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A counter-example for the heat-transfer condition in the Kinetic Theory of Gases

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Meccanica. — *A counter-example for the heat-transfer condition in the Kinetic Theory of Gases* (*). Nota (**) di MARIO PITTERI, presentata dal Socio straniero C. TRUESDELL.

RIASSUNTO. — In questa Nota si mostra, mediante un esempio, che la disuguaglianza di Maxwell sul trasferimento del calore non è valida, in generale, nella Teoria Cinetica dei Gas.

§ 1. INTRODUCTION.

In Chapter XI of their book [3], Truesdell and Muncaster mention a counter-exampe that I have constructed for the heat-transfer condition in the Kinetic Theory of Gases. In this Note I present that example. I assume the reader familiar with the content of the book [3], in particular with Chapter XI, and I use the same notations.

In § 2 I show by an example that Maxwell's heat-transfer condition

$$q_1 (\theta^W - \theta) \leqq 0 \quad \text{on } \partial\mathfrak{B} \tag{1.1}$$

does not necessarily hold for a body $\mathfrak{B}$ of kinetic gas confined by a *rough boundary*. *A fortiori*, it need not hold for a body confined by a linear boundary. Cercignani [1] and Darrozes and Guiraud [2] prove that, as a consequence of Boltzmann's H–theorem, a body of kinetic gas bounded by a linear wall satisfies the kinetic analogue of the heat-bath inequality:

$$\dot{H} \leqq \int_{\partial\mathfrak{B}} \frac{q_1}{2/3\, \varepsilon^W} \, dA . \tag{1.2}$$

We conclude that, nevertheless, the irreversibility expressed by that theorem is not completely consistent with the ideas of classical thermodynamics, which generally requires (1.1) to hold as well as (1.2).

§ 2. THE COUNTER-EXAMPLE.

At a given point on a perfectly rough material boundary for the kinetic gas and at a given time, the molecular density $F^e(\boldsymbol{v})$ for the emitted molecules is determined by the molecular density $F^i(\boldsymbol{v})$ for the incident ones through

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the relation

$$\mathrm{F}^e(\boldsymbol{v}) = \mathrm{AF}^{\mathrm{W}}(\boldsymbol{v}) \int_{c_1^* > 0} c_1^* \, \mathrm{F}^i(\boldsymbol{v}_*) \,, \qquad c_1 < 0 \,. \tag{2.1}$$

The condition

$$0 = \int_{c_1 > 0} c_1 \, \mathrm{F}^i(\boldsymbol{v}) + \int_{c_1 < 0} c_1 \, \mathrm{F}^e(\boldsymbol{v}) \tag{2.2}$$

fixes the value of the constant A in (2.1):

$$\mathrm{A} = \left(- \int_{c_1 < 0} c_1 \, \mathrm{F}^{\mathrm{W}}(\boldsymbol{v}) \right)^{-1} . \tag{2.3}$$

Putting

$$\Phi^{\mathrm{W}}(\boldsymbol{v}) = \mathrm{AF}^{\mathrm{W}}(\boldsymbol{v}) \,, \tag{2.4}$$

we can write $2\,q_1/\mathfrak{m}$, $2\,n\varepsilon$ and n in the following form:

$$\frac{2\,q_1}{\mathfrak{m}} = \int_{c_1 > 0} c_1 \, c^2 \, \mathrm{F}^i(\boldsymbol{v}) + \int_{c_1 < 0} c_1 \, c^2 \, \mathrm{F}^e(\boldsymbol{v}) = \tag{2.5}$$

$$= \int_{c_1 > 0} c_1 \, c^2 \left[\mathrm{F}^i(\boldsymbol{v}) - \Phi^{\mathrm{W}}(\boldsymbol{v}) \int_{c_1^* > 0} c_1^* \, \mathrm{F}^i(\boldsymbol{v}_*) \right] ,$$

$$2\,n\varepsilon = \int_{c_1 > 0} c^2 \, \mathrm{F}^i(\boldsymbol{v}) + \int_{c_1 < 0} c^2 \, \mathrm{F}^e(\boldsymbol{v}) = \tag{2.6}$$

$$= \int_{c_1 > 0} c^2 \left[\mathrm{F}^i(\boldsymbol{v}) + \Phi^{\mathrm{W}}(\boldsymbol{v}) \int_{c_1^* > 0} c_1^* \, \mathrm{F}^i(\boldsymbol{v}^*) \right] ,$$

$$n = \int_{c_1 > 0} (\mathrm{F}^i(\boldsymbol{v}) + \Phi^{\mathrm{W}}(\boldsymbol{v})) \,. \tag{2.7}$$

If there are a rough wall and a choice of $\mathrm{F}^i(\boldsymbol{v})$ such as to satisfy the relations

$$\int_{c_1 > 0} c_1 \, \mathrm{F}^i(\boldsymbol{v}) = 1$$

$$\int_{c_1 > 0} c_1 \, c^2 \, [\mathrm{F}^i(\boldsymbol{v}) - \Phi^{\mathrm{W}}(\boldsymbol{v})] > 0 \tag{2.8}$$

$$\int_{c_1 > 0} c^2 \, [\mathrm{F}^i(\boldsymbol{v}) + \Phi^{\mathrm{W}}(\boldsymbol{v})] < 2\,\varepsilon^{\mathrm{W}} \int_{c_1 > 0} (\mathrm{F}^i(\boldsymbol{v}) + \Phi^{\mathrm{W}}(\boldsymbol{v})) \,,$$

we conclude from (2.5) to (2.7) that

$$\frac{2\,q_1}{\mathfrak{m}} > 0 \qquad \text{and} \qquad 2\,n\,(\varepsilon - \varepsilon^{W}) < 0\,. \tag{2.9}$$

Hence that heat-transfer inequality (1.1), expressed in terms of the energetics ε and ε^{W} instead of the temperatures θ and θ^{W}, is violated.

PROPOSITION: *For any choice of* $F^{W}(\boldsymbol{v})$ *there is a continuously differentiable non-negative function* $F^{i}(\boldsymbol{v})$ *which satisfies* (2.8) *and is bounded by* $KF^{W}(\boldsymbol{v})$ *for large* $\|\boldsymbol{v}\|$ *and for some constant* $K > 0$.

Proof. I wish to satisfy (2.8) by means of a function $F^{i}(\boldsymbol{v})$ of the form

$$F^{i}(\boldsymbol{v}) = \Phi^{W}(\boldsymbol{v}) + f(\|\boldsymbol{v} - \boldsymbol{u}^{W}\|)\,, \tag{2.10}$$

where

$$f(x) = A_2\,e^{-(b^{W}/2)x^2} - A_3\,e^{-(b^{W}/3)x^2} + A_4\,e^{-(b^{W}/4)x^2} \tag{2.11}$$

and A_2, A_3, and A_4 are positive constants. The analogues of (2.6) and (2.7) for F^{W} imply that

$$\int\limits_{c_1>0} c^2\,\Phi^{W}(\boldsymbol{v}) = A\varepsilon^{W}\,n^{W}, \qquad \text{where} \quad n^{W} = 2\int\limits_{c_1>0} F^{W}(\boldsymbol{v})\,; \tag{2.12}$$

hence we can drop $\Phi^{W}(\boldsymbol{v})$ from both sides of $(2.8)_3$. Moreover, in this case $\boldsymbol{u} = \boldsymbol{u}^{W}$, as we can verify easily by using (2.2) and the fact that

$$n\boldsymbol{u} = \int\limits_{c_1>0} \boldsymbol{v}F^{i}(\boldsymbol{v}) + \int\limits_{c_1<0} \boldsymbol{v}F^{e}(\boldsymbol{v}) \tag{2.13}$$

and both F^{i} and F^{e} are functions of $\|\boldsymbol{v} - \boldsymbol{u}^{W}\|$. Then $\|\boldsymbol{v} - \boldsymbol{u}^{W}\| = c$ in (2.10). We can use in (2.8) the expression (2.10) for $F^{i}(\boldsymbol{v})$ and perform the integration over the angular variables. Moreover, taking into account (2.3) and (2.4), we reduce (2.8) to the form

$$\begin{aligned} &\int_0^\infty c^3 f(c)\,dc = 0\,, \\ &\int_0^\infty c^5 f(c)\,dc > 0\,, \\ &\int_0^\infty c^4 f(c)\,dc < 2\,\varepsilon^{W}\int_0^\infty c^2 f(c)\,dc\,, \end{aligned} \tag{2.14}$$

hence to the form

$$(2.15)\qquad \begin{aligned} &4A_2-9A_3+16A_4=0\,,\\ &2^3A_2-3^3A_3+4^3A_4>0\,,\\ &2^{5/2}A_2-3^{5/2}A_3+4^{5/2}A_4<2^{3/2}A_4-3^{3/2}A_3+4^{3/2}A_4\,. \end{aligned}$$

Here we have used the relations

$$(2.16)\qquad \begin{aligned} &\int_0^\infty c^{2n}\,e^{-bc^2}\,dc=\frac{1\cdot 3\cdot\cdots\cdot(2n-1)}{2^{n+1}\,b^n}\sqrt{\frac{\pi}{b}}\,,\\ &\int_0^\infty c^{2n+1}\,e^{-bc^2}\,dc=\frac{n!}{2\,b^{n+1}} \end{aligned}$$

and

$$(2.17)\qquad F^W=a^W\,e^{-(b^W/2)c^2}\quad,\quad \varepsilon^W=\frac{3}{4\,b^W}\,.$$

We can express A_4 in terms of A_2 and A_3 though $(2.15)_1$ and put the resulting expression into $(2.15)_{2,3}$. The latter reduce then to

$$(2.18)\qquad \frac{A_3}{A_2}>\alpha\quad,\quad\frac{A_3}{A_2}<\beta\,,$$

where

$$(2.19)\qquad \alpha=\frac{8}{9}\qquad\text{and}\qquad \beta=\frac{4}{3}\cdot\frac{3-\sqrt{2}}{9-4\sqrt{3}}\,.$$

It is easy to verify [1] that $\alpha<\beta$. Let us fix now any value of the ratio A_3/A_2 between α and β and determine A_4 as a function of A_2 through $(2.15)_1$. Then $f(c)$ is proportional to A_2, say $f(c)=A_2\hat{f}(c)$. Let $c_0=0$, let $c_1,\cdots,c_n$ be the critical points [2] of $\hat{f}(c)$ in $[0,+\infty)$ and let $\bar{c}$ be any one of $c_0,\cdots,c_n$ such that $\hat{f}(\bar{c})\leqq\hat{f}(c_i)$ for all i. If we choose A_2 such that $\Phi^W(\bar{c})+A_2\hat{f}(\bar{c})>0$, then (2.10) delivers a function $F^i(\boldsymbol{v})$ that satisfies (2.8) and moreover is non-negative, as necessary for a molecular density.

Remark 1. The function $F^i(\boldsymbol{v})$ that I have constructed is continuously differentiable and bounded by KF^W for large $\|\boldsymbol{v}\|$ and some constant K. Therefore it belongs to the set of functions $F^i(\boldsymbol{v})$ for which the heat-bath inequality (1.2) holds.

(1) In fact $3-\sqrt{2}>\frac{3}{2}$ and $9-4\sqrt{3}<2$. Therefore $\frac{3-\sqrt{2}}{9-4\sqrt{3}}>\frac{3}{4}$.

(2) $\hat{f}(c)$ is the composite function $P(g(c))$, where $P(y)$ is a polynomial in y and $g(c)$ is a negative exponential. Therefore it has a finite number of critical points.

Remark 2. The molecular density is in general a function $F = F(t, \boldsymbol{x}, \boldsymbol{v})$ not only of $\boldsymbol{v}$ but also of the position $\boldsymbol{x}$ and the time t. The variables $\boldsymbol{x}$ and t have been fixed in the considerations above and dropped from the notation, $\boldsymbol{x}$ being in particular the position of a point on $\partial\mathfrak{B}$. Because the choice of F at the initial time $t = 0$ is arbitrary, we can construct an $F(0, \boldsymbol{x}, \boldsymbol{v})$ such as to be continuously differentiable with respect to $\boldsymbol{x}$ and $\boldsymbol{v}$, and to have the form (2.10) at an arbitrary point $\boldsymbol{x}_0 \in \partial\mathfrak{B}$.

As a consequence of the proposition above, the motion of the kinetic gas violates the heat-transfer condition at $\boldsymbol{x}_0$ and at $t = 0$. This conclusion remains true at every point on $\partial\mathfrak{B}$ in a suitable neighborhood of $\boldsymbol{x}_0$ and over an interval of time, provided there be a continuous solution for the Maxwell-Boltzmann equation which is compatible with a rough boundary and with a class of initial conditions that allows us to fix $F(0, \boldsymbol{x}, \boldsymbol{v})$ at *one* point $\boldsymbol{x}_0$ on $\partial\mathfrak{B}$.

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