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On the derivation of the Onsager–Casimir reciprocal relations from the principles of thermodynamics

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Abstract. It is shown that for certain discrete systems the Casimir anti-symmetry relations follow from the basic principles of thermodynamics without assuming linear laws and microscopic reversibility.

It is well known how to derive the Onsager–Casimir relations from microscopic time reversal invariance and the assumption of linear laws for the thermodynamic variables [1]. However, the question has often been raised whether such relations could be obtained within the framework of thermodynamics only [2]. In this connection E. C. G. Stueckelberg and Scheurer [3] could only show that those relations were indeed consistent with the two principles of thermodynamics but were not able to derive them from those principles. In the following, we show that the Casimir anti-symmetry relation follows indeed from the two principles, at least for certain discrete systems, without assuming linear laws and microscopic reversibility.

We shall follow the phenomenology and notation of Reference [3] and restrict our discussion to elementary systems; the generalization to discrete systems is however straightforward. We recall that, by definition, an elementary system is a system such that the (thermodynamic) states are entirely defined by the independent state variables $(S, \xi^1, \dots, \xi^\omega)$ where S is the entropy and the ξ's are 'geometric' variables [3]. We shall only assume that the variables can be classified into three groups, namely:

$$\{\xi^a\}_{a=1,\dots,\omega} = \{\xi^i, v^i, \zeta^\alpha\}_{\substack{i=1,\dots,n \\ \alpha=1,\dots,m=\omega-2n}}$$

where

$v^i = d/(dt)\xi^i$ and that the variables $\{\xi^i, \zeta^\alpha\}$ are invariant under time reversal.[1])
From the first principle follows that:

$$H = H(S, \{\xi^a\}) \quad (H = \text{Energy})$$

and the irreversibility – or entropy production – is given by:

$$I = \left(\frac{\partial H}{\partial S}\right)^{-1}\left\{\sum_{i=1}^{n}\left(\Xi^{\text{ext}}_{\xi^i} - \frac{\partial H}{\partial \xi^i}\right)\dot{\xi}^i + \sum_{i=1}^{n}\left(\Xi^{\text{ext}}_{v^i} - \frac{\partial H}{\partial v^i}\right)\dot{v}^i + \sum_{\alpha=1}^{m}\left(\Xi^{\text{ext}}_{\zeta^\alpha} - \frac{\partial H}{\partial \zeta^\alpha}\right)\dot{\zeta}^\alpha\right\}$$

where $\Xi^{\text{ext}}_{\xi^a}$ denotes the external force associated with the variable ξ^a [3].

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[1]) This last condition is introduced for convenience only, but is not important.

Let us consider the case where the external forces are such that:

$$\Xi^{\text{ext}}_{\xi^i}(t) \neq 0 \qquad \Xi^{\text{ext}}_{\zeta^\alpha}(\mathrm{t}) \neq 0 \qquad \Xi^{\text{ext}}_{v^i}(t) \equiv 0$$

From the second principle (2a) $I(t) \geqslant 0$, it follows that there exists state functions $\lambda_{ab} = \lambda_{ab}(S, \{\xi^\cdot\})$ such that:

$$\left\{\left(\frac{\partial H}{\partial S}\right)^{-1} \lambda_{(ab)}(S, \{\xi^\cdot\})\right\} \geqslant 0, \quad \lambda_{(ab)} = \tfrac{1}{2}(\lambda_{ab} + \lambda_{ba})$$

and[2])

$$\Xi^{\text{ext}}_{\xi^i} - \frac{\partial H}{\partial \xi^i} = \lambda_{\xi^i\xi^j}\,\dot{\xi}^j + \lambda_{\xi^i v^j}\,\dot{v}^j + \lambda_{\xi^i\zeta^\beta}\dot{\zeta}^\beta \tag{1}$$

$$-\frac{\partial H}{\partial v^i} = \lambda_{v^i\xi^j}\,\dot{\xi}^j + \lambda_{v^i v^j}\,\dot{v}^j + \lambda_{v^i\zeta^\beta}\dot{\zeta}^\beta \tag{2}$$

$$\Xi^{\text{ext}}_{\zeta^\alpha} - \frac{\partial H}{\partial \zeta^\alpha} = \lambda_{\zeta^\alpha\xi^i}\,\dot{\xi}^j + \lambda_{\zeta^\alpha v^j}\,\dot{v}^j + \lambda_{\zeta^\alpha\zeta^\beta}\dot{\zeta}^\beta \tag{3}$$

But $\dot{v}^j$ and $\dot{\zeta}^\beta$ are not in general state functions, since the system is submitted to external forces [3]; on the other hand $\partial H/\partial v^i$, $\lambda_{\xi^a\xi^b}$, $\dot{\xi}^j = v^j$ are state functions. It then follows that:

$$\lambda_{v^i v^j} = 0 \qquad \lambda_{v^i\zeta^d} = 0$$

and therefore

$$-\frac{\partial H}{\partial v^i} = \lambda_{v^i\xi^j}\,\dot{\xi}^j \tag{2'}$$

We thus obtain for the irreversibility:

$$I = \left(\frac{\partial H}{\partial S}\right)^{-1}\left\{\sum_{i=1}^{n}\left(\Xi^{\text{ext}}_{\xi^i} - \frac{\partial H}{\partial \xi^i} + \lambda_{v^j\xi^i}\dot{v}^j\right)\dot{\xi}^i + \sum_{\alpha=1}^{m}\left(\Xi^{\text{ext}}_{\zeta^\alpha} - \frac{\partial H}{\partial \zeta^\alpha}\right)\dot{\zeta}^\alpha\right\}$$

Using again the second principle $I(t) \geqslant 0$, there exist state functions $\bar{\lambda}_{ab} = \bar{\lambda}_{ab}$ $(S, \{\xi^\cdot\})$ $a, b = 1, \ldots, n + m$ such that:

$$\left\{\left(\frac{\partial H}{\partial S}\right)^{-1} \bar{\lambda}_{(ab)}\right\} \geqslant 0$$

and

$$\Xi^{\text{ext}}_{\xi^i} - \frac{\partial H}{\partial \xi^i} + \lambda_{v^j\xi^i}\dot{v}^j = \bar{\lambda}_{\xi^i\xi^j}\dot{\xi}^j + \bar{\lambda}_{\xi^i\zeta^\beta}\dot{\zeta}^\beta \tag{1'}$$

$$\Xi^{\text{ext}}_{\zeta^\alpha} - \frac{\partial H}{\partial \zeta^\alpha} = \bar{\lambda}_{\zeta^\alpha\xi^j}\dot{\xi}^j + \bar{\lambda}_{\zeta^\alpha\zeta^\beta}\dot{\zeta}^\beta \tag{3'}$$

Comparing (1, 3) with (1′, 3′) and using the fact that the variables are independent, we obtain:

$$\lambda_{v^j\xi^i} = -\lambda_{\xi^i v^j}$$

$$\bar{\lambda}_{\xi^a\xi^b} = \lambda_{\xi^a\xi^b}$$

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[2]) With the notation: $\lambda_{ab} = \lambda_{\xi^a\xi^b}$.

In consequence we have obtained the Casimir anti-symmetric relations for the set of variables $\{\xi^i, \zeta^\alpha\}$ and $\{v^i\}$ (which transform with different signs with respect to time reversal) namely:

$$\lambda_{v^j\xi^i} = -\lambda_{\xi^i v^j} \quad i, j = 1 \ldots n$$

$$\lambda_{v^i\zeta^\alpha} = -\lambda_{\zeta^\alpha v^i} = 0 \quad i = 1, \ldots n, \alpha = 1, \ldots m$$

On the other hand the equations

$$\lambda_{v^i v^j} = 0$$

are special cases of Onsager relation.

To conclude this discussion, let us make the following remarks:

(1) In the terminology of Reference [3] $\lambda_{\xi^i v^j}\dot{v}^j$ is a 'force of inertia' and the tensor $\lambda_{ij} = \lambda_{\xi^i v^j}$ is a 'tensor of inertia'. (It is a state function and not necessarily a constant.) In particular if λ_{ij} is independent of the variables $\{v^i\}$ we have:

$$H(S, \{\xi^a\}) = \tfrac{1}{2}\lambda_{ij}(S, \{\xi^i\}, \{\zeta^\alpha\})v^i v^j + U(S, \{\xi^i\}, \{\zeta^\alpha\})$$

and it follows from the second principle (2b) that:

$$\left\{\left(\frac{\partial H}{\partial S}\right)^{-1} \lambda_{(ij)}\right\} \geqslant 0$$

(2) Equation (2′) could also be derived in the following manner; assuming the 'friction' forces $\Xi_a^{\mathrm{fr}} = -\Xi_{\xi^a}^{\mathrm{ext}} + \dfrac{\partial H}{\partial \xi^a}$ to be linearly independent, it follows from $I(t) \geqslant 0$ that:

$$\dot{\xi}^i = -\mathscr{L}_{\xi^i\xi^j}\Xi_{\xi^j}^{\mathrm{fr}} + \mathscr{L}_{\xi^i v^j}\left(-\frac{\partial H}{\partial v^j}\right) - \mathscr{L}_{\xi^i\zeta^\alpha}\Xi_{\zeta^\alpha}^{\mathrm{fr}}$$

However, since $\Xi_{\xi^i}^{\mathrm{fr}}$ and $\Xi_{\zeta^\alpha}^{\mathrm{fr}}$ are not state functions, while $\dot{\xi}^i$ and $\mathscr{L}_{ab}$ are [3], we obtain:

$$\dot{\xi}^i = -\mathscr{L}_{\xi^i v^j}(S, \{\xi^a\})\frac{\partial H}{\partial v^j}$$

and the conclusions follow as before.

References

[1] S. R. DE GROOT and P. MAZUR, *Non Equilibrium Thermodynamics* (North-Holland Publishing Company 1969).

[2] I. GYARMATI, *Non Equilibrium Thermodynamics* (Springer-Verlag 1970).

[3] E. C. G. STUECKELBERG DE BREIDENBACH and P. B. SCHEURER, *Thermocinétique Phénoménologique Galiléenne* (Birkhäuser-Verlag, Basel 1974).