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## LETTER TO THE EDITOR

# Coupling and uncoupling in irreversible thermodynamics

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**Abstract.** For convenience the Letter opens with a summary of the accepted elementary treatment of the coupled fluxes and forces in the flow of entropy and mass according to Onsager-based irreversible thermodynamics of the steady state. It is then shown that a simple transformation entirely consistent with that treatment shows that there also exists a set of uncoupled fluxes and forces. The physical significance of the uncoupled set is clear, and it is convenient to deal with operationally. Some important questions raised by the existence of this alternative set are discussed.

### Symbols

$G_0$	equilibrium Gibbs thermodynamic potential per unit mass
$J_m$	mass flux rate
$J_s$	entropy flux rate
$K$	thermal conductivity
$M^*$	function defined by equation (18) in terms of $S^*$ , $T$ , and $\psi$
$M_0$	as $M^*$ but in terms of $S_0$ , $T$ , and $\psi$
$r$	resistance
$S^*$	entropy transport parameter
$S_0$	equilibrium specific entropy
$T$	temperature
$\phi_0$	field potential
$\lambda_{11}$ , etc	coefficients in standard flux/force equations
$\psi$	total potential $G_0 + \phi_0$

We begin with a summary of the accepted elementary treatment of the coupled fluxes of entropy and mass according to Onsager-based irreversible thermodynamics. Its essentials will be found in such texts as Denbigh (1950), Zemansky (1957) and Benson (1967), and more fundamentally in De Groot (1961).

The rate of entropy generation per unit volume of a continuum maintained in a non-equilibrium steady state is stated to be given by

$$T \operatorname{div} J_s = -J_s \cdot \operatorname{grad} T - J_m \cdot \operatorname{grad} \psi. \quad (1)$$

The entropy flux  $J_s$  and the mass flux  $J_m$  are *each* responsive to the two forces  $\operatorname{grad} T$  and  $\operatorname{grad} \psi$  by the following relations:

$$J_s = \lambda_{11} \operatorname{grad} T + \lambda_{12} \operatorname{grad} \psi, \quad J_m = \lambda_{21} \operatorname{grad} T + \lambda_{22} \operatorname{grad} \psi. \quad (2)$$

It is also asserted, on the basis of statistical analysis of near-equilibrium conditions, that the cross-coupling coefficients are equal, i.e.

$$\lambda_{21} = \lambda_{12}. \quad (3)$$

All coefficients  $\lambda$  are constants for a given equilibrium condition, being equilibrium properties. They are evaluated from the phenomenology of the situation as follows.

When  $\text{grad } T$  is zero, i.e. under isothermal conditions, the ratio of entropy flux to mass flux is

$$(\mathbf{J}_s/\mathbf{J}_m)_{\text{grad } T=0} = \lambda_{12}/\lambda_{22}. \quad (4)$$

This is defined as the entropy transport parameter, denoted by a symbol such as  $S^*$ , which is the entropy carried by unit mass as it flows.

Thus  $\lambda_{12}$  is found as

$$\lambda_{12} = \lambda_{22}S^*, \quad (5)$$

and from equation (3), also

$$\lambda_{21} = \lambda_{22}S^*. \quad (6)$$

The coefficient  $\lambda_{22}$  itself is found by considering the concept of a resistance to mass flux also under the isothermal condition. The resistance concept then means

$$\mathbf{J}_m = -\text{grad } \psi/r = \lambda_{22} \text{ grad } \psi, \quad (7)$$

whence

$$\lambda_{22} = -1/r \quad (8)$$

Finally  $\lambda_{11}$  is found by considering the concept of thermal conductivity under conditions of zero mass flux. When mass flux is zero we have

$$(\mathbf{J}_s)_{J_m=0} = \mathbf{J}_q/T = -(K/T) \cdot \text{grad } T. \quad (9)$$

Also when mass flux is zero

$$\text{grad } \psi = -\lambda_{21} \text{ grad } T/\lambda_{22} = -S^* \text{ grad } T. \quad (10)$$

Substitution in the general equation for  $\mathbf{J}_s$  gives

$$-(K/T) \cdot \text{grad } T = (\lambda_{11} - \lambda_{12}S^*) \text{ grad } T = (\lambda_{11} + S^{*2}/r) \text{ grad } T. \quad (11)$$

Thus we find

$$\lambda_{11} = -(K/T + S^{*2}/r). \quad (12)$$

Thus all four coefficients are evaluated in terms of the concepts  $S^*$ ,  $K$  and  $r$ . This procedure for evaluating the four coefficients depends upon: (i) the  $\lambda$  being constant, so that the values inserted for specific situations can be used for others; (ii) the asserted equality  $\lambda_{21} = \lambda_{12}$ . Without this there would be only three situation equations (4), (7) and (9), while there are four unknowns.

The constancy of each  $\lambda$  is justified by the assumption of local equilibrium at each point, although the reference body as a whole is in a non-equilibrium steady state. Thus  $S^*$ ,  $r$  and  $K$  are equilibrium properties, constant for a given equilibrium condition. In general  $S^*$ , although it has the dimensions of specific entropy, is not identical with the equilibrium specific entropy  $S_0$ . It is frequently called the entropy transport parameter,

and its existence, with a value differing from  $S_0$ , is predicted by statistical analysis of small perturbations near equilibrium.

This summary of accepted theory and procedure has been given because we wish to draw attention to a feature which has unaccountably been neglected. The theory has quite correctly tended to emphasise the coupling of the entropy flux and mass flux as each being affected by *both* forces  $\text{grad } T$  and  $\text{grad } \psi$ , but in its concern to do this it appears to have overlooked the fact that an uncoupled flux affected only by  $\text{grad } T$  also emerges from the same equations. This can be seen readily from equation (2) by considering a flux defined by the relation

$$\mathbf{J}'_s = \mathbf{J}_s - \mathbf{J}_m S^*. \quad (13)$$

We then have immediately from equation (2)

$$\mathbf{J}'_s = (\lambda_{11} - \lambda_{21} S^*) \text{grad } T + (\lambda_{12} - \lambda_{22} S^*) \text{grad } \psi. \quad (14)$$

But from equation (5) the coefficient of  $\text{grad } \psi$  in equation (14) is necessarily zero, and from equations (12), (6) and (8), the coefficient of  $\text{grad } T$  in equation (14) is necessarily  $-K/T$ . Thus we have necessarily always

$$\mathbf{J}'_s = -(K/T) \cdot \text{grad } T. \quad (15)$$

It will be recalled that the inclusion of  $K$  arose from the assertion that when  $\mathbf{J}_m$  is zero the entropy flux can be only that due to what is commonly referred to as *heat* flux. The argument leading to equation (15) therefore shows that even when  $\mathbf{J}_m$  is not zero the quantity  $\mathbf{J}'_s$  can always be regarded as a heat flux.

There is a still further consequence. Inserting equation (13) into the entropy generation equation (1), we have

$$T \text{div } \mathbf{J}_s = -\mathbf{J}'_s \cdot \text{grad } T - \mathbf{J}_m \cdot (S^* \text{grad } T + \text{grad } \psi). \quad (16)$$

But also from equation (2) with the values which were established for  $\lambda_{21}$  and  $\lambda_{22}$

$$\mathbf{J}_m = -(1/r)(S^* \text{grad } T + \text{grad } \psi). \quad (17)$$

Thus the conjugate force with  $\mathbf{J}_m$  in equation (16) is the same expression as appears in equation (17). It follows that if we define the scalar quantity  $M^*$  such that

$$\text{grad } M^* = S^* \text{grad } T + \text{grad } \psi, \quad (18)$$

the basic equations (1) and (2) can be written as

$$T \text{div } \mathbf{J}_s = -\mathbf{J}'_s \cdot \text{grad } T - \mathbf{J}_m \cdot \text{grad } M^* \quad (19)$$

$$\mathbf{J}'_s = -(K/T) \cdot \text{grad } T, \quad \mathbf{J}_m = -\text{grad } M^*/r. \quad (20)$$

Thus by using the flux  $\mathbf{J}'_s$  instead of  $\mathbf{J}_s$  with the conjugate force  $\text{grad } T$ , and the conjugate force  $\text{grad } M^*$  instead of  $\text{grad } \psi$  with the flux  $\mathbf{J}_m$ , we have the entropy generation expressed directly in terms of uncoupled fluxes and forces. It is a simple transformation result using the same parameters  $S^*$ ,  $K$  and  $r$ , and giving the same value for the rate of entropy generation.

It is difficult to understand why so much emphasis is placed in contemporary irreversible thermodynamics on the set of coupled fluxes and forces when such a simple transformation to an uncoupled set exists, which is evidently much more convenient to deal with operationally.

The physical significance of the uncoupled set is perfectly clear.  $J'_s$  is the total entropy flux  $J_s$  less  $J_m S^*$ , which is the entropy transported with the mass flux. It can therefore be considered to be

$$J'_s = J_q/T. \quad (21)$$

$J_q$ , as shown by equation (15), is simply heat flux defined in the usual way as responsive to temperature gradient only, whether or not a mass flux  $J_m$  is also present.

Similarly  $\text{grad } M^*$  has a clear physical significance, since  $\psi$  is the equilibrium total potential, which may be written

$$\psi = G_0 + \phi_0.$$

Hence

$$\text{grad } \psi = V_0 \text{grad } p - S_0 \text{grad } T + \text{grad } \phi_0. \quad (22)$$

Thus

$$\text{grad } M^* = (S^* - S_0) \text{grad } T + V_0 \text{grad } p + \text{grad } \phi_0. \quad (23)$$

In equation (22) the terms  $V_0 \text{grad } p + \text{grad } \phi_0$  are recognisably the usual Newtonian forces which would be regarded as driving mass flux against the resistance  $r$ , i.e. in mechanics alone we should readily write

$$J_m = -(V_0 \text{grad } p + \text{grad } \phi_0)/r,$$

which comes from equations (20) and (23) if the difference between  $S^*$  and  $S_0$  is neglected. The inclusion of this difference is the correction which irreversible thermodynamics gives to simple mechanics. Indeed we might reasonably define for the idealised equilibrium situation

$$\text{grad } M_0 = V_0 \text{grad } p + \text{grad } \phi_0. \quad (24)$$

to which  $\text{grad } M^*$  tends as  $S^*$  tends to  $S_0$ .

None of this affects the well-known results of the accepted theory. There is still an effective 'heat' flux given by  $J_m T(S^* - S_0)$  additional to  $J_q$ , so that the concept of  $T(S^* - S_0)$  as a 'heat of transport' can be retained. The pressure/temperature gradient relation for the thermomechanical effect, the thermocouple relations, the thermo-diffusion phenomena—all of these stay the same. But it would seem desirable that much re-examination of the presentation of the theory should occur in the light of the uncoupled set of fluxes and forces which are so much more amenable to physical conceptualisation and experimental measurement.

There is indeed a more fundamental question raised. If we took an entirely simplistic 'classical' view, we should write heat flux  $J_q$  and mass flux  $J_m$  in the simple 'thermal' and 'mechanical' forms

$$J_q = -K \text{grad } T, \quad J_m = -(V_0 \text{grad } p + \text{grad } \phi_0)/r. \quad (25)$$

Then we could write, again classically,

$$V_0 \text{grad } p = \text{grad } G_0 + S_0 \text{grad } T, \quad (26)$$

giving

$$J_m = -(S_0 \text{grad } T + \text{grad } \psi)/r. \quad (27)$$

Then defining the total entropy flux  $\mathbf{J}_s$  as

$$\mathbf{J}_s = \mathbf{J}_q/T + \mathbf{J}_m S_0, \quad (28)$$

we should find

$$\mathbf{J}_s = -(K/T + S_0^2/r) \text{grad } T - (S_0/r) \text{grad } \psi. \quad (29)$$

Then equations (29) and (27) form a pair of the accepted coupled form with equal cross-coupling coefficients  $-S_0/r$ . Thus equality of cross coefficients in a coupled pair of equations has arisen directly from the simple equation (25) and the property relation (26)—with no need for appeal to microscopic reversibility. Of course we have the incorrect entropy value  $S_0$  instead of the correctly required  $S^*$ , but the implication is that, while statistical analysis using the theorem of microscopic reversibility may be necessary to prove the existence of  $S^*$  as a property of the near-equilibrium steady state, the *equality* of cross-coupling coefficients is inherent in the conceptual relations of the macroscopic properties.

Naturally since  $S_0$  appears in this simplistic treatment it fails to predict all the effects discussed above which depend on the difference  $S^* - S_0$ . But where an effect depends on  $S^*$  alone, this simple treatment in terms of  $S_0$  gives the correct form, although the arithmetical value will be incorrect. In retrospect it can be seen that Kelvin's treatment of the thermocouple was of this kind, and this is why he was able to predict the correct form of the relations between Seebeck, Peltier and Thomson coefficients.

## References

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