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Hamiltonian mechanics of complex fluids

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Abstract. Constitutive relations for complex fluids (e.g. polymeric fluids) are derived from the assumption that the equations that govern the time evolution of the complex fluids possess the generalised Hamiltonian structure. The constitutive relations consist of a configuration space kinetic equation, an extended local equilibrium relation, an expression for the extra stress tensor and an expression for the heat flux. In the particularly interesting case of complex fluids with spatially inhomogeneous internal structure, the extra stress tensor includes an extension of the Ericksen stress and the heat flux includes non-Fourier-type contributions.

1. Introduction

A comparison of the observed and the predicted macroscopic behaviour of fluids shows that for some fluids the time evolution of their macroscopic and microscopic characteristics cannot be separated. Such fluids will be called in this paper complex fluids. By macroscopic behaviour we mean the behaviour described by the five hydrodynamic fields of mass, momentum and energy densities. The predicted macroscopic behaviour is then the behaviour described by solutions of hydrodynamic equations. A microscopic characteristic of a fluid is a quantity (usually another field or a distribution function) that characterises the internal structure of the fluids under consideration. For example, a polymeric fluid (the reader can think about egg white) or a suspension are complex fluids. In the case of polymeric fluids, the internal structure is the structure of the macromolecules; in the case of suspensions it is the structure of suspended particles. Experience shows that for complex fluids any decoupling of hydrodynamic equations from the equations governing the time evolution of the internal structure leads to equations whose solutions do not agree with results of observations. An example of observations that cannot be predicted in the context of the five field and local-in-time hydrodynamic equations are the observations manifesting the so-called viscoelastic behaviour. Fluids that are not complex (i.e. the fluids for which the time evolution of their internal structure can be, with sufficient accuracy, decoupled from their hydrodynamic behaviour) will be called simple. By decoupling we mean here a separation that does not introduce into the time evolution equations integrals over the past time.

For simple fluids, the time evolution equations are introduced by requiring that their solutions agree with the following observations:

- (i) conservation of the total mass, momentum and energy;
- (ii) equilibrium thermodynamic experience (i.e. fluids that are isolated from their surroundings approach equilibrium states at which their behaviour is well described by equilibrium thermodynamics).

To guarantee agreement with the first observation, the time evolution equations have to have the form of a derivative with respect to time of a hydrodynamic field being equated to a divergence of a flux (this is, however, only true if we exclude non-local-in-space time evolution equations). The agreement with the second observation is guaranteed by an appropriate choice of the fluxes. The restrictions on the freedom of choice of the fluxes are usually expressed as the entropy inequality, the local equilibrium relation and the Onsager-Casimir symmetry (see § 2).

We shall try to follow the same route also in the context of complex fluids. Solutions to the time evolution equations of complex fluids will be required to agree with the same observations (i) and (ii) that we introduced in the context of simple fluids. It is not, however, evident how the analysis relating this requirement with the structure of the equations, that has been developed in the context of simple fluids, extends to complex fluids. The extension proposed in this paper is based on the following observation. It has been shown (Grmela 1986, also § 2 of this paper) that the entropy inequality, the local equilibrium relation and the Onsager-Casimir symmetry are consequences of a generalised Hamiltonian structure of the hydrodynamic equations of simple fluids. Moreover, the generalised Hamiltonian structure has been shown (Grmela 1986, 1988b) to express the compatibility of dynamical equations with equilibrium thermodynamics also on other levels of description (including for example the kinetic theory description). We shall therefore assume that the time evolution equations describing complex fluids will also possess the generalised Hamiltonian structure. It is quite straightforward to extend the Hamiltonian structure from simple to complex fluids (Grmela 1988a), where incompressible and isothermal fluids are considered, and § 3 of this paper, where the general complex fluids are discussed. Consequences of the generalised Hamiltonian structure are then interpreted as extensions of the entropy inequality, the local equilibrium relation and the the Onsager-Casimir symmetry. The results obtained as a consequence of the generalised structure also include expressions for the extra stress tensor and the heat flux.

In § 4 we confront the results obtained in § 3 with results obtained from other approaches. First, we turn our attention to kinetic theory of polymeric fluids (Kirkwood 1967, Bird *et al* 1987, Doi and Edwards 1986), which offers another approach to the analysis of complex fluids. A comparison of the kinetic theory approach and the approach followed in this paper will be made in § 4. Some results introduced in § 3 will be shown to agree with results obtained in kinetic theory. Most of the results arising in § 3 have not, however, been derived previously in kinetic theory. Finally, we can test our results against results of observations. We recall that we know already that solutions to equations introduced in this paper agree with the observations (i) and (ii) mentioned above (i.e. conservation of the total mass, momentum and energy, and compatibility with equilibrium thermodynamics). This is because the requirement for agreement with these two observations is the basis for the approach used in this paper. Other experimental observations with which we can confront the results obtained in this paper are rheological measurements. The new results appearing in this paper are particularly pertinent to the situation in which the internal structure is spatially inhomogeneous. This is the situation arising frequently for example in processing of polymeric liquid crystals (Denn 1986). Our results predict new stresses and a new heat flux arising due to the spatial inhomogeneity of the internal structure. The new stresses can be regarded as Ericksen stresses (Ericksen 1960) formulated on the kinetic theory level of description. The new heat flux has not been, to the best of our knowledge, introduced previously on any level of description. The question of which specific

experimental results could be used to test these predictions remains unanswered in this paper.

2. Hamiltonian mechanics of simple fluids

In this section we shall review the generalised Hamiltonian structure of simple fluids. We shall also present the entropy inequality, the local equilibrium relation and the Onsager-Casimir symmetry as a consequence of the Hamiltonian structure. The main objective of this section is to prepare the setting for § 3, where the complex fluids are considered.

Our interest in the macroscopic behaviour of fluids motivates us to choose five hydrodynamic fields ($\rho(\mathbf{r}, t)$ denoting mass density, $e(\mathbf{r}, t)$ denoting the total energy density and $\mathbf{u}(\mathbf{r}, t)$ denoting the momentum density; \mathbf{r} stands for the position coordinate and t for time) as state variables. The time evolution equations for (ρ, e, \mathbf{u}) will be introduced in two steps. First we focus our attention on the non-dissipative time evolution. We say that the time evolution is non-dissipative if there exists a functional S of the state variables (ρ, e, \mathbf{u}) that satisfies the following five properties.

(S1) The functional S is a convex functional of (ρ, e, \mathbf{u}) .

(S2) We limit ourselves only to functions of the type

$$S = \int d\mathbf{r} s(\mathbf{r}, t) \tag{2.1}$$

where $s(\mathbf{r}, t)$ is a sufficiently regular function of $\rho(\mathbf{r}, t)$, $e(\mathbf{r}, t)$, $\mathbf{u}(\mathbf{r}, t)$ pointwise for all \mathbf{r}, t .

$$(S3) \quad \frac{dS}{dt} = 0. \tag{2.2}$$

(S4) The transformation

$$(\rho, e, \mathbf{u}) \rightarrow (\rho, s, \mathbf{u}) \tag{2.3}$$

is one-to-one.

(S5) The functional S evaluated at equilibrium states (as will be defined in remark 2.1 of this section) is the equilibrium thermodynamic entropy of the fluid under consideration. For this reason, the functional S will be called an entropy. If we choose (ρ, e, \mathbf{u}) as state variables we speak about the energy representation, if we choose (ρ, s, \mathbf{u}) as state variables we speak about the entropy representation.

We now introduce the equations governing the non-dissipative time evolution. We shall introduce them first in the entropy representation. Let A, B, \dots , and all capital letters denote sufficiently regular functionals of (ρ, e, \mathbf{u}) . It has been shown (Iwinski and Turski 1976, Morrison *et al* 1980, Dzyaloshinskii and Volovick 1980) that

$$\frac{dA}{dt} = \int d\mathbf{r} \left(A_\rho \frac{\partial \rho}{\partial t} + A_s \frac{\partial s}{\partial t} + A_{u_\gamma} \frac{\partial u_\gamma}{\partial t} \right) \tag{2.4}$$

(where $A_\rho \equiv \delta A / \delta \rho(\mathbf{r}, t)$, \dots denotes the Volterra functional derivative; $\gamma = 1, 2, 3$, in this paper we use the summation convention) can be recast into the form

$$\frac{dA}{dt} = \{A, E\} \tag{2.5}$$

where

$$E = \int \mathbf{d}\mathbf{r} e(\mathbf{r}, t) \quad (2.6)$$

is the total energy, and $\{ , \}$ is the bracket operation

$$\begin{aligned} \{A, B\} = & \int \mathbf{d}\mathbf{r} \rho [\partial_\alpha(A_\rho)B_{u_\alpha} - \partial_\alpha(B_\rho)A_{u_\alpha}] + \int \mathbf{d}\mathbf{r} u_\gamma [\partial_\alpha(A_{u_\gamma})B_{u_\alpha} - \partial_\alpha(B_{u_\gamma})A_{u_\alpha}] \\ & + \int \mathbf{d}\mathbf{r} s [\partial_\alpha(A_s)B_{u_\alpha} - \partial_\alpha(B_s)A_{u_\alpha}]. \end{aligned} \quad (2.7)$$

The symbol ∂_α represents $\partial/\partial r_\alpha$. The bracket (2.7) is a Poisson bracket (i.e. $\{A, B\}$ depends linearly on $A_\rho, A_u, A_s, B_\rho, B_u, B_s$; $\{A, B\} = -\{B, A\}$; $\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0$). Equation (2.5), required to hold for all A , is called a non-canonical formulation of a Hamiltonian system (Marsden and Weinstein 1982, Olver 1986, Salmon 1988). The bracket (2.7) can be introduced by identifying the natural Lie algebraic structure of the hydrodynamic state space (Dzyaloshinskii and Volovick 1980, Marsden and Weinstein 1982, Holm and Kupersmidt 1983). The Hamiltonian structure of non-dissipative hydrodynamic equations has been first introduced in canonical form by Clebsh (1985). Transformations relating canonical and non-canonical formulations of Hamiltonian systems are discussed in detail in Holm *et al* (1986) and Salmon (1988).

We shall now rewrite (2.5) in the form

$$\begin{aligned} \frac{dA}{dt} = & \int \mathbf{d}\mathbf{r} A_\rho [-\partial_\alpha(\rho e_{u_\alpha})] + \int \mathbf{d}\mathbf{r} A_s [-\partial_\alpha(s e_{u_\alpha})] \\ & + \int \mathbf{d}\mathbf{r} A_{u_\alpha} [-\partial_\gamma(u_\alpha e_{u_\gamma}) - \rho \partial_\alpha(e_\rho) - u_\gamma \partial_\alpha(e_{u_\gamma}) - s \partial_\alpha(e_s)] \end{aligned} \quad (2.8)$$

where $e_\rho \equiv \partial e(\mathbf{r}, t)/\partial \rho(\mathbf{r}, t)$ etc. We used integration by parts and boundary conditions that make all the integrals over the surface of the region confining the fluid under consideration equal to zero. Since (2.8) holds for all A , we have

$$\frac{\partial \rho}{\partial t} = -\partial_\alpha(\rho e_{u_\alpha}) \quad (2.9a)$$

$$\frac{\partial s}{\partial t} = -\partial_\alpha(s e_{u_\alpha}) \quad (2.9b)$$

$$\frac{\partial u_\alpha}{\partial t} = -\partial_\gamma(u_\alpha e_{u_\gamma}) - \rho \partial_\alpha(e_\rho) - u_\gamma \partial_\alpha(e_{u_\gamma}) - s \partial_\alpha(e_s). \quad (2.9c)$$

Now we compare (2.9) with the non-dissipative hydrodynamic equations of simple fluids. Equation (2.9a) is equivalent to

$$\frac{\partial \rho}{\partial t} = -\partial_\alpha \dot{\rho}_\alpha \quad \dot{\rho}_\alpha = u_\alpha = \rho v_\alpha \quad (2.10)$$

where $\dot{\rho}$ denotes the flux of the mass density and \mathbf{v} the fluid velocity. If

$$e_{u_\alpha} = \frac{1}{\rho} u_\alpha = v_\alpha \quad (2.11)$$

then (2.9b) is the local form of (2.2) with the entropy flux

$$\dot{s}_\alpha = \frac{s}{\rho} u_\alpha. \tag{2.12}$$

Equation (2.9c) is identical to

$$\frac{\partial u_\alpha}{\partial t} = -\partial_\gamma(\dot{u}_{\alpha\gamma}) \tag{2.13}$$

where the momentum flux $\dot{\mathbf{u}}$ is given by

$$\dot{u}_{\alpha\gamma} = u_\alpha v_\gamma + p\delta_{\alpha\gamma} \tag{2.14}$$

if the scalar pressure p satisfies

$$\partial_\alpha p = \rho\partial_\alpha(e_\rho) + u_\gamma\partial_\alpha(e_{u_\gamma}) + s\partial_\alpha(e_s). \tag{2.15}$$

By combining

$$\partial_\alpha e = e_\rho\partial_\alpha\rho + e_{u_\gamma}\partial_\alpha u_\gamma + e_s\partial_\alpha s \tag{2.16}$$

and (2.15) we have

$$p = -e + se_s + \rho e_\rho + u_\gamma e_{u_\gamma}. \tag{2.17}$$

Equation (2.17), which holds pointwise for all \mathbf{r}, t , is known as the local equilibrium relation. It implies that the fields e, s, p, ρ are related, pointwise, as energy, entropy, pressure and mass introduced in equilibrium thermodynamics (at equilibrium states $\mathbf{u} \equiv 0$, as we shall see later in this section, so that the term in (2.17) which involves momentum \mathbf{u} disappears at equilibrium). We note that we have arrived at the local equilibrium relation (2.17) from the Hamiltonian structure. In the standard introduction of hydrodynamic equations the local equilibrium relation arises from the assumption of the local equilibrium.

Before introducing the irreversible part of the time evolution (i.e. the part which causes the entropy to grow), we shall rewrite the non-dissipative time evolution in the energy representation. By using the property (S4)—see equation (2.3)—we have

$$\begin{aligned} \delta/\delta\rho &\rightarrow \delta/\delta\rho + e_\rho\delta/\delta e & \delta/\delta s &\rightarrow e_s\delta/\delta e \\ \delta/\delta u_\alpha &\rightarrow \delta/\delta u_\alpha + e_{u_\alpha}\delta/\delta e \end{aligned} \tag{2.18}$$

where e_ρ (and similarly e_s and e_u) are functions of (ρ, e, \mathbf{u}) constructed as follows: first we differentiate e , considered as a function of (ρ, s, \mathbf{u}) with respect to ρ and then express the resulting function in terms of the state variables (ρ, e, \mathbf{u}) . If we insert (2.18) into (2.7) we obtain

$$\begin{aligned} \{A, B\} &= \int d\mathbf{r} \rho [\partial_\alpha(A_\rho)B_{u_\alpha} - \partial_\alpha(B_\rho)A_{u_\alpha}] + \int d\mathbf{r} u_\gamma [\partial_\alpha(A_{u_\gamma})B_{u_\alpha} - \partial_\alpha(B_{u_\gamma})A_{u_\alpha}] \\ &+ \int d\mathbf{r} \rho e_{u_\alpha} [\partial_\alpha(A_\rho)B_e - \partial_\alpha(B_\rho)A_e] + \int d\mathbf{r} u_\gamma e_{u_\alpha} [\partial_\alpha(A_{u_\gamma})B_e - \partial_\alpha(B_{u_\gamma})A_e] \\ &+ \int d\mathbf{r} s [\partial_\alpha(e_s A_e)B_{u_\alpha} - \partial_\alpha(e_s B_e)A_{u_\alpha}] + \int d\mathbf{r} (e_{u_\alpha}\rho e_\rho + e_{u_\alpha}u_\gamma e_{u_\gamma} + e_{u_\alpha}se_s) \\ &\times [\partial_\alpha(A_e)B_e - \partial_\alpha(B_e)A_e] + \int d\mathbf{r} \rho [\partial_\alpha(e_\rho A_e)B_{u_\alpha} - \partial_\alpha(e_\rho B_e)A_{u_\alpha}] \\ &+ \int d\mathbf{r} u_\gamma [\partial_\alpha(e_{u_\gamma} A_e)B_{u_\alpha} - \partial_\alpha(e_{u_\gamma} B_e)A_{u_\alpha}]. \end{aligned} \tag{2.19}$$

Equation (2.5) thus becomes (note that $E_e = 1$, $E_u \equiv 0$, $E_p \equiv 0$)

$$\begin{aligned} \frac{dA}{dt} = & \int \mathbf{dr} A_\rho [-\partial_\alpha(\rho e_{u_\alpha})] + \int \mathbf{dr} A_{u_\alpha} [-\partial_\gamma(u_\alpha e_{u_\gamma}) - s\partial_\alpha e_s - u_\gamma \partial_\alpha e_{u_\gamma} - \rho \partial_\alpha e_\rho] \\ & + \int \mathbf{dr} A_e [-\partial_\alpha(u_\gamma e_{u_\gamma} e_{u_\alpha}) - \partial_\alpha(\rho e_\rho e_{u_\alpha}) - \partial_\alpha(s e_s e_{u_\alpha})] \end{aligned} \quad (2.20)$$

which implies that

$$\frac{\partial \rho}{\partial t} = -\partial_\alpha(\rho e_{u_\alpha}) \quad (2.21a)$$

$$\frac{\partial u_\alpha}{\partial t} = -\partial_\gamma(u_\alpha e_{u_\gamma}) - s\partial_\alpha e_s - u_\gamma \partial_\alpha e_{u_\gamma} - \rho \partial_\alpha e_\rho \quad (2.21b)$$

$$\frac{\partial e}{\partial t} = -\partial_\alpha(u_\gamma e_{u_\gamma} e_{u_\alpha}) - \partial_\alpha(\rho e_\rho e_{u_\alpha}) - \partial_\alpha(s e_s e_{u_\alpha}). \quad (2.21c)$$

Equation (2.21a) is the same as (2.9a) and (2.10). Equation (2.21b) is equivalent to (2.13), (2.14) if (2.15) is used. Equation (2.20c) becomes, if (2.17) is used,

$$\frac{\partial e}{\partial t} = -\partial_\alpha(\dot{e}_\alpha) \quad (2.22)$$

where the energy flux \dot{e} is given by

$$\dot{e}_\alpha = (e + p)e_{u_\alpha}. \quad (2.23)$$

This is the equation governing the non-dissipative time evolution of the energy field of simple fluids. We have thus again, now in the energy representation, arrived at the result that the local equilibrium relation (2.17) guarantees the equivalence of the time evolution equations implied by the Hamiltonian structure (2.7) with the non-dissipative hydrodynamic equations of simple fluids. We note that the bracket (2.19) is again the Poisson bracket. This is because the brackets (2.7) and (2.19) are related by the one-to-one transformation (2.3). For the bracket (2.19), the entropy S is a Casimir (also called distinguished) functional. We say that a functional C is a Casimir functional for a bracket $\{ , \}$ if $\{A, C\} = 0$ holds for all functionals A (Marsden and Weinstein 1982). This property of the bracket (2.19) implies, in the energy representation, the non-dissipativity condition (2.2).

Now we turn our attention to the dissipative part of the time evolution of hydrodynamic fields ρ , e , \mathbf{u} . We want to add some terms to the right-hand side of (2.9) and (2.21) so that we shall preserve the conservation of the total mass, energy and momentum (i.e. we shall have $dM/dt = 0$, $dU/dt = 0$, $dE/dt = 0$ where $M = \int \mathbf{dr} \rho(\mathbf{r}, t)$ and $U_\alpha = \int \mathbf{dr} u_\alpha(\mathbf{r}, t)$) but the non-dissipative condition (2.2) will change into the dissipative condition

$$\frac{dS}{dt} \geq 0. \quad (2.24)$$

We shall first use the energy representation. Following Moreau (1970) and Edelen (1972) we begin by introducing first the so-called dissipative potential Φ . We say that

$\Phi: \mathbb{R}^n \rightarrow \mathbb{R}, (x_1, x_2, \dots, x_n) \rightarrow \Phi(x_1, \dots, x_n)$ is a dissipative potential if it satisfies the following properties:

$$\begin{aligned} (\Phi 1) \quad & \Phi(0, 0, \dots, 0) = 0 \\ (\Phi 2) \quad & \Phi \text{ reaches its minimum at } (0, 0, \dots, 0) \\ (\Phi 3) \quad & \Phi \text{ is convex in a neighbourhood of } (0, 0, \dots, 0). \end{aligned} \tag{2.25}$$

A straightforward consequence of the properties (2.25) is (Edelen 1972):

$$\varepsilon \stackrel{\text{def}}{=} x_i \Phi_{x_i} \geq 0. \tag{2.26}$$

For our purpose, we choose $\text{grad}(s_e)^{-1}$, $\text{Grad } \mathbf{v}$, $\text{div } \mathbf{v}$ as the independent variables x_1, \dots, x_n of the dissipative potential Φ . By Grad we denote a symmetric gradient, i.e. $(\text{Grad } \mathbf{v})_{\alpha\beta} = \frac{1}{2}(\partial v_\alpha / \partial r_\beta + \partial v_\beta / \partial r_\alpha)$. Now we modify (2.20) into

$$\frac{\partial \rho}{\partial t} = -\partial_\alpha (\rho e_{u_\alpha}) \tag{2.27a}$$

$$\frac{\partial u_\alpha}{\partial t} = -\partial_\gamma (u_\alpha e_{u_\gamma}) - s \partial e_s - u_\gamma \partial_\alpha e_{u_\gamma} - \rho \partial_\alpha e_\rho + \partial_\gamma \left(\frac{\delta \Phi}{\delta (\text{Grad } \mathbf{v})_{\alpha\gamma}} \right) + \partial_\alpha \left(\frac{\delta \Phi}{\delta (\text{div } \mathbf{v})} \right) \tag{2.27b}$$

$$\begin{aligned} \frac{\partial e}{\partial t} = & -\partial_\alpha (u_\gamma e_{u_\gamma} e_{u_\alpha}) - \partial_\alpha (\rho e_\rho e_{u_\alpha}) - \partial_\alpha (s e_s e_{u_\alpha}) + \partial_\gamma \left(v_\beta \frac{\delta \Phi}{\delta (\text{Grad } \mathbf{v})_{\gamma\beta}} \right) \\ & + \partial_\gamma \left(v_\gamma \frac{\delta \Phi}{\delta (\text{div } \mathbf{v})} \right) + \partial_\gamma \left(\frac{1}{s_e} \frac{\delta \Phi}{\delta (\text{grad}(s_e)^{-1})_\gamma} \right). \end{aligned} \tag{2.27c}$$

Equation (2.9b) governing the time evolution of the entropy density s now becomes

$$\frac{\partial s}{\partial t} = -\partial_\gamma \left(s e_{u_\gamma} - \frac{\delta \Phi}{\delta (\text{grad}(s_e)^{-1})_\gamma} \right) + s_e \varepsilon \tag{2.28}$$

where

$$\begin{aligned} \varepsilon(\mathbf{r}, t) = & (\text{grad}(s_e)^{-1})_\gamma \frac{\delta \Phi}{\delta (\text{grad}(s_e)^{-1})_\gamma} + \text{div } \mathbf{v} \frac{\delta \Phi}{\delta (\text{div } \mathbf{v})} \\ & + (\text{Grad } \mathbf{v})_{\alpha\gamma} \frac{\delta \Phi}{\delta (\text{Grad } \mathbf{v})_{\alpha\gamma}} \geq 0. \end{aligned} \tag{2.29}$$

The inequality (2.29) holds because the dissipative potential has been chosen to satisfy (2.26). By comparing (2.27b) with (2.13) we see that the momentum flux (2.14) has changed into

$$\dot{u}_{\alpha\beta} = u_\alpha v_\beta + p \delta_{\alpha\beta} + \sigma_{\alpha\beta}^{(\text{irr})} \tag{2.30}$$

where the irreversible extra stress tensor $\sigma^{(\text{irr})}$ is given by

$$\sigma_{\alpha\beta}^{(\text{irr})} = -\frac{\delta \Phi}{\delta (\text{Grad } \mathbf{v})_{\alpha\beta}} - \frac{\delta \Phi}{\delta (\text{div } \mathbf{v})} \delta_{\alpha\beta}. \tag{2.31}$$

By comparing (2.27c) with (2.22) we see that the energy flux (2.23) has changed into

$$\dot{e}_\alpha = (e + p) v_\alpha + \sigma_{\alpha\beta}^{(\text{irr})} v_\beta + q_\alpha^{(\text{irr})} \tag{2.32}$$

where the irreversible heat flux $q^{(\text{irr})}$ is given by

$$q_\alpha^{(\text{irr})} = -\frac{1}{s_e} \frac{\delta \Phi}{\delta (\text{grad}(s_e)^{-1})_\alpha}. \tag{2.33}$$

We note that in the particular case when Φ is chosen to be a quadratic potential, (2.27) become the Navier-Stokes-Fourier hydrodynamic equations. We end this section with two remarks.

Remark 2.1. Following Grmela (1984, 1986), Morrison (1984) and Kaufman (1984), we note that (2.27) can be formulated in the form (2.5) if we generalise the bracket $\{ , \}$ and the generating functional E . In order that (2.27) can be cast into the form

$$\frac{dA}{dt} = \langle A, G \rangle \tag{2.34}$$

we have to choose

$$\langle A, B \rangle = \{A, B\} + \{\{A, B\}\} \tag{2.35}$$

where $\{ , \}$ is the Poisson bracket (2.19):

$$\begin{aligned} \{\{A, B\}\} = & - \int d\mathbf{r} \left[(\text{Grad } A_u)_{\gamma\beta} \frac{\delta\Phi}{\delta(\text{Grad}(-B_u/B_e))_{\gamma\beta}} \right. \\ & + (\text{grad } A_e)_\gamma \left(-\frac{B_{u\beta}}{B_e} \frac{\delta\Phi}{\delta(\text{Grad}(-B_u/B_e))_{\gamma\beta}} \right) \\ & + \text{div } A_u \frac{\delta\Phi}{\delta(\text{div}(-B_u/B_e))} \\ & + (\text{grad } A_e)_\gamma \left(-\frac{B_{u\gamma}}{B_e} \frac{\delta\Phi}{\delta(\text{div}(-B_u/B_e))} \right) \\ & \left. + (\text{grad } A_e)_\gamma \left(\frac{1}{B_e} \frac{\delta\Phi}{\delta(\text{grad}(B_e)^{-1})_\gamma} \right) \right] \end{aligned} \tag{2.36}$$

and

$$G = E - k_B T_0 S \tag{2.37}$$

where k_B is the Boltzmann constant and T_0 is a constant equilibrium temperature. The equivalence of (2.34) and (2.27) can be directly verified. We note some properties of the bracket $\{\{ , \}\}$. First, we observe that $\{\{A, B\}\}$ depends linearly only on A_u, A_e, A_p . Its dependence on B_u, B_e, B_p is non-linear. Second, we note that the inequality (2.29) implies that

$$\{\{A, A\}\} \leq 0 \tag{2.38}$$

holds for all functionals A . Third, we note that E is the Casimir functional for the bracket $\{\{ , \}\}$ (i.e. $\{\{A, E\}\} = 0$ for all functionals A). We recall that S is the Casimir functional for the Poisson bracket $\{ , \}$. This degeneracy of the brackets $\{\{ , \}\}$ and $\{ , \}$ allows us to introduce a single generating functional G (see (2.37)) of the time evolution of simple fluids. Since E has the physical meaning of energy and S of entropy, the physical meaning of G introduced in (2.37) is a free energy. The states for which the functional G reaches its minimum are called equilibrium states. The functionals E, S and G evaluated at equilibrium states become the equilibrium energy, entropy and free energy. Equation (2.34) expresses the generalised Hamiltonian structure of simple fluids.

Remark 2.2. In § 1, we stated that the entropy inequality, the local equilibrium relation and the Onsager-Casimir symmetry are consequences of the generalised Hamiltonian

structure. So far, we have seen the entropy inequality (2.24) and the local equilibrium relation (2.17). It remains to introduce the Onsager-Casimir symmetry and to show that it is a consequence of the generalised Hamiltonian structure. Let us linearise (2.27) about an equilibrium state $(\rho_{eq}, e_{eq}, \mathbf{u}_{eq})$ defined in remark 2.1. Let us denote

$$\tilde{\rho} = \rho - \rho_{eq} \quad \tilde{e} = e - e_{eq} \quad \tilde{\mathbf{u}} = \mathbf{u} - \mathbf{u}_{eq}. \tag{2.39}$$

Equation (2.27) linearised about $(\rho_{eq}, e_{eq}, \mathbf{u}_{eq})$ becomes

$$\frac{\partial}{\partial t} \begin{pmatrix} \tilde{\rho} \\ \tilde{e} \\ \tilde{\mathbf{u}} \end{pmatrix} = P \begin{pmatrix} \tilde{\rho} \\ \tilde{e} \\ \tilde{\mathbf{u}} \end{pmatrix} \tag{2.40}$$

where P is a linear operator. It can be easily seen that the properties of the bracket \langle , \rangle introduced in (2.34) imply that P is a formally self-adjoint operator with respect to the indefinite inner product

$$(\cdot, \cdot)_{IG} \tag{2.41}$$

where \hat{G} is a Hessian matrix of the functional G evaluated at the equilibrium state $\rho_{eq}, e_{eq}, \mathbf{u}_{eq}$, I is the parity operator

$$(\tilde{\rho}, \tilde{e}, \tilde{\mathbf{u}}) \xrightarrow{I} (\tilde{\rho}, \tilde{e}, -\tilde{\mathbf{u}}) \tag{2.42}$$

and (\cdot, \cdot) is the L_2 inner product. The self-adjointness remains formal since we say nothing about the domain of the linear operator P . It has been shown (Grmela 1986 and references cited therein) that this property of the linearised time evolution equation is equivalent to the Onsager-Casimir reciprocity relations. We have suggested therefore calling the formal self-adjointness of the linearised vector field P an Onsager-Casimir symmetry. Any vector field obtained by linearising a generalised Hamiltonian vector field about an equilibrium state possesses the Onsager-Casimir symmetry.

3. Hamiltonian mechanics of complex fluids

In this section the analysis introduced in § 2 is extended to complex fluids. As we have mentioned already in § 1, experience shows that the time evolution equations involving only hydrodynamic fields are insufficient for describing the time evolution that agrees with the observed macroscopic behaviour (e.g. viscoelastic behaviour) of complex fluids. We recall that by a time evolution equation we mean in this paper always an equation that is local in time, i.e. an equation that does not involve integrals over the past time. The equations describing the time evolution of hydrodynamic fields have to be coupled to equations describing the time evolution of the internal structure.

The first question that has to be answered when dealing with complex fluids is how the internal structure will be described. In this paper we take inspiration from kinetic theory of polymeric fluids (Kirkwood 1967, Bird *et al* 1987, Doi and Edwards 1986) and choose the configuration space distribution function ψ as the quantity describing internal states; $\psi(\mathbf{r}, \mathbf{R}, t) d\mathbf{r} d\mathbf{R}$ is the probability of finding a molecule (or a suspended rod-like particle) at $(\mathbf{r}, \mathbf{r} + d\mathbf{r})$ with the end-to-end vector \mathbf{R} at $(\mathbf{R}, \mathbf{R} + d\mathbf{R})$ at time t . The complete set of state variables with which we shall describe states of complex fluids is thus $(\rho, e, \mathbf{u}, \psi)$. Everything introduced and derived in this section will reduce to the concepts and results introduced in § 2 if only the functionals that are independent of ψ are considered.

In the search for the equations that govern the time evolution of the state variables $\rho, e, \mathbf{u}, \psi$, we shall follow closely the presentation introduced in § 2. We begin with the non-dissipative time evolution. We shall assume that the non-dissipative time evolution equations possess the Hamiltonian structure. As a result, we obtain the non-dissipative time evolution equations for ψ , and similarly as in § 2, the scalar pressure, the extra stress tensor and the heat flux expressed in terms of the state variables and the entropy functional. Consideration, similar to those introduced in § 2, of the dissipative part of the time evolution then complete the results. The reader who wants to see only the results can proceed directly to § 4 where the main results are listed and discussed. The assumption that the equations governing the time evolution of $(\rho, e, \mathbf{u}, \psi)$ possess the same generalised Hamiltonian structure as the classical hydrodynamic equations governing the time evolution of (ρ, e, \mathbf{u}) is justified by the observation (see Grmela 1986, 1988b) that both the time evolution equations for (ρ, e, \mathbf{u}) and $(\rho, e, \mathbf{u}, \psi)$ have to be compatible with equilibrium thermodynamic experience and that it is the generalised Hamiltonian structure that guarantees this compatibility. An indirect justification of the assumption follows from the comparison of the consequences of the assumption (i.e. the constitutive relations) with the constitutive relations arising in the context of other types of considerations (see § 4).

We begin by introducing the entropy functional S , which is required to satisfy the following properties.

(S1)c The functional $-S$ is a convex functional of $(\rho, e, \mathbf{u}, \psi)$.

(S2)c We shall consider only functionals of the type

$$S = \int d\mathbf{r} s(\mathbf{r}, t) \quad (3.1)$$

where $s(\mathbf{r}, t)$ is a sufficiently regular function of $\rho(\mathbf{r}, t)$, $e(\mathbf{r}, t)$, $\psi(\mathbf{r}, \mathbf{R}, t)$, $\text{grad } \psi(\mathbf{r}, \mathbf{R}, t) \stackrel{\text{def}}{=} \partial/\partial \mathbf{r} \psi(\mathbf{r}, \mathbf{R}, t)$ pointwise for all \mathbf{r}, t . We allow for s to depend also on $\text{grad } \psi$ in order to introduce a setting in which we are able to consider equilibrium and dynamical aspects of spinodal-type decompositions that take place during isotropy-anisotropy transitions (see more about this in § 4).

(S3)c The non-dissipativity condition is again

$$\frac{dS}{dt} = 0. \quad (3.2)$$

(S4)c The transformation

$$(\rho, e, \mathbf{u}, \psi) \rightarrow (\rho, s, \mathbf{u}, \psi) \quad (3.3)$$

is one-to-one. We shall assume, moreover, in order to simplify some of the calculations arising later, that

$$\begin{aligned} s &= \hat{s}(\rho, e, \mathbf{u}, \psi) + \tilde{s}(\text{grad } \psi) \\ e &= \hat{e}(\rho, s, \mathbf{u}, \psi) + \tilde{e}(\text{grad } \psi). \end{aligned} \quad (3.4)$$

(S5)c The functional S evaluated at equilibrium states (defined similarly as in § 2—see remark 3.1) is the equilibrium thermodynamic entropy of the complex fluids under consideration. Some examples of polymeric fluids and the corresponding functionals S will be introduced in § 4.

As we have pointed out in § 1, the Hamiltonian structure is a property of the non-dissipative time evolution equations that is shared by many well established (i.e.

well tested against experimental results) time evolution equations on many levels of description (Grmela 1986, 1988b). We shall therefore assume that the equations governing the non-dissipative time evolution of $(\rho, s, \mathbf{u}, \psi)$ also possess the Hamiltonian structure and can be thus formulated in the form of (2.5). The generating functional will still be the total energy, the bracket will not, however, be the same as the bracket (2.7). The bracket involving the state variables (\mathbf{u}, ψ) has already been introduced in Grmela (1988a). By combining this bracket and the bracket (2.7) we arrive at

$$\begin{aligned} \{A, B\} = & \int d\mathbf{r} \rho [\partial_\alpha(A_\rho)B_{u_\alpha} - \partial_\alpha(B_\rho)A_{u_\alpha}] + \int d\mathbf{r} u_\gamma [\partial_\alpha(A_{u_\gamma})B_{u_\alpha} - \partial_\alpha(B_{u_\gamma})A_{u_\alpha}] \\ & + \int d\mathbf{r} s [\partial_\alpha(A_s)B_{u_\alpha} - \partial_\alpha(B_s)A_{u_\alpha}] \\ & + \int d\mathbf{r} \int d\mathbf{R} \psi \left[\partial_\alpha \left(\frac{\delta^{(\nu)}A}{\delta^{(\nu)}\psi} \right) B_{u_\alpha} - \partial_\alpha \left(\frac{\delta^{(\nu)}B}{\delta^{(\nu)}\psi} \right) A_{u_\alpha} \right] \\ & - \int d\mathbf{r} \int d\mathbf{R} \psi R_\beta \left[\partial_\beta(A_{u_\gamma}) \frac{\partial}{\partial R_\gamma} \left(\frac{\delta^{(\nu)}B}{\delta^{(\nu)}\psi} \right) - \partial_\beta(B_{u_\gamma}) \frac{\partial}{\partial R_\gamma} \left(\frac{\delta^{(\nu)}A}{\delta^{(\nu)}\psi} \right) \right]. \end{aligned} \quad (3.5)$$

The symbol $\delta^{(\nu)}A/\delta^{(\nu)}\psi$ denotes the variational derivative

$$\frac{\delta^{(\nu)}A}{\delta^{(\nu)}\psi} \stackrel{\text{def}}{=} A_\psi - \partial_\gamma A_{\partial_\gamma\psi}. \quad (3.6)$$

We now have to show that the bracket (3.5) is a Poisson bracket. The bracket (3.5) depends linearly on $A_\rho, A_s, A_u, A_\psi, B_\rho, B_s, B_u, B_\psi$ and $\{A, B\} = -\{B, A\}$. It thus remains to prove the Jacobi identity $\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0$. This can be done by a direct verification. In the calculations we can use the facts already known, as for example that if $\rho \equiv s \equiv 0$ or if only functionals that are independent of ψ are considered, then the Jacobi identity is satisfied, and the results proved in Morrison (1983). Alternatively, we can follow Holm and Kupercshmidt (1983) and use algebraic arguments. Similarly as we have transformed (2.5) into (2.8), we transform (3.5) into

$$\begin{aligned} \frac{dA}{dt} = & \int d\mathbf{r} A_\rho [-\partial_\alpha(\rho e_{u_\alpha})] + \int d\mathbf{r} A_s [-\partial_\alpha(s e_{u_\alpha})] \\ & + \int d\mathbf{r} A_{u_\alpha} \left[-\partial_\gamma(u_\alpha e_{u_\gamma}) - \rho \partial_\alpha e_\rho - u_\gamma \partial_\alpha e_{u_\gamma} - s \partial_\alpha e_s \right. \\ & - \left(\int d\mathbf{R} \left(-\psi \partial_\alpha e_\psi + \partial_\beta \left(\psi R_\beta \frac{\partial}{\partial R_\alpha} e_\psi \right) \right. \right. \\ & \left. \left. + \psi \partial_\alpha \partial_\gamma e_{\partial_\gamma\psi} - \partial_\beta \left(\psi R_\beta \frac{\partial}{\partial R_\alpha} \partial_\gamma e_{\partial_\gamma\psi} \right) \right) \right] \\ & + \int d\mathbf{r} \int d\mathbf{R} \frac{\delta^{(\nu)}A}{\delta^{(\nu)}\psi} \left[-\partial_\alpha(\psi e_{u_\alpha}) - \frac{\partial}{\partial R_\gamma} (\psi R_\beta \partial_\beta e_{u_\gamma}) \right] \end{aligned} \quad (3.7)$$

which implies

$$\frac{\partial \rho}{\partial t} = -\partial_\alpha(\rho e_{u_\alpha}) \quad (3.8a)$$

$$\frac{\partial s}{\partial t} = -\partial_\alpha(s e_{u_\alpha}) \quad (3.8b)$$

$$\frac{\partial u_\alpha}{\partial t} = -\partial_\gamma(u_\alpha e_{u_\gamma}) - \rho \partial_\alpha e_\rho - u_\gamma \partial_\alpha e_{u_\gamma} - s \partial_\alpha e_s + \int d\mathbf{R} \left(-\psi \partial_\alpha e_\psi + \psi \partial_\alpha \partial_\gamma e_{\partial_\gamma \psi} - \partial_\beta \left(\psi R_\beta \frac{\partial}{\partial R_\alpha} \partial_\gamma e_{\partial_\gamma \psi} \right) \right) \tag{3.8c}$$

$$\frac{\partial \psi}{\partial t} = -\partial_\alpha(\psi e_{u_\alpha}) - \frac{\partial}{\partial R_\gamma} (\psi R_\beta \partial_\beta e_{u_\gamma}). \tag{3.8d}$$

The sixth term on the right-hand side of (3.8c) will be rewritten as

$$\psi \partial_\alpha \partial_\gamma e_{\partial_\gamma \psi} = \partial_\alpha (\tilde{e} + \psi \partial_\gamma e_{\partial_\gamma \psi}) - \partial_\gamma (\partial_\alpha \psi e_{\partial_\gamma \psi}). \tag{3.9}$$

We have used the form of the energy functional introduced in (3.4). Equation (3.8c) can now be written in the form of (3.13) with

$$\hat{u}_{\alpha\gamma} = u_\alpha e_{u_\gamma} + p \delta_{\alpha\gamma} + \sigma_{\alpha\gamma}. \tag{3.10}$$

The extra stress tensor σ is

$$\sigma_{\alpha\beta} = - \int d\mathbf{R} \psi R_\beta \frac{\partial}{\partial R_\alpha} e_\psi + \int d\mathbf{R} \psi R_\beta \frac{\partial}{\partial R_\alpha} \partial_\gamma e_{\partial_\gamma \psi} + \int d\mathbf{R} \partial_\alpha \psi e_{\partial_\beta \psi} \tag{3.11}$$

and the scalar pressure p satisfies

$$\partial_\alpha p + \partial_\alpha \left(\tilde{e} + \int d\mathbf{R} \psi \partial_\gamma e_{\partial_\gamma \psi} \right) = \rho \partial_\alpha e_\rho + u_\gamma \partial_\alpha e_{u_\gamma} + s \partial_\alpha e_s + \int d\mathbf{R} \psi \partial_\alpha e_\psi. \tag{3.12}$$

Equation (3.12) together with

$$\partial_\alpha e = \partial_\alpha \tilde{e} + e_\rho \partial_\alpha \rho + e_{u_\rho} \partial_\alpha u_\rho + e_s \partial_\alpha s + \int d\mathbf{R} e_\psi \partial_\alpha \psi \tag{3.13}$$

implies

$$p = -e + s e_s + \rho e_\rho + u_\gamma e_{u_\gamma} + \int d\mathbf{R} \psi (e_\psi - \partial_\gamma e_{\partial_\gamma \psi}). \tag{3.14}$$

We note that in the context of complex fluids, the momentum flux \hat{u} in the non-dissipative time evolution equations involves the extra stress tensor σ . The local equilibrium relation (see (2.17) in the context of simple fluids) also changes (see (3.14)). We shall discuss (3.11) and (3.14) in more detail in § 4. Equation (3.8d) expresses the free advection of the vector \mathbf{R} by the flow. We shall see in § 4 that this is indeed the equation describing the non-dissipative time evolution of ψ that arises in kinetic theory.

Following § 2, we shall reformulate (3.5)–(3.8) into the energy representation. By applying the transformation (3.3) we have

$$\begin{aligned} \frac{\delta}{\delta \rho} &\rightarrow \frac{\delta}{\delta \rho} + e_\rho \frac{\delta}{\delta e} \\ \frac{\delta}{\delta s} &\rightarrow e_s \frac{\delta}{\delta e} \\ \frac{\delta}{\delta u_\alpha} &\rightarrow \frac{\delta}{\delta u_\alpha} + e_{u_\alpha} \frac{\delta}{\delta e} \\ \frac{\delta^{(v)}}{\delta^{(v)} \psi} &\rightarrow \frac{\delta^{(v)}}{\delta^{(v)} \psi} + e_\psi \frac{\delta}{\delta e} - \partial_\gamma \left(e_{\partial_\gamma \psi} \frac{\delta}{\delta e} \right). \end{aligned} \tag{3.15}$$

For the meaning of e_ρ etc, see the text following (2.18). By inserting (3.15) into (3.5) we have

$$\begin{aligned}
 \{A, B\} = & \int d\mathbf{r} \rho [\partial_\alpha (A_\rho) B_{u_\alpha} - \partial_\alpha (B_\rho) A_{u_\alpha}] + \int d\mathbf{r} u_\gamma [\partial_\alpha (A_{u_\gamma}) B_{u_\alpha} - \partial_\alpha (B_{u_\gamma}) A_{u_\alpha}] \\
 & + \int d\mathbf{r} \rho e_{u_\alpha} [\partial_\alpha (A_\rho) B_e - \partial_\alpha (B_\rho) A_e] \\
 & + \int d\mathbf{r} \left[e_{u_\alpha} (\rho e_\rho + u_\gamma e_{u_\gamma} + s e_s) + \int d\mathbf{R} \left(e_{u_\alpha} \psi e_\psi - e_{u_\alpha} \psi \partial_\gamma e_{\partial_\gamma \psi} \right. \right. \\
 & \left. \left. - \psi e_{u_\gamma} \partial_\gamma e_{\partial_\alpha \psi} - \psi R_\alpha e_{u_\gamma} \frac{\partial}{\partial R_\gamma} e_\psi + \psi R_\alpha e_{u_\beta} \frac{\partial}{\partial R_\beta} \partial_\gamma e_{\partial_\gamma \psi} \right. \right. \\
 & \left. \left. - \psi R_\beta \partial_\beta (e_{u_\gamma}) \frac{\partial}{\partial R_\gamma} (e_{\partial_\alpha \psi}) \right) \right] [\partial_\alpha (A_e) B_e - \partial_\alpha (B_e) A_e] \\
 & - \int d\mathbf{r} \int d\mathbf{R} \psi R_\beta e_{u_\alpha} e_\psi \left[\partial_\beta (A_e) \frac{\partial}{\partial R_\alpha} (B_e) - \partial_\beta (B_e) \frac{\partial}{\partial R_\alpha} (A_e) \right] \\
 & - \int d\mathbf{r} \int d\mathbf{R} \psi e_{u_\alpha} e_{\partial_\gamma \psi} [\partial_\alpha \partial_\gamma (A_e) B_e - \partial_\alpha \partial_\gamma (B_e) A_e] \\
 & + \int d\mathbf{r} \int d\mathbf{R} \psi R_\beta e_{u_\alpha} \frac{\partial}{\partial R_\alpha} (e_{\partial_\gamma \psi}) [\partial_\beta (A_e) \partial_\gamma (B_e) - \partial_\beta (B_e) \partial_\gamma (A_e)] \\
 & + \int d\mathbf{r} \int d\mathbf{R} \psi \left[\partial_\alpha \left(\frac{\delta^{(\nu)} A}{\delta^{(\nu)} \psi} \right) B_{u_\alpha} - \partial_\alpha \left(\frac{\delta^{(\nu)} B}{\delta^{(\nu)} \psi} \right) A_{u_\alpha} \right] \\
 & - \int d\mathbf{r} \int d\mathbf{R} \psi R_\beta \left[\partial_\beta (A_{u_\alpha}) \frac{\partial}{\partial R_\alpha} \left(\frac{\delta^{(\nu)} B}{\delta^{(\nu)} \psi} \right) - \partial_\beta (B_{u_\alpha}) \frac{\partial}{\partial R_\alpha} \left(\frac{\delta^{(\nu)} A}{\delta^{(\nu)} \psi} \right) \right] \\
 & + \int d\mathbf{r} u_\gamma e_{u_\alpha} [\partial_\alpha (A_{u_\gamma}) B_e - \partial_\alpha (B_{u_\gamma}) A_e] \\
 & + \int d\mathbf{r} s [\partial_\alpha (e_s A_e) B_{u_\alpha} - \partial_\alpha (e_s B_e) A_{u_\alpha}] \\
 & + \int d\mathbf{r} \rho [\partial_\alpha (e_{u_\gamma} A_e) B_{u_\alpha} - \partial_\alpha (e_{u_\gamma} B_e) A_{u_\alpha}] \\
 & + \int d\mathbf{r} \int d\mathbf{R} \psi [\partial_\alpha (e_\psi A_e) B_{u_\alpha} - \partial_\alpha (e_\psi B_e) A_{u_\alpha}] \\
 & + \int d\mathbf{r} u_\gamma [\partial_\alpha (e_{u_\gamma} A_e) B_{u_\alpha} - \partial_\alpha (e_{u_\gamma} B_e) A_{u_\alpha}] \\
 & - \int d\mathbf{r} \int d\mathbf{R} \psi [\partial_\alpha \partial_\gamma (e_{\partial_\gamma \psi} A_e) B_{u_\alpha} - \partial_\alpha \partial_\gamma (e_{\partial_\gamma \psi} B_e) A_{u_\alpha}] \\
 & - \int d\mathbf{r} \int d\mathbf{R} \psi R_\beta \left[\partial_\beta (A_{u_\alpha}) \frac{\partial}{\partial R_\alpha} (e_\psi B_e) - \partial_\beta (B_{u_\alpha}) \frac{\partial}{\partial R_\alpha} (e_\psi A_e) \right] \\
 & + \int d\mathbf{r} \int d\mathbf{R} \psi R_\beta \left[\partial_\beta (A_{u_\alpha}) \frac{\partial}{\partial R_\alpha} \partial_\gamma (e_{\partial_\gamma \psi} B_e) \right. \\
 & \left. - \partial_\beta (B_{u_\alpha}) \frac{\partial}{\partial R_\alpha} \partial_\gamma (e_{\partial_\gamma \psi} A_e) \right]. \tag{3.16}
 \end{aligned}$$

Equation (2.5) then yields (we use $E_e \equiv 1$, $E_u \equiv E_p \equiv E_\psi \equiv 0$, (3.14), (3.11))

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= -\partial_\gamma(\rho e_{u_\gamma}) \\ \frac{\partial u_\alpha}{\partial t} &= -\partial_\gamma(u_\alpha e_{u_\gamma} + p \delta_{\alpha\gamma}) \\ \frac{\partial e}{\partial t} &= -\partial_\gamma((e + p)e_{u_\alpha} + \sigma_{\gamma\beta} e_{u_\beta}) - \partial_\gamma q_\gamma \\ \frac{\partial \psi}{\partial t} &= -\partial_\alpha(\psi e_{u_\alpha}) - \frac{\partial}{\partial R_\gamma}(\psi R_\beta \partial_\beta e_{u_\gamma}) \end{aligned} \tag{3.17}$$

where

$$q_\alpha = \int d\mathbf{R} \left(\psi \partial_\gamma(e_{u_\gamma}) e_{\partial_\alpha \psi} - \psi \partial_\beta(e_{u_\gamma}) R_\beta \frac{\partial}{\partial R_\gamma}(e_{\partial_\gamma \psi}) \right). \tag{3.18}$$

The physical interpretation of (3.17) and (3.18) will be discussed in § 4. Now we turn our attention to the irreversible part of the time evolution equations.

As in § 2, our objective is to add to the right-hand side of (3.17) some terms so that the conservation of the total mass, momentum and energy is preserved and the non-dissipativity condition (3.2) changes into the dissipativity condition (2.24). Following the method used in § 2, we introduce first the dissipative potential Φ (see the text after (2.24)). The independent variables of Φ are now $\text{grad}(s_e)^{-1}$, $\text{Grad } \mathbf{v}$, $\text{div } \mathbf{v}$, $(1/s_e)(\partial/\partial \mathbf{R}(s_\psi - \partial_\gamma s_{\partial_\gamma \psi}))$ so that

$$\begin{aligned} \varepsilon(\mathbf{r}, t) &= (\text{grad}(s_e)^{-1})_\gamma \frac{\delta \Phi}{\delta (\text{grad}(s_e)^{-1})_\gamma} + \text{div } \mathbf{v} \frac{\delta \Phi}{\delta (\text{div } \mathbf{v})} \\ &+ (\text{Grad } \mathbf{v})_{\alpha\gamma} \frac{\delta \Phi}{\delta (\text{Grad } \mathbf{v})_{\alpha\beta}} + \frac{1}{s_e} \frac{\partial}{\partial R_\alpha}(s_\psi - \partial_\gamma s_{\partial_\gamma \psi}) \\ &\times \frac{\delta \Phi}{\delta ((1/s_e)(\partial/\partial R_\alpha)(s_\psi - \partial_\gamma s_{\partial_\gamma \psi}))} \geq 0. \end{aligned} \tag{3.19}$$

Equation (3.17) becomes

$$\frac{\partial \rho}{\partial t} = -\partial_\gamma(\rho e_{u_\gamma}) \tag{3.20a}$$

$$\frac{\partial u_\alpha}{\partial t} = -\partial_\gamma(u_\alpha e_{u_\gamma} + p \delta_{\alpha\gamma}) - \partial_\gamma \sigma_{\alpha\gamma} + \partial_\gamma \left(\frac{\delta \Phi}{\delta (\text{Grad } \mathbf{v})_{\alpha\gamma}} \right) + \partial_\alpha \left(\frac{\delta \Phi}{\delta (\text{div } \mathbf{v})} \right). \tag{3.20b}$$

$$\begin{aligned} \frac{\partial e}{\partial t} &= -\partial_\gamma((e + p)e_{u_\alpha} + \sigma_{\gamma\beta} e_{u_\beta}) - \partial_\gamma q_\gamma + \partial_\gamma \left(v_\beta \frac{\delta \Phi}{\delta (\text{Grad } \mathbf{v})_{\gamma\beta}} \right) \\ &+ \partial_\gamma \left(v_\gamma \frac{\delta \Phi}{\delta (\text{div } \mathbf{v})} \right) + \partial_\gamma \left(\frac{1}{s_e} \frac{\delta \Phi}{\delta (\text{grad}(s_e)^{-1})_\gamma} \right) \end{aligned} \tag{3.20c}$$

$$\frac{\partial \psi}{\partial t} = -\partial_\alpha(\psi e_{u_\alpha}) - \frac{\partial}{\partial R_\gamma}(\psi R_\beta \partial_\beta e_{u_\gamma}) - \frac{\partial}{\partial R_\alpha} \left(\frac{\delta \Phi}{\delta ((1/s_e)(\partial/\partial R_\alpha)(s_\psi - \partial_\gamma s_{\partial_\gamma \psi}))} \right). \tag{3.20d}$$

The quantities p , σ and q appearing in (3.20) are given by (3.14), (3.11) and (3.18). By comparing (3.20*b*) with (2.13), we find that the momentum flux $\hat{\mathbf{u}}$ is

$$\hat{u}_{\alpha\beta} = u_\alpha e_{u_\beta} + p\delta_{\alpha\beta} + \sigma_{\alpha\beta} + \sigma_{\alpha\beta}^{(irr)} \tag{3.21}$$

where the scalar pressure p is given by (3.14), the reversible extra stress tensor σ is given by (3.11) and the irreversible extra stress tensor $\sigma^{(irr)}$ is given by

$$\sigma_{\alpha\beta}^{(irr)} = -\frac{\delta\Phi}{\delta(\text{Grad } \mathbf{v})_{\alpha\beta}} - \frac{\delta\Phi}{\delta(\text{div } \mathbf{v})} \delta_{\alpha\beta}. \tag{3.22}$$

Similarly, by comparing (3.20*c*) with (2.22) we obtain the energy flux

$$\hat{e}_\alpha = (e + p)v_\alpha + \sigma_{\alpha\beta}v_\beta + \sigma_{\alpha\beta}^{(irr)}v_\beta + q_\alpha + q_\alpha^{(irr)} \tag{3.23}$$

where p , σ , $\sigma^{(irr)}$, q are given by (3.14), (3.11), (3.22), (3.18) and the irreversible heat flux $q^{(irr)}$ is given by

$$q_\alpha^{(irr)} = -\frac{1}{s_e} \frac{\delta\Phi}{\delta(\text{grad}(s_e)^{-1})_\alpha}. \tag{3.24}$$

The time evolution of the entropy density $s(\mathbf{r}, t)$ is governed by (2.28) with ε given by (3.19).

Remarks 2.1 and 2.2 made in § 2 can be easily adapted to the setting introduced in this section. The time evolution (3.20) can again be cast into the form (2.34) with the bracket $\{ , \}$ given by (3.16) and $\{ \{ , \} \}$ given by (3.16) with one additional term

$$+ \int d\mathbf{r} \int d\mathbf{R} \frac{\partial}{\partial R_\alpha} (A_\psi - \partial_\gamma A_{\partial_\gamma\psi}) \frac{\delta\Phi}{\delta((1/B_e)(\partial/\partial R_\alpha)(B_\psi - \partial_\gamma B_{\partial_\gamma\psi}))}. \tag{3.25}$$

If we linearise (3.20) about an equilibrium state $(\rho_{eq}, \mathbf{u}_{eq}, e_{eq}, \psi_{eq})$ (defined again as a state at which the generating functional G given by (2.37) reaches its minimum), we obtain

$$\frac{\partial}{\partial t} \begin{pmatrix} \tilde{\rho} \\ \tilde{e} \\ \tilde{\mathbf{u}} \\ \tilde{\psi} \end{pmatrix} = P \begin{pmatrix} \tilde{\rho} \\ \tilde{e} \\ \tilde{\mathbf{u}} \\ \tilde{\psi} \end{pmatrix} \tag{3.26}$$

where $\tilde{\rho}$, \tilde{e} , $\tilde{\mathbf{u}}$ are given by (2.29) and $\tilde{\psi} = \psi - \psi_{eq}$. Properties of the brackets $\{ , \}$ and $\{ \{ , \} \}$ imply again that the linear operator P is formally self-adjoint with respect to the indefinite inner product (2.41) with the parity operator I given by

$$(\tilde{\rho}, \tilde{e}, \tilde{\mathbf{u}}, \tilde{\psi}) \xrightarrow{I} (\tilde{\rho}, \tilde{e}, -\tilde{\mathbf{u}}, \tilde{\psi}). \tag{3.27}$$

4. Discussion

The main results of this paper are: (i) equation (3.20*d*) governing the time evolution of the configuration space distribution function ψ , (ii) the local equilibrium relation (3.14), (iii) the expressions (3.11) and (3.22) for the extra stress tensor, and (iv) the

expressions (3.18) and (3.24) for the heat flux. In this section, we shall compare these results with results derived previously in kinetic theory. A direct comparison with experimental results is not considered in this paper.

First, we compare the starting position taken in this paper with the starting position taken in kinetic theory. The assumption from which the results of this paper have been derived is that the time evolution equations of complex fluids possess a generalised Hamiltonian structure. Three types of argument have been advanced to justify this assumption. First, we have shown in § 2 that the ordinary hydrodynamic equations of simple fluids possess the generalised Hamiltonian structure. We have also seen in § 2 that the generalised Hamiltonian structure implies the entropy inequality, the local equilibrium relation and the Onsager-Casimir symmetry. These three properties of the time evolution equations of simple fluids have also been derived in other approaches to modelling of simple fluids (see, e.g., de Groot and Maxur 1969). Second, we have observed that the generalised Hamiltonian structure is also a structure of many other well established (i.e. well tested against experimental results) dynamical theories on many different levels of description. Third, the properties of solutions of the time evolution equations that are implied by the generalised Hamiltonian structure have been interpreted as an expression of the compatibility of a dynamical theory with equilibrium thermodynamics. In other words, the generalised Hamiltonian structure guarantees agreement of solutions of the time evolution equations with the observations on which equilibrium thermodynamics is based. Particularly well explored is the link between the Hamiltonian structure and the stability of certain stationary solutions (Arnold 1965, Holm *et al* 1985, 1986). Summing up, the results obtained in this paper arise from an attempt to formulate the time evolution equations whose consequences agree with results of observations. The focus has been put on the consequences that can be compared with the experience on which equilibrium thermodynamics is based. Now, we recall the starting position taken in kinetic theory. The foundation for kinetic theory is provided by quantum or classical mechanics of molecules composing the fluids under consideration. The macroscopic properties are searched as patterns in the set of molecular trajectories obtained by solving the dynamical equations of classical or quantum mechanics. The difficulties arise in: (i) associating the actual conditions under which the fluids are observed with initial and boundary conditions needed to solve the molecular dynamics; (ii) finding the trajectories (i.e. solving the equations governing the time evolution of the molecules); and (iii) identifying the patterns in the set of the trajectories expressing the macroscopic properties that are observed in hydrodynamic measurements. To overcome these difficulties, many unjustified or partially justified assumptions are usually introduced. The starting position of kinetic theory is thus classical or quantum mechanics and the assumptions introduced in the passage from the molecular description to the hydrodynamic description. The approach used in this paper (we shall call it a phenomenological approach) and the kinetic theory approach should be regarded as complementary. The phenomenological approach helps in the passage from the molecular to the hydrodynamic description; kinetic theory can be used on the other hand to specify the phenomenological quantities introduced in the phenomenological approach. For example, the generating functional G (see (2.37)) corresponding to the fluid under consideration can be suggested by using the Gibbs equilibrium statistical mechanics.

Now we shall discuss each of the main results of this paper separately. We begin with the configuration space kinetic equation (3.20*d*). We observe that its non-dissipative part (equation (3.8*d*)) is a Liouville (Liouville 1838) equation corresponding

to

$$\dot{r}_\alpha = v_\alpha \quad \dot{R}_\alpha = \frac{\partial v_\alpha}{\partial r_\beta} R_\beta. \quad (4.1)$$

These equations describe the time evolution of a macromolecule advected by the flow. Following the kinetic theory arguments, (3.8*d*) can thus be readily derived (Kirkwood 1967, Bird *et al* 1987). The phenomenological and kinetic theory arguments lead thus to identical non-dissipative configuration space kinetic equations. Next, we turn our attention to the dissipative (also called diffusion) part of the kinetic equation. This part arises in kinetic theory from a consideration of the effect of the Brownian motion and the Stokes drag forces on the motion of macromolecules. Kirkwood (1967) has considered inflexible macromolecules and arrived in this way to

$$-\frac{\partial}{\partial R_\alpha} \left(D \frac{\partial}{\partial R_\alpha} \psi \right) \quad (4.2)$$

where D is the diffusion coefficient that can depend on the configuration space distribution function ψ . It can easily be verified that (4.2) can be cast into the form of the third term on the right-hand side of (3.20*d*) if Φ is chosen to be quadratic and

$$s(\mathbf{r}, t) = - \int d\mathbf{R} \psi(\mathbf{r}, \mathbf{R}, t) \ln \psi(\mathbf{r}, \mathbf{R}, t). \quad (4.3)$$

In (4.3) we recognise the Boltzmann (Boltzmann 1968) expression for entropy. We see thus that in the particular case of polymeric fluids composed of inflexible macromolecules both the kinetic and the phenomenological approaches lead to the same dissipative part in the kinetic equation. The usefulness of the formulation of the dissipative term that appears in (3.20*d*) will be illustrated on the following example. Let the macromolecules composing the polymeric fluid under consideration be flexible, and not inflexible as assumed by Kirkwood (1967). Then, by following the kinetic theory approach, we first have to find how the change in the flexibility changes the Brownian motion and the Stokes drag forces. This turns out to be a difficult problem. By following the phenomenological approach, we look instead at the problem of how the change in flexibility influences the entropy functional. This problem has been considered, by using Gibbs equilibrium statistical mechanics, by Lifschitz (1968) and Khokhlov and Semenov (1985). Once we know the entropy functional, we can readily write the dissipative term by using the formulation appearing in (3.20*d*) (Grmela and Chhon Ly 1987). The phenomenological approach thus allows one to replace the difficult problem of specifying the Brownian motion of flexible macromolecules by a simpler problem of specifying the entropy functional for the flexible macromolecules.

The entropy functionals that have been considered in this paper depend not only on the configuration distribution function ψ but also on its derivatives with respect to the position coordinate \mathbf{r} . We shall explain now the reason why we have considered this general case. We recall that the configuration space distribution function ψ characterises the internal (molecular) structure of the fluids under consideration. Let, for example, the polymeric fluid under consideration be a polymeric liquid crystal (e.g. Ciferri 1982). It has been established experimentally (e.g. Onogi and Asada 1980) that the spatial inhomogeneities of the macromolecular structure play an important role in determining the equilibrium and hydrodynamic properties of polymeric liquid crystals. In particular, it has been observed that the inhomogeneities of the internal structure arise spontaneously during the isotropy-anisotropy phase transitions. This effect is

analogous to the spinodal decomposition observed in the liquid–solid phase transitions. In order to be able to model these phenomena, the free energy functional (in other words, the generating functional) has to depend on spatial gradients of the chosen internal state variable. This has already been established by Cahn (1961) in the context of the liquid–solid phase transitions in simple fluids (in this case the internal state variable is chosen to be the field of the mass density). Entropy functionals that depend non-locally on the configuration space distribution function ψ have been introduced by Priest (1973) and Straley (1973).

The second main result of this paper that we shall compare with results obtained in kinetic theory and in other approaches is the local equilibrium relation (3.14). We note that if e is independent of ψ and $\text{grad } \psi$ then this relation reduces to the familiar local equilibrium relation (2.17). This means that the relation (3.14) can be regarded as an extension of the local equilibrium relation (2.17) to complex fluids. The physical picture that is behind the local equilibrium relation (2.17) is that the fluid under consideration is locally at equilibrium and that the scalar pressure appearing in the hydrodynamic equations is the corresponding local equilibrium pressure. To the best of our knowledge, this picture cannot be directly extended to complex fluids. Neither has kinetic theory been able to provide an extension of the local equilibrium relation.

The third main result of this paper is the expressions (3.11) and (3.22) for the extra stress tensor σ . We note first that if Φ is a quadratic potential then (3.22) is the usual Navier–Stokes extra stress tensor. The first term on the right hand side of (3.11) is the well known Kramers (1944) stress derived by using the arguments of kinetic theory. The third term on the right-hand side of (3.11) is essentially the extra stress tensor introduced in the context of liquid crystals by Ericksen (1960). Ericksen’s analysis differs from ours in two respects. First, Ericksen uses a different internal state variable to ours; second, his arguments are based on completely different considerations than we use. The internal state variable chosen by Ericksen is a vector field $\mathbf{n}(\mathbf{r}, t)$ that can be related to the distribution function $\psi(\mathbf{r}, \mathbf{R}, t)$ by

$$\mathbf{n}(\mathbf{r}, t) = \frac{\int d\mathbf{R} \mathbf{R} \psi(\mathbf{r}, \mathbf{R}, t)}{|\int d\mathbf{R} \mathbf{R} \psi(\mathbf{r}, \mathbf{R}, t)|}. \quad (4.4)$$

One important advantage of choosing the configuration space distribution function ψ instead of the vector field \mathbf{n} is that with \mathbf{n} we cannot model the isotropy–anisotropy phase transitions. The fluid has to be already anisotropic if the vector field \mathbf{n} is chosen to describe its internal structure. If we would choose $\mathbf{n}(\mathbf{r}, t)$ instead of $\psi(\mathbf{r}, \mathbf{R}, t)$ and follow the phenomenological approach introduced in this paper then the term that would correspond to the third term on the right-hand side of (3.11) would be exactly the term derived by Ericksen (see Grmela 1989, where this analysis is done for incompressible and isothermal fluids). The second term on the right-hand side of (3.11) is a new term that has not been noticed before on any level of description. Summing up we note that $\sigma^{(\text{irr})}$ is a standard irreversible extra stress tensor, the first term on the right-hand side of (3.11) can be derived by using the kinetic theory arguments, the third term is an extension of the Ericksen stress to the configuration space kinetic theory setting (to the best of our knowledge, no kinetic theory derivation of this stress has appeared before) and the second term on the right-hand side of (3.11) is completely new even if considered in the setting used by Ericksen.

Finally, we shall comment on the heat flux (3.18) and (3.24). The irreversible heat flux $q^{(\text{irr})}$ given by (3.24) is (if Φ is chosen to be a quadratic potential) the usual Fourier heat flux. The reversible heat flux (3.18) is a new result that we cannot relate to any

other result derived previously in kinetic theory or other approaches. We note that this reversible heat flux is different from zero only if the free energy depends on the derivatives of the configuration space distribution function with respect to the position coordinate. The justification of the reversible heat flux (3.18) thus rests solely on the intrinsic consistency of the analysis presented in this paper. All results, including those that can be derived by using some other independent arguments, have been derived from the generalised Hamiltonian structure of the time evolution equations. An experimental evidence for a non-Fourier heat transfer and a non-Fickian mass transfer in spatially inhomogeneous polymeric fluids has been mentioned by Ocone and Astarita (1987) and Thomas and Windle (1982).

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