# SECONDARY EFFECTS IN IRREVERSIBLE THERMODYNAMICS

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## ABSTRACT

Linear phenomenological relations are recast to include relaxation effects. The relations are then written in a form suitable for general motion of the system and transformed to a coordinate system which is stationary relative to the observer. Generally, secondary fluxes are then observed which would be important in the fields of heat and mass transfer, for example. The Onsager relations are interpreted as reciprocal relations between the distribution functions of relaxation times. The principles on which these developments are based are that the thermodynamic properties of elements of a material are independent of the properties of neighbouring elements and also of the motion of the element in space, but may depend upon the thermodynamic history of the element.

## 1. INTRODUCTION

Many processes occur in which a specific physical quantity is transported through a sequence of non-equilibrium states of the system. Such transport processes are of a thermodynamically irreversible nature which is characterized by an irreducible increase in entropy.

The simpler aspects of these irreversible processes are usually treated on the macroscopic scale by *linear phenomenological laws* of which there are many, such as Newton's viscous law relating deformation stress with deformation strain rate in fluids, Fick's law relating flowrate of matter in a mixture with the concentration gradient of that matter, and Fourier's law relating heat energy flowrate with temperature gradient. Where one or more of these phenomena occur simultaneously then coupling occurs and important new phenomena are established such as the coupling between heat conduction and diffusion which gives rise to thermal diffusion.

In the subject of irreversible thermodynamics physical quantities such as temperature gradients and concentration gradients are termed 'forces' and the associated effects such as heat energy and mass flowrate are termed 'fluxes'. The product of 'forces' and 'fluxes' gives the entropy production rate or 'entropy source strength'. The identification of process source strengths and therefore the evolution of a system is the central theme of the subject of irreversible thermodynamics. In a published account de Groot[1] has outlined and interpreted many of the main features of the subject and its applications.

In the following work the theory is formulated in a convected coordinate framework which leads to important new results.

## 2. THE ONSAGER RELATIONS

In summarizing the previous comments on phenomenological laws it may be stated that the forces are linearly related to the fluxes and allowing for coupling, any force may, generally speaking, stimulate a response in any of the possible fluxes. This statement may be compactly represented by

$$J_\alpha = L_{\alpha\beta} X_\beta \quad (\alpha, \beta = 1, 2, 3, \ldots) \tag{1}$$

where summation over the repeated suffix is implied.

In equation 1 the $L_{\alpha\beta}$ are the phenomenological coefficients and those in which $\alpha = \beta$ are the direct coefficients whilst for $\alpha \neq \beta$ coupled or interference effects occur.

The important Onsager relations state that the *phenomenological coefficients are symmetrical,*

$$L_{\alpha\beta} = L_{\beta\alpha} \tag{2}$$

The proof of these relations is treated by de Groot[1] on the basis of statistical mechanics, microscopic reversibility and regression of fluctuations.

The hypothesis introduced by Onsager into the third part of the proof of the relations 2 is that on the average the decay of a fluctuation of the thermodynamic parameters of a system follows the ordinary linear macroscopic laws. Suppose that the *deviations* of the thermodynamic parameters have the values $a_\gamma(\gamma = 1, 2, 3, \ldots)$ then equation 1 may be written

$$J_\alpha = \bar{\dot{a}}_\alpha = L_{\alpha\beta} X_\beta \tag{3}$$

where the bar over $\dot{a}_\alpha$ denotes time averaged over *microscopic* fluctuations.

The hypothesis then implies that the time scale of the process $\Gamma_p$ is related to the time scale of fluctuation $\Gamma_f$ and the molecular time scale $\Gamma_m$ by the inequalities

$$\Gamma_m \ll \Gamma_p \ll \Gamma_f \tag{4}$$

where

$$\Gamma_{\gamma p} = \mathrm{O}\left(\frac{\bar{a}\gamma}{\bar{\dot{a}}\gamma}\right) \tag{5}$$

and

$$\Gamma_{\gamma f} = \mathrm{O}\left(\frac{\bar{\dot{a}}\gamma}{\bar{\ddot{a}}\gamma}\right) \tag{6}$$

Provided phase-shifting between the forces and fluxes does not impeach any of the fundamentals of irreversible thermodynamics, and this appears to be so, then there is the possibility of relaxing the inequality

$$\Gamma_p \ll \Gamma_f \tag{7}$$

and admitting *linear complex phenomenological* laws of the type

$$J_\alpha^+ = L_{\alpha\beta}^+ X_\beta^+ \tag{8}$$

The above development was implied in an isolated example by de Groot in which the relaxation associated with an internal redistribution of energy was treated.

In considering spatial distributions of the forces and fluxes it is necessary to note that tensor forces can only give rise to tensor fluxes *of the same rank.* This is an important consideration when treating coupled phenomena.

Up to the present, no mention has been made of possible motion of the reference frame in which the forces and fluxes are measured. In the following section the phenomenological equations are written in a reference frame which moves in space and this produces modifications in the phenomenological equations as seen by an observer with different motion.

## 3. GENERALIZATION OF THE EQUATIONS

### (i) Small variable strain rates

In this work spatial distributions of physical quantities will be denoted by Latin subscripts or superscripts whilst classes of physical quantities will continue to be denoted by Greek subscripts as before.

The general tensor form of the linear phenomenological laws of the type 8 for small variable strain rates is

$$J^{+\,ijk}_{\alpha\ rst} = L^{+}_{\alpha\beta} X^{+\,ijk}_{\beta\ rst} \tag{9}$$

because the fluctuation programme of the thermodynamic parameters could often be described by a Fourier series in real cases.

Since the phenomenological laws[9] are written in proper tensor form, which ensures invariance of form under a transformation of coordinates, then they are quite independent of the motion of any reference frame in space. When applied to a continuum in motion, addition of corresponding quantities throughout the whole history of motion is accomplished by writing the phenomenological equations in a reference frame which is convected, rotated and deformed with the continuum. Experimental observations are invariably made in a reference frame which is fixed relative to an observer who does not have the motion of all regions of the continuum. Transformation from the convected to the fixed reference frame will under certain circumstances introduce new terms into the phenomenological laws. But initial isotropy remains in the convected reference frame.

The formal apparatus for transforming rheological equations of state containing time derivatives and integrals has already been treated in some detail by Oldroyd[2]; for tensor quantities of general type and any rank of particular interest in practical cases there are phenomenological laws relating tensors of rank one. The linear differential form of 9 is then

$$\left(\sum_{N=0}^{N=P} \lambda_N \frac{\partial^N}{\partial t^N}\right) J^i_\alpha = L_{\alpha\beta} \left(\sum_{M=0}^{M=Q} \tau_M \frac{\partial^M}{\partial t^M}\right) x^i_\beta \tag{10}$$

where $\lambda_0 = \tau_0 = 1$.

For sufficiently slow fluctuations of the forces and fluxes terms containing higher time derivatives than the first in 10 can be neglected and the truncated linear differential equation is

$$\left(1 + \lambda_1 \frac{\partial}{\partial t}\right) J^i_\alpha = L_{\alpha\beta}\left(1 + \tau_1 \frac{\partial}{\partial t}\right) X^i_\beta \tag{11}$$

The general linear integral equation has the form

$$J^i_\alpha = \int_{-\infty}^{t} \psi_{\alpha\beta}(t - t') X^i_\beta(x, t')\, dt' \tag{12}$$

where $t$ is current time and $t'$ is non-current time and $x^j$ is the fixed coordinate system. The memory function $\psi_{\alpha\beta}(t - t')$ may take the form corresponding to the same type of function obtained in rheological equations of state, namely

$$\psi_{\alpha\beta}(t - t') = \int_0^\infty \frac{R_{\alpha\beta}(\tau)}{\tau} \exp - \frac{[t - t']}{\tau}\, d\tau \tag{13}$$

In 13 $R_{\alpha\beta}(\tau)$ is the distribution function of relaxation times associated with the $\alpha$ flux and $\beta$ force.

In generalizing 10, 11 and 12 it is noted that the phenomenological equations are not associated with a fixed point $x^j$ in space but rather with an element of material over all time in the interval $-\infty \leqslant t' \leqslant t$. Consequently the time differentiations and integration must follow the motion of the material and only under the special condition of small material velocities, i.e. creeping flow, can the time derivatives and integrals be interpreted in a simple way.

The differential equation 11 is a special case of the general integral form 12 obtained by substituting into 13 a distribution function of the type

$$R_{\alpha\beta}(\tau) = L_{\alpha\beta}(\tau_1/\lambda_1)\, \delta(\tau) + L_{\alpha\beta}\{(\lambda_1 - \tau_1)/\lambda_1\}\, \delta(\tau_1 - \lambda_1) \tag{14}$$

For the system characterized by 14 then it may easily be shown that fluctuations of a frequency $\omega$ give

$$J^+_\alpha = L_{\alpha\beta}/(1 + \omega^2\lambda_1^2)\,[(1 + \omega^2\tau_1\lambda_1) - i\omega(\lambda_1 - \tau_1)]X_\beta \tag{15}$$

**(ii) General motions**

Generalizations of the linear phenomenological equations 10, 11 and 12 are now considered in which the motion of the continuum in which the processes operate is arbitrary.

In the convected coordinate system introduced by Oldroyd[2] with coordinate surfaces $\xi^k$ = constant embedded in the deforming continuum, a material element which is located at $\xi^k$ at time $t$ occupies the same position at all prior and subsequent times. In this reference frame equation 12 takes on the form

$$\Pi^i_\alpha = \int_{-\infty}^{t} \psi_{\alpha\beta}(t - t')\, \chi^i_\beta(\xi, t')\, dt' \tag{16}$$

where $\Pi^i_\alpha$, $\chi^i_\beta$ are the convected components of the fluxes and forces respectively. The spatial distributions in 16 are written as contravariant tensors, but they might equally well be written as covariant tensors.

Transforming 16 to a coordinate system which is fixed relative to the observer, by the techniques introduced by Oldroyd, then

$$J^i_\alpha = \int_{-\infty}^{t} \psi_{\alpha\beta}(t - t')\, X^r_\beta(x', t') \frac{\partial x^i}{\partial x'^r} \mathrm{d}t' \tag{17}$$

The covariant form of the equation is

$$J_{i\alpha} = \int_{-\infty}^{t} \psi_{\alpha\beta}(t - t')\, X_{r\beta}(x', t') \frac{\partial x'^r}{\partial x^i} \mathrm{d}t' \tag{18}$$

Oldroyd has also considered generalizations of differential equations[3,4]. Considering equation 11 then the corresponding form in the convected coordinate system is

$$\left(1 + \lambda_1 \frac{\partial}{\partial t}\right) \Pi^i_\alpha = L_{\alpha\beta} \left(1 + \tau_1 \frac{\partial}{\partial t}\right) \chi^i_\beta \tag{19}$$

Transforming 19 back to a fixed coordinate system then the form equivalent to 19 is

$$\left(1 + \lambda_1 \frac{\bar{\delta}}{\bar{\delta} t}\right) J^i_\alpha = L_{\alpha\beta} \left(1 + \tau_1 \frac{\bar{\delta}}{\bar{\delta} t}\right) X^i_\beta \tag{20}$$

where

$$\frac{\bar{\delta} J^i_\alpha}{\bar{\delta} t} = \frac{\partial J^i_\alpha}{\partial t} + u^K J^i_{\alpha,K} - u^i_{,K} J^K_\alpha \tag{21}$$

with an identical form for

$$\frac{\bar{\delta} X^i_\beta}{\bar{\delta} t}$$

It may be noted from 21 that when the velocity field $u_k$ and its spatial gradients are not vanishingly small then the process of transforming time derivatives introduces additional terms into equation 20 and its expanded form becomes

$$J^i_\alpha + \lambda_1 \left[\frac{\partial J^i_\alpha}{\partial t} + u^K J^i_{\alpha,K} - u^i_{,K} J^K_\alpha\right]$$
$$= L_{\alpha\beta} \left(X^i_\beta + \tau_1 \left[\frac{\partial X^i_\beta}{\partial t} + u^r X^i_{\beta,r} - u^i_{,r} X^r_\alpha\right]\right) \tag{22}$$

Identical results are *not* obtained by taking the covariant equivalent of 20 namely

$$\left(1 + \lambda_1 \frac{\bar{\delta}}{\bar{\delta} t}\right) J_{\alpha i} = L_{\alpha\beta} \left(1 + \tau_1 \frac{\bar{\delta}}{\bar{\delta} t}\right) X_{\beta i} \tag{23}$$

for in this case

$$\frac{\bar{\delta} J_{\alpha i}}{\bar{\delta} t} = \frac{\partial J_{\alpha i}}{\partial t} + u^K J_{\alpha i, K} + u^K_{.i} J_{\alpha K} \tag{24}$$

and this should be compared with 21. There are important implications in these results as will be shown later. Other forms of 21 and 24 may be written which bring out more clearly their fundamental difference. To obtain a true comparison the equations are written in cartesian form in which there is no distinction between covariant and contravariant tensors. It is also convenient to take the velocity gradient in cartesian form.

$$u_{K,i} = \frac{1}{2}\left(\frac{\partial u_K}{\partial x_i} + \frac{\partial u_i}{\partial x_K}\right) + \frac{1}{2}\left(\frac{\partial u_K}{\partial x_i} - \frac{\partial u_i}{\partial x_K}\right) = e_{iK} - \omega_{iK} \tag{25}$$

Then 21 becomes

$$\frac{\bar{\delta} J_{\alpha i}}{\bar{\delta} t} = \frac{\partial J_{\alpha i}}{\partial t} + u_K \frac{\partial J_{\alpha i}}{\partial x_K} - (e_{Ki} + \omega_{Ki}) J_{\alpha K} \tag{26}$$

whilst 24 becomes

$$\frac{\bar{\delta} J_{\alpha i}}{\bar{\delta} t} = \frac{\partial J_{\alpha i}}{\partial t} + u_K \frac{\partial J_{\alpha i}}{\partial x_K} + (e_{iK} + \omega_{iK}) J_{\alpha K} \tag{27}$$

It may be seen from 25 that

$$e_{iK} = e_{Ki} \tag{28}$$

and

$$\omega_{iK} = -\omega_{Ki} \tag{29}$$

and hence 27 differs from 26 by the addition of $2e_{iK}J_{\alpha K}$

The simplest time derivative which takes account of both the translation of the continuum and *also its rotation* is just the common part of 26 and 27 and this is denoted by $\mathscr{D}J_{\alpha i}/\mathscr{D}t$ where [3,4]

$$\frac{\mathscr{D} J_{\alpha i}}{\mathscr{D} t} = \frac{\partial J_{\alpha i}}{\partial t} + u_K \frac{\partial J_{\alpha i}}{\partial x_K} + \omega_{iK} J_{\alpha K} \tag{30}$$

## 4. SIMPLE SHEARING

It is worthwhile from a practical viewpoint to examine some of the implications of the developments in Section 2 when the continuum is deformed in steady simple shearing motion.

Consider laminar motion of the continuum in which the velocity field has the pattern

$$u_i = (\gamma x_2, 0, 0) \tag{31}$$

where $\gamma$ is constant. This corresponds to steady simple shearing motion in which the shear planes move parallel to the $x_1$ axis. Suppose that there is a single thermodynamic force of unity tensor rank (vector), which has the distribution

$$X_K = (0, X_2, 0) \tag{32}$$

where $X_2$ is a constant. This could be for example a temperature or a concentration gradient in the $x_2$ direction. For simplicity it is taken that only direct fluxes are generated so that in the array of phenomenological coefficients only $L_{11}$ is non-zero.

Differences occur in the final results according to whether the contravariant differential equation 20 or covariant equation 23 is taken. Treating the contravariant equation first then

1 Direction $$J_1 - \lambda_1 \gamma J_2 = -L_{11}\tau_1 \gamma X_2 \tag{33}$$

2 Direction $$J_2 = L_{11} X_2 \tag{34}$$

or $$J_x = L_{11}\gamma X_y(\lambda_1 - \tau_1) \quad (34)$$

$$J_y = L_{11} X_y \tag{35}$$

where to avoid confusion the 1, 2 coordinates are now labelled $x$, $y$.

The flux $J_y$ in 35 is the ordinary direct flux produced by the force $X_y$ but the flux $J_x$ in 34 is a *secondary flux* which is only zero if $\gamma(\lambda_1 - \tau_1)$ becomes vanishingly small which it would in a stationary continuum.

The covariant case of the same differential equation gives

$$J_x = L_{11}\gamma X_y(\tau_1 - \lambda_1) \tag{36}$$

$$J_y = L_{11} X_y \tag{37}$$

Rheological equations of state have been formulated in which the partial time derivatives have been translated into the form 30 which allows for convection and rotation of the continuum *but not straining.* In this case it is easy to show that the differential equation 11 gives:

$$J_x = \frac{1}{2}\frac{L_{11}(\lambda_1 - \tau_1)}{(1 + \frac{1}{4}\lambda_1^2\gamma^2)}\gamma X_y \tag{38}$$

$$J_y = L_{11}\frac{(1 + \frac{1}{4}\lambda_1\tau_1\gamma^2)}{(1 + \frac{1}{4}\lambda_1^2\gamma^2)}X_y \tag{39}$$

In this case not only are there both direct and secondary fluxes, but a new feature arises in that they are both non-linear in the shear rate, but *the relation between the force and corresponding flux remains linear.*

Phenomenological relations between scalar forces and fluxes would not exhibit secondary effects because in general motion the time derivatives then are interpreted as the Eulerian time derivative $DS/Dt$ where

$$\frac{DS}{Dt} = \frac{\partial S}{\partial t} + u^r\frac{\partial S}{\partial x^r} \tag{40}$$

and $S$ is any scalar quantity.

Tensors of rank two have been treated by Oldroyd in the form of stress/strain rate relations.

## 5. CONCLUSION

The linear phenomenological relations of irreversible thermodynamics have been broadened to include relaxation effects in the coefficients. The well known Onsager reciprocal relations

$$L_{\alpha\beta} = L_{\beta\alpha} \tag{2}$$

which state that the array of phenomenological coefficients is symmetrical can then be restated as

$$R_{\alpha\beta} = R_{\beta\alpha} \tag{41}$$

The corresponding statement here is that the *distribution of relaxation times is symmetrical.*

The general effect of translation, rotation and deformation of the system is that new terms can occur in the thermodynamic equations of transport processes and these describe secondary fluxes. In rheological equations the secondary fluxes take the form of normal force effects in simple shearing; these have often been reported in the literature.

Scalar thermodynamic forces produce no secondary fluxes and in tensors of rank one the covariant form 23 produces negative secondary fluxes positive secondary fluxes in simple laminar shearing are present in the contravariant form and when time derivatives of the type 30 are used. It has already been noted[2] that in the rheological equations the corresponding covariant form produces results which are *not* in accord with experimental results. The contravariant form produces some of the correct types of effects but time derivatives of type 30 are perhaps the most successful[3, 4] in simple equations containing relaxation effects.

The secondary flux does not of course contribute to the evolution of entropy since the scalar product of this flux with the force is zero.

It is clear from equation 20 that 'cross' phenomena can also produce secondary fluxes. That is, $\beta$ forces can produce secondary $\alpha$ fluxes.

A fundamental principle implicit in this work is that the thermodynamic properties of a material element do not depend upon the properties of neighbouring elements but may depend upon the history of thermodynamic states of the element. The thermodynamic properties of the element are also independent of the motion of the element in space.

## 6. REFERENCES


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