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Autor: Wu, Ta-You

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The Theory of Irreversible Processes in Neutral and Ionized Gases

by **Ta-You Wu**
National Research Council, Ottawa, Canada
and Laboratoire de Physique, Université de Lausanne, Switzerland

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Abstract. The recent theory of irreversible processes in gases developed by PRIGOGINE and BALESCU is discussed. In this theory, the distribution function $f_N(x_1, \ldots, x_N, p_1 \ldots, p_N, t)$ is expressed in a Fourier series and the Liouville equation becomes an infinite system of equations for the Fourier components of f_N. The system is iterated to all powers of the intermolecular potential $\lambda V(|x_i - x_j|)$. By examining the asymptotic dependences of the various terms, to any given order in λ, on N, the volume and time in the limits $N \to \infty$, volume $\to \infty$, number density finite, $t \to \infty$, and by retaining only the dominant terms, some of the Fourier components are partially decoupled from the rest and are given by a closed set of 'reduced equations'. The main contention of the theory is that, by passing to the limits above, the reduced equations will describe the irreversible approach to thermodynamical equilibrium. It is shown in the present note that, without an additional hypothesis, these reduced equations will remain invariant upon time reversal and hence will not describe irreversible processes. On the same basis and also from a more technical point of view, the work of BALESCU on irreversible processes in fully ionized gases is discussed.

I. Introduction

Recently in a series of papers [1-5]), PRIGOGINE and BALESCU have developed a theory of irreversible processes in gases. The main ideas are as follows. The distribution function $f_N(x_1, \ldots x_N, p_1, \ldots p_N, t)$ is expressed in a Fourier series. The Liouville equation for f_N then becomes an infinite system of equations for the Fourier components of f_N. These equations are to be iterated, thereby leading to terms in all powers of the intermolecular interaction $\lambda V(|x_i - x_j|)$. The dependences of the various terms, to any given power of λ, on N, c and t in the limits

$$\begin{aligned} &N \to \infty\,, \\ &\text{volume} = 8\,\pi^3\,\Omega \to \infty\,, \qquad \text{with } c = N/\text{volume} = \text{finite}\,, \qquad (1) \\ &\text{time } t \to \infty\,, \end{aligned}$$

are studied. If only the dominant terms are retained, then the system of equations is, in the limits (1) above, partially decoupled and some of the Fourier components are given by a finite, closed set of equations, called the 'reduced equations'. This decoupling is interpreted as corresponding to an irreversibility in the time evolution of the system, and the reduced equations are taken to describe the irreversible approach to thermodynamical equilibrium. In particular, from the reduced equations involving only the 'diagonal transitions' arising from 'cycles', the so-called 'Master Equation' is derived for the momentum distribution function in the asymptotic sense (1) above.

The purpose of the present note is to study this interesting theory more closely, and to show that, if no additional hypothesis is introduced, these reduced equations will remain invariant upon time reversal and therefore cannot describe irreversible processes.

II. Resume of the theory of Prigogine and Balescu

To facilitate discussions, we shall briefly sketch the important steps of the theory. f_N is expressed (Eqs. (2.5) of ref. 1 and (1.2) of ref. 3) in a Fourier series. In the following, all the k, l, g, p are vectors, and $l \cdot g$, $k\,x$ scalar products.

$$f_N = (8\,\pi^3\,\Omega)^{-N} \Big\{ \varrho_0 + \frac{1}{\Omega} \sum_j^N \sum_{k_j}{}' \varrho_k^j \exp i\,k_j \left(x_j - \frac{p_j}{M} t\right) +$$

$$+ \frac{1}{\Omega^2} \sum_{j<m} \sum_{k_j}{}' \sum_{k_m}{}' [\varrho_{k_j k_m}^{jm} + \Omega\,\delta_{k_j + k_m}\,\varrho_{k_j, -k_j}^{jm}] \exp \Big[i\,k_j \left(x_j - \frac{p_j}{M}\,t\right) +$$

$$+ i\,k_m \left(x_m - \frac{p_m}{M}\right)\Big] + \ldots. \tag{2}$$

The Fourier components ϱ are functions of $p_1, \ldots p_N$ and t.

In particular,

$$\varrho_0 \equiv \varrho_0\,(p_1, \ldots p_N, t) = \int f_N\,(dq)^N\,.$$

Putting (2) and the Fourier expansion of the interaction

$$\lambda\,V\,(|x_m - x_j|) = \frac{\lambda}{\Omega} \sum_l V(l) \exp[i\,l\,(x_m - x_j)] \tag{3}$$

into the Liouville equation leads to an infinite system of equations, which is essentially equivalent to the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy, since both come from the Liouville equation. The first two members of the system can be written down:

$$\frac{\partial \varrho_0}{\partial t} = \frac{\lambda}{\Omega} \sum_{j<m} \sum_{l} V(l)\, i\, \beta_{jm} \exp(i\, \alpha_{jm}\, t)\, \varrho^{jm}_{-l\,l} \,, \tag{4}$$

$$\frac{\partial \varrho^{jm}_{-l\,l}}{\partial t} = -\lambda\, V(l) \exp(-i\, \alpha_{jm}\, t)\, i\, \beta_{jm}\, \varrho_0 + \dots \,, \tag{5}$$

where

$$\beta_{jm} \equiv (l \cdot D_{jm}) \equiv l \cdot \left(\frac{\partial}{\partial p_j} - \frac{\partial}{\partial p_m}\right), \tag{6}$$

$$\alpha_{jm} \equiv (l \cdot g_{jm}) \equiv l \cdot \frac{(p_j - p_m)}{M} \,, \tag{7}$$

and the dots in (5) represent terms coming from $\varrho^{jm}_{-l\,l}$, $\varrho^{jm}_{k\,k'}$, $\varrho^{jmn}_{k\,k'\,k''}$, $\varrho^{jmno}_{k\,k'\,k''\,k'''}$ (where $\Sigma\, k = 0$). On iterating between (4) and (5) and from the asymptotic dependences of the various terms on N, c and t, it is readily found that the dominant terms come from the 'diagonal transitions' (i.e., ϱ_0 contributing to $\partial \varrho_0/\partial t$, for example). On considering these dominant terms only, one obtains a pair of equations consisting of (4) and the following

$$\frac{\partial \varrho^{jm}_{-l\,l}}{\partial t} = -\lambda\, V(l) \exp(-i\, \alpha_{jm}\, t)\, i\, \beta_{jm}\, \varrho_0\, (p_1, \dots p_N, t) \,. \tag{8}$$

On iterating (4) and (8), one obtains the series

$$\begin{aligned}
\varrho_0(t) = {} & \varrho_0(0) + \left(\frac{\lambda}{\Omega}\right)^2 \sum_{j<m} \sum_{l} |V(l)|^2 \beta \int_0^t e^{i\alpha t'}\, dt' \int_0^{t'} e^{-i\alpha t_1}\, dt_1\, \beta\, \varrho_0(0) + \\
& + \dots \\
& + \left\{\left(\frac{\lambda}{\Omega}\right)^2 \sum_{j<m} \sum_{l} |V(l)|^2 \beta \int_0^t e^{i\alpha t'_{n+1}}\, dt'_{n+1} \int_0^{t'_{n+1}} e^{-i\alpha t_n}\, dt_n\, \beta\right\} \times \\
& \times \left\{\left(\frac{\lambda}{\Omega}\right)^2 \sum_{j<m} \sum_{l} |V(l)|^2 \beta \int_0^{t_n} e^{i\alpha t_n'}\, dt'_n \int_0^{t_n'} e^{-i\alpha t_{n-1}}\, dt_{n-1}\, \beta\right\} \times \dots \\
& \times \left\{\left(\frac{\lambda}{\Omega}\right)^2 \sum_{j<m} \sum_{l} |V(l)|^2 \beta \int_0^{t_2} e^{i\alpha t_2'}\, dt'_2 \int_0^{t_2'} e^{-i\alpha t_1}\, dt_1\, \beta\right\} \varrho(0) + \dots \,,
\end{aligned} \tag{9}$$

where for brevity we have written $\alpha \equiv \alpha_{jm}$, $\beta \equiv \beta_{jm}$ and

$$\varrho_0(0) = \varrho_0(p_1, \dots, p_N, t = 0) \,.$$

For the λ^2 term, these authors give, asymptotically for $t \to \infty$,

$$\lim_{t\to\infty} \frac{\lambda^2}{\Omega} \sum_{j<m} \int dl\, |V(l)|^2\, \beta_{jm} \int_0^t dt'\, e^{i\,\alpha_{jm} t'} \int_0^{t'} e^{-i\alpha_{jm} t_1}\, dt_1\, \beta_{jm}\, \varrho_0(0) =$$

$$= \frac{\lambda^2}{\Omega} \sum_{j<m} \int dl\, |V(l)|^2\, \beta_{jm} \int_0^t dt \lim_{t'\to\infty} \int_0^{t'} e^{i\,\alpha_{jm}(t'-t_1)}\, dt_1\, \beta_{jm}\, \varrho_0(0) =$$

$$= t\, \frac{\lambda^2}{\Omega} \sum_{j<m} \int dl\, |V(l)|^2\, \beta_{jm}\, \pi\, \delta(\alpha_{jm})\, \beta_{jm}\, \varrho_0(0)\,, \tag{10}$$

use having been made of the relation

$$\lim_{t\to\infty} \int_0^t e^{i\,\alpha x}\, dx = \delta_+(\alpha) = \pi\, \delta(\alpha) + i\, \frac{P}{\alpha}\,. \tag{11}$$

Similarly, by allowing the intermediate limits $t'_1, t'_2, \ldots t'_n$ in (9) to go to ∞ *first* and then performing the integrations over $t_1, t_2, \ldots t_n$ as in (10), they obtain for the series (9)

$$\varrho_0(t) = \exp\Big[t \sum_{j<m} 0_{2,jm}\Big]\, \varrho_0(0)\,, \tag{12}$$

where

$$0_{2,jm} = \frac{\lambda^2}{\Omega} \int dl\, |V(l)|^2\, \beta_{jm}\, \pi\, \delta(\alpha_{jm})\, \beta_{jm} \tag{13}$$

is an operator operating of $p_1, p_2, \ldots p_N$ according to (6) and (7). From (12), they arrive at the following equation

$$\frac{\partial \varrho_0}{\partial t} = \frac{\pi\, \lambda^2}{\Omega} \sum_{j<m} \int dl\, |V(l)|^2\, l \cdot \Big(\frac{\partial}{\partial p_j} - \frac{\partial}{\partial p_m}\Big)\, \delta\Big(l\, \frac{p_j - p_m}{M}\Big)\, l \cdot \Big(\frac{\partial}{\partial p_j} - \frac{\partial}{\partial p_m}\Big) \times$$

$$\times\, \varrho_0\, (p_1 \ldots p_N, t)\,, \tag{14}$$

which is their 'Master Equation' for the momentum distribution function $\varrho_0(p_1, \ldots, p_N, t)$ in the limits (1)*).

III. Discussions of the theory

We wish now to point out the following curious result in the theory above. One starts from the Liouville equation which is invariant upon time reversal and thus describes only reversible processes. The infinite system of equations for the Fourier components of f_N, of which (4) and (5) are two members, is hence also invariant upon time reversal. It is

*) Equations (10), (13) here are Equations (5.8) of ref. 1, and (12), (14) are (3.2), (3.4) respectively of ref. 2.

seen from the explicit forms of (4) and the 'reduced' equation (8) that the pair (4) and (8) are also invariant upon time reversal. Then how is it possible to obtain from (4) and (8), without the introduction of an additional hypothesis, the 'Master Equation' (14) which is *not* invariant upon time reversal? Of course the main result of the whole theory, namely, that the 'reduced equations' in the limits (1) describe irreversible processes, depends on this non-invariance of equations such as (14) upon time reversal.

A little closer examination of theory, as summarized in the preceding section, shows that this curious result arises entirely from the manner in which the integrations of (10) and (9) have been carried out. From the 'telescope' nature of the integrals in (10) and (9), one should have obtained for (10)

$$\lim_{t\to\infty} \frac{\lambda^2}{\Omega} \sum_{j<m} \int dl \, |V(l)|^2 \, \beta_{j\,m} \int e^{i\alpha_{j\,m} t'} \frac{e^{-i\alpha_{j\,m} t'}-1}{-i\,\alpha_{j\,m}} \, \beta_{j\,m}\, \varrho_0(0) =$$

$$= \frac{\lambda^2}{\Omega} \sum_{j<m} \int dl \, |V(l)|^2 \, \beta_{j\,m} \frac{t-\delta_+(\alpha_{j\,m})}{-i\,\alpha_{j\,m}} \, \beta_{j\,m}\, \varrho_0(0) =$$

$$= t \frac{\lambda^2}{\Omega} \sum_{j<m} \int dl \, |V(l)|^2 \, \beta_{j\,m} \frac{1}{-i\,\alpha_{j\,m}} \, \beta_{j\,m}\, \varrho_0(0) \,. \tag{15}$$

The corresponding changes in (13) and (14) are the replacement of $\delta(\alpha_{j\,m})$ by $-1/i\,\alpha_{j\,m}$, leading to

$$0_{2,j\,m} = \frac{\lambda^2}{\Omega} \int dl \, |V(l)|^2 \, \beta_{j\,m} \frac{1}{i\,\alpha_{j\,m}} \, \beta_{j\,m} \,, \tag{16}$$

and

$$\frac{\partial p_0}{\partial t} = \frac{\lambda^2}{\Omega} \sum_{j<m} \int dl \, |V(l)|^2 \, l \left(\frac{\partial}{\partial p_j} - \frac{\partial}{\partial p_m}\right) \frac{-1}{i\,(l\cdot g_{j\,m})} \, l \cdot \left(\frac{\partial}{\partial p_j} - \frac{\partial}{\partial p_j}\right) \times$$
$$\times \, \varrho_0\,(p_1 \ldots p_N, t) \,. \tag{17}$$

The difference between (15), (16), (17) and (10), (13), (14) respectively lies not only in the nature of the singularity, but much more importantly in the symmetry with respect to time reversal. It is seen from (17) that, in contrast to (14), it is invariant upon time reversal and therefore cannot describe irreversible processes. This is just as expected, since, without introducing any additional hypothesis one should not arrive at an equation having a different symmetry in time such as (14), by starting from a time-reversible theory, such as the Liouville equation.

It remains to see whether the integration procedure made in (10) thereby leading to the $\delta(\alpha_{j\,m}) = \delta(l \cdot g_{j\,m})$ and consequently to the Master Equation (14), can be taken on a postulational basis for a theory of irreversible processes as summarized in the two preceding sections. For this purpose, it may first be noted that the dropping of terms in the iteration of the infinite system of equations (4), (5), ..., does not affect the invariance property with respect to time reversal, as is seen from (4) and (8). If irreversibility, according to the theory of these authors, is consequent upon the dropping of terms in the limits (1) to form the 'reduced equations', then, by including more and more terms one should get in the limit (of including all terms) the original complete (Liouville) system which describes reversible processes. Such a *change in the symmetry property* with respect to time reversal cannot be brought about by dropping or including terms, as noted above. It is easy to see that if the procedure of integration in (10) is postulated leading to the $\delta(l \cdot g_{jm})$ consistently everywhere in the theory, one will *not* pass back from (14), by the inclusion of more terms, to an equation which is invariant upon time reversible. Thus the procedure of introducing irreversibility through the manner of integration in (10) is not consistent with the theory that the dropping of terms (in the limit (1)) to form the 'reduced equations' from the original infinite system leads to irreversibility.

In this connection, we may perhaps emphasize the distinction between (1) understanding the reason for *irreversibility* in the *statistical* sense, and (2) the formulation of a basic *equation* which describes the irreversible, monotonic approach to equilibrium in the macroscopic view. The former is well known since BOLTZMANN, GIBBS and EHRENFEST. From the Liouville equation, one can understand the observed macroscopic irreversibility and fluctuations, but one does not have an equation which describes only and explicitly irreversible processes. To obtain such an equation BOLTZMANN introduced the Stosszahlansatz. But if one attempts to start from the Liouville equations and to arrive at the Boltzmann equation, then it has been shown by KIRKWOOD that *additional* Ansatz or hypotheses are necessary. Similarly, in the theory of BOGOLINBOV[6]), it is the initial condition Ansatz*) concerning the correlation among the particles that is *the* postulate responsible for rendering the time-reversible kinetic equation

$$\frac{\partial F_1}{\partial t}(x_1, p_1, t) = \{H_1, F_1\} + \lambda c \int \{V(x_1 - x_2), F_2(x_1, x_2, p_1, p_2, t)\}\, dx_2\, dp_2 \tag{18}$$

(where c = number density of particles and the curly brackets are the

*) In the theory of PRIGOGINE and BALESCU[1])[2]), initial conditions are also introduced which require the initial dependences of the Fourier components of f_N on N, c to be the same as in the equilibrium state. Since these dependences, as stated already by the authors, are preserved in time by the equations of the Fourier components themselves, it follows that the initial conditions in their theory cannot be relevant for the question of irreversibility.

Poisson bracket expressions) of the B-B-G-K-Y hierarchy, into the generalized Boltzmann equation which is not invariant upon time reversal[7]). The relation between the introduction of a time arrow (and hence irreversibility) and an additional Ansatz has been discussed recently[8]). Thus it seems untenable to have arrived at an equation irreversible in time from the Liouville equation without an Ansatz of one form or another.

IV. Balescu's theory of irreversible processes in ionized gases

In a recent paper[9]), Balescu has applied the theory [1])[2])[3]) to ionized gases for which $V(|x_i - x_j|)$ is the Coulomb interaction. The same procedure integration as in (10) has led to the appearance of $\delta(l \cdot g_{j\,m})$ in the final equations (4.19) and (5.11)[9]). Thus the same considerations as given in the preceding section apply to this work. Hence if one follows the usual procedure of integrations of (15), the $\delta(l \cdot g_{j\,m})$ would have been replaced by $1/i(l \cdot g_{j\,m})$, and Eqs. (4.19) and (5.11) would have been invariant upon time reversal and therefore would not describe irreversible processes.

From a more 'technical' point of view, the following points might also be raised in this connection.

(i) Equation (14) represents the sum of the series of terms (9) which are the 'dominant' ones and which can be represented by the diagrams[1])[2])

 (19)

On integrating (14) over all the momenta except p_α, one readily obtains (on assuming the product relation $\varphi_2(p_1, p_2, t) = \varphi_1(p_1, t) \cdot \varphi_1(p_2, t)$) the equation (1.3) in the paper of Balescu[8]),

$$\frac{\partial \varphi_1(p_\alpha, t)}{\partial t} = 16\,\pi^3\, e^4\, c \int \frac{1}{l^4}\, dl \int dp_1\, l \cdot \frac{\partial}{\partial p_\alpha}\, \delta(l \cdot g_{j\,m})\, l \cdot \left(\frac{\partial}{\partial p_\alpha} - \frac{\partial}{\partial p_1}\right) \times$$
$$\varphi_1(p_\alpha, t)\, \varphi_1(p_1, t)\,. \tag{20}$$

The integral over l in (20) diverges at $l = 0$, corresponding to large interionic distances. Balescu hence discards the series of terms (19).

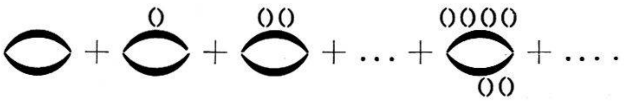
This divergence, however, is present in all theories in which charges of one sign are described by distribution functions while charges of the opposite sign are represented by a uniformly spread out background to maintain electrical neutrality. Thus from the perfectly general equation (18) above, it can be seen that a uniformly spread out background contributes nothing to the integral, and the integral diverges at large distances for Coulomb interactions between charges of the same sign. This does not seem to have been realized in many studies of the problem and has led to the introduction of the unsatisfactory 'cut-off' artifice.

However, if one represents the coordinates and momenta of charged particles of the opposite sign by X_j, P_j and include them in the distribution functions, then Equation (18) would have read

$$\frac{\partial F_1(x_1, p_1, t)}{\partial t} = \{H_1, F_1\} + c \int \left\{\frac{e^2}{|x_1 - x_2|}, F_2(x_1, x_2, p_1, p_2, t)\right\} dx_2\, dp_2 + + c \int \left\{\frac{-e^2}{|x_1 - X_1|}, F_2(x_1, X_1, p_1, P_1, t)\right\} dX_1\, dP_1. \tag{21}$$

While each integral in (21) diverges at large distances, the divergent parts of the two integrals cancel each other*).

(ii) BALESCU discards Equation (20) representing the series (19), of the 'dominant' terms and chooses the terms represented by the following series of diagrams



(22)

The argument for considering these diagrams is that, in the expression for the Debye-Hückel length

$$\frac{1}{r_D} = \left(\frac{4\,\pi\, e^2\, c}{k\,T}\right)^{1/2}, \qquad c = \text{number density of ions}, \tag{23}$$

the combination $e^2\, c \equiv \lambda c$ appears, which is the contribution of each 'bubble' $\underline{0}$. The series (22) includes all diagonal diagrams involving 'rings' (i.e., 'cycle' with 'bubbles') to all orders of λc. The summation of (22) is elegantly carried out (with the integration procedure (10)) and leads to Equation (4.19)[9]) in place of (20) above.

But r_D does not give the combination of e and c uniquely. From the pertinent dimensionless quantity

$$\frac{1}{c\, r_D^3} = \left[\frac{64\,\pi^3\, e^6\, c}{(k\,T)^3}\right]^{1/2}, \tag{24}$$

it would seem that the combination $e^6\, c = \lambda^3 c$ is the combination to look for. However, one must not make any such argument the basis for the choice of terms (diagrams) since one should *arrive at* the Debye screening in the equilibrium state *from* the theory. In any case, the second term in (19), of order $(\lambda^2\, N\, c\, t)^2$, is more 'dominant' than the third term of (22), of order $\lambda^2 N\, c\, t (\lambda c)^2$, by a 'large' factor $N\, t/c$. Thus there seems to be really no convincing argument to include the terms in (22) but to exclude the 'dominant' ones in (19).

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*) To the approximation $F_2(x_1, x_2, p_1, p_2, t) = F_1(x_1, p_1, t)\, F_1(x_2, p_2, t)$ and $F_2(x_1, X_1, p_1, P_1, t) = F_1(x_1, p_1, t)\, F_1(X_1, P_1, t)$, Equation (21) leads immediately to the Vlasov-Landau equation.

In a recent work, GUERNSEY[10]) starts with the theory of Bogoliubov but introduces two expansion parameters, namely e^2 and $e^2 c$. To the first order in e^2 but all orders in $e^2 c$, the kinetic equation obtained agrees with (4.19)[9]) of Balescu, for the case of a spatially homogeneous system. The relation between the two treatments and the meaning of the equation (20) are discussed by WU and ROSENBERG[10]) elsewhere.

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