4. K. Ito, *Proc.Japan Acad.,Tokyo*, **22** (1946) .
5. Yu.L Klimontovich, *Theoretical and Mathematical Physics*, **96** (1993) 385–415.
6. G.I. Zmievskaya, A.A. Piarnpuu, and V.I. Shematovich, *Doklady Academii Nauk, USSR*, **266** (1982) 573–576.
7. G.I. Zmievskaya and T.V. Zin'kovskaya, *Doklady Academii Nauk, USSR*, **309** (1989) 301–305.
8. Pugachev V.S. and Sinitsin I.N., *Stochastic Differential System* (Nauka, Moscow, 1985).
9. V.A. Gribkov and G.I. Zmievskaya, in *Rarefied Gas Dynamics* (A.E. Beylich VCH Verlagsgesellschaft mbH, 1991), pp. 469–478.
10. G.I. Zmievskaya and T.V. Zin'kovskaya, in *XX International Conference on Phenomena in Ionized Gases* (, 1991), pp. 1303–1304.
11. T.A. Averina and S.S. Artemiev, *Doklady Academii Nauk, USSR*, **288** (1986) 777–780.
12. T.A. Averina and S.S. Artemiev, *Soviet Numerical Anal. Math. Modelling*, **3** (1988) 267–285.
13. L. Liboff, *Phys. Lett.*, **74A** (26/11/1979) .
14. L.G. Christophorou, in *Contributed Papers of XX International Conference on Phenomena in Ionized Gases, Pisa, Italy* (, 1991).
15. Krasheninnikov S.I. Zmievskaya G.I., Soboleva T.K., *Influence of Kinetic Effects on Divertor Plasma Parameters* (Keldysh Institute of Applied Mathematics Akademy of Sciences of the USSS, Moscow, 1990).
16. ed. Yu. S. Sigov, *Discrete Plasma Simulation* (Institute of Applied Mathematics, 1990).
17. S.I. Krasheninnikov, T.K. Soboleva, O.V. Batischev, G.I. Zmievskaya, V.D. Levchenko, P.A. Ovchenkov, Yu.S. Sigov, and I.I. Silaev, *Journal of Nuclear Materials*, **196-198** (1992) 899–903.
18. Schurz H. Kloeden P.E., Platen E., *Numerical Solution of SDE through Computer Experiment* (Springer-Verlag,Berlin, Heidelberg, New York, 1994).

From Kinetic Equation to Clausius Inequality

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1. Introduction

In the framework of classical mechanics the first equation of B.B.G.K.Y. hierarchy gives an exact and detailed microscopic description of a dynamical system. Even if this equation cannot be solved exactly, it still plays an important role insofar as it is the starting point for the derivation of the kinetic and momentum equations. We recall that the thermodynamic and the fluidodynamic equations provide a macroscopic description of many physical processes, yet it still is essential to establish the limits of their validity and to understand the approximations inherent in them.

The kinetic equation is useful to set these limits because the macroscopic equations are a reduced (or integrated) form of it. The purpose of this paper is to derive the second law of thermodynamics beginning with the first B.B.G.K.Y. equation, or derive the Boltzmann equation. Resorting to the H theorem it follows that the evolution of the entropy S is given by [1], [2]

$$\frac{\partial S}{\partial t} + \vec{\nabla} \cdot \vec{J}_s = \sigma$$

where

$$\vec{J}_s = \int_{R_3} \vec{v}\ f \ln f \, d\vec{v}$$

and σ is the entropy production. From this equation we will obtain the Clausius inequality that expresses the second law of thermodynamics.

2. Clausius' Inequality

Starting from the kinetic equation [3], [4]

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \frac{\partial f}{\partial \vec{r}} + \frac{\vec{F}}{m} \cdot \frac{\partial f}{\partial \vec{v}} = \left(\frac{\partial f}{\partial t}\right)_{coll} \tag{1}$$

where the r.h.s. takes into account the collision effects on the distribution function $f(\vec{r}, \vec{v}; t)$, we consider a system of particles interacting with each-other.

For the moment, we do not specify the r.h.s. term, which could be the Boltzmann collision integral, the Fokker-Plank collision term, or the BBGKY term depending on the

two-particle distribution function.

According to Boltzmann's theory, the entropy S is defined as $S = - K H_0$ [4], with k the Boltzmann constant and

$$H_0 = \int_V H \, d\vec{r} \tag{2}$$

where

$$H = \int_{R_3} f \ln f \, d\vec{v} \tag{3}$$

is the Boltzmann H function.

Relation (2) gives the space integration of the H function extended over a volume V. Thus the expression $S = - k H_0$ gives the average value of the entropy in the volume V.

From Eqs (1) and (3) it follows that:

$$\frac{\partial H}{\partial t} = \int_{R_3} (1 + \ln f) \left\{ \left(\frac{\partial f}{\partial t}\right)_{coll} - \vec{v} \cdot \frac{\partial f}{\partial \vec{r}} - \frac{\vec{F}}{m} \cdot \frac{\partial f}{\partial \vec{v}} \right\} d\vec{v}\ , \tag{4}$$

where last term in the above expression, i.e. the integral proportional to the force $\vec{F}$, vanishes if $\vec{F}$ is independent of the velocity $\vec{v}$, is the some as that in ref. [4].

We will extend this statement to the case of Lorentz force

$$\vec{F} = q\vec{E} + q\vec{v} \times \vec{B}, \tag{5}$$

so that the effects of an external magnetic field, $\vec{B}$, do not influence the time evolution of entropy. In fact, in this case, each component F_i, of $\vec{F}$, with i = x; y; z, does not depend on the component v_i of the velocity $\vec{v}$, and consequently

$$\frac{\partial}{\partial \vec{v}} \cdot \vec{F} = 0. \tag{6}$$

We also observe that

$$\int_{R_3} (1 + \ln f)\, \frac{\vec{F}(\vec{v})}{m} \cdot \frac{\partial f}{\partial \vec{v}}\, d\vec{v} = \int_{R_3} \frac{\vec{F}(\vec{v})}{m} \cdot \frac{\partial}{\partial \vec{v}} (f \ln f)\, d\vec{v} =$$

$$= -\frac{1}{m}\int_{R_3} f \ln f \, \frac{\partial}{\partial \vec{v}} \cdot \vec{F}(\vec{v})\, d\vec{v} = 0. \qquad (7)$$

This result has been obtained by integrating by parts and observing that

$$\left| f \ln f \right|_{-\infty}^{+\infty}, \qquad (8)$$

must vanish for each component of the velocity under "normal conditions". Thus, for the Lorentz force, Eq (7) vanishes since Eq (6) is obeyed.

Considering now the second term on r.h.s. of Eq (4), we introduce the peculiar velocity $\vec{c} = \vec{v} - \vec{v}_0$, where $\vec{v}_0$ is the mean velocity of the particles given by

$$\vec{v}_0 = \frac{1}{n}\int_{R_3} \vec{v} f(\vec{v})\, d\vec{v} \qquad (9)$$

and

$$n = \int_{R_3} f\, d\vec{v} \qquad (10)$$

is the number-density. We have

$$\int_{R_3} \vec{v} \cdot \frac{\partial}{\partial \vec{r}} (f \ln f)\, d\vec{v} = \frac{\partial}{\partial \vec{r}} \cdot \int_{R_3} \vec{v}_0 f \ln f \, d\vec{v} + \frac{\partial}{\partial \vec{r}} \cdot \int_{R_3} \vec{c} f \ln f \, d\vec{v} =$$

$$= \frac{\partial}{\partial \vec{r}} \cdot \left(\vec{v}_0 H\right) + \frac{\partial}{\partial \vec{r}} \cdot \int_{R_3} \vec{c} f \ln f \, d\vec{v} \ . \qquad (11)$$

The first term on the second line of (8) represents the variation of the function H due to the presence of the mean velocity $\vec{v}_0$ (i.e. an open system), whereas the meaning of the second term will be now elucidated.

Writing the distribution function as

$$f = f_0 + f_1 = f_0(1 + \Phi_1), \qquad (12)$$

where f_0 is taken to be a local Maxwellian, we observe that the distribution function can always be written in thi: form, without making any assumption concerning the function Φ_1.

Taking the logarithm of (12) we get

$$\ln f = \ln f_0 + \ln(1 + \Phi_1), \qquad (13)$$

recalling that

$$\ln f_0 = \ln n + \frac{3}{2} \ln \frac{m}{2\pi kT} - \frac{mc^2}{2kT}, \qquad (14)$$

and substituting the term ln f appearing in the integral in Eq (11) with Eqs (13) and (14), we obtain

$$\frac{\partial}{\partial \vec{r}} \cdot \int_{R_3} \vec{c} f \ln f \, d\vec{v} = \frac{\partial}{\partial \vec{r}} \cdot \left\{ \ln n \int_{R_3} \vec{c} f \, d\vec{v} + \frac{3}{2} \ln \frac{m}{2\pi kT} \int_{R_3} \vec{c} f \, d\vec{v} + \right.$$

$$\left. - \frac{1}{kT} \int_{R_3} \vec{c}\, \frac{1}{2} mc^2 f \, d\vec{v} + \int_{R_3} \vec{c} f \ln(1 + \Phi_1)\, d\vec{v} \right\} \qquad (15)$$

Observing that the mean value of the peculiar velocity is zero, the first two integrals on the r.h.s. of Eq (15) vanish, whereas the third term is equal to

$$\frac{\vec{q}}{kT} \qquad (16)$$

where $\vec{q}$ is the heat flux defined as

$$\vec{q} = \int_{R_3} \vec{c}\, \frac{1}{2} mc^2 f \, d\vec{v}. \qquad (17)$$

Moreover, if we assume

$$\Phi_1 = \frac{f_1}{f_0} << 1, \qquad (18)$$

we have

$$\ln(1 + \Phi_1) = \sum_{p=1}^{\infty} (-1)^{p+1} \frac{\Phi^p}{p} \cong \Phi_1 \qquad (19)$$

and the second term on the r.h.s. of Eq (4) becomes

$$\frac{\partial}{\partial \vec{r}} \cdot \int \vec{c}\, f \ln f\, d\vec{v} = \frac{\partial}{\partial \vec{r}} \cdot \left(\vec{v}_0\, H\right) - \frac{\partial}{\partial \vec{r}} \cdot \frac{\vec{q}}{kT} + \frac{\partial}{\partial \vec{r}} \cdot \vec{\Phi}_1 \qquad (20)$$

where

$$\vec{\Phi}_1 = \int_{R_3} \vec{c}\, f\, \Phi_1\, d\vec{v}. \qquad (21)$$

The last two terms in Eq (20) concern the divergence of the heat flux and the divergence of the vector $\vec{\Phi}_1$, which takes into account the "flux of the distortion" of the distribution function in comparison with the local Maxwellian.

In order to obtain the time evolution of the entropy of a system with volume V, we will integrate each term of Eq (4) with respect to $\vec{r}$. According to the divergence theorem

$$\int_V \frac{\partial}{\partial \vec{r}} \cdot \left(\vec{v}_0\, H\right) d\vec{r} = \int_\Sigma H\, \vec{v}_0 \cdot \hat{n}\, d\Sigma, \qquad (22a)$$

$$\int_V \frac{\partial}{\partial \vec{r}} \cdot \frac{\vec{q}}{kT}\, d\vec{r} = \int_\Sigma \frac{\vec{q}}{kT} \cdot \hat{n}\, d\Sigma \qquad (22b)$$

and

$$\int_V \frac{\partial}{\partial \vec{r}} \cdot \vec{\Phi}_1\, d\vec{r} = \int_\Sigma \vec{\Phi}_1 \cdot \hat{n}\, d\Sigma\ , \qquad (22c)$$

where Σ is the surface surrounding the volume V, and $\hat{n}$ is the outward unit vector normal of element $d\Sigma$.

Finally, we obtain

$$\frac{\partial S}{\partial t} - k \int_\Sigma H\, \vec{v}_0 \cdot \hat{n}\, d\sigma + \int_\Sigma \frac{\vec{q}}{T} \cdot \hat{n}\, d\sigma - k \int_\Sigma \vec{\Phi}_1 \cdot \hat{n}\, d\Sigma$$

$$= -k \int (1 + \ln f) \left(\frac{\partial f}{\partial t}\right)_{coll} d\vec{v}\, d\vec{r}. \qquad (23)$$

If we take as the Boltzmann integral, the collision term assume $\vec{v}_0 = 0$ (closed system, the matter is conserved [1], [2]), and neglect the flux $\vec{\Phi}_1$ (local Maxwellian approximation for ln f), Eq (23) reduces to

$$\frac{\partial S}{\partial t} + \frac{k}{4} \int \ln \frac{f f_B}{f' f'_B} \left(f' f'_B - f f_B\right) g\, b\, d\, b\, d\, \varphi\, d\vec{v}_B\, d\vec{v}\, d\vec{r} = - \int_\Sigma \frac{\vec{q}}{T} \cdot \hat{n}\, d\Sigma. \qquad (24)$$

By virtue of the Boltzmann H theorem, the second term on the l.h.s. is either negative or zero, so

$$\frac{\partial S'}{\partial t} \geq - \int_\Sigma \frac{q_\perp}{T}\, d\Sigma\ , \qquad (25)$$

which is the Clausius inequality, or the second law of thermodynamic. In fact, if $q_\perp < 0$ (heat flux entering into the closed system from its environment), the r.h.s. of Eq (24) is positive and Eq (25) must be obeyed.

On the contrary, if $q_\perp > 0$ (heat flux outcoming from the volume V), the r.h.s. of Eq (24) is negative and then $\frac{\partial S}{\partial t}$ can be positive, and then Eq (25) is true, or it can be negative. However

$$\left|\frac{\partial S}{\partial t}\right| < \int_\Sigma \frac{q_\perp}{T}\, d\Sigma.$$

Consequently, Eq (25) is obeyed also in this case. Finally, if f is the Maxwellian distribution, the collision term vanishes and the equal sign applies.

Hence, we have proved the existence of the inequality given by Eq (25), which expresses the second law of thermodynamics, starting from Boltzmann equation. Moreover, we have shown under what conditions Eq (25) can be obtained.

3. Clausius Inequality for a Fully Ionized Plasma

In the previous section, we derived the equation of the time evolution of the entropy for a single gas and, in particular, the Clausius inequality has been demonstrated under the hypothesis that the Boltzmann collision integral is a suitable approximation. This is certainly true for a perfect gas.

Now we wish to demonstrate the Clausius inequality for a fully ionized plasma (of only one type of positive ions with Z = 1) which - we recall - is not a perfect gas.

The kinetic equations for electrons and positive ions are

$$\frac{\partial f^-}{\partial t} + \vec{v} \cdot \frac{\partial f^-}{\partial \vec{r}} + \frac{\vec{F}^- + \vec{F}'^-}{m} \cdot \frac{\partial f^-}{\partial \vec{v}} = \left(\frac{\partial f^-}{\partial t}\right)_{coll} \tag{26a}$$

and

$$\frac{\partial f^+}{\partial t} + \vec{v} \cdot \frac{\partial f^+}{\partial \vec{r}} + \frac{\vec{F}^+ + \vec{F}'^+}{M} \cdot \frac{\partial f^+}{\partial \vec{v}} = \left(\frac{\partial f^+}{\partial t}\right)_{coll} \tag{26b}$$

Whereas respectively the forces $\vec{F}^{\mp}$ refer to the external fields, the forces $\vec{F}'^{\mp}$ are the self-consistent forces (Vlasov forces) given by

$$\vec{F}'^- = \int_V \vec{F}_{ee} (n^- - n^+) \, d\vec{r} \tag{27a}$$

and

$$\vec{F}'^+ = \int_V \vec{F}_{ii} (n^+ - n^-) \, d\vec{r}. \tag{27a}$$

$\vec{F}_{ee}$ and $\vec{F}_{ii}$ are the Coulomb forces for electron-electron and ion-ion interactions respectively. These expressions can be obtained on the assumption that the particles are not correlated; that is, the two-particle distribution function $f^{(2)}$ is given in terms of the product of two one-particle distribution functions [5], [6]

$$f^{(2)} (\vec{r}_1, \vec{r}_2, \vec{v}_1, \vec{v}_2, t) = f^{(1)} (\vec{r}_1, \vec{v}_1, t) \, f^{(1)} (\vec{r}_2, \vec{v}_2, t). \tag{28}$$

The r.h.s. of Eqs (26) takes into account the change in the distribution function due to the short-range collisions; i.e. the binary-collision rate, which is appropriately described by the Boltzmann collision integral.

Hence, in a plasma, the interactions have been properly divided roughly into two parts [5], [7]: one part, given by the self-consistent forces $\vec{F}'$, due to the long-range multi-particles interactions, and the other part connected with the short-range binary collisions.

Following the same procedure as in section 2, Eq (2) becomes

$$\frac{\partial H^-}{\partial t} = \int_{R_3} (1 + \ln f^-) \left\{ \left(\frac{\partial f^-}{\partial t}\right)_{coll} - \vec{v} \cdot \frac{\partial f^-}{\partial \vec{r}} - \frac{\vec{F}^- + \vec{F}'^-}{m} \cdot \frac{\partial f^-}{\partial \vec{v}} \right\} d\vec{v} \tag{29a}$$

for electrons and

$$\frac{\partial H^+}{\partial t} = \int_{R_3} (1 + \ln f^+) \left\{ \left(\frac{\partial f^+}{\partial t}\right)_{coll} - \vec{v} \cdot \frac{\partial f^+}{\partial \vec{r}} - \frac{\vec{F}^+ + \vec{F}'^+}{M} \cdot \frac{\partial f^+}{\partial \vec{v}} \right\} d\vec{v} \tag{29b}$$

for ions.

Since $\vec{F}^{\mp}$ are electrostatic forces, the independent of velocity and the terms proportional to the forces, again, vanish. Thus, Eq (23) for electrons and ions can be written as

$$\frac{\partial S^-}{\partial t} - k \int_\Sigma H^- \vec{v}_0^- \cdot \hat{n} \, d\Sigma + \int_\Sigma \frac{\vec{q}^-}{T^-} \cdot \hat{n} \, d\Sigma - k \int_\Sigma \vec{\Phi}_1^- \cdot \hat{n} \, d\Sigma =$$

$$= -k \int (1 + \ln f^-) \left(\frac{\partial f^-}{\partial t}\right)_{coll} d\vec{v} \, d\vec{r}, \tag{30a}$$

$$\frac{\partial S^+}{\partial t} - k \int_\Sigma H^+ \vec{v}_0^+ \cdot \hat{n} \, d\Sigma + \int_\Sigma \frac{\vec{q}^+}{T^+} \cdot \hat{n} \, d\Sigma - k \int_\Sigma \vec{\Phi}_1^+ \cdot \hat{n} \, d\Sigma =$$

$$= -k \int (1 + \ln f^+) \left(\frac{\partial f^+}{\partial t}\right)_{coll} d\vec{v} \, d\vec{r} \tag{30b}$$

For the case of vanishing average velocities, $\vec{v}_0^- = \vec{v}_0^+ = 0$, and $\ln f^{\mp}$ approximated by a local Maxwellian distribution, Eq (24) becomes

$$\frac{\partial S^-}{\partial t} + \frac{k}{4} \int \ln \frac{f^- f_B^-}{f'^- f_B'^-} (f'^- f_B'^- - f^- f_B^-) \, g^{--} b \, db \, d\varphi \, d\vec{v}_B \, d\vec{v} \, d\vec{r} +$$

$$+ \frac{k}{2} \int \ln \frac{f_B^-}{f_B'^-} (f_B'^- f_C'^+ - f_B^- f_C^+) \, g^{+-} b \, db \, d\varphi \, d\vec{v}_B \, d\vec{v}_C \, d\vec{r} = - \int_\Sigma \frac{\vec{q}^-}{T^-} \cdot \hat{n} \, d\Sigma, \tag{31a}$$

and

$$\frac{\partial S^+}{\partial t}+\frac{k}{4}\int \ln \frac{f^+f_C^+}{f^{+'}f_C^{+'}}\left(f^{+'}f_C^{+'}-f^+f_C^+\right) g^{++}b\, d b\, d \varphi\, d\vec{v}_C\, d\vec{v}\, d\vec{r} \,+$$

$$+\frac{k}{2}\int \ln \frac{f_C^+}{f_C^{+'}}\left(f_B^{'}f_C^{+'}-f_Bf_C^+\right) g^{-+}b\, d b\, d \varphi\, d\vec{v}_C\, d\vec{v}_B\, d\vec{r} = -\int_\Sigma \frac{\vec{q}^{\,+}}{T^+}\cdot\hat{n}\, d\Sigma, \qquad (31b)$$

where we assumed that the Boltzmann integral collision describes binary collisions [4]. We observe that, in general, the electron temperature T^- is different than T^+ (the ion temperature), $T^- \neq T^+$, as a consequence of the heat flux and the external forces.

Now, recalling that the entropy is additive, if $S = S^- + S^+$ is the entropy of the plasma, in addition to Eq (31a) and Eq (31b), we obtain [4]

$$\frac{\partial S}{\partial t}+\frac{k}{4}\left\{\int \ln \frac{f^-f_B^-}{f^{-'}f_B^{-'}}\left(f^{-'}f_B^{-'}-f^-f_B^-\right) g^{--}b\, d b\, d \varphi\, d\vec{v}_B\, d\vec{v}\, d\vec{r} \,+\right.$$

$$\left.+\int \ln \frac{f^+f_C^+}{f^{+'}f_C^{+'}}\left(f^{+'}f_C^{+'}-f^+f_C^+\right) g^{++}b\, d b\, d \varphi\, d\vec{v}_C\, d\vec{v}\, d\vec{r}\right\} +$$

$$+\frac{k}{2}\int \ln \frac{f_B^-f_C^+}{f_B^{-'}f_C^{+'}}\left(f_B^{-'}f_C^{+'}-f_B^-f_C^+\right) g^{-+}b\, d b\, d \varphi\, d\vec{v}_C\, d\vec{v}_B\, d\vec{r} =$$

$$= -\int_\Sigma \left(\frac{\vec{q}^{\,-}}{T^-}+\frac{\vec{q}^{\,+}}{T^+}\right)\cdot\hat{n}\, d\Sigma, \qquad (32)$$

Since the three integrals on the l.h.s. of Eq (32) cannot be positive, it follows that

$$\frac{\partial S}{\partial t} \geq -\int_\Sigma \left(\frac{q_\perp^-}{T^-}+\frac{q_\perp^+}{T^+}\right) d\Sigma, \qquad (33)$$

which express the Clausius inequality for a fully ionized plasma.

References

[1] Yu.L. Klimontovich, *Statistical Physics*, Harwood Academic Publishers, Chur Switzerland, 1986.

[2] L.C. Woods, *The Thermodynamics of Fluid Systems*, Claredon Press, Oxford, 1986.

[3] R.L. Liboff, *Kinetic Theory*, Prentice Hall, Englewood Cliffs, New Jersey, 1990.

[4] S. Chapman and T.G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, Cambridge University Press, New York, 1970.

[5] N.A. Krall and A.W. Trivelpiece, *Principles of Plasma Physics*, McGraw-Hill, New York, 1973.

[6] J.L. Delcroix, *Physique des Plasmas*, Dunod, Paris, 1963.

[7] L. Spitzer and R. Härm, "Phys. Rev.", 89, 977 (1953).