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1986 J. Phys. A: Math. Gen. 19 L295

(http://iopscience.iop.org/0305-4470/19/5/014)

J. Phys. A: Math. Gen. 19 (1986) L295-L297. Printed in Great Britain

LETTER TO THE EDITOR

# Lagrangian formulation of non-linear extended irreversible thermodynamics

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Received 12 December 1985

**Abstract.** Landau and Lifshitz showed that phenomenological equations of extended non-equilibrium thermodynamics, reciprocity included, can be cast in Langrangian form, so long as the kinetic equations are linear in time derivatives of the even variables. It is shown that this formalism can be extended to the general non-linear case.

A closed system is described by a set $\{\alpha_i\}$ of variables even with respect to time reversal and a set $\{\eta_i\}$, where $\eta_i = \dot{\alpha}_i$, which are odd. By an extension of the Zwanzig (1960, 1961) projection operator technique, a derivation has been given (Nettleton 1985) of the phenomenological equations

$$\dot{\alpha}_i = \sum_j L_{ij}^{(2)} F_j^* \tag{1a}$$

$$\dot{\eta}_i = \sum_j L_{ij}^{(4)} F_j^* + \sum_j L_{ij}^{(3)} F_j \tag{1b}$$

with the reciprocity relations

$$L_{ij}^{(2)} = -L_{ji}^{(3)} \qquad L_{ij}^{(4)} = L_{ji}^{(4)}. \tag{2}$$

Here $F_j = -\partial F/\partial \alpha_j$, $F_j^* = -\partial F/\partial \eta_j$, and the free energy $F$ and $L_{ij}^{(k)}$ are non-linear in the $\eta$ variables and in the deviations $\{\alpha_i - \alpha_{i0}\}$ from equilibrium.

In the case where the $L_{ij}^{(k)}$ are independent of the $\eta$ variables and the $\{F_j^*\}$ are linear therein, Landau and Lifshitz (1958) (see also Casas-Vásques *et al* 1984, p 25) have shown that ($1a$, $b$) and (2) are equivalent to

$$F = T + V \equiv L + 2V \tag{3a}$$

$$(\partial/\partial t)(\partial L/\partial \eta_i) - \partial L/\partial \alpha_i = R_i \tag{3b}$$

where $T$ represents the terms in $F$ which are bilinear in the $\eta$ variables, and $R_i = -\partial R/\partial \eta_i$ is a non-conservative force which is minus the $\eta_i$ derivative of a dissipation function, $R$. Landau and Lifshitz (1958) assumed the coefficients in $T$ and $R$ to be constant, but we shall see that they can be $\alpha$-dependent, so that the assumption is unnecessary. By postulating functions $L$ and $R$ of appropriate symmetry, one can derive macroscopic equations of motion more directly by ($3b$) than by ($1a$, $b$) (Sannikov 1962a, b). It remains to explore whether ($3a$, $b$) can be extended to the general non-linear case.

0305-4470/86/050295+03$02.50  

Suppose

$$F = F_0 + \sum_{n\geqslant 1} \sum_{\mu(1)\ldots\mu(2n)} F^{(2n)}_{\mu(1)\ldots\mu(2n)} \eta_{\mu(1)} \cdots \eta_{\mu(2n)} \tag{4}$$

where the $F^{(2n)}$ coefficients depend on the set $\{\alpha_i\}$. This permits us to define $\tilde{F}_{ij}$ so that $F_i^* = \Sigma_j \tilde{F}_{ij}\eta_j$. Setting $L = 2T - F$ in $(3b)$, we have

$$\sum_j \left(2\frac{\partial^2 T}{\partial\eta_i\partial\eta_j} - \frac{\partial^2 F}{\partial\eta_i\partial\eta_j}\right)\dot{\eta}_j + \sum_j \left(2\frac{\partial^2 T}{\partial\eta_i\partial\alpha_j} - \frac{\partial^2 F}{\partial\eta_i\partial\alpha_j}\right)\eta_j - 2\frac{\partial T}{\partial\alpha_j} + \frac{\partial F}{\partial\alpha_j} = R_i. \tag{5}$$

Let us determine $T$ so that

$$2\partial^2 T/\partial\eta_i\partial\eta_j - \partial^2 F/\partial\eta_i\partial\eta_j = -\tilde{F}_{ij} \tag{6}$$

i.e. $T$ is even in the $\eta$ variables, with

$$T^{(2n)}_{\mu(1)\ldots\mu(2n)} = \frac{1}{2}\,\frac{2n}{2n-1} F^{(2n)}_{\mu(1)\ldots\mu(2n)}. \tag{7}$$

That this is a natural way to calculate $T$ is seen if we note that

$$\dot{\alpha}_i = \eta_i = \sum_j \tilde{F}^{-1}_{ij} F_j^* \tag{8a}$$

$$L^{(2)}_{ij} = \tilde{F}^{-1}_{ij}. \tag{8b}$$

Equation (6) ensures that the $F_j$ term in (5) is consistent with the corresponding term in $(1b)$. Putting $(1b)$ into (5) and using (7), we find

$$-\sum_{jm} \tilde{F}_{ij} L^{(4)}_{jm} F_m^* + \sum_j (2\partial^2 T/\partial\eta_i\partial\alpha_j - \partial^2 F/\partial\eta_i\partial\alpha_j)\eta_j - 2\partial T/\partial\alpha_i = R_i. \tag{9}$$

Equations (9) and (7) imply that

$$-\sum_i \eta_i R_i = \sum_{jm} F_j^* L^{(4)}_{jm} F_m^* \tag{10}$$

which is the rate of irreversible entropy production. This must hold if $R_i$ is a non-conservative force. Equations (6) and (7) are thus consistent with this requirement.

Corresponding to the Lagrangian, there is also a Hamiltonian formulation. Defining $p_i \equiv \partial L(\alpha, \eta)/\partial\eta_i$, we set

$$H \equiv \sum_i p_i\eta_i - L = F \tag{11}$$

since we can verify from (7) that $\Sigma_i\, p_i\eta_i = 2T$. With this $H$, we find that $\partial H(\alpha, p)/\partial p_i = \eta_i$ and $\partial H(\alpha, p)/\partial\alpha_i = -\partial L(\alpha, \eta)/\partial\alpha_i$, so that the Lagrangian equations (3) go over into canonical Hamiltonian form.

In the Lagrangian derivation of the equations of motion, an ansatz is made for $R$, with coefficients ultimately to be found from experiment. We want to see how this ansatz becomes more complicated in the general non-linear case. Referring to (9) for $R_i$, and given that $F$ is presumed known and $T$ is determined above, we concentrate on the first term on the left. The coefficients in this term have the form

$$\sum_{jkm} \tilde{F}_{ij} L^{(4)}_{jk} \tilde{F}_{km} = c_{im} = c_{mi} \tag{12}$$

where $c_{im}$ is not constant, as it was when equations (1) were linear in the $\{\eta_i\}$. Inspection of the microscopically derived expression for $L^{(4)}_{ij}$ (Nettleton 1985, equation (27)) shows that if $c_{ij}$ is expanded in powers and products of $\{F_j^*\}$, the coefficients are not symmetric with respect to the interchange of all indices. In first approximation

$$c_{ij} = c_{ij}^{(0)}(\{\alpha_i\}) + \sum_k \bar{c}_{ikj}\eta_k \qquad (13)$$

where $\bar{c}_{ijk} \neq \bar{c}_{ijk}$.

From (9) and (13), we see that we can find $L$ so that ($1a, b$) are equivalent to (2). However, $R_i$ is no longer the derivative of a simple quadratic dissipation function. The more complicated structure of (13) removes many of the advantages of the Lagrangian approach. The Onsager–Casimir formulation has an advantage in that it has been shown (Nettleton 1967) explicitly for $n=2$ that if we can calculate $F_0$ and ($1b$) from a model, then, with the antireciprocity relation of (2), we can find $F^{(2)}_{\mu(1)\mu(2)}$. The reciprocity relations can thus be invoked to calculate the $\eta$ dependence of $F$ if the $\alpha$ dependence can be found from a model.

## References

Casas-Vásquez J, Jou D and Lebon G (ed) 1984 *Recent Developments in Nonequilibrium Thermodynamics* (Berlin: Springer)
Landau L D and Lifshitz E M 1958 *Statistical Physics* (Oxford: Pergamon)
Nettleton R E 1967 *Phys. Lett.* **24A** 231
—— 1985 *Physica* **132A** 143
Sannikov D G 1962a *Sov. Phys.-JETP* **14** 98
——1962b *Sov. Phys.-Solid State* **4** 1187
Zwanzig R 1960 *J. Chem. Phys.* **33** 1338
—— 1961 *Phys. Rev.* **124** 983