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Annual Technical Report
ONR Contract Nonr-228(23)

Authority NR 013-307/1-11-62 (Physics Branch)

SOME ASPECTS OF THE THEORY OF IRREVERSIBLE
STATISTICAL MECHANICS

by

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INTRODUCTION

Substantial progress has been made in the last several years in the field of statistical mechanics of irreversible phenomena. Not only the important problem of the irreversibility itself has been clarified to a large extent, but also it can be claimed now that we do have a way of describing kinetic equations describing particular physical situations.^{a,b} These can be eventually solved, at least in principle, and provide the transport coefficients of the particular physical system under consideration. We refer in particular to the work of Prigogine and his collaborators, which has influenced the whole field.^{a,c,d,e} Insofar as classical systems without external correlation sources* are concerned, the problem of finding the kinetic equations (for the probability distributions) can be considered to be solved.^f On the other hand, there is little doubt that the derivation of the particular form of this solution, based on an infinite perturbation expansion and the use of Fourier vectors in the place of the coordinates, shall be simplified and that alternative forms of kinetic equations still might be found.

In view of this generality of the results of Prigogine and his group, it is imperative to compare the other kinds of approaches with Prigogine's results; such a comparison can not only clarify some physical or mathematical aspects of either theory, but also can evaluate the extent of generality and the inherent limitations involved. We attempt such a comparison with respect to the theory advanced by Bogolyubov in 1946.^g

Bogolyubov has proposed a systematic procedure of solving by successive approximations the Bogolyubov-Born-Green-Kirkwood-Yvon hierarchy of integro-differential equations for the probability distributions for sub-sets of s ($s \ll N$) particles of an N -particle system. Actually there are two versions of the Bogolyubov theory--one uses the concentration $C = N/V$ as the expansion parameter, whereas in the other version the potential energy of intermolecular forces, U , is replaced by λU and an expansion in powers of λ is used. In the first version one tries to reduce the problem of N -body motion to that of finding trajectories and momenta predicted by an exact solution of equations of motion for 2, 3, . . . s , bodies. The potential then has to be assumed to be

* e.g., turbulence; the extent of this limitation has not yet been fully clarified.

repulsive, in order to ensure that the considered s bodies would be found in an uncorrelated state (all relative distances very large) if one goes to the limit $t \rightarrow -\infty$. This version has been considered by Choh and Uhlenbeck, Hollinger,* Green,* and Cohen,* and substantial results have been derived. In the second version the reduction to the 2, 3, . . . body problem is obscured by the use of a different counting parameter (i.e., λ) and, indeed, a collective motion of an electron gas can be described; on the other hand, the boundary conditions are much simpler and there is no use to assume that the potential is only repulsive.

Since the Prigogine theory is based on a weak coupling expansion, a comparison with the first version would involve a rearrangement of Prigogine's equations so that terms would be ordered with regard to the number of particles involved or, alternatively, an expansion of Bogolyubov results in powers of λ . For that reason we attempted a comparison of the weak coupling version of Bogolyubov's theory.

The weak coupling version has been applied to the plasma problem, but it has never been formally solved to all orders of λ . Chapter I deals with this problem; the Bogolyubov procedure is strictly followed and the formal solution is given in the form of recursion relations between scattering operators.

In a second chapter now in preparation we express the results of Chapter I in terms of Fourier components of the distribution function and show how the resulting expressions are related to the kinetic equations of Prigogine.

* References to earlier work of this author can also be found in Chapter I.

References

- a. I. Prigogine, Non-equilibrium Statistical Mechanics, Wiley-Interscience (1962).
- b. Reference a, Chapter 14.
- c. R. Zwanzig, in Lectures in Theoretical Physics, Vol. III, Boulder, Colorado (1960), pp. 106-141.
- d. E. Montroll, ibid., 221-325; see also Summer School on Statistical Mechanics (ed., E. G. D. Cohen) (1962).
- e. S. Rice and H. L. Frisch, Ann. Rev. of Phys. Chem. (1961).
- f. Reference a, Chapter 12.
- g. N. N. Bogolyubov, "Problems of a Dynamical Theory in Statistical Physics," in Studies in Statistical Mechanics, de Boer and Uhlenbeck, editors, North-Holland Publishing Co., Amsterdam (1962).

CHAPTER I

Chapter I is a reproduction of a paper by J. Stecki, and has been submitted to the Journal of Chemical Physics for publication.

THE WEAK COUPLING VERSION OF BOGOLYUBOV'S KINETIC THEORY OF GASES*)

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Abstract

The version of Bogolyubov's theory of irreversible phenomena in gases, in which the coupling constant is used as an expansion parameter, is generalized to all orders.

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In 1946 Bogolyubov outlined a new approach to the classical statistical mechanics of irreversible phenomena in gases. This theory has been applied by Choh and Uhlenbeck² to derive a generalized form of Boltzmann equation in which ternary collisions were taken into account. Recently Hollinger³ has derived equations valid to all orders of concentration. The generalization of Bogolyubov's treatment to all orders of concentration was also considered by Cohen⁴ and Green and

¹
N.N. Bogolyubov, Problems of a Dynamical Theory in Statistical Physics, in Studies in Statistical Mechanics, de Boer and Uhlenbeck, Editors (North-Holland Publ. Co., Amsterdam, 1962)

²
S. T. Choh and G. E. Uhlenbeck, Technical Report, Navy Theor. Phys. Contract No. Nonr 1224(15) (1958)

*) This work was supported by the Office of Naval Research, Physics Branch, under contract No. Nonr 228(23) NR 013-307

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 Piccirelli . The alternative approach which uses a coupling constant, λ , as an expansion parameter, has also been given by Bogolyoubov and has been applied to a derivation of a kinetic equation for a homogeneous electron plasma in a positive background ^{6,7,8} . This equation has also been derived by Balescu, significantly, in a very different way, namely, by using the theory developed by Prigogine and his coworkers ^{9,10,11} ^{2,4,5,12} . Several authors have pointed out that the significance

³
 H. B. Hollinger, J. Chem. Phys. 36, 3208 (1962); H. B. Hollinger and C F Curtiss
 ibid. 33, 1386 (1960)

⁴
 E. G. D. Cohen, Physica 28, 1025, 1045, 1060 (1962)

⁵
 M. S. Green and R. A. Piccirelli, private communication

⁶
 reference 1, Chapter 11

⁷
 A. Lenard, Ann. Phys. 10, No. 3, 390 (1960) (1960)

⁸
 R. L. Guernsey, Technical Report, Navy Theor. Phys. Contract No. Nonr. 1224(15) ✓

⁹
 R. Balescu, Phys. Fluids 3, 52 (1960); R. Balescu and H. S. Taylor, ibid. 4, 85 (1961)

¹⁰
 I. Prigogine, Non-equilibrium Statistical Mechanics (Wiley-Interscience, 1962) §
 where further references can be found.

¹¹
 R. Balescu, Statistical Mechanics of Charged Particles, to be published

¹²
 reference 10, Chapter 11, par. 5

of Bogolyoubov assumptions and the extent of generality of final kinetic equations to which his procedure leads, are important and open questions. Recently this problem has been given preliminary consideration by Resibois ¹³ who considered briefly the generalization ² of Boltzmann equation in terms of the recently completed general theory ¹⁰ ¹⁴ . We intend to present a discussion of this version of Bogolyoubov ¹⁰ method within the framework of that general theory given by Prigogine ¹⁰ . In this

¹³
 P. Resibois, Physics Letters, 2, 60 (1962) ; J. Brocas (to be published)

¹⁴
 J. Stecki and H. S. Taylor, to be published

paper an explicit formal calculation is presented which leads to kinetic equations valid to all orders of λ .

THE BOGOLYUBOV PROCEDURE

Let us introduce the N -particle distribution function of momenta, $\underline{p}_i$, and positions, $\underline{q}_i$, normalized to unity and depending on time t . Let $\underline{K}_s$ be the s -particle Liouville operator, without the customary i -factors, defined as

$$K_s = K_s^0 - \lambda \delta K_s, \quad (s=1, 2, \dots, N) \quad (1)$$

$$K_s^0 = \sum_{i \in \{s\}} K_1^0(i), \quad (2)$$

$$\delta K_s = \sum_{i < j \in \{s\}} \theta_{ij}, \quad (3)$$

$$K_1^0(i) = v_i \frac{\partial}{\partial q_i}, \quad (v_i \equiv p_i m^{-1}) \quad (4)$$

$$\theta_{ij} = \frac{\partial u_{ij}}{\partial q_i} \frac{\partial}{\partial p_i} + \frac{\partial u_{ij}}{\partial q_j} \frac{\partial}{\partial p_j}. \quad (5)$$

The phase of the particle " i " is denoted by $\underline{x}_i$ which is understood to be the 6-vector $\{\underline{p}_i, \underline{q}_i\}$. This is also abbreviated as (i) . Vector notation for $\underline{p}_i, \underline{q}_i, \underline{v}_i$ is not used. The operator $\underline{K}_s$ corresponds to a Poisson bracket with a hamiltonian

$$H_s = \sum_{i \in \{s\}} p_i^2 (2m)^{-1} + \lambda U_s, \quad (6)$$

with intermolecular potential

$$U_s = \sum_{i < j \in \{s\}} u_{ij}(|q_i - q_j|). \quad (7)$$

Along the mechanical trajectory of the system, $\underline{f}_N$ is a constant of motion

$$(\partial_t + K_N^*) f_N = 0 \quad (8)$$

and from this the well-known B-B-G-K-Y hierarchy of equations, ^{**)}

$$(\partial_t + K_s) f_s = \int dx_{s+1} \sum_{i \in \{s\}} \lambda \theta_{i, s+1} f_{s+1} \quad (9)$$

^{1,10}
is derived.
**) ~~*)~~

Bogolyubov, Born and Green, Kirkwood, Yvon

The reduced distribution functions $f_s(\underline{x}_1, \dots, \underline{x}_s; \underline{t})$ are probability densities for finding a set of any s particles at specified phases $\underline{x}_1, \dots, \underline{x}_s$. The spatial part of f_1 in a homogeneous system is $\underline{c} = N/V$, where V is volume and $\underline{c}$, number density; the spatial part of f_s reduces to $\underline{c}^s$ if all particles are uncorrelated, i. e. if all relative distances between the s particles are very large. For this reason it is convenient to define

$$F_s = \underline{c}^{-s} f_s \quad (10)$$

with the restriction $s \ll N$ insofar as the system is finite, so that (9) takes the form

$$(\partial_t + K_s^0) F_s = \lambda \delta K_s F_s + \lambda c \int d\underline{x}_{s+1} \sum_{i=1}^s \theta_{i,s+1} F_{s+1} \quad (11)$$

This system of equations is not closed - in contrast to macroscopic transport equations. Bogolyubov then proceeded to assume that all higher distribution functions are functionals of one-particle distribution function, or rather of the set of F_1 's having positions and momenta of different particles as arguments: $F_1(1, \underline{t})$, $F_1(2, \underline{t})$, This allows us to write

$$F_s = O_s \{ F_1(j, \underline{t}) \} \quad (12)$$

where O_s is a time-independent operator, and the time $\underline{t}$ is the same either as argument of F_1 's or of F_s .

Suppose now one is somehow entitled to expand

$$F_s = \sum_0^{\infty} \lambda^n F_s^m \quad (13)$$

This could be substituted into (11) and the same powers of λ collected. However, the first of the equations (11) reads

$$(\partial_t + K_i^0(i)) F_i(i) = \lambda c \int d\underline{x}_\alpha \theta_{i\alpha} F_2(i, \alpha) \quad (14)$$

so that to be consistent with (13) for $s = 2$ we have to expand the time derivative of F_1 :

$$\partial_t F_1 = \sum_0^{\infty} \lambda^n A_n \quad (15)$$

with

$$A_0(i) \equiv -K_1^0 F_1(i) , \quad (16)$$

$$A_n(i) \equiv c \int dx_\alpha \theta_{i\alpha} F_2^{n-1}(i, \alpha) \quad (n \geq 1). \quad (17)$$

Therefore we do not expand F_1 itself; it follows that the assumed expansion (13) is to be interpreted as the expansion of the operator O_S in powers of λ :

$$F_S^m = O_S^m \{ F_1(j; t) \} \quad (17)$$

The time derivative of F_S^n is then

$$\partial_t F_S^m = \sum_j \frac{\delta F_S^m}{\delta F_1(j)} \cdot \frac{\partial F_1(j)}{\partial t} = \sum_j \frac{\delta F_S^m}{\delta F_1(j)} \sum_0^\infty \lambda^m A_m(j) \equiv \sum_0^\infty \lambda^m \mathcal{D}_m F_S^m , \quad (18)$$

or

$$\partial_t F_S = \sum_0^\infty \sum_0^\infty \lambda^{n+m} \mathcal{D}_m F_S^n , \quad (19)$$

where the operator $\mathcal{D}_m$ stands for differentiation with respect to t followed by substitution of $A_m(j)$ for $\partial_t F_1(j)$, for each j . Using (11) and collecting the same powers of λ , we arrive at the basic set of equations

$$(\partial_t + K_S^0) F_S^0 = 0 , \quad (21)$$

$$(\partial_t + K_S^0) F_S^m = - \sum_{n=1}^m \mathcal{D}_n F_S^{m-n} + \delta K_S^0 F_S^{m-1} + c \int dx_{s+1} \sum_0^\infty \lambda^{m-1} \theta_{i,s+1} F_{s+1}^{m-1} . \quad (22)$$

which can be solved successively, when following the prescription given by Bogolyubov. There is a variety of choices for the zeroth approximation. Indeed, the equation:

$$(\partial_t + K_S^0) f = 0 \quad (23)$$

has a solution

$$f = f_0(p_1, q_1^*; \dots; p_s, q_s^*; t_0) , \quad q_i^* \equiv q_i - v_i t , \quad (24)$$

reducing to a prescribed arbitrary function $f_0(1, \dots, s; t_0)$ at $t = 0$. Guided by the form of the Boltzmann equation, we want

$$F_S^0 = \prod_{j=1}^s F_1(j) . \quad (25)$$

This is obtained with the aid of "boundary condition" introduced by Bogolyubov.

Consider expression (24) which can also be written as

$$\exp(-\tau K_s^0) f_0$$

which is nothing else than a Taylor expansion of (24) around $t=0$. The exponential operator shifts the positions backwards along straight lines of unperturbed motion. Then, for t large enough, a situation will be reached, when all the s particles will be distant from one another, so that F_s will reduce to a product of F_1 's. So we put

$$\lim_{\tau \rightarrow +\infty} \exp(-\tau K_s^0) F_s = \prod_{j \in \{s\}} F_1(j, t), \quad (26)$$

or in terms of F_s^n .

$$\lim_{\tau \rightarrow +\infty} \exp(-\tau K_s^0) F_s^0 = \prod_{j \in \{s\}} F_1(j, t), \quad (27)$$

$$\lim_{\tau \rightarrow +\infty} \exp(-\tau K_s^0) F_s^m = 0 \quad (m \geq 1). \quad (28)$$

These are Bogolyubov boundary conditions for homogeneous systems. In that case $F_1 = F_1(p, t)$ does not depend on position. In the inhomogeneous case some care has to be exercised, since F_s depends on a given q_j explicitly and implicitly through F_1 's which do depend on positions now. The operator has a property of shifting everything which is to its right, so that F_1 's have to be shifted separately in the opposite direction in order to compensate for the unwanted shift of their arguments. In Bogolyubov's notation, writing $F_s(x_1, \dots, x_s; F_1)$ instead of (12), we have

$$\lim_{\tau \rightarrow +\infty} \exp(-\tau K_s^0) F_s(1, \dots, s; \exp(+\tau K_1^0) F_1) = \prod_{j \in \{s\}} F_1(j). \quad (29)$$

The exponential operator was denoted by Bogolyubov by $S_{-\tau}^{(s)}$. We split (29) into

$$\lim_{\tau \rightarrow +\infty} \exp(-\tau K_s^0) F_s^0(1, \dots, s; \exp(+\tau K_1^0) F_1) = \prod_{j \in \{s\}} F_1(j, t), \quad (30)$$

$$\lim_{\tau \rightarrow +\infty} \exp(-\tau K_s^0) F_s^m(1, \dots, s; \exp(+\tau K_1^0) F_1) = 0, \quad (m \geq 1). \quad (31)$$

These conditions have been used by Bogolyubov to derive (25) as the solution of the homogeneous equation (21) and to show that the solution of an inhomogeneous equation

$$(\mathcal{O}_0 + K_s^0) F_s^m = g_s^m(x_1, \dots, x_s; F_1) \quad (32)$$

is

$$F_s^m = \int_0^\infty d\tau \exp(-\tau K_s^0) g_s^m(x_1, \dots, x_s; \exp(+\tau K_1^0) F_1), \quad (33)$$

where g_s^n may stand for the r.h.s. of (22).

FORMAL SOLUTION

Using (33) in (21) and (22) Bogolyubov derived the next approximation, which reads

$$F_s^1 = \int_0^\infty d\tau \exp(-\tau K_s^0) \delta K_s \exp(+\tau K_s^0) \prod_{j \in \{s\}} F_1(x_j, \tau). \quad (34)$$

The following features are clear. The last term of the r.h.s. of (22) as well as the $\mathcal{O}$ -operators through the A -functions introduce F_1 's of additional variables which are always integrated over, as indicated in (22) and in (17). To each variable there corresponds a power of c . We denote these "dummy variables" by subscripts $\alpha_1, \alpha_2, \dots$ or α, β . The variables represent the "average particles of the medium" allowed to interact with the fixed set of s particles whose positions and momenta are the arguments of F_s^n . For given n there can be at most $n-1$ dummy variables. Also F_1 's appear only as a product. Therefore we assert that (18) can be replaced by

$$F_s^m = \sum_{l=0}^{n-1} c^l \Omega_s^{m,l}(\{s\}) \prod_{j \in \{s\}} F_1(j) \prod_{\alpha_i \in \{l\}} F_1(\alpha_i), \quad (35)$$

where the operators $\Omega_s^{m,l}$ are to be determined. It is understood that they act on the main set $\{s\}$ and on the set of dummy variables $\alpha_1, \dots, \alpha_l$. Now the results of action of $\mathcal{O}$ -operators can be written down explicitly. When making use of (17) and (35), we obtain

$$\begin{aligned} \mathcal{O}_m F_s^0 &= \mathcal{O}_m \prod_{j \in \{s\}} F_1(j) = \sum_{i \in \{s\}} \prod_{j \neq i} F_1(j) A_m(i) \\ &= \sum_{l=1}^{n-1} c^l \int dx_\alpha \sum_{i \in \{s\}} \theta_{i\alpha} \Omega_s^{m-1, l-1}(i, \alpha) \prod_{j \in \{s\}} F_1(j) F_1(\alpha) \prod_{\beta \in \{l-1\}} F_1(\beta) \end{aligned} \quad (36)$$

$$\begin{aligned}
 \varphi_{n-m} F_s^m &= \sum_{\nu=0}^{m-1} \varphi_{n-m} c^\nu \Omega_s^{m\nu} \prod_{j \in \{s\}} F_1(j) \prod_{\beta \in \{v\}} F_1(\beta) \\
 &= \sum_{\nu=0}^{m-1} c^{\nu+1} \Omega_s^{m\nu} \int dx_\alpha \left(\sum_{i \in \{s\}} + \sum_{i \in \{v\}} \right) \theta_{i\alpha} F_2^{n-m-1}(i, \alpha) \prod_{j \in \{s\}} F_1(j) \prod_{\beta \in \{v\}} F_1(\beta) \\
 &= \sum_{\nu=0}^{m-1} \sum_{\nu'=0}^{m-m-1} c^{\nu+\nu'+1} \Omega_s^{m\nu} \int dx_\alpha \left(\sum_{i \in \{s\}} + \sum_{i \in \{v\}} \right) \theta_{i\alpha} \Omega_2^{n-m-1, \nu'}(i, \alpha) \prod_{j \in \{s\}} F_1(j) F_1(\alpha) \prod_{\substack{\beta \in \{v\} \\ \beta \in \{v'\}}} F_1(\beta)
 \end{aligned} \tag{37}$$

This term can exist for $n \geq 3$. Finally

$$\varphi_l F_s^{n-1} = \sum_{l=1}^{n-1} c^l \Omega_s^{n-1, l-1} \int dx_\alpha \left(\sum_{i \in \{s\}} + \sum_{i \in \{l-1\}} \right) \theta_{i\alpha} \prod_{j \in \{s\}} F_1(j) F_1(\alpha) \prod_{\beta \in \{l-1\}} F_1(\beta). \tag{38}$$

We now substitute these expressions into (22) and (33). We find $\frac{n}{s}$ in the form (35), which proves (35) by induction, (34) being given. When collecting the same powers of λ and $\underline{c}$ we find three separate recursions - two particular cases

$$l=0 \quad \Omega_s^{n,0} = \int_0^\infty d\tau_m \exp(-\tau_m K_s^0) \delta K_s \Omega_s^{n-1,0} \exp(+\tau_m K_s^0) \tag{39}$$

$$\begin{aligned}
 l=n-1 \quad \Omega_s^{n,n-1} &= \int_0^\infty d\tau_m \exp(-\tau_m K_s^0) \int dx_\alpha \left[\sum_{i \in \{s\}} \theta_{i\alpha} (\Omega_{s+1}^{n-1, n-2}(\{s\}, \alpha) - \Omega_2^{n-1, n-2}(i, \alpha)) + \right. \\
 &\quad \left. - \Omega_s^{n-1, n-2} \left(\sum_{i \in \{s\}} + \sum_{i \in \{n-2\}} \right) \theta_{i\alpha} \right] \exp(+\tau_m K_{s+n-1}^0),
 \end{aligned} \tag{40}$$

and the general one

$$\begin{aligned}
 1 \leq l \leq n-2 \\
 \Omega_s^{n,l} &= \int_0^\infty d\tau_m \exp(-\tau_m K_s^0) \left\{ \delta K_s \Omega_s^{n-1, l} \exp(+\tau_m K_{s+l}^0) + \int dx_\alpha \left[\sum_{i \in \{s\}} \theta_{i\alpha} (\Omega_{s+1}^{n-1, l-1}(\{s\}, \alpha) - \right. \right. \\
 &\quad \left. \left. - \Omega_2^{n-1, l-1}(i, \alpha)) \exp(+\tau_m K_{s+l}^0(\{s\}, \alpha, \{l-1\})) - \sum_{\substack{m'+m''=n-1 \\ m' \geq \nu' \geq 0 \\ m'' \geq \nu'' \geq 0}} \sum_{\nu'+\nu''=l-1} \Omega_s^{m', \nu'} \left(\sum_{i \in \{s\}} + \right. \right. \\
 &\quad \left. \left. + \sum_{i \in \{v'\}} \right) \theta_{i\alpha} \Omega_2^{m'', \nu''}(i, \alpha) \exp(+\tau_m K_{s+l}^0(\{s\}, \alpha, \{v'\}, \{v''\})) \right] \right\},
 \end{aligned} \tag{41}$$

with

$$\Omega_s^{1,0} = \int_0^\infty d\tau_1 \exp(-\tau_1 K_s^0) \delta K_s \exp(+\tau_1 K_s^0). \tag{42}$$

This is the formal solution, valid for all $n \geq 1$. Now the operators Ω can be calculated successively by simple algebra. Some minor simplifications are achieved by ma-

king the integrals explicit; there are n integrations over $\tau_1, \dots, \tau_n$ and l integrations over $x_\alpha, x_\beta, \dots$. We note that there is a separate recursion for $l=0$; the operators $\Omega_s^{n,0}$ represent approximations to the s -body problem of isolated s particles involved in F_s . The other separate recursion involves the largest power of c possible for given power of λ . These terms have been considered by Guernsey⁸. For a homogeneous system they lead to Balescu-Lenard equation.

THE HOMOGENEOUS SYSTEM

Considerable simplifications occur if it is assumed that F_1 does not depend on position. Then

$$\exp(-\tau K_1^0) F_1 = F_1. \quad (43)$$

Also, due to spherical symmetry of the interaction potential

$$\int dx_\alpha \theta_{i\alpha} F_1(i) F_1(\alpha) = 0. \quad (44)$$

We can also now identify the τ -integrals with the free propagators familiar from the scattering theory, for which many equivalent representations are known.¹⁰ Hence we introduce the abbreviation

$$\int_0^\infty d\tau \exp(-\tau K_s^0) \equiv \mathcal{Q}_s. \quad (45)$$

With (25) unchanged, we obtain

$$\Omega_s^{1,0} = \mathcal{Q}_s \delta K_s \quad (46)$$

and the following recursions resulting from (39)-(41)

$$l=0 \quad \Omega_s^{n,0} = \mathcal{Q}_s \delta K_s \Omega_s^{n-1,0} \quad (47)$$

$$1 \leq l \leq n-2 \quad \Omega_s^{n,l} = \mathcal{Q}_s \left[\delta K_s \Omega_s^{n-1,l} + \sum_{i \in \{s\}} \int dx_\alpha \theta_{i\alpha} (\Omega_{s+1}^{n-1,l-1}(\{s\}, \alpha) - \Omega_2^{n-1,l-1}(i, \alpha)) + \right. \\ \left. - \sum_{m', m''} \sum_{\nu', \nu''} \Omega_s^{m', \nu'} \sum_{i \in \{s\}} \int dx_\alpha \theta_{i\alpha} \Omega_2^{m'', \nu''}(i, \alpha) \right] \quad (48)$$

$$\Omega_s^{n,n-1} = \mathcal{Q}_s \sum_{i \in \{s\}} \int dx_\alpha \theta_{i\alpha} [\Omega_{s+1}^{n-1,n-2}(\{s\}, \alpha) - \Omega_2^{n-1,n-2}(i, \alpha)] \quad (49)$$

DISCUSSION

The last recursion, (49), is of remarkable simplicity. It has been examined by Guernsey⁸ in a different but equivalent form and shown to lead for $s = 2$ and when used in conjunction with (15)-(17) to the Balescu-Lenard kinetic equation. Notably $\Omega_s^{n,n-1}$ is a sum of binary terms, so that $\Omega_2(i, \alpha)$ just cancels a term in Ω_{s+1} . The general term is of the form

$$\mathcal{Q} \int dx_\alpha \sum \theta_{ij} \mathcal{Q} \int dx_\beta \sum \theta_{ij}, \dots,$$

so that no two propagators follow one another without being separated by (a sum of) scattering operators θ_{ij} . This can be traced back to the fact that only $\mathcal{Q}_{nF_s}^0$ contributes here. As can be seen from (47), that is no longer true in the general term, $1 \leq \ell \leq n-2$. Each Ω -operator contains always one $\mathcal{Q}_s$ at the outmost left resulting directly from (33). Therefore the last term of the r.h.s. of (48) will introduce a $\mathcal{Q}_s \mathcal{Q}_s$ sequence, which will reappear later to give rise to a $\mathcal{Q} \mathcal{Q} \theta_{ij} \mathcal{Q} \mathcal{Q} \theta_{ij}$ sequence, etc. We see that, indeed, the terms with $\lambda^{n,n-1}$ are exceptionally simple.

The Markovian character is assumed explicitly as early as in (12). A non-Markovian behaviour could result, if we would allow the operator $\mathcal{Q}_s$ to depend on time t and it is not clear how this could be done without departing radically from the Bogolyubov procedure. On the other hand we know that the most general kinetic equations are non-Markovian¹⁰.

Owing to the simplicity of the boundary conditions, there is no need to assume that the intermolecular potential is only repulsive^{1,3,4} and all expressions are in principle amenable to explicit calculations. On the other hand, some individual integrals can diverge owing to the repulsive force being infinite at the center of

the particle for common potentials; hence some resummation procedure may be needed¹³
- a common feature of all weak-coupling theories.

ACKNOWLEDGEMENTS

The author is indebted to Dr Howard S. Taylor, from this University, for suggesting the problem and for several helpful discussions.