambda'$  is a time constant,  $\eta_0$  and  $\eta_{\infty}$  are the zero and infinite shear-rate viscosities, respectively. This equation, which is based on molecular network theories, is known to fit experimental data very well and can be used for smoothly changing flows of polymer melts and polymer solutions as well [1].

Substituting the viscosity  $\eta$  given by Eqn. (18) into relation (17) one obtains the following equality:

$$\pi \frac{\psi_1(x/\lambda')}{4\beta\lambda'(\eta_0 - \eta_{\infty})} = \int_0^{\infty} \frac{(1 + x^2)^{-N} - (1 + t^2)^{-N}}{t^2 - x^2} dt \quad (19)$$

where  $x = \lambda' \dot{\gamma}$ .

Denoting the integrand in Eqn. (19) by  $f(x, t)$  one can see that

$$\lim_{t \rightarrow x} \frac{\partial f}{\partial x}(x, t) = \frac{-N(N+1)x}{(1+x^2)^{N+2}} \quad (20)$$

and  $\partial f/\partial x$  is bounded and continuous for all  $x \in \langle 0, A \rangle$ ,  $t \leq 2A$ , ( $A > 0$ ). For  $t > 2A$ , there exists an integrable majorant,  $|\partial f/\partial x| \leq ct^{-3}$ , and the integral in Eqn. (19) can be differentiated with respect to the parameter  $x$ .

Let us further denote

$$F(x) = \int_0^\infty \frac{(1+x^2)^{-N} - (1+t^2)^{-N}}{t^2 - x^2} dt \equiv \int_0^\infty f(x, t) dt. \quad (21)$$

Since

$$\frac{\partial f}{\partial x}(x, t) = \frac{\partial f}{\partial t}(t, x), \quad (22)$$

one can write

$$\frac{dF}{dx} = \int_0^\infty \frac{\partial f}{\partial t}(t, x) dt = - \frac{1 - (1+x^2)^{-N}}{x^2}. \quad (23)$$

Integration of this equation yields

$$F(0) - F(x) = - \frac{1 - (1+x^2)^{-N}}{x} + 2N \int_0^x (1+u^2)^{-(N+1)} du. \quad (24)$$

The last term of this equation can be transformed into the incomplete beta function  $B_x(\nu, \mu)$  [11]. The function  $F$  is then given by the following relation:

$$F(0) - F\left(\sqrt{\frac{x}{1-x}}\right) = - \frac{1 - (1-x)^N}{\sqrt{x}} \sqrt{1-x} + NB_x\left(\frac{1}{2}, N + \frac{1}{2}\right). \quad (25)$$

The value of  $F(0)$  can be computed by substitution of  $t = s^{1/2}$  followed by integration by parts:

$$\begin{aligned} F(0) &= \int_0^\infty \frac{1 - (1+t^2)^{-N}}{t^2} dt = \frac{1}{2} \int_0^\infty \frac{1 - (1+s)^{-N}}{s^{3/2}} ds \\ &= N \int_0^\infty s^{-1/2} (1+s)^{-N-1} ds = NB\left(\frac{1}{2}, N + \frac{1}{2}\right) \end{aligned} \quad (26)$$

where  $B(\frac{1}{2}, N + \frac{1}{2})$  is the beta function [11].

Substituting Eqn. (26) into Eqn. (25) one obtains

$$\begin{aligned} F\left(\sqrt{\frac{x}{1-x}}\right) &= \frac{1 - (1-x)^N}{\sqrt{x}} \sqrt{1-x} \\ &\quad + N \left[ B\left(\frac{1}{2}, N + \frac{1}{2}\right) - B_x\left(\frac{1}{2}, N + \frac{1}{2}\right) \right]. \end{aligned} \quad (27)$$

Finally, the primary normal stress coefficient  $\psi_1$  is given by the following expression:

$$\begin{aligned} \psi_1(\dot{\gamma}) &= \frac{4\beta\lambda'(\eta_0 - \eta_\infty)}{\pi} \left\{ (\lambda'\dot{\gamma})^{-1} \left[ 1 - (1 + (\lambda'\dot{\gamma})^2)^{-N} \right] + \right. \\ &\quad \left. + N \left[ B\left(\frac{1}{2}, N + \frac{1}{2}\right) - B_z\left(\frac{1}{2}, N + \frac{1}{2}\right) \right] \right\} \end{aligned} \quad (28)$$

where  $z = (\lambda'\dot{\gamma})^2 / (1 + (\lambda'\dot{\gamma})^2)$ .

Let us note that the factor  $\beta$  cannot be obtained from the Goddard expansion [2];  $\beta$  has been added as an empirical factor by Bird et al. [1] since Eqn. (17) (without  $\beta$ ) predicts  $\psi_1$ -values lower than the experimentally measured quantities. Limitations of the presented relation between  $\psi_1(\dot{\gamma})$  and  $\eta(\dot{\gamma})$  are due to the assumptions (1–3) of the quasilinear thermodynamic theory. These limitations do not violate the Clausius-Duhem inequality.

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