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Non-hydrodynamic transport theory of charged particle swarms in neutral gases

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Abstract. The transport properties of a swarm of charged test particles in a rarefied neutral gas subjected to time-dependent and *nonuniform* external field are studied within the framework of the linear Boltzmann equation (BE). We develop a new theoretical approach for the description of the pre-hydrodynamic stage of evolution of charged particle swarms. The initial value problem of the BE is studied by using the time-dependent perturbation theory generalized to non-Hermitian operators. The main result of this paper is a generalized diffusion equation (GDE) valid for all times, with an infinite set of transport coefficients which are expressed in terms of the solutions of a hierarchy of coupled linear integrodifferential equations. It is established that the time derivatives of spatial moments of the number density can be expressed as spatial moments of generalized transport coefficients.

Keywords: exact results, transport processes/heat transfer (theory)

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1. Introduction

Transport theory of charged particle swarms plays a fundamental role in understanding the physics of discharges, gas lasers, radiation detectors, ionospheric phenomena, planetary atmospheres and modern technologies associated with various gas discharges [1]–[4]. The studies of the short-time development (non-hydrodynamic regime) of charged particle swarms both in time-dependent and spatially nonuniform electric field are important in many applications such as high speed switching techniques, neutral and ion beam sources, and gas phase chemical reactions using hot electrons. In swarm physics, the studies of the approach to the hydrodynamic regime [5]–[10] are important in the design of swarm experiments to ensure that the measured transport coefficients correspond to the theoretical calculations obtained by means of a hydrodynamic assumption in the solution of the Boltzmann equation.

The non-hydrodynamic description of charged particle transport in nonuniform electric fields [11]–[13] is of primary importance for the modelling of gas-filled proportional counters [14]. In a typical example, the amplification of the gain signal in the gas counters is determined by the behaviour of electron ionization processes in the cylindrically or spherically symmetric electric field around a thin wire or tiny sphere anode.

In this paper, we present the Boltzmann equation description for the charged particle swarm under the influence of a time-dependent and *nonuniform* external field. One of the purposes of this paper is to develop a unified analysis of the transport properties of charged particle swarms in both hydrodynamic and non-hydrodynamic regimes by the Boltzmann equation method. An additional purpose is to give a new insight to the basic theoretical research of the short-time development of charged particle swarms.

A swarm is the name given to an ensemble of *independent* charged particles moving through a background of dilute neutral gas molecules. The number density of the swarm is so low that both mutual interactions between the charged particles and the influence of the swarm on the neutral gas distribution can be neglected. The behaviour of the swarm is then determined by the interactions between the charged particles and the neutral molecules and by the forces exerted by externally applied electric and magnetic fields. This ensemble of charged particles can be described by the one-particle distribution function $f(\vec{r},\vec{v},t)$, where $\vec{r}$ and $\vec{v}$ denote respectively the position and velocity coordinates of a swarm particle, and t is the time. The knowledge of $f(\vec{r},\vec{v},t)$ yields all physically measurable quantities of swarm particles. The one-particle distribution function can be found from the corresponding Boltzmann equation (BE) [15]

$$\left[\frac{\partial}{\partial t}+\vec{v}\cdot\frac{\partial}{\partial \vec{r}}+\vec{a}\cdot\frac{\partial}{\partial \vec{v}}\right]f(\vec{r},\vec{v},t)=J[f](\vec{r},\vec{v},t), \tag{1.1}$$

where vector $\vec{a}$ is the acceleration on a particle produced by external electric $\vec{E}(\vec{r},t)$ and/or magnetic $\vec{B}(\vec{r},t)$ fields, which are both *space* and *time* dependent. The collision integral $J[f]$ represents the rate of change of f due to collisions. The collision processes can be elastic and inelastic, particle conserving processes and non-conservative collisions (e.g., attachment and ionization). The operator J is an integral operator whose explicit form is given elsewhere [15]–[17]. 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 gas distribution function and scattering cross sections. By virtue of the low charged particle concentrations 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. This allows us to make use of the vast array of techniques available for linear operators.

Here a basis for non-hydrodynamic transport theory of charged particle swarms in a *nonuniform* external field is reported. The analytical method we follow parallels our previous work on the transport theory of granular swarms [18]. Using the time-dependent perturbation theory generalized to non-Hermitian operators [10], we construct a transport theory of swarm particles as an initial value problem for a linear Boltzmann kinetic equation. Our definition of the transport coefficients for swarm particles is applicable for arbitrary non-stationary and nonuniform external fields. We shall also provide evidence that our proposed method can be used 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. Special emphasis will be put on the relationship between the time derivatives of spatial moments of the number density and transport coefficients. This is important in order to implement the calculation of transport coefficients in a non-hydrodynamic regime by means of the direct simulation Monte Carlo method. For these reasons, the theory presented in this paper is not only a conceptual generalization of the hydrodynamic transport theory, but also, we believe, is a significant advancement in the still rather unexplored areas of the large domain of the particle kinetic and transport theory.

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The outline of the paper is as follows. In section 2 the initial value problem for the linear Boltzmann kinetic equation is introduced and the corresponding transport theory is developed. In section 3 we derive the non-hydrodynamic extension of the diffusion equation, and establish the connection between swarm particle flux and transport coefficients in the presence of the non-conservative collision processes. Section 4 is devoted to the analysis of the long-time behaviour of the transport coefficients. Finally, in the conclusion, we summarize our main results. Some technical details of the calculations are given in the appendices.

2. Preliminaries

In this section we introduce the initial value problem for the Boltzmann kinetic equation (1.1) and develop its formal solution. We study the solution of this equation for a system of infinite volume, assuming that the one-particle distribution function $f(\vec{r},\vec{v},t)$ and its derivatives all vanish at large $\vec{r}$. This allows us to apply Fourier transform to equation (1.1) to obtain

$$\frac{\partial}{\partial t}\Phi_{\vec{q}}(\vec{v},t) = \mathcal{L}_{\vec{q}}(t)\Phi_{\vec{q}}(\vec{v},t), \tag{2.1}$$

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

$$\Phi_{\vec{q}}(\vec{v},t) = \int \mathrm{d}\vec{r}\ \mathrm{e}^{-\mathrm{i}\vec{q}\cdot\vec{r}} f(\vec{r},\vec{v},t). \tag{2.2}$$

In equation (2.1) the operator $\mathcal{L}_{\vec{q}}(t)$ is

$$\mathcal{L}_{\vec{q}}(t) = \mathcal{M}_{\vec{q}}(t) + \mathcal{P}_{\vec{q}}, \tag{2.3}$$

with

$$\mathcal{M}_{\vec{q}}(t)\Phi_{\vec{q}}(\vec{v},t) = -\frac{1}{(2\pi)^3}\frac{1}{m}\vec{F}_{\vec{q}}(t)\cdot\frac{\partial}{\partial\vec{v}}\star\Phi_{\vec{q}}(\vec{v},t) + J\Phi_{\vec{q}}(\vec{v},t), \tag{2.4}$$

$$\mathcal{P}_{\vec{q}}\Phi_{\vec{q}}(\vec{v},t) = -\mathrm{i}\vec{q}\cdot\vec{v}\Phi_{\vec{q}}(\vec{v},t). \tag{2.5}$$

Above, $\vec{F}_{\vec{q}}(t)$ is the spatial Fourier transform of the external force acting on a swarm particle of charge e and mass m. The symbol $\star$ denotes the convolution of the functions, i.e.,

$$\frac{1}{(2\pi)^3}\frac{1}{m}\vec{F}_{\vec{q}}(t)\cdot\frac{\partial}{\partial\vec{v}}\star\Phi_{\vec{q}}(\vec{v},t) = \frac{1}{(2\pi)^3}\int \mathrm{d}\vec{q}\,'\ \frac{1}{m}\vec{F}_{\vec{q}-\vec{q}\,'}(t)\cdot\frac{\partial}{\partial\vec{v}}\Phi_{\vec{q}\,'}(\vec{v},t). \tag{2.6}$$

In general a swarm of charged particles may undergo reactive interactions as well as conservative collisions. Here we interpret a reactive collision as any collision which produces a change in the number of swarm particles. In the present work we are interested in unidirectional reactions, which are irreversible ones of the type *swarm particle + gas molecule → products*, and lead to a net increase or decrease in particle numbers. If reactions are present the collision operator J may be split into a particle-conserving J^{PC} and a reactive part J^{R}, i.e. $J = J^{\mathrm{PC}} + J^{\mathrm{R}}$. Then we introduce the following operators:

$$\mathcal{M}^{\mathrm{PC}}_{\vec{q}}(t) = \mathcal{M}_{\vec{q}}(t) - J^{\mathrm{R}}, \qquad \mathcal{M}^{\mathrm{R}}_{\vec{q}}(t) = \mathcal{M}_{\vec{q}}(t) - J^{\mathrm{PC}}. \tag{2.7}$$

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It is convenient to use an abstract linear vector space notation borrowed from quantum mechanics. We interpret $\Phi_{\vec{q}}(\vec{v},t)$ as the velocity–space representation of the corresponding proper vector $|\Phi_{\vec{q}}(t)\rangle$ in an abstract Hilbert space $\mathcal{H}$, i.e., $\Phi_{\vec{q}}(\vec{v},t) = \langle\vec{v}|\Phi_{\vec{q}}(t)\rangle$. In Hilbert space $\mathcal{H}$, the scalar (inner) product between two arbitrary vectors $|\varphi\rangle$ and $|\psi\rangle$ is defined as

$$\langle\varphi|\psi\rangle = \int \mathrm{d}\vec{v}\,\frac{1}{\phi^0(\vec{v},t)}\varphi^*(\vec{v})\psi(\vec{v}), \tag{2.8}$$

where φ^* denotes the complex conjugate of φ. Here $\phi^0(\vec{v},t) > 0$ is an arbitrary scalar function of $\vec{v}$ and t. According to equation (2.8) we have

$$\hat{I} = \int \mathrm{d}\vec{v}\,\frac{1}{\phi^0(\vec{v},t)}|\vec{v}\rangle\langle\vec{v}|, \tag{2.9}$$

and

$$\langle\vec{v}|\vec{v}\,'\rangle = \phi^0(\vec{v}\,',t)\;\delta(\vec{v}-\vec{v}\,'), \tag{2.10}$$

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

Likewise, a formal correspondence between operators $\mathcal{L}_{\vec{q}}(t)$, $\mathcal{M}_{\vec{q}}(t)$, $\mathcal{M}_{\vec{q}}^{\mathrm{PC}}(t)$, $\mathcal{M}_{\vec{q}}^{\mathrm{R}}(t)$ and $\mathcal{P}_{\vec{q}}$, and linear operators on the Hilbert space $\mathcal{H}$ can be established:

$$\begin{aligned}&\mathcal{M}_{\vec{q}}(t)\rightarrow\hat{H}_{0\vec{q}}(t), \qquad \mathcal{M}_{\vec{q}}^{\mathrm{PC}}(t)\rightarrow\hat{H}_{0\vec{q}}^{\mathrm{PC}}(t), \qquad \mathcal{M}_{\vec{q}}^{\mathrm{R}}(t)\rightarrow\hat{H}_{0\vec{q}}^{\mathrm{R}}(t),\\ &\mathcal{P}_{\vec{q}}\rightarrow\hat{H}'_{\vec{q}}, \qquad \mathcal{L}_{\vec{q}}(t) = \mathcal{M}_{\vec{q}}(t)+\mathcal{P}_{\vec{q}}\rightarrow\hat{H}_{\vec{q}}(t) = \hat{H}_{0\vec{q}}(t)+\hat{H}'_{\vec{q}}.\end{aligned} \tag{2.11}$$

For instance, the convective operator $\hat{H}'_{\vec{q}} = -\mathrm{i}\vec{q}\cdot\hat{\vec{v}}$ acts on vector $|\psi\rangle\in\mathcal{H}$, according to

$$\hat{H}'_{\vec{q}}|\psi\rangle = \int \mathrm{d}\vec{v}\,\frac{1}{\phi^0(\vec{v},t)}\psi(\vec{v})(-\mathrm{i}\vec{q}\cdot\hat{\vec{v}})|\vec{v}\rangle, \qquad |\psi\rangle\in\mathcal{H}, \tag{2.12}$$

where $\hat{\vec{v}}$ is a vector operator defined by its components $\hat{v}_i$, $i = 1,\ldots,3$ along three orthogonal axes, and $\hat{v}_i$, $i = 1,\ldots,3$, are the usual multiplicative operators [19]. From equations (2.12) and (2.10) it follows that the velocity–space representation of the Hilbert space vector $\hat{H}'_{\vec{q}}|\psi\rangle$ is

$$\varphi(\vec{v}) = \langle\vec{v}|\hat{H}'_{\vec{q}}|\psi\rangle = -\mathrm{i}\vec{q}\cdot\vec{v}\;\psi(\vec{v}). \tag{2.13}$$

It is obvious that the convective operator $\hat{H}'_{\vec{q}}$ is anti-Hermitian,

$$\langle\varphi|\hat{H}'_{\vec{q}}|\psi\rangle = -\langle\psi|\hat{H}'_{\vec{q}}|\varphi\rangle^*, \qquad |\psi\rangle,|\varphi\rangle\in\mathcal{H}. \tag{2.14}$$

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2.1. Initial value problem

After these technical preliminaries, we formulate the transport problem of swarm particles starting from the abstract initial value problem:

$$\frac{\partial}{\partial t}|\Phi_{\vec{q}}(t)\rangle = \hat{H}_{\vec{q}}(t)|\Phi_{\vec{q}}(t)\rangle, \qquad |\Phi_{\vec{q}}(t_0)\rangle = |\Phi^I_{\vec{q}}\rangle, \quad t \geqslant t_0. \tag{2.15}$$

Knowing that vector $|\Phi^I_{\vec{q}}\rangle$ represents a certain state of the swarm at time $t = t_0$, 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 (2.15). The correspondence between $|\Phi^I_{\vec{q}}\rangle$ and $|\Phi_{\vec{q}}(t)\rangle$ is linear and defines a linear evolution operator $\hat{U}_{\vec{q}}(t, t_0)$:

$$|\Phi_{\vec{q}}(t)\rangle = \hat{U}_{\vec{q}}(t, t_0)|\Phi^I_{\vec{q}}\rangle, \qquad t \geqslant t_0. \tag{2.16}$$

Since $\hat{H}_{\vec{q}}$ is not a Hermitian operator, it is obvious that the evolution operator $\hat{U}_{\vec{q}}(t, t_0)$ is not unitary.

Our procedure, based on the time-dependent perturbation theory which has been developed for Hermitian operators in quantum mechanics [19], is to determine the evolution operator $\hat{U}_{\vec{q}}(t, t_0)$ by perturbation calculus, considering the operator $\hat{H}'_{\vec{q}}$ as a perturbation.

Let $\hat{U}_{0\vec{q}}(t, t_0)$ be the evolution operator corresponding to the unperturbed operator $\hat{H}_{0\vec{q}}(t)$; consequently the operator $\hat{U}_{0\vec{q}}(t, t_0)$ satisfies the differential equation

$$\frac{\partial}{\partial t}\hat{U}_{0\vec{q}}(t, t_0) = \hat{H}_{0\vec{q}}(t)\hat{U}_{0\vec{q}}(t, t_0) = \hat{U}_{0\vec{q}}(t, t_0)\hat{H}_{0\vec{q}}(t), \qquad \hat{U}_{0\vec{q}}(t_0, t_0) = \hat{I}. \tag{2.17}$$

The evolution operator $\hat{U}_{\vec{q}}(t, t_0)$ can be expressed in terms of the operator $\hat{U}_{0\vec{q}}(t, t_0)$:

$$\hat{U}_{\vec{q}}(t, t_0) = \hat{U}^{(0)}_{\vec{q}}(t, t_0) + \sum_{p=1}^{\infty} \hat{U}^{(p)}_{\vec{q}}(t, t_0), \qquad \hat{U}^{(0)}_{\vec{q}}(t, t_0) = \hat{U}_{0\vec{q}}(t, t_0), \tag{2.18}$$

$$\begin{aligned}\hat{U}^{(p)}_{\vec{q}}(t, t_0) = &\int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t_1} \mathrm{d}t_2 \cdots \int_{t_0}^{t_{p-1}} \mathrm{d}t_p\, \hat{U}^{(0)}_{\vec{q}}(t, t_1)\hat{H}'_{\vec{q}} \\ &\times \hat{U}^{(0)}_{\vec{q}}(t_1, t_2)\hat{H}'_{\vec{q}} \cdots \hat{U}^{(0)}_{\vec{q}}(t_{p-1}, t_p)\hat{H}'_{\vec{q}}\, \hat{U}^{(0)}_{\vec{q}}(t_p, t_0), \\ &t \geqslant t_1 \geqslant t_2 \geqslant \cdots \geqslant t_{p-1} \geqslant t_0, \quad p \geqslant 1.\end{aligned} \tag{2.19}$$

The steps in the evaluation of equations (2.18) and (2.19) that differ from the Hermitian case are outlined in appendix A.

Using equations (2.16) and (2.18), one obtains the expansion of $|\Phi_{\vec{q}}(t)\rangle$,

$$|\Phi_{\vec{q}}(t)\rangle = \sum_{p=0}^{\infty} |\Phi^{(p)}_{\vec{q}}(t)\rangle, \qquad t \geqslant t_0, \tag{2.20}$$

where

$$|\Phi^{(p)}_{\vec{q}}(t)\rangle = \hat{U}^{(p)}_{\vec{q}}(t, t_0)|\Phi^I_{\vec{q}}\rangle, \qquad t \geqslant t_0. \tag{2.21}$$

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Inserting an explicit form of the convective operator $\hat{H}'_{\vec{q}} = -\mathrm{i}\vec{q}\cdot\hat{\vec{v}}$ into equation (2.19), and by using equations (2.20) and (2.21), we find that the vector $|\Phi_{\vec{q}}(t)\rangle$ can be expressed as

$$|\Phi_{\vec{q}}(t)\rangle = \sum_{p=0}^{\infty}(-\mathrm{i}\vec{q})^p \odot_p \|\varkappa_{\vec{q}}^{(p)}(t)\rangle\!\rangle, \qquad t \geqslant t_0, \tag{2.22}$$

where

$$\|\varkappa_{\vec{q}}^{(0)}(t)\rangle\!\rangle = \hat{U}_{\vec{q}}^{(0)}(t,t_0)|\Phi_{\vec{q}}^I\rangle, \qquad t \geqslant t_0, \tag{2.23}$$

$$\begin{aligned}\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\!\rangle = \int_{t_0}^{t}\mathrm{d}t_1\int_{t_0}^{t_1}\mathrm{d}t_2\cdots\int_{t_0}^{t_{p-1}}\mathrm{d}t_p\,\hat{U}_{\vec{q}}^{(0)}(t,t_1)\hat{\vec{v}}\\ \times\hat{U}_{\vec{q}}^{(0)}(t_1,t_2)\hat{\vec{v}}\cdots\hat{U}_{\vec{q}}^{(0)}(t_{p-1},t_p)\hat{\vec{v}}\hat{U}_{\vec{q}}^{(0)}(t_p,t_0)|\Phi_{\vec{q}}^I\rangle,\\ t\geqslant t_1\geqslant t_2\geqslant\cdots\geqslant t_{p-1}\geqslant t_0, \quad p\geqslant 1.\end{aligned} \tag{2.24}$$

The quantities $(-\mathrm{i}\vec{q})^p$ and $\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\!\rangle$ are tensors of rank p. The notation $\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\!\rangle$ signifies that such an object is a tensor of rank p whose components are not the usual $\mathbb{C}$-numbers, but rather are vectors in the Hilbert space $\mathcal{H}$. The symbol $\odot_p$ denotes the appropriate p-fold scalar product, i.e., $\hat{A}^{(p)}\odot_p\hat{B}^{(p)} = \sum_{\alpha_1\cdots\alpha_p}A^{(p)}_{\alpha_1\cdots\alpha_p}B^{(p)}_{\alpha_1\cdots\alpha_p}$ for any tensors $\hat{A}^{(p)}$ and $\hat{B}^{(p)}$ of rank p. The Cartesian components $\alpha_1,\ldots,\alpha_p = 1,2,3$, $p\geqslant 1$, of the tensor $(-\mathrm{i}\vec{q})^p$ are $\mathbb{C}$-numbers given by

$$[(-\mathrm{i}\vec{q})^p]_{\alpha_1,\ldots,\alpha_p} = (-\mathrm{i})^p q_{\alpha_1}q_{\alpha_2}\cdots q_{\alpha_p}, \tag{2.25}$$

while the components of tensors $\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\!\rangle$ are vectors of the Hilbert space $\mathcal{H}$ given by

$$\begin{aligned}\left[\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\!\rangle\right]_{\alpha_1,\ldots,\alpha_p} = \int_{t_0}^{t}\mathrm{d}t_1\int_{t_0}^{t_1}\mathrm{d}t_2\cdots\int_{t_0}^{t_{p-1}}\mathrm{d}t_p\,\hat{U}_{\vec{q}}^{(0)}(t,t_1)\hat{v}_{\alpha_1}\\ \times\hat{U}_{\vec{q}}^{(0)}(t_1,t_2)\hat{v}_{\alpha_2}\cdots\hat{U}_{\vec{q}}^{(0)}(t_{p-1},t_p)\hat{v}_{\alpha_p}\,\hat{U}_{\vec{q}}^{(0)}(t_p,t_0)|\Phi_{\vec{q}}^I\rangle\in\mathcal{H},\\ t\geqslant t_1\geqslant t_2\geqslant\cdots\geqslant t_{p-1}\geqslant t_0, \quad p\geqslant 1.\end{aligned} \tag{2.26}$$

Expressions (2.22)–(2.24) represent a formal solution of initial value problem (2.15). They allow us in principle to calculate the one-particle distribution function at time t if its initial value is known. However, these formal expressions are of no great help until we know how to operate with the evolution operator $\hat{U}_{\vec{q}}^{(0)}(t,t_0)$, which is very complicated and cannot be evaluated in closed form. In order to circumvent this difficulty, we shall develop the hierarchy of kinetic equations for determining the tensors $\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\!\rangle$, $p\geqslant 0$.

3. Short-time development of charged particle swarms and transport coefficients

We now perform the first part of the program sketched in the introduction, namely, deriving a hierarchy of kinetic equations for charged particle swarms. In addition, we derive general expressions for the transport coefficients valid at *all* times, including the initial non-hydrodynamic stage of the evolution of the swarm particles.

Taking the time derivative of equations (2.23) and (2.24), with the help of equation (2.17), we find that the tensors $\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\!\rangle$ obey the following hierarchy of coupled

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differential equations (see appendix B):

$$\frac{\partial}{\partial t}\|\varkappa_{\vec{q}}^{(0)}(t)\rangle\rangle = \hat{H}_{0\vec{q}}(t)\|\varkappa_{\vec{q}}^{(0)}(t)\rangle\rangle, \qquad \|\varkappa_{\vec{q}}^{(0)}(t_0)\rangle\rangle = |\Phi_{\vec{q}}^{I}\rangle, \qquad t \geqslant t_0, \tag{3.1}$$

$$\frac{\partial}{\partial t}\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\rangle = \hat{H}_{0\vec{q}}(t)\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\rangle + \hat{\vec{v}}\,\|\varkappa_{\vec{q}}^{(p-1)}(t)\rangle\rangle, \qquad \|\varkappa_{\vec{q}}^{(p)}(t_0)\rangle\rangle = 0, \quad t \geqslant t_0, \quad p \geqslant 1. \tag{3.2}$$

The action of the vector operator $\hat{\vec{v}} = (\hat{v}_1, \hat{v}_2, \hat{v}_3)$ on tensor $\|\varkappa_{\vec{q}}^{(p-1)}(t)\rangle\rangle$, $p \geqslant 1$, raises its rank by one, and is defined as

$$\begin{aligned} \left[\hat{\vec{v}}\|\varkappa_{\vec{q}}^{(0)}(t)\rangle\rangle\right]_{\alpha_1} &= \hat{v}_{\alpha_1}\|\varkappa_{\vec{q}}^{(0)}(t)\rangle\rangle, \qquad \alpha_1 = 1,2,3, \\ \left[\hat{\vec{v}}\|\varkappa_{\vec{q}}^{(p-1)}(t)\rangle\rangle\right]_{\alpha_1,\ldots,\alpha_p} &= \hat{v}_{\alpha_1}\left[\|\varkappa_{\vec{q}}^{(p-1)}(t)\rangle\rangle\right]_{\alpha_2,\ldots,\alpha_p}, \qquad \alpha_1,\ldots,\alpha_p = 1,2,3, \quad p \geqslant 2. \end{aligned} \tag{3.3}$$

It is convenient to introduce an infinite set of tensors

$$\hat{N}^{(p)}(\vec{q},t) = \langle\phi^0(t)\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\rangle, \qquad p \geqslant 0. \tag{3.4}$$

The quantities $\hat{N}^{(p)}(\vec{q},t)$ are analogous to the spatial moments of the number density $n(\vec{r},t)$ [15]. Since $n_{\vec{q}}(t) = \langle\phi^0(t)|\Phi_{\vec{q}}(t)\rangle$, we get:

$$n_{\vec{q}}(t) = \sum_{p=0}^{\infty}(-\mathrm{i}\vec{q})^p \odot_p \hat{N}^{(p)}(\vec{q},t), \qquad t \geqslant t_0. \tag{3.5}$$

Finally, to set up our transport theory we define the transport coefficients by

$$\frac{\partial}{\partial t}\hat{N}^{(p)}(\vec{q},t) = \hat{\omega}_{\vec{q}}^{(p)}(t)\hat{N}^{(0)}(\vec{q},t) + \sum_{r=0}^{p-1}\hat{\omega}_{\vec{q}}^{(r)}(t) \otimes \hat{N}^{(p-r)}(\vec{q},t), \qquad p \geqslant 0, \tag{3.6}$$

where $\hat{\omega}_{\vec{q}}^{(r)}(t)$ denote tensor transport coefficients of rank r, and the symbol $\otimes$ denotes the standard symmetrized outer tensor product defined as

$$\left[\hat{\omega}_{\vec{q}}^{(r)}(t) \otimes \hat{N}^{(p-r)}(\vec{q},t)\right]_{i_1,\ldots,i_p} = \frac{1}{p!}\sum\nolimits_{(j_1,\ldots,j_p)\in P(i_1,\ldots,i_p)}\left[\hat{\omega}_{\vec{q}}^{(r)}(t)\right]_{j_1,\ldots,j_r} N_{j_{r+1},\ldots,j_p}^{(p-r)}(\vec{q},t). \tag{3.7}$$

The summation in equation (3.7) extends over all of the indices $(j_1,\ldots,j_p)$ that are permutations $P(i_1,\ldots,i_p)$ of the indices on the left-hand side.

It should be stressed that the $\vec{q}$ dependence of the transport coefficients $\hat{\omega}_{\vec{q}}^{(p)}$, $p \geqslant 0$, has its origin not only in the initial vector $|\Phi_{\vec{q}}^{I}\rangle$ (see equations (2.23) and (2.24)) but also in external force $\vec{F}_{\vec{q}}(t)$. For a homogeneous external field, i.e., $\vec{F}_{\vec{q}}(t) = \delta(\vec{q})\vec{F}_{\mathrm{H}}(t)$, the transport coefficients are time-dependent functionals of the initial conditions.

From definitions (3.6) and equation (3.5) it follows that

$$\frac{\partial}{\partial t}n_{\vec{q}}(t) - \sum_{p=0}^{\infty}(-\mathrm{i}\vec{q})^p \odot_p \hat{\omega}_{\vec{q}}^{(p)}(t)n_{\vec{q}}(t) = 0. \tag{3.8}$$

Details of the derivation are given in appendix C. This last equation is often called the generalized diffusion equation (GDE). It describes the temporal evolution of the $n_{\vec{q}}(t)$ in

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terms of an infinite set $\{\hat{\omega}^{(p)}_{\vec{q}} | p \geqslant 0\}$ of transport coefficients. The GDE (3.8) is valid for *all* times and for *arbitrary* initial conditions.

Let us go back to configuration space. Fourier inversion $\mathcal{F}^{-1}$ of the GDE (equation (3.8)) gives

$$\frac{\partial}{\partial t} n(\vec{r}, t) - \sum_{p=0}^{\infty} \left(-\frac{\partial}{\partial \vec{r}}\right)^p \odot_p \int \mathrm{d}\vec{r}_1 \; \hat{\omega}^{(p)}(\vec{r} - \vec{r}_1, t) n(\vec{r}_1, t) = 0, \tag{3.9}$$

where $\mathcal{F}^{-1}\left[\hat{\omega}^{(p)}_{\vec{q}}(t)\right] \equiv \hat{\omega}^{(p)}(\vec{r}, t)$, $p \geqslant 0$. Previous equation (3.9) involves a non-local dependence on the number density $n(\vec{r}, t)$. Otherwise, the transport coefficients $\hat{\omega}^{(p)}(\vec{r}, t)$, $p \geqslant 0$ connect the time evolution of $n(\vec{r}, t)$ at an arbitrary point $\vec{r}$ to its value at other points.

The derivative with respect to time occurring in equation (3.6) can be eliminated with the help of equations (3.1) and (3.2). Combining (3.4), (3.6) and (3.1), (3.2) we obtain

$$\hat{\omega}^{(0)}_{\vec{q}}(t) = \frac{1}{\langle \phi^0(t) \| \varkappa^{(0)}_{\vec{q}}(t) \rangle\!\rangle} \langle \phi^0(t) | \hat{H}^{\mathrm{R}}_{0\vec{q}}(t) \| \varkappa^{(0)}_{\vec{q}}(t) \rangle\!\rangle, \tag{3.10}$$

$$\begin{aligned} \hat{\omega}^{(p)}_{\vec{q}}(t) = \frac{1}{\langle \phi^0(t) \| \varkappa^{(0)}_{\vec{q}}(t) \rangle\!\rangle} \Bigg[& \langle \phi^0(t) | \hat{\vec{v}} \, \| \varkappa^{(p-1)}_{\vec{q}}(t) \rangle\!\rangle + \langle \phi^0(t) | \hat{H}^{\mathrm{R}}_{0\vec{q}}(t) \| \varkappa^{(p)}_{\vec{q}}(t) \rangle\!\rangle \\ & - \sum_{r=0}^{p-1} \hat{\omega}^{(r)}_{\vec{q}}(t) \otimes \langle \phi^0(t) \| \varkappa^{(p-r)}_{\vec{q}}(t) \rangle\!\rangle \Bigg], \qquad p \geqslant 1. \end{aligned} \tag{3.11}$$

The details of this calculation are given in appendix D. For a given initial condition $|\Phi^I_{\vec{q}}\rangle$, the kinetic equations (3.1) and (3.2) and expressions (3.10) and (3.11) determine both the time-dependent tensors $\| \varkappa^{(r)}_{\vec{q}}(t) \rangle\!\rangle$ and the transport coefficients $\hat{\omega}^{(r)}_{\vec{q}}(t)$ for all $r \leqslant p$ and $p \geqslant 0$.

Note that when non-conservative processes are present the calculation of a transport coefficient of rank p requires solutions of the kinetic equations (3.1) and (3.2) up to order p. In the absence of non-conservative processes, solutions of kinetic equations to the order $p - 1$ suffice for the same purpose. We must bear in mind that, although the reactions affect the transport coefficients $\hat{\omega}^{(r)}_{\vec{q}}(t)$ explicitly through $\hat{H}^{\mathrm{R}}_{0\vec{q}}$-dependent terms in equations (3.10) and (3.11), they also have an implicit effect through the influence of reactive collisions on tensors $\| \varkappa^{(p)}_{\vec{q}}(t) \rangle\!\rangle$.

3.1. Bulk and flux transport coefficients

Here we want to establish the connection between the swarm particle flux $\vec{\Gamma}(\vec{r}, t) = \int \mathrm{d}\vec{v} \, \vec{v} f(\vec{r}, \vec{v}, t)$ and the transport coefficients $\hat{\omega}^{(p)}_{\vec{q}}(t)$, $p \geqslant 0$. From definition (2.2) we have that the Fourier transform of $\vec{\Gamma}(\vec{r}, t)$ is given by

$$\vec{\Gamma}_{\vec{q}}(t) = \langle \phi^0(t) | \hat{\vec{v}} \, | \Phi_{\vec{q}}(t) \rangle. \tag{3.12}$$

Inserting equation (2.22) into (3.12), we arrive at

$$\vec{\Gamma}_{\vec{q}}(t) = \sum_{p=0}^{\infty} (-\mathrm{i}\vec{q})^p \odot_p \langle \phi^0(t) | \hat{\vec{v}} \, \| \varkappa^{(p)}_{\vec{q}}(t) \rangle\!\rangle. \tag{3.13}$$

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From equations (3.13), (D.2) and (D.3), using definition (3.6) and equation (3.5), we obtain

$$\vec{\Gamma}_{\vec{q}}(t) = \sum_{p=0}^{\infty}(-\mathrm{i}\vec{q})^p \odot_p \hat{\Omega}_{\vec{q}}^{(p+1)}(t) n_{\vec{q}}(t), \tag{3.14}$$

where

$$\hat{\Omega}_{\vec{q}}^{(p)}(t) = \hat{\omega}_{\vec{q}}^{(p)}(t) - \hat{R}_{\vec{q}}^{(p)}(t), \qquad p \geqslant 1, \tag{3.15}$$

$$\hat{R}_{\vec{q}}^{(p)}(t) = -\frac{1}{n_{\vec{q}}(t)}\langle\phi^0(t)|\left[\hat{\omega}_{\vec{q}}^{(0)}(t)\hat{I} - \hat{H}_{0\vec{q}}^{\mathrm{R}}(t)\right]\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\rangle, \qquad p \geqslant 1. \tag{3.16}$$

For completeness we put $\hat{\Omega}_{\vec{q}}^{(0)}(t) \equiv \hat{\omega}_{\vec{q}}^{(0)}(t)$.

In the present work we will refer to the $\hat{\Omega}_{\vec{q}}^{(p)}(t)$ as the '*flux*' components of the transport coefficients and the $\hat{R}_{\vec{q}}^{(p)}(t)$ as the 'reactive' components. The reaction-corrected transport coefficients $\hat{\omega}_{\vec{q}}^{(p)}(t)$ are often called '*bulk*' transport coefficients. In the absence of reactive processes $\hat{R}_{\vec{q}}^{(p)}(t)$ vanishes for any $p \geqslant 1$, and the 'bulk' and 'flux' transport coefficients become *identical*.

Applying the well-known convolution theorem for Fourier transforms on equation (3.14), we get immediately

$$\vec{\Gamma}(\vec{r},t) = \sum_{p=0}^{\infty}\left(-\frac{\partial}{\partial\vec{r}}\right)^p \odot_p \int \mathrm{d}\vec{r}_1\ \hat{\Omega}^{(p+1)}(\vec{r}-\vec{r}_1,t)n(\vec{r}_1,t), \tag{3.17}$$

where $\mathcal{F}^{-1}\left[\hat{\Omega}_{\vec{q}}^{(p)}(t)\right] \equiv \hat{\Omega}^{(p)}(\vec{r},t)$, $p \geqslant 1$.

4. Space–time evolution of charged particles swarms

The objective of this section is to analyse the long-time behaviour of the transport coefficients $\hat{\omega}_{\vec{q}}^{(p)}(t)$, $p \geqslant 0$, and one-particle distribution function $f(\vec{r},\vec{v},t)$.

Recently, we have analysed the foundations of the transport theory of charged particle swarms in neutral gases in the presence of a *static* and *uniform* external electric field [10]. In that case, the corresponding unperturbed collision operator $\hat{H}_{0\vec{q}}(t)$ (equation (2.11)) is both time and $\vec{q}$ independent, i.e. $\hat{H}_{0\vec{q}}(t) \equiv \hat{H}_0$. We have performed an analysis of the long-time behaviour of tensors $\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\rangle$, $p \geqslant 0$. Except for minor technical details, our strategy was the same as the one we followed in sections 2 and 3 to establish the generalized diffusion equation (equation (3.8)) from the Boltzmann equation. The remarkable theorem has been proved that a sufficient condition for the existence of a hydrodynamics regime is the existence of an isolated eigenvalue $\hat{\omega}_*^{(0)}$ of the operator $\hat{H}_0$ which is separated from the rest of the spectrum by the gap along the real axis [5, 10]. Such an assumption implies the separation of the relaxation timescale $\tau_0 \propto (d_0)^{-1}$ (d_0 is the length of gap in the spectrum), and the hydrodynamic timescale $\tau_{\mathrm{h}} \propto (q(k_{\mathrm{B}}T)^{1/2})^{-1}$ [20] (τ_{h} is the time a swarm particle needs to travel the length of macroscopic gradients; $k_{\mathrm{B}}T$ is the mean random energy of a swarm particle). This means that in the long-time limit ($t \gg \tau_0$) all

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$\hat{\omega}_{\vec{q}}^{(p)}(t)$ become time *and* $\vec{q}$ independent in the *same* characteristic time and achieve their hydrodynamics values:

$$\hat{\omega}_{\vec{q}}^{(p)}(t) \simeq \hat{\omega}_{*}^{(p)}, \qquad t \gg \tau_0, \quad p \geqslant 0. \tag{4.1}$$

The transport coefficients $\hat{\omega}_{*}^{(p)}$ can be expressed in terms of microscopic quantities [10]:

$$\hat{\omega}_{*}^{(0)} = \langle \tilde{\psi}_{\bar{n}}^{(0)} | \hat{H}_0 \| \chi_{\bar{n}}^{(0)} \rangle\rangle, \qquad \hat{\omega}_{*}^{(p)} = \langle \tilde{\psi}_{\bar{n}}^{(0)} | \hat{\vec{v}} \, \| \chi_{\bar{n}}^{(p-1)} \rangle\rangle, \qquad p \geqslant 1, \tag{4.2}$$

where

$$\begin{aligned} &\| \chi_{\bar{n}}^{(0)} \rangle\rangle = | \psi_{\bar{n}}^{(0)} \rangle, \qquad \| \chi_{\bar{n}}^{(1)} \rangle\rangle = [\hat{\omega}_{*}^{(0)} - \hat{H}_0]^{-1} \hat{Q} \, \hat{\vec{v}} \, \| \chi_{\bar{n}}^{(0)} \rangle\rangle, \\ &\| \chi_{\bar{n}}^{(p)} \rangle\rangle = [\hat{\omega}_{*}^{(0)} - \hat{H}_0]^{-1} \hat{Q} \left[\hat{\vec{v}} \, \| \chi_{\bar{n}}^{(p-1)} \rangle\rangle - \sum_{r=1}^{p-1} \hat{\omega}_{*}^{(r)} \otimes \| \chi_{\bar{n}}^{(p-r)} \rangle\rangle \right], \qquad p \geqslant 2. \end{aligned} \tag{4.3}$$

The vectors $|\psi_{\bar{n}}^{(0)}\rangle$ and $|\tilde{\psi}_{\bar{n}}^{(0)}\rangle$ are eigenvectors of the operator $\hat{H}_0$ and its adjoint operator $\hat{H}_0^{\dagger}$ respectively, corresponding to the nondegenerate isolated eigenvalue $\hat{\omega}_{*}^{(0)}$. The operator $\hat{Q} = \hat{I} - |\psi_{\bar{n}}^{(0)}\rangle\langle\tilde{\psi}_{\bar{n}}^{(0)}|$ is a projector (but not orthogonal) onto subspace complementary to the subspace spanned by the basic eigenvector $|\psi_{\bar{n}}^{(0)}\rangle$. Previous results show that hydrodynamic behaviour is always linked to the forgetting of the initial conditions through the relaxation.

Finally, we have shown under previous assumptions that after time $t \gg \tau_0$, the one-particle distribution function $|f(\vec{r}, t)\rangle$ (i.e. the solution of the initial value problem (2.15)) is given by [10]

$$|f(\vec{r}, t)\rangle = \sum_{p=0}^{\infty} \| \chi_{\bar{n}}^{(p)} \rangle\rangle \odot \left(-\frac{\partial}{\partial \vec{r}} \right)^{p} \mathrm{e}^{\hat{\omega}_{*}^{(0)} t} \int \mathrm{d}\vec{q} \; c_{\bar{n}}^{0(I)}(\vec{q}) \times \mathrm{e}^{+\mathrm{i}\vec{q}\cdot\vec{r}} \prod_{s=1}^{\infty} \mathrm{e}^{(-\mathrm{i}\vec{q})^{s} \odot \, \hat{\omega}_{*}^{(s)} t}, \qquad t \gg \tau_0. \tag{4.4}$$

The coefficients $c_{\bar{n}}^{0(I)}(\vec{q}) = \langle \tilde{\psi}_{\bar{n}}^{(0)} | \Phi_{\vec{q}}^{I} \rangle$ depend on $\vec{q}$ through their dependence on the initial state of the swarm $|\Phi_{\vec{q}}^{I}\rangle$. 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 results of more fundamental assumptions on the spectral properties of operators involved in the Boltzmann equation.

Our perturbation formalism (sections 2 and 3) describes the transport phenomena produced by external forces with arbitrary space and time variations. To extract any information about the long-time behaviour of either the transport coefficients $\hat{\omega}_{\vec{q}}^{(p)}(t)$, $p \geqslant 0$ or the one-particle distribution function $f(\vec{r}, \vec{v}, t)$, we must analyse the asymptotic behaviour of the tensors $\| \varkappa_{\vec{q}}^{(p)}(t) \rangle\rangle$, $p \geqslant 0$. The tensors $\| \varkappa_{\vec{q}}^{(p)}(t) \rangle\rangle$ involve the evolution operator $\hat{U}_{0\vec{q}}(t, t_0)$, which is very complicated and cannot be evaluated in closed form. For this reason it is difficult to analyse the long-time behaviour of transport coefficients for arbitrary initial conditions. In the discussion that follows, we assume an initial distribution of the form

$$|\Phi_{\vec{q}}^{I}\rangle = |f_0\rangle \, n_{\vec{q}}(t_0). \tag{4.5}$$

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Inserting this initial value into equations (2.23) and (2.24) we obtain

$$\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\!\rangle = \|\xi_{\vec{q}}^{(p)}(t)\rangle\!\rangle n_{\vec{q}}(t_0), \qquad p \geqslant 0, \quad t \geqslant t_0, \tag{4.6}$$

where

$$\|\xi_{\vec{q}}^{(0)}(t)\rangle\!\rangle = \hat{U}_{\vec{q}}^{(0)}(t, t_0)|f_0\rangle, \qquad t \geqslant t_0, \tag{4.7}$$

$$\begin{aligned}\|\xi_{\vec{q}}^{(p)}(t)\rangle\!\rangle = &\int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t_1} \mathrm{d}t_2 \cdots \int_{t_0}^{t_{p-1}} \mathrm{d}t_p\, \hat{U}_{\vec{q}}^{(0)}(t, t_1)\hat{\vec{v}} \\ &\times \hat{U}_{\vec{q}}^{(0)}(t_1, t_2)\hat{\vec{v}} \cdots \hat{U}_{\vec{q}}^{(0)}(t_{p-1}, t_p)\hat{\vec{v}}\, \hat{U}_{\vec{q}}^{(0)}(t_p, t_0)|f_0\rangle, \\ &t \geqslant t_1 \geqslant t_2 \geqslant \cdots \geqslant t_{p-1} \geqslant t_0, \quad p \geqslant 1.\end{aligned} \tag{4.8}$$

Hence, the tensors $\|\xi_{\vec{q}}^{(p)}(t)\rangle\!\rangle$, $p \geqslant 0$, are independent of the spatial part of the initial state (4.5). From equations (3.10), (3.11) and (4.6) we conclude that the spatial dependence of the transport coefficients arises only from their implicit dependence on the inhomogeneous external field.

For a spatially homogeneous but time-dependent external field, $\vec{F}_{\vec{q}}(t) = \delta(\vec{q})\vec{F}_{\mathrm{H}}(t)$, we find that all transport coefficients $\hat{\omega}_{\vec{q}}^{(p)}(t)$, $p \geqslant 0$, become $\vec{q}$ independent, i.e.,

$$\hat{\omega}_{\vec{q}}^{(p)}(t) \equiv \hat{\omega}^{(p)}(t), \qquad p \geqslant 0, \quad t \geqslant t_0. \tag{4.9}$$

From equations (3.15), (3.16) and (4.6) we obtain that the flux transport coefficients $\hat{\Omega}_{\vec{q}}^{(p)}$, $p \geqslant 1$ also become $\vec{q}$ independent when the velocity and space–time dependence of the initial conditions separate:

$$\begin{aligned}&\hat{\Omega}_{\vec{q}}^{(p)}(t) \equiv \hat{\Omega}^{(p)}(t) = \hat{\omega}^{(p)}(t) - \hat{R}^{(p)}(t), \qquad p \geqslant 1, \quad t \geqslant t_0, \\ &\hat{R}_{\vec{q}}^{(p)}(t) \equiv \hat{R}^{(p)}(t) = -\langle\phi_0(t)| \left[\hat{\omega}^{(0)}(t)\hat{I} - \hat{H}_0^{\mathrm{R}}(t)\right] \|\xi^{(p)}(t)\rangle\!\rangle, \qquad p \geqslant 1, \quad t \geqslant t_0,\end{aligned} \tag{4.10}$$

where the tensors $\|\xi^{(p)}(t)\rangle\!\rangle$, $p \geqslant 1$, are $\vec{q}$ independent. Fourier inversion $\mathcal{F}^{-1}$ of equations (4.9) and (4.10) gives

$$\begin{aligned}&\mathcal{F}^{-1}\left[\hat{\omega}_{\vec{q}}^{(p)}(t)\right] \equiv \hat{\omega}^{(p)}(\vec{r}, t) = \hat{\omega}^{(p)}(t)\ \delta(\vec{r}), \qquad p \geqslant 0, \quad t \geqslant t_0, \\ &\mathcal{F}^{-1}\left[\hat{\Omega}_{\vec{q}}^{(p)}(t)\right] \equiv \hat{\Omega}^{(p)}(\vec{r}, t) = \hat{\Omega}^{(p)}(t)\ \delta(\vec{r}), \qquad p \geqslant 1, \quad t \geqslant t_0.\end{aligned} \tag{4.11}$$

According to equation (4.11), from equations (3.9) and (3.17) we get immediately the generalized diffusion equation [15, 16]

$$\frac{\partial}{\partial t} n(\vec{r}, t) - \sum_{p=0}^{\infty} \hat{\omega}^{(p)}(t) \odot_p \left(-\frac{\partial}{\partial \vec{r}}\right)^p n(\vec{r}, t) = 0, \tag{4.12}$$

and an expression for the swarm particle flux

$$\vec{\Gamma}(\vec{r}, t) = \sum_{p=0}^{\infty} \hat{\Omega}^{(p+1)}(t) \odot_p \left(-\frac{\partial}{\partial \vec{r}}\right)^p n(\vec{r}, t). \tag{4.13}$$

These equations are exact for *all* times if the initial condition separates the velocity and space–time dependences (equation (4.5)).

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To make some further points about the nature of the transport coefficients, we now derive expressions which relate the transport coefficients $\hat{\omega}^{(p)}(\vec{r},t)$, $p \geqslant 0$, with the time derivatives of the spatial moments of the number density $n(\vec{r},t)$. Let $\psi(\vec{r})$ be any function of $\vec{r}$ and let us define

$$\langle\psi(\vec{r})\rangle_n \equiv \frac{1}{N(t)}\int \mathrm{d}\vec{r}\;\psi(\vec{r})n(\vec{r},t), \qquad N(t) = \int \mathrm{d}\vec{r}\;n(\vec{r},t). \tag{4.14}$$

Assuming that $n(\vec{r},t)$, together with its derivatives, vanish at $|\vec{r}| \to \infty$, we obtain from equation (3.9) the following equation for the time development of the averages $\langle\psi(\vec{r})\rangle_n$:

$$\frac{\partial}{\partial t}\langle\psi(\vec{r})\rangle_n + \frac{1}{N(t)}\frac{\mathrm{d}N(t)}{\mathrm{d}t}\langle\psi(\vec{r})\rangle_n - \frac{1}{N(t)}\sum_{p=0}^{\infty}\int \mathrm{d}\vec{r}_1\;\hat{\omega}^{(p)}(\vec{r}_1,t)$$
$$\odot_p \int \mathrm{d}\vec{r}\;n(\vec{r}-\vec{r}_1,t)\left(\frac{\partial}{\partial\vec{r}}\right)^p\psi(\vec{r}) = 0. \tag{4.15}$$

The details of the derivation of equation (4.15) are given in appendix E.

If $\psi(\vec{r})$ is a polynomial of order s in $\vec{r}$, then in equation (4.15) only the transport coefficients of order $p \leqslant s$ occur. Taking successive moments ($\psi(\vec{r}) = 1, \vec{r}, \vec{r}\otimes\vec{r}, \ldots$), after some algebra (see appendix F) we have

$$\frac{1}{N(t)}\frac{\mathrm{d}N(t)}{\mathrm{d}t} = \int \mathrm{d}\vec{r}\;\hat{\omega}^{(0)}(\vec{r},t), \tag{4.16}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\vec{r}\rangle_n = \int \mathrm{d}\vec{r}\;\hat{\omega}^{(1)}(\vec{r},t) - \int \mathrm{d}\vec{r}\;\hat{\omega}^{(0)}(\vec{r},t)\vec{r}, \tag{4.17}$$

and

$$\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\left(\langle\vec{r}\otimes\vec{r}\rangle_n - \langle\vec{r}\rangle_n\otimes\langle\vec{r}\rangle_n\right)$$
$$= \int \mathrm{d}\vec{r}\;\hat{\omega}^{(2)}(\vec{r},t)\otimes 1 - \int \mathrm{d}\vec{r}\;\hat{\omega}^{(1)}(\vec{r},t)\otimes\vec{r} + \tfrac{1}{2}\int \mathrm{d}\vec{r}\;\hat{\omega}^{(0)}(\vec{r},t)\vec{r}\otimes\vec{r}, \tag{4.18}$$

where the operation $\otimes$ has its usual meaning as defined in equation (3.7). Thus, the temporal evolution of the spatial moment of number density of sth order depends on the generalized transport coefficients $\hat{\omega}^{(p)}(\vec{r},t)$ of order $0 \leqslant p \leqslant s$.

Let us consider the time derivatives of the spatial moments of the number density for the case of a spatially homogeneous external field $\vec{F}_{\mathrm{H}}(t)$. We limit ourselves again to the case where the initial state $f(\vec{r},\vec{v},t_0) = f_0(\vec{v})n(\vec{r},t_0)$ separates the velocity and space–time dependence (equation (4.5)). According to equation (4.11), from equations (4.16) to (4.18) we get immediately the following expressions for the transport coefficients:

$$R(t) \equiv -\hat{\omega}^{(0)}(t) = -\frac{1}{N(t)}\frac{\mathrm{d}N(t)}{\mathrm{d}t}, \tag{4.19}$$

$$\vec{W}(t) \equiv \hat{\omega}^{(1)}(t) = \frac{\mathrm{d}}{\mathrm{d}t}\langle\vec{r}\rangle_n, \tag{4.20}$$

$$\hat{D}(t) \equiv \hat{\omega}^{(2)}(t) = \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\left(\langle\vec{r}\otimes\vec{r}\rangle_n - \langle\vec{r}\rangle_n\otimes\langle\vec{r}\rangle_n\right) = \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\left\langle(\vec{r}-\langle\vec{r}\rangle_n)\otimes(\vec{r}-\langle\vec{r}\rangle_n)\right\rangle_n. \tag{4.21}$$

The above equations are exact for *all* times if the initial condition has the assumed form.

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Let us now return to the case of an external field which is uniform in space and independent of time. We have seen that for the long-time limit all the transport coefficients achieve their hydrodynamics values given by microscopic expressions (4.2). Consequently, the corresponding averages in the equations (4.19)–(4.21) must be *linear* in time.

5. Concluding remarks

In the present work we have addressed the problem of the non-hydrodynamic transport of a swarm of charged test particles in a neutral gas subjected to an arbitrary time-dependent and nonuniform external field. Non-hydrodynamic effects may be important at short times after emission from the source, close to boundaries or wherever the density $n(\vec{r}, t)$ varies rapidly over distances of the order of a mean free path and/or times of the order of the mean free time between collisions [15].

Without specifying the collision operator, a linear Boltzmann equation was used to describe the kinetics of the swarm particles in a dilute neutral gas. We have applied the time-dependent perturbation method to study the evolution of the swarm from an arbitrary initial distribution. The results presented here are not restricted to small gradients in the density of swarm particles.

Several new aspects of charged particle transport theory have been introduced.

(1) The transport theory has been extended with the introduction of spatially dependent transport coefficients.

(2) We have derived exact algebraic expressions for the transport coefficients (equations (3.10) and (3.11)), which are valid for all times including the initial non-hydrodynamic regime. Any transport coefficient can be represented as a function of the solutions to the hierarchy of kinetic equations (equations (3.1) and (3.2)).

(3) We have obtained equation (3.8), which is a non-hydrodynamic extension of the diffusion equation with transport coefficients that are time dependent and explicitly depend on the wavevector.

(4) On the basis of these formulae we have discussed the asymptotic behaviour of the generalized transport coefficients. We have established that our definition of generalized transport coefficients is consistent with the hydrodynamic expressions for transport coefficients in a space–time-independent external field (see equations (4.1) and (4.4)).

(5) We have demonstrated the separation of the 'flux' and 'reactive' components of the transport coefficients (equations (3.15) and (4.10)).

(6) We have established the connection between the time derivatives of the spatial moments of the number density and the spatial moments of the generalized transport coefficients (equations (4.16)–(4.18)).

The theory given here is for an infinite medium, with no boundaries. This is an idealized situation. Future investigations of non-hydrodynamic effects, based on the Boltzmann equation, should involve boundaries. When the effects of boundaries are taken into account, a modification of the kinetic equation is needed. These effects may be dealt with by introducing a boundary operator which can be specified by considering an interaction potential of the boundary layer [15].

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Moreover, the formalism developed in this paper may be considered more generally than only within the framework of the transport theory of charged particle swarms. We need not confine ourselves to the strict usage of this theory for the Boltzmann equation (1.1) with a collision integral as specified in the introduction. In other words, we may use the derived equations for the case of an arbitrary kinetic equation with a *linear* collision integral [18]. We hope that the formalism developed in this paper will be used to solve various actual problems in related fields as well as in other fields in physics.

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Appendix A. Time-dependent perturbation method

The methods briefly described below are based on the time-dependent perturbation theory which has been developed for Hermitian operators in quantum mechanics [19].

Let the linear operator $\hat{U}_{\vec{q}}(t,s)$ map the solution $|\Phi_{\vec{q}}(s)\rangle$ of equation (2.15) at time s to the solution $|\Phi_{\vec{q}}(t)\rangle$ at time $t \geqslant s$:

$$|\Phi_{\vec{q}}(t)\rangle = \hat{U}_{\vec{q}}(t,s)|\Phi_{\vec{q}}(s)\rangle, \qquad t \geqslant s \geqslant t_0. \tag{A.1}$$

The uniqueness of the solution of equation (2.15) implies that the family of evolution operators $\{\hat{U}_{\vec{q}}(t,s)|t \geqslant s \geqslant t_0\}$ satisfies

$$\begin{aligned} &\hat{U}_{\vec{q}}(t,s)\hat{U}_{\vec{q}}(s,r) = \hat{U}_{\vec{q}}(t,r), \qquad t \geqslant s \geqslant r \geqslant t_0, \\ &\hat{U}_{\vec{q}}(t,t) = \hat{I}, \qquad t \geqslant t_0. \end{aligned} \tag{A.2}$$

Furthermore, the evolution operator family $\{\hat{U}_{\vec{q}}(t,s), t \geqslant s \geqslant t_0\}$ governing equation (2.15) satisfies the following differential equations [21]:

$$\begin{aligned} &\frac{\partial}{\partial t}\hat{U}_{\vec{q}}(t,s) = \hat{H}_{\vec{q}}(t)\hat{U}_{\vec{q}}(t,s) = \hat{U}_{\vec{q}}(t,s)\hat{H}_{\vec{q}}(t), \qquad \hat{U}_{\vec{q}}(s,s) = \hat{I} \\ &\frac{\partial}{\partial s}\hat{U}_{\vec{q}}(t,s) = -\hat{U}_{\vec{q}}(t,s)\hat{H}_{\vec{q}}(s) = -\hat{H}_{\vec{q}}(s)\hat{U}_{\vec{q}}(t,s), \qquad \hat{U}_{\vec{q}}(t,t) = \hat{I}. \end{aligned} \tag{A.3}$$

The evolution operator $\hat{U}_{\vec{q}}(t,t_0)$ can be expressed in terms of the operator $\hat{S}_{\vec{q}}(t,t_0)$ defined as

$$\hat{U}_{\vec{q}}(t,t_0) = \hat{U}_{0\vec{q}}(t,t_0)\hat{S}_{\vec{q}}(t,t_0). \tag{A.4}$$

Here $\hat{U}_{0\vec{q}}(t,t_0)$ is the solution of equation (2.17). From equations (A.3), (2.17), and (A.4) it follows that the time dependence of $\hat{S}_{\vec{q}}(t,t_0)$ is given by

$$\frac{\partial}{\partial t}\hat{S}_{\vec{q}}(t,t_0) = \hat{P}_{\vec{q}}(t)\hat{S}_{\vec{q}}(t,t_0), \qquad \hat{S}_{\vec{q}}(t_0,t_0) = \hat{I}. \tag{A.5}$$

Here the operator $\hat{P}_{\vec{q}}(t)$ is the perturbation operator $\hat{H}'_{\vec{q}}$ in the 'interaction picture':

$$\hat{P}_{\vec{q}}(t) = \hat{U}^{-1}_{0\vec{q}}(t,t_0)\hat{H}'_{\vec{q}}\,\hat{U}_{0\vec{q}}(t,t_0). \tag{A.6}$$

Equation (A.5) is equivalent to the integral equation

$$\hat{S}_{\vec{q}}(t,t_0) = \hat{I} + \int_{t_0}^{t} \mathrm{d}t_1\, \hat{P}_{\vec{q}}(t_1)\hat{S}_{\vec{q}}(t_1,t_0), \tag{A.7}$$

which can be solved by iteration (in powers of $\hat{P}_{\vec{q}}$) yielding

$$\hat{S}_{\vec{q}}(t,t_0) = \hat{I} + \sum_{p=1}^{\infty} \hat{S}_{\vec{q}}^{(p)}(t,t_0), \tag{A.8}$$

where

$$\hat{S}_{\vec{q}}^{(p)}(t,t_0) = \int_{t_0}^{t} \mathrm{d}t_1\, \hat{P}_{\vec{q}}(t_1) \int_{t_0}^{t_1} \mathrm{d}t_2\, \hat{P}_{\vec{q}}(t_2) \cdots \int_{t_0}^{t_{p-1}} \mathrm{d}t_p\, \hat{P}_{\vec{q}}(t_p),$$
$$t \geqslant t_1 \geqslant t_2 \geqslant \cdots \geqslant t_{p-1} \geqslant t_0, \quad p \geqslant 1. \tag{A.9}$$

From this result, with the aid of definitions (A.4) and (A.6), we get the expansion (2.18) for $\hat{U}_{\vec{q}}(t,t_0)$.

Appendix B. Derivation of the hierarchy of the kinetic equations (3.1) and (3.2)

We present here the detailed derivation of equations (3.1) and (3.2) only for $p = 0, 1$. By induction, it is easy to verify equation (3.2) for arbitrary $p > 1$.

Differentiating (2.23) with respect to t, we use the identity (2.17) to obtain (3.1).

Taking the time derivative of (2.24), with the help of

$$\hat{U}_{\vec{q}}^{(0)}(t,t_1) = \hat{U}_{\vec{q}}^{(0)}(t,t_0)\left[\hat{U}_{\vec{q}}^{(0)}(t_1,t_0)\right]^{-1}, \qquad t \geqslant t_1 \geqslant t_0, \tag{B.1}$$

we get

$$\frac{\partial}{\partial t}\|\varkappa_{\vec{q}}^{(1)}(t)\rangle\!\rangle = \left[\frac{\partial}{\partial t}\hat{U}_{\vec{q}}^{(0)}(t,t_0)\right]\int_0^t \mathrm{d}t_1 \left[\hat{U}_{\vec{q}}^{(0)}(t_1,t_0)\right]^{-1}\hat{\vec{v}}\,\hat{U}_{\vec{q}}^{(0)}(t_1,t_0)|\Phi_{\vec{q}}^{I}\rangle$$
$$+\, \hat{U}_{\vec{q}}^{(0)}(t,t_0)\left[\hat{U}_{\vec{q}}^{(0)}(t,t_0)\right]^{-1}\hat{\vec{v}}\,\hat{U}_{\vec{q}}^{(0)}(t_1,t_0)|\Phi_{\vec{q}}^{I}\rangle, \qquad t \geqslant t_1 \geqslant t_0. \tag{B.2}$$

Equation (3.2) for $p = 1$ follows immediately from equations (2.17), (B.1) and (B.2).

Appendix C. Derivation of the generalized diffusion equation (3.8)

Taking the time derivative of (3.5), with the help of definition (3.6) we get

$$\frac{\partial}{\partial t}n_{\vec{q}}(t) = \sum_{p=0}^{\infty}(-\mathrm{i}\vec{q})^p \odot_p \left[\hat{\omega}_{\vec{q}}^{(p)}(t)\hat{N}^{(0)}(\vec{q},t) + \sum_{r=0}^{p-1}\hat{\omega}_{\vec{q}}^{(r)}(t)\otimes \hat{N}^{(p-r)}(\vec{q},t)\right]. \tag{C.1}$$

This expression can be transformed as follows:

$$\frac{\partial}{\partial t}n_{\vec{q}}(t) = \sum_{r=0}^{\infty}\sum_{p=r}^{\infty}(-\mathrm{i}\vec{q})^p \odot_p \left[\hat{\omega}_{\vec{q}}^{(p-r)}(t)\otimes \hat{N}^{(r)}(\vec{q},t)\right]. \tag{C.2}$$

After some algebra, we readily obtain

$$\frac{\partial}{\partial t}n_{\vec{q}}(t) = \sum_{p=0}^{\infty}(-\mathrm{i}\vec{q})^p \odot_p \hat{\omega}_{\vec{q}}^{(p)}(t)\sum_{p=0}^{\infty}(-\mathrm{i}\vec{q})^p \odot_p \hat{N}^{(p)}(\vec{q},t). \tag{C.3}$$

Inserting equation (3.5) into (C.3), we get GDE (3.8).

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Appendix D. Derivation of equations (3.10) and (3.11)

Since the time derivative of $\hat{N}^{(p)}(\vec{q},t)$ is (see definition (3.4))

$$\frac{\partial}{\partial t}\hat{N}^{(p)}(\vec{q},t) = \langle\phi^0(t)|\frac{\partial}{\partial t}\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\rangle, \qquad p \geqslant 0, \tag{D.1}$$

we obtain from equations (3.1) and (3.2)

$$\frac{\partial}{\partial t}\hat{N}^{(0)}(\vec{q},t) = \langle\phi^0(t)|\hat{H}_{0\vec{q}}(t)\|\varkappa_{\vec{q}}^{(0)}(t)\rangle\rangle, \tag{D.2}$$

$$\frac{\partial}{\partial t}\hat{N}^{(p)}(\vec{q},t) = \langle\phi^0(t)|\hat{H}_{0\vec{q}}(t)\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\rangle + \langle\phi^0(t)|\hat{\vec{v}}\,\|\varkappa_{\vec{q}}^{(p-1)}(t)\rangle\rangle, \qquad p \geqslant 1. \tag{D.3}$$

Now notice that the operator $\hat{H}_{0\vec{q}}(t)$ contains two terms: the particle conserving term $\hat{H}_{0\vec{q}}^{\mathrm{PC}}(t)$ and the 'reactive' term $\hat{H}_{0\vec{q}}^{\mathrm{R}}(t)$ (see equation (2.11)). Since

$$\langle\phi^0(t)|\hat{H}_{0\vec{q}}(t)\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\rangle = \langle\phi^0(t)|\hat{H}_{0\vec{q}}^{\mathrm{R}}(t)\|\varkappa_{\vec{q}}^{(p)}(t)\rangle\rangle \neq 0, \qquad p \geqslant 0, \tag{D.4}$$

non-particle-conserving terms will survive in equations (D.2) and (D.3). Inserting equation (D.4) into equations (D.2) and (D.3), with the help of definition (3.6), we arrive at the expressions (3.10) and (3.11).

Appendix E. Derivation of equation (4.15)

Multiplying equation (3.9) by function $\psi(\vec{r})$ and integrating over $\vec{r}$, we obtain

$$\frac{\partial}{\partial t}\int \mathrm{d}\vec{r}\;\psi(\vec{r})n(\vec{r}) - \sum_{p=0}^{\infty}\int \mathrm{d}\vec{r}_1\;\hat{\omega}^{(p)}(\vec{r}_1,t)\odot_p \int \mathrm{d}\vec{r}\;\psi(\vec{r})\left(-\frac{\partial}{\partial\vec{r}}\right)^p n(\vec{r}-\vec{r}_1,t) = 0. \tag{E.1}$$

We suppose that $n(\vec{r},t)$ together with its derivatives vanish at the boundaries of the domain of integration:

$$\left(\frac{\partial}{\partial\vec{r}}\right)^p n(\vec{r},t) \to 0, \qquad |\vec{r}| \to \infty; \quad p \geqslant 0. \tag{E.2}$$

By partial integration, we get immediately

$$\frac{\partial}{\partial t}\int \mathrm{d}\vec{r}\;\psi(\vec{r})n(\vec{r},t) - \sum_{p=0}^{\infty}\int \mathrm{d}\vec{r}_1\;\hat{\omega}^{(p)}(\vec{r}_1,t)\odot_p \int \mathrm{d}\vec{r}\;n(\vec{r}-\vec{r}_1,t)\left(\frac{\partial}{\partial\vec{r}}\right)^p \psi(\vec{r}) = 0. \tag{E.3}$$

Using, in addition, equality

$$\frac{\partial}{\partial t}\int \mathrm{d}\vec{r}\;\psi(\vec{r})n(\vec{r},t) = N(t)\frac{\partial}{\partial t}\langle\psi(\vec{r})\rangle_n + \frac{\mathrm{d}N(t)}{\mathrm{d}t}\langle\psi(\vec{r})\rangle_n\,, \tag{E.4}$$

we readily obtain equation (4.15).

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Appendix F. Derivation of equations (4.16)–(4.18)

We demonstrate here formula (4.18). For $\psi(\vec{r}) = r_p r_q$ $(p, q = 1, 2, 3)$, it is easy to show that equation (4.15) reduces to

$$\frac{\partial}{\partial t}\langle r_p r_q\rangle_n + \frac{1}{N(t)}\frac{\mathrm{d}N(t)}{\mathrm{d}t}\langle r_p r_q\rangle_n - \frac{1}{N(t)}\int \mathrm{d}\vec{r}_1\ \omega^{(0)}(\vec{r}_1,t)\int \mathrm{d}\vec{r}\ n(\vec{r},t)(r_p - r_{1p})(r_q - r_{1q}) - \frac{1}{N(t)}\int \mathrm{d}\vec{r}_1\ \omega_p^{(1)}(\vec{r}_1,t)\int \mathrm{d}\vec{r}\ n(\vec{r},t)(r_q - r_{1q}) - \frac{1}{N(t)}\int \mathrm{d}\vec{r}_1\ \omega_q^{(1)}(\vec{r}_1,t) \times \int \mathrm{d}\vec{r}\ n(\vec{r},t)(r_p - r_{1p}) - \int \mathrm{d}\vec{r}_1\ \omega_{qp}^{(2)}(\vec{r}_1,t) - \int \mathrm{d}\vec{r}_1\ \omega_{pq}^{(2)}(\vec{r}_1,t) = 0. \qquad \text{(F.1)}$$

Straightforward algebraic manipulations then lead to

$$\frac{\partial}{\partial t}\langle r_p r_q\rangle_n + T_{\mathrm{I}}(t) + T_{\mathrm{II}}(t) - \int \mathrm{d}\vec{r}_1\ \omega^{(0)}(\vec{r}_1,t) r_{1p} r_{1q} + \int \mathrm{d}\vec{r}_1\ \omega_p^{(1)}(\vec{r}_1,t) r_{1q} + \int \mathrm{d}\vec{r}_1\ \omega_q^{(1)}(\vec{r}_1,t) r_{1p} - \int \mathrm{d}\vec{r}_1\left[\omega_{qp}^{(2)}(\vec{r}_1,t) + \omega_{pq}^{(2)}(\vec{r}_1,t)\right] = 0, \qquad \text{(F.2)}$$

where

$$T_{\mathrm{I}}(t) = \frac{1}{N(t)}\left[\int \mathrm{d}\vec{r}_1\ \omega^{(0)}(\vec{r}_1,t) r_{1q} - \int \mathrm{d}\vec{r}_1\ \omega_q^{(1)}(\vec{r}_1,t)\right]\int \mathrm{d}\vec{r}\ n(\vec{r},t) r_p, \qquad \text{(F.3)}$$

$$T_{\mathrm{II}}(t) = \frac{1}{N(t)}\left[\int \mathrm{d}\vec{r}_1\ \omega^{(0)}(\vec{r}_1,t) r_{1p} - \int \mathrm{d}\vec{r}_1\ \omega_p^{(1)}(\vec{r}_1,t)\right]\int \mathrm{d}\vec{r}\ n(\vec{r},t) r_q. \qquad \text{(F.4)}$$

According to equation (4.17) we have

$$T_{\mathrm{I}}(t) + T_{\mathrm{II}}(t) = -\frac{\mathrm{d}}{\mathrm{d}t}\langle r_p\rangle_n \langle r_q\rangle_n . \qquad \text{(F.5)}$$

Inserting this expression into equation (F.2), we readily obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[\langle r_p r_q\rangle_n - \langle r_p\rangle_n\langle r_q\rangle_n\right] - \int \mathrm{d}\vec{r}_1\ \omega^{(0)}(\vec{r}_1,t) r_{1p} r_{1q} + \int \mathrm{d}\vec{r}_1\ \omega_p^{(1)}(\vec{r}_1,t) r_{1q} + \int \mathrm{d}\vec{r}_1\ \omega_q^{(1)}(\vec{r}_1,t) r_{1p} - \int \mathrm{d}\vec{r}_1\left[\omega_{qp}^{(2)}(\vec{r}_1,t) + \omega_{pq}^{(2)}(\vec{r}_1,t)\right] = 0. \qquad \text{(F.6)}$$

From this result, with the aid of definition (A.4), we arrive at equation (4.18).

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