Applications of Extended Thermodynamics ...Part II.

Sergey Sobolev
Review Article

Applications of Extended Thermodynamics to Chemical, Rheological, and Transport Processes: A Special Survey Part II. Vector Transport Processes, Shear Relaxation and Rheology

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4. Vector transport processes

The transport processes to be taken up here are heat conduction and diffusion plus dielectric relaxation and electrical conduction. The first two are clearly coupled, since

1 The sections of this second part are numbered consecutively to those of the first part, published in Vol. 20, Issue 3, Pages 205–229. Similarly, new bibliographical references start with reference 100, the first 99 references being listed at the end of Part 1.

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diffusing molecules can carry energy, and they are often treated together in the same formalism, which would make it difficult not to combine them in a single section. Since the polarization current is a component of the total current, relaxation of electric polarization and of the current of free charges are usually treated together. We add a third sub-section on superfluidity. Applications of the phenomenology of vector processes fall into four classes: (1) Use of reciprocity in calculating linear transport coefficients from models. (2) Non-linear effects in heat conduction and diffusion. (3) temperature and polarization waves. (4) correlation functions. Category (1) is old, since molecular models have given way to molecular dynamics, and effects in (2) are small. Papers on (3) and (4) have tended to give more attention to formulating the theory than to predictions tested against experiment.

4.1. Heat conduction and diffusion

The earliest extended thermodynamic treatment [100] of thermal conduction was designed to fit the Cattaneo-Vernot equation (24) into the scheme of de Groot [12], discussed in Part I, Section 2.2. The phenomenological coefficients were evaluated with the aid of a phonon model of Debye. This work was extended by coupling the phonon component of heat flow to a self-diffusion component [101] and to a binary diffusion flow [102]. The first of these extensions was designed to estimate numerically the coefficient of \((\nabla \rho)^2\) in the free energy density, which was earlier exploited by Cahn and Hilliard [103] to calculate the density profile across a liquid-vapour phase boundary. The extended treatment of binary diffusion [102] led to a formal expression for the thermal diffusion coefficient, but not a numerical value. These papers show how Onsager reciprocity can be exploited, in conjunction with molecular models, in calculating transport coefficients. The models are now old, but the formalism formed the basis of more recent studies, discussed below, of non-linear heat and matter transport. A substantial number of contemporary studies incorporate both heat flow \(\mathbf{J}\) and viscous pressure \(P\). Most of these will be discussed in Section 5 on viscoelasticity.

The possibility of non-linear effects in heat conduction arises from the fact that \(\gamma \equiv \lambda / \tau\) in equation (24) may have a term \(O(J^2)\). This term was estimated microscopically by adding [104] to the Liouville equation a term representing coupling of the system to two reservoirs at different \(T\), which maintain a steady heat flow. From the resulting Liouville equation with reservoir term included, one extracts an equation for \(\partial g / \partial t\), where [105]

\[
g'(v) = \int f_x \delta(J - v) dx. \tag{63}
\]

Here \(\mathbf{J}\) is the heat flux operator, \(f_x\) is the solution of the Liouville equation, \(g'(v)\) is the probability amplitude for the distribution of values of \(\mathbf{J}\). The first moment of the equation for \(\partial g / \partial t\) has the form of equation (24), with

\[
\gamma = m^{-1} P \tilde{C}_p + P_0 n^{-1} \alpha_p \tag{64}
\]

where \(\tilde{C}_p\) = specific heat per particle; \(n\) = number density; and \(\alpha_p\) = coefficient of volume expansion. The \(O(J^2)\) term in \(P\) is calculated from the integrability condition

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for $dF$ in equation (23):

$$\partial P / \partial \mathbf{J} = \partial X / \partial V.$$  

(65)

With this, one can estimate the $O(J^2)$ contribution to thermal conductivity $\lambda = \gamma T$. For a hard-sphere model of Ar at 87 K, this non-linear contribution to $\lambda$ was unobservably small [104], a common property of non-linear transport effects in simple fluids, except in the case of viscoelasticity discussed in Section 5.

Considerations similar to those used in calculating the $O(J^2)$ contribution to $\lambda$ can be applied to the extended theory of diffusion, where the diffusion coefficient $D$ can depend quadratically on the diffusion flux, $\mathbf{J}_d$. The Gibbs equation in this case has the form:

$$T \, dS = dU + P \, dV - \mu_1 \, dM_1 - \mu_2 \, dM_2 + \mathbf{\Phi} \cdot d\mathbf{J}_d,$$

(66)

and the extended Fick's law is

$$\mathbf{J}_d = (L/V) \, \mathbf{\Phi} - \gamma_d V T (\mu_1 - \mu_2) - \lambda T^{-1} \nabla T.$$  

(67)

$\gamma_d$ can be evaluated by reasoning analogous to that which led to (64). One adds to the Liouville equation a term which couples the system to reservoirs of particles. This term is proportional to $P_{xx}$, if diffusion is along $x$. The leading contribution of $J_{dx}$ to $P_{xx}$ is estimated to be

$$P_{xx} = P_0 + J_{dx} J_{dx} (\rho_1^{-1} + \rho_2^{-1}).$$  

(68)

Numerical estimates [106] for an isotropic mixture of $^{36}$Ar and $^{40}$Ar at 87 K led to the conclusion that the $O(J_d^2)$ terms in $\gamma_d$ and $P$ would be less than one percent of the zero-order term unless $J_d \geq 17 \times 10^3$ kg/m$^2$s. Accordingly, steady-state computer simulations in simple fluids at high $T$ and concentration gradients are not expected to reveal appreciable non-linearities in $\lambda$ and $D$.

If we calculate $dF$ from (66), we have the integrability condition

$$\partial \mu_i / \partial \mathbf{J}_d = - \partial \mathbf{\Phi} / \partial M_i \quad (i = 1, 2).$$

(69)

From (69), one can calculate [106]

$$\mu_i = \mu_{i0} + \mu_{i2} J_d^2 + O(J_d^4) \quad (i = 1, 2)$$

(70a)

$$\mu_{i2} = - (2 m_i \gamma_{i00}) [P_0^{-1} (\partial P_0 / \partial n) + m_i (\rho_1^{-1} - \rho_2^{-1}) - n^{-1}].$$

(70b)

Since the chemical potentials depend on the squares of the fluxes, the temperature at which two phases are in equilibrium can be affected by a large vector flux. Non-linear effects, however, are most pronounced in viscoelasticity, and so existing treatments involve the effect of shear on phase stability, to be discussed in Section 5.
In contrast to the foregoing applications, the majority of extended thermodynamic treatments of diffusion and heat conduction have employed the Müller and Barcelona extensions of rational thermodynamics discussed in Part I, Section 2.3. The objective is to infer the structure of the evolution equations for \( \mathbf{J} \) and \( \mathbf{J}_s \) so that, by elimination of fast variables, one can derive hyperbolic wave equations for temperature or concentration. Also from the evolution equations, one can calculate time-correlations of the fluxes. From Einstein-Smoluchowski theory, one can evaluate correlations of fluctuations from equilibrium.

One of the earliest examples of this type of formulation [44] assumed as set of extensive state variables \( \{ a^s \} \), appropriate to a classical non-equilibrium description, obeying balance equations

\[
\rho \, \dot{a}^s = - \nabla \cdot \mathbf{q}^s + \sigma^s. \tag{71}
\]

The \( \mathbf{q}^s \) are fluxes associated with the variables. The variable set was extended by adding \( \{ \mathbf{q}^i \} \) and one second-rank tensor flux \( \mathbf{Q} \) to the set of state variables. One postulates a Gibbs equation

\[
\dot{\sigma} = T \dot{\mathbf{S}} + \sum_i \Gamma^s \, \dot{a}^s + \sum_i \mathbf{A}_i J_i \tag{72}
\]

where the \( \{ J_i \} \) are the fluxes associated with \( \{ q^i \} \) and \( \mathbf{Q} \). Also, one assumes the entropy flux,

\[
\mathbf{J}_s = \sum_i (\phi_i^s \, \mathbf{Q} + \phi_i^s \mathbf{Q} \cdot \mathbf{Q}) \cdot \mathbf{q}^i. \tag{73}
\]

Substituting (72) and (73) into the entropy principle (29), one gets

\[
\sigma_s = \sum_i J_i X^i \tag{74}
\]

where the \( X^i \) are sums of terms extracted from the calculation. One then assumes

\[
J^s = \sum_i \mathbf{F}_i X^i \tag{75}
\]

with coefficients chosen to make \( \sigma_s \geq 0 \). (74) and (75) correspond to (36) and (37a–c).

A special case of a formalism of this kind [107] chooses the heat flux \( \mathbf{J} \), the traceless viscous pressure, \( \mathbf{P}^s \), and the trace \( \rho^s \) of the viscous pressure as the \( J_i \)-variables. The Gibbs equation provides an expansion of \( \delta S \) in powers of \( \delta u, \delta v, \delta P^s, \delta \rho^s \), and \( \delta J \) which, in conjunction with Einstein’s fluctuation theory, yields the correlation functions \( \langle (\delta u)^2 \rangle, \langle (\delta v)^2 \rangle, \langle \delta u \delta v \rangle, \langle \delta J_1 \, \delta J_1 \rangle, \langle (\delta P^s)^2 \rangle, \) and \( \langle \delta P_{ij} \delta P_{ij} \rangle \). These results are compared with a simple relaxation-time approximation to the gas-kinetic Boltzmann equation. Many calculations of this type have been made [108–110]. Another early formulation [111] extracts a Cattaneo-Vernotte equation from the entropy principle.

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by requiring that temperature, heat flux, and their derivatives plus the rate at which energy is supplied by radiation should be arbitrary. In respect of inclusion of radiation, this is closer to rational thermodynamics.

These early formulations do not include gradients of $\mathbf{J}$, $\mathbf{P}^t$, or $\mathbf{J}_d$ in the evolution equations. These have been introduced [20] by adding non-linear terms to the entropy flux, $\mathbf{J}_s$, as in equation (32) where, in the Barcelona approach, $\beta = T^{-1}$. This leads to

$$\nabla T^{-1} - T_0^{-1} \sigma_{10} \mathbf{J}_s + \mu_{10} \mathbf{J}_s + (\mu_{13} - \beta^t) \nabla \cdot \mathbf{P}^t + (\mu_{14} - \beta^s) \nabla p^s$$

(76)

and an equation for $d \mathbf{P}^s / dt$ which depends on $(\nabla \mathbf{J}_s)^2$, the symmetrized traceless gradient of $\mathbf{J}$. The $\mu_{ij}$ are those of (37a–c). The terms $\mathbf{V} \cdot \mathbf{P}^t$ and $\nabla p^s$ are allowed by the equipresence principle and have featured in most formulations inspired by rational thermodynamics. Introduction of these terms has been supported by the circumstance that Grad’s treatment of the gas-kinetic Boltzmann equation [20] yields non-zero theoretical expressions for $\mu_{13} - \beta^t$ and $\mu_{14} - \beta^s$. If these terms are retained, in spite of arguments to the contrary [62, 63], then they can be invoked as a source of non-local effects. We remark later that this explanation of non-local effects is not unique.

Such effects of interaction with the surroundings are represented by a term linear in $\nabla^2 \mathbf{J}$ in the equation for $\mathbf{J}$. It occurs if $\mathbf{P}^s$ depends on $(\nabla \mathbf{J}_s)^2$ provided the relaxation time for $\mathbf{P}^s$ is short enough. One then obtains the equation derived by Guyer and Krumhansl [111] to explain second sound in crystals,

$$\mathbf{J} + \tau_v^{-1} \mathbf{J} + (1/3) \rho C_v c_0^2 \nabla T - (3/5) c_0^2 \tau_n [\nabla^2 \mathbf{J} + 2 \nabla (\nabla \cdot \mathbf{J})] = 0$$

(77)

where $C_v$ is specific heat, and $c_0$ is the first-sound velocity. $\tau_v$ and $\tau_n$ are characteristic times for umklapp and normal processes, respectively. Equation (77) does not yield a finite velocity as $\omega \to \infty$, and so there are problems if we apply it to a continuum. A way around this difficulty introduces an evolution equation for the tensor flux of $\mathbf{J}$, as described in the discussion of equation (35) [112]. However, this mechanism for introducing the $\nabla^2 \mathbf{J}$ term in (77) is not unique. It is possible to derive ‘statistically’ [42, 113] a set of phenomenological equations which involve second-order spatial derivatives, providing for non-local effects, without the first-order derivatives whose presence has been invoked to derive (77).

A derivation of (77) has also been given [114] in the frame work of an extension of rational thermodynamics to include an evolution equation for $\mathbf{J}$, as developed at the beginning of Section 2.3 (Part I) rather than the Barcelona modification thereof. One postulates a generalized version of (34a, b) in the form

$$\tau \partial \mathbf{J}/\partial t = - \nabla \cdot \mathbf{J}^s + \mathbf{s}$$

(78a)

$$\tau_v \partial \mathbf{J}^s/\partial t = - \nabla \cdot \mathbf{J}^s^v + \mathbf{s}^v.$$  

(78b)

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The constitutive equations are:

\[ J^{\delta} = \lambda (\delta) \]  
\[ \sigma^{v} = -J \]  
\[ s^{\mu} = -J^{v} + [B_1(T) + B_2 Tr J^{v}] \delta. \]  

(79a)  
(79b)  
(79c)

The Guyer-Krumhansl equation (77) in this case is not extracted directly from (79a–c), but rather from a variational principle,

\[ \delta/T \sigma^v dV = 0 \]

subject to \( V \cdot J = 0 \).

In the case of diffusion, a derivation [115] has been given, using the Barcelona formalism, of an equation analogous to (76). For the diffusion flow \( J_d \) and \( J_a \) the flux of \( J_a \), one postulates the Gibbs equation, the entropy flux \( J_s \), and the entropy production, \( \sigma_s \), in the form:

\[ T ds/dt = -\mu dc/dt + \nu \mu \beta \frac{J_a \cdot J_a}{dV/dt} = \beta_{10} \beta_{10} J_a \cdot J_a \]

(81a)

\[ J_s = \beta_{00} J_a + \beta_{10} \beta_{10} J_a \cdot J_a \]

(81b)

\[ \sigma_s = \mu_1 \beta_{10}^2 + \mu_2 \beta_{10} J_a \cdot J_a. \]

(81c)

Using these in the entropy principle, one finds

\[ -\tau_j d J_a/dt = J_a - (\mu_{10})^{-1} \nabla (\mu/T) = \ell \nabla \cdot J_a \]

(82)

\[ -\tau_j d J_a/dt = J_a - \ell \cdot \nabla J_a. \]

(82b)

If \( \tau_j \) is sufficiently small, we neglect it in (82b) and substitute the result into (82a), obtaining

\[ -\tau_j d J_a/dt = J_a + T \cdot J_a \]

(83)

which resembles the Guyer-Krumhansl equation in respect of the non-local term.

With a view to applications to glassy polymers, the EIT of diffusion has been applied [116] to the case of a solution with \( J_d \) the solute diffusion flux and \( \beta^{p}, p^v \) included among the variables, but not the heat flux \( J_a \). A Gibbs equation is postulated and an entropy flux,

\[ J_s = J T^{-1} - T^{-1} \beta_0 J_a + \beta_2 \beta^{p} \cdot J_a + \beta_{0p} p^v J_a. \]

(84)
According to the scheme of (37a–c), one obtains coupled relaxation equations of the form:

\[
\tau_1 \dot{J}_d + J_d = - D \nabla c_1 + \vec{D} TV \cdot (\beta_2 \vec{P}^\nu) + \vec{D} TV(\beta_0 p') \tag{85a}
\]

\[
\tau_0 \dot{p'} + p' = - \zeta \nabla \cdot \vec{v} + \zeta T \beta_0 \nabla \cdot J_d \tag{85b}
\]

\[
\tau_2 (\vec{P}^\nu)^+ + \vec{P}^\nu = - 2 \eta (\nabla v')^2 + 2 \eta T \beta_2 (\nabla J_d)^2. \tag{85c}
\]

By solving formally (85b,c) and substituting back into (85a), one gets a diffusion equation with memory which can be compared with the equations of this kind found in the literature on polymers. A somewhat similar set of equations has been derived [117] for polymers, by a similar method, which includes the heat flux rather than \( p' \).

A still more general equation has been derived [4] by the methods of Müller, imposing objectivity on constitutive and evolution equations and including heat flow and stress. It does not have the term in \( \nabla^2 J_d \). Elimination of \( J_d \) gives a hyperbolic equation for \( c \). Similar methods have been applied [118] to the case of a non-magnetic material diffusing in a paramagnet, with evolution equations for the fluxes of matter and heat.

A different approach to both heat conduction and diffusion can be found in Gyarmati’s procedure [45]. In the case of heat transport, a general formulation has been given [119] and applied to radiation [120]. This formalism [120] introduces a set \( \{ \vec{P}^{(k)} \} \) of independent vector variables related to components of the heat flux. In accord with Gyarmati’s formalism, one postulates that

\[
s = s_{eq}(u) - \frac{1}{2} \sum_{k=1}^{n} (\vec{P}^{(k)})^2 \tag{86a}
\]

\[
d \mu = T \, ds + T \sum_{k} \vec{P}^{(k)} \cdot d \vec{P}^{(k)} \tag{86b}
\]

\[
\rho \frac{d \mu}{dt} = - \nabla \cdot \vec{J}. \tag{86c}
\]

Substitution into the entropy principle yields

\[
\sigma_d = T^{-1} \left[ - T^{-1} \vec{J} \cdot \nabla T - T \sum_{k} \vec{P}^{(k)} \cdot d \vec{P}^{(k)}/dt \right]. \tag{87}
\]

One assumes, to make \( \sigma_d \geq 0 \), that the fluxes \( \vec{J} \) and \( \{ \vec{P}^{(k)} \} \) are linear sums of \( \nabla T \) and \( \{ d \vec{P}^{(k)}/dt \} \). One extracts the equations:

\[
\vec{J} = \sum_{k} \vec{J}^{(k)} \tag{88a}
\]

\[
\vec{J}^{(k)} + \tau^{(k)} d \vec{J}^{(k)}/dt = - \lambda^{(k)} \nabla T \quad (k = 1, \ldots, n). \tag{88b}
\]
In the special case of radiation [121] one neglects the conduction component of \( \mathbf{J} \) in favour of the radiation component. The internal energy and entropy per unit mass are:

\[
u = u_m + u_e/\rho \tag{89a}
\]

\[
s = s_m(u_m) + \rho^{-1} s_e(u_e) - \frac{1}{2} m J^2 \tag{89b}
\]

whilst (86c) is postulated. One defines

\[
T_m^{-1} = ds_m/du_m, \quad T_e^{-1} = ds_e/du_e. \tag{90}
\]

From

\[
\sigma_s = \rho (du_m/dt)(T_m^{-1} - T_e^{-1}) + J \cdot [\nabla T_e^{-1} - m d\mathbf{J}/dt] \tag{91}
\]

it can be concluded that \( du_m/dt \) and \( \mathbf{J} \) are linear sums of \( (T_e - T_m)/T_e T_m \) and \( (-T_e^{-2} \nabla T_e - md\mathbf{J}/dt) \). The application of Gyarmati's approach has been extended [122] to add phonon and electron transport to the components summed in (88a).

This approach to radiation, based on Gyarmati's principle, may be compared to a radiation hydrodynamics [123] in which the evolution equations are obtained from the radiative transfer equation for \( dI_s/dt \), \( I_s \) is the spectral density of the intensity of radiation travelling in a narrow pencil surrounding a given direction. By integrating the radiative transfer equation over frequencies and directions, one obtains evolution equations for mass and energy density, radiation flux density, and radiation pressure. A Gibbs equation is introduced for entropy density. Entropy is produced only at points of space where radiation interacts with matter. If radiation travels between two plates at different temperature, entropy is produced at the surface of the plates. This observation appears to be in accord with others [124] concerning the non-local character of entropy production in such a system and concerning failure of radiation to fit into the classical local equilibrium formulation of non-equilibrium thermodynamics.

In applying the Gyarmati approach to diffusion [125], one takes

\[
s = s(u) - \sum_i (2c_i)^{-1} \dot{\mathbf{j}}_i^2 \tag{92}
\]

where \( \dot{\mathbf{j}}_i \) is an independent diffusion flux. The evolution equations are extracted from the variational principle [6, 127]

\[
\sigma_s - (\Phi + \Psi) = \max \tag{93}
\]

where \( \Phi \) is a homogeneous quadratic function of the rate-type variables and \( \Psi \) a quadratic function of the remaining variables.

For the case of diffusion of heat and particles in porous solids there is still another approach, previously reviewed in Section 2.3 (Part I), which has received extensive

application. This is the Mexican variational method [34]. In application to diffusive flow $J_w$ of water through a soil matrix, one defines the soil-water matrix potential $\psi$ by [129]

$$J_w = -K \nabla \psi$$

(94)

and assumes $s = s(\psi, J_w)$ which obeys the entropy principle with constitutive equations

$$\dot{J}_w = \beta_{21}(\psi) J_w$$

(95a)

$$\sigma_s = \beta_{21}(\psi) J_w^2.$$  

(95b)

From the entropy principle, one obtains

$$\tau \frac{\partial}{\partial t} J_w = J_w + K \nabla \psi$$

(96)

from which one can derive a generalization of the parabolic Richards equation [130] for $\psi$ in the form

$$\tau \frac{\partial^2 \psi}{\partial t^2} - \gamma K \nabla^2 \psi + \psi \frac{\partial \psi}{\partial t} = \gamma (\frac{\partial K}{\partial x}) (\nabla \psi)^2 + \tau \gamma^{-1} \frac{\partial}{\partial x} (\frac{\partial \psi}{\partial t})^2$$

(97)

where $\gamma$ is a constitutive coefficient in $s$.

To apply the variational approach to the soil-water problem, one varies the functional

$$L = \int \left[ \rho \frac{ds}{dt} + \nabla \cdot J_w - \sigma_s \right] dV$$

(98)

with respect to the functional dependence of non-conserved variables [131]. Assuming $s = s(\psi, J_w)$, one obtains via the variational approach

$$[(2 \frac{\partial \psi}{\partial x_{20}} \frac{\partial I}{\partial J_w} + x_{20} \delta) \cdot \delta J_w/\partial t = -\nabla x_{30} + 2 \frac{\partial J_w}{\partial x_{1}} \frac{\partial I}{\partial \psi} + \frac{\partial \psi}{\partial x_{1}} \frac{\partial I}{\partial J_w}$$

$$- 2 (\frac{\partial \psi}{\partial x_{1}} (x_{30} - x_{4)}}) (\nabla \cdot J_w) J_w - 2 (J_w \cdot \nabla \psi) (\frac{\partial \psi}{\partial t}) J_w$$

(99)

where $I = J_w^2$, and the $x$-coefficients depend on $\psi$. Constitutive equations are postulated for them, leading to a generalization of (96). A very formal extension of the diffusion problem has been made [132] to include heat conduction.

4.2. Dielectric relaxation and electrical conduction

Since the diffusion of free charge in a conductor is a vector process analogous to particle diffusion, the extended thermodynamics can be formulated in a similar way, with the electrochemical potential replacing $\mu_1 - \mu_2$ in the formalisms of the preceding subsection. This vector process can be coupled to heat conduction, since energy is carried by both phonons and free charges. In a polarizable medium, the total current is the sum of the polarization current plus the electrical flux carried by free charges. The dielectrical relaxation can be coupled to relaxation of the flows of heat and charge.
Most of the formulations we examine yield a set of formal evolution equations. In principle, the solutions thereof can be used in calculating time correlation functions whilst elimination of fast variables leads to equations for the propagation of polar waves. An introduction to these topics can be found in the books [306] and [307].

The earliest extended thermodynamic theory of dielectric relaxation was given by Sannikov [25]. This generalized the Lagrangian formulation of Landau and Lifshitz to continuous media, discussed in Part I, Section 2. The free energy is taken to be the sum of kinetic terms quadratic in \( \partial \mathbf{P} / \partial t \) and \( \partial \mathbf{u} / \partial t \) plus an expansion in powers of polarization \( \mathbf{P} \) and \( \mathbf{V} \mathbf{P} \) to fourth order, appropriate to discussion of ferroelectrics. The Lagrangian approach yields a wave equation for \( \mathbf{P} \).

More recent treatments have followed the Barcelona approach, discussed in (36–37c). The simplest of these [132] introduces the electric current density, \( \mathbf{J}_e \), as the only extended variable. The postulated Gibbs equation is

\[
T \, ds = du - \mu_e \, dc_e + \rho^{-1} \gamma \mathbf{J}_e \cdot d \mathbf{J}_e
\]

where \( c_e \) is the electron density. This leads to an evolution equation,

\[
d \mathbf{J}_e / dt = - \tau^{-1} (\mathbf{J}_e - \sigma \mathbf{E}).
\]

Solutions of this can be used in calculating correlation functions of current fluctuations at equal and at different times. These equations can also be used [134] to calculate mixed correlations of 

The approach based on (100) and (101) was extended to include the heat flux \( \mathbf{J} \) as well as \( \mathbf{J}_e \). We replace \([135] \) (100) by

\[
T \, ds = du - \eta \, dc_e + v ( \gamma_1 \mathbf{J} + \gamma_2 \mathbf{J}_e ) \cdot d \mathbf{J} + v ( \gamma_1 \mathbf{J} + \gamma_2 \mathbf{J}_e ) \cdot d \mathbf{J}_e,
\]

with the entropy flux given by

\[
\mathbf{J}_s = - T^{-1} (\mathbf{J} + \mu_e \mathbf{J}_e).
\]

Here \( \mu_e \) is the electrochemical potential. On insertion of (103) and the Gibbs equation into the entropy balance equation, one obtains:

\[
\sigma_s = \mathbf{J} \cdot (V T^{-1} + T^{-1} \gamma_1 \mathbf{J} + T^{-1} \gamma_2 \mathbf{J}_e) + \mathbf{J}_e \cdot (T^{-1} \mathbf{E} - \mathbf{V} (\mu_e T^{-1}))
\]

\[
+ T^{-1} \gamma_2 \mathbf{J} + T^{-1} \gamma_2 \mathbf{J}_e.
\]

From \( \sigma_s \), one extracts evolution equations for \( \mathbf{J} \) and \( \mathbf{J}_e \) by assuming that the brackets which multiply \( \mathbf{J} \) and \( \mathbf{J}_e \) in (104) are each linear combinations of these two fluxes chosen to make \( \sigma_s \geq 0 \). For \( \mathbf{J} \) one gets an equation of the form (77) used by Guyer and Krumhansl [111] to discuss second sound.

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The foregoing theory can be specialized to the case of electrical conduction in a membrane [136]. The electric current in a membrane should obey the equation

$$\tau \partial J_e / \partial t + J_e = \sigma E$$  \hspace{1cm} (105)

having the entropy and entropy production

$$s(u, J_e) = s_{eq}(u) - \frac{1}{2} (\tau \nu / \sigma) J^2_e$$  \hspace{1cm} (106a)

$$\sigma_s = (1 / \sigma T) J^2_e.$$  \hspace{1cm} (106b)

If a pore has two states, with $N_0$ of them open and $N_1$ closed, the chemical potentials are:

$$\mu_0 = \mu_{0,eq} + \frac{1}{2} (\tau \nu / \sigma) J^2_0$$  \hspace{1cm} (107a)

$$\mu_1 = \mu_{1,eq} + \frac{1}{2} (\tau \nu / \sigma) J^2_1.$$  \hspace{1cm} (107b)

The numbers $N_0$, $N_1$ are given by

$$N_i = \exp\left[-(1 / \kappa T) (\vartheta_{i,eq} + \frac{1}{2} (\tau \nu / \sigma) J^2_i)\right] \quad (i = 0, 1).$$  \hspace{1cm} (108)

As remarked above, the free charge current in a solid is accompanied by a polarization current, $\partial P / \partial t$. Thus, the total current density $J_e$ and charge density $\rho_t$ satisfy [139]

$$J_e = J_f + \partial P / \partial t + \text{curl} \ M$$  \hspace{1cm} (109a)

$$\rho_t = \rho_f + \rho_p, \quad \rho_p = - \nabla \cdot P.$$  \hspace{1cm} (109b)

Also,

$$J_e = \beta_1 J + \beta_2 J_e$$  \hspace{1cm} (110a)

$$\sigma_s = X_1 \cdot J + X_2 \cdot J_e.$$  \hspace{1cm} (110b)

where $X_1$, $X_2$ are linear combinations of $J$, $J_e$, and $T_0^{-1} (E + \nabla \phi_0)$, with $T_0$ the local equilibrium temperature and $\phi_0$ the electric potential at local equilibrium. For $P$ one obtains

$$\tau_1 \partial^2 P / \partial t^2 + \tau_2 \partial P / \partial t - (\epsilon_0 E - P) = \gamma_1 \nabla (T_0^{-1}) - \gamma_2 J.$$  \hspace{1cm} (111)

By solving this equation, one can calculate

$$\Phi = \langle P(k, t) \cdot P(k, 0) \rangle.$$  \hspace{1cm} (112)
and the frequency-dependent dielectric constant. The latter has been fitted approximately [138] to an experimental Cole-Davidson plot for polypropylene glycol. An equation for complex \(\varepsilon(\omega)\) has been obtained [139] by solving a differential equation for the correlation \(\langle \mathbf{P}(k, t) \cdot \mathbf{P}(k, 0) \rangle\).

In a deformable medium, the elastic strain \(\varepsilon\) is added to \(\mathbf{J}\) and \(\mathbf{J}_e\). Such a theory has been given [140] for deformable semiconductors, where the variables include the charge densities \(n, p\) of negative and positive carriers, the currents \(\mathbf{J}_n, \mathbf{J}_p, \mathbf{V}_T, \mathbf{V}_n, \mathbf{V}_p\), the heat flux \(\mathbf{J}\), and \(\varepsilon\). The formalism is the axiomatic extension of rational thermodynamics discussed in Part I, Section 2.3. One derives for \(\mathbf{J}\) an equation linear in all the vector variables. To the foregoing variables, one can add a magnetic field \(\mathbf{B}\) [141,142]. The effect of dislocations can be included by adding the dislocation core tensor and its flux to the list of variables [143]. An analysis of waves in deformable semiconductors is given in Section 6.4.

A number of papers have appeared which use some of the other methods mentioned in Part I, Section 2. One of these [144] uses Gyarmati's approach [45]. Another [145] introduces a field Lagrangian description of interaction of charged particles with an electromagnetic field. A series of papers discuss dielectric relaxation via the internal variable method. In this approach [146–148], one assumes for the total specific polarization \(\mathbf{P}\) the sum

\[
\mathbf{P} = \sum_{k=0}^{s} \mathbf{P}^{(k)}
\]  

whilst \(s = s(u, e, \{\mathbf{P}^{(k)}\})\). One calculates \(\sigma\) in terms of forces and fluxes and erects equations for \(d\mathbf{P}^{(k)}/dt\) according to the scheme of de Groot discussed in Part I, Section 2.2. Elimination of internal variables yields an equation for \(d\mathbf{T}/dt\) and, in similar fashion [149], a differential equation for \(\mathbf{P}(t)\). Completely general, but formal, expressions for the phenomenological equations have also been given [150].

For the discussion of elastic paramagnets, the magnetization can be expressed [151] as a sum of internal variables in a fashion analogous to (113). Through elimination of internal variables, one obtains a wave equation for the magnetization with time-derivatives of arbitrary order, depending on the number of internal variables eliminated.

### 4.3. Liquid \(^4\)He

The application of EIT to superfluid He couples relaxation of heat flow \(\mathbf{J}\) to that of the stress \(T\). The objective is to predict superfluid properties without invoking Landau's two-fluid model [152]. An application of EIT to the two-fluid model, with a derivation of Landau's equations, is given in [4]. The formalism which avoids this model follows Liu and Müller [153]. In addition to \(\mathbf{J}\) and \(T\), the variables include \(\rho\) and \(T\) [154]. The balance equations postulated for \(\mathbf{J}\) and \(T\) involve higher-order fluxes, \(m_{\text{ijk}}\) and \(m_{\text{ijk}}\), for which constitutive equations are written down. One obtains
(114a) coupled evolution equations
\[
\begin{align*}
\tau_0 \partial \rho / \partial t + \lambda_0 \nabla \cdot \mathbf{v} - p' T \lambda_0 \nabla \cdot \mathbf{J} &= - p' \\
\tau_2 \partial T / \partial t + 2\lambda_2 (\nabla \mathbf{v}) - 2\beta \lambda_2 (\nabla \cdot \mathbf{J}) &= - T \\
\tau_3 \partial \mathbf{J} / \partial t + \lambda_1 \nabla T - \beta \lambda_1 \nabla p' - \beta T^2 \lambda_1 (\nabla \cdot \mathbf{T}) &= - \mathbf{J}.
\end{align*}
\]

These are specialized to He II by setting \( \lambda_0 = 0 = \lambda_2, \lambda_1 = \infty \), since viscosity is low and thermal conductivity very high. From the evolution equations, one derives wave equations for two propagating modes, corresponding to first and second sound. A similar derivation of the equation for temperature modes has been made by Greco and Müller [156].

The constitutive equations for \( T, s \), and \( m_{\text{ak}} \) in the superfluid phase have been compared [157] with the Landau two-fluid model. In the case
\[
\dot{T} = \bar{a}(\mathbf{J} \cdot \mathbf{J})
\]
the two-fluid model yields an \( \bar{a} \) which differs by a factor 5/9 from the result of EIT. The fountain effect has been explained [158] on the basis of the dependence of \( s \) on \( J^2 \).

Equations (114a–c) can be regarded as elaborating on earlier work [159] which postulated
\[
\begin{align*}
s &= s(u, \mathbf{v}, \xi) \\
T ds &= d u + P d v + \mathbf{A} \cdot d \xi,
\end{align*}
\]
where \( \xi \) is an initially undefined internal variable and \( v \) the mass velocity. One also postulates
\[
\mathbf{J} = T^{-1} \mathbf{J}
\]
and Newtonian stress
\[
\begin{align*}
p' &= -(\zeta/3) \nabla \cdot \mathbf{v} \\
\dot{T} &= 2\eta (\nabla \mathbf{v})^2
\end{align*}
\]
so that there are no evolution equations for \( dp' / dt \) and \( d \dot{T} / dt \). The condition \( \sigma_z \geq 0 \) yields
\[
\begin{align*}
\frac{d \xi}{dt} &= - \lambda_3 T^{-1} \nabla T - \lambda_4 \rho \xi \\
\mathbf{J} &= \lambda_1 T^{-1} \nabla T - \lambda_2 \rho \xi \xi
\end{align*}
\]
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in addition to the hydrodynamic equations. ξ may be one of several fast variables coupled to \( \mathbf{J} \), but the absence of any identification of it renders this approach more formal and mathematical than (114a–c) which is in accord with much of the recent literature on viscoelasticity linked to heat flow.

5. Shear relation and rheology

In this section we concentrate on evolution equations which involve the viscous pressure deviator \( \mathbf{P}^{v} \), the viscous pressure trace \( p^{v} \), and rheological models representing special cases of these equations. We shall include work which couples relaxation of \( \mathbf{P}^{v} \) to that of the heat flux \( \mathbf{J} \). We first review in Section 5.1 the various approaches, based on e.g. the EIT of Sections 2.2 and 2.3 (Part I) or rational thermodynamics with memory introduced into the constitutive equations. In 5.2 we complement these with some statistically-derived evolution equations. The latter can be used to calculate a complex frequency- and wave vector-dependent viscosity and to generate various rheological models discussed in Section 5.4. Section 5.3 discusses liquid suspensions, but not from a rheological point of view. By eliminating fast or internal variables from the evolution equations we can obtain wave equations whose derivation and solution form the subject of Section 6. There we do not concentrate on viscoelasticity, and we consider phenomena such as shock waves. In Section 5.5 we consider shear-induced phase transitions.

5.1. Review of extended thermodynamics of viscoelasticity

The works considered here specialize the approaches of Section 2 (Part I) to viscoelastic relaxation, and therefore they tend to be viewed by their authors as applications of the various general methods. This could be disputed, because most do not make a direct fit to experiment. They can, however, be compared with the rheological models discussed in Section 5.4 and thus be said to find application as a thermodynamic basis for the latter.

An early formulation of EIT for shear relaxation [160] assumed for the specific entropy

\[
s = s(u, v, \mathbf{P}^{v})
\]

where \( u \) is the specific internal energy and \( v \) the specific volume. This yields for the specific free energy differential, \( df \), the expression:

\[
df = - s dT - P dv - \kappa \mathbf{P}^{v} : d \mathbf{P}^{v}.
\]

(121)

Assuming that \( \zeta = (\tau \epsilon/2\mu T) \exp (2\gamma) \), one could show that stability conditions on the derivatives of \( f \) restrict the possible values of \( \gamma \). These considerations have been applied to shock waves [161] and instabilities they induce. A more general treatment [162] assumed

\[
s = s(T, \epsilon_{ij}, \tau_{ij}, \mathbf{J})
\]

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where $\epsilon_{ij}$ is the strain and $\tau_{ij}$ the stress tensor. The entropy balance equation reads

$$
\rho s + \mathbf{V} \cdot \mathbf{J}_e - \rho (r/T) = \sigma_s \geq 0.
$$

(123)

$r$ is the rate of energy supply by radiation which, in rational thermodynamics, is eliminated with the aid of the energy-conservation equation. The result is discussed in the framework of various rheological models.

As a variant of the choice of variables in (122), the "inelastic" part of $\tau_{ij}$, labeled $\tau''_{ij}$, has been chosen [163]. The trace $\tau''$ and deviator $\tau''_{ij}$ obey:

$$
\tau'' = J_{kk} + s_s,
$$

(124a)

$$
(\tau''_{ij})' = (J_{ijkl})' + (s_{ij})'.
$$

(124b)

where $J_k$ and $J_{ikl}$ are fluxes and $s_s$, $(s_{ij})'$ dissipative parts. Superscript $s$ means a traceless, symmetric tensor. For all four, constitutive equations are assumed. The resulting evolution equations can be specialized to the Maxwell and Kelvin-Voigt rheological models. The possibilities have been discussed [164] of applying these viscoelastic equations to dilute polymer solutions.

A different division of the stress has been made with regard to an application to relaxation of $\mathbf{P}_\nu$ in gases [165]. This divides $\mathbf{P}_\nu$ into independent kinetic and potential parts, with $\mathbf{P}_v^k$ and $\mathbf{P}_v^p$ as independent state variables. Via fluctuation theory, correlation functions of these are calculated.

For the case of a suspension of spherical particles in a fluid, separate components, $\mathbf{P}_f$ and $\mathbf{P}_s$, have been introduced [166] for contributions of fluid and spheres, respectively. The fluxes associated with these variables are $\mathbf{S}_f$ and $\mathbf{S}_s$ which appear as additional variables in axiomatic EIT, discussed in (31a–c). The coefficients in the evolution equations are identified with those appearing in a calculation [167] by Bedeaux, Kapral, and Mazur of the viscosity $\eta(k, \omega)$ in a suspension of spheres.

An extension of the foregoing approaches, which use $\mathbf{P}_\nu$, and possible independent tensor components thereof, as independent variables, has been given for non-local effects [168]. These are introduced by adding a hierarchy of fluxes as state variables, in the manner employed for derivation of the Guyer-Krumhansl equation [77] in Section 4.

There are a considerable number of approaches, in addition to [162], which couple relaxation of the viscous pressure, $p''$ and $\mathbf{P}_\nu$, to that of the heat flow $\mathbf{J}$ or the electric current $J_e$. These were not listed in Section 4 because in most the emphasis appears to be on viscoelastic properties. An early work of this kind [169] postulated constitutive equations for $\mathbf{J}$ and $(\mathbf{P}_\nu)'$ which were made to conform to the entropy principle. Application was to ideal gases. This work was extended [170] and used in conjunction with the Einstein-Smoluchowski theory to calculate correlations of fluctuations in $\mathbf{J}$ and in internal energy $u$. A more general version [171], which is closer to the Barcelona approach of (36–37c), has been used to calculate the relation between dynamic and

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static structure factors for comparison with an alternative derivation [172] which relates the dynamic structure factor to mechanical creep compliance and the longitudinal stress modulus of a viscoelastic liquid. In a formalism which neglects non-local effects, the $\omega \to \infty$ limiting velocities of shear and thermal waves are related to shear viscosity and thermal conductivity and to the correlation function or $\mathbf{P}$ an $P^e$ [173].

For the description of an elastic semiconductor, the variables include not only elastic strain and heat flux $\mathbf{J}$, but also the current flows carried by electrons and holes [174, 175]. The conservation equations are supplemented by Maxwell equations and evolution equations for the heat and current fluxes. Constitutive equations are limited by the entropy inequality. Applications of the evolution equations to experimental problems are not discussed. In the case of an explicit treatment of effects of dislocations in elastic semiconductors [143, 176] an internal variable $a_{ij}$ is added to represent the strain field produced by the dislocation core.

The work of Liu and Müller [153] combines both shear relaxation and an extended theory of heat conduction in a gas in a single formalism which incorporates 13 moments of the single-particle distribution function. This can be extended, as has been done by Kremer [177] to the case of a $v$-component mixture, where 13 generalized hydrodynamic variables appear. A different kind of extension [178] has been made to include 14 moments, which is the number that occurs naturally in a relativistic treatment. The fourteenth variable in this case is a contracted fifth moment, written $\rho_{ijkl}$, which may be compared to pressure $P_{ij}$. In a polyatomic gas with internal degrees of freedom, one needs 17 moments [93], including the density and flux of the internal energy.

In addition to the approaches related to or descended from rational thermodynamics, there are also derivations of stress-relaxation equations which stem from the methods of Gibrated. One of these [179] introduces a field variable, $a$, and assumes

$$s = s(u, a) = s_0(u) - \frac{1}{2} \gamma a : \mathbf{a}. \quad (125)$$

Elimination of $a$ yields

$$P^e + \tau^e = -2\eta (d + \tau^e d) \quad (\tau^e > \tau_d > 0, \eta > 0) \quad (126)$$

where $d$ is the deformation tensor, and time-derivatives are objective. This approach has been extended [180, 181] to the case of many internal variables. An application to plasticity [182] has utilized the variational principle which minimizes the space and time integral of $\sigma - \mathbf{Y} - \mathbf{R}$, where $\mathbf{Y}$ and $\mathbf{R}$ are quadratic functions of the forces and fluxes, respectively, appearing in $\sigma$. The same principle has been applied [183] to nematic liquid crystals.

Beside these approaches, there exist thermodynamic theories which follow the $\phi$ Groot formalism described in Part I, Section 2.2. One of these introduces inelastic strain as an internal variable [38] and later generalizes this [184] to the case where the inelastic strain has many independent components, $a^{ij}$, all introduced as internal variables. If $n$ internal variables are used, their elimination yields an equation with time-derivatives out to order $n$ in stress and strain.
A possible aesthetic difficulty with such an internal-variable approach occurs in highly viscous materials where different mechanisms have different timescales and one can distinguish the rates of inelastic strain contributed by different models more readily than inelastic strain components themselves. Those who prefer to use quantities directly observable as variables should use the elastic component of strain, which is proportional to stress and vanishes with it, plus the contributions of the various creep mechanisms to the inelastic strain-rate.

In accord with this idea, consider a macroscopically small, but microscopically large system described by \( V, T, \) traceless elastic train \( \hat{\epsilon}_{ij} \), and traceless inelastic strain-rate \( \dot{\hat{C}}_{ij} \). \( \hat{C}_{ij} \) may have many independent components [185]. We may also have a scalar parameter, \( \zeta \), representing the fraction of molecules situated in a particular kind of structural environment, e.g. a local expansion or "hole". There are thermodynamic forces,

\[
\Phi_{ij} = T \frac{\partial S}{\partial \epsilon_{ij}}, \quad \Psi_{ij} = T \frac{\partial S}{\partial \hat{C}_{ij}}
\]

(127)

for which constitutive equations, in general non-linear, are given:

\[
\Psi_{ij} = a_\zeta \hat{C}_{ij}, \quad \Phi_{ij} = a_\tau \hat{\epsilon}_{ij}.
\]

(128)

Then the statement that the total strain-rate, \( (\hat{S}_{ij})^\tau = (\dot{\hat{C}}_{ij})^\tau + (\hat{\epsilon}_{ij})^\tau \) becomes

\[
(\hat{\epsilon}_{ij})^\tau = -(1/a_\zeta) \Psi_{ij} + (\hat{S}_{ij})^\tau
\]

(129)

A set of anti-reciprocity relations, which are necessary if \( \sigma_i \geq 0 \), give

\[
(\dot{\hat{C}}_{ij})^\tau = \kappa \Psi_{ij} - \chi \Phi_{ij}, \quad \chi = (a_\zeta)^{-1}
\]

(130a)

\[
\dot{\hat{\epsilon}}_{ij} = V^{-1} \Phi_{ij} = -\lambda_2 \hat{\epsilon}_{ij}
\]

(130b)

\[
\lambda_2 = -V^{-1} a_\tau.
\]

(130c)

At low frequencies, we neglect \( (\dot{\hat{C}}_{ij})^\tau \), so that \( \hat{\epsilon}_{ij} \) is proportional to \( \dot{\hat{C}}_{ij} \), the latter being proportional to the total strain-rate. This yields for the shear viscosity

\[
\eta = -(\kappa/\chi) a_\zeta V^{-1} = \kappa a_\zeta^2 V^{-1}.
\]

(131)

\( \kappa a_\zeta = \tau^{-1} \), with \( \tau \) being the shear relaxation frequency.

This theory [185] was designed for plastic creep in polycrystals, but it may be extended to viscous liquids in general. The integrability conditions for free energy lead to terms \( O(C^2) \) in \( P \) which, in a steadily creeping specimen, are seen as effective contributions to third-order elastic constants. The same tensor equations, augmented by

\[
\hat{z} = z Z
\]

(132)
with \( Z \) a thermodynamic force associated with \( \zeta \), have been applied [98] to Couette flow at very high shear-rates. Computer simulations [186] have been made which remove the heat generated, keeping \( T \) constant, by rescaling particle velocities. The non-analyticities in [186,187] could be explained [98] if we let \( Z \) depend non-linearly on \( C_{ij} \) and on \( (\zeta - \zeta_{eq}) \). At high shear-rate, the steady-state equation \( Z = 0 \) has an asymptotic solution which, on substitution into \( P \), causes the latter to depend on the \( 3/2 \) power of \( C \equiv C_{xy} \). One can explain similarly the shear-thinning effect, in which \( \eta \) depends negatively on \( C^{3/2} \) [188].

Viscoelasticity is the only phenomenon in which computer simulations have turned up non-analyticity far from equilibrium. Simulations have been made of heat conduction [189] and diffusion [190] in simple fluids undergoing Couette flow at high shear-rate. By generalizing the thermodynamics of visco-elasticity to include heat flow \( J \) and diffusion flux, \( J_{ij} \), one can predict many of the shear-induced anisotropies in the thermal conductivity and diffusion tensors.

To complete the record on formulations of visco-elasticity with memory, we should mention an approach [46] which uses objective constitutive equations which depend on the history of the system, i.e. they are functional of the variables over a period of time preceding the present. By expanding the functionals in powers of time-derivatives of the variables, one can make them explicit functions of these derivatives, resembling EIT. The field equations, obtained by using the constitutive equations in the balance equations, have been applied [47] to the flow of fluids in channels with fixed walls. One can predict the velocity profile across the channel for comparison with experiment. This has been done for the tube flow of blood [49].

An extension has been made [191] which sets up a continuum theory of micropolar fluids, e.g. liquid crystals. A vector field is introduced called the “director” in terms of which micro-inertia and deformation tensors may be expressed. An additional evolution equation is required for the former of these. This formalism is applied [192] to describe the flow of fluids with uniaxial symmetry. Internal variables such as micro-inertia are introduced to provide for deformations of micro-elements of the fluid in a generalized hydrodynamic continuum model.

5.2. Balance equations from kinetic theory

As we have noted in Part I, Section 2.4, evolution equations postulated by EIT have been influenced heavily by the self-consistent moment method of Grad [20]. This approach assumed an expansion for the single particle distribution \( f(c) \) for peculiar velocity \( c \) in a sum of Hermite functions of \( c \) with coefficients depending on moments. This procedure yields evolution equations for \( \rho, T, v, \) as well as \( J \) and \( P^{e} \). Here we shall mention alternative ways of using the gas-kinetic Boltzmann equation to extract such evolution equations.

Of these [55,193] calculate for \( \rho, M, M_{i}, M_{a}, \) equations (45a,b) plus

\[
\frac{\partial M}{\partial t} + \frac{\partial M_{k}}{\partial x_{k}} = 0 \tag{133a}
\]

\[
P_{ij} = m \int dc c_{i} c_{j} J(f) \tag{133b}
\]

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where the external force field $\mathbf{F}$, obeys, in (45a, b),

$$F_i = R_i + c_n R_n.$$

Repeated indices are summed, and curved brackets denote symmetrization with respect to the indices they enclose. To obtain a closed set of balance equations, one uses an expression for $P_{\text{on}}$ which holds rigorously only for Maxwell molecules and a closure approximation for $M_{\text{inh}}$, as described in Part I, Section 2.4. These equations can provide information about the shear-rate dependence of viscosity [194].

A different moment method, which has found extensive application [51] to a wide variety of transport problems, including rheology, viscoelasticity, and non-Newtonian viscosity, modified Grad’s approach by using an exponential ansatz in which the exponent is a sum of hermite functions. The coefficients are determined, not by Grad’s self-consistency condition, but rather to yield a Gibbs equation from the Boltzmann $H$-theorem. When the ansatz has been so determined, substitution into the Boltzmann equation and taking of moments of the result yields moment equations [51]. A set of phenomenological postulates has been erected for a version [195] of EIT which brings the latter into formal agreement with the kinetic theory of [51]. A problem exists because a distribution which depends on time only through the moments is not an exact solution of the Boltzmann equation and cannot obey the $H$-theorem exactly. Any inconsistencies which arise from neglecting this fact have been found to be small [196].

5.3. Colloidal suspensions and liquid crystals

There exists an extensive literature on applications of EIT to suspensions other than the polymer solutions whose rheology is treated in Section 5.4. We shall collect and review some of these here. The objective in general is to introduce internal variables to represent solute orientation and solute contributions to stress and strain tensors. From the evolution equations, complex moduli can be obtained for comparison with the rheological literature.

As an example of an application of the theory of Verhás to globular colloids, we can assume [197] that $s = s(u, \kappa_{ij})$, where $\kappa_{ij}$ is a strain tensor associated with the solute. From the hydrodynamic equations and the entropy principle, one may extract a complex viscosity which can be compared with one given earlier by Oldroyd [198]. This viscosity corresponds to a model of springs and dash-pots. This work has been extended [199] to suspensions at high concentrations subjected to uniaxial tension.

A different approach to suspensions of spheres, where $P^e$ was expressed as a sum of $P^e_f$ and $P^e_r$ [5] was extended and applied to dilute solutions of dumbbell molecules [200]. The possibility was raised of having a number of components of $P^e$ arising from different degrees of freedom of the solute. A microscopic calculation [200] was made of the phenomenological coefficients, based on a Boltzmann equation for the distribution function for the dumbbell configuration. This was done for both rigid and elastically-extensible dumbbells. The Einstein-Smoluchowski theory was used [201] to evaluate correlations of the components of $P^e$. The method can be extended to the rod and Rouse-Zimm models.

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When the EIT of simple suspensions is generalized to nematic liquid crystals, one requires that a director field, \( \mathbf{e} \), a tensor \( \mathbf{V} \), and the electric polarization \( \mathbf{P} \) be added to the set of variables [182, 202]. Then \( s - s_0(u, T) \) is a negative definite quadratic form in the components of these vectors and tensors. Rate equations are calculated via Gyarmati's principle with a dissipation potential (88) quadratic in \( \mathbf{V} \times \mathbf{V} \) and the time-derivatives of \( \mathbf{e} \) and \( \mathbf{V} \). This work has been extended [203] to biaxial nematics, for which three director fields are needed.

More general and formal treatments of suspensions and liquid crystals have been given by A. C. Eringen, who uses constitutive equations with memory. In the early work [204,205], conservation equations were postulated for mass, momentum, energy, moment of momentum, and microinertia. This work was generalized [206] by introducing constitutive equations dependent on past motion and thermal history. In liquid crystals, the director field is added. Extensions of this work have been proposed [208] for dense suspensions of fibers and rigid spheres.

5.4. Special cases: rheological models

The methods [197–210] described in the preceding section for deformable spherical suspensions and elastically extensible dumbbells can be applied to other types of suspensions, such as polymer solutions in which there are deformable molecular solutes. In this section, we shall include such applications to polymers. However, the emphasis here is not on basic mathematical postulates, but rather on comparison of viscoelastic kinetic equations with rheological models. The discussion will be more phenomenological and re-examine from the rheological point-of-view equations given previously.

The first rheological observation we make is that a wide class of materials, such as polymer suspensions, soap solutions, some honeys, asphalts, and physiological fluids, do not obey the linear Newtonian constitutive law. Viscosity is shear-dependent, or stress is not directly proportional to the deformation. Rheological models for both linear viscoelasticity and nonlinear generalized Newtonian fluids can also be derived [5,163,164,200,201,211–216], as we have pointed out in Section 5.1., by specializing the evolution equations of EIT. We proceed to give concrete cases. An extensive review of models is given in ref. [5, Chapter 7], to which we are indebted for many of the examples given here.

A. Linear viscoelasticity

To describe viscoelastic bodies, many versions of EIT introduce (cf. equations 119a, b) as an additional variable the tensor \( \mathbf{P}^{\sigma} \), which is the inelastic part of the pressure tensor, \( \mathbf{P} \) (cf. equation 119b):

\[
\mathbf{P} = \mathbf{P}^{\sigma} + \mathbf{P}^{\nu} \tag{135a}
\]

\[
P_{ij}^{\sigma} = -2G\varepsilon_{ij} + \lambda^i (Tr \varepsilon) \delta_{ij} \tag{135b}
\]

The parameters \( \lambda^i \) and \( G \) are Lamé coefficients; \( \varepsilon_{ij} \) is the symmetric strain tensor. The choice of \( \mathbf{P}^{\sigma} \) as additional variable is based on the fact that its behaviour is similar to that of the other fluxes. \( \mathbf{P}^{\sigma} \) satisfies a material conservation law. Its relaxing character makes the inelastic behaviour over long times.

EIT assumes that the non-equipartition tensor and on the classical equation 117:

\[
s = s(u, e, l, \rho, \rho^* , \mathbf{P}^*)
\]

where \( e, \rho^* , \) and \( l \) are the corresponding Gibbs equation.

\[
ds = T^{-1} du + (\mathbf{P}^*/\rho T)
\]

where \( c \) and \( \dot{c} \) are constitutive balance equation for energy, where

\[
\rho T \dot{c} \delta t = \sum \rho_{\delta} \delta t_{\gamma} \delta p_{\delta} \delta t_{\gamma}
\]

To make \( \sigma_{ij} \geq 0 \), one assumes a and b scalar respectively, with a and b scalar Section 2.3.

\[
\tau_{ij} \dot{\varepsilon}_{ij} \delta t + \dot{\mathbf{P}}_{ij} = -2\eta \dot{\varepsilon}_{ij} \delta t + \dot{\mathbf{P}}_{ij} = -\dot{\varepsilon}_{ij} \delta t
\]

where \( 2\eta = a, \sigma_{ij} = \dot{\varepsilon}_{ij} b^{-1} \) a. According to these equations in the high-frequency limit. Adf for the deviator \( \dot{\mathbf{P}} \) and isotrops

\[
\tau_{ij} \dot{\varepsilon}_{ij} \delta t + \dot{\mathbf{P}}_{ij} = -2G \dot{\varepsilon}_{ij} \delta t + \dot{\mathbf{P}}_{ij} = -3K \dot{\varepsilon}_{ij} \delta t
\]

\[
K = \lambda^i + (2/3)G; \tau_{ij} = \dot{\varepsilon}_{ij}
\]

Thus, EIT leads to the constitutive

In the limit \( \tau_{ij} \rightarrow 0, \) (140a) reduces to body,

\[
\dot{\mathbf{P}}_{ij} = -2G \dot{\varepsilon}_{ij} + 2\mathbf{P}_{ij} \delta t
\]

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that of the other fluxes. $P^\ast$ is a fast variable and generally does not satisfy a conservation law. Its relaxing character may provide for elastic behaviour over short times and inelastic behaviour over longer times.

EIT assumes that the non-equilibrium entropy depends both on the inelastic pressure tensor and on the classical variables (internal energy $u$ and strain tensor $\varepsilon_{ij}$) (cf. equation 117):

$$s = s(u, e, \varepsilon_{ij}, p^\ast, \dot{P}^\ast)$$

(136)

where $e$, $p^\ast$, and $\varepsilon_{ij}$, $P^\ast$ are the trace of $\varepsilon_{ij}$, $P^\ast$, respectively, and the deviators. The corresponding Gibbs equations is:

$$ds = T^{-1} du + (P^\ast/3 \rho T) de + \sum_{ij} (\dot{P}^\ast_{ij}/\rho T) \dot{d}e_{ij} = -(c/\rho T) dp^\ast - (\dot{\mathcal{C}}/\rho T) \dot{d}P^\ast$$

(137)

where $c$ and $\dot{\mathcal{C}}$ are constitutive functions. Using the Gibbs equation and the linearized balance equation for energy, we can cast the entropy balance equation in the form:

$$\rho T \dot{d}S/\dot{c}t = \sum_{ij} \dot{P}^\ast_{ij}(\partial e_{ij}/\partial t + a \dot{e} \dot{P}^\ast_{ij}/\partial t) - p^\ast(\partial e/\partial t + \beta \dot{p^\ast}/\partial t).$$

(138)

To make $\sigma_\epsilon \geq 0$, one assumes the curved brackets to be proportional to $a \dot{P}^\ast$ and $b \dot{p^\ast}$, respectively, with $a$ and $b$ scalars. Then, according to the Barcelona scheme discussed in Section 2.3,

$$\tau_\epsilon \dot{e} \dot{P}^\ast_{ij}/\partial t + \dot{P}^\ast_{ij} = -2 \eta \dot{e} e_{ij}/\partial t$$

(139a)

$$\tau_\epsilon \dot{e} \dot{p^\ast}/\partial t + \dot{p^\ast} = -\zeta \dot{e} e/\partial t$$

(139b)

where $2\eta = a^{-1}$, $a/2\eta = \tau_\epsilon$; $b^{-1} = \zeta/\beta = \tau_\epsilon$; and the coefficients $a$ and $b$ may depend on $u$. According to these equations, $\dot{P}^\ast$ is not purely inelastic, since it is proportional to $\dot{e}_{ij}$ in the high-frequency limit. After some algebra, one can obtain the evolution equations for the deviator $\dot{P}$ and isotropic part $p$ of the total pressure, $P$:

$$\tau_\epsilon \dot{e} \dot{P}_{ij}/\partial t + \dot{P}_{ij} = -2G \ddot{e}_{ij} + \tau_\epsilon \dot{e} e_{ij}/\partial t$$

(140a)

$$\tau_\epsilon \dot{e} \dot{p}/\partial t + \dot{p} = -3K (e + \tau_\epsilon \dot{e} e/\partial t)$$

(140b)

$$K = \lambda^2 + (2/3) G; \; \tau_\epsilon = (\eta/G) + \tau_\epsilon; \; \tau_\epsilon = (\zeta/3K) + \tau_\epsilon.$$  

(140c)

Thus, EIT leads to the constitutive equations for a Poynting-Thomson body [211].

In the limit $\tau_\epsilon \rightarrow 0$, (140a) reduces to the constitutive equation for a Kelvin-Voigt body,

$$\dot{P}_{ij} = -2G \ddot{e}_{ij} - 2\eta \dddot{e}_{ij}/\partial t.$$  

(141)

*}
In the other limit $G \to 0$, (135a) leads to the basic equation of Maxwell's model:

$$\tau_i \partial \dot{P}_{ij} / \partial t + \dot{P}_{ij} = -2\eta \partial \theta \partial_{ij} / \partial t. \quad (142)$$

Note that the material coefficients in these equations are subject to some constraints imposed by the entropy principle and the condition that entropy is a convex function about equilibrium [5, 163, 211–214].

**B. Polymer solutions**

The thermodynamic functions of polymer solutions under flow may depend on shear-rate [5]. The internal energy of a solution of elastic dumbbells is not the same in equilibrium as in shear. The rheological models for polymer solutions [5, 164, 200, 201, 215–219] assume that the roles of solvent and polymer can be separated. The viscous pressure tensor is decomposed [218, 219] into two parts

$$P^v = P^o + P_p \quad (143)$$

where subscripts "o" and "p" denote the contribution of the solvent and polymer, respectively. $P_p$ is decomposed into $N$ normal modes

$$P_p = \sum_{i=1}^{N} P_i. \quad (144)$$

As usual, the pressure contribution $P_i$ from mode $i$ can be decomposed into a trace $p_i$ and traceless part $\dot{P}_{ij}$. According to the basic hypothesis of EIT, the thermodynamic potentials are assumed to depend on $p_i$ and $\dot{P}_{ij}$ in addition to the classical variables, i.e.

$$s = s(u, v, \{p_i\}, \{\dot{P}_{ij}\}). \quad (145)$$

Via a procedure similar to that in sub-section A, we obtain

$$\tau_i \partial p_i / \partial t + p_i = -\zeta_i \nabla \cdot v \quad (i = 0, \ldots, N) \quad (146a)$$

$$\tau_i \partial \dot{P}_{ij} / \partial t + \dot{P}_{ij} = -2\eta_i \dot{v} \quad (i = 0, \ldots, N). \quad (146b)$$

The components $\dot{P}_{ij}$ are analogous to the internal variables in the formalism of Kluiberg [38], $\tau_i$ and $\eta_i$ are the relaxation time and shear viscosity associated with $\dot{P}_{ij}$; $\nabla$ is the traceless symmetric part of the velocity gradient. Assuming that the solvent may be considered as a Newtonian fluid, i.e. $\tau_0 \ll \tau_i$ and $\tau_0 \ll \tau_0$, one obtains for the solvent the classical Newton-Stokes equations

$$p_0 = -\zeta_0 \nabla \cdot v \quad (147a)$$

$$\dot{P}_0 = -2\eta_0 \dot{v}. \quad (147b)$$

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Relations (146b) and (147b) are the Rouses-Zimm model [218, 219] which was derived from statistical arguments.

Different kinds of dumbbells, rigid dumbbells, Hookean dumbbells, and so-called finitely extensible nonlinear elastic (FENE) dumbbells are considered in [200, 201, 216]. The entropy is evaluated microscopically for comparison with macroscopic EIT.

C. Non-linear models

In the non-linear case, the generalized thermodynamic force $X$ (cf. 36–37c) takes the form [5, 214–216]

$$ X = -a_1 \mathbf{P}^\tau - a_2 (\mathbf{P}^\tau \cdot \mathbf{P}^\tau - \pi^\tau \delta) $$

where $\pi^\tau = (1/3) \mathbf{P}^\tau \cdot \mathbf{P}^\tau$; $a_1$ and $a_2$ are functions of $u$ and the invariants of $\mathbf{P}^\tau$. The entropy principle requires that $a_1 > 0$ and restricts dependence of $a_1$ and $a_2$ on the invariants. The evolution equation for $\mathbf{P}^\tau$ can be cast in the form:

$$ \tau D_j \mathbf{P}^\tau = -2\eta \mathbf{V} - \mathbf{P}^\tau - \chi (\mathbf{P}^\tau \cdot \mathbf{P}^\tau - \pi^\tau \delta), $$

where $\tau$ is the relaxation time; $\eta$ is viscosity; $D_j$ is the Jaumann derivative; and $\mathbf{V}$ is the symmetrical part of the velocity gradient. $\chi$ is a coefficient that provided for the non-linear correction to Newton’s law. A similar result was obtained by Müller and Wilmanski [220]. For $\tau \to 0$ and $\chi \to 0$, (149) reduces to Newton’s law. The thermodynamic restrictions lead to

$$ \tau > 0, \quad \eta > 0. $$

No information about the sign of $\chi$ is available. The parameters $\eta$, $\tau$, and $\chi$ should be determined from experiment or molecular models. To investigate the relation between (149) and other models, e.g. Rivlin-Ericksen [221] and Reiner-Rivlin [5], one should rewrite (149) in terms of the Rivlin-Ericksen time-derivative, $\mathbf{P}^{(2)}$:

$$ \mathbf{P}^\tau = -2\eta \mathbf{V} - \tau \mathbf{P}^{(2)} - \chi (\mathbf{P}^\tau \cdot \mathbf{P}^\tau - \pi^\tau \delta) + \tau (\mathbf{P}^\tau \cdot \mathbf{V} + \mathbf{V} \cdot \mathbf{P}^\tau). $$

In first approximation and in the limit $\tau \to 0$, this relation reduces to Navier-Stokes (cf. ref. [5]):

$$ (1) \mathbf{P}^\tau = -2\eta \mathbf{V}. $$

For $\tau > 0$ and also in the first-order approximation, one has

$$ (2) \mathbf{P}^\tau = -2\eta \mathbf{V} - \tau \mathbf{\dot{P}}^{(2)} \delta t. $$

This is the basic equation of Maxwell’s model. The second-order approximation with $\tau = 0$ gives the Reiner-Rivlin equation,

$$ (3) \mathbf{P}^\tau = -2\eta \mathbf{V} - 4\eta^2 \chi (\mathbf{V} \cdot \mathbf{V} - (1/3) \mathbf{V} \cdot \mathbf{V}). $$

References:

The second-order approximation with \( \tau > 0 \) allows one to express the first and second normal stress coefficients, \( \psi_1 \) and \( \psi_2 \), in terms of \( \eta, \tau \), and \( z \) [5]. It turns out that \( \psi_1 > 0 \).

Equation (149) has been extended by Oldroyd [222] to include all possible products of \( P^r \) and \( V \).

D. Steady shearing flow

Evolution equation (149) can be used to study polymer solutions in a steady shear flow between two parallel horizontal plates [5, 215]. If the lower plate is at rest and the upper plate in motion in the \( x \)-direction with a constant velocity \( v_0 \), the fluid velocity field is given by

\[
v = (\dot{\gamma} y, 0, 0).
\]

(155)

Here \( \dot{\gamma} = v_0/h \); \( y \) is the direction normal to the plates; \( h \) is the distance between the plates; and \( \dot{\gamma} \) is the constant shear-rate. The first and second normal stress differences are defined as

\[
N_1 = P^{rr}_{xx} - P^{rr}_{yy} \quad (156a)
\]

\[
N_2 = P^{rr}_{yy} - P^{rr}_{zz} \quad (156b)
\]

They are related to viscometric functions \( \psi_1 \) and \( \psi_2 \) by

\[
N_1 = -\psi_1 (\dot{\gamma}) \dot{\gamma}^2 \quad (\psi_1 > 0) \quad (157a)
\]

\[
N_2 = -\psi_2 (\dot{\gamma}) \dot{\gamma}^2 \quad (\psi_2 < 0) \quad (157b)
\]

Experimental data indicate that \( \psi_1 \) is positive and \( \psi_2 \) generally negative [5]. The apparent viscosity can be introduced by

\[
P^{rr}_{xy} = -\eta(\dot{\gamma}) \dot{\gamma} \quad (\eta > 0). \quad (158)
\]

Inserting the velocity field \( v_x = \dot{\gamma} y \) into the evolution equation and using (157a, b, 158), one obtains the set of non-linear algebraic equations [5]:

\[
4\tau \mu^2 - \psi_1 (2\eta - \tau \dot{\psi}_1 \dot{\gamma}^2) = 0 \quad (159a)
\]

\[
\tau \mu (\psi_1 + 2\psi_2) + 2 \dot{\psi}_1 \dot{\psi}_2 (\psi_1 + \psi_2) \dot{\gamma}^2 - \tau \mu^2 \psi_1 = 0 \quad (159b)
\]

\[
3\psi_1 - 6\mu \tau - 2 \dot{\psi}_1 (\psi_1 + 2\psi_2) \dot{\gamma}^2 = 0. \quad (159c)
\]

Here \( \mu, \psi_1 \), and \( \psi_2 \) are unknowns, whilst \( \dot{\gamma} \) is the independent variable. Preliminary information can be obtained by assuming that \( \tau \) and \( \eta \) are constant and that \( z = 0 \). Then (159a–c) yields:

\[
\mu = \eta/(1 + \tau^2 \dot{\gamma}^2), \quad \psi_1 = 2\tau \eta/(1 + \tau^2 \dot{\gamma}^2), \quad \psi_2 = -\frac{1}{2} \psi_1 \quad (160)
\]

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These results indicate that the three viscometric functions are even functions of $\dot{\gamma}$ and that $\psi_1 > 0$ and $\psi_2 < 0$. A more realistic model is obtained by supposing that $\eta$, $\tau$, and $\alpha$ depend on the invariants of $P$.

Taking into account the fact that the apparent viscosity $\mu$ and the first normal stress coefficient $\psi_1$ can be described by Ostwald power laws [5], and that $\psi_2$ is proportional to $\dot{\gamma}$, one finds that $\eta$, $\tau$, and $\alpha$ also satisfy Ostwald power laws:

$$\eta = \eta_0 (\dot{\gamma}/\dot{\gamma}_0)^n; \quad \tau = \tau_0 (\dot{\gamma}/\dot{\gamma}_0)^n; \quad \alpha = \alpha_0 (\dot{\gamma}/\dot{\gamma}_0)^n.$$  \hspace{1cm} (161)

The unknown constant parameters are related by

$$n_1 = n_2 = n_\alpha - 1; \quad n_\alpha = -1 - n_2; \quad n_1 = -1; \quad n_\alpha = n_\alpha,$$

(162)

where $n_\alpha$, $n_1$, and $n_2$ are constants in the power laws of $\mu$, $\psi_1$, and $\psi_2$, respectively.

Comparison with experimental data [223, 224] is made in the cases of three polymeric solutions: a 2.5% solution of polyacrylamide in a 50% water and 50% glycerine solution (PAA), a 1.1% polyisobutylene solution in dechydronaphthalene (Oppanol B200), and a 8.7% polyisobutylene-decalin solution “D2b” (Oppanol B30) [5, 215]. The EIT model gives a very satisfactory agreement with the experimental data.

A powerful way of investigating fluids at high, steady shear rates and isothermal conditions not readily realizable in the laboratory is provided by molecular dynamics simulation. One study in polymers used a Brownian model in which interaction with the solvent was provided by a friction constant [225]. Many-body effects were neglected, corresponding to the Rouse rheological model. The object of this study was to investigate formation of molecular agglomerates and resultant phase separation.

Most of the computer studies involve Lennard-Jones liquids under steady Couette flow. Kinetic energy, used as a measure of temperature, is kept constant by rescaling velocities or by introduction of artificial damping terms into the equations of particle motion. The earlier studies [226-228] gave attention to the “shear thinning effect”. A small decrease in shear viscosity at low shear-rates becomes more pronounced [226] as $\dot{\gamma}$ increases. At large $\dot{\gamma}$, it was found [229] that

$$\eta = \eta_0 - 2\dot{\gamma}^{1/2},$$

(163)

For shearing of the $xy$ plane, we have

$$P_{xx} - P_{zz} = \alpha_0 + \chi_1 \dot{\gamma}^{3/2},$$

(164)

and similarly for $P_{yy} - P_{zz}$ [229]. Such effects can be understood on the basis of EIT via the theory [186] reviewed in (122-125c) augmented by addition of a relaxing scalar parameter which, at large $\dot{\gamma}$, depends on shear rate through a term linear in $\dot{\gamma}^{1/2}$ [186].

These results agree with the non-analyticities found by Hanley and Evans [187] and explained by EIT [185, 186]. The simulations which determined the internal energy...
and the pressure as functions of $\gamma$ have been extended to include anisotropies in the diffusion tensor $D_{ij}$ in steady Couette flow [190, 230–232]. The methods are still being developed, and the colour field method used in the earlier work [233–235] on diffusion has been found [232] to be inaccurate at high shear-rates. To apply EIT to the analysis of shear-induced anisotropy in $D_{ij}$, one needs a nonlinear formalism with the shear and heat flows, an internal variable proportional to $\mathbf{P}$, and the traceless inelastic strain-rate, as the set on which the thermodynamic potentials are assumed to depend.

E. The Giesekus four-parameter model

The Giesekus model [236] can be obtained from EIT if it is admitted that (139) holds. It is also assumed that the solvent is an incompressible Newtonian fluid, so that

$$P_0 = -2\eta_0 V.$$  \hspace{1cm} (165)

$\eta_0$ is the shear viscosity of the solvent. The Gibbs equation takes the form

$$Td\mathbf{s} = du - (1/p) A_{p'} P_{p'} : d \mathbf{P}_p$$  \hspace{1cm} (166)

where one takes into account the fact that $P_0$ is not an independent variable. In the usual way, EIT yields the evolution equation [5]

$$\tau_p D P_p = -2\eta_P V - P_p - a_p (P_p \cdot P_p - \pi_p \delta)$$  \hspace{1cm} (167)

which contains three parameters, $\tau_p, \eta_p$, and $a_p; \pi_p = (1/3) P_p : P_p$. $D$ is an objective time-derivative. After some algebra, one can obtain the evolution equation for the total viscous pressure, $P^v$:

$$\tau_p D P^v + P^v - (\tau_p / \eta_0) (P^v \cdot P^v - \pi_0 \delta) - 2\lambda (V \cdot P^v + P^v \cdot V - \pi_0 \delta)$$

$$= -2\eta_0 (V + \lambda D V - 2\lambda \lambda / \tau_p) (V \cdot V - \pi_0 \delta)$$  \hspace{1cm} (168)

where

$$\eta = \eta_0 + \eta_p; \quad \tau_p = \eta_0 \tau_p; \quad \lambda = \lambda_0 \tau_p / \eta; \quad \pi = (2/3) P^v : V; \quad \pi_0 = (1/3) V : V.$$  \hspace{1cm} (169)

(163) is the same as the Giesekus constitutive equation [236, 237] except for the terms in $\pi^v, \pi$, and $\pi$ which appear as a consequence of the hypothesis of the absence of bulk effects [5, 212]. This equation contains four independent parameters, $\eta_0, a_p, \tau_p$, and $\eta_p$, or equivalently $\eta, \tau, \lambda$, and $\tau_p$.

F. Burgers media

We have described [38] in Part I, Section 2 how elimination of internal variables in a viscoelastic medium can lead to a linear equation relating stress and strain components.
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and the time-derivatives of both to order \( n \). In the general case, the equation has the form:

\[
\begin{align*}
R^{(r)}_{i,j,k} \dddot{\varepsilon}_{g} &= \sum_{m=1}^{n-1} R^{(r)}_{i,j,m} \dddot{\varepsilon}_{g} + (d^{m}/dt^{m}) \dddot{\varepsilon}_{g} + \sum_{m=1}^{n+1} R^{(r)}_{i,j,m} (d^{m}/dt^{m}) \dddot{\varepsilon}_{g} \\
R^{(r)}_{i,j,k} (\tau - \tau^{0}) &= \sum_{m=1}^{n-1} (d^{m}/dt^{m}) \tau + (d^{m}/dt^{m}) \tau = R^{(r)}_{i,j,k} \tau + \sum_{m=1}^{n+1} R^{(r)}_{i,j,k} (d^{m}/dt^{m}) \tau
\end{align*}
\]  

(170a)

(170b)

where \( \varepsilon_{g} \) is the strain tensor, \( \tau_{g} \) the stress tensor, \( \varepsilon \) and \( \tau \) their traces, respectively, and the tilde denotes a traceless tensor. \( \tau^{0} \) is a constant reference value. The \( R \)-coefficients satisfy inequalities imposed by the entropy principle.

When \( n = 2 \), we have the “Burgers equation”, and the versions with higher \( n \) are obtained by including more internal variables \([184, 238]\). A study has been made \([239]\) of the propagation of non-linear dissipative waves in generalized Burgers media.

Solutions of the Burgers equation for linear and non-linear models are discussed in Part III, Section 6.5. These include the various rheological models we have mentioned in this section which are special cases of (170a, b).

5.5. Shear-induced phase transitions

In the discussion of Section 4, equations (70a, b), it was remarked that the chemical potentials in a mixture depend quadratically on the fast variables, causing the latter to affect chemical and phase equilibrium when \( \mathcal{F} \) and \( \mathcal{J} \) become sufficiently large. As an example \([240]\) we find for a polymer solution that the specific Gibbs function for Rouse polymers obeys

\[
G = G_{eq} + (1/4)(\varepsilon K) T^{-1} \hat{\mathcal{P}} : \hat{\mathcal{P}}
\]

(171)

where \( \varepsilon K T \) is the polymer elastic modulus. This follows if \( G \) depends on a configurational tensor analogous to the elastic strain in reference \([185]\). According to the Flory-Huggins theory, \( G_{eq} \) depends on \( \phi \), the volume fraction of polymer. If \( \mu_{1} \) is the chemical potential of polymers, the spinodal line is given by \( \partial \mu_{1} / \partial \phi = 0 \), where the derivative is at constant \( P_{eq}^{1} \), this is the non-zero component of \( \hat{\mathcal{P}} \). The resulting curves, which depend on \( P_{eq}^{1} \), were fitted to experiment. An extension of this theory \([242]\) has been made to include the flux of the polymer solute as an independent fast variable. A fit was also made \([243]\) to experimental data by Wolf \([244]\) for a solution of polystryrene in trans-decalin. This paper uses an expression given by Wolf for the steady-state shear compliance. The same study examines the non-Newtonian viscosity in the light of data by Wolf et al. \([244, 245]\).

EIT has also been applied \([246]\) in calculating the course of phase separation in a generalized van der Walls-Kac fluid with interaction potential

\[
\phi(r) = \infty, \quad r \leq \sigma
\]

(172a)

\[
\phi(r) = (\lambda/2\pi) r_{d}^{2} (\gamma r)^{-1} \exp(-\gamma r), \quad r > \sigma.
\]

(172b)

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From EIT, one gets the equation

$$\frac{\partial \rho}{\partial t} + \tau \frac{\partial \rho}{\partial t^2} = M_0 V^2 \mu$$

(173)

where \( \mu \) is calculated from a functional Taylor expansion for the free energy. Equation (173) is obtained by taking the divergence of the relaxation equation for \( \mathbf{J}_r \), equation (82a), neglecting \( \nabla \cdot \nabla \cdot \mathbf{J}_k \), and using the mass conservation equation for the solute.

That the critical point, determined by setting

$$\frac{\partial P}{\partial V} = 0 = \frac{\partial^2 P}{\partial V^2}$$

(174)

where \( P \) is the thermodynamic pressure, is affected by steady shear is seen from equation (121) which implies

$$\frac{\partial P}{\partial \tilde{P}} = \tilde{F} \frac{\partial \xi}{\partial V}$$

(175)

so that

$$P = P_0(V, T) + \frac{1}{2} \tilde{F} \frac{\partial \xi}{\partial V} \tilde{P}; \tilde{P}$$

(176)

Using this equation to determine \( T_c \) and the circumstance that \( x < 0 \), one can predict [248] that \( T_c \) is lowered by a steady shear. The lowering is predicted to be quadratic in the shear-rate \( \dot{\gamma} \), whereas the experiments [249] yield a lowering \( O(\dot{\gamma}^{0.53}) \), resembling the non-analyticities found in [187]. Thus they could arise from a non-linear dependence of \( P \) on a structural parameter \( \xi \), rather than from its explicit dependence on \( \tilde{P} \).

In addition to the critical point, it has been predicted [250] that a steady shear-rate \( \dot{\gamma} \) can depress the melting point. One starts with

$$\mu(T, P, \dot{\gamma}) = \mu_{eq}(T, P) + RT \ln \Delta_q$$

(177a)

$$\Delta_q = \exp[(\eta/\rho RT) \dot{\gamma}^2]$$

(177b)

\( \eta \) is shear viscosity:

$$\eta = \eta_0 \quad \text{(Newtonian fluids)}$$

(178a)

$$\eta = \eta_0 \sinh^{-1}(\tau \dot{\gamma})/\tau \dot{\gamma} \quad \text{(non-Newtonian fluids)}$$

(178b)

From \( \mu \), one calculates the temperature derivative of the specific enthalpy, and on integrating, one can predict that \( T_c \) is lowered by steady shear. As in the preceding case of the critical point, any effects actually observed at large \( \dot{\gamma} \) may not necessarily be those predicted by this theory, since \( \mu \) can depend indirectly on \( \dot{\gamma} \) through the coupling of shear-rate to liquid structure.
There are other types of phase transitions which can be induced by high shear-rate. One of these is flocculation in a suspension discussed previously in a review of molecular dynamics [225]. Another [229] is the formation of long chains of diffusing particles oriented along the direction of diffusion. The chains have a hexagonal structure in a plane perpendicular to x. A thermodynamic theory of such a phenomenon must couple diffusion to viscoelasticity and provide for non-linear effects.

References


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