Colloquia: ICTT2009

Extension of the Clausius inequality to quantum gases from a kinetic equation approach

V. Molinari, D. Mostacci(*) and F. Pizzio

Laboratorio di Ingegneria Nucleare di Montecuccolino, Alma Mater Studiorum
Università di Bologna - via dei Colli 16, I-40136 Bologna, Italy

Summary. — Starting from the appropriate quantum kinetic equation, with the Boltzmann, Uehling and Uhlenbeck collision term, an expression is derived for the time evolution of entropy and, upon time integration, a corresponding entropy inequality is obtained valid for quantum systems of particles following either the Bose-Einstein, or the Fermi-Dirac statistics.

PACS `05.30.-d` – Quantum statistical mechanics.
PACS `05.30.Fk` – Fermion systems and electron gas.
PACS `05.30.Jp` – Boson systems.

1. – Introduction

Clausius inequality is a cornerstone of Thermodynamics: however its traditional applicability is confined to conductive and convective heat transfer in classical systems. Recent work has extended the inequality to include radiative transfer [1]. Still, the question of applicability of the inequality to quantum gases remains open. The present investigation aims at deriving the analogue of Clausius inequality for quantum systems, viz., systems of particles following either the Bose-Einstein, or the Fermi-Dirac statistics. To this effect, a volume V will be considered, bounded by a surface Σ, and containing an assembly of either fermions or bosons. For simplicity, the volume will be considered fixed in time. The particles may be subjected to an external force or to a self-consistent field, with the sole limitation that the only velocity-dependent force be the Lorentz force.

The tool needed for the present purpose is a quantum kinetic equation (QKE) with an appropriate collision term. To determine the required QKE, first recall how, according to De Broglie, Bohm and others, quantum mechanics (QM) may be interpreted causally, the wave function playing the role of the trajectory generating function. Hence, in contrast to

---

(*) E-mail: `domiziano.mostacci@unibo.it`

the more usual Copenhagen interpretation, Bohm's alternative view leads to individual systems in precisely defined kinetic states, obeying deterministic laws. In this framework, a QKE (quantum kinetic equation) can be derived exhibiting the familiar form of the classical kinetic theory. As this derivation can be found in several papers by the present authors, it will not be repeated here; the interested reader may find all further details in refs. [2-5]. The final result will be utilized in the present work, *i.e.* the kinetic equation for the single-particle distribution function f_1, for particle of mass m, that is

$$(1) \qquad \frac{\partial f_1}{\partial t} + \mathbf{v} \cdot \frac{\partial f_1}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \frac{\partial f_1}{\partial \mathbf{v}} = \left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}},$$

where the force term $\mathbf{F} = \mathbf{F}_Q + \mathbf{F}_{\text{oth}}$ is to be interpreted as the sum of the force $\mathbf{F}_Q$ due to the quantum potential U

$$(2) \qquad \mathbf{F}_Q = -\frac{\partial}{\partial \mathbf{r}} U = \frac{\partial}{\partial \mathbf{r}} \left(\frac{\hbar^2}{2m} \frac{\nabla^2 R}{R}\right)$$

and a possible force $\mathbf{F}_{\text{oth}}$ due to any other source. In (2), R is the modulus of the wave function and $\hbar = h/2\pi$, with h the Planck constant.

In the present case, close collisions are modeled with the Boltzmann, Uehling and Uhlenbeck (BUU) collision term which takes into account the effects of quantum statistics, and that can be written as follows (see [6], p. 371, [7] p. 333):

$$(3) \qquad \left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}}^{\text{BUU}} = \int_{\Re^3} \int_{4\pi} \left\{ f_1' f_{1B}' \left(1 \pm \frac{f_1}{g}\right) \left(1 \pm \frac{f_{1B}}{g}\right) \right.$$
$$\left. - f_1 f_{1B} \left(1 \pm \frac{f_1'}{g}\right) \left(1 \pm \frac{f_{1B}'}{g}\right) \right\} v_{\text{rel}} \sigma\left(v_{\text{rel}}, \mu\right) \mathrm{d}_2 \Omega \, \mathrm{d}_3 \mathbf{v}',$$

where the upper sign is to be taken for bosons, the lower one for fermions and the constant g is given by

$$(4) \qquad g = \gamma \frac{m^3}{h^3},$$

where γ is the statistical weight. Reduced quantities can be defined conveniently as follows:

$$(5) \qquad f = \frac{f_1}{g}; \quad f_B = \frac{f_{1B}}{g}; \qquad \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = \frac{1}{g} \left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}}^{\text{BUU}}.$$

The collision term then becomes

$$(6) \qquad \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = g \int_{\Re^3} \int_{4\pi} \left\{ f' f_B'(1 \pm f)(1 \pm f_B) \right.$$
$$\left. - f f_B(1 \pm f')(1 \pm f_B') \right\} v_{\text{rel}} \sigma(v_{\text{rel}}, \mu) \mathrm{d}_2 \Omega \mathrm{d}_3 \mathbf{v}'$$

and finally the dimensionless QKE is written as

$$(7) \qquad \frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}} - \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} - \frac{\mathbf{F}}{m} \cdot \frac{\partial f}{\partial \mathbf{v}}.$$

2. – H-function for quantum systems

Define as follows the H-function for the present quantum case (see [8] p. 377, [9]) (once again, upper sign for bosons, lower one for fermions):

$$(8) \qquad H_Q = g \int_{\Re^3} \{f \ln f \mp (1 \pm f) \ln(1 \pm f)\} \, \mathrm{d}_3 \mathbf{v}$$

and consider derivatives of H_Q with respect to α, where α stands for any one of the independent variables t, x, y or z:

$$(9) \qquad \frac{\partial H_Q}{\partial \alpha} = g \int_{\Re^3} \frac{\partial}{\partial \alpha} \left[f \ln f \mp (1 \pm f) \ln(1 \pm f) \right] \mathrm{d}_3 \mathbf{v}$$

$$= g \int_{\Re^3} \frac{\mathrm{d}}{\mathrm{d}f} \left[f \ln f \mp (1 \pm f) \ln(1 \pm f) \right] \frac{\partial f}{\partial \alpha} \mathrm{d}_3 \mathbf{v},$$

or

$$(10) \qquad \frac{\partial H_Q}{\partial \alpha} = g \int_{\Re^3} \left[\ln f - \ln(1 \pm f) \right] \frac{\partial f}{\partial \alpha} \mathrm{d}_3 \mathbf{v}.$$

Applying the above prescription to the time derivative, and introducing the time derivative of the distribution function as given by (7),

$$(11) \qquad \frac{\partial H_Q}{\partial t} = g \int_{\Re^3} \left[\ln f - \ln(1 \pm f) \right] \left\{ \left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}} - \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} - \frac{\mathbf{F}}{m} \cdot \frac{\partial f}{\partial \mathbf{v}} \right\} \mathrm{d}_3 \mathbf{v}.$$

Consider now the three integrals in eq. (11) separately. The first

$$(12) \qquad I_1 = g \int_{\Re^3} \left[\ln f - \ln(1 \pm f) \right] \left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}} \mathrm{d}_3 \mathbf{v}$$

can be seen to be always ≤ 0 (see, *e.g.*, [10]). The third,

$$(13) \qquad I_3 = -g \int_{\Re^3} \left[\ln f - \ln(1 \pm f) \right] \frac{\mathbf{F}}{m} \cdot \frac{\partial f}{\partial \mathbf{v}} \mathrm{d}_3 \mathbf{v}$$

vanishes, just as in the classical case, for forces not depending on velocity (which is the case for the Bohm force), and likewise for the Lorentz force; therefore it brings no contribution in the present case (see, *e.g.*, [11]). The second term is more conveniently

written in terms of the peculiar velocity $\mathbf{c} = \mathbf{v} - \mathbf{v_0}$, with $\mathbf{v_0}$ the velocity averaged over the distribution function.

$$(14) \qquad I_2 = g \int_{\Re^3} [\ln f - \ln(1 \pm f)] \, \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} \mathrm{d}_3 \mathbf{v}$$

$$= g \frac{\partial}{\partial \mathbf{r}} \cdot \int_{\Re^3} (\mathbf{v_0} + \mathbf{c}) \left[f \ln f \mp (1 \pm f) \ln(1 \pm f) \right] \mathrm{d}_3 \mathbf{c}.$$

Now,

$$(15) \qquad g \frac{\partial}{\partial \mathbf{r}} \cdot \int_{\Re^3} \mathbf{v_0} \left[f \ln f \mp (1 \pm f) \ln(1 \pm f) \right] \mathrm{d}_3 \mathbf{c} = \frac{\partial}{\partial \mathbf{r}} \cdot [\mathbf{v_0} H_Q].$$

since the term between brackets is the local value of H_Q. To calculate the integral with the peculiar velocity the following positions will be made:

$$(16) \qquad f = f_0 \Phi_1; \qquad 1 \pm f = (1 \pm f_0) \Phi_2,$$

where f_0 is the equilibrium distribution function (as usual, upper sign for bosons, lower one for fermions)

$$(17) \qquad f_0 = \frac{1}{e^{-\frac{\mu}{K_B T}} e^{\frac{mc^2}{2 K_B T}} \mp 1}.$$

Here no assumption is made on Φ_1, which is left therefore completely general: on the other hand, Φ_2 is just a shorthand, and is connected to Φ_1 by the following relation:

$$(18) \qquad \Phi_2 = \frac{1 \pm f_0 \Phi_1}{1 \pm f_0}.$$

Introducing these quantities,

$$(19) \qquad f \ln f \mp (1 \pm f) \ln(1 \pm f) = f \ln \frac{f_0}{1 \pm f_0} \mp \ln(1 \pm f_0) + f \ln \Phi_1 \mp (1 \pm f) \ln \Phi_2$$

and, given the expression (17) for f_0, the first logarithm on the r.h.s. of (19) is

$$(20) \qquad \ln \frac{f_0}{1 \pm f_0} = \frac{\mu}{K_B T} - \frac{mc^2}{2 K_B T},$$

so that the first term on the r.h.s. of (19), once inserted in the integral on the r.h.s. of (14), yields

$$(21) \qquad \int_{\Re^3} \mathbf{c} \left[\frac{\mu}{K_B T} - \frac{mc^2}{2 K_B T} \right] g f \mathrm{d}_3 \mathbf{c} = -\frac{1}{K_B T} \int_{\Re^3} \mathbf{c} \frac{mc^2}{2} g f \mathrm{d}_3 \mathbf{c} = -\frac{\mathbf{q}}{K_B T},$$

where $\mathbf{q}$ is seen to be the usual heat flux.

The second term on the r.h.s. of (19) leads to a vanishing integral on the r.h.s. of (14), since the integrand is an odd function in all three components of the peculiar velocity $\mathbf{c}$, so that

$$(22) \qquad g \int_{\Re^3} \mathbf{c} \ln \left[\frac{e^{-\frac{\mu}{K_B T}} e^{\frac{mc^2}{2K_B T}}}{e^{-\frac{\mu}{K_B T}} e^{\frac{mc^2}{2K_B T}} \mp 1} \right] \mathrm{d}_3 \mathbf{c} = 0.$$

The remainder of (19) yields a third term that has the dimensions of a flux and is connected with the departure of f from the equilibrium distribution. In the following it will be named $\mathbf{Z}$:

$$(23) \qquad g \int_{\Re^3} \mathbf{c} \left[f \ln \Phi_1 \mp (1 \pm f) \ln \Phi_2 \right] \mathrm{d}_3 \mathbf{c} = \mathbf{Z}.$$

So finally the time derivative of the H-function becomes

$$(24) \qquad \frac{\partial H_Q}{\partial t} = g \int_{\Re^3} \left[\ln f - \ln(1 \pm f) \right] \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} \mathrm{d}_3 \mathbf{v} - \frac{\partial}{\partial \mathbf{r}} \cdot \left[[\mathbf{v}_0 H_Q] - \frac{\mathbf{q}}{K_B T} + \mathbf{Z} \right].$$

3. – Entropy

Entropy per unit volume can be tied to the function H_Q [12]:

$$(25) \qquad S_V = -K_B H_Q$$

and hence the total entropy calculated as the integral over the volume V considered is given by

$$(26) \qquad S = \int_V S_V \mathrm{d}_3 \mathbf{r} = -K_B \int_V H_Q \mathrm{d}_3 \mathbf{r} = -K_B H_0^q.$$

This relation connects H_0^q, as defined implicitly in (26), with the entropy when the gas is in a uniform steady state: out of equilibrium, entropy is not defined in a thermodynamical sense. Yet, the concept of entropy may be generalized to non-equilibrium states, if the quantity is redefined by (25) and (26). The quantity so defined coincides with entropy when the system considered is at equilibrium (see, *e.g.*, [13], pp. 78-79, for an analogous discussion).

Hence, the time derivative of S can be calculated as (recalling that the volume V is fixed in time)

$$(27) \qquad \frac{\mathrm{d}S}{\mathrm{d}t} = -K_B \int_V \left\{ g \int_{\Re^3} \left[\ln f - \ln(1 \pm f) \right] \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} \mathrm{d}_3 \mathbf{v} \right.$$
$$\left. - \frac{\partial}{\partial \mathbf{r}} \cdot \left[[\mathbf{v}_0 H_Q] - \frac{\mathbf{q}}{K_B T} + \mathbf{Z} \right] \right\} \mathrm{d}_3 \mathbf{r}.$$

Referring to the surface Σ enclosing the volume V, and using the divergence theorem:

$$(28) \qquad \frac{\mathrm{d}S}{\mathrm{d}t} = -K_B \int_V \left\{ g \int_{\Re^3} [\ln f - \ln(1 \pm f)] \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} \mathrm{d}_3\mathbf{v} \right\} \mathrm{d}_3\mathbf{r}$$
$$+ \int_\Sigma \left[K_B[\mathbf{v}_0 H_Q] - \frac{\mathbf{q}}{T} + K_B \mathbf{Z} \right] \cdot \hat{\mathbf{n}} \mathrm{d}S.$$

Recalling that the integral between brackets in the first term of the r.h.s. is always non positive, and hence that the volume integral is always less or equal zero, the above expression can be rewritten as

$$(29) \qquad \frac{\mathrm{d}S}{\mathrm{d}t} - K_B \left| \int_V \left\{ g \int_{\Re^3} [\ln f - \ln(1 \pm f)] \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} \mathrm{d}_3\mathbf{v} \right\} \mathrm{d}_3\mathbf{r} \right| =$$
$$\int_\Sigma \left[K_B[\mathbf{v}_0 H_Q] - \frac{\mathbf{q}}{T} + K_B \mathbf{Z} \right] \cdot \hat{\mathbf{n}} \mathrm{d}S$$

or in "Clausius inequality" form,

$$(30) \qquad \frac{\mathrm{d}S}{\mathrm{d}t} \geq \int_\Sigma \mathbf{v}_0 [K_B H_Q] \cdot \hat{\mathbf{n}} \mathrm{d}S - \int_\Sigma \frac{\mathbf{q}}{T} \cdot \hat{\mathbf{n}} \mathrm{d}S + \int_\Sigma K_B \mathbf{Z} \cdot \hat{\mathbf{n}} \mathrm{d}S.$$

The first term contains the quantity $\mathbf{v}_0[K_B H_Q] = -\mathbf{v}_0 S_V$ which represents the convective flow of the entropy per unit surface and time: then the integral represents the inflow of entropy towards the volume V, carried by the incoming flow of particles (this term only exists if a collective motion through the boundary is present, that is, if the system is open).

The second term represents the inflow of the quantity $\frac{\mathbf{q}}{T}$ towards the volume V. This is the conductive inflow of entropy, to wit, the one due to thermal exchanges across the boundary. If, in particular, temperature does not vary over the surface Σ, the integral gives the familiar $\frac{\dot{Q}}{T}$ term (where $\dot{\mathbf{Q}}$ is the heat flow, the positive direction being, as usual, towards the volume V).

In particular, for a closed system with a uniform temperature over the heat exchange surface, (30) becomes simply

$$(31) \qquad \frac{\mathrm{d}S}{\mathrm{d}t} \geq \frac{\dot{\mathbf{Q}}}{T} + \int_\Sigma K_B \mathbf{Z} \cdot \hat{\mathbf{n}} \mathrm{d}S.$$

4. – Conclusions

Starting from the QKE, an equation has been derived for the time evolution of the H_0^q function, and hence, through (26), of the generalized entropy, in quantum systems. This equation highlights the various phenomena determining the behavior of the entropy in time. Among the different contributions, it is noteworthy to remark the one due to the flux $\mathbf{Z}$: this term could not appear in balance equations for entropy that have macroscopic equations as a starting point and therefore cannot account for effects connected with the departure of the distribution function from equilibrium. The terms in (28) highlight the processes leading, as a consequence, to the 2nd Principle of Thermodynamics. Finally, in this work the Clausius inequality has been derived from the QKE for a quantum system of bosons or fermions.

REFERENCES

[1] WRIGHT S. E., *Int. J. Eng. Sci.*, **45** (2007) 1007.
[2] MOSTACCI D., MOLINARI V. and PIZZIO F., *Transp. Theory Stat. Phys.*, **37** (2008) 589.
[3] MOSTACCI D., MOLINARI V. and PIZZIO F., *J. Stat. Mech.* (2009) P04008.
[4] MOSTACCI D., MOLINARI V. and PIZZIO F., *Europhys. Lett.*, **82** (2008) 20002.
[5] MOSTACCI D., MOLINARI V. and PIZZIO F., *Physica A*, **382** (2008) 6771.
[6] LIBOFF R. L., *Kinetic Theory. Classical, Quantum, Relativistic Descriptions* (Prentice Hall, Englewood Cliffs, U.S.A.) 1990, p. 371.
[7] CHAPMAN S. and COWLING T. G., *The Mathematical Theory of Non-Uniform Gases*, 3rd ed. (University Press, Cambridge, UK) 1961, p. 333.
[8] LIBOFF R. L., *Kinetic Theory. Classical, Quantum, Relativistic Descriptions* (Prentice Hall, Englewood Cliffs, U.S.A.) 1990, p. 377.
[9] TOLMAN R. C., *Principles of Statistical Mechanics* (University Press, Oxford) 1967, p. 456.
[10] HAUG H. and JAUHO A. P., *Quantum Kinetics in Transport and Optics of Semiconductors*, 2nd ed. (Springer, Berlin) 2008, pp. 5-8.
[11] DELCROIX J. L., *Plasma Physics* (Wiley & Sons, London) 1965, pp. 160-162.
[12] SOMMERFELD A., *Thermodynamics and Statistical Mechanics* (Academic Press, New York) 1964, p. 268.
[13] CHAPMAN S. and COWLING T. G., *The Mathematical Theory of Non-Uniform Gases*, 3rd ed. (University Press, Cambridge, UK) 1961, pp. 78-79.