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Internal variables for relaxation phenomena in heat and mass transfer

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Abstract—A general theory is developed for relaxation phenomena in heat and mass transfer, based on an internal variables approach. The model equations are systematically derived from the description of the dissipation and the extended free energy of the system (Hamiltonian) in terms of the traditional (equilibrium) thermodynamic variables and internal variables characterizing heat and mass flux. The resulting equations generalize the most important from the previously used empirical models. The meaning of the internal variables is clarified through a comparison with the results of the kinetic theory of gases. Mass transfer relaxation phenomena in polymers are also discussed.

1. INTRODUCTION

THE TRADITIONAL description of heat and mass transfer, including Fourier's law for heat conduction and Fick's law for mass diffusion, although adequate for steady-state problems, results in an infinitely fast propagation of signals, due to the parabolic nature of the resulting equations. Although this aphysical behavior does not affect most engineering applications, even transient ones, there are cases where finite wave speeds of propagation are experimentally observed, such as in anomalous diffusion in polymers [1–4]. In these cases, the above paradoxical behavior is corrected by explicitly taking into consideration relaxation phenomena in the constitutive equation for mass flux.

So far, with the exception of Maxwellian gases [5], the development of constitutive equations describing relaxation phenomena associated with heat and mass transfer is based upon empirical phenomenological relationships governing the corresponding fluxes [1–4, 6–9]. The purpose of this work is to reveal the relation of the relaxation phenomena observed in heat conduction and mass diffusion with corresponding relaxation processes of the structure of the physical systems under consideration through the recently developed generalized bracket description [10–12]. This formalism provides a formulation for local equilibrium thermodynamics based on internal variables which also incorporates a Hamiltonian description for flow phenomena. Previous publications have demonstrated the consistency of this formalism in the description of transport phenomena for (multi-component) Newtonian [10] and viscoelastic [11] fluids. Thus, a thermodynamically consistent theoretical framework is developed for the description of transport processes influenced by relaxation changes of the internal microstructure. It is shown that this framework is rich enough to explain the most important of the observed phenomena, consistent with the only (so far) case where a microscopic analysis is available (Maxwellian gases) and that it is potentially helpful in bridging the gap between macroscopic (phenomenological) models and microscopic (based on first principles) ones in explaining anomalous mass transfer behavior in polymeric systems.

2. FLUX RELAXATION MODELS

The most general linear form for heat and mass flux relaxation phenomena can be obtained through an integral equation which represents a weighted average of the corresponding affinity over the time history of the material

$$J_\alpha = \int_{-\infty}^{t} \psi(t-t')\nabla_\alpha \Phi(\underline{x}, t')\,\mathrm{d}t' \qquad (1)$$

where $\underline{x}$ is the spatial coordinate. In equation (1), the kernel $\psi(s)$ is a positive, monotonically-decreasing relaxation function that tends to zero as $s \to \infty$, and Φ is the corresponding potential. For anisotropic materials, ψ is expected to have a tensorial character, so that equation (1) becomes

$$J_\alpha = \int_{-\infty}^{t} \psi_{\alpha\beta}(t-t')\nabla_\beta \Phi(\underline{x}, t')\,\mathrm{d}t'. \qquad (2)$$

Depending on the form of the kernel $\psi(s)$, one can recover various flux relaxation models. For example, by assuming a single, exponentially-decreasing expression in time for the relaxation kernel

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NOMENCLATURE

A_1	1.37 in kinetic theory
A_2	2.68 in kinetic theory
a	Helmholtz free energy density
C	structural variable in kinetic theory
c	solute concentration
$\underline{c}$	speed relative to the center of mass (in kinetic theory)
c_p	phonon speed
f	mass distribution function in kinetic theory
F	generic functional, equation (12)
$\underline{F}$	$\partial\underline{\phi}_{eq}/\partial T$ or $\partial\underline{\theta}_{eq}/\partial\rho$
H	Hamiltonian functional
$\underline{J}$	heat or mass flux
$\underline{J}^s$	entropy flux
k	generic diffusivity
K	force constant, in kinetic theory characterizes the interaction between molecules
m	molecular mass in kinetic theory
p	thermodynamic pressure
P	operating space of thermodynamic variables
q, $\underline{q}$	heat, heat flux
$\underline{\underline{Q}}$	symmetric matrix, $\partial^2 a/\partial\underline{\phi}\partial\underline{\phi}$ or $\partial^2 a/\partial\underline{\theta}\partial\underline{\theta}$
s	entropy density
S	entropy functional
T	temperature
t	time
u	energy density
$\underline{x}$	spatial coordinate.

Greek symbols

α_i	internal variables in heat transfer
β	rate parameter in Crank's model
$\underline{\underline{\delta}}$	unit second order tensor
Δ	first difference, i.e. $\Delta\mu \equiv \mu_1 - \mu_2$
$\underline{\theta}$	internal variable in mass transfer
λ	generic relaxation time
μ_i	chemical potential of species i, $\equiv \delta H/\delta\rho_i$
$\underline{\xi}_i$	absolute velocity coordinate for species i
ρ	mass density
σ	volumetric rate of heat production
σ^s	volumetric rate of internal entropy production
τ_N	relaxation time for normal processes that preserve the phonon momentum
τ_R	relaxation time for the momentum-nonconserving processes
$\underline{\phi}$	internal variable in heat transfer
Φ	generic thermodynamic potential
Ω	spatial domain.

Subscripts

i	different species
α	spatial coordinates.

Superscript

e	value at thermodynamic equilibrium.

Miscellaneous symbols

$[\cdot,\cdot]$	dissipation bracket
$\{\cdot,\cdot\}$	Poisson bracket.

$$\psi(s) = (k/\lambda)\exp(-s/\lambda) \tag{3}$$

one can obtain upon differentiation the equivalent differential model

$$J_\alpha + \lambda\frac{\partial J_\alpha}{\partial t} = -k\nabla_\alpha\Phi \tag{4}$$

where λ is the relaxation time and k the corresponding diffusivity. An equation of this type was originally proposed by Cattaneo [6, 7] for heat transfer. For a lucid description of the relaxation-type phenomena occurring in heat transfer, from a mathematical point of view, see Joseph and Preziosi [8, 9]. Ocone and Astarita [13] used Cattaneo's equation in their model for heat transfer in polymers accompanied by crystallization. An analogous equation was assumed by Kalospiros *et al.* [14, 15] in a model describing sorption and transport phenomena in solid polymers. Note that equation (4), when considered with the corresponding conservation equation, results in hyperbolic equations, thus allowing for the development of heat and concentration waves, propagating with finite speed.

Pao and Banerjee [16] have remarked that a natural generalization of equation (4) to anisotropic media is

$$J_\alpha + \lambda_{\alpha\beta}\frac{\partial J_\beta}{\partial t} = -k_{\alpha\beta}\nabla_\beta\Phi \tag{5}$$

where the tensors $\underline{\underline{\lambda}}$ and $\underline{\underline{k}}$ are positive semi-definite and generally depend on Φ and the morphology of the material.

When the kernel in equation (1) is defined by the superposition of an exponentially decreasing term and a delta function

$$\psi(s) = k_1\delta(s) + (k_2/\lambda)\exp(-s/\lambda) \tag{6}$$

then an equation arises which is similar to the well-known model of Jeffreys (see p. 261 of ref. [17]) for the stress and strain rate in viscoelastic liquids

$$J_\alpha + \lambda\frac{\partial J_\alpha}{\partial t} = -k\nabla_\alpha\Phi - \lambda k_1\frac{\partial\nabla_\alpha\Phi}{\partial t} \tag{7}$$

where k_1 is an effective diffusivity corresponding to an instantaneous response to changes in the affinity. The relationship between k and k_1 is given by

$$k = k_1 + k_2. \tag{8}$$

Note that k_2 is an elastic diffusivity arising from slow relaxation modes. The Pao and Banerjee generalization is also applicable to equations (7) and (8). A discussion of the physical ideas leading to equation (7) is given by Joseph and Preziosi [8, 9] for the heat transfer case. The analogous model for mass transfer was proposed by Neogi [1, 2], and used by Camera-Roda and Sarti [4] in their model for diffusion in polymers. The dependence of the diffusion coefficient upon the concentration history considered by Crank [3] also results in a similar mass flux model. Inclusion of an effective diffusivity is meant to represent fast decaying modes in practical applications involving much longer timescales where the parabolic nature of the resulting equations and consequently the infinitely fast wave propagation associated with equation (7) is not of concern.

In addition to the relaxation models discussed above for heat conduction, there is another category of relaxation models in heat transfer originating from an effort to describe a different phenomenon, namely the second sound in dielectric crystals [8]. These models have never formally been connected with the ones of the Cattaneo-type and involve a qualitatively different equation for the heat flux which does not reduce to Fourier's law even under steady-state conditions. The original equation, proposed for the description of heat waves in dielectric crystals at low temperatures, was obtained by Guyer and Krumhansl [18] through a solution of the linearized Boltzmann equation for the pure phonon field in terms of the normal-process collision operator. An interpretation of their results in terms of fluxes led to the system of two equations [8]

$$\gamma \frac{\partial T}{\partial t} + \underline{\nabla} \cdot \underline{J} = 0 \tag{9}$$

$$J_\alpha + \tau_R \frac{\partial J_\alpha}{\partial t} = -\tau_R \frac{c_p^2}{3} \nabla_\alpha T + \tau_R \tau_N \frac{c_p^2}{5} (\nabla^2 J_\alpha + 2\nabla_\alpha \nabla_\varepsilon J_\varepsilon) \tag{10}$$

where γ is the heat capacity of the material, τ_R a relaxation time for the momentum-nonconserving processes (the umklapp processes in which momentum is lost from the phonon system), c_p the average sound speed of the phonons and τ_N a relaxation time for normal processes that preserve the phonon momentum [8]. It is interesting to note that the original equations were expressed in terms of internal variables α_0 and $\underline{\alpha}_1$ rather than the heat flux [18]. These variables characterize the non-equilibrium modification of the distribution function of the phonons. In the limit of low temperature, under the assumption of a dispersionless and isotropic phonon spectrum, these components are proportional to the local thermal energy density (i.e. the temperature) and the heat current, respectively (see p. 768 of ref. [18]). Under these conditions, the heat current is proportional to the momentum of the phonon gas [18].

Finally note that equation (10) does not reduce to Fourier's law under steady-state conditions and that one can have according to equation (10) heat flux not necessarily down the temperature gradient. This new type of heat transport was subsequently found experimentally in helium IV crystals [19, 20]. Corresponding phenomena for mass transfer, although entirely possible from a theoretical point of view, have not been reported in the literature.

3. THE BRACKET FORMULATION OF RELAXATION PHENOMENA IN HEAT CONDUCTION

In this section we are concerned with the description of relaxation phenomena associated with heat conduction only. Relaxation phenomena associated with mass transfer are discussed separately in the next section. An internal variable (structural parameter), $\underline{\phi}$, is introduced in addition to the usual thermodynamic variables characterizing the system at equilibrium, i.e. the mass and entropy densities, ρ and s, respectively. If so desired, a macroscopic flow field can also be introduced following the approach detailed in Edwards and Beris [10–12], but the analysis of its effect is not addressed here in order to keep the introduction of the new ideas in this paper clearer. Also, for simplicity, we consider an incompressible medium. Thus, without loss of generality, the (constant) density can be considered equal to unity and the dependent variables of the system are just the entropy density, s, and the internal variable, $\underline{\phi}$.

As an example of the physical interpretation of the internal variable, in the case of an idealized solid, $\underline{\phi}$ can be associated with a vector parameter describing the anisotropic deviation from equilibrium of the distribution density function of phonons [18, 21]. This is proportional to the momentum flux of the phonon gas. The nature of the conformation vector in other systems (Maxwellian gases) is discussed in Section 5.

The operating space for this problem in terms of the above variables is

$$P \equiv \begin{cases} \phi(\underline{x}, t) : \phi \in \mathbb{R}^3 \\ s(\underline{x}, t) : s \in \mathbb{R} \end{cases} \tag{11}$$

(and appropriate initial and boundary conditions) where s is the entropy density and $\underline{\phi}$ the internal state variable, with the corresponding equilibrium value, $\underline{\phi}^{\text{eq}}$, depending only on s; i.e. $\underline{\phi}^{\text{eq}} = \underline{\phi}^{\text{eq}}(s)$. The additional variable, $\underline{\phi}$, is called *internal* in the sense that, unlike s (and ρ in the compressible case), it can alter without any corresponding changes occurring outside the system (see p. 44 of ref. [22]). It is used to characterize a 'local' equilibrium state (defined for a particular time and length scale) which corresponds to all possible microstates which are compatible with the particular value of $\underline{\phi}$. Within the context of irreversible thermodynamics, the internal variables are continuum tensor fields of arbitrary order (i.e. scalar, vector, second order tensor, etc.) and character (absolute or relative)—see Table 1 in Section 5. In this section and the following one, we deal with absolute vector internal variables. Furthermore, of importance for the specification of the dissipation is that $\underline{\phi}$ has odd parity upon time inversion; i.e. $\underline{\phi}(t) = -\underline{\phi}(-t)$. This property arises from the special physical character of $\underline{\phi}$. For example, in the modeling of second-sound phenomena in dielectric crystals, $\underline{\phi}$ can be identified with the momentum flux of the phonon gas (see discussion at the end of the previous section) and therefore, similar to the velocity, it has to be odd under time inversion.

In the generalized-bracket description, the governing equations are generated from the description of the time evolution of an arbitrary functional, F, defined as

$$F = F[s, \underline{\phi}] = \int_\Omega f(s, \underline{\phi})\, \mathrm{d}^3x \tag{12}$$

of the system. This is given by the dynamical equation [10–12]

$$\mathrm{d}F/\mathrm{d}t = \{F, H\} + [F, H] \tag{13}$$

where H is the corresponding Hamiltonian and $\{\cdot,\cdot\}$, $[\cdot,\cdot]$ are the Poisson and dissipation brackets, respectively. The Hamiltonian functional represents the total energy of the system. In the absence of kinetic and potential energies, it may be written solely as a volume integral of the internal energy density, u, over the entire system Ω

$$H[s, \underline{\phi}] = \int_\Omega u(s, \underline{\phi})\, \mathrm{d}^3x. \tag{14}$$

The Poisson bracket expresses the (reversible) macroscopic flow (convection) effects [10–12]. Since no macroscopic flow is present in this case, $\{F, H\} = 0$, and we need to be concerned with the definition of the dissipation bracket only. The dissipation bracket expresses the influence of dissipative (irreversible) effects on the system. It is thermodynamically constrained to satisfy two relations. From the first law, since H is the total energy of the system

$$[H, H] = 0 \tag{15}$$

(so that $\mathrm{d}H/\mathrm{d}t = 0$) and the total energy of the system (in the absence of external interactions) is conserved. From the second law of thermodynamics, the entropy of the system (in the absence of external interactions) cannot decrease with time. Thus

$$[S, H] \geqslant 0 \tag{16}$$

(so that $\mathrm{d}S/\mathrm{d}t \geqslant 0$), where S is the total entropy of the system

$$S = \int_\Omega s\, \mathrm{d}^3x. \tag{17}$$

Thus, provided that the model parameters are selected in such a way so that the inequality (16) is satisfied, the thermodynamic consistency of the resulting equations is guaranteed. Subject to the constraints imposed by equations (15) and (16), and according to coordinate invariance and the equipresence principle, the most general expression for $[F, G]$ close to equilibrium (where only linear terms are retained) is given as a sum of bilinear functionals in F, G [10–12]. For the operating space specified by equation (11), this gives

$$\begin{aligned}
[F, G] = &-\int_\Omega K_{\alpha\beta} \frac{\delta F}{\delta\phi_\alpha} \frac{\delta G}{\delta\phi_\beta}\, \mathrm{d}^3x \\
&+ \int_\Omega \frac{1}{T} \frac{\delta F}{\delta s} K_{\alpha\beta} \frac{\delta G}{\delta\phi_\alpha} \frac{\delta G}{\delta\phi_\beta}\, \mathrm{d}^3x \\
&- \int_\Omega \Lambda_{\alpha\beta} \left[\nabla_\alpha \left(\frac{\delta F}{\delta s} \right) \frac{\delta G}{\delta\phi_\beta} - \frac{\delta F}{\delta\phi_\beta} \nabla_\alpha \left(\frac{\delta G}{\delta s} \right) \right] \mathrm{d}^3x \\
&- \int_\Omega M_{\alpha\beta} \nabla_\alpha \left(\frac{\delta F}{\delta s} \right) \nabla_\beta \left(\frac{\delta G}{\delta s} \right) \mathrm{d}^3x \\
&+ \int_\Omega \frac{1}{T} \frac{\delta F}{\delta s} M_{\alpha\beta} \nabla_\alpha \left(\frac{\delta G}{\delta s} \right) \nabla_\beta \left(\frac{\delta G}{\delta s} \right) \mathrm{d}^3x \\
&- \int_\Omega N_{\alpha\beta\gamma\varepsilon} \nabla_\alpha \left(\frac{\delta F}{\delta\phi_\beta} \right) \nabla_\gamma \left(\frac{\delta G}{\delta\phi_\varepsilon} \right) \mathrm{d}^3x \\
&+ \int_\Omega \frac{1}{T} \frac{\delta F}{\delta s} N_{\alpha\beta\gamma\varepsilon} \nabla_\alpha \left(\frac{\delta G}{\delta\phi_\beta} \right) \nabla_\gamma \left(\frac{\delta G}{\delta\phi_\varepsilon} \right) \mathrm{d}^3x
\end{aligned} \tag{18}$$

where $\underline{\underline{K}}$, $\underline{\underline{\Lambda}}$, $\underline{\underline{M}}$, ${}_4\underline{\underline{N}}$ (where the ${}_4\underline{\underline{}}$ denotes a fourth order tensor) are phenomenological coefficients, which are in general functions of the primary variables, and $\delta/\delta s$, $\delta/\delta\underline{\phi}$ are functional derivatives, which for spaces with no constraints or gradient dependencies (such as P) reduce simply to the partial derivatives of the corresponding integrands.

Note that the dissipation bracket defined by equation (18) consists of four parts, each one represented by a bilinear form in F, G and its corresponding entropy production. Also notice that the second pair of terms is antisymmetric due to the assumed parity of ϕ (odd). The first three parts can be considered together as coupling the vector affinities present in the system, $\delta H/\delta\underline{\phi}$ and $\underline{\nabla}(\delta H/\delta s)$. Thus, the phenomenological coefficient matrices $\underline{\underline{K}}$ and $\underline{\underline{M}}$ should be symmetric and non-negative definite to satisfy the Onsager and thermodynamic relations [12]. The matrix $\underline{\underline{K}}$ is inversely proportional to a characteristic relaxation time, whereas the matrices $\underline{\underline{\Lambda}}$ and $\underline{\underline{M}}$ are related to the elastic and effective conductivity, respectively. To preserve the finite speed of propagation of heat waves, $\underline{\underline{M}}$ should always be taken to be identically zero. However (see also Joseph and Preziosi [8]), in practical applications the fast relaxation modes can be approximated using an 'effective' (in general, anisotropic) conductivity $\underline{\underline{M}}$, which is meant to represent all the modes that have decayed within the time scale of the observation (phonon/phonon interactions in the case of idealized solids). The elastic conductivity on the other hand, takes into account slow modes, for example free-electron/phonon interactions. The fourth pair of terms in equation (18) represents nonhomogeneous structural effects and is usually neglected as corresponding to higher order corrections to the dissipation; however, it becomes important in systems where the primary dissipation is absent ($\underline{\underline{M}} = \underline{\underline{0}}$). The fourth order tensor ${}_4\underline{N}$ should also satisfy corresponding symmetry and inequality constraints [12].

Equating the right-hand side of equation (13) with the one relating the rate of change of an arbitrary functional $F[s, \underline{\phi}]$ to the time derivatives of the primary variables

$$\frac{\mathrm{d}F}{\mathrm{d}t} = \int_{\Omega} \left(\frac{\delta F}{\delta \underline{\phi}} \cdot \frac{\partial \underline{\phi}}{\partial t} + \frac{\delta F}{\delta s} \frac{\partial s}{\partial t} \right) \mathrm{d}^3 x \tag{19}$$

yields the evolution equations for $\underline{\phi}$ and s

$$\frac{\partial \phi_\alpha}{\partial t} = -K_{\alpha\beta} \frac{\delta H}{\delta \phi_\beta} + \Lambda_{\alpha\beta} \nabla_\beta T + \nabla_\beta \left(N_{\beta\alpha\gamma\varepsilon} \nabla_\gamma \frac{\delta H}{\delta \phi_\varepsilon} \right) \tag{20a}$$

$$\begin{aligned} \frac{\partial s}{\partial t} = {} & \nabla_\alpha \left(\Lambda_{\alpha\beta} \frac{\delta H}{\delta \phi_\beta} \right) + \nabla_\alpha (M_{\alpha\beta} \nabla_\beta T) \\ & + \frac{1}{T} \left(K_{\alpha\beta} \frac{\delta H}{\delta \phi_\alpha} \frac{\delta H}{\delta \phi_\beta} + M_{\alpha\beta} \nabla_\alpha T \nabla_\beta T \right. \\ & \left. + N_{\alpha\beta\gamma\varepsilon} \nabla_\alpha \frac{\delta H}{\delta \phi_\beta} \nabla_\gamma \frac{\delta H}{\delta \phi_\varepsilon} \right) \end{aligned} \tag{20b}$$

where we have used the thermodynamic identity $T = \delta H / \delta s$. By comparison with the macroscopic relationship

$$\partial s / \partial t = -\nabla \cdot J^s + \sigma^s \tag{21}$$

equation (20b) implies the following expression for the entropy flux

$$J_\alpha^s = -\left(\Lambda_{\alpha\beta} \frac{\delta H}{\delta \phi_\beta} + M_{\alpha\beta} \nabla_\beta T \right) \tag{22}$$

and the rate for internal entropy production

$$\begin{aligned} \sigma^s = \frac{1}{T} \Bigg[& K_{\alpha\beta} \frac{\delta H}{\delta \phi_\alpha} \frac{\delta H}{\delta \phi_\beta} + M_{\alpha\beta} (\nabla_\alpha T)(\nabla_\beta T) \\ & + N_{\alpha\beta\gamma\varepsilon} \nabla_\alpha \left(\frac{\delta H}{\delta \phi_\beta} \right) \nabla_\gamma \left(\frac{\delta H}{\delta \phi_\varepsilon} \right) \Bigg]. \end{aligned} \tag{23}$$

Furthermore, substituting equation (13) in

$$\frac{\partial u}{\partial t} = \frac{\partial u}{\partial \underline{\phi}} \cdot \frac{\partial \underline{\phi}}{\partial t} + \frac{\partial u}{\partial s} \frac{\partial s}{\partial t} = \frac{\delta H}{\delta \underline{\phi}} \cdot \frac{\partial \underline{\phi}}{\partial t} + T \frac{\partial s}{\partial t} \tag{24}$$

and using the symmetry property of $\underline{\underline{\Lambda}}$, gives

$$\begin{aligned} \frac{\partial u}{\partial t} = -\nabla_\alpha \Bigg[-\Bigg(& \Lambda_{\alpha\beta} T \frac{\delta H}{\delta \phi_\beta} + M_{\alpha\beta} T \nabla_\beta T \\ & + N_{\alpha\beta\gamma\varepsilon} \frac{\delta H}{\delta \phi_\beta} \nabla_\gamma \frac{\delta H}{\delta \phi_\varepsilon} \Bigg) \Bigg]. \end{aligned} \tag{25}$$

Finally, according to the local equilibrium assumption and in the absence of mass transfer

$$\frac{\mathrm{d}q}{\mathrm{d}t} \equiv T \frac{\partial s}{\partial t} \equiv -\underline{\nabla} \cdot \underline{J} + \sigma \tag{26}$$

where J, σ are the rate of heat flux and volumetric heat production evaluated by substituting $\partial s / \partial t$ from equation (20b) into equation (26) as

$$J_\alpha = -\left(\Lambda_{\alpha\beta} T \frac{\delta H}{\delta \phi_\beta} + M_{\alpha\beta} T \nabla_\beta T \right) \tag{27a}$$

$$\begin{aligned} \sigma = {} & K_{\alpha\beta} \frac{\delta H}{\delta \phi_\alpha} \frac{\delta H}{\delta \phi_\beta} - \Lambda_{\alpha\beta} \nabla_\alpha T \frac{\delta H}{\delta \phi_\beta} \\ & + N_{\alpha\beta\gamma\varepsilon} \nabla_\alpha \left(\frac{\delta H}{\delta \phi_\beta} \right) \nabla_\gamma \left(\frac{\delta H}{\delta \phi_\varepsilon} \right). \end{aligned} \tag{27b}$$

To examine more clearly the implications of the general model presented above without obscuring the physical issues with a complex mathematical formalism, let us assume a simple Taylor expansion of the Helmholtz free energy density, $a = a(T, \underline{\phi})$, in terms of an equilibrium configuration, $\underline{\phi}^e = \underline{\phi}^e(T)$

$$\underline{\phi}^e \approx \underline{\phi}^0 + \underline{F}(T - T^0) \tag{28}$$

$$a(T, \underline{\phi}) \approx a^e(T) + \tfrac{1}{2} \underline{\underline{Q}}(T) : (\underline{\phi} - \underline{\phi}^e)(\underline{\phi} - \underline{\phi}^e) \tag{29}$$

where $\underline{\underline{Q}} \equiv \partial^2 a / \partial \underline{\phi} \partial \underline{\phi}$ is a symmetric matrix. Note that $\underline{\underline{Q}}$, $\underline{\phi}^0$ and $\underline{F}$ are in general anisotropic for anisotropic materials, such as certain crystalline solids, in which case their dependence on an anisotropic structural parameter, in addition to T and $\underline{\phi}$, has to be taken into account. For simplicity, we will consider here only isotropic media, in which case $\underline{\phi}^0 = \underline{F} = \underline{0}$, as in the case of a Maxwellian gas (see Table 1 in Section 5)

$$\underline{\underline{Q}} = Q \underline{\underline{\delta}} \tag{30}$$

and, without loss of generality, $T^0 = 0$. Thus, we have

$$a(T, \underline{\phi}) = a_e(T) + \tfrac{1}{2} Q \underline{\phi} \cdot \underline{\phi} \tag{31}$$

which implies that [10]

$$\left. \frac{\delta H}{\delta \underline{\phi}} \right|_s = \left. \frac{\partial a}{\partial \underline{\phi}} \right|_T = Q \underline{\phi}. \tag{32}$$

Furthermore, for an isotropic medium

$$\underline{\underline{K}} = K \underline{\underline{\delta}}; \quad \underline{\underline{\Lambda}} = \Lambda \underline{\underline{\delta}}; \quad \underline{\underline{M}} = M \underline{\underline{\delta}} \tag{33a}$$

$$N_{\alpha\beta\gamma\varepsilon} = N_1 (\delta_{\alpha\gamma} \delta_{\beta\varepsilon} + \delta_{\alpha\varepsilon} \delta_{\beta\gamma}) + N_2 (\delta_{\alpha\beta} \delta_{\gamma\varepsilon}) \tag{33b}$$

where K, M, N_1 and N_2 are subject to the inequality constraints

$$K, M, N_1, 2N_1 + 3N_2 \geqslant 0 \tag{34}$$

(Λ can be either positive or negative) which are obtained by application of the thermodynamic inequality (16) [12]. Note that equation (33b) is the most general isotropic fourth order expression which is consistent with the symmetries $(\alpha,\gamma)\leftrightarrow(\beta,\varepsilon)$, $\alpha\leftrightarrow\beta$ and $\gamma\leftrightarrow\varepsilon$ [12]. Then, incorporating equations (31)–(33) into equations (20)–(23) yields

$$\frac{\partial\phi_\alpha}{\partial t} = -KQ\,\phi_\alpha+\Lambda\nabla_\alpha T+N_1\nabla^2(Q\phi_\alpha)+(N_1+N_2)\nabla_\alpha[\nabla_\varepsilon(Q\,\phi_\varepsilon)] \tag{35a}$$

$$J_\alpha = -[\Lambda\,TQ\phi_\alpha+M\,T(\nabla_\alpha T)]. \tag{35b}$$

Let us now further assume that $\Lambda\,TQ$ and $M\,T$ are independent of the temperature. Then, if in addition we set $N_1 = N_2 = 0$ and the dependence on ϕ is eliminated between equations (35a) and (35b), we get

$$J_\alpha+\frac{1}{KQ}\frac{\partial J_\alpha}{\partial t} = -\left(M+\frac{\Lambda^2}{K}\right)T\nabla_\alpha T-\frac{M\,T}{KQ}\frac{\partial}{\partial t}(\nabla_\alpha T) \tag{36a}$$

which reduces exactly to the Jeffreys-type model, equation (7). If instead we use $M = 0$ and $N_1 = N_2 = N$, we get

$$J_\alpha+\frac{1}{KQ}\frac{\partial J_\alpha}{\partial t} = -\frac{\Lambda^2}{K}T\nabla_\alpha T-N\frac{\Lambda}{K}T[\nabla^2(Q\phi_\alpha)+2\nabla_\alpha\nabla_\varepsilon(Q\phi_\varepsilon)] \tag{36b}$$

which reduces exactly to the Guyer and Krumhansl model, equation (9). Therefore, we see that for the first time, the two most often used heat transfer relaxation models appear as limiting cases of the same general evolution equations, equation (20).

4. THE BRACKET DESCRIPTION OF MASS DIFFUSION

In order to analyze relaxation phenomena in mass transfer alone we assume that the (mean) velocity is zero and that the temperature is constant. The operating system in this case is defined as

$$P \equiv \begin{cases} \underline{\theta}(\underline{x},t):\underline{\theta}\in\mathbb{R}^3 \\ \rho_i(\underline{x},t):\rho_i\in\mathbb{R}^+\,;\ \Sigma_i\rho_i = \rho,\ i = 1,\ldots,n \\ s(\underline{x},t):s\in\mathbb{R} \end{cases} \tag{37}$$

where $\underline{\theta}$ is (similar to $\underline{\phi}$ in the previous section) an internal state variable [22], ρ_i the mass density of component i, n the number of components and s, as usual, the entropy density. Notice that, here and in the following, Latin subscripts denote chemical components, as opposed to Greek ones which are reserved for the Cartesian coordinates. Therefore, following Einstein's summation convention, repeated indices imply a summation over that index, from 1 to n if the indices denote chemical components (Latin) and from 1 to 3 if they denote spatial coordinates (Greek). The internal state vector variable, $\underline{\theta}$, characterizes the diffusion process and can be associated with the flux (inertia) of the diffusing species (in terms of the theory of interpenetrating continua [23]) or, in the case of diffusion in polymers, with the rate of change of the microscopic structure of the system. As with any internal state variable, its equilibrium value, $\underline{\theta}^{\mathrm{eq}}$, depends only on the other thermodynamic equilibrium variables, which are, in this case, s (or T), and ρ_i; i.e. $\underline{\theta}^{\mathrm{eq}} = \underline{\theta}^{\mathrm{eq}}(T,\rho_i)$. Furthermore, of importance is that $\underline{\theta}$ (similar to $\underline{\phi}$) has odd parity upon time inversion; i.e. $\underline{\theta}(t) = -\underline{\theta}(-t)$.

The dissipation bracket can be constructed in an analogous fashion to the heat transfer case, equation (18). For the operating space specified by equation (37), this gives (ignoring terms affecting the entropy and heat transfer)

$$\begin{aligned}[F,G] = &-\int_\Omega \Phi_{\alpha\beta}\frac{\delta F}{\delta\theta_\alpha}\frac{\delta G}{\delta\theta_\beta}\,\mathrm{d}^3x \\ &-\sum_{i=1}^{n}\int_\Omega X^i_{\alpha\beta}\left[\nabla_\alpha\left(\frac{\delta F}{\delta\rho_i}\right)\frac{\delta G}{\delta\theta_\beta}-\frac{\delta F}{\delta\theta_\alpha}\nabla_\beta\left(\frac{\delta G}{\delta\rho_i}\right)\right]\mathrm{d}^3x \\ &-\sum_{i=1}^{n}\sum_{j=1}^{n}\int_\Omega \Psi^{ij}_{\alpha\beta}\nabla_\alpha\left(\frac{\delta F}{\delta\rho_i}\right)\nabla_\beta\left(\frac{\delta G}{\delta\rho_j}\right)\mathrm{d}^3x \\ &-\int_\Omega \Omega_{\alpha\beta\gamma\varepsilon}\nabla_\alpha\left(\frac{\delta F}{\delta\theta_\beta}\right)\nabla_\gamma\left(\frac{\delta G}{\delta\theta_\varepsilon}\right)\mathrm{d}^3x \end{aligned} \tag{38}$$

where $\underline{\underline{\Phi}}$, $\underline{\underline{X}}^i$, $\underline{\underline{\Psi}}^{ij}$, ${}_4\underline{\underline{\Omega}}$, i, $j = 1,\ldots,n$ are phenomenological coefficients, which are in general functions of the primary variables. The dissipation bracket defined by equation (37) is very similar to the one defined by equation (18); as such, similar arguments as the ones mentioned after equation (18) lead to similar symmetry conditions for the phenomenological coefficients. Likewise, there are similarities in the physical interpretation: the tensor $\underline{\underline{\Phi}}$ is inversely proportional to a relaxation time characteristic of the evolution of the internal state variable $\underline{\theta}$, whereas the tensors $\underline{\underline{X}}^i$ and $\underline{\underline{\Psi}}^{ij}$, i, $j = 1,\ldots,n$, are related to the elastic and effective diffusivity, respectively. Finally, there are similarities in the mathematical consequences: in order to preserve the finite speed of propagation of mass waves, $\underline{\underline{\Psi}}$ should be taken to be identically zero. For diffusion in polymers, the effective diffusivity, following Crank's arguments [3], is meant to represent the (almost) instantaneous response to changes in the affinity attributed to movements of individual molecular groups and small segments of chains, while the elastic diffusivity takes into account slow modes associated with the relatively slow uncoiling and displacement of large segments of the polymer chains. The fourth couple of terms in equation (38) represents non-homogeneous structural effects and will be neglected in the following as corresponding to higher order corrections to the dissipation; however, they might become important in systems where the primary dissipation is absent ($\underline{\underline{\Psi}}^{ij} = \underline{\underline{0}}$; see also the similar discussion in the previous section).

However, there are also differences which are not only restricted by the fact that there are now n variables, ρ_i, $i = 1, \ldots, n$, but they are rather due primarily to the fact that not all of the phenomenological coefficients entering the description of the dissipation bracket can be independently defined. Rather, they are constrained to satisfy the following equations [12]

$$\sum_{i=1}^{n} \underline{\underline{X}}^{i} = \underline{\underline{0}} \tag{39a}$$

$$\sum_{i=1}^{n} \underline{\underline{\Psi}}_{ij} = \underline{\underline{0}} \quad j = 1, \ldots, n \tag{39b}$$

due to the fact that the total mass has to be conserved. The above constraints simplify, when only two components are present (taking also into account Onsager's reciprocal relations, $\underline{\underline{\Psi}}^{12} = \underline{\underline{\Psi}}^{21}$), to

$$\underline{\underline{X}}^{1} = -\underline{\underline{X}}^{2} \equiv \underline{\underline{X}} \tag{40a}$$

$$\underline{\underline{\Psi}}^{11} = -\underline{\underline{\Psi}}^{12} = -\underline{\underline{\Psi}}^{21} = \underline{\underline{\Psi}}^{22} \equiv -\underline{\underline{\Psi}} \tag{40b}$$

where $\underline{\underline{X}}$, $\underline{\underline{\Psi}}$ are the only independent (tensorial) parameters entering in the description of the dissipation bracket which reduces to

$$\begin{aligned}[F, G] = &- \int_{\Omega} \Phi_{\alpha\beta} \frac{\delta F}{\delta\theta_{\alpha}} \frac{\delta G}{\delta\theta_{\beta}} \mathrm{d}^3x \\ &- \int_{\Omega} X_{\alpha\beta}\left(\nabla_{\alpha}\left(\frac{\delta F}{\delta\rho_1} - \frac{\delta F}{\delta\rho_2}\right)\frac{\delta G}{\delta\theta_{\beta}}\right. \\ &\left. - \frac{\delta F}{\delta\theta_{\alpha}} \nabla_{\beta}\left(\frac{\delta G}{\delta\rho_1} - \frac{\delta G}{\delta\rho_2}\right)\right)\mathrm{d}^3x \\ &- \int_{\Omega} \Psi_{\alpha\beta}\nabla_{\alpha}\left(\frac{\delta F}{\delta\rho_1} - \frac{\delta F}{\delta\rho_2}\right)\nabla_{\beta}\left(\frac{\delta G}{\delta\rho_1} - \frac{\delta G}{\delta\rho_2}\right)\mathrm{d}^3x \\ &- \int_{\Omega} \Omega_{\alpha\beta\gamma\varepsilon}\nabla_{\alpha}\left(\frac{\delta F}{\delta\theta_{\beta}}\right)\nabla_{\gamma}\left(\frac{\delta G}{\delta\theta_{\varepsilon}}\right)\mathrm{d}^3x. \end{aligned} \tag{41}$$

Now, equating the right-hand side of equation (41) with the one relating the rate of change of a general functional $F(\underline{\theta}, \rho_i)$ to the evolution equations for the primary variables

$$\frac{\mathrm{d}F}{\mathrm{d}t} = \int_{\Omega} \left(\frac{\delta F}{\delta\underline{\theta}} \cdot \frac{\partial\underline{\theta}}{\partial t} + \frac{\partial F}{\partial\rho_i}\frac{\partial\rho_i}{\partial t}\right)\mathrm{d}^3x \tag{42}$$

yields the following evolution equations for $\underline{\theta}$ and ρ_i:

$$\frac{\partial\theta_{\alpha}}{\partial t} = -\Phi_{\alpha\beta}\frac{\delta H}{\delta\theta_{\beta}} + X_{\alpha\beta}\nabla_{\beta}(\Delta\mu) + \nabla_{\beta}\left[\Omega_{\beta\alpha\gamma\varepsilon}\nabla_{\gamma}\left(\frac{\delta H}{\delta\theta_{\varepsilon}}\right)\right] \tag{43a}$$

$$\frac{\partial\rho_1}{\partial t} = \nabla_{\alpha}\left(X_{\alpha\beta}\frac{\delta H}{\delta\theta_{\beta}}\right) + \nabla_{\alpha}[\Psi_{\alpha\beta}\nabla_{\beta}(\Delta\mu)] \tag{43b}$$

$$\frac{\partial\rho_2}{\partial t} = -\nabla_{\alpha}\left(X_{\alpha\beta}\frac{\delta H}{\delta\theta_{\beta}}\right) - \nabla_{\alpha}[\Psi_{\alpha\beta}\nabla_{\beta}(\Delta\mu)] \tag{43c}$$

where $\Delta\mu \equiv \mu_1 - \mu_2$ and $\mu_i \equiv \delta H/\delta\rho_i$. Equations (43b) and (43c) imply that the mass fluxes are

$$J_{\alpha}^{1} = -J_{\alpha}^{2} \equiv J_{\alpha} = -\left(X_{\alpha\beta}\frac{\delta H}{\delta\theta_{\beta}} + \Psi_{\alpha\beta}\nabla_{\beta}(\Delta\mu)\right) \tag{44}$$

whereas the requirement of a non-negative entropy production (not calculated here) necessitates constraints in the character of the tensors $\underline{\underline{\Phi}}$, $\underline{\underline{\Psi}}$, and ${}_4\underline{\underline{\Omega}}$.

Again, to examine more clearly the implications of the general model presented above without obscuring the physical issues with a complex mathematical formalism, let us assume a simple free energy expression for the Hamiltonian, provided again by a Taylor expansion around equilibrium, the latter corresponding to the constant temperature T and the local instantaneous densities ρ_i. Since at equilibrium the free energy is minimized with respect to $\underline{\theta}$, the linear term in the Taylor expansion is zero. Hence, similarly to equations (28) and (29), the Taylor expansion of the free energy density, $a = a(T, \rho_i, \underline{\theta})$, in terms of an equilibrium configuration, $\underline{\theta}^{c} = \underline{\theta}^{c}(T)$, is

$$\underline{\theta}^{c} \approx \underline{\theta}^{o} + \tfrac{1}{2}\underline{F}(\Delta\rho - \Delta\rho^{o}) \tag{45}$$

$$a(T, \rho_i, \underline{\theta}) \approx a^{c}(T, \rho_i) + \tfrac{1}{2}\underline{\underline{Q}}(T, \rho_i) : (\underline{\theta} - \underline{\theta}^{c})(\underline{\theta} - \underline{\theta}^{c}) \tag{46}$$

where $\underline{\underline{Q}} \equiv \partial^2 a/\partial\underline{\theta}\partial\underline{\theta}$ is a symmetric matrix. For simplicity, we consider here only isotropic media, where $\underline{\theta}_{o} = \underline{F} = \underline{0}$ and $\underline{\underline{Q}} = Q\underline{\underline{\delta}}$ (analogous to equation (30) in heat transfer). Then, using without loss of generality $\Delta\rho^{o} = 0$, we have

$$a(T, \rho_i, \underline{\theta}) = a_{c}(T, \rho_i) + \tfrac{1}{2}Q\underline{\theta} \cdot \underline{\theta} \tag{47}$$

which implies that [10]

$$\left.\frac{\delta H}{\delta\underline{\theta}}\right|_{s,\rho_i} = \left.\frac{\partial a}{\partial\underline{\theta}}\right|_{T,\rho_i} = Q\underline{\theta}. \tag{48}$$

Furthermore, for an isotropic medium

$$\underline{\underline{\Phi}} = \Phi\underline{\underline{\delta}}; \quad \underline{\underline{X}} = X\underline{\underline{\delta}}; \quad \underline{\underline{\Psi}} = \Psi\underline{\underline{\delta}} \tag{49a}$$

$$\Omega_{\alpha\beta\gamma\varepsilon} = \Omega_1(\delta_{\alpha\gamma}\delta_{\beta\varepsilon} + \delta_{\alpha\varepsilon}\delta_{\beta\gamma}) + \Omega_2(\delta_{\alpha\beta}\delta_{\gamma\varepsilon}) \tag{49b}$$

where Φ, Ψ, Ω_1, and Ω_2 are subject to inequality constraints analogous to the ones provided by equation (34) for heat transfer. Note that equation (49b) is the most general isotropic fourth order expression which is consistent with the symmetries $(\alpha, \gamma) \leftrightarrow (\beta, \varepsilon)$, $\alpha \leftrightarrow \beta$ and $\gamma \leftrightarrow \varepsilon$ [12]. Then, incorporating equations (47) and (48) into equations (43) and (44) yields

$$\begin{aligned}\frac{\partial\theta_{\alpha}}{\partial t} = &-\Phi Q\theta_{\alpha} + X\nabla_{\alpha}(\Delta\mu) + \Omega_1\nabla^2(Q\theta_{\alpha}) \\ &+ (\Omega_1 + \Omega_2)\nabla_{\alpha}\nabla_{\varepsilon}(Q\theta_{\varepsilon})\end{aligned} \tag{50}$$

$$J_{\alpha} = -[XQ\theta_{\alpha} + \Psi\nabla_{\alpha}(\Delta\mu)] \tag{51}$$

in complete analogy to the corresponding heat transfer equations, equations (33) and (34). Let us also assume for simplicity that $\underline{\underline{X}}Q$ and Ψ are constant. Then, if in addition we set $\Omega_1 = \Omega_2 = 0$ and the dependence on $\underline{\theta}$ is eliminated between equations (50) and (51), we get

$$J_\alpha + \frac{1}{\Phi Q}\frac{\partial J_\alpha}{\partial t} = -\left(\Psi + \frac{X^2}{\Phi}\right)\nabla_\alpha(\Delta\mu) - \frac{\Psi}{\Phi Q}\frac{\partial}{\partial t}(\nabla_\alpha(\Delta\mu)) \tag{52}$$

which reduces exactly to the Jeffreys-type model, equation (7). This is similar to the equation used by Camera-Roda and Sarti [4] in their model. When $\Psi = 0$, equation (52) coincides with the Cattaneo-type mass flux equation used by Kalospiros *et al.* [14, 15] in their model and also the one derived by Aifantis [23], who arrived at it by considering solute and polymer as interpenetrating continua. Of course, if $Q \rightarrow \infty$, or equivalently, $Q^{-1} \rightarrow 0$—which also means that $\underline{\theta} = \underline{0}$ at all times—Fick's law, equation (4) with $\lambda = 0$, is recovered.

If instead we use $\Psi = 0$ and $\Omega_1 = \Omega_2 = \Omega$ we get

$$J_\alpha + \frac{1}{\Phi Q}\frac{\partial J_\alpha}{\partial t} = -\frac{X^2}{\Phi}\nabla_\alpha(\Delta\mu) + \Omega\frac{X}{\Phi}[\nabla^2(J_\alpha/X) + 2\nabla_\alpha\nabla_\varepsilon(J_\varepsilon/X)] \tag{53}$$

which reduces exactly to the Guyer and Krumhansl model, equation (9), in heat transfer in dielectrics. As far as we know, equation (53) has not found as yet any applications in mass transfer problems.

5. HEAT AND MASS FLUX RELAXATION IN THE CLASSICAL KINETIC THEORY OF GASES

Maxwell's classical kinetic theory of gases [5] represents the first (and, perhaps, greatest) attempt to develop a microscopic theory accounting for transport phenomena. It is interesting to note here that Maxwell first arrived at a Cattaneo-type equation for heat flux, but immediately proceeded to cast out the time derivative term by assuming that the rate of conduction quickly establishes itself. In a subsequent treatment, Natanson [24] showed how the kinetic theory can also account for relaxation phenomena in mass transfer. However, his treatment for mass flux relaxation was not recognized till 85 years later [25, 26]. An independent derivation was provided by Sandler and Dahler [27], who studied the case of equimolar counterdiffusion in a mixture of two very similar chemical species.

An interesting comment can be made, based on the kinetic theory results, regarding the relation of each one of the transport phenomena to a *different structural variable* of the Maxwellian gas. These results are summarized in Table 1. The fundamental molecular mechanism for relaxation is associated in all cases with the effect of the collision process on the evolution of the corresponding structural variables. However, the structural variables associated with the various transport phenomena have rates of evolution which are characterized, in general, by *different* relaxation times. The latter may possibly be related to each other through the underlying collision process. Regarding the value of the aforementioned analysis, it allows us to physically interpret and directly relate the relevant phenomenological coefficients of the macroscopic models developed in Sections 3 and 4 to the diffusivities and relaxation times obtained by the kinetic theory arguments.

Of course, in the case of gases, relaxation phenomena are very fast and unimportant to (most) engineering applications. However, within more complex systems, such as polymeric solids discussed in the next section, relaxation times can be determined of the order of several seconds or larger. Unfortunately, a microscopic theory, analogous to kinetic theory, which will have allowed us to obtain a microscopic physical picture of the macroscopic phenomena, is still missing.

6. MASS TRANSFER RELAXATION PHENOMENA IN POLYMERIC SYSTEMS

A plethora of phenomena associated with mass transfer of small solutes in polymers has been reported in the literature that cannot be explained by classical (Fickian) diffusion theory [30]. *Two-stage sorption* is a phenomenon usually observed in linear perturbation experiments, where the weight uptake initially reaches an apparent equilibrium value, only to subsequently grow at a much smaller rate to a significantly larger final equilibrium solute content [31]. In *Case-II transport*, in a neighborhood of time zero the weight uptake grows linearly with time, often up to the time of complete saturation of the sample [32]. Another experimental observation is *Overshoot*: the amount of solute absorbed reaches a maximum and subsequently decreases towards its final equilibrium value. In some instances [33–35], the effect has been attributed to crystallization occurring at time scales comparable to the time scale of the experiment. However, in well-documented cases [36–38] overshoots are observed in the absence of crystallization.

Several models, in addition to the mass flux relaxation models introduced in Section 2, have been proposed to explain the aforementioned observations. All of the previously mentioned phenomena (except, possibly, Case-II transport which can be explained through a coupling of the mass transfer with the stress) invariably necessitate modeling of relaxation phenomena extending over macroscopic time scales up to several seconds. However, the various models differ from each other, with respect to the mechanism of the relaxation. One mechanism involves the direct

Table 1. Characteristic parameters for relaxation in transport phenomena for Maxwellian gases

Type of flux, $\underline{J}$	Character of flux	Corresponding structural variable, C	Proportionality constant, A, $J = AC$	Relaxation time from Maxwell's theory
Stress, $\underline{\underline{\tau}}$	Tensor	$\int \underline{cc} f \, \mathrm{d}\underline{\xi}$	1	$\frac{1}{3}\sqrt{\left(\frac{2m}{K}\right)}\frac{m}{\rho A_2}$
Heat flux, $\underline{q}$	Vector	$\int \underline{c} c^2 f \, \mathrm{d}\underline{\xi}$	1/2	$\frac{1}{3}\sqrt{\left(\frac{2m}{K}\right)}\frac{m}{\rho A_2}$†
Mass flux, $\underline{J}_1$	Vector	$\int \underline{\xi}_1 f_1 \, \mathrm{d}\underline{\xi}_1$	1	$\sqrt{\left(\frac{2m}{K}\right)}\frac{m}{\rho A_1}$

† Note that the relaxation time for heat flux has a coefficient of 1/2 instead of 1/3 in the more complete Grad [28] and Truesdell [29] formulations.

coupling of the well documented stress relaxation phenomena with diffusion processes [39–42]. Others, like the Crank model [3] or the proposed Vrentas *et al.* mechanism [12, 37], rely only indirectly on the stress relaxation process. They involve rather the relaxation of the polymer structure in general as far as it affects the diffusion coefficient or the chemical potential of the solute. In other instances, phenomenological models relying on the relaxation of an inertial quantity (like the flux, or $\underline{\theta}$ in Section 4) have been utilized to explain phenomena such as the sorption overshoot [4, 14]. Finally, more than one mechanism can be involved in more complex models [12, 43].

In addition to the flux relaxation models discussed previously, the bracket formalism can actually reproduce most of the models discussed in the last paragraph. Space constraints do not allow us to present the bracket formulations of these models in detail. The interested reader can find them in ref. [12]. We will rather focus on the implications that the bracket analysis on Section 4 has on the still unanswered questions related to the appropriateness of the use of mass-flux relaxational models with large relaxation times in explaining the diffusion of solutes in polymers. More specifically, the internal variables necessarily introduced through the bracket formalism in order to reproduce flux relaxation models presented in Section 2 (for example, $\underline{\theta}$), are inertial in nature with an odd parity upon time reversal. This observation is consistent with the findings from the kinetic theory of gases (see Section 5) where the relaxation times are very small. However, it raises the question on how it is possible to associate a large relaxation time with inertial variables, such as the time associated with the experimental observations of mass transport phenomena with polymers.

This question is really related to the overall problem of introducing inertial phenomena in polymer fluid dynamics. It is only recently that awareness on this issue has arisen (see, for example, discussion on the Hinch [44] and the two-mode Giesekus [45]). Clearly, more work is warranted in order to clarify all the issues related with this subject.

7. CONCLUDING REMARKS

In conclusion, the most significant contribution of the above theoretical development is the unification of all relaxation processes associated with transport phenomena. Granted, the bracket formalism cannot distinguish a priori which one of the many available mechanisms for transport is more important and dominates a particular application. However, it offers the flexibility to accommodate the mechanics under a common theoretical framework. By modeling relaxation phenomena associated with heat and mass transfer using an internal-variables approach, which is extensively used in describing viscoelastic stress-relaxation behavior, we begin to see a common framework for the description of all these cases. In addition, this approach allows for the straightforward description of coupling between various transport processes through their dependence on the same relaxing internal variable. Finally, the validity of the internal variables approach has been reinforced by showing its consistency with the kinetic theory of gases.

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