Collisional coupling of fluctuations in plasmas

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Abstract. The transition probability function approach is extended to plasmas in which the fluctuations in the various particle species are coupled through the collisions. The collisions may be either particle conserving or particle non-conserving (chemical reactions). Particular attention is paid to the case of particle non-conserving collisions, because certain difficulties connected with the use of the fluctuation dissipation theorem then arise. This does not mean that the fluctuation dissipation theorem is erroneous, but only that the appropriate force–response pair is at best difficult to find. Such is the case for the density fluctuation spectrum. The transition probability function approach avoids this difficulty.

1. Introduction

Present theories of linear fluctuations in a plasma usually belong to one of two main categories. Thus Swartz and Farley (1979) and Seasholtz (1971) use a generalised version of the fluctuation dissipation theorem (further references are available in these works). An alternative approach, the transition probability function theory, was developed by e.g. Grewal (1964), Hagfors and Brockelman (1971) and Uddholm (1982). Here one first calculates the fluctuation spectra with the collective fields neglected. Following Theimer and Theimer (1973) we shall refer to these spectra as the random spectra. We also use the term 'undressed spectra', as opposed to 'dressed spectra' when collective effects are included. The collective effects are then introduced by means of a superposition principle.

The fluctuation dissipation theorem is an exact thermodynamical relation which is valid for any system in thermal equilibrium. The transition probability approach is not restricted to Maxwellian velocity distribution functions but, on the other hand, its domain of validity is the same as that of the Boltzmann equation (1). Although the two theories are fundamentally different, they yield identical results when both apply.

The above is true for plasmas for which the particles are conserved in the collisions. The purpose of this paper is to extend the method of Uddholm (1982) to include the effects of collisional coupling of the fluctuations by means of chemical reactions (i.e. particle *non*-conserving collisions) as well as particle conserving collisions. The calculation of actual spectra will be postponed to later papers, however. We shall see that the velocity spectra thus obtained always agree with those calculated by means of the fluctuation dissipation theorem. In the presence of chemical reactions, however, a *straightforward* application of the fluctuation dissipation theorem yields *density* spectra quite different from those obtained using the theory presented here. In fact, the

former are associated with *non*-causal response functions and are hence unphysical. Their validity is also to be doubted owing to more elementary considerations (§ 7). It should be emphasised that we never claim that the fluctuation dissipation theorem is wrong; only that it has to be applied with some care. This theorem yields the correct velocity- and potential-fluctuation spectra, because those quantities can be directly associated with the work done on the plasma by (hypothetical) external forces, whereas the density fluctuation spectrum cannot if particle non-conserving collisions are assumed. In the absence of chemical reactions it is often calculated from the velocity fluctuation spectrum, using the continuity equation. In this paper we thus show how this procedure should be altered for plasmas, in which the particle *non*-conserving collisions are important, and formulate a formalism which correctly allows for such collisions.

Our results will also be valid for systems where the particles *are* conserved in the collisions but, nevertheless, the fluctuations in the various particle species are coupled through the cross species collision operators. Examples of this are the collisional coupling between the ions and the electrons in a fully ionised plasma (Cheng 1973) and between the charged particles and the background neutral gas in a weakly ionised plasma (Tanenbaum 1968). These can be treated as particular cases of our theory and, for such plasmas, there is no conflict with any calculations based on the fluctuation dissipation relation. Moreover, Theimer and Sandalov (1979), Theimer *et al* (1980) and Theimer and Theimer (1981) have pointed out the importance of high-Z impurity ion collisions in dense, low-temperature fusion plasmas. Depending on the impurity ion concentration the dominant collisional damping is due to ion–ion, ion–impurity or impurity–impurity collisions. To the author's knowledge, our theory is the first one that correctly includes the effects of the light ion-impurity collisions.

The disposition of this paper will be as follows. In § 2 we discuss and solve the linearised Boltzmann equation. In order to clarify the exposition somewhat we review the fluctuation dissipation theorem and the transition probability function method in §§ 3 and 4, respectively. In § 5 we discuss how the use of the continuity equation (when deriving the density fluctuation spectrum from the velocity fluctuation spectrum) should be altered in the presence of chemical reactions. In the absence of collective effects, it is easy to verify that the resulting expression agrees with the results derived by the transition probability function theory. In order to calculate the dressed spectra, that relation is quite useless, however. We conclude the section by presenting the dressed electron density fluctuation spectrum, where the collective effects have been included through the dielectric superposition principle. In § 6 we show that the total intensity in the electron density fluctuation spectrum is *not* changed in the presence of chemical reactions, if the plasma is isothermal. We devote § 7 to a short discussion of the results obtained in this paper and comparison with a previous work (Kockarts and Wisemberg 1981). The presentation has to be rather terse, due to the lengthy algebra.

2. The Boltzmann equation

We consider a plasma described by the linearised Boltzmann equation

$$[\mathrm{i}(\omega - \boldsymbol{k} \cdot \boldsymbol{v}) - C_\sigma]f_{\sigma 1} + \frac{n_{\sigma 0}}{m_\sigma}(q_\sigma \boldsymbol{E}_1 + \boldsymbol{F}_\sigma) \cdot \frac{\partial f_{\sigma 0}}{\partial \boldsymbol{v}} - \sum_{\sigma'} C_{\sigma\sigma'}(f_{\sigma'1}) = f_{\sigma 1}(\boldsymbol{k}, \boldsymbol{v}, t = 0) \tag{1}$$

where the index σ denotes the particle species, C_σ is an ordinary particle conserving charged particle–neutral collision operator (e.g. a BGK or Lorentz term), $n_{\sigma 0}$ is the unperturbed particle number density, $f_{\sigma 0}$ is the unperturbed velocity distribution function, normalised so that $\int d\boldsymbol{v}\, f_{\sigma 0} = 1$, $f_{\sigma 1}$ is the perturbation of the distribution function, m_σ and q_σ are the particle mass and charge, $\boldsymbol{F}_\sigma$ is an external fictitious force which only couples (directly) with particles of species σ and the collision operators $C_{\sigma\sigma'}$ account for the effects of the collisional and chemical coupling of the linear fluctuations in the different species.

We have separated out the operator C_σ. This is, of course, not necessary but in the following we shall find it convenient, since we may then let the operators $C_{\sigma\sigma'}$ refer to the chemical reactions exclusively. From this point we consider only the case of particle *non*-conserving collisions, but neglect the exchange of momentum and energy, between the various particle species, due to particle *conserving* collisions. This is only because the former is the most difficult case to treat, but as stated previously, the theory below applies to both cases. Furthermore, we assume that the collective electric field $\boldsymbol{E}_1$ is longitudinal, that there are no net particle drifts and that, except for the fictitious forces $\boldsymbol{F}_\sigma$, there are no external fields applied to the plasma. Generalisation of the theory to include such effects presents no difficulties, however.

In the ionospheric plasma, only the reaction $n + e^- \rightleftharpoons J^-$ is of interest ($\sigma = n$, e and J for neutrals, electrons and negative ions, respectively). Whether there are other reactions, which may be of interest in incoherent scattering experiments, for instance associated with ionisation waves in laboratory discharges, is not known to the author. We consider the general problem, however, since it does not complicate the matter appreciably.

It should be noticed that equation (1) does, in fact, not describe the exact microscopic fluctuations. It contains no information as to exactly when or where each collision or chemical reaction occurs but only the probabilities per unit time for these processes to take place. Thus, given some initial values $f_{\sigma 1}(\boldsymbol{r}, \boldsymbol{v}, t = 0)$, the solutions $f_{\sigma 1}$ are only the averages, at times $t > 0$, of the microscopic fluctuations satisfying this initial value. We must therefore draw the conclusion that any properties, of the quantities $f_{\sigma 1}$, $n_{\sigma 1}$ etc, which are derived from the Boltzmann equation (1) cannot be transferred to the ensemble averages $\langle f_{\sigma 1} f^*_{\sigma' 1} \rangle_k$, $\langle n_{\sigma 1} n^*_{\sigma' 1} \rangle_k$ etc without further reference.

Let us now solve equation (1). To this end we introduce the operator matrix $\mathbf{g}^{-1}$ with the element

$$g^{-1}_{\sigma'\sigma''} = [i(\omega - \boldsymbol{k} \cdot \boldsymbol{v}) - C_{\sigma'}]\delta_{\sigma'\sigma''} - C_{\sigma'\sigma''} \tag{2}$$

at the position $\sigma'\sigma''$ ($\delta_{\sigma'\sigma''}$ being the Kronecker delta, $\delta_{\sigma'\sigma''} = 1$ if $\sigma' = \sigma''$ and $\delta_{\sigma'\sigma''} = 0$ if $\sigma' \neq \sigma''$) and its inverse $\mathbf{g}$ with the elements $g_{\sigma'\sigma''}$. Thus

$$\sum_{\sigma'''} g_{\sigma'\sigma'''} g^{-1}_{\sigma'''\sigma''} = \sum_{\sigma'''} g^{-1}_{\sigma'\sigma'''} g_{\sigma'''\sigma''} = \delta_{\sigma'\sigma''}. \tag{3}$$

The algebra is quite straightforward so we omit the details and only present the results. Hence if we define the generalised susceptibilities

$$\chi_{\sigma'\sigma''} = i \frac{q_{\sigma'} q_{\sigma''} n_{\sigma''0}}{m_{\sigma''} \varepsilon_0 k^2} \int d\boldsymbol{v}\, g_{\sigma'\sigma''} \left(\boldsymbol{k} \cdot \frac{\partial f_{\sigma''0}}{\partial \boldsymbol{v}} \right), \tag{4}$$

$$\chi'_{\sigma''} = \sum_{\sigma'} \chi_{\sigma'\sigma''}, \tag{5}$$

$$\chi_{\sigma'}'' = \sum_{\sigma''} \chi_{\sigma'\sigma''}, \tag{6}$$

the dielectric number

$$\varepsilon = 1 + \sum_{\sigma',\sigma''} \chi_{\sigma'\sigma''} \tag{7}$$

and the generalised conductivities

$$\Delta_{\sigma'\sigma''} = i \frac{q_{\sigma'}q_{\sigma''}n_{\sigma''0}}{m_{\sigma''}\varepsilon_0 k^2} \int d\boldsymbol{v} \, \boldsymbol{k} \cdot \boldsymbol{v} g_{\sigma'\sigma''} \left(\boldsymbol{k} \cdot \frac{\partial f_{\sigma''0}}{\partial \boldsymbol{v}} \right), \tag{8}$$

$$\Delta_{\sigma''}' = \sum_{\sigma'} \Delta_{\sigma'\sigma''}, \tag{9}$$

$$\Delta_{\sigma'}'' = \sum_{\sigma''} \Delta_{\sigma'\sigma''}, \tag{10}$$

we derive from equation (1)

$$n_{\sigma 1} = \sum_{\sigma'} \left(\delta_{\sigma\sigma'} - \frac{\chi_\sigma''}{\varepsilon} \right) \frac{q_{\sigma'}}{q_\sigma} n_{\sigma'1}^{(r)} + \sum_{\sigma'} i \frac{\varepsilon_0 \boldsymbol{k} \cdot \boldsymbol{F}_{\sigma'}}{q_\sigma q_{\sigma'}} \left(\chi_{\sigma\sigma'} - \frac{\chi_\sigma' \chi_\sigma''}{\varepsilon} \right) \tag{11}$$

for the particle number density perturbations,

$$\rho_{\text{tot}} = \frac{\rho_{\text{tot}}^{(r)}}{\varepsilon} + \sum_{\sigma'} i \frac{\varepsilon_0 \boldsymbol{k} \cdot \boldsymbol{F}_{\sigma'}}{q_{\sigma'}} \frac{\chi_{\sigma'}'}{\varepsilon} \tag{12}$$

for the total charge density perturbation,

$$n_{\sigma 0} \boldsymbol{u}_{\sigma 1} = \sum_{\sigma'} \left(\delta_{\sigma\sigma'} - \frac{\Delta_\sigma''}{\omega\varepsilon} \right) \frac{q_{\sigma'}}{q_\sigma} n_{\sigma'0} \boldsymbol{u}_{\sigma'1}^{(r)} + \sum_{\sigma'} i \frac{\varepsilon_0 \boldsymbol{F}_{\sigma'}}{q_\sigma q_{\sigma'}} \left(\Delta_{\sigma\sigma'} - \frac{\chi_\sigma' \Delta_\sigma''}{\varepsilon} \right) \tag{13}$$

for the σ-particle flux density perturbations and

$$\boldsymbol{j}_{\text{tot}} = \frac{\boldsymbol{j}_{\text{tot}}^{(r)}}{\varepsilon} + \sum_{\sigma'} i \frac{\varepsilon_0 \boldsymbol{F}_{\sigma'}}{q_{\sigma'}} \frac{\Delta_{\sigma'}'}{\varepsilon} \tag{14}$$

for the total current perturbation.

In equations (11)–(14) we assume that the forces $\boldsymbol{F}_\sigma$ are longitudinal for all σ, and the superscript (r) denotes random quantities, i.e. the appropriate moments of

$$f_{\sigma 1}^{(r)}(\boldsymbol{k}, \boldsymbol{v}, \omega) = \sum_{\sigma'} g_{\sigma\sigma'}[f_{\sigma'}(\boldsymbol{k}, \boldsymbol{v}, t = 0)]. \tag{15}$$

We have thus kept both the initial value terms and the fictitious forces $\boldsymbol{F}_\sigma$ in (11)–(14). When using the fluctuation dissipation theorem we neglect the former but retain the latter and conversely, when using the transition probability function approach, we keep the former but neglect the latter.

The total electric charge is always conserved, $\omega\rho_{\text{tot}} = \boldsymbol{k} \cdot \boldsymbol{j}_{\text{tot}}$. Neglecting the initial value terms in (11)–(14), one therefore easily shows that

$$\Delta_\sigma' = \omega\chi_\sigma' \tag{16}$$

and hence also

$$\varepsilon = 1 + \sum_\sigma \Delta_\sigma'/\omega. \tag{17}$$

On the other hand we do *not* generally have the relation $\Delta_{\sigma'\sigma} = \omega\chi_{\sigma'\sigma''}$ which is only valid if there are no chemical reactions. Equations (16) and (17) are important when showing that the velocity fluctuation spectrum is the same, whether calculated by means of either the fluctuation dissipation theorem or the transition probability function approach.

3. The fluctuation dissipation theorem

Before stating the fluctuation dissipation theorem, we establish a notational convention. Let the matrix **A**, with the elements $A_{\alpha\beta}$ at the position $\alpha\beta$, be given. We then denote the *transpose* to **A**, i.e. the matrix which has the elements $A_{\beta\alpha}$ at the position $\alpha\beta$, by $\mathbf{A}^{\mathrm{T}}$, and we denote by $\mathbf{A}^{+}$ the *transpose conjugate* to **A**, i.e. the matrix which has the elements $A_{\beta\alpha}^{*}$ at the position $\alpha\beta$. The indices α and β are not necessarily related to the particle species σ.

We shall use the following version of the fluctuation dissipation theorem. Consider a system in thermal equilibrium, with the temperature T (in energy units). Let F_{α} be a set of small external perturbations acting on the system and let V_{α} be a set of linear responses to these perturbations, such that the work done on the system by the perturbations F_{α} is $w = \int dk \, (2\pi)^{-4} \sum_{\alpha} F_{\alpha} V_{\alpha}^{*}$. Let the symbols V and F denote the column vectors with the elements V_{α} and F_{α} at the position α. If we then define the response matrix **A** as the matrix which satisfies the relation $V = \mathbf{A} \cdot F$, the theorem states that

$$\langle VV^{+}\rangle_{k} = T(\mathbf{A} + \mathbf{A}^{+}) \tag{18}$$

where $\langle VV^{+}\rangle_{k}$ has the element $\langle V_{\alpha}V_{\beta}^{*}\rangle_{k}$ at the position $\alpha\beta$.

For instance, if the set of perturbations F_{α} has only one element $F = \phi_{\mathrm{ext}}$, where ϕ_{ext} is an external electrostatic potential, we have $V = -i\omega\rho$. It is now easy to determine the response function A, and we obtain $\langle |V|^{2}\rangle_{k} = \omega^{2}\langle |\rho|^{2}\rangle_{k} = 2\omega\varepsilon_{0}k^{2}T \, \mathrm{Im}(\varepsilon^{-1})$ from equation (18).

In order to calculate the velocity fluctuation spectrum, we choose $F_{\sigma} = \hat{k} \cdot F_{\sigma}$ and hence $V_{\sigma} = n_{\sigma 0}\hat{k} \cdot u_{\sigma 1}$; $\hat{k}$ is the unit vector in the direction of k. The response matrix **A** is then found from equation (13) and according to the fluctuation dissipation theorem we thus have

$$\langle n_{\sigma 0}k \cdot u_{\sigma 1} n_{\sigma'0}k \cdot u_{\sigma'1}^{*}\rangle_{k} = \frac{i\varepsilon_{0}T}{q_{\sigma}q_{\sigma'}}\left[\left(\Delta_{\sigma\sigma'} - \frac{\Delta_{\sigma}'\cdot\Delta_{\sigma}''}{\omega\varepsilon}\right) - \left(\Delta_{\sigma'\sigma} - \frac{\Delta_{\sigma}'\Delta_{\sigma}''}{\omega\varepsilon}\right)^{*}\right] \tag{19}$$

where we have also used equation (16).

We now demonstrate the effect of a direct application of the continuity equation

$$(\omega - i\mathbf{K})N = k\,\Gamma \tag{20}$$

where N and Γ are column vectors with the elements $n_{\sigma 1}$ and $n_{\sigma 0}\hat{k} \cdot u_{\sigma 1}$ at the position σ. The matrix **K**, with the constant $K_{\sigma\sigma'}$ at the position $\sigma\sigma'$, accounts for the chemical reactions in the plasma. This is equivalent to the simple model $C_{\sigma\sigma'}\varphi = -K_{\sigma\sigma'}f_{\sigma 0}\int dv' \, \varphi$. If we wish to use the fluctuation dissipation theorem to calculate the density fluctuation spectrum instead of the velocity fluctuation spectrum, we replace the set of responses Γ with N and we introduce new external perturbations Φ_{σ} such that the work integrals $\int dk(2\pi)^{-4}F^{+}V$ and $\int dk(2\pi)^{-4}\Phi^{+}N$ are equal. This is achieved by setting $\Phi = k^{-1}(\omega - i\mathbf{K})^{+}F$. The response matrix appropriate for the calculation of $\langle NN^{+}\rangle_{k}$, using

equation (18), then becomes

$$\hat{\mathbf{A}} = k^2(\omega - i\mathbf{K})^{-1}\mathbf{A}[(\omega - i\mathbf{K})^{-1}]^{\dagger} \tag{21}$$

where $\mathbf{A}$ is the matrix used in the calculation of the velocity spectrum (19). This result can also be derived by means of a direct substitution of equation (20) in the velocity spectrum.

However, the particle *non*-conserving collisions are a damping mechanism, just as any other collision process is. Hence the matrix $(\omega - i\mathbf{K})^{-1}$ has poles in the upper ω-half plane. As a consequence $[(\omega - i\mathbf{K})^{-1}]^{\dagger}$ has poles in the lower ω-half plane. The response matrix $\hat{\mathbf{A}}$ in equation (21) thus has poles in both the upper and the lower ω-half planes. This response matrix is accordingly non-causal and hence unphysical.

The reason why this occurs is, of course, that the continuity equation (20) only describes the average evolution of the system for times $t > 0$. In order to describe the plasma before $t = 0$, at which time a complete knowledge about the system was assumed, we require another equation. Thus the continuity equation cannot be Fourier transformed directly and it must accordingly be applied very carefully. We return to this point in § 5. The results of the method leading to equation (21) will be further discussed in § 7.

If there are no particle non-conserving collisions, the operator $(\omega - i\mathbf{K})^{-1}$ reduces to the scalar ω^{-1} which has no poles in the lower ω-half plane. In this case no problems associated with non-causal response operators therefore appear.

4. The transition probability method

A straightforward extension of Uddholm (1982) yields the undressed density and velocity fluctuation spectra

$$\langle n_{\sigma'1}^{(r)} n_{\sigma''1}^{(r)*} \rangle_k = n_{\sigma''0} \int dv \, g_{\sigma'\sigma''}(f_{\sigma''0}) + n_{\sigma'0} \int dv \, g_{\sigma''\sigma'}(f_{\sigma'0}) \tag{22}$$

and

$$\langle \mathbf{k} \cdot \mathbf{u}_{\sigma'1}^{(r)} \mathbf{k} \cdot \mathbf{u}_{\sigma''1}^{(r)*} \rangle_k = n_{\sigma'0}^{-1} \int dv \, \mathbf{k} \cdot \mathbf{v} g_{\sigma'\sigma''}(\mathbf{k} \cdot \mathbf{v} f_{\sigma''0}) + n_{\sigma''0}^{-1} \int dv \, \mathbf{k} \cdot \mathbf{v} g_{\sigma''\sigma'}^*(\mathbf{k} \cdot \mathbf{v} f_{\sigma'0}) \tag{23}$$

where the integrals $n_{\sigma''0} \int dv (\cdot) g_{\sigma'\sigma''}(\cdot \cdot)$ are the Fourier–Laplace transforms of the forward-time correlation functions, e.g. $S_{\sigma'\sigma''}^+(\mathbf{k}, \omega)$ where $S_{\sigma'\sigma''}^+(\mathbf{k}, t) = \langle n_{\sigma'1}(t) n_{\sigma''1}^*(0) \rangle_k$ if $t > 0$ and $S_{\sigma'\sigma''}^+(\mathbf{k}, t) = 0$ if $t < 0$. Due to time and space reversibility we have $S_{\sigma'\sigma''}^+(\mathbf{k}, t) = S_{\sigma''\sigma'}^+(\mathbf{k}, t)$, or equivalently,

$$n_{\sigma''0} \int dv \, g_{\sigma'\sigma''}(f_{\sigma''0}) = n_{\sigma'0} \int dv \, g_{\sigma''\sigma'}(f_{\sigma'0}), \tag{24}$$

a relation which we shall find useful later.

The collective effects are then included by assuming that the relations (11)–(14) are also valid for the exact microscopic distribution functions, and not only for the averages $f_{\sigma1}$ and $f_{\sigma1}^{(r)}$. In particular, we obtain the electron velocity fluctuation spectrum

$$\langle |\mathbf{k} \cdot \mathbf{u}_{e1}|^2 \rangle_k = \sum_{\sigma',\sigma''} \frac{q_{\sigma'} q_{\sigma''} n_{\sigma'0} n_{\sigma''0}}{q_e^2 n_{e0}^2} \left(\delta_{e\sigma'} - \frac{\Delta_e''}{\omega\varepsilon} \right) \left(\delta_{e\sigma''} - \frac{\Delta_e''}{\omega\varepsilon} \right)^* \langle \mathbf{k} \cdot \mathbf{u}_{\sigma'1}^{(r)} \mathbf{k} \cdot \mathbf{u}_{\sigma''1}^{(r)*} \rangle_k \tag{25}$$

by multiplying equation (13) with its complex conjugate and taking the averages. The fictitious forces $\boldsymbol{F}_\sigma$ are neglected, in accordance with § 2. We refer to this calculation as the dielectric superposition principle, and it has been discussed by several authors, e.g. Ichimaru (1973) and Rosenbluth and Rostoker (1962). It is also possible to establish a linear relation between the external forces $\boldsymbol{F}_\sigma$ and the random variables $n_{\sigma 1}^{(r)}$ or $\boldsymbol{u}_{\sigma 1}^{(r)}$, such that both terms on the RHS of equations (11)–(14) become identical. The random quantities can accordingly be directly interpreted in terms of the fictitious forces (and *vice versa*). This version of the superposition principle has often been used to extend the fluctuation dissipation theorem to many-temperature plasmas.

It is thus standard to use the superposition principle and since it would be quite outside the scope of this paper to prove it, we shall accept it without further justification.

Let us now assume Maxwellian velocity distribution functions. If we consider at first only the random spectra (i.e. neglect the term $\varepsilon^{-1}\Delta'_\sigma \cdot \Delta''_\sigma$ in equation (19)) it is easy to see that equations (19) and (23) are equivalent. The collective effects can then be included by means of the superposition principle above. In the collective case, the verification of the equivalence between equations (19) and (25) is a straightforward but lengthy calculation. The details must therefore be omitted, but we mention that the key step is to notice the identity

$$\Delta_{\sigma\sigma'} - \frac{\Delta'_\sigma \cdot \Delta''_\sigma}{\omega\varepsilon}$$

$$\equiv -\sum_{\sigma'' \neq \sigma} \Delta_{\sigma''\sigma'} + \left(1 - \frac{\Delta''_\sigma}{\omega\varepsilon}\right)\left(1 - \frac{\Delta''_{\sigma'}}{\omega\varepsilon}\right)^* \sum_{\sigma''} \Delta_{\sigma''\sigma'}$$

$$+ \left(\frac{\Delta''_\sigma}{\omega\varepsilon}\right)^* \left(1 - \frac{\Delta''_\sigma}{\omega\varepsilon}\right) \sum_{\sigma''} (\Delta_{\sigma''\sigma'} - \Delta_{\sigma\sigma''}) + \left(\frac{\Delta''_\sigma}{\omega\varepsilon}\right)\left(\frac{\Delta''_{\sigma'}}{\omega\varepsilon}\right)^* \left(\omega + \sum_{\sigma'' \neq \sigma}\sum_{\sigma'''} \Delta_{\sigma''\sigma'''}\right)$$

$$\tag{26}$$

and to calculate the factors before $\Delta_{\sigma\sigma'}$, $\Delta_{\sigma''\sigma'}$, $\Delta_{\sigma\sigma'''}$ and $\Delta_{\sigma''\sigma'''}$ where $\sigma'' \neq \sigma$ and $\sigma''' \neq \sigma'$. Thus, the two methods yield the same velocity spectra.

We have formulated the theory in terms of the Boltzmann equation operators $g_{\sigma'\sigma'''}$. It is also possible to use the Green functions (or the transition probability functions) $W_{\sigma'\sigma''}(k, \boldsymbol{v}|\boldsymbol{v}')$ of the operators $g_{\sigma'\sigma''}$ (Hagfors and Brockelman 1971). For instance, equation (22) then assumes the form

$$\langle n_{\sigma'1}^{(r)} n_{\sigma''1}^{(r)*} \rangle_k = n_{\sigma''0} \int d\boldsymbol{v}\, d\boldsymbol{v}'\, W_{\sigma'\sigma''}(k, \boldsymbol{v}|\boldsymbol{v}')f_{\sigma''0}(\boldsymbol{v}')$$

$$+ n_{\sigma'0} \int d\boldsymbol{v}\, d\boldsymbol{v}'\, W_{\sigma''\sigma'}^*(k, \boldsymbol{v}|\boldsymbol{v}')f_{\sigma'0}(\boldsymbol{v}'). \tag{27}$$

The functions $W_{\sigma'\sigma''}$ have a simple physical interpretation. Let a particle of species σ'' be given at the origin $\boldsymbol{r} = \boldsymbol{0}$ with the velocity $\boldsymbol{v}'$ at the time $t = 0$. Due to the chemical reactions (or the collisions with the other species) this particle will also give contributions to the distribution functions for the other particle species. With the collective fields neglected, $W_{\sigma'\sigma''}(\boldsymbol{r}, \boldsymbol{v}, t|\boldsymbol{v}')$ is then the average contribution to the σ'-particle distribution function from this particle.

In this work we use the $g_{\sigma'\sigma''}$ operator formalism, because it is more suitable for algebraic operations. We might, of course, just as well have used the physically more appealing formalism in equation (27). However, in that case it would have been

necessary to derive an adjoint Boltzmann equation[+] in the initial coordinates for the functions $W_{\sigma'\sigma''}$ and to use this equation repeatedly.

We close this section by noticing that according to equation (27)

$$\int d\omega (2\pi)^{-1} \langle n^{(r)}_{\sigma'1} n^{(r)*}_{\sigma''1} \rangle_k = n_{\sigma'0} \delta_{\sigma'\sigma''} \tag{28}$$

or in other words, if the collective fields are negligible, the total scattered intensity is *not* affected by the presence of chemical reactions in the plasma.

5. Density fluctuations

Let us consider the density autocorrelation function matrix $\langle N(r, t)N^{\mathrm{T}}(r' t')\rangle$, which only depends on $|r - r'|$ and $|t - t'|$. We have seen (§ 3) that we obtain a non-physical result if we assume that the continuity equation (20) can be applied to both $N(r, t)$ and $N(r', t')$ in $\langle N(r, t)N^{\mathrm{T}}(r', t')\rangle$, i.e.

$$(\partial/\partial t + \mathbf{K})\langle N(r, t)N^{\mathrm{T}}(r', t')\rangle(\partial/\partial t' + \mathbf{K}^{\mathrm{T}}) = \langle D(r, t)D^{\mathrm{T}}(r', t')\rangle \tag{29}$$

where $D(r, t)$ is the column vector with the element

$$D_\sigma(r, t) = \partial/\partial r \cdot \Gamma_\sigma(r, t) \equiv n_{\sigma 0}\partial/\partial r \cdot u_{\sigma 1}(r, t)$$

at the position σ, and in order to make our expressions more concise, we let the operator $(\partial/\partial t' + \mathbf{K}^{\mathrm{T}})$ operate on its left. Equation (29) is also in disagreement with our formulae (22) and (23). This is an example of the fact that the *average properties* of the fluctuating quantities, such as equation (20), derived from the Boltzmann equation, cannot be transferred to the correlation functions in a straightforward manner (§ 2). If the matrix $\mathbf{K}$ vanishes, the continuity equation (20) is exact and equation (29) then applies. However, if the matrix $\mathbf{K}$ is finite, equation (20) only describes the average evolution of the system for times $t > 0$, and equation (29) accordingly does not apply.

The purpose of this section is thus to modify equation (29) in such a way that the chemical reactions (i.e. the matrix $\mathbf{K}$) are included in a correct manner. When the collective effects are negligible, the resulting equation is a relation between the random density and velocity autocorrelation functions. We shall show that this relation agrees with the transition probability theory, i.e. with equations (22) and (23).

It is not difficult to derive the appropriate version of equation (29). To this end we define the forward-time correlation function $\mathbf{S}^+$,

$$\mathbf{S}^+(r, t|r', t') = H(t - t')\langle N(r, t)N^{\mathrm{T}}(r', t')\rangle \tag{30}$$

which vanishes for $t' > t$ (the Heaviside unit step function $H(\tau)$ vanishes for $\tau < 0$ and equals unity for $\tau > 0$). There is of course also a backward-time correlation function $\mathbf{S}^-$, which vanishes for $t' < t$, such that $\mathbf{S}^+ + \mathbf{S}^- = \langle NN^{\mathrm{T}}\rangle$. These functions have similar properties, so we need only consider $\mathbf{S}^-$, however. In the presence of chemical reactions in the plasma, it is necessary to consider the function(s) $\mathbf{S}^+$ (and $\mathbf{S}^-$) instead of $\langle NN^{\mathrm{T}}\rangle$. The reason for this is that then the discontinuities at $t = t'$ give rise to terms which do not cancel out in the density fluctuation spectrum, when we add the forward- and backward-time correlation functions $\mathbf{S}^+$ and $\mathbf{S}^-$. The random spectrum (see

[+] cf Uddholm, British Libraries Supplementary Publication Scheme, PS ref no 90057 (appendix).

equation (38)) does, in fact, consist of two parts: one which contains chemical effects in addition to *all* the thermal effects, and another which corresponds to chemical fluctuations in a plasma without any thermal effects. The former vanishes in the limit of a 'cold' plasma, i.e. when diffusion effects are so weak that the plasma particles are virtually stationary on the timescale of the chemical reactions. We shall, somewhat improperly, use the notations 'thermal' and 'chemical' parts. It is the 'chemical' part that originates from the discontinuities at $t = t'$.

We now derive the relation between the velocity and density correlation functions, which replaces equation (29). To this end we let t be constant and vary $t' < t$. If we increase t' by a small amount dt', the correlation function $\langle \boldsymbol{D}(\boldsymbol{r}, t)\boldsymbol{N}^{\mathrm{T}}(\boldsymbol{r}', t')\rangle$ will change by the infinitesimal quantities $\langle \boldsymbol{D}\boldsymbol{N}^{\mathrm{T}}\rangle\boldsymbol{K}^{\mathrm{T}} \, dt'$ and $\langle \boldsymbol{D}\boldsymbol{D}^{\mathrm{T}}\rangle \, dt$, which are due to the chemical reactions and the particle fluxes, respectively. Hence, bearing in mind that an increase of t' must increase our knowledge about the system since $|t - t'|$ decreases, we obtain

$$\langle \boldsymbol{D}(\boldsymbol{r}, t)\boldsymbol{N}^{\mathrm{T}}(\boldsymbol{r}', t')\rangle(\partial/\partial t' - \boldsymbol{K}^{\mathrm{T}}) = \langle \boldsymbol{D}(\boldsymbol{r}, t)\boldsymbol{D}^{\mathrm{T}}(\boldsymbol{r}', t')\rangle \tag{31}$$

if $t' < t$ and where the operator $(\partial/\partial t' - \boldsymbol{K}^{\mathrm{T}})$ operates on its left. On the other hand, if we keep t' fixed and vary $t > t'$, we derive

$$(\partial/\partial t + \boldsymbol{K})\boldsymbol{S}^{+}(\boldsymbol{r}, t|\boldsymbol{r}', t') = \langle \boldsymbol{D}(\boldsymbol{r}, t)\boldsymbol{N}^{\mathrm{T}}(\boldsymbol{r}', t')\rangle \tag{32}$$

if $t > t'$. Including the contributions from the discontinuity at $t = t'$, equations (31) and (32) yield

$$[(\partial/\partial t + \boldsymbol{K})\boldsymbol{S}^{+}(\boldsymbol{r}, t|\boldsymbol{r}', t') - \delta(t - t')\langle \boldsymbol{N}(\boldsymbol{r}, t)\boldsymbol{N}^{\mathrm{T}}(\boldsymbol{r}', t')\rangle](\partial/\partial t' - \boldsymbol{K}^{\mathrm{T}})$$
$$= H(t - t')\langle \boldsymbol{D}(\boldsymbol{r}, t)\boldsymbol{D}^{\mathrm{T}}(\boldsymbol{r}', t')\rangle - \delta(t - t')\langle \boldsymbol{D}(\boldsymbol{r}, t)\boldsymbol{N}^{\mathrm{T}}(\boldsymbol{r}', t')\rangle \tag{33}$$

where we have used the fact that the delta function $\delta(\tau)$ is the derivative of the unit step function $H(\tau)$. Equation (33) is the appropriate formula to use instead of equation (29). Taking the Fourier transforms of equation (33), we obtain

$$(\omega - \mathrm{i}\boldsymbol{K})\boldsymbol{S}^{+}(\boldsymbol{k})(\omega - \mathrm{i}\boldsymbol{K}^{\mathrm{T}})$$
$$= \int_0^\infty \mathrm{d}\tau \, \mathrm{e}^{-\mathrm{i}\omega\tau}\langle \boldsymbol{D}(t' + \tau)\boldsymbol{D}^{+}(t')\rangle_{\boldsymbol{k}} - \mathrm{i}\langle \boldsymbol{N}(t = t')\boldsymbol{N}^{+}(t')\rangle_{\boldsymbol{k}}(\omega - \mathrm{i}\boldsymbol{K}^{\mathrm{T}})$$
$$- \langle \boldsymbol{D}(t = t')\boldsymbol{N}^{+}(t')\rangle_{\boldsymbol{k}} \tag{34}$$

where

$$(2\pi)^4\delta(\boldsymbol{k} - \boldsymbol{k}')\boldsymbol{S}^{+}(\boldsymbol{k}) = \int \mathrm{d}\boldsymbol{r} \, \mathrm{d}t \, \mathrm{d}\boldsymbol{r}' \, \mathrm{d}t' \exp[-\mathrm{i}(\omega t - \omega't' - \boldsymbol{k} \cdot \boldsymbol{r} + \boldsymbol{k}' \cdot \boldsymbol{r}')]\boldsymbol{S}^{+}(\boldsymbol{r}, t|\boldsymbol{r}', t').$$
$$\tag{35}$$

For uncorrelated particles we have the formulae

$$\langle n_{\sigma 1}^{(\mathrm{r})}(t = t')n_{\sigma'1}^{(\mathrm{r})*}(t')\rangle_{\boldsymbol{k}} = n_{\sigma 0}\delta_{\sigma\sigma'} \tag{36}$$

where $\delta_{\sigma\sigma'}$ is the Kronecker delta and

$$\langle \boldsymbol{k} \cdot \boldsymbol{u}_{\sigma 1}^{(\mathrm{r})}(t = t')n_{\sigma'1}^{(\mathrm{r})}(t')\rangle_{\boldsymbol{k}} = 0. \tag{37}$$

When inserted in equation (34) these formulae yield the random density, forward-time correlation function

$$\boldsymbol{S}^{+(\mathrm{r})}(\boldsymbol{k}) = k^2(\omega - \mathrm{i}\boldsymbol{K})^{-1}\int_0^\infty \mathrm{d}\tau \, \mathrm{e}^{-\mathrm{i}\omega\tau}\langle \boldsymbol{\Gamma}^{(\mathrm{r})}(t' + \tau)\boldsymbol{\Gamma}^{(\mathrm{r})+}(t')\rangle_{\boldsymbol{k}}(\omega - \mathrm{i}\boldsymbol{K}^{\mathrm{T}})^{-1} - \mathrm{i}\boldsymbol{M} \tag{38}$$

where we have used that $D_\sigma = -ik\Gamma_\sigma$ and have introduced the matrix **M** with the element $n_{\sigma'0}(\omega - i\mathbf{K})^{-1}_{\sigma\sigma'}$ at the position $\sigma\sigma'$. The first term on the RHS in equation (38) corresponds to the 'thermal part' of the spectrum and the second term, which arises due to the discontinuities at $t = t'$, corresponds to the 'chemical part'. We obtain the spectrum $\langle NN^+ \rangle_k = 2 \operatorname{Re} \mathbf{S}^+(k)$ by taking the real parts in equation (38).

Let us now consider the transition probability function method. The results (36) and (37) are immediate consequences of this theory, cf equation (28). Moreover, according to the definition of the operators $g_{\sigma\sigma'}$, equation (3), we have

$$\sum_{\sigma''} (\omega\delta_{\sigma\sigma''} - iK_{\sigma\sigma''}) \int d\boldsymbol{v}\, g_{\sigma''\sigma'}(f_{\sigma'}0) - \int d\boldsymbol{v}\, \boldsymbol{k} \cdot \boldsymbol{v}g_{\sigma\sigma'}(f_{\sigma'}0) = -i\delta_{\sigma\sigma'} \tag{39}$$

where the constants $K_{\sigma\sigma'}$ are the elements in the matrix **K**. This relation is equivalent to

$$\left[\int d\boldsymbol{v}\, g_{\sigma\sigma'}(f_{\sigma'}0)\right] = (\omega - i\mathbf{K})^{-1}\left[\int d\boldsymbol{v}\, \boldsymbol{k} \cdot \boldsymbol{v}g_{\sigma\sigma'}(f_{\sigma'}0)\right] - i(\omega - i\mathbf{K})^{-1} \tag{40}$$

where $[h_{\sigma\sigma'}]$ is short for the matrix which has the element $h_{\sigma\sigma'}$ at the position $\sigma\sigma'$. In an analogous way we also find

$$\left[\int d\boldsymbol{v}\, \boldsymbol{k} \cdot \boldsymbol{v}g_{\sigma\sigma'}(f_{\sigma'}0)\right] = \left[\int d\boldsymbol{v}\, \boldsymbol{k} \cdot \boldsymbol{v}g_{\sigma\sigma'}(\boldsymbol{k} \cdot \boldsymbol{v}f_{\sigma'}0)\right](\omega - i\mathbf{K})^{-1}. \tag{41}$$

When we substitute equation (41) in the RHS of equation (40), equation (38) follows upon multiplication with the diagonal matrix $[\delta_{\sigma\sigma'}n_{\sigma0}]$, if we use $(\omega - i\mathbf{K})^{-1}[\delta_{\sigma\sigma'}n_{\sigma0}] = [\delta_{\sigma\sigma'}n_{\sigma0}](\omega - i\mathbf{K}^\mathrm{T})^{-1}$ which is due to the condition for balance between the loss and production of particles $K_{\sigma\sigma'}n_{\sigma'0} = K_{\sigma'\sigma}n_{\sigma0}$. This also follows if we apply equation (24) to the 'chemical part' of the spectrum or from arguments similar to those in the appendix.

If the chemical reactions are sufficiently frequent, the 'thermal part' in equation (38) is small and the 'chemical part' dominates. However, if the chemical reaction rate is low the 'chemical part' $-i\mathbf{M}$ does not vanish. Nevertheless, if there are no chemical reactions, there can be no chemical terms in the spectrum in spite of this. We can understand this by expressing the integrals $\int d\boldsymbol{v}\, \boldsymbol{k} \cdot \boldsymbol{v}g_{\sigma\sigma'}(\boldsymbol{k} \cdot \boldsymbol{v}f_{\sigma'}0)$ as a linear combination of the integrals $\int d\boldsymbol{v}\, g_{\sigma\sigma'}(f_{\sigma'}0)$ by means of equations (40) and (41). It is then seen that the 'thermal part' of equation (38) can be expressed as

$$(\omega - i\mathbf{K})^{-1}\left[n_{\sigma'0}\int d\boldsymbol{v}\, \boldsymbol{k} \cdot \boldsymbol{v}g_{\sigma\sigma'}(\boldsymbol{k} \cdot \boldsymbol{v}f_{\sigma'}0)\right](\omega - i\mathbf{K}^\mathrm{T})^{-1} = \left[n_{\sigma'0}\int d\boldsymbol{v}\, g_{\sigma\sigma'}(f_{\sigma'}0)\right] + i\mathbf{M}.$$

When this is substituted in equation (38), the second term on the RHS and the 'chemical part' cancel, and equation (38) reduces to equation (22). The 'thermal part' in (38) thus also involves a chemical term. The notations 'thermal and chemical part' are therefore not quite adequate. However, Im **M** is equal to the chemical part of Kockarts and Wisemberg (1981) and the 'thermal part' contains all the thermal effects and it is small when these effects are weak.

The failure of equation (29) can also be demonstrated in a much more elementary manner. Since the quantities $\langle \boldsymbol{N}(\boldsymbol{r}, t)\boldsymbol{N}^\mathrm{T}(\boldsymbol{r}', t')\rangle$ and $\langle \boldsymbol{D}(\boldsymbol{r}, t)\boldsymbol{D}^\mathrm{T}(\boldsymbol{r}', t')\rangle$ only depend on $|\boldsymbol{r} - \boldsymbol{r}'|$ and $|t - t'|$, they must remain invariant under the change of variables $(\boldsymbol{r}, t) \rightleftharpoons (\boldsymbol{r}', t')$ and we must also have $\partial/\partial t = -\partial/\partial t'$ on the LHS. These facts lead to a contradiction, because equation (29) then assumes a form where the operators on its LHS are

replaced with $(\partial/\partial t - \mathbf{K})$ and $(\partial/\partial t' - \mathbf{K}^T)$. If we consider equation (33), on the other hand, the change of variables $(r, t) \rightleftharpoons (r', t')$ and transposition (or use of $\partial/\partial t = -\partial/\partial t'$) yields the equation corresponding to (33) for $\mathbf{S}^-(r, t|r', t')$, as we should expect.

We have thus found the correct relation between the random density and velocity correlation functions, equation (38). We have also seen that this relation is a simple consequence of the transition probability function approach. The transition probability approach is in fact more general than equation (38). Whereas the latter is restricted to the model for the particle non-conserving collisions introduced in § 3, the former is valid for arbitrary collision terms $C_{\sigma'\sigma''}$. As a matter of fact, for general particle non-conserving collision operators $C_{\sigma'\sigma''}$, it is not possible to derive continuity equations corresponding to equation (20) or (38).

Although equation (34) is much simplified when we consider the random spectra, it is highly impractical to use, if we wish to consider the dressed spectra. The collective fields are easily included, however, by means of the superposition principle, as discussed previously. Omitting the extensive algebra, we thus derive the dressed electron density fluctuation spectrum

$$\frac{1}{n_{e0}} \langle |n_{e1}|^2 \rangle_k = 2 \left| 1 - \frac{\chi_e''}{\varepsilon} \right|^2 \mathrm{Re} \int \mathrm{d}v\, g_{ee}(f_{e0})$$

$$- 4 \, \mathrm{Re}\left[\left(1 - \frac{\chi_e''}{\varepsilon}\right)\left(\frac{\chi_e''}{\varepsilon}\right)^* \right] \sum_{\sigma \neq e} \frac{q_\sigma}{q_e} \mathrm{Re} \int \mathrm{d}v\, g_{\sigma e}(f_{e0})$$

$$+ 2 \left| \frac{\chi_e''}{\varepsilon} \right|^2 \sum_{\sigma, \sigma' \neq e} \frac{q_\sigma q_{\sigma'} n_{\sigma'0}}{q_e^2 n_{e0}} \mathrm{Re} \int \mathrm{d}v\, g_{\sigma\sigma'}(f_{\sigma'0}) \tag{42}$$

where equation (24) has been used in the second term on the RHS. This expression is valid both for plasmas in which the fluctuations in the various species are coupled through particle conserving collisions, and for plasmas where this coupling is due to particle *non*-conserving collisions. All non-standard symbols appearing in equation (42) have been defined in § 2.

6. The total scattered intensity

Let us consider a Maxwellian, isothermal plasma, i.e. a plasma in which all the particle species have the same temperature, and show that the total intensity in the electron density fluctuation spectrum is *not* changed in the presence of particle non-conserving collisions. Since we assume Maxwellian velocity distribution functions

$$f_{\sigma0}(v) = (2\pi v_{T\sigma})^{-3/2} \exp(-v^2/2v_{T\sigma}^2) \tag{43}$$

we can rewrite equation (4) as

$$\chi_{\sigma\sigma'} = \frac{q_\sigma}{\varepsilon_0 k^2 T} \int \mathrm{d}v\, g_{\sigma\sigma'}\left(-\mathrm{i}\omega q_{\sigma'} n_{\sigma'0} f_{\sigma'0} + \sum_{\sigma''} g_{\sigma'\sigma'}^{-1} (q_{\sigma''} n_{\sigma''0} f_{\sigma''0}) \right) \tag{44}$$

where we have used that all species have the same temperature $T = m_\sigma v_{T\sigma}^2$ together with equations (2), (43) and the relation

$$\sum_{\sigma''} C_{\sigma'\sigma''}(q_{\sigma''} n_{\sigma''0} f_{\sigma''0}) = 0. \tag{45}$$

The formula (45) is not obvious, and a heuristic derivation is therefore presented in the appendix. Although we do not prove it rigorously, for general collision operators $C_{\sigma\sigma'}$, the arguments in the appendix are quite sufficient for showing that this relation is true for any collision operators which can be written in the Boltzmann form, e.g. the collision model introduced in § 3. The Boltzmann form is suitable for the collisions with the neutrals and the particle non-conserving collisions. For small-angle Coulomb collisions, the collision operators assume a different mathematical form, however, so the simple model in the appendix does not quite apply. Nevertheless, this is probably only a mathematical detail of very restricted physical interest.

Combining equation (45) with equations (6) and (3), it is now easy to show that

$$\chi_\sigma'' = \frac{\omega_{p\sigma}^2}{k^2 v_{T\sigma}^2}\left(1 - i\omega \sum_{\sigma'} \frac{q_{\sigma'} n_{\sigma'0}}{q_\sigma n_{\sigma 0}} \int d\boldsymbol{v}\, g_{\sigma\sigma'}(f_{\sigma'0})\right), \tag{46}$$

where $\omega_{p\sigma}$ is the plasma frequency for species σ, $\omega_{p\sigma}^2 = n_{\sigma 0} q_\sigma^2/(m_\sigma \varepsilon_0)$. If we use this formula together with the relation $\varepsilon = 1 + \Sigma_\sigma \chi_\sigma'$ and equation (24) we derive

$$\frac{-k^2 v_{Te}^2}{\omega_{pe}^2}\mathrm{Im}\left(\frac{(\varepsilon - \chi_e'')\chi_e''}{\varepsilon}\right)$$

$$= \left|1 - \frac{\chi_e''}{\varepsilon}\right|^2 \mathrm{Re}\int d\boldsymbol{v}\, g_{ee}(f_{e0}) + \left(\left|1 - \frac{\chi_e''}{\varepsilon}\right|^2 + \left|\frac{\chi_e''}{\varepsilon}\right|^2\right) \sum_{\sigma \neq e} \frac{q_\sigma}{q_e} \mathrm{Re}\int d\boldsymbol{v}\, g_{\sigma e}(f_{e0})$$

$$+ \left|\frac{\chi_e''}{\varepsilon}\right|^2 \sum_{\sigma,\sigma' \neq e} \frac{q_{\sigma'} q_\sigma n_{\sigma 0}}{q_e^2 n_{e0}} \mathrm{Re}\int d\boldsymbol{v}\, g_{\sigma'\sigma}(f_{\sigma 0}) \tag{47}$$

where the straightforward algebra has been omitted. We notice that equations (42) and (47) are quite similar, apart from the factor in front of the second term on the RHS. Combining these two equations we will, in fact, find that

$$\frac{1}{n_{e0}}\langle |n_{e1}|^2\rangle_k = \frac{-2k^2 v_{Te}^2}{\omega \omega_{pe}^2}\mathrm{Im}\left(\frac{(\varepsilon - \chi_e'')\chi_e''}{\varepsilon}\right) - 2\sum_{\sigma \neq e}\frac{q_\sigma}{q_e}\mathrm{Re}\int d\boldsymbol{v}\, g_{\sigma e}(f_{e0}). \tag{48}$$

In the case of no collisional coupling between the various particle species, we see that this formula reduces to the familiar version of the fluctuation dissipation theorem.

We are not interested in equation (48) for its resemblance to the fluctuation dissipation theorem, but because it is quite easy to calculate the frequency integral of the RHS of this equation. The first term is integrated as in Dougherty and Farley (1963) and it is then seen that the result only depends on $\chi_e''(\omega = 0)$ and $\varepsilon(\omega = 0)$, which are easily calculated from equation (46). The second term does not contribute. This is clear if we rewrite it in terms of the transition probability functions $W_{\sigma e}$ and use the same arguments as in the end of § 4. We thus find

$$\int \frac{d\omega}{2\pi}\frac{1}{n_{e0}}\langle |n_{e1}|^2\rangle_k = 1 - \left(1 + \sum_\sigma \frac{\omega_{p\sigma}^2}{k^2 v_{T\sigma}^2}\right)^{-1}\frac{\omega_{pe}^2}{k^2 v_{Te}^2}. \tag{49}$$

This equation generalises (28) (valid for $\omega_{pe}/k v_{Te} = 0$) to the collective case $\omega_{pe}/k v_{Te} \neq 0$, for isothermal plasmas. Both (28) and (49) are identical to the corresponding results in the absence of chemical fluctuations (Fukuyama and Kofman 1980). The total intensity in the electron density fluctuation spectrum is accordingly not changed in the presence of chemical reactions, if the plasma is isothermal, and the same result probably also holds for general collision processes.

Our formula (49) for the total intensity requires microscopic reversibility (see appendix). As pointed out by Professor Kockarts this need not be true for, e.g., photo-ionisation. However, in a fluid theory the chemical reactions are only introduced through the continuity equation (20), which does not include any information as to whether microscopic reversibility holds or not. Equation (20) can, in fact, be obtained by taking the velocity moments of the simple kinetic model in § 3, which satisfies the microscopic reversibility requirement. In order to investigate effects associated with the failure of this requirement, detailed kinetic theories must be employed. Moreover, in the presence of photo-ionisation the plasma is not likely to be in thermodynamic equilibrium, so the use of the fluctuation dissipation theorem is questionable and kinetic theories may have to be used also for this reason.

7. Discussion

We have formulated a theory for fluctuations in a plasma, where the fluctuations in the various particle species are coupled through the collision operators. The collisions may be particle conserving, particle *non*-conserving or both. We have concentrated our attention on the effects of particle non-conserving collisions, since in this case the theory becomes much more difficult. The need for such a theory has recently been pointed out by Kockarts and Wisemberg (1981), who considered the mesosphere at heights below 80 km. The main result in the present work is equation (42), which is valid independently of the collision processes. It can thus also be used in completely different situations, for instance to allow correctly for the collisional transfer of momentum (and energy) between the light ions and high-Z impurities in dense, low-temperature plasmas. This collisional effect has previously been neglected.

Our approach is different from that of Kockarts and Wisemberg (1981). Their method is equivalent to first calculating the velocity fluctuation spectrum and then using the continuity equation, i.e. our equation (29), when calculating the density fluctuation spectrum. This method only works in the absence of chemical reactions, however. In the presence of chemical reactions, it is incompatible with the well known fact that $\langle n_{e1}(k, t) n_{e1}^*(k, t') \rangle$ only depends on $|t - t'|$. The reason for this is quite straightforward. In the presence of chemical reactions the dissipative part of the continuity equation would yield extra damping factors to both $n_{e1}(\boldsymbol{k}, t)$ and $n_{e1}^*(\boldsymbol{k}, t')$. As we increase t and t', $\langle n_{e1}(\boldsymbol{k}, t) n_{e1}^*(\boldsymbol{k}, t') \rangle$ thus tends to zero, even if we keep $|t - t'|$ constant. This is obviously in disagreement with the fact that the correlation function only depends on $|t - t'|$. This situation occurs because the dissipative terms were not correctly included in equation (29). In order to treat the problem correctly we have to differentiate between the two cases $t > t'$ and $t < t'$. If $t > t'$ our knowledge about the system decreases when t increases, but increases when t' increases. If $t < t'$, on the other hand, our knowledge about the system increases when t increases, but decreases when t' increases. As a result, the dissipative term $\mathbf{K}$, in the factor with the derivative with respect to the *smallest* of t and t', in equation (29) must change sign. This analysis is presented in some detail in § 5. If we use equation (29) directly, without changing the sign of $\mathbf{K}$ as we have just described, the factors $(\omega - i\mathbf{K})^{-1}$ and $[(\omega - i\mathbf{K})^{-1}]^+$ will appear in the spectrum. As we have also seen before, the appearance of the non-causal response functions in § 3 is thus due to this erroneous use of the continuity equation. The theory of Kockarts and Wisemberg (1981) had therefore to be corrected. Their main result was that the electron density fluctuation spectrum

falls into two parts. To an excellent approximation, these are the (narrow) chemical part, discussed in our § 5, and a (broad) part which is equal to the fluctuation spectrum in the absence of chemical reactions. Both parts may contain approximately the same power, so they also find that the total intensity may become doubled in the presence of chemical fluctuations. These calculations were performed assuming an isothermal plasma. We have seen, however, that the chemical reactions do not change the total power in the spectrum, if the plasma is isothermal and unless extremely complicated kinetic models are used. The effects of the chemical reactions are, in fact, very small for the short-wavelength fluctuations ($k \approx 40$ m^{-1}) considered by Kockarts and Wisemberg (1981).

As we increase the wavelength of the fluctuations, the effects of the chemical reactions increase due to collisional narrowing of the spectrum. Significant modifications will appear when the negative ion life time is comparable to or shorter than the period of a typical plasma oscillation. This can be expected for $k \leqslant 5\text{-}10$ m^{-1}, even in the isothermal case when the total power is not changed. The incoherent scatter technique may thus provide a possible means for direct measurements of the life times of mesospheric negative ions.

Acknowledgment

Appendix

We wish to prove equation (45). To this end we consider some arbitrary chemical reaction $\Sigma_\sigma A_\sigma \sigma \rightleftarrows \Sigma_\sigma B_\sigma \sigma$, where the numbers A_σ and B_σ are non-negative integers. We shall derive a general expression on the Boltzmann form, for the contribution from this reaction to the linearised collision integral. This derivation is related to the discussion of the collisions in Hagfors and Brockelman (1971), since in both approaches the collisions are described by means of the particle 'scattering' probabilities (per unit time). We assume that the collisions are microscopically reversible, i.e. any reaction (with the initial and the final particle velocities given) going from the left to the right is (in equilibrium) exactly as probable as the same reaction going from the right to the left. This does, of course, not imply macroscopic reversibility. Equation (45) is then a very simple consequence of charge conservation

$$\sum_\sigma A_\sigma q_\sigma = \sum_\sigma B_\sigma q_\sigma \tag{A1}$$

as we shall see below.

In order to find an expression for the collisional integral, let us first consider the unperturbed state, i.e. when the σ-particle distribution functions are $n_{\sigma 0} f_{\sigma 0}$. We then denote by

$$dP = P(\{\{v_\sigma^{(l)}\}_{l=1}^{A_\sigma + B_\sigma}\}_\sigma) \prod_\sigma \prod_{l=1}^{A_\sigma + B_\sigma} dv_\sigma^{(l)} \tag{A2}$$

the number of reactions, per unit time and volume, in which A_σ particles of species

σ, with velocities in $\{d\boldsymbol{v}_\sigma^{(l)}\}_{l=1}^{A_\sigma}$ about $\{\boldsymbol{v}_\sigma^{(l)}\}_{l=1}^{A_\sigma}$, react so that B_σ particles of species σ emerge from the reaction with velocities in $\{d\boldsymbol{v}_\sigma^{(l)}\}_{l=A_\sigma+1}^{A_\sigma+B_\sigma}$ about $\{\boldsymbol{v}_\sigma^{(l)}\}_{l=A_\sigma+1}^{A_\sigma+B_\sigma}$ and where the index σ goes over all the particle species involved in the reaction. The expression $\{a_\sigma^{(l)}\}_{l=1}^N$ denotes the sequence $a_\sigma^{(1)}, a_\sigma^{(2)}, \ldots, a_\sigma^{(N)}$. Hence, the elements in the sequences $\{\boldsymbol{v}_\sigma^{(l)}\}_{l=1}^{A_\sigma}$ and $\{\boldsymbol{v}_\sigma^{(l)}\}_{l=A_\sigma+1}^{A_\sigma+B_\sigma}$ are the velocities of the σ-particles immediately before and after the reaction. The quantity dP thus contains all the information as to how the particles are 'scattered' in the reaction. Since we have assumed microscopic reversibility, dP is also the number of reactions, per unit time and volume, going in the opposite direction.

Now suppose that the distribution functions are slightly perturbed. Linearising, we then find the number of reactions going from the left to the right:

$$dP\left(1 + \sum_\sigma \sum_{l=1}^{A_\sigma} \{f_{\sigma 1}(\boldsymbol{v}_\sigma^{(l)})/[n_{\sigma 0} f_{\sigma 0}(\boldsymbol{v}_\sigma^{(l)})]\}\right)$$

and the number of reactions going from the right to the left:

$$dP\left(1 + \sum_\sigma \sum_{l=A_\sigma+1}^{A_\sigma+B_\sigma} \{f_{\sigma 1}(\boldsymbol{v}_\sigma^{(l)})/[n_{\sigma 0} f_{\sigma 0}(\boldsymbol{v}_\sigma^{(l)})]\}\right).$$

Having thus determined the number of reactions going in each direction, it is not difficult to construct the collision integral. This integral consists of four terms. When the reaction goes from the left to the right, a loss term arises due to the particles on the LHS (which are destroyed in the reaction), and a gain term arises due to the particles on the RHS (which are created in the reaction). If the reaction goes in the opposite direction, another loss term and another gain term arise for analogous reasons. The derivations of these four terms are quite similar. It is therefore sufficient to present the calculation of only one of them. We shall calculate the loss term, when the reaction goes from the left to the right.

Consider the infinitesimal element $d\boldsymbol{v}$ about $\boldsymbol{v}$ in velocity space. Due to the chemical reactions, the element $d\boldsymbol{v}$ will experience a loss of particles of species σ. The magnitude of this loss is

$$d\boldsymbol{v}\, A_\sigma \int dP\, \delta(\boldsymbol{v} - \boldsymbol{v}_\sigma^{(1)})\left(1 + \sum_{\sigma'} \sum_{l'=1}^{A_{\sigma'}} \{f_{\sigma'1}(\boldsymbol{v}_{\sigma'}^{(l')})/[n_{\sigma'0} f_{\sigma'0}(\boldsymbol{v}_{\sigma'}^{(l')})]\}\right)$$

per unit time and volume. The factor A_σ is included in front of the integral because we must add the contributions from each of the terms where $d\boldsymbol{v} = d\boldsymbol{v}_\sigma^{(l)}$ and $\boldsymbol{v} = \boldsymbol{v}_\sigma^{(l)}$ for any l, $1 \leq l \leq A_\sigma$, and all these terms are equal.

Calculating also the three remaining terms, we then find the linearised chemical collision integral

$$\left(\frac{df_{\sigma 1}}{dt}\right)_{\text{chem}} \equiv \sum_{\sigma'} C_{\sigma\sigma'}(f_{\sigma'1})$$

$$= -\int dP[A_\sigma \delta(\boldsymbol{v} - \boldsymbol{v}_\sigma^{(1)}) - B_\sigma \delta(\boldsymbol{v} - \boldsymbol{v}_\sigma^{(A_\sigma+1)})]$$

$$\times \sum_{\sigma'}\left(\sum_{l'=1}^{A_{\sigma'}} \frac{f_{\sigma'1}(\boldsymbol{v}_{\sigma'}^{(l')})}{n_{\sigma'0} f_{\sigma'0}(\boldsymbol{v}_{\sigma'}^{(l')})} - \sum_{l'=A_{\sigma'}+1}^{A_{\sigma'}+B_{\sigma'}} \frac{f_{\sigma'1}(\boldsymbol{v}_{\sigma'}^{(l')})}{n_{\sigma'0} f_{\sigma'0}(\boldsymbol{v}_{\sigma'}^{(l')})}\right) \tag{A3}$$

where the straightforward algebra has been omitted. Equation (45) now follows directly from (A1) if we put $f_{\sigma 1} = q_0 n_{\sigma 0} f_{\sigma 0}$.

The calculation above only holds if the collisions can be viewed as discrete events. This is certainly true for chemical reactions. If $A_\sigma = B_\sigma$ for all species σ, the chemical reaction reduces to a particle conserving collision process, and the theory thus applies for this case, too, provided the collisions are discrete, e.g., charged particle–neutral collisions. Coulomb collisions, on the other hand, cannot be considered as discrete and are often described by means of Fokker–Planck collision operators. However, it is not difficult to show that, if we generalise the collision operators of, e.g., Dougherty (1964) to account for cross species collisions, the quantities $C_{\sigma\sigma'}(f_{\sigma'0})$ always vanish. We notice that this is also the case for the collision operators in equation (A3) if particle conservation is assumed. There is an obvious physical interpretation of this. The velocity distribution functions $f_{\sigma0}$ represent an equilibrium state, and a small density perturbation $\varepsilon_{\sigma'}n_{\sigma'0}f_{\sigma'0}$ ($\varepsilon_{\sigma'}$ being a small number) does not change the velocity distribution functions. Hence, for particle conserving collisions $C_{\sigma\sigma'}(f_{\sigma'0}) = 0$, and equation (45) follows.

Equation (45) can probably also be proven for Coulomb collisions, by successively approximating the collision operators with expressions such as (A3). Such a procedure would be very lengthy and technical and is therefore not included in this report.

References

Cheng C S 1973 *J. Math. Phys.* **14** 947–56
Dougherty J P 1964 *Phys. Fluids* **7** 1788–99
Dougherty J P and Farley D T 1963 *J. Geophys. Res.* **68** 5473–86
Fukuyama K and Kofman W 1980 *J. Geomag. Geoelectr.* **32** 67–81
Grewal M S 1964 *Phys. Rev.* **134** A86–93
Hagfors T and Brockelman R A 1971 *Phys. Fluids* **14** 1143–51
Ichimaru S 1973 *Basic Principles of Plasma Physics* (New York: W A Benjamin) ch 9
Kockarts G and Wisemberg J 1981 *J. Geophys. Res.* **86** 5793–800
Rosenbluth M N and Rostoker N 1962 *Phys. Fluids* **5** 776–88
Seasholtz R G 1971 *J. Geophys. Res.* **76** 1793–802
Swartz W E and Farley D T 1979 *J. Geophys. Res.* **84** 1930–2
Tanenbaum B S 1968 *Phys. Rev.* **171** 215–21
Theimer O and Sandalov A N 1979 *Phys. Fluids* **22** 488–90
Theimer O, Sandalov A N and Theimer M M 1980 *Phys. Fluids* **23** 931–3
Theimer O and Theimer M M 1981 *Nuovo Cimento* **65** 207–23
Theimer O and Theimer R 1973 *Plasma Physics* **15** 837–52
Uddholm P 1982 *J. Phys. A: Math. Gen.* **15** 1701–4