

Giovanni Gallavotti (Ed.)

CIME Summer Schools

Statistical Mechanics

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ROBERTO CONTI

Giovanni Gallavotti (Ed.)

Statistical Mechanics

Lectures given at a Summer School of the
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STATISTICAL MECHANICS

Coordinatore: Prof. Giovanni Gallavotti

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P. CARTIER

Théorie de la mesure

Introduction à la mécanique statistique classique.

(Testo non pervenuto)

CENTRO INTERNAZIONALE MATEMATICO ESTIVO
(C.I.M.E.)

A SKETCH OF THE THEORY
OF THE BOLTZMANN EQUATION

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Corso tenuto a Bressanone dal 21 giugno al 24 giugno 1976

A Sketch of the Theory of the
Boltzmann equation

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In this seminar, I shall briefly review the theory of the Boltzmann equation. How the latter arises from the Liouville equation has been discussed in O.Lanford's lectures.

We shall write the Boltzmann equation in this form

$$\frac{\partial f}{\partial t} + \underline{x} \cdot \frac{\partial f}{\partial \underline{x}} = Q(f, f) \quad (1)$$

where t , \underline{x} , $\underline{\xi}$ denote the time, space and velocity variables, while f is the distribution function, normalized in such a way that

$$\int f d\underline{x} d\underline{\xi} = M \quad (2)$$

where M is the mass contained in the region over which the integration with respect to \underline{x} extends.

$Q(f, f)$ is the so called collision term, explicitly obtainable from the following definition

$$Q(f, g) = \frac{1}{2m} \int (f' g'_* + f'_* g' - f g_* - f_* g) B(\theta, V) d\underline{\xi}_* d\theta d\underline{e} \quad (3)$$

where $\underline{\xi}_*$ is an auxiliary velocity vector, V is the relative speed, i.e. the magnitude of the vector $\underline{V} = \underline{\xi} - \underline{\xi}_*$, $f' = f(\underline{\xi}')$, $g'_* = g(\underline{\xi}'_*)$ etc., where $\underline{\xi}'$ and $\underline{\xi}'_*$ are related to $\underline{\xi}$ and $\underline{\xi}_*$ through the relations expressing conservation of momentum and energy in a collision

$$\underline{\xi}' + \underline{\xi}'_* = \underline{\xi} + \underline{\xi}_* \quad (4)$$

$$\xi'^2 + \xi'^*{}^2 = \xi^2 + \xi_*^2 \quad (5)$$

equivalent to

$$\underline{\xi}' = \underline{\xi} - \underline{n} (\underline{n} \cdot \underline{V}) \quad (6)$$

$$\underline{\xi}'_* = \underline{\xi}_* + \underline{n} (\underline{n} \cdot \underline{V}) \quad (7)$$

where \underline{n} is a unit vector, whose polar angles are θ and ϵ in a polar coordinate system with \underline{V} as polar axis. Integration extends to all values of $\underline{\xi}_*$ and between 0 and $\pi/2$ with respect to θ , from 0 to 2π with respect to ϵ . Finally $B(\theta, V)$ is related to the differential cross section $\sigma(\theta, V)$ by the relation

$$B(\theta, V) = V \sin \theta \sigma(\theta, V) \quad (8)$$

and m is the mass of a gas molecule. For further details one should consult one of my books [1,2].

Eq. (1) is valid for monatomic molecules and is more general than the Boltzmann equation considered by Lanford in his lectures, because it is not restricted to rigid spheres, but allows molecules with any differential cross section. The case of rigid spheres is obtained by specializing $B(\theta, V)$ as follows

$$B(\theta, V) = V d^2 \sin\theta \cos\theta \quad (9)$$

where d is the sphere diameter. Another important case is offered by the so called Maxwell molecules.

The latter are classical point masses interacting with a central force inversely proportional to the fifth power of their mutual distance; as a consequence, it turns out that

$B(\theta, V)$ is independent of V .

It is clear that initial and boundary conditions are required in order to solve the Boltzmann equation, since the latter contains the time and space derivatives of f . The boundary conditions are particularly important since they describe the interaction of the gas molecules with solid walls, but particularly difficult to establish; the difficulties are due, mainly, to our lack of knowledge of the structure of the surface layers of solid bodies and hence of the interaction potential of the gas molecules with molecules of the solid. When a molecule impinges upon a surface, it is adsorbed and may form chemical bonds, dissociate, become ionized or displace surface atoms.

The simplest possible model of the gas-surface interaction is to assume that the molecules are specularly reflected at the solid boundary. This assumption is extremely unrealistic in general and can be used only in particular cases. In general, a molecule striking a surface at a velocity $\underline{\xi}'$ reflects from it at a velocity $\underline{\xi}$ which is strictly determined only if the path of the molecule within a wall can be computed exactly. This computation is impossible because it depends upon a great number of details, such as the locations and velocities of all the molecules of the wall. Hence we may only hope to compute the probability density $R(\underline{\xi}' \rightarrow \underline{\xi})$ that a molecule

striking the surface with velocity between $\underline{\xi}'$ and $\underline{\xi}' + d\underline{\xi}'$ re-emerges with velocity between $\underline{\xi}$ and $\underline{\xi} + d\underline{\xi}$. If R is known, it is easy to write the boundary condition for f [1,2] :

$$|\underline{\xi} \cdot \underline{n}| f(\underline{x}, \underline{\xi}, t) = \int_{\underline{\xi}' \cdot \underline{n} < 0} R(\underline{\xi}' \rightarrow \underline{\xi}) f(\underline{\xi}') |\underline{\xi}' \cdot \underline{n}| d\underline{\xi}' \quad (10)$$

where \underline{n} is the unit vector normal to the wall and we assumed the wall to be at rest (otherwise $\underline{\xi}$, $\underline{\xi}'$ must be replaced by $\underline{\xi} - \underline{u}_0$, $\underline{\xi}' - \underline{u}_0$, \underline{u}_0 denoting the wall's velocity.)

In general, R will be different at different points of the wall and different times; the dependence on \underline{x} and t is not shown explicitly to make the equations shorter.

If the wall restitutes all the gas molecules (i.e. it is non-porous and nonadsorbing), the total probability for an impinging molecule to be re-emitted, with no matter what velocity $\underline{\xi}$, is unity:

$$\int_{\underline{\xi}' \cdot \underline{n} < 0} R(\underline{\xi}' \rightarrow \underline{\xi}) d\underline{\xi}' = 1 \quad (11)$$

An obvious property of the kernel $R(\underline{\xi}' \rightarrow \underline{\xi})$ is that it cannot assume negative values

$$R(\underline{\xi}' \rightarrow \underline{\xi}) \geq 0 \quad (12)$$

Another basic property of the kernel R , which can be called the "reciprocity law" or the "detailed balance", is written as follows [1, 2] :

$$|\underline{\xi}' \cdot \underline{n}| f_0(\underline{\xi}') R(\underline{\xi}' \rightarrow \underline{\xi}) = |\underline{\xi} \cdot \underline{n}| R(-\underline{\xi} \rightarrow -\underline{\xi}') f_0(\underline{\xi}) \quad (13)$$

where $f_0(\underline{\xi})$ is proportional to $\exp[-\underline{\xi}^2/(2kT_0)]$, where T_0 is

the temperature of the wall (in other words, $f_0(\underline{\xi})$ is a Maxwellian distribution for a gas at rest at the temperature of the wall).

We note a simple consequence of reciprocity; if the incoming distribution is the wall Maxwellian f_0 and mass is conserved at the wall according to Eq. (11), then the distribution function of the emerging molecules is again f_0 or, in other words, the wall Maxwellian satisfies the boundary conditions. In fact, if we integrate Eq. (13) with respect to $\underline{\xi}'$ and use Eq. (11) we obtain

$$\int_{\underline{\xi} \cdot \underline{n} < 0} |\underline{\xi}' \cdot \underline{n}| f_0(\underline{\xi}') R(\underline{\xi}' \rightarrow \underline{\xi}) d\underline{\xi}' = |\underline{\xi} \cdot \underline{n}| f_0(\underline{\xi}) \quad (\underline{\xi} \cdot \underline{n} > 0) \quad (14)$$

and this equation proves our statement, according to Eq. (10). It is to be remarked that Eq. (14), although a consequence of Eq. (13) (when Eq. (11) holds) is less restrictive than Eq. (13) and could be satisfied even if Eq. (13) failed.

As a consequence of the above properties, one can prove [2] the following remarkable theorem:

Let $C(g)$ be a strictly convex continuous function of its argument g . Then for any scattering kernel $R(\underline{\xi}' \rightarrow \underline{\xi})$ satisfying Eqs. (11), (12), (14), the following inequality holds

$$\int f_0 \underline{\xi} \cdot \underline{n} C(g) d\underline{\xi} \leq 0 \quad (15)$$

where f_0 is the wall Maxwellian, $g = f/f_0$ and integration extends to the full ranges of values of the components of $\underline{\xi}$, the values of f for $\underline{\xi} \cdot \underline{n} > 0$ being related to those for $\underline{\xi} \cdot \underline{n} < 0$ through Eq. (1.6). Equality in Eq. (15) holds if and only if $f = g$ almost everywhere, unless $R(\underline{\xi}' \rightarrow \underline{\xi})$ is proportional

to a delta function.

As a corollary, the following inequality holds [2] :

$$\int \underline{\xi} \cdot \underline{n} f \log f d\underline{\xi} \leq -\frac{1}{R T_0} [q \cdot \underline{n}]_{\text{solid}} \quad (16)$$

where $[q \cdot \underline{n}]_{\text{solid}}$ denotes the normal heat flux fed into the gas by the solid constituting the wall and R is the gas constant.

We want to generalize the H-theorem, considered in O. Lanford's lectures, to the case of a gas bounded by solid walls which may or may not be at rest. To this end we define

$$\mathcal{H} = \int f \log f d\underline{\xi} \quad (17)$$

$$\mathcal{H}_i = \int \xi_i f \log f d\underline{\xi} \quad (i=1,2,3) \quad (18)$$

and observe that

$$\frac{\partial \mathcal{H}}{\partial t} + \frac{\partial \mathcal{H}_i}{\partial x_i} = \int \log f Q(f, f) d\underline{\xi} \quad (19)$$

(A sum with respect to i from 1 to 3 is understood).

Now, the following identity holds for any φ, f, g provided the integrals make sense:

$$\int \varphi Q(f, g) d\underline{\xi} = \frac{1}{8m} \int (\varphi + \varphi_* - \varphi' - \varphi'_*) (f' g'_* + f'_* g' - f g_* - f_* g) B(\theta, V) d\underline{\xi}_* d\theta d\varepsilon \quad (20)$$

This identity follows by straightforward manipulations; for details, see [1,2] .

Applying Eq. (20) to the case $\varphi = \log f, g = f$ ($f \geq 0$), we obtain

$$\int \log f Q(f, f) d\underline{\xi} = \frac{1}{8m} \left(\log \frac{f f_*}{f' f'_*} \right) \left(1 - \frac{f f_*}{f' f'_*} \right) f' f'_* B(\theta, V) d\underline{\xi}_* d\theta d\varepsilon \leq 0 \quad (21)$$

where the inequality follows from the fact that $(1-\lambda) \log \lambda$ is always negative, except for $\lambda = 1$, where it is zero. Hence equality in Eq. (21) is valid if and only if

$$ff_* = f'f'_* \quad (22)$$

or letting φ denote $\log f$

$$\varphi + \varphi_* = \varphi' + \varphi'_* \quad (23)$$

This equation is satisfied trivially by $\varphi = 1$ and, as a consequence of Eqs. (4) and (5), by $\varphi = \xi_i$ ($i = 1, 2, 3$) and $\varphi = \xi^2$; it can be shown [2] that there are no other linearly independent collision invariants (such is the name for the solutions of Eq. (23)). As a consequence, the most general distribution function satisfying Eq. (22) is given by

$$f = \exp(a + \underline{b} \cdot \underline{\xi} + c \xi^2) \quad (24)$$

where a, \underline{b}, c are constant. Eq. (24) can be rewritten in the following form

$$f = \rho (2\pi RT)^{-3/2} \exp\left[-\frac{(\underline{\xi} - \underline{v})^2}{2RT}\right] \quad (25)$$

where ρ, \underline{v}, T are new constants related to the previous ones and have the meaning of density, mass velocity and temperature associated with the distribution function f according to well-known formulas [1, 2]. Eq. (25) gives a Maxwellian distribution.

Eqs. (19) and (21) imply that

$$\frac{\partial \mathcal{H}}{\partial t} + \frac{\partial \mathcal{H}_i}{\partial \kappa_i} \leq 0 \quad (26)$$

where the equality sign applies if and only if f is Maxwellian, i.e. is given by Eq. (25).

If we integrate, both sides of Eq. (26) with respect to \underline{x} over a region R bounded by solid walls, we have, if the boundary ∂R of R moves with velocity \underline{u}_0 :

$$\frac{dH}{dt} - \int_{\partial R} (\mathcal{H} \cdot \underline{n} - \mathcal{H} \underline{u}_0 \cdot \underline{n}) dS \leq 0 \quad (27)$$

where dS is a surface element of the boundary ∂R and \underline{n} the inward normal. The second term in the integral comes from the fact that, if the boundary is moving, when forming the time derivative of H we have to take into account that the region of integration changes with time.

If we use Eq. (16), Eq. (27) becomes:

$$\frac{dH}{dt} \leq -\frac{1}{R} \int \frac{(q \cdot \underline{n})_{\text{solid}} dS}{T_0} \quad (28)$$

where we replaced \underline{F} by $\underline{F} - \underline{u}_0$ in Eq. (16) as required. Eq. (28) generalizes the H-theorem, showing that H decreases with time if there is no heat exchange between the gas and the walls. Also, equality in Eq. (28) applies if and only if f is Maxwellian. Eq. (28) suggests that H be interpreted as $-\eta/g$ where η is the entropy of the gas, since it satisfies the same inequality (Clausius-Duhem inequality). This identification is validated by evaluating H at equilibrium, when f must have the form indicated in Eq. (25); in such a case $\eta = -RH$ turns out to have the same dependence on g and T as the entropy in ordinary thermodynamics.

Let us now briefly examine the problem of solving the Boltzmann equation; because of the nonlinear nature of the collision term $Q(f, f)$, this is a difficult problem. A very particular

class of solutions is offered by Maxwellian distributions, Eq. (25), which describe states characterized by the fact that neither heat flux nor stresses other than isotropic pressure are present. If we want to describe more realistic nonequilibrium situations, we have to rely upon approximate methods, typically perturbation techniques. The simplest approach is to write

$$f = f_0 (1 + \varepsilon h_1 + \varepsilon^2 h_2 + \dots) \quad (29)$$

where f_0 is a Maxwellian and ε is a "small parameter", which may or may not appear in the Boltzmann equation. In the second case, ε will appear in the initial and boundary conditions and the equation for $h = h_1$ will be

$$\frac{\partial h}{\partial t} + \underline{\xi} \cdot \frac{\partial h}{\partial \underline{x}} = L h \quad (30)$$

where

$$L h = \frac{2}{f_0} Q(f_0, f_0 h) \quad (31)$$

is called the linearized Boltzmann operator. Eq. (30), in turn, is called linearized Boltzmann equation. If one introduces a Hilbert space \mathcal{H} where the scalar product is given by

$$(g, h) = \int f_0 g h d\underline{\xi} \quad (32)$$

then L is a symmetric operator in \mathcal{H} :

$$(g, L h) = (L g, h) \quad (33)$$

In addition, L is non-negative

$$(h, L h) \leq 0 \quad (34)$$

and the equality sign holds if and only if h is a collision invariant. In such a case

$$Lh = 0 \quad (35)$$

i.e. the collision invariants are eigenfunctions associated with the fivefold degenerate eigenvalue $\lambda = 0$ of the operator L . All these properties follow immediately from Eq. (31) and (20), if the circumstance that f_0 satisfies Eq. (22) is properly taken into account.

Eq. (35) suggests investigating the spectrum of L ; this problem arises when we look for the solution of Eq. (30) in the space homogeneous case ($\partial h / \partial \underline{x} = 0$). Eq. (34) shows that the spectrum is contained in the negative real semiaxis of the λ -plane; it turns out that the spectrum is extremely dependent upon the form of the choice of the function $B(\theta, V)$ appearing in Eq. (3). It is completely discrete for the case of Maxwell molecules, while it is partly discrete and partly continuous in the case of rigid spheres. For further details, one should consult Refs. [1,2].

An interesting problem arises when one investigates the solutions which do not depend on time t and two space coordinates, say x_2 and x_3 ; in this case one has to solve the equation

$$\xi_1 \frac{\partial h}{\partial x_1} = Lh \quad (36)$$

in the unknown $h = h(x_1, \xi_1, \xi_2, \xi_3) = h(x_1, \underline{\xi})$. The similarity between this equation and Eq. (30) with $\partial h / \partial \underline{x} = 0$ suggests that we look for solutions of the form

$$h = e^{\lambda x_1} g(\underline{\xi}) \quad (37)$$

where g satisfies

$$Lg = \lambda \xi_1 g \quad (38)$$

which is the analogue of $Lh = \lambda h$. The first question is whether the solutions of Eq. (38) are sufficient to construct the general solution of Eq. (36) by superposition. Next comes a study of the set of values of λ for which Eq. (38) has a solution (different from $g = 0$).

The problem here is more difficult because there is an interplay between L and the multiplicative operator ξ_1 . In addition the existence of the collision invariants satisfying Eq. (35) prevents L from being a strictly negative operator. In spite of this, it is possible to show [2] that the general solution of Eq. (36) can be written as follows:

$$h = \sum_{\alpha=0}^4 A_{\alpha} \psi_{\alpha} + \int_{-\lambda_0}^{\lambda_0} B_{\alpha} [L^{-1}(\xi_1 \psi_{\alpha}) + x_1 \psi_{\alpha}] + \left[\int_{-\lambda_0}^{\lambda_0} + \int_{\lambda_0}^{-\lambda_0} \right] g_{\lambda} \left(\frac{x}{\xi} \right) \cdot A_{\lambda} e^{\lambda x_1} d\lambda. \quad (A_{\alpha}, B_{\alpha} = \text{const.}; A_{\lambda} = A(\lambda)) \quad (39)$$

where g_{λ} are the eigensolutions of Eq. (38), ψ_{α} are the five collision invariants $\psi_0 = 1$, $\psi_i = \xi_i$ ($i = 1, 2, 3$), $\psi_4 = \xi^2 - 5R T_0$ (T_0 being the temperature in the basic Maxwellian f_0). Here we have assumed that the λ 's form a continuous set, otherwise the corresponding integral has to be replaced by the sum $\sum_{\lambda} e^{\lambda x_1} g_{\lambda} \left(\frac{x}{\xi} \right) A_{\lambda}$.

It is clear that the general solution given in Eq. (39) is made up of two parts, h_A and h_B , given by

$$h_A = \sum_{\alpha=0}^4 A_{\alpha} \psi_{\alpha} + \int_{-\lambda_0}^{\lambda_0} B_{\alpha} [x_1 \psi_{\alpha} + L^{-1}(\xi_1 \psi_{\alpha})] \quad (40)$$

$$h_B = \int_{-\lambda_\infty}^{-\lambda_0} + \int_{\lambda_0}^{\lambda_\infty} e^{\lambda x_1} g_\lambda\left(\frac{x}{\lambda}\right) A_\lambda d\lambda \quad (41)$$

where the "eigenvalues" λ are of the order of the inverse of the mean free path [2]. It is clear that h_B describes space transients which are of importance in the neighbourhood of boundaries and become negligible a few mean free paths far from them. The circumstance that Eq. (41) contains exponentials with both $\lambda > 0$ and $\lambda < 0$ is exactly what is required to describe a decay either for $x > \bar{x}_1$ or $x_1 < \bar{x}_1$, where \bar{x}_1 is the location of a boundary.

The general solution given by Eq. (39) then shows that, if the region where the gas is contained (either a half space or a slab of thickness d , because of the assumption that h is independent of two space coordinates) is much thicker than the mean free path ℓ , then h_B will be negligible except in boundary layers a few mean free paths thick. These layers receive the name of "Knudsen layers" or "Kinetic boundary layers". Outside them the solution is accurately described by the asymptotic part h_A , defined by Eq. (40); it can be shown [2] that if we compute the stress tensor and heat flux vectors arising from h_A , they turn out to be related to the velocity and temperature gradients by the Navier-Stokes-Fourier relations, with the following expressions for the viscosity coefficient μ and the heat conduction coefficient k :

$$\mu = -(RT_0)^{-1} \int \xi_1 \xi_2 L^{-1}(\xi_1 \xi_2) d\xi \quad (42)$$

$$k = (4RT_0^2)^{-1} \int \xi_1 \xi_2^2 L^{-1}[\xi_1 (\xi_2^2 - 5RT_0)] d\xi \quad (43)$$

These results can be extended to more general problems [3]

Very interesting problems arise when the inequality $d \gg \ell$ is not satisfied, i.e. the mean free path is comparable with the slab thickness [1, 2] ; their treatment is, however, beyond the limits of the present seminar.

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CENTRO INTERNAZIONALE MATEMATICO ESTIVO
(C.I.M.E.)

QUALITATIVE AND STATISTICAL THEORY
OF DISSIPATIVE SYSTEMS

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Qualitative and Statistical Theory
of Dissipative Systems

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Chapter I. Elementary Qualitative Theory of Differential Equations.

This series of lectures will be concerned with the statistical theory of dissipative systems and, at least metaphorically, with its applications to hydrodynamics. The principal objective will be to try to clarify the question of how to construct the appropriate ensemble for the statistical theory of turbulence. We will not, however, come to this point for some time. It should be noted at the outset that the relevance of our discussion to the theory of turbulence is dependent on the guess that, despite the fact that fluid flow problems have infinite-dimensional state spaces, the important phenomena are essentially finite dimensional.* This point of view is not universally accepted [4]. On the other hand, the theory is not restricted to fluid flow problems; it also applies to a large number of model systems arising, for example, in mathematical biology [7].

The methods we will discuss are limited in that they appear not to have anything to say about such traditionally central issues as the characteristic spatial properties of turbulent flow, the dynamics of vorticity, etc. Instead, they attempt to clarify the apparently stochastic character of the flow and its peculiar dependence-independence on initial conditions. To explain what this means, let us look briefly at two important but not completely precise distinctions — between conservative and dissipative systems and between stable and unstable ones. Intuitively, when we say that a system is conservative, we mean that, once it has been started in motion, it will keep going forever without

* It may be that this ceases to be true for "fully developed turbulence" and that what we say here applies to turbulence at relatively low Reynolds numbers and not at high Reynolds numbers.

further external driving. Mathematically this is usually reflected in the fact that the equations of motion may be written in Hamiltonian form, with the consequent conservation of energy and phase space volume. Among numerous examples, let us note

- a. the Newtonian two-body problem
- b. the motion of a finite number of frictionless and perfectly elastic billiard balls on a rectangular table.

These examples illustrate the distinction between stable and unstable systems. The Newtonian two-body system is stable in the sense that the effects of small perturbations of the initial conditions grow slowly if at all and hence that long-term predictions about the state of the system are possible on the basis of approximate information about the initial state. In the billiard system, on the other hand, even very small changes in the initial state are soon amplified so that they have large effects. If the system is started out repeatedly, in almost but not exactly the same way, the long-term histories will almost certainly be totally different. In this sense, although the motion is strictly speaking deterministic, it is from a practical point of view effectively random; the coarse features of the state of the system at large times depend on unobservably fine details of the state at time zero.

Consider next dissipative systems. Intuitively, these have some sort of frictional mechanism which tends to damp out motion and must therefore be driven by external forces if they are not simply to stop. A mathematical transcription of this notion which is as general as the correspondence "conservative \equiv Hamiltonian" does not seem to exist, but it is generally not difficult to agree on whether a given dynamical system is dissipative or not. We will consider systems driven by time-