The solid state isomerization of **2**b and **2**c is quite unusual and joins rare examples of solids that undergo chemical transformation in solid state, spontaneously. Interestingly, **2**d does not isomerize in solid state, though it does in solution. This indicates clearly that the solid state isomerization depends on the crystalline structure of the solid.

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On Stability of the Steady State, Thermodynamic Stability and Corresponding States in Rheology of Dense Simple Fluids†

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It is shown that the linear stability coincides with the thermodynamic stability in the case of stress tensor evolution for simple dense fluids even if the constitutive (evolution) equation for the stress tensor is nolinear. The domain of coincidence can be defined in the space of parameters appearing in the constitutive equation and we find the domain is confined in an elliptical cone in a three-dimensional parameter space. The corresponding state theory in rheology of simple dense fluids is also further examined. The validity of the idea is strengthened by the examination.

Introduction

Viscous phenomena[1] have attracted attention from physical scientists and engineers over a few decades by now since the subject is relevant to various engineering questions as well as some fundamental physical aspects of matter. Especially, non-Newtonian viscous flow of polymeric materials presents an interesting object of study since they are not only important substances in our everyday life but also present often intriguing and challenging topics of investigation in chemistry and physics. In the past a great deal of effort has been invested into the investigations[2] of empirical rheological equations of state and their statistical foundations which are generally studied by means of the Brownian motion model of a polymer taken as a bead-spring.[3]

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Studies[4-7] on non–Newtonian viscous flow in simple dense fluids begun relatively recently and there are now available some molecular dynamics calculations[4,5] on viscosities of simple fluids and also theories[6,7] of transport processes in simple dense fluids which are based on the kinetic theory. An important motivation for research on rheology of simple dense fluids is in formulating irreversible thermodynamics of nonlinear transport processes[8] since viscous flow is an important example of nonequilibrium phenomena and non–Newtonian viscous flow is in essence a transport phenomena in the domain of nonlinear nonequilibrium processes. We mean by a nonlinear nonequilibrium process a transport process to which a linear force–flux relation, e.g., Newton's viscosity law, Fourier's heat conduction law or Fick's diffusion law, no longer applies. Viscous flow in simple dense fluids is shown to be amenable to investigation from the microsopic viewpoint and the stress–strain relationship can be derived from the solution of the kinetic equation[6], e.g., the generalized Boltzmann equation[9]. Since such kinetic equation is generally not possible to solve exactly, it is practically necessary to solve the equation to an approximation. Unfortunately, approximate solutions of the kinetic equation are not assured to satisfy the thermodynamic laws despite the fact that all macroscopic natural phenomena are subject to the requirements of thermodynamic laws. The modified moment method[10] developed by Eu provides approximate solutions and the evolution equations (rheological constitutive equations) which strictly conform to the thermodynamic laws. Moreover, the method helps us systematically formulate a theory of irreversible thermodynamics for systems removed far from equilibrium. The rheological constitutive equations derived by the method have been applied to some dense fluids especially in regard to the shear rate dependence of viscosity. The steady state solution of the rheological constitutive equation yields the stress as a function of the strain rate and the non–Newtonian viscosity in general. Furthermore it was possible to show that the steady state is stable in the sense of Liapounov[11], but its connection with thermodynamic stability has not been considered despite its obviously interesting aspect. In this paper we will show that the linear stability of the steady state of the rheological equation of state coincides with the thermodynamic stability. These two stability criteria combine to give the domain of stability for the coefficients appearing in the rheological constitutive equation. We will also discuss an aspect of the rheological corresponding states that has not been discussed before but strengthens the concept from the experimental standpoint. It is reported by some research workers[12,13] that the normal stress coefficients change their signs as the shear rate or the frequency of shear oscillation changes. We find that they can change their signs without violating the stability, and the thermodynamic stability, criterion and therefore the phenomenon is fully in conformation to the thermodynamic second law. The discussions on these points are presented in the subsequent sections.

Nonlinear Stress Evolution Equation

In isothermal plane Couette flow of a single component, incompressible, non–heat–conducting simple fluid the velocity gradient tensor $\vec{\nabla}\vec{u}$ and the traceless symmetric part $\rho\hat{P}$ of the stress tensor $\overleftrightarrow{P}$ are given as follows:

$$\vec{\nabla}\vec{u} = \begin{bmatrix} 0 & 0 & 0 \\ 2\gamma & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \qquad \gamma = (\partial u_x/\partial y)/2$$

$$\rho\hat{P} = \begin{bmatrix} P_{xx}-p & P_{xy} & 0 \\ P_{yx} & P_{yy}-p & 0 \\ 0 & 0 & P_{zz}-p \end{bmatrix} \equiv \begin{bmatrix} \Pi_{xx} & \Pi_{xy} & 0 \\ \Pi_{yx} & \Pi_{yy} & 0 \\ 0 & 0 & \Pi_{zz} \end{bmatrix} \equiv \overleftrightarrow{\Pi}$$

$$\Pi_{xy} = \Pi_{yx}$$
$$\Pi_{xx} + \Pi_{yy} + \Pi_{zz} = 0.$$

Here we have assumed that the flow is in the x–direction while the gradient of velocity is in the y direction. The tensor $\vec{\nabla}\vec{u}$ may be decomposed into strain rate tensor $\overleftrightarrow{\Gamma}$ and spin tensor $\overleftrightarrow{W}$

$$\vec{\nabla}\vec{u} = \overleftrightarrow{\Gamma} + \overleftrightarrow{W}$$

where

$$\overleftrightarrow{\Gamma} = \begin{bmatrix} 0 & \gamma & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\overleftrightarrow{W} = \begin{bmatrix} 0 & -\gamma & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

The stress evolution equation can be derived from the generalized Boltzmann equation and its general form[6] is

$$\frac{d}{dt}\overleftrightarrow{\Pi} = -\vec{\nabla}\cdot\overleftrightarrow{\psi} - 2[\overleftrightarrow{\Gamma}\cdot\overleftrightarrow{\Pi}]^{(2)} + [\overleftrightarrow{W}, \overleftrightarrow{\Pi}] - 2p\overleftrightarrow{\Gamma} + [\overleftrightarrow{V}^{(2)}]^{(2)} + \overleftrightarrow{\Lambda} \quad (1)$$

where

$$[\overleftrightarrow{W}, \overleftrightarrow{\Pi}] = \overleftrightarrow{W}\cdot\overleftrightarrow{\Pi} - \overleftrightarrow{\Pi}\cdot\overleftrightarrow{W}$$

and $[A]^{(2)}$ is the traceless symmetric part of tensor A, p is the hydro–static pressure, $\overleftrightarrow{\psi}$ and $\overleftrightarrow{V}^{(2)}$ are respectively a third and second rank tensor whose definitions can be found in ref. 6. They are identically equal to zero in the approximation that neglects heat conduction. The term $\overleftrightarrow{\Lambda}$ represents the collisional dissiaptive term which is generally a nonlinear function of $\overleftrightarrow{\Pi}$.

Since (1) is derived in a space–fixed frame of reference the vorticity term $[\overleftrightarrow{W}, \overleftrightarrow{\Pi}]$ and the rate of change in $\overleftrightarrow{\Pi}$, $(d\overleftrightarrow{\Pi}/dt)$, are in variance with the corresponding terms in the stress evolution equation commonly used in continuum mechanics which obey the frame indifference principle.[14] The variance referred to above can be removed if a corotational frame of reference is adopted instead of a fixed frame.[15] In the corotational frame formulation the rate of change in time for stress tensor $\overleftrightarrow{\Pi}$ is expressed in terms of the Jaumann derivative[16]:

$$\frac{\mathcal{D}\overleftrightarrow{\Pi}}{\mathcal{D}t} = \frac{d\overleftrightarrow{\Pi}}{dt} + [\overleftrightarrow{W}, \overleftrightarrow{\Pi}]$$

and with this corotational frame formulation the stress evolution equation does not involve the vorticity term explicitly and the equation becomes materially objective:

$$\frac{\mathcal{D}\overleftrightarrow{\Pi}}{\mathcal{D}t} = -2[\overleftrightarrow{\Gamma}\cdot\overleftrightarrow{\Pi}]^{(2)} - 2p\overleftrightarrow{\Gamma} + \overleftrightarrow{\Lambda} \quad (2)$$

When this form of evolution equation is reverted back to a space–fixed reference frame the evolution equation for $\overleftrightarrow{\Pi}$ takes the following form:

$$\frac{d\overleftrightarrow{\Pi}}{dt} = -2\,[\overleftrightarrow{\Gamma}\cdot\overleftrightarrow{\Pi}]^{(2)} - [\overleftrightarrow{W}, \overleftrightarrow{\Pi}] - 2p\overleftrightarrow{\Gamma} + \overleftrightarrow{\Lambda} \tag{3}$$

where the vorticity term now has the opposite sign to the fixed frame version (1). This form of evolution equation for $\overleftrightarrow{\Pi}$ is taken as a model for studying stress evolution in a dense fluid in this paper. It is a model since we take the coefficients (collision integrals) appearing in the equation as phenomenological parameters. We seek the justilication of such an evolution equation a posteriori by its utility in comparison with experiment.

According to the modified moment method, the dissipative term $\overleftrightarrow{\Lambda}$ is ultimately related to the entropy production σ due to the process in question in the following manner:

$$\sigma/k_B = \beta\overleftrightarrow{X} : \overleftrightarrow{\Lambda} \tag{4}$$

where k_B is the Boltzmann constant, $\beta = 1/k_BT$, X is a second order traceless symmetric tensor which can be determined from the following consistency condition

$$\overleftrightarrow{X} : (2\,[\overleftrightarrow{\Gamma}\cdot\overleftrightarrow{\Pi}]^{(2)} + 2p\overleftrightarrow{\Gamma}) + \overleftrightarrow{\Pi} : \Gamma = 0. \tag{5}$$

We remark that the solution of this equation provides $\overleftrightarrow{X}$ to be used in the subsequent calculation.

The entropy production can be calculated by means of a cumulant expansion and to the first order cumulant approximation σ and $\overleftrightarrow{\Lambda}$ take the following forms[6b]:

$$\sigma/k_B = \beta g^{-1}\ \overleftrightarrow{X}\overleftrightarrow{X} :: R^{(4)}\ (\sinh x/x) \tag{6a}$$

$$\overleftrightarrow{\Lambda} = g^{-1}\overleftrightarrow{X} : \overleftrightarrow{R}^{(4)}\ (\sinh x/x) \tag{6b}$$

where

$$x = \beta \ll (\overleftrightarrow{X} : \overleftrightarrow{h})^2 \gg^{\frac{1}{2}}$$

$$\overleftrightarrow{R}^{(4)} = \beta^2 \ll \overleftrightarrow{h}\overleftrightarrow{h} \gg,$$

with $\overleftrightarrow{h}$ standing for the molecular expression for the stress tensor, « » is the reduced collision integral, g is the scaling parameter for the collision integral

$$g = \beta\,(m_r\,\beta/2)^{1/2}/(nd)^2,$$

m_r is the reduced mass, n and d are respectively the number density and the diameter of the molecule. Since $\overleftrightarrow{h}$ is a second rank tensor, $\overleftrightarrow{R}^{(4)}$ is a tensor of rank four. The details of $\overleftrightarrow{R}^{(4)}$ and related collision integrals can be found in ref. 6 to which the reader is referred. The tensor $\overleftrightarrow{R}^{(4)}$ can be calculated in principle in terms of n, T and the potential parameters, but in this work we will regard them as phenomenological coefficients which can be determined from experimental data, since our aim in this paper is to determine constraints implied on them by the thermodynamic laws and stability of equilibrium and the steady state of the evolution equation (3).

It is shown in a previous work[6] that $\overleftrightarrow{X}$ can be given by

$$X = -\overleftrightarrow{\Pi}/2p + [\overleftrightarrow{\Pi}\cdot\overleftrightarrow{\Pi}]^{(2)}/2p^2. \tag{7}$$

By using (6b) and (7) and defining the following abbreviations for shear stress, primary and secondary normal stress difference

$$S = \Pi_{xy}/p,$$

$$N_1 = (\Pi_{xx} - \Pi_{yy})/p,$$

$$N_2 = (\Pi_{yy} - \Pi_{zz})/p,$$

we write the evolution for three independent components of $\overleftrightarrow{\Pi}$ as follows:

$$\frac{d}{dt}S = -2\gamma\,(1+2N_1/3+N_2/3) - C_sS\,(1-N_1/3-2N_2/3) \cdot (\sinh x/x) \tag{8a}$$

$$\frac{d}{dt}N_1 = 4\gamma S - \{(C_x - C_{xy})N_1\,(1-N_1/3-2N_2/3) + (C_x - C_y)\,[N_2\,(1+2N_1/3+N_2/3) - S^2]\} \cdot (\sinh x/x) \tag{8b}$$

$$\frac{d}{dt}N_2 = -4\gamma S - \{(C_x+2C_{xy})N_1\,(1-N_1/3-2N_2/3) + (C_x+2C_y+3C_{xy})\,[N_2\,(1+2N_1/3+N_2/3) - S^2]\} \cdot (\sinh x/x) \tag{8c}$$

where

$$C_x = \beta^2 \ll h_{xx}h_{xx} \gg /2pg,$$

$$C_y = \beta^2 \ll h_{yy}h_{yy} \gg /2pg,$$

$$C_{xy} = \beta^2 \ll h_{xx}h_{yy} \gg /2pg,$$

$$Cs = \beta^2 \ll h_{xy}^2 \gg /2pg.$$

Eqs. (8a–c) are the rheological constitutive equations derived by the modified moment method from the generalized Boltzmann equation for dense simple fluids. They provide algebraic relations between the three independent components of $\overleftrightarrow{\Pi}$ and the rate of strain γ which we investigate in the following section.

Solution of Evolution Equations at a Moderate Strain Rate

Since (8a–c) are generally not amenable to analytic solution, either numerical solution method or approximate methods must be developed. Since it would be preferable to have some analytic relation between γ and S, N_1, and N_2 to discuss some formal aspects of viscosity and normal stress coefficients, we look for a suitable approximate but analytic form of solution. When the shear rate is not too large, the magnitudes of shear and normal stresses are smaller than the hydrostatic pressure so that the following inequalities hold:

$$|S| \ll 1, \quad |N_1| \ll 1, \quad |N_2| \ll 1.$$

In fact the stresses measured on viscous flow in polymeric solutions are generally within the range of values obeying the inequalities above. When the inequalities hold, (8a–c) can be put to a good approximation into the following forms:

$$\frac{d}{dt}S = -2\gamma - C_sS\,(\sinh x_o/x_o) \tag{9a}$$

$$\frac{d}{dt}N_1 = 4\gamma S - [(C_x - C_{xy})N_1 + (C_x - C_y)N_2]\ \ (\sinh x_o/x_o) \tag{9b}$$

$$\frac{d}{dt}N_2 = -4\gamma S - [(C_x+2C_{xy})N_1 + (C_x+2C_y+3C_{xy})N_2]\ \ (\sinh x_o/x_o) \tag{9c}$$

which is the result of dropping the quadratic terms and replacing x with $x_0 = (C_s pg/2)^{1/2}S$ in the evolution equations. To the same order of approximation the entropy production is given as follows:

$$\sigma/k_B = (\beta p/2)\,[C_sS^2 + C_xN_1^2 + 2\,(C_x + C_{xy})N_1N_2 + (C_x+C_y+2C_{xy})N_2^2]\ \ (\sinh x_o/x_o) \tag{10}$$

We then find the following steady state solution for (9a–c)

$$pS^{(s)} = -2\eta_o\gamma q_e \tag{11a}$$

$$pN_1^{(s)} = -4\psi_{10}\gamma^2 q_e^2 \tag{11b}$$

$$pN_2^{(s)} = -4\psi_{20}\gamma^2 q_e^2 \tag{11c}$$

$$q_e = \sinh^{-1}\tau\gamma/\tau\gamma$$

where

$$\eta_o = p/C_s, \tag{12a}$$

$$\tau = (2\eta_o g)^{1/2}, \tag{12b}$$

$$\psi_{10} = (2/3)\eta_o(2C_x+C_y+3C_{xy})/(C_xC_y-C_{xy}^2) \tag{12c}$$

$$\psi_{20} = -(2/3)\eta_o(2C_x+C_{xy})/(C_xC_y-C_{xy}^2). \tag{12d}$$

From the following definitions of transport coefficients

$$pS^{(s)} = -2\eta\gamma,$$

$$pN_1^{(s)} = -4\psi_1\gamma^2,$$

$$pN_2^{(s)} = -4\psi_2\gamma^2,$$

we obtain the formulas for non-Newtonian viscosity, primary normal stress coefficient and secondary normal stress coefficient:

$$\eta = \eta_o q_e \tag{13a}$$

$$\psi_1 = \psi_{10} q_e^2 \tag{13b}$$

$$\psi_2 = \psi_{20} q_e^2 \tag{13c}$$

The details of derivation of these formulas appear in ref. 6b. These formulas will be used for the discussions below.

Stability of the Steady State and the Second Law of Thermodynamics

The steady state solutions presented in the previous section are simply the mathematical solutions satisfying the conditions.

$$dS/dt = 0, \quad dN_1/dt = 0, \quad dN_2/dt = 0$$

In order for them to be physically meaningful the longtime limits of the solutions for the differential equations must coincide with the steady state solutions for arbitrary initial conditions. In other words, if the experiment is of steady condition, the stresses must evolve to their value at the steady condition and this means the observed steady stress must be represented by stable steady state solutions of (9a–c).

The stability question of nonlinear ordinary differential equations can be handled if the theory of Liapounov[11] is applied to the differential equations linearized around the steady state. If (8a–c) is linearized by expanding the nonlinear terms in Taylor series and retaining only the linear terms, the following linearized ordinary differential equations arise:

$$\frac{d}{dt}S = -C_s(1+\gamma^2\tau^2)^{1/2}(S-S^{(S)}) \tag{14a}$$

$$\begin{aligned}\frac{d}{dt}N_1 = {} & [8\gamma+2S^{(S)}(1+\gamma^2\tau^2)^{1/2}/\eta_0](S-S^{(S)}) \\ & +(2\gamma\eta_0/S^{(S)})[(C_x-C_{xy})(N_1-N_1^{(S)}) \\ & +(C_x-C_y)(N_2-N_2^{(S)})]\end{aligned} \tag{14b}$$

$$\begin{aligned}\frac{d}{dt}N_2 = {} & -[8\gamma+2S^{(S)}(1+\gamma^2\tau^2)^{1/2}/\eta_0](S-S^{(S)}) \\ & +(2\gamma\eta_0/S^{(S)})[(C_x+2C_{xy})(N_1-N_1^{(S)}) \\ & +(C_x+2C_y+3C_{xy})(N_2-N_2^{(S)})].\end{aligned} \tag{14c}$$

With the definitions of new dependent variables

$$Y_1 = S - S^{(S)}$$

$$Y_2 = N_1 - N_1^{(S)}$$

$$Y_3 = N_2 - N_2^{(S)}$$

and a column vector Y

$$\vec{Y} = \begin{bmatrix} Y_1 \\ Y_2 \\ Y_3 \end{bmatrix}$$

(14a–c) can be put into the form

$$\frac{d}{dt}\vec{Y} = M\cdot\vec{Y} \tag{15}$$

where the 3×3 matrix **M** has the following components: with $f = 4\gamma(1+\gamma^2\tau^2)^{1/2}$

$$M = \begin{pmatrix} -C_s f/4\gamma & 0 & 0 \\ 8\gamma - f\eta/\eta_0 & -(C_x-C_{xy})\eta_0/\eta & -(C_x-C_y)\eta_0/\eta \\ -8\gamma+f\eta/\eta_0 & -(C_x+2C_{xy})\eta_0/\eta & -(C_x+2C_y+3C_{xy})\eta_0/\eta \end{pmatrix}$$

According to the theory of linear stability, all the eigenvalues of **M** must have a negative real part in order for the steady state to be stable. If the Routh–Hurwitz conditions[17] are applied to the linear stability condition on the eigenvalues of **M**, the following three inequalities arise:

$$C_s > 0, \tag{16a}$$

$$C_x+C_y+C_{xy} > 0, \tag{16b}$$

$$C_xC_y - C_{xy}^2 > 0. \tag{16c}$$

On the other hand, since the entropy production σ must be always positive for nonequilibrium processes, the following inequalities can be deduced from (10):

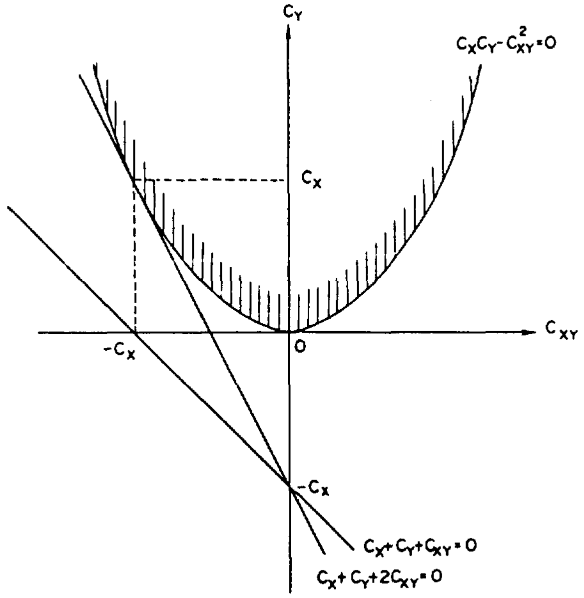

Figure 1. The stability parabola. The shaded region inside the parabola is the common area of $C_x>0$, $C_y>0$, $C_x+C_y+2C_{xy}>0$, and $C_xC_y - C_{xy}^2>0$.

$$C_s > 0 \tag{17a}$$

$$C_x > 0, \tag{17b}$$

$$C_x + C_y + 2C_{xy} > 0, \tag{17c}$$

$$C_xC_y - C_{xy}^2 > 0. \tag{17d}$$

We would like to show that there is a relation between the inequalities (16a–c) deduced from the linear stability condition and the inequalities (17a–d) implied by the second law of thermodynamics.

Clearly, the inequalities (16a) and (17a) for the coefficient C_s coincide. Therefore as far as C_s is concerned, the linear stability condition and the second law of thermodynamics yield the same condition on C_s and they may be regarded as equivalent. We now consider other inequalities. Recalling that C_x and C_y and defined as collisional integrals of quadratic terms related to the virial tensor for stress and they are always $C_x > 0$, $C_y > 0$ and that C_xC_y must be always larger than C_{xy}^2 by the Schwartz inequality[18], it is easy to see that the inequality $C_xC_y - C_{xy}^2 > 0$ is sufficient for the conditions on C_x, C_y and C_{xy} as shown graphically in Figure 1. The values of the coefficient must be within the shaded region bounded by the parabola. This means that in the moderate shear rate range under consideration the requirements by the second law of thermodynamics on C_x, C_y and C_{xy} exactly coincide with the linear stability criterion for the steady state of the stress evolution equations (8a–c). In order to understand this aspect in a more general setting, we form a three-dimensional orthogonal space spanned by (C_x, C_y, C_{xy}) and consider a surface $C_xC_y - C_{xy}^2 = 0$. This surface is a quadric whose traces are the axes C_x and C_y. Therefore the surface is that of an elliptical cone in the positive half space as shown in Figure 2. In the three dimensional space the subspace $C_xC_y - C_{xy}^2 > 0$ is then a space bounded by the elliptical cone, and only the values of the coefficients C_x, C_y, C_{xy} within the cone can give rise to a stable steady state for which the entropy production is positive, that is, the second law of thermodynamics is satisfied in those cases. The present analysis is also significant in settling the question of which of the two formulations, fixed frame and corotating frame, must be used. We have argued that the fixed frame evolution equation leads to incorrect signs for primary and secondary normal stress coefficients and thus must be abandoned. If the fixed frame evolution were used for the present discussion the inequality (16c) would have been reversed and it would mean that not only the second law of thermodynamics is contradicted by it but also the kinetic theory prediction for the inequality would be broken; recall that the definitions of C_x, C_y and C_{xy} imply the inequality (16c) by the Schwartz ine-

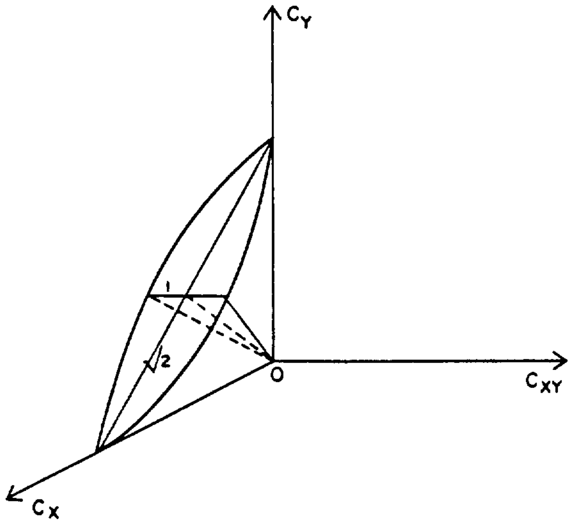

Figure 2. The stability cone: subspace $C_xC_y - C_{xy}^2 > 0$ in the parameter space.

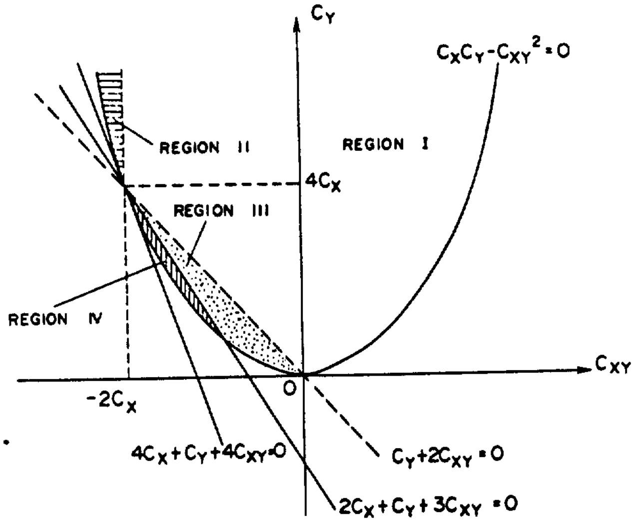

Figure 3. Regions in which the normal stress coefficients have different signs and relative magnitudes.

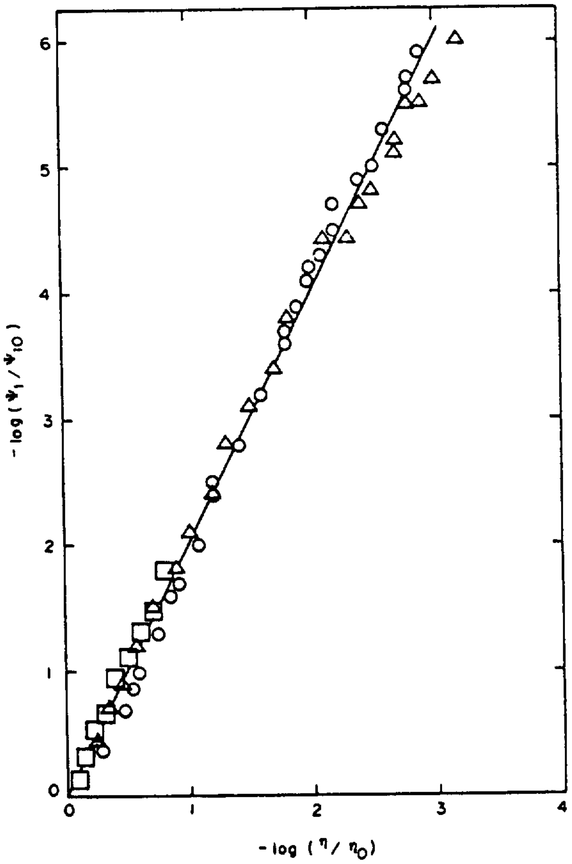

Figure 4. Corresponding state relation between the shear viscosity and the first normal stress coefficient. The straight line is the theoretical prediction, $\psi_1/\psi_{10} = (\eta/\eta_0)^2$; △, PAA(Ref.20); ○, Separan AP30(Ref.19); □, Oppanol B200(Ref.21).

quality. Therefore we see that the reason for using a corotating frame formulation is further strengthened by the analysis presented above.

The signs of the normal stress coefficients defined by (12a,b) can be examined in close connection with the stability criterion established here. Since the denominator in (12a,b) is always positive, the signs of the zero shear rate normal stress coefficients will be determined by the numerators. The numerators are planes in (C_x, C_y, C_{xy}) and, when projected, are lines in the (C_y, C_{xy}) plane as shown in Fig. 3. They cut the stability parabola $C_xC_y - C_{xy}^2 = 0$ and the shaded regions bounded by the stability parabola and the lines $C_y + 2C_{xy} = 0$ and $2C_x + C_y + 3C_{xy} = 0$. In the regions bounded from below by the stability parabola the linear stability criterion coincide with the thermodynamic stability criterion, but the normal stress coefficients can have various signs as indicated below:

Region I : $\psi_{10} > 0$, $\psi_{20} < 0$; $\psi_{10} > -\psi_{20}$
Region II : $\psi_{10} > 0$, $\psi_{20} > 0$; $\psi_{10} > \psi_{20}$
Region III : $\psi_{10} > 0$, $\psi_{20} < 0$; $\psi_{10} < -\psi_{20}$
Region IV : $\psi_{10} < 0$, $\psi_{20} < 0$; $-\psi_{10} < -\psi_{20}$.

Note that Region I is the domain bounded by the stability parabola minus the shaded regions. The above analysis shows that there is nothing mysterious about the change in sign of normal stress coefficients from the standpoints of thermodynamic laws as long as the thermodynamic stability criterion is met by the coefficients C_x, C_y and C_{xy}. As far as we are aware of, this result is new.

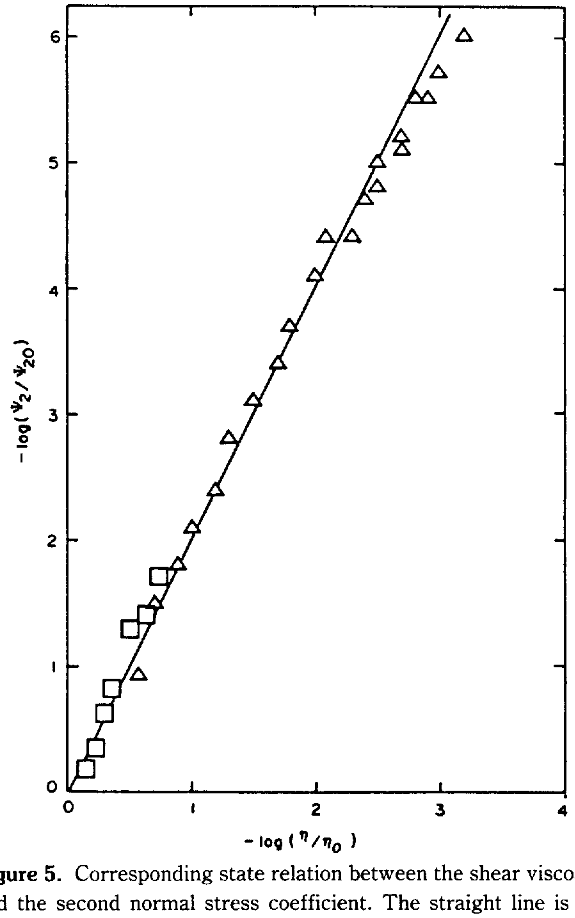

Figure 5. Corresponding state relation between the shear viscosity and the second normal stress coefficient. The straight line is the theoretical prediction, $\psi_2/\psi_{20} = (\eta/\eta_0)^2$; △, PAA(Ref.20); □, Oppanol B200(Ref.21).

Table 1. Paraetric Values of Polymer Solutions Studied in this and Previous Papers (Ref. 6).

	PAA[a]	Separan AP30[b]	Oppanol B200[c]
η_0 Pa sec	4.5×10^3	3.0×10^2	4.0×10^{-1}
ψ_{10} Pa sec^2	2.5×10^6	2.8×10^4	3.5×10^{-1}
ψ_{20} Pa sec^2	-1.5×10^5	—	-5.5×10^{-2}

[a] PAA = 2.5% polyacrylamide in 50-50 water-glycerine solution (Ref.20). [b] Separan AP30 = 1.5% polyacrylamide in 50-50 water-glycerine solution(Ref.19). [c] Oppanol B200 = 1.1% polyisobutylene in decaline(Ref.21).

Application to Polymetric Solutions

Since (13a-c) are determined from a kinetic equation for simple dense fluids the material functions derived cannot be expected to be applicable to other materials. However, when the evolution equation (3) with (7) is compared with the rheological constitutive equations commonly used in the phenomenological approach to rheology, its structure is quite similar to the structure of the phenomenological equations. Therefore it appears that (3) may be used for studying the shear rate dependence of material functions if the coefficients appearing in the equations are taken as phenomenlogical coefficients. In fact, the coefficients C_s, C_x, C_y, and C_{xy} in (8a-c) can be related to the zero shear rate material functions as shown already. Especially, if we define reduced material functions in reference to the zero shear rate material functions already introduced

$$\eta^* = \eta/\eta_0$$
$$\psi_1^* = \psi_1/\psi_{10}$$
$$\psi_2^* = \psi_2/\psi_{20}$$
$$\gamma^* = \gamma\tau$$

then the following universal reduced material functions are obtained which we call the corresponding state material functions

$$\eta^* = q_e^*$$
$$\psi_1^* = \psi_2^* = q_e^{*2} \tag{18a}$$
$$q_e^* = \sinh^{-1}\gamma^*/\gamma^*. \tag{18b}$$

These equations suggest that there is a universal (corresponding state) relationship between the reduced material functions:

$$\psi_1^* = \psi_2^* = \eta^{*2}. \tag{19}$$

These relations were indicated in a previous paper but not ascertained in comparison with experimental data.[20-21] We show that they indeed hold excellently. We treat η_0, ψ_{10}, ψ_{20}, τ, as adjustable parameters and then reduce the measured material functions for some polymeric solutions. As is shown in Figures. 4 and 5, the relationships as given in (19) are obeyed to a very good accuracy. The figures also demonstrate the fact that the corresponding state theory is obeyed to the same degree of accuracy for the polymeric solutions studied. Therefore it is possible to conclude that the idea of corresponding states in rheology appears to have experimental support at least for the systems studied in this and previous papers[6]

(Table 1). Its theoretical basis can be founded by using the genralized Boltzmann equation.

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Synthesis and Ring-Opening Polymerization of 1,2-Disubstituted Cyclobutanes

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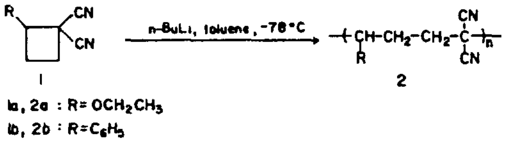
1,1-Dicyano-2-ethoxycyclobutane (**1a**) was prepared by [2+2] cycloaddition reaction of vinylidene cyanide with ethyl vinyl ether. 1,1-Dicyano-2-phenylcyclobutane (**1b**) was prepared by the reactions involving the reduction of cinnamyl alcohol, chlorination, cyanomethylation, bromination, and ring-closure reaction. Compound **1a** was ring-opening polymerized with NaCN or n-butyllithium to give a low molecular weight polymer. The compound **1b** however, failed to polymerize by either anionic or radical catalysts.

Introduction

Previously we have reported ring-opening polymerization of various substituted cyclopropanes[1-4] with radical or anionic initiators. These substituted cyclopropanes have various radical- or anion-stabilizing groups at the proper position of the cyclopropane ring. This substituent effect was also demonstrated in the ring-opening polymerization of 2-methylene-4-phenyl-1,3-dioxolane[5] and 2-phenyl-3-vinyloxirane.[6] We have extended this concept to the substituted cycobutanes and the present report describes the synthesis and ring-opening polymerization of 1,1-dicyano-2-ethoxycyclobutane (**1a**) and 1,1-dicyano-2-phenylcyclobutane (**1b**).



1 2

1a, 2a : R= OCH_2CH_3
1b, 2b : R= C_6H_5

Results and Discussion

Monomer **1a** was prepared[7] as shown in Scheme I, by reacting ethyl vinyl ether and vinylidene cyanide. Vinylidene cyanide.[8] Monomer **1b** was synthesized by the reactions involving the reduction of cinnamyl alcohol, chlorination, cyanomethylation, bromination, and ring-closure reaction, as