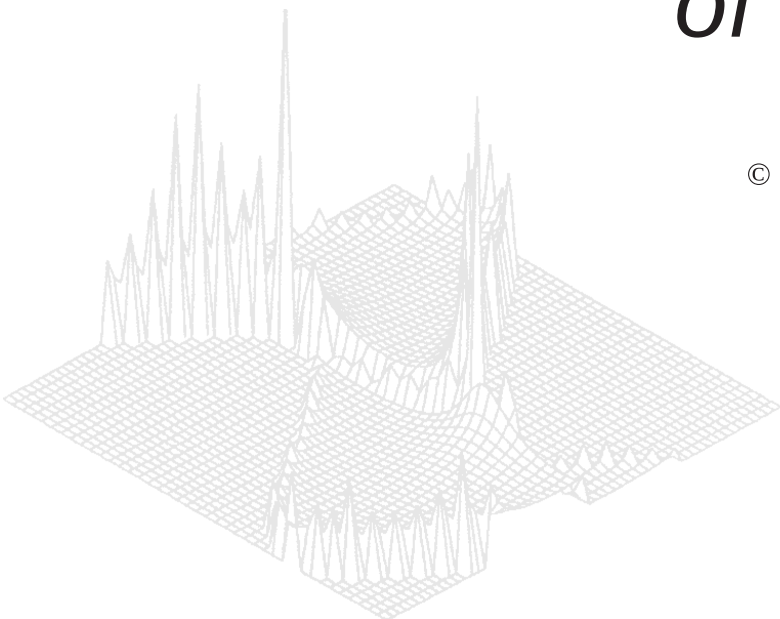
CSIRO PUBLISHING

Australian Journal of Physics



Volume 52, 1999

A journal for the publication of
original research in all branches of physics

www.publish.csiro.au/journals/ajp

All enquiries and manuscripts should be directed to
Australian Journal of Physics
CSIRO PUBLISHING
PO Box 1139 (150 Oxford St)
Collingwood
Vic. 3066
Australia

Telephone: 61 3 9662 7626
Facsimile: 61 3 9662 7611
Email: peter.robertson@publish.csiro.au

Published by **CSIRO** PUBLISHING
for CSIRO Australia and
the Australian Academy of Science

Aust. J. Phys., 1999, **52**, 999–1024

Boltzmann Equation Theory of Charged Particle Transport in Neutral Gases: Perturbation Treatment

Slobodan B. Vrhovac and Zoran Lj. Petrović

Institute of Physics, PO Box 57, 11001 Belgrade, Yugoslavia.

Abstract

This paper examines the formal structure of the Boltzmann equation (BE) theory of charged particle transport in neutral gases. The initial value problem of the BE is studied by using perturbation theory generalised to non-Hermitian operators. The method developed by Résibois was generalised in order to be applied for the derivation of the transport coefficients of swarms of charged particles in gases. We reveal which intrinsic properties of the operators occurring in the kinetic equation are sufficient for the generalised diffusion equation (GDE) and the density gradient expansion to be valid. Explicit expressions for transport coefficients from the (asymmetric) eigenvalue problem are also deduced. We demonstrate the equivalence between these microscopic expressions and the hierarchy of kinetic equations. The establishment of the hydrodynamic regime is further analysed by using the time-dependent perturbation theory. We prove that for times $t \gg \tau_0$ (τ_0 is the relaxation time), the one-particle distribution function of swarm particles can be transformed into hydrodynamic form. Introducing time-dependent transport coefficients $\hat{\omega}_*^{(p)}(\vec{q},t)$, which can be related to various Fourier components of the initial distribution function, we also show that for the long-time limit all $\hat{\omega}_*^{(p)}(\vec{q},t)$ become time and $\vec{q}$ independent in the same characteristic time and achieve their hydrodynamic values.

1. Introduction

One of the most important contributions of Résibois (1970) to nonequilibrium statistical mechanics is his analysis of linearised hydrodynamic modes. He formulated the problem of linear hydrodynamic modes from a microscopic point of view. The concept of hydrodynamic modes plays an important role in many problems in kinetic theory where long-wavelength, low-frequency behaviour dominates, such as in the critical behaviour of transport coefficients (Résibois and Prigogine 1960) or the slow power-law decay of correlation functions (Résibois and Leaf 1960). Résibois treated the eigenvalue problem associated with the linear generalised BE by the degenerate perturbation method in powers of the uniformity parameter q. As a result, the hydrodynamic frequencies appear as five eigenvalues calculated up to the order q^2 which tend to zero when $q \to 0$. In this procedure, the usual expressions for the transport coefficients in neutral gases come out as q^2-coefficients of the eigenvalues. This analysis clarifies the microscopic interpretation of transport coefficients with respect to the traditional approach, which was based on the Chapman–Enskog method for dilute gases. On

 10.1071/PH99053 0004-9506/99/060999$10.00

the other hand, the eigenfunctions associated with the hydrodynamic frequencies furnish a microscopic expression for the above-mentioned hydrodynamic modes.

In this paper we present both the stationary and time-dependent perturbation treatment of the BE. The stationary treatment is a generalisation of the technique developed by Résibois to the transport of charged particles swarms in neutral gases. The basic idea is to construct the hydrodynamic form of one-particle distribution function from the more basic principles rather than impose it. If the time-dependent perturbation method is applied it is possible to obtain a deeper understanding of the relationship between the initial conditions and the time dependence of the transport coefficients and of the one-particle distribution function that is built into the transport theory. In other words, one may obtain fundamental knowledge on the limitations of the applicability of the hydrodynamic theory of swarms.

The issue of the definition of transport coefficients, their comparisons and the adequacy of theoretical calculations arose as the accuracy of experiments obtained under different conditions improved and also as Monte Carlo simulations were used more extensively with more complete scattering models. Nevertheless, the assumptions of the hydrodynamic expansion and the GDE were always taken as the basic assumptions. In particular, it was always assumed that density gradient expansion is applicable under the assumption of small gradients, but the criterion on just how small the gradients should be was not established clearly.

The starting point for this work is the study by Kumar (1981), where the connection between the hydrodynamic behaviour and the spectral properties of the operators occurring in the BE was established. Basically, he applied a time-dependent perturbation technique to a hierarchy of equations for spatial moments of the one-particle distribution function. He was able to show that, in the hydrodynamic limit, both spatial moments and time-dependent transport coefficients should approach time-independent limits. Standish (1987) has developed Kumar's ideas further by applying a projection operator method to the Fourier transform of the BE which resulted in a simpler procedure, but the final results were essentially the same. Kondo (1987) has also applied the projection operator method in the study of the initial relaxation processes. In order to derive the evolution equation which describes the development of the number density at all times, Kondo assumed that the initial distribution separates the spatio-temporal and the velocity part of the one-particle distribution function. Thus the resulting GDE which was developed from the BE originates from a very special form of the initial conditions.

Keeping in mind the importance of the application of the hydrodynamic theory and the need to extend the swarm analysis to situations where either large gradients may occur or some form of non-equilibrium (spatial or temporal or both) may develop, we have attempted to develop a theory that would not rely in any way on the assumptions of the GDE and density gradient expansion and which would allow us to correlate the temporal development of the swarms with the very general initial conditions.

These issues often arise in the application of the transport theory to modeling of rf plasmas used in the processing of very large scale integrated electronic circuits (Nakano *et al*. 1994). Large gradients occur in the proximity of the electrodes of glow discharges (Boeuf and Marode 1982) at all pressures, but the non-hydrodynamic behaviour is particularly observable at low pressures in Townsend and obstructed glow discharges (Petrović and Phelps 1997).

The paper is organised as follows. In the remainder of the introduction we outline the basic definitions of the kinetic theory of charged particle swarms. In Section 2 we recall briefly the initial value problem of the BE, together with a few useful properties of the operators involved in this equation. In Section 3 we develop the time-independent version of the theory, namely we construct asymptotic (long-time) solutions to the BE and discuss their analogy with solutions obtained by different methods. Section 4 is devoted to the time-dependent part of the theory. Finally, after the conclusions in Section 5, more detailed mathematical developments can be found in the Appendices.

(1a) Outline of the Relevant Kinetic Theory

For the purpose of this paper a swarm is defined as an ensemble of *independent* charged particles moving in a neutral background gas. The motion of the swarm particles is determined by the forces exerted by the external electric field $\vec{E}$ and collisions with gas molecules. Throughout this paper the electric field is assumed to be uniform in space and independent of time. We assume that the swarm particles are described by a one-particle distribution function, denoted here as $f(\vec{r}, \vec{v}, t)$.

First, we can reproduce the arguments for neglecting the nonlinearity. To simplify, we assume that, at $t = 0$, the neutral gas molecules are distributed uniformly in space and their distribution function, simply denoted by f_0, is then $f_0(\vec{r}, \vec{v}, 0) = f^{(0)}(\vec{v})$. If we suppose that the swarm density $n(\vec{r}, t)$ is very small compared with the gas density n_0 then:

(a) The probability of collision between two swarm particles is extremely small compared with the probability of their collision with gas molecules (by a factor n/n_0).

(b) Similarly, the neutral gas distribution function is only slightly perturbed (again by a factor n/n_0) from its spatially uniform form by the very rare collisions of swarm particles with the neutral gas.

Hence, the relation $f_0(\vec{r}, \vec{v}, t) = f^{(0)}(\vec{v}) + o(n/n_0)$ remains approximately valid at all times.

The Boltzmann equation for swarms in *free space* has the form (Kumar *et al.* 1980):

$$\left[\frac{\partial}{\partial t} + \vec{v} \cdot \frac{\partial}{\partial \vec{r}} + \vec{a} \cdot \frac{\partial}{\partial \vec{v}}\right] f(\vec{r}, \vec{v}, t) = J(f)\,, \tag{1}$$

where $\vec{a} = e\vec{E}/m$ is the acceleration of the particle with charge e and mass m in the electric field $\vec{E}$. The operator J is the collision integral which includes the elastic and inelastic particle conserving processes and the effects of attachment and ionisation, i.e. annihilation and creation of charged particles (Kumar *et al.* 1980; Kumar 1984; Wang-Chang *et al.* 1964). The collision operator J maps the function f onto another function, say $\tilde{f}$, $f \to \tilde{f} = J(f)$ and depends functionally on the neutral distribution and scattering cross sections. It is a *linear* operator which acts on f only through its $\vec{v}$ dependence. The operator J is local in space and in time.

Let us briefly review some results of the standard BE theory of charged particle transport which will be useful hereafter.

The connection between the swarm experiments (Huxley and Crompton 1974) and the theory proceeds by first making an assumption about the time development of the number density $n(\vec{r},t)$ (Kumar *et al*. 1980; Kumar 1984):

$$\left[\frac{\partial}{\partial t} - \sum_{p=0}^{\infty} \hat{\omega}^{(p)} \odot \left(-\frac{\partial}{\partial \vec{r}}\right)^{p}\right] n(\vec{r},t) = 0. \tag{2}$$

This equation is known as the generalised diffusion equation (GDE). The constants $\hat{\omega}^{(p)}$ are tensorial transport coefficients of order p, and $\odot$ indicates a p-fold scalar product.

In the context of static fields (Kumar *et al*. 1980), the term 'hydrodynamic regime' (HDR) is usually employed to describe the situation where the system has evolved to a state independent of the initial state of the system and the space–time dependence of one-particle distribution function $f(\vec{r},\vec{v},t)$ is entirely carried by the number density $n(\vec{r},t)$. A sufficient functional relationship between $f(\vec{r},\vec{v},t)$ and $n(\vec{r},t)$ in the HDR is the density gradient expansion (Kumar *et al*. 1980)

$$f(\vec{r},\vec{v},t) = \sum_{p=0}^{\infty} \hat{f}^{(p)}(\vec{v}) \odot \left(-\frac{\partial}{\partial \vec{r}}\right)^{p} n(\vec{r},t). \tag{3}$$

The coefficients $\hat{f}^{(p)}(\vec{v})$ are velocity-dependent tensors of rank p. The density gradient expansion (3) is *a priori* assumed for the one-particle distribution function $f(\vec{r},\vec{v},t)$ in the HDR. This form of functional relationship makes it possible to derive transport coefficients which are independent of time. The hydrodynamic regime does not pre-suppose small relative gradients $n^{-1}(\partial/\partial\vec{r})n$, yet equations (2) and (3) can be expected to hold only when the density gradients are small.

The connection between kinetic theory and transport coefficients is established via the BE (1). Substitution of the expansion (3) into equation (1) and making use of the GDE (2) leads to the following hierarchy of kinetic equations (Kumar *et al*. 1980)

$$\left(\vec{a}\cdot\frac{\partial}{\partial \vec{v}} - J\right)\hat{f}^{(0)} = -\hat{\omega}^{(0)}\hat{f}^{(0)}, \tag{4}$$

$$\left(\vec{a}\cdot\frac{\partial}{\partial \vec{v}} - J\right)\hat{f}^{(p)} = \vec{v}\hat{f}^{(p-1)} - \sum_{j=0}^{p}\hat{\omega}^{(j)}\hat{f}^{(p-j)}, \quad p \geq 1. \tag{5}$$

Integration of equations (4) and (5) with respect to velocity $\vec{v}$ gives

$$\hat{\omega}^{(0)} = \int d^3\vec{v} J^R \hat{f}^{(0)}, \tag{6}$$

$$\hat{\omega}^{(p)} = \int d^3\vec{v}\vec{v}\hat{f}^{(p-1)} + \int d^3\vec{v}J^R\hat{f}^{(p)}, \quad p \geq 1. \tag{7}$$

The tensor functions $\hat{f}^{(p)}$ have the following normalisation:

$$\int d^3\vec{v}\hat{f}^{(0)} = 1, \quad \int d^3\vec{v}\hat{f}^{(p)} = 0, \quad p \geq 1. \tag{8}$$

Condition (8) is needed to make $\hat{f}^{(p)}$ unique. The operator J^R is the part of the collision operator J responsible for reactions.

Our aim is to reveal which intrinsic properties of the operators occurring in the kinetic equation (1) are sufficient for the validity of the GDE (2) and the density gradient expansion (3). We approached this problem by developing a formal but very general frame that applies in principle to the most general case of charged particle transport, using the formal language and the tools developed in quantum many-body theory.

2. Initial Value Problem

We first write the BE (1) in Fourier space. Applying the Fourier transform to equation (1) one obtains

$$\frac{\partial}{\partial t}\Phi(\vec{q},\vec{v},t) = \mathcal{L}\Phi(\vec{q},\vec{v},t), \tag{9}$$

where $\Phi(\vec{q},\vec{v},t)$ is the spatial Fourier transform of the distribution function

$$\Phi(\vec{q},\vec{v},t) = \int d^3\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} f(\vec{r},\vec{v},t). \tag{10}$$

In equation (9) the operator $\mathcal{L}$ is

$$\mathcal{L} = \mathcal{M} + \mathcal{P}, \tag{11}$$

with

$$\mathcal{M} = -\vec{a}\cdot\frac{\partial}{\partial\vec{v}} + J, \tag{12}$$

$$\mathcal{P} = -i\vec{q}\cdot\vec{v}. \tag{13}$$

For the sake of compact notation, we introduce an abstract Hilbert space $\mathbf{H}$ to represent any function ψ of velocity $\vec{v}$. In other words, we consider $\psi(\vec{v})$ as the velocity-space representation of the vector $|\psi\rangle \in \mathbf{H}$ (Messiah 1974):

$$\psi(\vec{v}) = \langle\vec{v}|\psi\rangle. \tag{14}$$

In Hilbert space **H**, the scalar (inner) product between two arbitrary vectors $|\varphi\rangle$ and $|\psi\rangle$ is defined as

$$\langle\varphi|\psi\rangle = \int d^3\vec{v}\frac{1}{f^{(0)}(\vec{v})}\varphi^*(\vec{v})\psi(\vec{v}). \tag{15}$$

Otherwise, we are free to choose the $f^{(0)}(\vec{v})$ arbitrarily. The norm induced by the scalar product $\langle\cdot|\cdot\rangle$ is denoted by $||\cdot||$. According to equation (15) we have

$$\hat{I} = \int d^3\vec{v}\frac{1}{f^{(0)}(\vec{v})}|\vec{v}\rangle\langle\vec{v}|, \tag{16}$$

$$\langle\vec{v}|\vec{v}^{\,'}\rangle = f^{(0)}(\vec{v}^{\,'})\delta(\vec{v}-\vec{v}^{\,'})\,, \tag{17}$$

where $\hat{I}$ is the unit operator and δ is the delta function.

Likewise, we have established a formal correspondence between the operators $\mathcal{L}$, $\mathcal{M}$ and $\mathcal{P}$, and the linear operators on Hilbert space **H**:

$$\mathcal{M} \to \hat{H}_0, \quad \mathcal{P} \to \hat{H}', \quad \mathcal{L} = \mathcal{M} + \mathcal{P} \to \hat{H} = \hat{H}_0 + \hat{H}'. \tag{18}$$

For instance, acting convective operator $\hat{H}' = -i\vec{q}\cdot\hat{\vec{v}}$ on vector $|\psi\rangle \in \mathbf{H}$, according to equation (16), is defined as

$$\hat{H}'|\psi\rangle = \int d^3\vec{v}\frac{1}{f^{(0)}(\vec{v})}\psi(\vec{v})(-i\vec{q}\cdot\hat{\vec{v}})|\vec{v}\rangle, \quad |\psi\rangle \in \mathbf{H}, \tag{19}$$

where $\hat{\vec{v}}$ is a vector operator (Messiah 1974). A vector operator $\hat{\vec{v}}$ is defined by its components $\hat{v}_1$, $\hat{v}_2$ and $\hat{v}_3$ along three orthogonal axes, where $\hat{v}_1$, $\hat{v}_2$, $\hat{v}_3$ are operators in the ordinary sense of the term. If we use equation (17), from (19) we obtain that the velocity-space representation of the vector $\hat{H}'|\psi\rangle$ is

$$\phi(\vec{v}) = \langle\vec{v}|\hat{H}'|\psi\rangle = -i\vec{q}\cdot\vec{v}\psi(\vec{v}). \tag{20}$$

Consider an abstract Cauchy problem (or initial value problem)

$$\frac{\partial}{\partial t}|\Phi(\vec{q},t)\rangle = \hat{H}|\Phi(\vec{q},t)\rangle, \quad |\Phi(\vec{q},0)\rangle = |\Phi_I(\vec{q})\rangle. \tag{21}$$

The formal solution of (21) is

$$|\Phi(\vec{q},t)\rangle = e^{t\hat{H}}|\Phi_I(\vec{q})\rangle, \tag{22}$$

where the exponential of an operator $\hat{H}$ is defined by the expansion

$$e^{t\hat{H}} = \sum_{l=0}^{\infty}\frac{1}{l!}(t\hat{H})^l. \tag{23}$$

Here, however, $\hat{H}$ is *not* a Hermitian operator. Indeed, it is obvious that the convective operator $\hat{H}'$ is an anti-Hermitian

$$\langle\varphi|\hat{H}'|\psi\rangle = -\langle\psi|\hat{H}'|\varphi\rangle^*, \quad |\psi\rangle, |\varphi\rangle \in \mathbf{H}, \tag{24}$$

where * represents complex conjugation.

For simplicity we shall assume the spectrum of $\hat{H}$ to be entirely discrete. Consider then the non-Hermitian eigenvalue problem of the operator $\hat{H}$

$$\hat{H}|\psi_{n\lambda}(\vec{q})\rangle = \Lambda_n(\vec{q})|\psi_{n\lambda}(\vec{q})\rangle, \tag{25}$$

where $|\psi_{n\lambda}\rangle$ is an eigenvector and Λ_n the corresponding eigenvalue. The number λ distinguishes between different eigenvectors belonging to some degenerate eigenvalue. Eigenvalues Λ_n are generally not real. We should also consider the eigenvalue problem of the adjoint operator $\hat{H}^\dagger$:

$$\hat{H}^\dagger|\tilde{\psi}_{n\lambda}(\vec{q})\rangle = \tilde{\Lambda}_n(\vec{q})|\tilde{\psi}_{n\lambda}(\vec{q})\rangle, \tag{26}$$

assuming that its eigenvectors can be orthonormalised according to

$$\langle\tilde{\psi}_{n\lambda}(\vec{q})|\psi_{n'\lambda'}(\vec{q})\rangle = \delta_{nn'}\delta_{\lambda\lambda'}. \tag{27}$$

For the non-Hermitian case an expansion theorem in series of eigenvectors seldom can be established in a rigorous manner. Here we *assume* that both $\{|\psi_{n\lambda}\rangle\}$ and $\{|\tilde{\psi}_{n\lambda}\rangle\}$ are complete sets of vectors in Hilbert space $\mathbf{H}$. Therefore any vector $|\Phi\rangle \in \mathbf{H}$ can be represented by the series

$$|\Phi\rangle = \sum_{n\lambda} c_{n\lambda}|\psi_{n\lambda}\rangle, \tag{28}$$

with coefficients given by

$$c_{n\lambda} = \langle\tilde{\psi}_{n\lambda}|\Phi\rangle. \tag{29}$$

Equations (28) and (29) can be summarised in a closure relation

$$\sum_{n\lambda} |\psi_{n\lambda}\rangle\langle\tilde{\psi}_{n\lambda}| = \hat{I}, \tag{30}$$

which generalises the well-known result for Hermitian operators.

Let us now return to the solution of the initial value problem (21). With the expansion (28) for the vector $|\Phi_I(\vec{q})\rangle$, which represents the state of the system at time $t = 0$, we obtain a formal solution for any time t:

$$|\Phi(\vec{q}, t)\rangle = \sum_{n\lambda} c_{n\lambda}^{(I)}(\vec{q}) e^{t\Lambda_n(\vec{q})}|\psi_{n\lambda}(\vec{q})\rangle. \tag{31}$$

Here, we have

$$c_{n\lambda}^{(I)}(\vec{q}) = \langle\tilde{\psi}_{n\lambda}(\vec{q})|\Phi_I(\vec{q})\rangle. \tag{32}$$

3. The Stationary Perturbation Solution

We now show how, in the limit of small wave vectors and long times, the solution of the BE leads to the hydrodynamic (macroscopic) description (Section 1*a*). We formulate the transport problem, starting from the BE by means of an analysis of its eigenvalue problem. In addition, we establish explicit microscopic expressions for the transport coefficients of swarm particles. These microscopic expressions give the transport coefficients in terms of the solutions of the eigenvalue problem associated with the BE. In macroscopic theory (Section 1*a*) these transport coefficients were introduced as phenomenological constants.

We limit ourselves to looking at the phenomena varying slowly in space; this means that in the Fourier transform (10), the only coefficients that are relevant correspond to the small values of $\vec{q}$. When the wave vector $\vec{q}$ is small, equation (21) can be treated as composed of the principal kinetic equation for homogeneous evolution of the one-particle distribution

$$\frac{\partial}{\partial t}|\Phi(t)\rangle = \hat{H}_0|\Phi(t)\rangle, \tag{33}$$

and the perturbation $\hat{H}'$ (convective term).

Our procedure, based on the Résibois (1970) method of derivation of linear transport coefficients is to solve equation (21) by perturbation calculus, considering $\hat{H}'$ as a small perturbation in the long-wavelength limit $\vec{q}\to 0$.

We have thus to discuss first the spectral properties of the unperturbed operator $\hat{H}_0$. For simplicity we assume that the spectrum of $\hat{H}_0$ is entirely discrete. The unperturbed eigenvalue problem has the form

$$\hat{H}_0|\psi_{n\lambda}^{(0)}\rangle = \Lambda_n^{(0)}|\psi_{n\lambda}^{(0)}\rangle. \tag{34}$$

Since $\hat{H}_0$ is not a symmetric operator, we are obliged to use a biorthonormal set of eigenvectors; thus, together with equation (34), we have to study the adjoint eigenvalue problem

$$\hat{H}_0^{\dagger}|\tilde{\psi}_{n\lambda}^{(0)}\rangle = \tilde{\Lambda}_n^{(0)}|\tilde{\psi}_{n\lambda}^{(0)}\rangle. \tag{35}$$

The sets $\{|\psi_{n\lambda}^{(0)}\rangle\}$ and $\{|\tilde{\psi}_{n\lambda}^{(0)}\rangle\}$ can always be made biorthonormal:

$$\langle\tilde{\psi}_{n\lambda}^{(0)}|\psi_{n'\lambda'}^{(0)}\rangle = \delta_{nn'}\delta_{\lambda\lambda'}, \tag{36}$$

and again we *assume* that these sets are complete, i.e.

$$\sum_{n\lambda}|\psi_{n\lambda}^{(0)}\rangle\langle\tilde{\psi}_{n\lambda}^{(0)}| = \hat{I}. \tag{37}$$

Further discussion requires additional assumptions about the spectral properties of the operators $\hat{H}_0$ and $\hat{H}$.

Assumption I: *There exists an isolated eigenvalue* $\Lambda_{\bar{n}}^{(0)}$ *such that*

$$\mathrm{Re}\,\Lambda_n^{(0)} < \mathrm{Re}\,\Lambda_{\bar{n}}^{(0)}, \quad \forall n \neq \bar{n}. \tag{38}$$

Let

$$\frac{1}{\tau_0} = d_0 = \inf_{n\neq\bar{n}} |\mathrm{Re}\,\Lambda_n^{(0)} - \mathrm{Re}\,\Lambda_{\bar{n}}^{(0)}|. \tag{39}$$

In the kinetic theory of neutral gases, such an assumption implies separation of the relaxation timescale $\tau_0 \propto (d_0)^{-1}$, and the hydrodynamic timescale $\tau_h \propto (q(k_BT)^{\frac{1}{2}})^{-1}$ (Sirovich and Thurber 1969) (τ_h is the time a swarm particle needs to travel the length of macroscopic gradients and k_BT is the mean random energy of a swarm particle). Macroscopic lengths and collisional invariants play a significant role in the neutral gas theory approach to hydrodynamics (Balescu 1975). The swarm may freely exchange momentum and energy with the neutral gas. The number of particles may also change if reactions are allowed. Thus, there are no collisional invariants. In the transport theory of charged particles the role of condition (38) was clearly established in the work by Kumar (1981), a study of short-time development of swarms. He has shown that, subject to Assumption I, the time-dependent transport coefficients (Kumar 1984) all approach their hydrodynamic values in the same characteristic time.

The spectrum of $\hat{H}$ varies continuously with $\vec{q}$, coinciding with the spectrum of $\hat{H}_0$ when $\vec{q}=0$, i.e. $\hat{H}'=0$. We wish to calculate the eigenvalue $\Lambda_{\bar{n}}(\vec{q})$ of $\hat{H}$ that tends to $\Lambda_{\bar{n}}^{(0)}$ when $\vec{q}\to 0$, and to determine the corresponding eigenvectors of $\hat{H}$. We assume that the eigenvalue $\Lambda_{\bar{n}}^{(0)}$ is *nondegenerate*. Eigenvalue $\Lambda_{\bar{n}}(\vec{q})$ will also be non-degenerate. The corresponding eigenvector, $|\psi_{\bar{n}}(\vec{q})\rangle$, is defined to within a constant which may be arbitrarily fixed so we impose the normalisation condition

$$\langle\tilde{\psi}_{\bar{n}}^{(0)}|\psi_{\bar{n}}(\vec{q})\rangle = \langle\tilde{\psi}_{\bar{n}}^{(0)}|\psi_{\bar{n}}^{(0)}\rangle = 1. \tag{40}$$

With this condition, $|\psi_{\bar{n}}(\vec{q})\rangle$ tends to $|\psi_{\bar{n}}^{(0)}\rangle$ when $\vec{q}\to 0$.

The second assumption is always implicit in any microscopic approach to transport problem (Résibois and De Leener 1977; Kato 1966):

Assumption II (upper semicontinuity of spectrum):

The small perturbation $\hat{H}'$ shifts slightly the eigenvalues of $\hat{H}_0$ (and introduces the dependence on $\vec{q}$), but assumption (38) remains valid for eigenvalues of $\hat{H}$ in the long-wavelength limit $\vec{q}\to 0$:

$$\mathrm{Re}\,\Lambda_n(\vec{q}) < \mathrm{Re}\,\Lambda_{\bar{n}}(\vec{q}), \quad \forall n \neq \bar{n}; \quad \vec{q}\to 0. \tag{41}$$

This assumption, which plays a crucial role in derivation of the GDE, states that the spectrum $\sigma(\hat{H}_0)$ of the unperturbed operator $\hat{H}_0$ does not expand suddenly when $\vec{q}$ is changed continuously. Note that *Assumptions I* and *II* are yet to be proven for classes of operators occurring in the kinetic theory of swarm particles.

Therefore, for all $n \neq \bar{n}$, we have

$$\lim_{t\to\infty} \lim_{\vec{q}\to 0} \frac{|c_{n\lambda}^{(I)}(\vec{q})e^{t\Lambda_n(\vec{q})}|\psi_{n\lambda}(\vec{q})\rangle\ |}{|c_{\bar{n}}^{(I)}(\vec{q})e^{t\Lambda_{\bar{n}}(\vec{q})}|\psi_{\bar{n}}(\vec{q})\rangle\ |} = 0. \tag{42}$$

Consequently, as the prevailing contribution to the solution (31) in the double limit ($\vec{q} \to 0$, $t \to \infty$) is given by the perturbed eigenvector $|\psi_{\bar{n}}(\vec{q})\rangle$ associated with the perturbed eigenvalue $\Lambda_{\bar{n}}(\vec{q})$, we obtain an asymptotic formula:

$$|\Phi(\vec{q},t)\rangle \simeq c_{\bar{n}}^{(I)}(\vec{q})e^{t\Lambda_{\bar{n}}(\vec{q})}|\psi_{\bar{n}}(\vec{q})\rangle, \quad \vec{q} \to 0, \quad t \gg \tau_0. \tag{43}$$

Taking the time derivative of (43), we get

$$\frac{\partial}{\partial t}|\Phi(\vec{q},t)\rangle = \Lambda_{\bar{n}}(\vec{q})|\Phi(\vec{q},t)\rangle, \quad \vec{q} \to 0. \tag{44}$$

Since the Fourier transform $n_{\vec{q}}(t)$ of the swarm particle density is

$$n_{\vec{q}}(t) = \langle f^{(0)}|\Phi(\vec{q},t)\rangle, \tag{45}$$

we also get

$$\frac{\partial}{\partial t}n_{\vec{q}}(t) = \Lambda_{\bar{n}}(\vec{q})n_{\vec{q}}(t), \quad \vec{q} \to 0. \tag{46}$$

By taking the limit where t becomes large and $\vec{q}$ small, we have reduced the solution of the BE problem (1) to the calculation of one single eigenvalue of the problem (25) in the limit where $\vec{q}$ becomes small.

The fact that $\vec{q}$ is small suggests that we evaluate the basic eigenvalue $\Lambda_{\bar{n}}(\vec{q})$ and the eigenvector $|\psi_{\bar{n}}(\vec{q})\rangle$ by perturbation calculus. We assume that $\Lambda_{\bar{n}}(\vec{q})$ and $|\psi_{\bar{n}}(\vec{q})\rangle$ can be expanded into the converging series

$$\Lambda_{\bar{n}}(\vec{q}) = \Lambda_{\bar{n}}^{(0)} + \Lambda_{\bar{n}}^{(1)} + \Lambda_{\bar{n}}^{(2)} + \cdots + \Lambda_{\bar{n}}^{(p)} + \cdots, \tag{47}$$

$$|\psi_{\bar{n}}(\vec{q})\rangle = |\psi_{\bar{n}}^{(0)}\rangle + |\psi_{\bar{n}}^{(1)}\rangle + |\psi_{\bar{n}}^{(2)}\rangle + \cdots + |\psi_{\bar{n}}^{(p)}\rangle + \cdots, \tag{48}$$

where $\Lambda_{\bar{n}}^{(p)}$ and $|\psi_{\bar{n}}^{(p)}\rangle$ are the pth order perturbation contributions to $\Lambda_{\bar{n}}(\vec{q})$ and $|\psi_{\bar{n}}(\vec{q})\rangle$, respectively. The perturbation method consists of determining the successive expansion terms in (47) and (48).

We have shown that the orthogonality property and the closure relation can be generalised to non-Hermitian operators, if we use biorthonormal sets of eigenvectors. It can be proved that the standard formulae of perturbation calculus remain valid in non-Hermitian perturbation with minor modifications. The equations for corrections are obtained from equation (25) using the expansions (47) and (48), treating the perturbation $\hat{H}'$ as the first order term, and grouping terms of the same order. Solutions for the pth order corrections can be presented in the form

$$\Lambda_{\bar{n}}^{(1)} = \langle \tilde{\psi}_{\bar{n}}^{(0)} | \hat{H}' | \psi_{\bar{n}}^{(0)} \rangle, \tag{49}$$

$$\Lambda_{\bar{n}}^{(p)} = \langle \tilde{\psi}_{\bar{n}}^{(0)} | \hat{H}' | \psi_{\bar{n}}^{(p-1)} \rangle, \quad p \geq 2, \tag{50}$$

$$|\psi_{\bar{n}}^{(1)}\rangle = [\Lambda_{\bar{n}}^{(0)} - \hat{H}_0]^{-1} \hat{Q} \hat{H}' |\psi_{\bar{n}}^{(0)}\rangle, \tag{51}$$

$$|\psi_{\bar{n}}^{(p)}\rangle = [\Lambda_{\bar{n}}^{(0)} - \hat{H}_0]^{-1} \hat{Q} \left[\hat{H}' |\psi_{\bar{n}}^{(p-1)}\rangle - \sum_{s=1}^{p-1} \Lambda_{\bar{n}}^{(s)} |\psi_{\bar{n}}^{(p-s)}\rangle \right], \quad p \geq 2. \tag{52}$$

The steps in the evaluation of equations (49)–(52) that differ from the Hermitian case are outlined in Appendix A. These equations effectively determine $\Lambda_{\bar{n}}^{(p)}$ and $|\psi_{\bar{n}}^{(p)}\rangle$ in terms of the lower order corrections. Condition (40) becomes

$$\langle \tilde{\psi}_{\bar{n}}^{(0)} | \psi_{\bar{n}}^{(1)} \rangle = \langle \tilde{\psi}_{\bar{n}}^{(0)} | \psi_{\bar{n}}^{(2)} \rangle = \cdots = \langle \tilde{\psi}_{\bar{n}}^{(0)} | \psi_{\bar{n}}^{(p)} \rangle = \cdots = 0. \tag{53}$$

The operator

$$\hat{Q} = \hat{I} - |\psi_{\bar{n}}^{(0)}\rangle \langle \tilde{\psi}_{\bar{n}}^{(0)}| \tag{54}$$

is a projector (but not orthogonal) onto the subspace complementary to the subspace spanned by the basic eigenvector $|\psi_{\bar{n}}^{(0)}\rangle$. Since the operator $\Lambda_{\bar{n}}^{(0)} - \hat{H}_0$ is singular, it is clear that the inverse operator $[\Lambda_{\bar{n}}^{(0)} - \hat{H}_0]^{-1}$ cannot be defined on the whole Hilbert space $\mathbf{H}$. In equations (51) and (52) the operator $[\Lambda_{\bar{n}}^{(0)} - \hat{H}_0]^{-1}$ is well defined because the range of $\hat{Q}$ does not contain the vectors of the kernel of $\Lambda_{\bar{n}}^{(0)} - \hat{H}_0$, $\mathrm{im}\hat{Q} \cap \ker(\Lambda_{\bar{n}}^{(0)} - \hat{H}_0) = \emptyset$. Furthermore, from the closure relation (37) and definition (54), it is obvious that the operator $[\Lambda_{\bar{n}}^{(0)} - \hat{H}_0]^{-1}\hat{Q}$ can be written in the form of a series of elementary, non-orthogonal projectors:

$$[\Lambda_{\bar{n}}^{(0)} - \hat{H}_0]^{-1} \hat{Q} = \sum_{n \neq \bar{n}} \sum_{\lambda} \frac{1}{\Lambda_{\bar{n}}^{(0)} - \Lambda_{n}^{(0)}} |\psi_{n\lambda}^{(0)}\rangle \langle \tilde{\psi}_{n\lambda}^{(0)}|. \tag{55}$$

The higher order corrections involve an increasing number of the operators $[\Lambda_{\bar{n}}^{(0)} - \hat{H}_0]^{-1} \hat{Q} \hat{H}'$, the norm of which is the scale of relative perturbation. Consequently, the magnitude of the perturbative corrections is a rapidly diminishing function of the order p.

The projector $\hat{I} - \hat{Q}$ is an essential part of the theory of Kondo (1987). Projector operators occurring in our analysis play a less important role.

(3a) Hydrodynamic Regime and Transport Coefficients

Using the explicit form of the convective operator $\hat{H}' = -i\vec{q} \cdot \hat{\vec{v}}$, let us show how equation (46) leads to the GDE, with microscopic expressions for the transport coefficients, as well. First we introduce the quantities $\omega^{(p)}$ and $\chi^{(p)}$ which are defined through a set of coupled recursive relations:

$$\hat{\omega}^{(0)} = \langle \tilde{\psi}_{\bar{n}}^{(0)} | \hat{H}_0 | \psi_{\bar{n}}^{(0)} \rangle, \tag{56}$$

$$|| \chi_{\bar{n}}^{(0)} \rangle\rangle = | \psi_{\bar{n}}^{(0)} \rangle, \tag{57}$$

$$\hat{\omega}^{(1)} = \langle \tilde{\psi}_{\bar{n}}^{(0)} | \hat{\vec{v}} \, || \chi_{\bar{n}}^{(0)} \rangle\rangle, \tag{58}$$

$$|| \chi_{\bar{n}}^{(1)} \rangle\rangle = [\hat{\omega}^{(0)} - \hat{H}_0]^{-1} \hat{Q} \hat{\vec{v}} \, || \chi_{\bar{n}}^{(0)} \rangle\rangle, \tag{59}$$

$$\hat{\omega}^{(p)} = \langle \tilde{\psi}_{\bar{n}}^{(0)} | \hat{\vec{v}} \, || \chi_{\bar{n}}^{(p-1)} \rangle\rangle, \quad p \geq 2, \tag{60}$$

$$|| \chi_{\bar{n}}^{(p)} \rangle\rangle = [\hat{\omega}^{(0)} - \hat{H}_0]^{-1} \hat{Q} \left[\hat{\vec{v}} \, || \chi_{\bar{n}}^{(p-1)} \rangle\rangle - \sum_{s=1}^{p-1} \hat{\omega}^{(s)} \otimes \, || \chi_{\bar{n}}^{(p-s)} \rangle\rangle \right], \quad p \geq 2, \tag{61}$$

with notation

$$\hat{\vec{v}} \, || \chi_{\bar{n}}^{(0)} \rangle\rangle = \left(\hat{v}_{\alpha_1} \, || \chi_{\bar{n}}^{(0)} \rangle\rangle \right), \quad \alpha_1 = 1, 2, 3, \tag{62}$$

$$\hat{\omega}^{(s)} \otimes \, || \chi_{\bar{n}}^{(p-s)} \rangle\rangle = \left(\hat{\omega}_{\alpha_1, \ldots, \alpha_s}^{(s)} \, || \chi_{\bar{n}}^{(p-s)} \rangle\rangle_{\alpha_{s+1}, \ldots, \alpha_p} \right),$$
$$\alpha_1, \ldots, \alpha_p = 1, 2, 3; \quad s = 1, \ldots, p-1; \quad p \geq 2, \tag{63}$$

$$\hat{\vec{v}} \, | \chi_{\bar{n}}^{(p-1)} \rangle\rangle = \left(\hat{v}_{\alpha_1} \, | \chi_{\bar{n}}^{(p-1)} \rangle\rangle_{\alpha_2, \ldots, \alpha_p} \right), \quad \alpha_1, \ldots, \alpha_p = 1, 2, 3; \quad p \geq 2. \tag{64}$$

Inserting corrections (49)–(52) into equations (47) and (48), and having in mind equations (56)–(61) we find that the perturbed eigenvector (48) can be expressed as

$$| \psi_{\bar{n}}(\vec{q}) \rangle = \sum_{p=0}^{\infty} | \psi_{\bar{n}}^{(p)} \rangle = \sum_{p=0}^{\infty} (-i\vec{q})^p \otimes \, || \chi_{\bar{n}}^{(p)} \rangle\rangle, \tag{65}$$

and the basic, perturbed eigenvalue (47) has the form

$$\Lambda_{\bar{n}}(\vec{q}) = \sum_{p=0}^{\infty} \Lambda_{\bar{n}}^{(p)} = \sum_{p=0}^{\infty} (-i\vec{q})^p \odot \hat{\omega}^{(p)}. \tag{66}$$

The symbol $\odot$ indicates the k-fold scalar product. The condition (53) becomes

$$\langle \tilde{\psi}_{\bar{n}}^{(0)} || \chi_{\bar{n}}^{(1)} \rangle\rangle = 0, \quad \langle \tilde{\psi}_{\bar{n}}^{(0)} || \chi_{\bar{n}}^{(2)} \rangle\rangle = 0, \quad \cdots, \quad \langle \tilde{\psi}_{\bar{n}}^{(0)} || \psi_{\bar{n}}^{(p)} \rangle\rangle = 0. \tag{67}$$

Substituting equation (66) into equation (46) we obtain the spatial Fourier transform of GDE (2):

$$\frac{\partial}{\partial t} n_{\vec{q}}(t) - \sum_{p=0}^{\infty} (-i\vec{q})^p \odot \hat{\omega}^{(p)} n_{\vec{q}}(t) = 0. \tag{68}$$

The transport coefficients are determined with the microscopic expressions (56)–(61). These equations give the transport coefficients $\hat{\omega}^{(p)}$ for all $p \geq 0$ in terms of solutions of the eigenvalue problems (34) and (35). For example, using the equations (50) and (51) together with the spectral decomposition of the operator $[\Lambda_{\bar{n}}^{(0)} - \hat{H}_0]^{-1}\hat{Q}$ (see equation 55), the diffusion tensor $\hat{D} \equiv \hat{\omega}^{(2)}$ can be expressed as

$$\hat{D} \equiv \hat{\omega}^{(2)} = \sum_{n \neq \bar{n}} \sum_{\lambda} \frac{1}{\hat{\omega}^{(0)} - \Lambda_n^{(0)}} \langle \tilde{\psi}_{\bar{n}}^{(0)} | \hat{\vec{v}} | \psi_{n\lambda}^{(0)} \rangle \langle \tilde{\psi}_{n\lambda}^{(0)} | \hat{\vec{v}} | \psi_{\bar{n}}^{(0)} \rangle. \tag{69}$$

An explicit expression for the third order transport coefficient $\hat{\omega}^{(3)}$ can be derived by using expressions (56)–(61). Using equation (55) and condition (36), one obtains for the third order transport coefficients $\hat{\omega}^{(3)}$ the expression:

$$\begin{aligned}\hat{\omega}^{(3)} = & \sum_{n \neq \bar{n}} \sum_{\lambda} \sum_{n' \neq \bar{n}} \sum_{\lambda'} \frac{1}{\hat{\omega}^{(0)} - \Lambda_n^{(0)}} \frac{1}{\hat{\omega}^{(0)} - \Lambda_{n'}^{(0)}} \langle \tilde{\psi}_{\bar{n}}^{(0)} | \hat{\vec{v}} | \psi_{n\lambda}^{(0)} \rangle \\ & \times \langle \tilde{\psi}_{n\lambda}^{(0)} | \hat{\vec{v}} | \psi_{n'\lambda'}^{(0)} \rangle \langle \tilde{\psi}_{n'\lambda'}^{(0)} | \hat{\vec{v}} | \psi_{\bar{n}}^{(0)} \rangle - \langle \tilde{\psi}_{\bar{n}}^{(0)} | \hat{\vec{v}} | \psi_{\bar{n}}^{(0)} \rangle \\ & \sum_{n \neq \bar{n}} \sum_{\lambda} \frac{1}{\left(\hat{\omega}^{(0)} - \Lambda_n^{(0)}\right)^2} \langle \tilde{\psi}_{\bar{n}}^{(0)} | \hat{\vec{v}} | \psi_{n\lambda}^{(0)} \rangle \langle \tilde{\psi}_{n\lambda}^{(0)} | \hat{\vec{v}} | \psi_{\bar{n}}^{(0)} \rangle. \end{aligned} \tag{70}$$

In the case of transport coefficients of order higher than three, one can proceed in an analogous way.

To summarise the results of this section, we have obtained the generalised diffusion equation and the transport coefficients of swarm particles from the eigenvalue problem associated with the inhomogeneous BE.

(3b) Hierarchy of Kinetic Equations for Transport Coefficients

In previous sections we have proved under Assumptions I and II that if we take times $t \gg \tau_0$, and provided $\vec{q}$ is small enough, the solution of the initial value problem (21) is given by equation (43), where the basic perturbed eigenvector

$|\psi_{\bar{n}}(\vec{q})\rangle$ and eigenvalue $\Lambda_{\bar{n}}(\vec{q})$ can be expressed as (65) and (66), respectively. Combining (43), (45) and (65), we finally get

$$|\Phi(\vec{q},t)\rangle = \sum_{p=0}^{\infty} ||\chi_{\bar{n}}^{(p)}\rangle\rangle \otimes (-i\vec{q})^p \bar{n}_{\vec{q}}(t), \tag{71}$$

where

$$\bar{n}_{\vec{q}}(t) = c_{\bar{n}}^{(I)}(\vec{q}) e^{t\Lambda_{\bar{n}}(\vec{q})} = \frac{1}{\langle f^{(0)}|\psi_{\bar{n}}(\vec{q})\rangle} n_{\vec{q}}(t). \tag{72}$$

Notice that vectors $||\chi_{\bar{n}}^{(p)}\rangle\rangle$ satisfy the normalisation conditions (67), and that

$$c_{\bar{n}}^{(I)}(\vec{q}) = \langle\tilde{\psi}_{\bar{n}}(\vec{q})|\Phi_I(\vec{q})\rangle \to c_{\bar{n}}^{0(I)}(\vec{q}) = \langle\tilde{\psi}_{\bar{n}}^{(0)}|\Phi_I(\vec{q})\rangle, \quad \vec{q} \to 0. \tag{73}$$

Taking the inverse Fourier transform of equation (71), the one-particle distribution function has the form

$$|f(\vec{r},t)\rangle = \sum_{p=0}^{\infty} ||\chi_{\bar{n}}^{(p)}\rangle\rangle \otimes \left(-\frac{\partial}{\partial\vec{r}}\right)^p \bar{n}(\vec{r},t), \tag{74}$$

where $\bar{n}(\vec{r},t)$ is the inverse Fourier transform of $\bar{n}_{\vec{q}}(t)$. Since

$$\bar{n}(\vec{r},t) = \langle\tilde{\psi}_{\bar{n}}^{(0)}|f(\vec{r},t)\rangle \neq \langle f^{(0)}|f(\vec{r},t)\rangle = n(\vec{r},t), \tag{75}$$

the gradient expansions (3) and (74) are not identical. Their forms are equivalent in the sense of separation of velocity and space–time dependence of the one-particle distribution function. The difference between the two expansions arises from different normalisation procedures. The normalisation as used by Kumar is given in equation (8). It should be compared to our choice given in equation (67) which was made in order to make it possible to derive microscopic expressions of transport coefficients based only on solutions to the eigenvalue problems for $\hat{H}_0$ and $\hat{H}_0^\dagger$. Inserting equations (66) and (73) into (72), equation (74) can be written in the form

$$|f(\vec{r},t)\rangle = \sum_{p=0}^{\infty} ||\chi_{\bar{n}}^{(p)}\rangle\rangle \otimes \left(-\frac{\partial}{\partial\vec{r}}\right)^p e^{\hat{\omega}^{(0)}t} \int d^3\vec{q} c_{\bar{n}}^{0(I)}(\vec{q}) e^{+i\vec{q}\vec{r}} \prod_{s=1}^{\infty} e^{(-i\vec{q})^s \odot \hat{\omega}^{(s)} t}. \tag{76}$$

Our approach strongly suggests that the solution (76) of the BE, obtained for arbitrary initial conditions, properly describes the long-time behaviour of a swarm of charged particles with slowly varying inhomogeneities.

We are now able to demonstrate the equivalence between the microscopic expressions for the transport coefficients (56)–(61) and the hierarchy of kinetic equations (4)–(5). Since $\langle\tilde{\psi}_{\bar{n}}^{(0)}\, ||\chi_{\bar{n}}^{(0)}\rangle\rangle = 1$, equation (56) implies that

$$\hat{H}_0\, ||\chi_{\bar{n}}^{(0)}\rangle\rangle = \hat{\omega}^{(0)}\, ||\chi_{\bar{n}}^{(0)}\rangle\rangle. \tag{77}$$

Applying the operator $\hat{\omega}^{(0)} - \hat{H}_0$ to both sides of equations (59) and (61) and using equations (58), (60) and (67) yields:

$$(-\hat{H}_0)\,||\chi_{\bar{n}}^{(p)}\rangle\!\rangle = \hat{\vec{v}}\,||\chi_{\bar{n}}^{(p-1)}\rangle\!\rangle - \sum_{s=0}^{p} \hat{\omega}^{(s)} \otimes\, ||\chi_{\bar{n}}^{(p-s)}\rangle\!\rangle, \quad p \geq 1. \tag{78}$$

Thus we have obtained that the expansion vectors $||\chi_{\bar{n}}^{(p)}\rangle\!\rangle$ and transport coefficients $\hat{\omega}^{(p)}$ satisfy the hierarchy of equations (77) and (78). This result is equivalent to the formulae (4) and (5) of Kumar's theory.

Projecting equations (77) and (78) onto the basic eigenvector $|\psi_{\bar{n}}^{(0)}\rangle$ gives

$$\hat{\omega}^{(0)} = \frac{1}{||\,|\psi_{\bar{n}}^{(0)}\rangle\,||^2} \langle \psi_{\bar{n}}^{(0)}|\hat{H}_0\,||\chi_{\bar{n}}^{(0)}\rangle\!\rangle, \tag{79}$$

$$\hat{\omega}^{(p)} = \frac{1}{||\,|\psi_{\bar{n}}^{(0)}\rangle\,||^2} \Bigg[\langle \psi_{\bar{n}}^{(0)}|\hat{\vec{v}}\,||\chi_{\bar{n}}^{(p-1)}\rangle\!\rangle - \langle \psi_{\bar{n}}^{(0)}|(-\hat{H}_0)\,||\chi_{\bar{n}}^{(p)}\rangle\!\rangle - \sum_{s=0}^{p-1} \hat{\omega}^{(s)} \odot \langle \psi_{\bar{n}}^{(0)}\,||\chi_{\bar{n}}^{(p-s)}\rangle\!\rangle \Bigg], \quad p \geq 1. \tag{80}$$

The third term in expression (80) exists due to the fact that in the non-Hermitian case, the normalisation condition (67) implies $\langle \psi_{\bar{n}}^{(0)}\,||\chi_{\bar{n}}^{(p)}\rangle\!\rangle \neq 0$. These equations show that the transport coefficients $\hat{\omega}^{(p)}$ depend only on the velocity-dependent part of the one-particle distribution function. This condition was never imposed, it arises naturally and it also implies that the final values of the transport coefficients are reached regardless of initial conditions.

In this section we have applied the technique of Résibois which was originally developed for transport of neutral particles. Applying it to swarms of charged particles in an electric field proved to be straightforward, i.e. without major difficulties.

4. Time-dependent Perturbation Method

In the preceding sections, we have treated the problem of charged particle transport by the stationary perturbation method which consists of determining eigenvectors and eigenvalues for the perturbed operator $\hat{H}$ differing little from the unperturbed operator $\hat{H}_0$. This section is devoted to methods of investigating the time evolution of a system of charged particles based on a time-dependent perturbation theory.

Knowing that vector $|\Phi_I(\vec{q})\rangle$ (equation 21) represents a certain state of the swarm at time $t = 0$, we wish to determine its state $|\Phi(\vec{q}, t)\rangle$ at a later time t. The problem, therefore, is to determine the operator describing the evolution in time of the swarm particles in accordance with the kinetic equation (21). The correspondence between $|\Phi_I(\vec{q})\rangle$ and $|\Phi(\vec{q}, t)\rangle$ is linear and defines a linear evolution operator $\hat{U}(t)$:

$$|\Phi(\vec{q}, t)\rangle = \hat{U}(t)|\Phi_I(\vec{q})\rangle. \tag{81}$$

According to equations (22) and (30), the operator $\hat{U}(t)$ can be formally written as

$$\hat{U}(t) = e^{t\hat{H}} = \sum_{n,\lambda} e^{t\Lambda_n} |\psi_{n\lambda}\rangle\langle\tilde{\psi}_{n\lambda}|. \tag{82}$$

The operator $\hat{U}(t)$ is the solution of the differential equation

$$\frac{d}{dt}\hat{U}(t) = \hat{H}\hat{U}(t), \quad \hat{U}(0) = \hat{I}. \tag{83}$$

Since $\hat{H}$ is not a Hermitian operator, it is obvious that evolution operator $\hat{U}(t)$ is not unitary. We wish to determine as exactly as possible the operator $\hat{U}(t)$ without any reference to the eigenvalue problem of the perturbed operator $\hat{H}$. The methods briefly described below are based on the time-dependent perturbation theory which has been developed for Hermitian operators in quantum mechanics (Messiah 1974).

Let $\hat{U}_0(t)$ be the evolution operator corresponding to the unperturbed operator $\hat{H}_0$; consequently operator $\hat{U}_0$ satisfies the differential equation

$$\frac{d}{dt}\hat{U}_0(t) = \hat{H}_0\hat{U}_0(t), \quad \hat{U}_0(0) = \hat{I}. \tag{84}$$

In our case when $\hat{H}_0$ is time independent, the evolution operator $\hat{U}_0(t)$ becomes simply

$$\hat{U}_0(t) = e^{t\hat{H}_0} = \sum_{n,\lambda} e^{t\Lambda_n^{(0)}} |\psi_{n\lambda}^{(0)}\rangle\langle\tilde{\psi}_{n\lambda}^{(0)}|. \tag{85}$$

The properties of $\hat{U}_0(t)$ are thus directly related to those of $\hat{H}_0$. Since $\hat{U}_0(t)$ is known, $\hat{U}$ will be determined if we can form the operator $\hat{U}_I$ defined as

$$\hat{U}(t) = \hat{U}_0(t)\hat{U}_I(t). \tag{86}$$

A simple calculation shows that the time dependence of $\hat{U}_I(t)$ is determined by the equation

$$\frac{d}{dt}\hat{U}_I(t) = \hat{H}'_I(t)\hat{U}_I(t), \quad \hat{U}_I(0) = \hat{I}, \tag{87}$$

where operator $\hat{H}'_I(t)$ is a perturbation operator $\hat{H}'$ in the 'interaction picture':

$$\hat{H}'_I(t) = \hat{U}_0^{-1}(t)\hat{H}'\hat{U}_0(t). \tag{88}$$

Equation (87) is equivalent to the integral equation

$$\hat{U}_I(t) = \hat{I} + \int_0^t dt_1 \hat{H}'_I(t_1)\hat{U}_I(t_1). \tag{89}$$

The integral in equation (89) can be solved by iteration (in powers of $\hat{H}'_I$) yielding

$$\hat{U}_I(t) = \hat{I} + \sum_{p=1}^{\infty} \hat{U}_I^{(p)}(t), \tag{90}$$

where

$$\hat{U}_I^{(p)}(t) = \int_0^t dt_1 \hat{H}'_I(t_1) \int_0^{t_1} dt_2 \hat{H}'_I(t_2) \cdots \int_0^{t_{p-1}} dt_p \hat{H}'_I(t_p), \quad p \geq 1. \tag{91}$$

From this result, with the aid of definitions (86) and (88), we get the following expansion for $\hat{U}$:

$$\hat{U}(t) = \hat{U}^{(0)}(t) + \sum_{p=1}^{\infty} \hat{U}^{(p)}(t), \tag{92}$$

$$\hat{U}^{(0)}(t) = \hat{U}_0(t), \tag{93}$$

$$\begin{aligned}\hat{U}^{(p)}(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{p-1}} dt_p \hat{U}^{(0)}(t-t_1)\hat{H}'\hat{U}^{(0)}(t_1-t_2)\hat{H}' \cdots \\ \cdots \hat{U}^{(0)}(t_{p-1}-t_p)\hat{H}'\hat{U}^{(0)}(t_p), \quad p \geq 1\,.\end{aligned} \tag{94}$$

Using equations (81) and (92), one obtains the expansion of $|\Phi(\vec{q},t)\rangle$

$$|\Phi(\vec{q},t)\rangle = \sum_{p=0}^{\infty} |\Phi^{(p)}(\vec{q},t)\rangle, \tag{95}$$

where

$$|\Phi^{(p)}(\vec{q},t)\rangle = \hat{U}^{(p)}(t)|\Phi_I(\vec{q})\rangle. \tag{96}$$

Inserting the explicit form of the convective operator $\hat{H}' = -i\vec{q}\hat{\vec{v}}$ into equation (94), and by using (95) and (96), we get that the vector $|\Phi(\vec{q},t)\rangle$ can be expressed as

$$|\Phi(\vec{q},t)\rangle = \sum_{p=0}^{\infty} (-i\vec{q})^p \otimes \; ||^{(p)}(\vec{q},t)\rangle\rangle, \tag{97}$$

where

$$||^{(0)}(\vec{q},t)\rangle\rangle = e^{t\hat{H}_0}|\Phi_I(\vec{q})\rangle, \tag{98}$$

$$||^{(p)}(\vec{q},t)\rangle\!\rangle = \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{p-1}} dt_p e^{(t-t_1)\hat{H}_0} \hat{\vec{v}} e^{(t_1-t_2)\hat{H}_0} \hat{\vec{v}} \cdots$$
$$\cdots e^{(t_{p-1}-t_p)\hat{H}_0} \hat{\vec{v}} e^{t_p \hat{H}_0} |\Phi_I(\vec{q})\rangle, \quad p \geq 1. \tag{99}$$

As may be checked by direct differentiation of equations (98) and (99), the vectors $||^{(p)}(\vec{q},t)\rangle\!\rangle$ satisfy the following infinite set of equations:

$$\frac{\partial}{\partial t}\, ||^{(0)}(\vec{q},t)\rangle\!\rangle = \hat{H}_0\, ||^{(0)}(\vec{q},t)\rangle\!\rangle, \tag{100}$$

$$\frac{\partial}{\partial t}\, ||^{(p)}(\vec{q},t)\rangle\!\rangle = \hat{H}_0\, ||^{(p)}(\vec{q},t)\rangle\!\rangle + \hat{\vec{v}}\, ||^{(p-1)}(\vec{q},t)\rangle\!\rangle, \quad p \geq 1. \tag{101}$$

Replacing the exponential operators in (98) and (99) with corresponding expansions in series of non-orthogonal projectors (equation 85), one finds

$$||^{(0)}(\vec{q},t)\rangle\!\rangle = \sum_{n,\lambda} c_{n\lambda}^{0(I)}(\vec{q}) |\psi_{n\lambda}^{(0)}\rangle e^{t\Lambda_n^{(0)}}, \tag{102}$$

$$||^{(p)}(\vec{q},t)\rangle\!\rangle = \sum_{n,\lambda} c_{n\lambda}^{0(I)}(\vec{q}) \sum_{n_1,\lambda_1} \sum_{n_2,\lambda_2} \cdots \sum_{n_p,\lambda_p} \langle \tilde{\psi}_{n_p\lambda_p}^{(0)} | \hat{\vec{v}} | \psi_{n_{p-1}\lambda_{p-1}}^{(0)} \rangle \cdots$$
$$\cdots \langle \tilde{\psi}_{n_2\lambda_2}^{(0)} | \hat{\vec{v}} | \psi_{n_1\lambda_1}^{(0)} \rangle \langle \tilde{\psi}_{n_1\lambda_1}^{(0)} | \hat{\vec{v}} | \psi_{n\lambda}^{(0)} \rangle |\psi_{n_p\lambda_p}^{(0)}\rangle \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \tag{103}$$
$$\cdots \int_0^{t_{p-1}} dt_p e^{t_p\Lambda_n^{(0)}} e^{(t_{p-1}-t_p)\Lambda_{n_1}^{(0)}} \cdots e^{(t_1-t_2)\Lambda_{n_{p-1}}^{(0)}} e^{(t-t_1)\Lambda_{n_p}^{(0)}}, \quad p \geq 1.$$

Here

$$c_{n\lambda}^{0(I)}(\vec{q}) = \langle \tilde{\psi}_{n\lambda}^{(0)} | \Phi_I(\vec{q}) \rangle. \tag{104}$$

Since $n_{\vec{q}}(t) = \langle f^{(0)} | \Phi(\vec{q},t) \rangle$, we also get

$$n_{\vec{q}}(t) = \sum_{p=0}^{\infty} (-i\vec{q})^p \odot \hat{N}_*^{(p)}(\vec{q},t), \tag{105}$$

where

$$\hat{N}_*^{(p)}(\vec{q},t) = \langle f^{(0)}\, ||^{(p)}(\vec{q},t)\rangle\!\rangle, \quad p = 0, 1, 2, \ldots, \tag{106}$$

are tensors of order p. The quantities $\hat{N}_*^{(p)}(\vec{q},t)$ are analogous to the spatial moments of the number density $n(\vec{r},t)$ (Kumar 1981).

A hierarchy of tensor functions $\hat{\omega}_*^{(p)}(\vec{q},t)$ of rank p is now introduced by the definitions

$$\frac{\partial}{\partial t}\hat{N}_*^{(p)}(\vec{q},t)=\sum_{r=0}^{p}\hat{\omega}_*^{(r)}(\vec{q},t)\odot\hat{N}_*^{(p-r)}(\vec{q},t),\quad p=0,1,2,\ldots. \tag{107}$$

It easily follows from definitions (107) and equation (105) that

$$\frac{\partial}{\partial t}n_{\vec{q}}(t)-\sum_{p=0}^{\infty}(-i\vec{q})^p\odot\hat{\omega}_*^{(p)}(\vec{q},t)n_{\vec{q}}(t)=0. \tag{108}$$

Guided by analogies with the Fourier transform of the GDE (2), tensors $\hat{\omega}_*^{(p)}(\vec{q},t)$ may be regarded as time-dependent transport coefficients. Since the $\vec{q}$ dependence of the transport coefficients $\hat{\omega}_*^{(p)}(\vec{q},t)$ has its origin in the $\vec{q}$ dependence of the initial vector $|\phi_I(\vec{q})\rangle$ [see equations (102) – (104)], we conclude that $\hat{\omega}_*^{(p)}(\vec{q},t)$ can be related to various Fourier components of the initial distribution function.

We shall try to find vector $|\Phi(\vec{q},t)\rangle$ (equation 97) for times $t\gg\tau_0$ and *arbitrary* values of $\vec{q}$. This will be carried out by using only Assumption I (equation 38). It will be shown that for the long-time limit, the vector $|\Phi(\vec{q},t)\rangle$ (equation 97) can be transformed into the hydrodynamics form (71). We shall also show that for the long-time limit all $\hat{\omega}_*^{(p)}(\vec{q},t)$ become time *and* $\vec{q}$ independent in the same characteristic time and achieve their hydrodynamic values given by the microscopic expressions (56), (58) and (60).

First let us try to find vectors $||^{(p)}(\vec{q},t)\rangle\rangle$ for times $t\gg\tau_0$. Starting from equations (102)–(103) and using only Assumption I, we obtain the following asymptotic formulae for the first four vectors:

$$||^{(0)}(\vec{q},t)\rangle\rangle\simeq c_{\bar{n}}^{0(I)}(\vec{q})e^{t\Lambda_{\bar{n}}^{(0)}}\;||\chi_{\bar{n}}^{(0)}\rangle\rangle,\quad t\gg\tau_0, \tag{109}$$

$$||^{(1)}(\vec{q},t)\rangle\rangle\simeq c_{\bar{n}}^{0(I)}(\vec{q})e^{t\Lambda_{\bar{n}}^{(0)}}\left[t\hat{\omega}^{(1)}\otimes\;||\chi_{\bar{n}}^{(0)}\rangle\rangle+\;||\chi_{\bar{n}}^{(1)}\rangle\rangle\right],\quad t\gg\tau_0, \tag{110}$$

$$\begin{aligned}||^{(2)}(\vec{q},t)\rangle\rangle\simeq c_{\bar{n}}^{0(I)}(\vec{q})e^{t\Lambda_{\bar{n}}^{(0)}}\Bigg[&\frac{t^2}{2}\hat{\omega}^{(1)}\odot\hat{\omega}^{(1)}\otimes\;||\chi_{\bar{n}}^{(0)}\rangle\rangle+t\hat{\omega}^{(1)}\otimes\;||\chi_{\bar{n}}^{(1)}\rangle\rangle\\&+t\hat{\omega}^{(2)}\otimes\;||\chi_{\bar{n}}^{(0)}\rangle\rangle+\;||\chi_{\bar{n}}^{(2)}\rangle\rangle\Bigg],\quad t\gg\tau_0,\end{aligned} \tag{111}$$

$$\begin{aligned}||^{(3)}(\vec{q},t)\rangle\rangle\simeq c_{\bar{n}}^{0(I)}(\vec{q})e^{t\Lambda_{\bar{n}}^{(0)}}\Bigg[&\frac{t^3}{6}\hat{\omega}^{(1)}\odot\hat{\omega}^{(1)}\odot\hat{\omega}^{(1)}\otimes\;||\chi_{\bar{n}}^{(0)}\rangle\rangle\\&+\frac{t^2}{2}\hat{\omega}^{(1)}\odot\hat{\omega}^{(1)}\otimes\;||\chi_{\bar{n}}^{(1)}\rangle\rangle+\frac{t^2}{2}\hat{\omega}^{(1)}\odot\hat{\omega}^{(2)}\otimes\;||\chi_{\bar{n}}^{(0)}\rangle\rangle\\&+t\hat{\omega}^{(1)}\otimes\;||\chi_{\bar{n}}^{(2)}\rangle\rangle+\frac{t^2}{2}\hat{\omega}^{(2)}\odot\hat{\omega}^{(1)}\otimes\;||\chi_{\bar{n}}^{(0)}\rangle\rangle\\&+t\hat{\omega}^{(2)}\otimes\;||\chi_{\bar{n}}^{(1)}\rangle\rangle+t\hat{\omega}^{(3)}\otimes\;||\chi_{\bar{n}}^{(0)}\rangle\rangle+\;||\chi_{\bar{n}}^{(3)}\rangle\rangle\Bigg],\quad t\gg\tau_0.\end{aligned} \tag{112}$$

The details of the calculation for $||^{(0)}(\vec{q},t)\rangle\rangle, \ldots, ||^{(3)}(\vec{q},t)\rangle\rangle$ are given in Appendix B. In practice the calculation of these vectors becomes increasingly complicated with higher orders. Tensors $\hat{\omega}^{(1)}$, $\hat{\omega}^{(2)}$ and $\hat{\omega}^{(3)}$ are given by microscopic expressions (58), (69) and (70). Vectors $||\chi_{\bar{n}}^{(1)}\rangle\rangle, \ldots, ||\chi_{\bar{n}}^{(3)}\rangle\rangle$, defined by equations (57), (59) and (61), can also be expressed in terms of the solution of the eigenvalue problems (34) and (35) [see equations (141)–(142) in Appendix B.

Replacing the above asymptotic expressions for $||^{(p)}(\vec{q},t)\rangle\rangle$ into equation (97), after a suitable rearrangement of the terms, leads to the following form of $|\Phi(\vec{q},t)\rangle$ for $t \gg \tau_0$:

$$|\Phi(\vec{q},t)\rangle = \sum_{p=0}^{\infty} ||\chi_{\bar{n}}^{(p)}\rangle\rangle \otimes (-i\vec{q})^p c_{\bar{n}}^{0(I)}(\vec{q}) e^{t\Lambda_{\bar{n}}^{(0)}} \Omega_{\vec{q}}(t), \tag{113}$$

where

$$\begin{aligned}
\Omega_{\vec{q}}(t) &= 1 + (-i\vec{q}) \odot \hat{\omega}^{(1)} t + (-i\vec{q})^2 \odot \hat{\omega}^{(1)} \odot \hat{\omega}^{(1)} \frac{t^2}{2} + (-i\vec{q})^2 \odot \hat{\omega}^{(2)} t \\
&\quad + (-i\vec{q})^3 \odot \hat{\omega}^{(1)} \odot \hat{\omega}^{(1)} \odot \hat{\omega}^{(1)} \frac{t^3}{6} + (-i\vec{q})^3 \odot \hat{\omega}^{(1)} \odot \hat{\omega}^{(2)} \frac{t^2}{2} \\
&\quad + (-i\vec{q})^3 \odot \hat{\omega}^{(2)} \odot \hat{\omega}^{(1)} \frac{t^2}{2} + (-i\vec{q})^3 \odot \hat{\omega}^{(3)} t + \cdots \\
&= \left[1 + (-i\vec{q}) \odot \hat{\omega}^{(1)} t + \tfrac{1}{2}(-i\vec{q})^2 \odot (\hat{\omega}^{(1)})^2 t^2 + \tfrac{1}{6}(-i\vec{q})^3 \odot (\hat{\omega}^{(1)})^3 t^3 + \cdots\right] \\
&\quad \times \left[1 + (-i\vec{q})^2 \odot \hat{\omega}^{(2)} t + \tfrac{1}{2}(-i\vec{q})^4 \odot (\hat{\omega}^{(2)})^2 t^2 + \cdots\right] \\
&\quad \times \left[1 + (-i\vec{q})^3 \odot \hat{\omega}^{(3)} t + \cdots\right] [1 + \cdots] \cdots .
\end{aligned} \tag{114}$$

By induction, it is easy to verify that

$$\Omega_{\vec{q}}(t) = \prod_{s=1}^{\infty} \left\{ 1 + \sum_{r=1}^{\infty} [(-i\vec{q})^s]^r \odot \left[\hat{\omega}^{(s)}\right]^r t^r \right\} = \prod_{s=1}^{\infty} e^{(-i\vec{q})^s \odot \hat{\omega}^{(s)} t}. \tag{115}$$

Introducing the expression (115) into (113) leads to

$$|\Phi(\vec{q},t)\rangle = \sum_{p=0}^{\infty} ||\chi_{\bar{n}}^{(p)}\rangle\rangle \otimes (-i\vec{q})^p \bar{n}_{\vec{q}}^0(t), \quad t \gg \tau_0, \tag{116}$$

where

$$\bar{n}_{\vec{q}}^0(t) = c_{\bar{n}}^{0(I)}(\vec{q}) e^{\sum_{s=0}^{\infty} (-i\vec{q})^s \odot \hat{\omega}^{(s)} t}. \tag{117}$$

Thus we have found an explicit expression for the arbitrary wave number Fourier coefficient $|\Phi(\vec{q},t)\rangle$ in the limit of long times, $t \gg \tau_0$. One should note that the inverse Fourier transform of equation (116) and expression (76) are identical.

We have accomplished the first part of our plan: the long-time behaviour of the one particle distribution function. In the following we shall carry out the second part: the determination of the time-dependent transport coefficient $\hat{\omega}_*^{(p)}(\vec{q},t)$ for long times.

We start from the definitions (107). The derivative with respect to time occurring in equation (107) can be eliminated with the help of (100)–(101). Combining (107), (106) and (100)–(101) we can write

$$\hat{\omega}_*^{(0)}(\vec{q},t) = \frac{1}{\langle f^{(0)} \,||^{(0)}(\vec{q},t)\rangle\!\rangle} \langle f^{(0)}|\hat{H}_0 \,||^{(0)}(\vec{q},t)\rangle\!\rangle, \tag{118}$$

$$\hat{\omega}_*^{(p)}(\vec{q},t) = \frac{1}{\langle f^{(0)}||^{(0)}(\vec{q},t)\rangle\rangle} \Bigg[\langle f^{(0)}|\hat{\vec{v}}||^{(p-1)}(\vec{q},t)\rangle\rangle + \langle f^{(0)}|\hat{H}_0 \,||^{(p)}(\vec{q},t)\rangle\!\rangle$$

$$-\sum_{s=0}^{p-1} \hat{\omega}_*^{(s)}(\vec{q},t) \odot \langle f^{(0)} \,||^{(p-s)}(\vec{q},t)\rangle\!\rangle\Bigg], \quad p \geq 1. \tag{119}$$

We are interested in times $t \gg \tau_0$. Introducing asymptotic expressions for vectors $||^{(p)}(\vec{q},t)\rangle\!\rangle$ [see equations (109)–(112)] into (118) and (119), and using the hierarchy of equations (77) and (78), we obtain that

$$\hat{\omega}_*^{(p)}(\vec{q},t) \simeq \hat{\omega}^{(p)}, \quad t \gg \tau_0; \quad p = 0,1,2,\ldots. \tag{120}$$

The present derivation, which can be carried out for any $\vec{q}$, shows that all time-dependent transport coefficients $\hat{\omega}_*^{(p)}(\vec{q},t)$ achieve their hydrodynamic values $\hat{\omega}^{(p)}$ in the same characteristic time. As a result, for $t \gg \tau_0$, equation (108) reduces directly to the spatial Fourier transform of the GDE (2).

5. Conclusion

In this paper we have analysed the foundations of the transport theory of charged particle swarms in neutral gases. In particular, we have studied the properties of operators $\hat{H}_0$ and $\hat{H}$ occurring in the BE and their relationship to transport coefficients and the one-particle distribution function by applying perturbation theory.

In the first part of the paper we studied weakly inhomogeneous swarms (i.e. with small relative density gradients). The method of Résibois was generalised for the case of charged particle transport in the presence of a static and uniform electric field. Two critical assumptions were required about the spectrum of the operator $\hat{H}_0$:

(A1) There is an isolated eigenvalue of the operator $\hat{H}_0$ which is separated from the rest of the spectrum by the gap along the real axis.

(A2) The perturbation $\hat{H}'$, for small values of the wave vector $\vec{q}$, has a small effect on the spectrum of the operator $\hat{H}_0$; i.e. the spectrum of the perturbed operator $\hat{H}$ also has an isolated eigenvalue separated from the rest of the spectrum along the real axis.

Furthermore it was possible to obtain the GDE in a double limit ($\vec{q} \to 0,\ t \to \infty$), a result (in this theory it is not an assumption) arising from the application of the stationary perturbation theory for non-Hermitian operators to BE.

The isolated point of the unperturbed operator $\hat{H}_0$ may be associated with the corresponding reaction rate. Its perturbation correction of the pth order may be associated with the pth order transport coefficients. According to the theoretical derivation presented here, any transport coefficient may be represented as a function of the solutions to the eigenvalue problem for the operators $\hat{H}_0$ and $\hat{H}_0^\dagger$. We have also shown a full equivalence of those microscopic equations and the hierarchy of kinetic equations for the transport coefficients.

Finally, we have described the asymptotic behaviour of the solution of the Cauchy problem for the BE. For any initial distribution of the swarm at moment $t = 0$ after $t \gg \tau_0$, a separation between the spatio-temporal and the velocity part of the one-particle distribution function occurs. At the same time, the transport coefficients only depend on the velocity part of the one-particle distribution function.

In the second part of the paper we have studied the time evolution of the one-particle distribution function of a swarm of charged particles in an electric field. In this section we have not limited our analysis to weakly inhomogeneous swarms (i.e. small relative density gradients). Time-dependent perturbation theory was applied to follow the evolution of the system from an arbitrary initial distribution. The difference between our approach and that of Kumar (1981) is that we apply time-dependent perturbation theory to the BE itself, while Kumar applied it to a hierarchy of equations for spatial moments of one-particle distribution function. Thus, he analysed the time dependence of spatial moments and consequently of the transport coefficient, but not of the distribution function.

We obtained the equation (108) which is analogous to the GDE with transport coefficients that are time dependent and implicitly depend on the wave vector. The spatial dependence of the transport coefficients arises from their explicit dependence on the initial distribution. In other words, every Fourier component of the initial distribution has corresponding transport coefficients which, according to (108), describes the temporal evolution of the corresponding Fourier component of the number density $n(\vec{r}, t)$.

In this section we require only the assumption (A1) and by using it we have shown that after a time $t \gg \tau_0$ any time-dependent transport coefficient becomes a constant. The limiting values are also independent of the wave vector and are equal to the corresponding hydrodynamic values which were derived in the first section of the paper.

To summarise, the basic result of this paper is the asymptotic form of the one-particle distribution function of charged particle swarms. Only the assumption (A1) is required to prove that by solving the BE for times $t \gg \tau_0$, the one-particle distribution function has the form given by equation (76). Therefore, it was shown that after time $t \gg \tau_0$ the distribution function separates to spatio-temporal and velocity dependent parts. In standard hydrodynamic theories this was always one of the basic assumptions, together with the assumption of the validity of the GDE. In the present theory both are the results of more fundamental assumptions on the spectral properties of operators involved in Boltzmann equation.

Acknowledgment

The authors are grateful to Professor Bob Crompton (Australian National University) for his help and encouragement. The work was partially funded by project MNTRS 01E03.

References

Balescu, R. (1975). 'Equilibrium and Nonequilibrium Statistical Mechanics' (Wiley: New York).
Boeuf, J. P., and Marode, E. (1982). *J. Phys.* D **15**, 2169.
Huxley, L. G. H., and Crompton, R. W. (1974). 'The Diffusion and Drift of Electrons in Gases' (Wiley: New York).
Kato, T. (1966). 'Perturbation Theory for Linear Operators' (Springer: Berlin).
Kondo, K. (1987). *Aust. J. Phys.* **40**, 367.
Kumar, K. (1981). *J. Phys.* D **14**, 2199.
Kumar, K. (1984). *Phys. Reports* **112**, 319.
Kumar, K., Skullerud, H. R., and Robson, R. E. (1980). *Aust. J. Phys.* **33**, 343.
Messiah, A. (1974). 'Quantum Mechanics' (North Holland: Amsterdam).
Nakano, N., Shimura, N., Petrović, Z. Lj., and Makabe, T. (1994). *Phys. Rev.* E **49**, 4455.
Petrović, Z. Lj., and Phelps, A. V. (1997). *Phys. Rev.* E **56**, 5920.
Résibois, P. (1970). *J. Statist. Phys.* **2**, 21.
Résibois, P., and De Leener, M. (1977). 'Classical Kinetic Theory of Fluids' (Wiley: New York).
Résibois, P., and Leaf, B. (1960). *Bull. Acad. Roy. Belg. Cl. Sc.* **46**, 148.
Résibois, P., and Prigogine, I. (1960). *Bull. Acad. Roy. Belg. Cl. Sc.* **46**, 53.
Sirovich, L., and Thurber, K. (1969). *J. Math. Phys.* **10**, 239.
Standish, R. K. (1987). *Aust. J. Phys.* **40**, 519.
Wang-Chang, C. S., Uhlenbeck, G. E., and De Boer, J. (1964). 'Studies in Statistical Mechanics' (Eds J. De Boer and G. E. Uhlenbeck), Vol. II, p. 241 (Wiley: New York).

Appendix A

We substitute expressions (47) and (48) into both sides of equation (25), which then becomes an equality between two series. In order that this equality is satisfied, the terms of the same order must be equal separately, giving, successively:

$$\hat{H}_0|\psi_{\bar{n}}^{(0)}\rangle = \Lambda_{\bar{n}}^{(0)}|\psi_{\bar{n}}^{(0)}\rangle, \tag{121}$$

$$\hat{H}_0|\psi_{\bar{n}}^{(1)}\rangle + \hat{H}'|\psi_{\bar{n}}^{(0)}\rangle = \Lambda_{\bar{n}}^{(0)}|\psi_{\bar{n}}^{(1)}\rangle + \Lambda_{\bar{n}}^{(1)}|\psi_{\bar{n}}^{(0)}\rangle, \tag{122}$$

$$\hat{H}_0|\psi_{\bar{n}}^{(p)}\rangle + \hat{H}'|\psi_{\bar{n}}^{(p-1)}\rangle = \Lambda_{\bar{n}}^{(0)}|\psi_{\bar{n}}^{(p)}\rangle + \sum_{s=1}^{p-1}\Lambda_{\bar{n}}^{(s)}|\psi_{\bar{n}}^{(p-s)}\rangle + \Lambda_{\bar{n}}^{(1)}|\psi_{\bar{n}}^{(0)}\rangle, \quad p \geq 2. \tag{123}$$

Equation (121) determines the eigenvalue and eigenvector to the zeroth order. With conditions (53), equation (123) determines the pth order corrections to these two quantities. Projecting equation (123) onto eigenvector $|\tilde{\psi}_{\tilde{n}}^{(0)}\rangle$ and taking into account equation (53) and the identity

$$\Lambda_n^{(0)} = \left(\tilde{\Lambda}_n^{(0)}\right)^*, \quad \forall n, \tag{124}$$

we obtain equation (50). From equations (123) and (122), with the aid of definition (54), we obtain the expressions (51) and (52).

Appendix B

We present here the detailed calculation of $||^{(0)}(\vec{q},t)\rangle\rangle$, $||^{(1)}(\vec{q},t)\rangle\rangle$ and $||^{(2)}(\vec{q},t)\rangle\rangle$ for long times. From equations (102) and (103), we have

$$||^{(0)}(\vec{q},t)\rangle\rangle = \sum_{n,\lambda} c_{n\lambda}^{0(I)}(\vec{q}) e^{t\Lambda_n^{(0)}} |\psi_{n\lambda}^{(0)}\rangle, \tag{125}$$

$$\begin{aligned} ||^{(1)}(\vec{q},t)\rangle\rangle = {} & \sum_{n,\lambda} c_{n\lambda}^{0(I)}(\vec{q}) t e^{t\Lambda_n^{(0)}} \langle\tilde{\psi}_{n\lambda}^{(0)}|\hat{\vec{v}}|\psi_{n\lambda}^{(0)}\rangle |\psi_{n\lambda}^{(0)}\rangle + \sum_{n,\lambda} \sum_{n_1\neq n,\lambda_1} c_{n\lambda}^{0(I)}(\vec{q}) \\ & \times \frac{1}{\Lambda_n^{(0)} - \Lambda_{n_1}^{(0)}} \left(e^{t\Lambda_n^{(0)}} - e^{t\Lambda_{n_1}^{(0)}}\right) \langle\tilde{\psi}_{n_1\lambda_1}^{(0)}|\hat{\vec{v}}|\psi_{n\lambda}^{(0)}\rangle |\psi_{n_1\lambda_1}^{(0)}\rangle, \end{aligned} \tag{126}$$

$$\begin{aligned} ||^{(2)}(\vec{q},t)\rangle\rangle = {} & ||K_1(\vec{q},t)\rangle\rangle + ||K_2(\vec{q},t)\rangle\rangle + ||K_3(\vec{q},t)\rangle\rangle + ||K_4(\vec{q},t)\rangle\rangle \\ & + ||K_5(\vec{q},t)\rangle\rangle + ||K_6(\vec{q},t)\rangle\rangle, \end{aligned} \tag{127}$$

where

$$||K_1(\vec{q},t)\rangle\rangle = \sum_{n,\lambda} c_{n\lambda}^{0(I)}(\vec{q}) \frac{t^2}{2} e^{t\Lambda_n^{(0)}} \langle\tilde{\psi}_{n\lambda}^{(0)}|\hat{\vec{v}}|\psi_{n\lambda}^{(0)}\rangle \langle\tilde{\psi}_{n\lambda}^{(0)}|\hat{\vec{v}}|\psi_{n\lambda}^{(0)}\rangle |\psi_{n\lambda}^{(0)}\rangle, \tag{128}$$

$$\begin{aligned} ||K_2(\vec{q},t)\rangle\rangle = {} & \sum_{n,\lambda} c_{n\lambda}^{0(I)}(\vec{q}) \sum_{n_2\neq n,\lambda_2} \left[\frac{1}{\Lambda_n^{(0)} - \Lambda_{n_2}^{(0)}} t e^{t\Lambda_n^{(0)}} \right. \\ & \left. - \frac{1}{\left(\Lambda_n^{(0)} - \Lambda_{n_2}^{(0)}\right)^2} e^{t\Lambda_n^{(0)}} + \frac{1}{\left(\Lambda_n^{(0)} - \Lambda_{n_2}^{(0)}\right)^2} e^{t\Lambda_{n_2}^{(0)}} \right] \\ & \times \langle\tilde{\psi}_{n_2\lambda_2}^{(0)}|\hat{\vec{v}}|\psi_{n\lambda}^{(0)}\rangle \langle\tilde{\psi}_{n\lambda}^{(0)}|\hat{\vec{v}}|\psi_{n\lambda}^{(0)}\rangle |\psi_{n_2\lambda_2}^{(0)}\rangle, \end{aligned} \tag{129}$$

$$||K_3(\vec{q},t)\rangle\!\rangle = \sum_{n,\lambda} c_{n\lambda}^{0(I)}(\vec{q}) \sum_{n_1\neq n,\lambda_1} \frac{1}{\Lambda_n^{(0)} - \Lambda_{n_1}^{(0)}} t e^{t\Lambda_n^{(0)}}$$

$$\times \langle\tilde{\psi}_{n\lambda}^{(0)}|\hat{\vec{v}}|\psi_{n_1\lambda_1}^{(0)}\rangle\langle\tilde{\psi}_{n_1\lambda_1}^{(0)}|\hat{\vec{v}}|\psi_{n\lambda}^{(0)}\rangle|\psi_{n\lambda}^{(0)}\rangle, \tag{130}$$

$$||K_4(\vec{q},t)\rangle\!\rangle = \sum_{n,\lambda} c_{n\lambda}^{0(I)}(\vec{q}) \sum_{n_1\neq n,\lambda_1}\sum_{n_2\neq n,\lambda_2} \left[\frac{1}{\Lambda_n^{(0)} - \Lambda_{n_1}^{(0)}}\frac{1}{\Lambda_n^{(0)} - \Lambda_{n_2}^{(0)}} e^{t\Lambda_n^{(0)}}\right.$$

$$\left. - \frac{1}{\Lambda_n^{(0)} - \Lambda_{n_1}^{(0)}}\frac{1}{\Lambda_n^{(0)} - \Lambda_{n_2}^{(0)}} e^{t\Lambda_{n_2}^{(0)}}\right]$$

$$\times \langle\tilde{\psi}_{n_2\lambda_2}^{(0)}|\hat{\vec{v}}|\psi_{n_1\lambda_1}^{(0)}\rangle\langle\tilde{\psi}_{n_1\lambda_1}^{(0)}|\hat{\vec{v}}|\psi_{n\lambda}^{(0)}\rangle|\psi_{n_2\lambda_2}^{(0)}\rangle, \tag{131}$$

$$||K_5(\vec{q},t)\rangle\!\rangle = -\sum_{n,\lambda} c_{n\lambda}^{0(I)}(\vec{q}) \sum_{n_1\neq n,\lambda_1} \frac{1}{\Lambda_n^{(0)} - \Lambda_{n_1}^{(0)}} t e^{t\Lambda_{n_1}^{(0)}}$$

$$\times \langle\tilde{\psi}_{n_1\lambda_1}^{(0)}|\hat{\vec{v}}|\psi_{n_1\lambda_1}^{(0)}\rangle\langle\tilde{\psi}_{n_1\lambda_1}^{(0)}|\hat{\vec{v}}|\psi_{n\lambda}^{(0)}\rangle|\psi_{n_1\lambda_1}^{(0)}\rangle, \tag{132}$$

$$||K_6(\vec{q},t)\rangle\!\rangle = -\sum_{n,\lambda} c_{n\lambda}^{0(I)}(\vec{q}) \sum_{n_1\neq n,\lambda_1}\sum_{n_2\neq n_1,\lambda_2} \left[\frac{1}{\Lambda_n^{(0)} - \Lambda_{n_1}^{(0)}}\frac{1}{\Lambda_{n_1}^{(0)} - \Lambda_{n_2}^{(0)}} e^{t\Lambda_{n_1}^{(0)}}\right.$$

$$\left. - \frac{1}{\Lambda_n^{(0)} - \Lambda_{n_1}^{(0)}}\frac{1}{\Lambda_{n_1}^{(0)} - \Lambda_{n_2}^{(0)}} e^{t\Lambda_{n_2}^{(0)}}\right]$$

$$\times \langle\tilde{\psi}_{n_2\lambda_2}^{(0)}|\hat{\vec{v}}|\psi_{n_1\lambda_1}^{(0)}\rangle\langle\tilde{\psi}_{n_1\lambda_1}^{(0)}|\hat{\vec{v}}|\psi_{n\lambda}^{(0)}\rangle|\psi_{n_2\lambda_2}^{(0)}\rangle. \tag{133}$$

For $t \gg \tau_0$, using the Assumption I (see equation 38), we have from equations (125)–(127),

$$||^{(0)}(\vec{q},t)\rangle\!\rangle = c_{\bar{n}}^{0(I)}(\vec{q}) e^{t\Lambda_{\bar{n}}^{(0)}} |\psi_{\bar{n}}^{(0)}\rangle, \quad t \gg \tau_0, \tag{134}$$

$$||^{(1)}(\vec{q},t)\rangle\!\rangle = c_{\bar{n}}^{0(I)}(\vec{q}) e^{t\Lambda_{\bar{n}}^{(0)}} \langle\tilde{\psi}_{\bar{n}}^{(0)}|\hat{\vec{v}}|\psi_{\bar{n}}^{(0)}\rangle|\psi_{\bar{n}}^{(0)}\rangle + c_{\bar{n}}^{0(I)}(\vec{q}) e^{t\Lambda_{\bar{n}}^{(0)}}$$
$$\times \sum_{n_1\neq\bar{n},\lambda_1} \frac{1}{\Lambda_{\bar{n}}^{(0)} - \Lambda_{n_1}^{(0)}} \langle\tilde{\psi}_{n_1\lambda_1}^{(0)}|\hat{\vec{v}}|\psi_{\bar{n}}^{(0)}\rangle|\psi_{n_1\lambda_1}^{(0)}\rangle, \quad t \gg \tau_0, \tag{135}$$

$$||^{(2)}(\vec{q},t)\rangle\!\rangle = ||L_1(\vec{q},t)\rangle\!\rangle + ||L_2(\vec{q},t)\rangle\!\rangle + ||L_3(\vec{q},t)\rangle\!\rangle$$

$$+ ||L_4(\vec{q},t)\rangle\!\rangle, \quad t \gg \tau_0, \tag{136}$$

where

$$||L_1(\vec{q},t)\rangle\rangle = c_{\bar{n}}^{0(I)}(\vec{q})\frac{t^2}{2}e^{t\Lambda_{\bar{n}}^{(0)}}\langle\tilde{\psi}_{\bar{n}}^{(0)}|\hat{\vec{v}}|\psi_{\bar{n}}^{(0)}\rangle\langle\tilde{\psi}_{\bar{n}}^{(0)}|\hat{\vec{v}}|\psi_{\bar{n}}^{(0)}\rangle|\psi_{\bar{n}}^{(0)}\rangle, \tag{137}$$

$$\begin{aligned}||L_2(\vec{q},t)\rangle\rangle = c_{\bar{n}}^{0(I)}(\vec{q})te^{t\Lambda_{\bar{n}}^{(0)}}\langle\tilde{\psi}_{\bar{n}}^{(0)}|\hat{\vec{v}}|\psi_{\bar{n}}^{(0)}\rangle \sum_{n_2\neq\bar{n},\lambda_2}\frac{1}{\Lambda_{\bar{n}}^{(0)}-\Lambda_{n_2}^{(0)}}\\ \times\langle\tilde{\psi}_{n_2\lambda_2}^{(0)}|\hat{\vec{v}}|\psi_{\bar{n}}^{(0)}\rangle|\psi_{n_2\lambda_2}^{(0)}\rangle,\end{aligned} \tag{138}$$

$$\begin{aligned}||L_3(\vec{q},t)\rangle\rangle = c_{\bar{n}}^{0(I)}(\vec{q})te^{t\Lambda_{\bar{n}}^{(0)}}\sum_{n_1\neq\bar{n},\lambda_1}\frac{1}{\Lambda_{\bar{n}}^{(0)}-\Lambda_{n_1}^{(0)}}\\ \times\langle\tilde{\psi}_{\bar{n}}^{(0)}|\hat{\vec{v}}|\psi_{n_1\lambda_1}^{(0)}\rangle\langle\tilde{\psi}_{n_1\lambda_1}^{(0)}|\hat{\vec{v}}|\psi_{\bar{n}}^{(0)}\rangle|\psi_{\bar{n}}^{(0)}\rangle,\end{aligned} \tag{139}$$

$$\begin{aligned}||L_4(\vec{q},t)\rangle\rangle = c_{\bar{n}}^{0(I)}(\vec{q})e^{t\Lambda_{\bar{n}}^{(0)}}\Bigg[\sum_{n_1\neq\bar{n},\lambda_1}\sum_{n_2\neq\bar{n},\lambda_2}\frac{1}{\Lambda_{\bar{n}}^{(0)}-\Lambda_{n_1}^{(0)}}\frac{1}{\Lambda_{\bar{n}}^{(0)}-\Lambda_{n_2}^{(0)}}\\ \times\langle\tilde{\psi}_{n_2\lambda_2}^{(0)}|\hat{\vec{v}}|\psi_{n_1\lambda_1}^{(0)}\rangle\langle\tilde{\psi}_{n_1\lambda_1}^{(0)}|\hat{\vec{v}}|\psi_{\bar{n}}^{(0)}\rangle|\psi_{n_2\lambda_2}^{(0)}\rangle\\ -\langle\tilde{\psi}_{\bar{n}}^{(0)}|\hat{\vec{v}}|\psi_{\bar{n}}^{(0)}\rangle\sum_{n_2\neq\bar{n},\lambda_2}\frac{1}{(\Lambda_{\bar{n}}^{(0)}-\Lambda_{n_2}^{(0)})^2}\langle\tilde{\psi}_{n_2\lambda_2}^{(0)}|\hat{\vec{v}}|\psi_{\bar{n}}^{(0)}\rangle|\psi_{n_2\lambda_2}^{(0)}\rangle.\end{aligned} \tag{140}$$

By means of spectral decomposition in equation (55), we obtain from equations (56)–(61)

$$||\chi_{\bar{n}}^{(1)}\rangle\rangle = \sum_{n\neq\bar{n},\lambda}\frac{1}{\hat{\omega}^{(0)}-\Lambda_n^{(0)}}\langle\tilde{\psi}_{n\lambda}^{(0)}|\hat{\vec{v}}|\psi_{\bar{n}}^{(0)}\rangle|\psi_{n\lambda}^{(0)}\rangle, \tag{141}$$

$$\begin{aligned}||\chi_{\bar{n}}^{(2)}\rangle\rangle = \sum_{n\neq\bar{n},\lambda}\sum_{n_1\neq\bar{n},\lambda_1}\frac{1}{\hat{\omega}^{(0)}-\Lambda_n^{(0)}}\frac{1}{\hat{\omega}^{(0)}-\Lambda_{n_1}^{(0)}}\\ \times\langle\tilde{\psi}_{n\lambda}^{(0)}|\hat{\vec{v}}|\psi_{n_1\lambda_1}^{(0)}\rangle\langle\tilde{\psi}_{n_1\lambda_1}^{(0)}|\hat{\vec{v}}|\psi_{\bar{n}}^{(0)}\rangle|\psi_{n\lambda}^{(0)}\rangle\\ -\langle\tilde{\psi}_{\bar{n}}^{(0)}|\hat{\vec{v}}|\psi_{\bar{n}}^{(0)}\rangle\sum_{n\neq\bar{n},\lambda}\frac{1}{(\hat{\omega}^{(0)}-\Lambda_n^{(0)})^2}\langle\tilde{\psi}_{n\lambda}^{(0)}|\hat{\vec{v}}|\psi_{\bar{n}}^{(0)}\rangle|\psi_{n\lambda}^{(0)}\rangle.\end{aligned} \tag{142}$$

Equations (109)–(111) follow immediately from (134)–(136), by using (58), (69), (70) and (141)–(142).

Manuscript received 2 June, accepted 29 June 1999