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ONSAGER'S RECIPROCAL RELATIONS AND SOME BASIC LAWS

József Verhás
Department of Chemical Physics, Budapest University of Technology and Economy
H-1521 Budapest, Hungary
verhas@phy.bme.hu

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Abstract. This paper presents some ideas and doubts about some assumptions on the validity and proofs of the Onsager–Casimir reciprocal relations. Presuming the validity of the Onsager–Casimir reciprocal relations, exact proofs can be constructed for Newton's second and third laws, moreover, for the formula of the Lorentz–force. This way, the axioms of both mechanics and electrodynamics would become theorems in a theory in which the Onsager–Casimir reciprocal relations have been proved phenomenologically. We incline to believe that neither the axioms mentioned nor the Onsager–Casimir reciprocal relation can be proved, nevertheless, they are valid. The statement that if something is true then it can be proved is false.

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1. Introduction

The Onsager–Casimir reciprocal relations play important role in non-equilibrium thermodynamics [1, 2, 3, 4, 5, 6]; their validity deserves attention even if they have been discussed several times, (see e.g. [7,8,9,10,11] and [12], especially, [13,14,15,16,17,18, 19, 20] as weel as [21, 22]). Furthermore they are somehow related to the celebrated and persistent problems of the increase in the entropy and thermalization in statistical manifolds [23, 24].

The original proof based on the principle of microscopic reversibility suggests that they hold for statistical ensembles — in accordance with the opinion that entire thermodynamics does — and other methods introducing them did not result in anything new [5]. The generality and some applications hardly belonging to the realm of statistics inspired efforts for a phenomenological proof. The attempts to prove the reciprocal relations on a phenomenological basis have failed. One may think that the failure proves the statistical validity. Here we show that the reciprocal relations are closely related to very basic principles. We show here that the desired phenomenological proof of the reciprocal relations would be equivalent to a proof of fundamental laws of physics.

The equivalence of the reciprocal relations and the principle of detailed balance are well known. What is more the latter has hardly any meaning, e.g., in particle mechanics or in Maxwell's theory. The thermodynamic theory of diffusion—see e.g. [25]— shows that the reciprocal relations for the diffusion coefficients are equivalent to Newton's third law.

Some simple models can elucidate the intimate relation of the reciprocity to Newton's laws and to the fundamental principles of electromagnetism.

2. The diffusion

The entropy production density in an isothermal multicomponent system is (see [5] eq. XI.171, p. 265.)

$$\sigma = \frac{1}{T}\sum_{k=1}^{n} \mathbf{J}_k^a\{\mathbf{F}_k - (\operatorname{grad}\mu_k)_T\}, \tag{2.1}$$

where the vectors $\mathbf{J}_k^a = \rho_k(\mathbf{v}_k - \mathbf{v})$ are the diffusion flows with respect to any reference velocity $(\mathbf{v})$, $\mathbf{F}_k$ stands for the body forces acting on the unit amount of each chemical species in a frame travelling and accelerating together with the local center of mass, the scalars μ_k are the chemical potentials, and T is the thermodynamic temperature. Here ρ_k stands for the densities and $\mathbf{v}_k$ for the velocities of the components. The Onsager equations read

$$\mathbf{F}_i - (\operatorname{grad}\mu_i)_T = \sum_{k=1}^{n} R_{ik}\mathbf{J}_k^a. \tag{2.2}$$

From the fact that a simple translation of the material does not result in any dissipation,

$$\sum_{k=1}^{n} R_{ik}\rho_k = 0 \tag{2.3}$$

follows. Eliminating the diagonal elements from the right-hand side of equation (2.2), we get

$$\mathbf{F}_i - (\operatorname{grad}\mu_i)_T = \sum_{k\neq 1} R_{ik}\rho_k(\mathbf{v}_k - \mathbf{v}_i). \tag{2.4}$$

The right-hand side gives account of the forces exertied by the other components on the unit amount of the i-th one. Referring to unit volume, equation (2.4) transforms into

$$\rho_i(\mathbf{F}_i - (\operatorname{grad}\mu_i)_T) = \sum_{k\neq 1} R_{ik}\rho_k\rho_i(\mathbf{v}_k - \mathbf{v}_i). \tag{2.5}$$

One can see that Onsager's reciprocal relations follow from Newton's third law; exactly as Truesdell concluded [25]. To decide whether they are equivalent or not needs a detailed axiomatic investigation difficult for such a complex system. The possibilities are more transparent in case of simpler models.

3. Newton's second law

The simplest model we use is a small – point like – particle and its motion is discussed by recalling the ideas of thermodynamics. The idea of work and Galilean relativity are presumed but Newton's second and third axioms are not. Remember that the idea of work is much older than Newton's theory (Archimedes). The reciprocal relation and the possibility of reversible motion yields Newton's second axiom.

Assume the conservation of energy for a particle. Heat – unlike pure mechanical considerations – is also taken into account as friction or drag may always be present.

$$\frac{de}{dt} = I_q + \mathbf{F}\mathbf{v}. \tag{3.1}$$

Here e is the energy of the thermodynamic system (i.e. the particle and its immediate environment, e.g. in a fluid), I_q is the heat flow into, and $\mathbf{F}$ is the force exerted on it. The entropy is supposed to depend on the energy and on a – not yet specified – β-type vector variable;

$$s = s(e, \boldsymbol{\beta}). \tag{3.2}$$

The Morse – lemma [26] ensures that the form of the above function becomes

$$s = s(e - \frac{1}{2}\boldsymbol{\beta}^2) \tag{3.3}$$

with a suitable independent variable. The second law of thermodynamics reads

$$\frac{ds}{dt} = \frac{I_q}{T} + P_s \tag{3.4}$$

with non-negative entropy production;

$$P_s \geq 0\,.$$

If we do not want to take on the difficulties of discussing the possible details of heat exchange we had better suppose reversible heat effects, which results in

$$\frac{\partial s}{\partial e} = \frac{1}{T}\,.$$

The actual form of the entropy production is

$$P_s = \frac{1}{T}\left\{\mathbf{F}\mathbf{v} - \boldsymbol{\beta}\,\frac{d\boldsymbol{\beta}}{dt}\right\}. \tag{3.5}$$

The Onsager equations are

$$\begin{aligned} \mathbf{F} &= R_{11}\mathbf{v} + R_{12}\frac{d\boldsymbol{\beta}}{dt}, \\ -\boldsymbol{\beta} &= R_{21}\mathbf{v} + R_{22}\frac{d\boldsymbol{\beta}}{dt} \end{aligned} \tag{3.6}$$

with Casimir's reciprocal relation

$$R_{21} = -R_{12}\,. \tag{3.7}$$

The energy dissipation rate – TP_s – is given by

$$TP_s = R_{11}\mathbf{v}^2 + R_{22}\left\{\frac{d\boldsymbol{\beta}}{dt}\right\}^2 .$$

In the reversible limit both R_{11} and R_{22} equal zero; Onsager's equations turn into

$$\mathbf{F} = R_{12}\frac{d\boldsymbol{\beta}}{dt},$$
$$-\boldsymbol{\beta} = -R_{12}\mathbf{v}, \tag{3.8}$$

which results in

$$\mathbf{F} = R_{12}^2\frac{d\mathbf{v}}{dt}; \tag{3.9}$$

obviously, the positive quantity R_{12}^2 is m, the mass of the particle. The dropped coefficient R_{11} may give account of drag if the particle moves in a fluid, while the coefficient R_{22} results in a term approximating electromagnetic radiation [27] or emission of acoustic waves, etc.

The entropy function (3.3) in the reversible case is

$$s = s(e - \frac{1}{2}\,m\mathbf{v}^2)\,.$$

Newton's second law has been shown by Onsager's linear theory. The relativistic formulae result in a non-linear theory.

4. Newton's third law

Combining two particles and applying the previous result as well as the homogeneity of space lead to the third axiom if and only if the Onsager–Casimir reciprocal relation holds. For the sake of simplicity, suppose that no external forces act on the particles; the change of the energy is due to heat. The first law of thermodynamics reads

$$\frac{de}{dt} = I_q\,. \tag{4.1}$$

Take the entropy in the form

$$s = s\big(e - \frac{1}{2}m_1\mathbf{v}_1^2 - \frac{1}{2}m_2\mathbf{v}_1^2, \mathbf{r}_1 - \mathbf{r}_2\big). \tag{4.2}$$

The entropy function expresses the fact that the space is homogeneous and the interaction of the two particles is influenced by their distance. Dropping again the heat effects and evaluating the entropy production leads to

$$TP_s = \boldsymbol{\Gamma}(\mathbf{v}_1 - \mathbf{v}_2) - m_1\mathbf{v}_1\frac{d\mathbf{v}_1}{dt} - m_2\mathbf{v}_2\frac{d\mathbf{v}_2}{dt}$$

or rearranged

$$TP_s = \left(\boldsymbol{\Gamma} - m_1\frac{d\mathbf{v}_1}{dt}\right)\mathbf{v}_1 \;-\left(\boldsymbol{\Gamma} + m_2\frac{d\mathbf{v}_2}{dt}\right)\mathbf{v}_2, \tag{4.3}$$

where the symbol $\boldsymbol{\Gamma}$ stands for the gradient of the entropy with respect to $\mathbf{r}_1$;

$$\boldsymbol{\Gamma} = \frac{\partial s}{\partial(\mathbf{r}_1 - \mathbf{r}_2)}.$$

The Onsager equations are

$$\left(\mathbf{\Gamma} - m_1 \frac{d\mathbf{v}_1}{dt}\right) = R_{11}\mathbf{v}_1 + R_{12}\mathbf{v}_2,$$
$$-\left(\mathbf{\Gamma} + m_2 \frac{d\mathbf{v}_2}{dt}\right) = R_{21}\mathbf{v}_1 + R_{22}\mathbf{v}_2, \tag{4.4}$$

where Onsager's reciprocity is not assumed. Galilean invariance requires

$$R_{11} + R_{12} = 0,$$
$$R_{21} + R_{22} = 0,$$

as the left hand sides of the equations (4.4) contain only differences of position vectors and velocities—they are objective— while on the right hand sides absolute velocities stand except the above equalities hold. The sum of the equations—after multiplying both sides by -1—results

$$m_1 \frac{d\mathbf{v}_1}{dt} + m_2 \frac{d\mathbf{v}_2}{dt} = (R_{21} - R_{12})(\mathbf{v}_1 - \mathbf{v}_2), \tag{4.5}$$

which leads to the conservation of the linear momentum if and only if Onsager's reciprocity holds.

5. **Lorentz–force**

The idea of the electric field and a β-type field – generated by the motion of charges – is presumed. Onsager's reciprocal relation gives the formula of Lorentz's force together with the definition for the **B**-vector.

The balance equation for the internal energy $u = e - 1/2m\mathbf{v}^2$ reads

$$\frac{du}{dt} = I_q + q\mathbf{E}\mathbf{v}\,, \tag{5.1}$$

where q is the electric charge and $\mathbf{E}$ is the electric field strength. The entropy function is

$$s = s(u) \tag{5.2}$$

and the entropy production reads

$$P_s = \frac{1}{T} q\mathbf{E}\mathbf{v}. \tag{5.3}$$

The form of Onsager's equation is

$$q\mathbf{E} = \mathbf{R}\mathbf{v}\,, \tag{5.4}$$

where the resistivity tensor $\mathbf{R}$ depends on the aforementioned β-type field quantity $\boldsymbol{\beta}$, the tensorial order of which has not been specified. Onsager's reciprocal relation takes the form

$$\mathbf{R}^T(\boldsymbol{\beta}) = \mathbf{R}(-\boldsymbol{\beta}), \tag{5.5}$$

which says that the skew-symmetric part of the resistivity tensor is an odd function on $\boldsymbol{\beta}$ while the symmetric part is even. Denote the symmetric part by $\mathbf{R}^+$, and the vector invariant of the skew-symmetric part by $-q\mathbf{B}$. Equation (5.4) turns into

$$q\mathbf{E} = \mathbf{R}^+\mathbf{v} - q\mathbf{B} \times \mathbf{v}. \tag{5.6}$$

The last term on the right–hand side is proportional to the charge q; it can be reasoned the same way as for the electric force $q\mathbf{E}$. The quantity $\mathbf{B}$ is characteristic for the field and may be accepted – trivially – as the magnetic field strength. The first term on the right–hand side gives account of drag.

6. Conclusion

The arguments presented show clearly that a general phenomenological proof for the Onsager–Casimir reciprocal relations would be also proof for Newton's axioms and for the axioms of electromagnetism.

I hardly believe that it is possible.

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