

NON-LINEAR HYDRODYNAMIC FLUCTUATION THEORY FOR A CHARGED TWO COMPONENT FLUID IN EQUILIBRIUM

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A scheme introduced recently for the description of non-linear hydrodynamic fluctuations of a one-component fluid is extended to the case of a two-component charged fluid. The random fluxes which are introduced are assumed to be Gaussian processes with white noise. It is found that the usual expressions for the systematic parts of the dissipative fluxes are only consistent with this assumption, if the Onsager coefficients are constant.

1. Introduction

In most approaches to hydrodynamic fluctuation theory, one writes the dissipative fluxes as the sum of a systematic part and a random part, which is usually assumed to be a random variable with Gaussian white noise¹). The consistency of such a procedure can easily be checked if one restricts oneself to the case in which all equations are fully linearized. However, the above approach has usually also been followed in mode-mode coupling calculations; in this case, some non-linear terms (usually the convective ones) are retained in the analysis. The limitations to the use of this kind of non-linear equations for the fluctuations are less wellknown. This led Van Saarloos, Bedeaux and Mazur^{3,4,5}) to investigate in two recent papers, to be referred to as papers I and II, whether a hydrodynamic fluctuation theory, based on the splitting of the dissipative fluxes into systematic and random parts, can be consistently set up if one wants to retain all non-linearities. It was concluded that the non-linearities due to the presence of reversible convective terms and also to the non-linear functional dependence of the thermodynamic functions on the state parameters, can all be taken into account. However, there is a severe restriction to be imposed on the phenomenological laws for the dissipative fluxes, in order to make such a fluctuation theory consistent. Thus, although the expressions for the dissipative fluxes are of the usual form found in

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thermodynamics of irreversible processes⁶), they are more restricted in that the Onsager coefficients (i.e. the viscosities divided by the temperature and the heat conduction divided by the temperature squared) should be constants.

The analysis in papers I and II was based on the equivalence of the stochastic differential equations with Gaussian white noise with a Fokker-Planck equation. However, the derivation of a Fokker-Planck equation for fields is beset with divergency problems inherent in a continuum description. To circumvent these, the hydrodynamic equations were discretized first according to certain rules, and the continuum limit was only taken in the final stage of the calculation. These discretization rules were formulated for conserved variables. In the present paper, we investigate a simple case in which the state of the system cannot be characterized by conserved variables alone: a fluid system consisting of two charged components, in which polarization and magnetization effects can be neglected. It is indeed found that similar restrictions on the phenomenological laws have to be imposed as in the case of an uncharged one-component fluid.

In section 2, we recapitulate the macroscopic equations describing a charged two-component fluid. In section 3 we introduce the stochastic differential equations and give the correlations for the random fluxes. On the basis of the assumption that these random fluxes are Gaussian, we obtain in section 4 the Fokker-Planck equation equivalent with the discretized stochastic equations. The form of the dissipative fluxes in the continuum limit, consistent with the assumptions made for the random fluxes and the known equilibrium distribution for the hydrodynamic variables, is obtained in section 5. Finally, in section 6, we indicate how the linear response analysis of paper II can be extended to the present case. The relevant fluctuation dissipation theorems for the response to an external electric potential are listed.

2. Fundamental macroscopic laws

In this section we recapitulate the thermodynamics of irreversible processes for a binary charged mixture in the presence of an electromagnetic field. The mixture will be assumed to be unpolarizable and unmagnetizable. The total charge of the system will be assumed to be zero.

For the case under consideration the following conservation laws of mass, charge, momentum and energy, hold⁶)

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \rho v, \quad (2.1)$$

$$\frac{\partial \rho_e}{\partial t} = -\nabla \cdot \rho_e v - \nabla \cdot i, \quad (2.2)$$

$$\frac{\partial \mathbf{g}}{\partial t} = -\nabla \cdot (\mathbf{j}\mathbf{v} + p - \mathbf{T}) - \nabla \cdot \mathbf{\Pi}, \quad (2.3)$$

$$\frac{\partial e_v}{\partial t} = -\nabla \cdot \left\{ (e_v - \frac{1}{2}\mathbf{E}^2 - \frac{1}{2}\mathbf{B}^2 + p)\mathbf{v} + c\mathbf{E} \wedge \mathbf{B} \right\} - \nabla \cdot (\mathbf{J} + \mathbf{\Pi} \cdot \mathbf{v}). \quad (2.4)$$

Here ρ is the mass density, ρ_e the charge density, \mathbf{g} the total momentum density of matter and field, \mathbf{v} the velocity, \mathbf{j} ($= \rho\mathbf{v}$) the momentum density of matter, p the hydrostatic pressure, \mathbf{T} Maxwell's electromagnetic stress tensor, e_v the total energy of matter and field, \mathbf{E} and \mathbf{B} are the electric and magnetic field in Gaussian units, and c is the velocity of light, while \mathbf{i} , $\mathbf{\Pi}$ and \mathbf{J} are the dissipative fluxes, the conduction current, the viscous pressure tensor and the heat current, respectively. The total momentum density \mathbf{g} and the momentum density of matter are related by

$$\mathbf{g} = \mathbf{j} + \frac{1}{c}\mathbf{E} \wedge \mathbf{B}, \quad (2.5)$$

and Maxwell's stress tensor is given by

$$\mathbf{T} = \mathbf{E}\mathbf{E} + \mathbf{B}\mathbf{B} - \frac{1}{2}(\mathbf{E}^2 + \mathbf{B}^2)\mathbf{U}, \quad (2.6)$$

where \mathbf{U} is the unit matrix.

For a complete description the above conservation laws have to be supplemented with the phenomenological laws for the dissipative fluxes and the Maxwell equations, which in the present case may be written as

$$\frac{\partial \mathbf{E}}{\partial t} = c\nabla \wedge \mathbf{B} - \rho_e\mathbf{v} - \mathbf{i}, \quad (2.7)$$

$$\frac{\partial \mathbf{B}}{\partial t} = -c\nabla \wedge \mathbf{E}, \quad (2.8)$$

$$\nabla \cdot \mathbf{E} = \rho_e, \quad (2.9)$$

$$\nabla \cdot \mathbf{B} = 0. \quad (2.10)$$

In thermodynamics of irreversible processes the phenomenological laws are established on the basis of the expression for the entropy production. Of course, eqs. (2.2) and (2.7)–(2.10) are not fully independent. If we take the divergence of eq. (2.7) and use eq. (2.2), we obtain $\partial \nabla \cdot \mathbf{E} / \partial t = \partial \rho_e / \partial t$; similarly eq. (2.8) implies that $\partial \nabla \cdot \mathbf{B} / \partial t = 0$. Hence, if eqs. (2.9) and (2.10) are obeyed

initially, eqs. (2.2), (2.7) and (2.8) ensure that they are obeyed at all later times. We will therefore in this paper consider eqs. (2.2), (2.7) and (2.8) as the basic equations describing the time dependence of \mathbf{E} , \mathbf{B} and ρ_e , while eqs. (2.9) and (2.10) will be viewed as equations prescribing initial conditions for these fields. The balance equation for the entropy density s_v may be derived from the above equations and the Gibbs-equation, written in the form

$$T ds_v = du_v - \frac{\mu_1 - \mu_2}{z_1 - z_2} d\rho_e - \frac{\mu_2 z_1 - \mu_1 z_2}{z_1 - z_2} d\rho, \quad (2.11)$$

where T is the temperature, and where μ_1 , μ_2 , z_1 and z_2 are the chemical potentials and the charges per unit mass of components 1 and 2, respectively*, while the internal energy density u_v is given by

$$u_v = e_v - \left(\frac{1}{2}\rho v^2 + \frac{1}{2}\mathbf{E}^2 + \frac{1}{2}\mathbf{B}^2\right). \quad (2.12)$$

One obtains

$$\frac{\partial s_v}{\partial t} = -\nabla \cdot \left(\frac{\mathbf{J} - \mu_1 \mathbf{J}_{d_1} - \mu_2 \mathbf{J}_{d_2}}{T} \right) + \sigma, \quad (2.13)$$

where \mathbf{J}_{d_1} and \mathbf{J}_{d_2} are the diffusion flows of component 1 and 2, and where the entropy production σ is given by**

$$\sigma = -\frac{1}{T^2} \mathbf{J} \cdot \nabla T - \frac{1}{T} \mathbf{i} \cdot \left\{ T \nabla \left[\frac{\mu_1 - \mu_2}{T(z_1 - z_2)} \right] - \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \wedge \mathbf{B} \right) \right\} - \frac{1}{T} \mathbf{\Pi} : \nabla \mathbf{v}. \quad (2.14)$$

In thermodynamics of irreversible processes, the entropy production is written as a bilinear expression in the fluxes and forces. In the present case, the fluxes are

$$\mathbf{i}, \quad \mathbf{\Pi} \quad \text{and} \quad \mathbf{J}; \quad (2.15)$$

on the basis of eq. (2.14), one therefore associates the thermodynamic forces with

$$-\frac{1}{T^2} \nabla T, \quad -\frac{1}{T} \nabla \mathbf{v},$$

and

$$-\frac{1}{T} \left\{ T \nabla \left[\frac{\mu_1 - \mu_2}{T(z_1 - z_2)} \right] - \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \wedge \mathbf{B} \right) \right\}. \quad (2.16)$$

* One immediately obtains eq. (2.11) from the more familiar form, viz. $T ds_v = du_v - \mu_1 d\rho_1 - \mu_2 d\rho_2$ (where ρ_1 and ρ_2 are the mass densities of components 1 and 2) by transforming to the variables $\rho = \rho_1 + \rho_2$ and $\rho_e = z_1 \rho_1 + z_2 \rho_2$.

** We have eliminated the diffusion flows \mathbf{J}_{d_1} and \mathbf{J}_{d_2} from the expression for σ given in ref. 6 with the aid of the equations $\mathbf{i} = z_1 \mathbf{J}_{d_1} + z_2 \mathbf{J}_{d_2}$ and $\mathbf{J}_{d_1} + \mathbf{J}_{d_2} = 0$.

From these identifications and using symmetry considerations (the Curie-principle), the usual linear laws are obtained. We will not give these expressions, as it is the purpose of this paper to derive the appropriate laws for a *fluctuating* system. This will be discussed in the next sections.

3. Stochastic differential equations

As discussed by Landau and Lifshitz¹), one may obtain fluctuating equations for the case under consideration by writing the dissipative fluxes Π , J and i as the sum of systematic and random parts,

$$\Pi = \Pi^s + \Pi^R, \quad J = J^s + J^R, \quad i = i^s + i^R, \quad (3.1)$$

where the quantities with a superscript s obey phenomenological laws in terms of the fluctuating variables and where the quantities with a superscript R are random variables with zero mean,

$$\overline{\Pi^R(r, t)} = 0, \quad \overline{J^R(r, t)} = 0, \quad \overline{i^R(r, t)} = 0. \quad (3.2)$$

Here we have employed the notation of paper II to denote an average over an ensemble of random forces of systems with the same initial conditions for the hydrodynamical and electromagnetic fields by a bar.

In order to form a closed set of stochastic equations, the phenomenological laws for the systematic parts in eq. (3.1) should be specified, as well as the correlations of the random parts.* We will not specify the phenomenological laws as yet, *as it is the aim of this paper to investigate which form of the phenomenological laws is compatible with the assumption that the random fields Π^R , J_q^R and i^R are Gaussian variables with correlations which are delta-correlated in space and time.*

The above assumption, together with symmetry considerations, fully determine the correlations of the 'random forces'. Since quantities with a different tensorial character cannot be correlated, one immediately finds that

$$\overline{J^R(r, t)\Pi^R(r', t')} = 0, \quad \overline{i^R(r, t)\Pi^R(r', t')} = 0. \quad (3.3)$$

In view of the isotropy of the system, the non-zero correlations must be of the form (the factor $2k$, where k is Boltzmann's constant, is introduced for

* Moreover, because of the presence of the term $\nabla \cdot (\Pi \cdot v)$ in the energy equation, one must also specify whether the stochastic equations are interpreted in the Itô or in the Stratonovich sense⁷). One may show that either of the two interpretations lead to identical results. As the analysis is completely analogous to the one in paper II, where this point is discussed in extenso, it will not be given here. Throughout the rest of this paper, we shall adopt the Stratonovich interpretation.

convenience)

$$\overline{J_j^R(\mathbf{r}, t) J_k^R(\mathbf{r}', t')} = 2kL_{qq} \delta_{jk} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \quad (3.4)$$

$$\overline{J_j^R(\mathbf{r}, t) i_k^R(\mathbf{r}', t')} = 2kL_{qi} \delta_{jk} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \quad (3.5)$$

$$\overline{i_j^R(\mathbf{r}, t) i_k^R(\mathbf{r}', t')} = 2kL_{ii} \delta_{jk} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \quad (3.6)$$

$$\overline{\Pi_{jk}^R(\mathbf{r}, t) \Pi_{im}^R(\mathbf{r}', t')} = 2kL_{ijklm} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (3.7)$$

$$= 2k \left[L \left(\delta_{jl} \delta_{km} + \delta_{jm} \delta_{kl} - \frac{2}{3} \delta_{jk} \delta_{lm} \right) + L_v \delta_{ij} \delta_{kl} \right] \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \quad (3.8)$$

In these equations, the coefficients L , L_v , L_{ii} , L_{qq} and L_{qi} are phenomenological constants; they do not depend on the fluctuating fields, but may depend on the equilibrium quantities of the system.

In the next section we obtain the Fokker–Planck equation corresponding to the above stochastic equations on the basis of which we derive the form of the phenomenological laws compatible with the assumptions made in this section and the known equilibrium statistical properties of the system.

4. The Fokker–Planck equation

It is well known that one may derive in general a Fokker–Planck equation from a set of stochastic differential equations of the Langevin-type if the noise is Gaussian and white. However, if one tries to derive a Fokker–Planck equation from the stochastic differential equations introduced in the previous section, one encounters difficulties in the interpretation of some terms in this equation as a consequence of the fact that we are dealing with *fields*. The way to avoid these difficulties, which was employed in papers I and II, is to start with a derivation of a Fokker–Planck equation corresponding to an analogous set of stochastic differential equations for a discrete set of variables, and to go over to the continuum limit only in the final stage of the calculations. We will now carry out this program explicitly along the lines set forth in papers I and II.

To arrive at a discrete set of variables, we discretize the system in coordinate space by dividing the system into cubic cells of size Δ^3 . The position of a cell is denoted by $\mathbf{r} = \mathbf{n}\Delta$, where \mathbf{n} is a vector of which the components are integer numbers. To every field-quantity considered before, there now corresponds a variable defined on the cubic lattice. For instance, $\rho_{\mathbf{n}}(t)$ and $\mathbf{g}_{\mathbf{n}}(t)$ are the mass-density and the total momentum density in the

cell with position $r = n\Delta$, which converge in the continuum limit to the fields $\rho(r, t)$ and $g(r, t)$. The other variables are defined in an analogous way.

The discretized variables are now postulated to obey equations of motion which are of the same form as the equations of the field variables, and which indeed reduce to these equations in the continuum limit. These equations are

$$\frac{\partial \rho_n}{\partial t} = -\nabla_n \cdot \rho_n v_n, \quad (4.1)$$

$$\frac{\partial \rho_{c,n}}{\partial t} = -\nabla_n \cdot \rho_{c,n} v_n - \nabla_n \cdot i_n, \quad (4.2)$$

$$\frac{\partial g_n}{\partial t} = -\nabla_n \cdot (j_n v_n + p_n - T_n) - \nabla_n \cdot \Pi_n, \quad (4.3)$$

$$\frac{\partial e_{v,n}}{\partial t} = -\nabla_n \cdot \left\{ (e_{v,n} - \frac{1}{2} E_n^2 - \frac{1}{2} B_n^2 + p_n) v_n + c E_n \wedge B_n \right\} - \nabla_n \cdot (J_n + \Pi_n \cdot v_n), \quad (4.4)$$

$$\frac{\partial E_n}{\partial t} = c \nabla_n \wedge B_n - \rho_{c,n} v_n - i_n, \quad (4.5)$$

$$\frac{\partial B_n}{\partial t} = -c \nabla_n \wedge E_n. \quad (4.6)$$

In these equations, action of the discrete gradient operator on an arbitrary quantity A_n is given by

$$\nabla_n A_n \equiv \sum_{i=1}^3 \frac{\hat{e}_i}{2\Delta} [A_{n+\hat{e}_i} - A_{n-\hat{e}_i}], \quad (4.7)$$

where the \hat{e}_i 's are unit vectors along the Cartesian axes. These equations have to be supplemented with the discrete analogues of eqs. (2.9) and (2.10), viz.

$$\nabla_n \cdot E_n = \rho_{c,n}, \quad (4.8)$$

$$\nabla_n \cdot B_n = 0, \quad (4.9)$$

and the equations for the fluxes Π_n , J_n and i_n . The discrete analogue of eq. (3.1) is

$$\Pi_n = \Pi_n^s + \Pi_n^R, \quad J_n = J_n^s + J_n^R, \quad i_n = i_n^s + i_n^R. \quad (4.10)$$

The random parts are again Gaussian random variables with zero mean. In analogy with eqs. (3.4)–(3.8), we may write the correlations of these variables as

$$\overline{J_{j,n}^R(t) J_{k,n}^R(t')} = 2kL_{qq} \delta_{jk} \Delta^{-3} \delta_{nn'} \delta(t-t'), \quad (4.11)$$

$$\overline{J_{j,n}^R(t) i_{k,n}^R(t')} = 2kL_{qi} \delta_{jk} \Delta^{-3} \delta_{nn'} \delta(t-t'), \quad (4.12)$$

$$\overline{i_{j,n}^R(t)i_k^R(t')} = 2kL_{ij}\delta_{jk}\Delta^{-3}\delta_{nn'}\delta(t-t'), \quad (4.13)$$

$$\overline{\Pi_{jk}^R(t)\Pi_{lm}^R(t')} = 2kL_{ijklm}\Delta^{-3}\delta_{nn'}\delta(t-t'). \quad (4.14)$$

It should be emphasized that the above discretized equations are postulated; they cannot be *derived* from the field equations. In fact, one can introduce different discretized equations which also reduce to the field equations in the continuum limit but which would lead to different results in the analysis given below. For reasons discussed in papers I and II, the most convincing scheme appears to discretize the conservation equations for the conserved hydrodynamic variables. It is for this reason that we will take below ρ , ρ_e , \mathbf{g} and e , as our basic hydrodynamic variables. The fields \mathbf{E} and \mathbf{B} are of course not conserved. However, eqs. (4.5) and (4.6) appear to be the natural discretized analogues of eqs. (2.7) and (2.8), and, as will turn out later, our conclusions concerning the phenomenological laws would not be affected if eqs. (2.7) and (2.8) would be discretized in a different way.

We will now derive the Fokker-Planck equation for the density distribution function P of the variables ρ , ρ_e , \mathbf{g} , e , \mathbf{E} and \mathbf{B} . To do so, it is convenient to write these variables as the components of a vector

$$\alpha_n \equiv (\rho_n, \rho_{e,n}, e_{v,n}, \mathbf{g}_n, \mathbf{E}_n, \mathbf{B}_n),$$

so that

$$\alpha_{1,n} \equiv \rho_n, \quad \alpha_{2,n} \equiv \rho_{e,n}, \quad \alpha_{3,n} \equiv e_{v,n}, \quad (4.15)$$

$$\alpha_{3+j,n} \equiv \mathbf{g}_{j,n}, \quad \alpha_{6+j,n} \equiv \mathbf{E}_{j,n}, \quad \alpha_{9+j,n} \equiv \mathbf{B}_{j,n}, \quad (\text{for } j = 1, 2, 3).$$

With the aid of this notation, we may write eqs. (4.1)–(4.6) together with (4.10) in the compact form*

$$\frac{\partial \alpha_{\beta,n}}{\partial t} = F_{\beta,n}^{\text{rev}} + F_{\beta,n}^{\text{irr}} + \sum_{n'} \sum_{\gamma\delta} M_{\beta\gamma\delta,nn'} f_{\gamma\delta,n'}. \quad (4.16)$$

Here $F_{\beta,n}^{\text{rev}}$ and $F_{\beta,n}^{\text{irr}}$ denote the reversible and irreversible parts of the rates of change of the quantities $\alpha_{\beta,n}$, respectively. Comparison with eqs. (4.1)–(4.6) and (4.10) shows that for eq. (4.16) to be equivalent with these equations, we need to define

$$\begin{aligned} F_{1,n}^{\text{rev}} &\equiv -\nabla_n \cdot \rho_n \mathbf{v}_n, & F_{2,n}^{\text{rev}} &\equiv -\nabla_n \cdot \rho_{e,n} \mathbf{v}_n, \\ F_{3,n}^{\text{rev}} &\equiv -\nabla_n \cdot [(e_{v,n} - \frac{1}{2}(\mathbf{E}_n^2 + \mathbf{B}_n^2) + p_n) \mathbf{v}_n + c \mathbf{E}_n \wedge \mathbf{B}_n], \\ F_{3+j,n}^{\text{rev}} &\equiv -[\nabla_n \cdot (\mathbf{j}_n \mathbf{v}_n + p_n - \mathbf{T}_n)]_j, \\ F_{6+j,n}^{\text{rev}} &\equiv c(\nabla_n \wedge \mathbf{B}_n)_j - \rho_{e,n} v_{n,j}, & F_{9+j,n}^{\text{rev}} &\equiv -c(\nabla_n \wedge \mathbf{E}_n)_j, \end{aligned} \quad (4.17)$$

* From here on, Greek indices run from 1 to 12, whereas Latin indices can vary from 1 to 3.

and

$$\begin{aligned}
 F_{i,n}^{\text{irr}} &\equiv 0, & F_{2,n}^{\text{irr}} &\equiv -\nabla_n \cdot i_n^s, \\
 F_{3,n}^{\text{irr}} &\equiv -\nabla_n \cdot [\Pi_n^s \cdot v_n + J_n^s], & F_{3+j,n}^{\text{irr}} &\equiv -(\nabla_n \cdot \Pi_n^s)_j, \\
 F_{6+j,n}^{\text{irr}} &\equiv -i_{j,n}^s, & F_{9+j,n}^{\text{irr}} &\equiv 0.
 \end{aligned} \tag{4.18}$$

The quantities $M_{\beta\gamma\delta,nn'}$ and the 'random forces' $f_{\gamma\delta,n'}$ give account of the stochastic source terms in the conservation equations and the Maxwell equations. There is some freedom in choosing these quantities such that these terms in eq. (4.16) coincide with the stochastic terms in eqs. (4.1)–(4.6). We will take

$$\begin{aligned}
 M_{24j,nn'} &\equiv -\nabla_{j,n} \delta_{nn'}, & M_{3jk,nn'} &\equiv -v_{k,n} \nabla_{j,n} \delta_{nn'}, \\
 M_{35j,nn'} &\equiv -\nabla_{j,n} \delta_{nn'}, & M_{(3+j)kl,nn'} &\equiv -\delta_{jl} \nabla_{k,n} \delta_{nn'}, \\
 M_{(6+j)6k,nn'} &\equiv -\delta_{jk} \delta_{nn'}
 \end{aligned} \tag{4.19}$$

and

$$f_{jk,n} \equiv \Pi_{jk,n}^R, \quad f_{4j,n} \equiv i_{j,n}^R, \quad f_{5j,n} \equiv J_{j,n}^R. \tag{4.20}$$

The other elements of $M_{\beta\gamma\delta,nn'}$ and $f_{\beta\gamma,n}$ are all zero. In view of eq. (4.20) the random forces f also have zero mean; if we write their variances as

$$\overline{f_{\beta\gamma,n}(t) f_{\delta\epsilon,n'}(t')} = 2\Lambda_{\beta\gamma\delta\epsilon,nn'} \delta(t-t'), \tag{4.21}$$

we may identify the nonzero elements of Λ from eqs. (4.11)–(4.14) as

$$\begin{aligned}
 \Lambda_{jklm,nn'} &\equiv kL_{jklm} \Delta^{-3} \delta_{nn'}, \\
 \Lambda_{5j5l,nn'} &\equiv kL_{qq} \Delta^{-3} \delta_{jl} \delta_{nn'}, \\
 \Lambda_{4j4l,nn'} &\equiv kL_{ii} \Delta^{-3} \delta_{jl} \delta_{nn'}, \\
 \Lambda_{4j5l,nn'} &= \Lambda_{5l4j,nn'} \equiv kL_{qi} \Delta^{-3} \delta_{jl} \delta_{nn'}.
 \end{aligned} \tag{4.22}$$

We now turn to the derivation of the Fokker–Planck equation for the density distribution $P(\{\alpha_n\}, t)$ in the "phase space" of discretized variables. Since we viewed, as explained in section 2, eqs. (2.9) and (2.10) as initial conditions to be satisfied by the solutions of eqs. (2.1)–(2.8), we will also tacitly assume that the distribution functions we consider are consistent with the initial conditions (4.8) and (4.9). As is well known⁷, the stochastic differential equations (4.16), interpreted in the Stratonovich sense, are

equivalent to the Fokker–Planck equation

$$\begin{aligned} \frac{\partial P(\{\alpha_n\}, t)}{\partial t} = & \sum_n \sum_\beta \frac{\partial}{\partial \alpha_{\beta,n}} \left[-F_{\beta,n}^{\text{rev}} - F_{\beta,n}^{\text{irr}} \right. \\ & \left. + \sum_{\substack{n''n'''' \\ n''''\gamma'\delta'}} M_{\beta\gamma\delta,nn''} \frac{\partial}{\partial \alpha_{\beta',n''}} M_{\beta'\gamma'\delta',n''n''''} \Lambda_{\beta\gamma\beta'\gamma',n''n''''} \right] P(\{\alpha_n\}, t). \end{aligned} \quad (4.23)$$

With the aid of the identity*

$$\sum_{\substack{n''n'''' \\ n''''\gamma'\delta'}} M_{\beta'\gamma'\delta',n''n''''} \Lambda_{\gamma\delta\gamma'\delta',n''n''''} \left(\frac{\partial}{\partial \alpha_{\beta',n''}} M_{\beta\gamma\delta,nn''} \right) = 0, \quad (4.24)$$

which follows in a straightforward way from the explicit expressions for M and Λ , the Fokker–Planck equation (4.26) can be rewritten in the form

$$\begin{aligned} \frac{\partial P(\{\alpha_n\}, t)}{\partial t} = & \sum_n \sum_\beta \frac{\partial}{\partial \alpha_{\beta,n}} \left[-F_{\beta,n}^{\text{rev}} - F_{\beta,n}^{\text{irr}} \right. \\ & \left. + \sum_{n'} \sum_{\beta'} \frac{\partial}{\partial \alpha_{\beta',n'}} D_{\beta\beta',nn'} \right] P(\{\alpha_n\}, t). \end{aligned} \quad (4.25)$$

Here we have introduced the matrix $D_{\beta\beta',nn'}$ defined by

$$D_{\beta\beta',nn'} \equiv \sum_{n''n''''} \sum_{\substack{\gamma\delta \\ \gamma'\delta'}} M_{\beta\gamma\delta,nn''} M_{\beta'\gamma'\delta',n''n''''} \Lambda_{\gamma\delta\gamma'\delta',n''n''''}. \quad (4.26)$$

For the elements of this matrix, one finds with the help of the explicit expressions (4.19) and (4.22)

$$\begin{aligned} D_{22,nn'} &= kL_{ii}\Delta^{-3}\nabla_n \cdot \nabla_{n'}\delta_{nn'}, \\ D_{23,nn'} &= D_{32,n'n} = kL_{qi}\Delta^{-3}\nabla_n \cdot \nabla_{n'}\delta_{nn'}, \\ D_{2(6+j),nn'} &= D_{(6+j)2,n'n} = kL_{ii}\Delta^{-3}\nabla_{j,n}\delta_{nn'}, \\ D_{33,nn'} &= kL_{qq}\Delta^{-3}\nabla_n \cdot \nabla_{n'}\delta_{nn'} + 2kL\Delta^{-3}\nabla_n v_n : \overline{\nabla_{n'} v_{n'}}\delta_{nn'} \\ &\quad + kL_\nu\Delta^{-3}\nabla_{n'}\nabla_n : v_n v_{n'}\delta_{nn'}, \\ D_{3(3+j),nn'} &= D_{(3+j)3,n'n} = k\Delta^{-3}(2L\nabla_n \cdot \overline{\nabla_{n'} v_{n'}}\delta_{nn'} + L_\nu\nabla_n \nabla_{n'} \cdot v_{n'}\delta_{nn'}), \\ D_{3(6+j),nn'} &= D_{(6+j)3,n'n} = kL_{qi}\Delta^{-3}\nabla_{j,n}\delta_{nn'}, \end{aligned} \quad (4.27)$$

* As eqs. (4.19) show, only $M_{3jk,nn'}$ depends on the variables; this is a consequence of the appearance of the $\nabla \cdot (\Pi^R \cdot v)$ term in the energy equation. Since this term is the same as in the pure hydrodynamic case (no electromagnetic fields), we refer to appendix A of paper II for an explicit verification of eq. (4.24). As is also discussed there, it is this equation which ensures the equivalence of the Itô and Stratonovich interpretations in this case.

$$D_{(3+j)(3+k),nn'} = D_{(3+k)(3+j),n'n} = k\Delta^{-3}(LU\nabla_n \cdot \nabla_n \delta_{nn'} + (L_v + \frac{1}{3}L)\nabla_n \nabla_n \delta_{nn'})_{jk},$$

$$D_{(6+j)(6+k),nn'} = D_{(6+k)(6+j),n'n} = kL_{ij}\delta_{jk}\Delta^{-3}\delta_{nn'}.$$

All the other elements of D are zero. In these expressions, the discrete gradient-operators act on all factors at their right.

The Fokker-Planck equation can be rewritten once more, using the fact that

$$\sum_{\beta} \frac{\partial F_{\beta,n}^{\text{rev}}}{\partial \alpha_{\beta,n}} = 0. \tag{4.28}$$

To verify this equation, one should notice that for $\beta = 1-6$, $F_{\beta,n}^{\text{rev}}$ does not depend on the variables α_n in cell n , due to the definition of the gradient operator (cf. eqs. (4.17) and (4.7)). In taking the derivative with respect to $E_{i,n}$ of $F_{(6+j),n}^{\text{rev}}$ the field \mathbf{B}_n is kept fixed. Hence the term arising from curl \mathbf{B} in $F_{(6+j),n}^{\text{rev}}$ does not contribute in taking this derivative (of course this term also vanishes as a consequence of the definition of the discrete gradient operator); for similar reasons the term arising from curl \mathbf{E} in taking the derivative of $F_{(6+j),n}^{\text{rev}}$ with respect to $B_{j,n}$ does not contribute. To evaluate the contribution from the term $-\rho_{e,n}v_{j,n}$ in $F_{(6+j),n}^{\text{rev}}$; we have to write $v_{j,n}$ in terms of our basic variables α_n , i.e.

$$-\rho_{e,n}v_{j,n} = -\frac{\rho_{e,n}}{\rho_n} [g_{j,n} - c^{-1}(\mathbf{E}_n \wedge \mathbf{B}_n)_j]$$

$$= -\frac{\alpha_{2,n}}{\alpha_{1,n}} \left[\alpha_{j,n} - c^{-1} \sum_{kl} \epsilon_{jkl} \alpha_{(6+k),n} \alpha_{(9+l),n} \right], \tag{4.29}$$

Here ϵ_{jkl} is the Levi-Civita symbol. One easily sees that the derivative of the right hand side of eq. (4.29) with respect to $\alpha_{(6+j),n}$ vanishes. This finally establishes the result (4.28). Similarly, one may show from the explicit expressions for D , that

$$\sum_{n'} \sum_{\beta'} \frac{\partial D_{\beta\beta',nn'}}{\partial \alpha_{\beta',n'}} = 0. \tag{4.30}$$

Using eqs. (4.28) and (4.29), we may rewrite the Fokker-Planck equation (4.25) in the form

$$\frac{\partial P(\{\alpha_n\}, t)}{\partial t} = \sum_n \sum_{\beta} \left[-F_{\beta,n}^{\text{rev}} \frac{\partial}{\partial \alpha_{\beta,n}} + \frac{\partial}{\partial \alpha_{\beta,n}} \right.$$

$$\left. \times \left(-F_{\beta,n}^{\text{irr}} + \sum_{n'} \sum_{\beta'} D_{\beta\beta',nn'} \frac{\partial}{\partial \alpha_{\beta',n'}} \right) \right] P(\{\alpha_n\}, t). \tag{4.31}$$

In the next section, expressions for the systematic parts of the dissipative fluxes will be obtained from this Fokker-Planck equation.

5. The form of the dissipative currents

We will now obtain the form of the dissipative currents, compatible with the assumption made in section 3 for the random fluxes. We will require that the solutions of the Fokker–Planck equation satisfy detailed balance. This is ensured for a Fokker–Planck equation of the form (4.31) if the following two conditions are fulfilled⁶⁾

$$\sum_n \sum_\beta F_{\beta,n}^{\text{rev}} \frac{\partial P^{\text{eq}}}{\partial \alpha_{\beta,n}} = 0, \quad (5.1)$$

$$F_{\beta,n}^{\text{irr}} = \sum_{n'} \sum_{\beta'} D_{\beta\beta',nn'} \frac{\partial \ln P^{\text{eq}}}{\partial \alpha_{\beta',n'}}. \quad (5.2)$$

Here P^{eq} is the equilibrium distribution for the variables α_n . The above conditions will be analysed in the continuum-limit, in which the discretized variables α_n approach to the fields $\alpha(\mathbf{r})$. In this limit, the terms $F_{\beta,n}^{\text{rev}}$ converge to the reversible parts of the rate of change of the fields $\alpha(\mathbf{r})$, e.g. $\lim_{\Delta \rightarrow 0} F_{2,n}^{\text{rev}} = -\nabla \cdot \rho_e(\mathbf{r})\mathbf{v}(\mathbf{r})$. We will therefore write

$$\lim_{\Delta \rightarrow 0} F_{\beta,n}^{\text{rev}} = F_\beta^{\text{rev}}(\mathbf{r}), \quad (5.3)$$

where $F_\beta^{\text{rev}}(\mathbf{r})$ is the rate of change of $\alpha(\mathbf{r})$ in the ideal case (no dissipative effects). With this notation, eq. (5.1) becomes in the continuum limit

$$\sum_\beta \int d\mathbf{r} F_\beta^{\text{rev}}(\mathbf{r}) \frac{\delta P^{\text{eq}}(\{\alpha(\mathbf{r})\})}{\delta \alpha_\beta(\mathbf{r})} = 0. \quad (5.4)$$

Here $\delta/\delta\alpha_\beta(\mathbf{r})$ denotes a functional derivative. According to eq. (5.4) P^{eq} must depend on the variables α via quantities that are conserved in the case of ideal flow.* In particular, the Einstein equilibrium distribution for a materially and energetically isolated system,

$$P^{\text{eq}}(\{\alpha(\mathbf{r})\}) \sim e^{S(\{\alpha(\mathbf{r})\})/k}, \quad (5.5)$$

where S is the total entropy of the system, defined by

$$S(\{\alpha(\mathbf{r})\}) \equiv \int d\mathbf{r} s_v(\mathbf{r}), \quad (5.6)$$

obeys eq. (5.4) since the total entropy is conserved in the case of ideal fluid

* In the pure hydrodynamic case^{3,4)}, where we had Poisson-bracket expressions for F_β^{rev} , the analogous statement was that P^{eq} should be a stationary solution of the Liouville-equation. In this connection, it should be noted that the first condition is only valid in the form (5.1) if eq. (4.28) holds. The latter equation expresses the incompressibility of the ideal flow in phase space. (cf. paper I, section 4).

flow. We will base our subsequent discussion on the equilibrium distribution (5.5).

The second condition, (5.2), determines the form of the dissipative fluxes. With the definitions

$$F_{\beta}^{\text{irr}}(\mathbf{r}) \equiv \lim_{\Delta \rightarrow 0} F_{\beta, n}^{\text{irr}}, \quad D_{\beta\beta'}(\mathbf{r}, \mathbf{r}') \equiv \lim_{\Delta \rightarrow 0} D_{\beta\beta', nn'} \quad (5.7)$$

we may write eq. (5.2) in the continuum limit as

$$F_{\beta}^{\text{irr}}(\mathbf{r}) = \sum_{\beta'} \int d\mathbf{r}' D_{\beta\beta'}(\mathbf{r}, \mathbf{r}') \frac{\delta \ln P^{\text{eq}}(\{\alpha(\mathbf{r})\})}{\delta \alpha_{\beta}(\mathbf{r}')} \quad (5.8)$$

From the definition (5.7) and (4.18), one obtains for $F_{\beta}^{\text{irr}}(\mathbf{r})$

$$\begin{aligned} F_1^{\text{irr}}(\mathbf{r}) &= 0, & F_2^{\text{irr}}(\mathbf{r}) &= -\nabla \cdot \mathbf{i}^s(\mathbf{r}), \\ F_3^{\text{irr}}(\mathbf{r}) &= -\nabla \cdot [\mathbf{II}^s(\mathbf{r}) \cdot \mathbf{v}(\mathbf{r}) + \mathbf{J}^s(\mathbf{r})], & \\ F_{6+j}^{\text{irr}}(\mathbf{r}) &= -i_j^s(\mathbf{r}), & F_{9+j}^{\text{irr}}(\mathbf{r}) &= 0, \end{aligned} \quad (5.9)$$

while, according to eqs. (5.7) and (4.27), the non-zero elements of $D_{\beta\beta'}(\mathbf{r}, \mathbf{r}')$ are explicitly given by (as before, the gradient operators act on everything to the right of them)

$$\begin{aligned} D_{22}(\mathbf{r}, \mathbf{r}') &= kL_{ii} \nabla \cdot \nabla' \delta(\mathbf{r} - \mathbf{r}'), \\ D_{23}(\mathbf{r}, \mathbf{r}') &= D_{32}(\mathbf{r}', \mathbf{r}) = kL_{qi} \nabla \cdot \nabla' \delta(\mathbf{r} - \mathbf{r}'), \\ D_{2(6+j)}(\mathbf{r}, \mathbf{r}') &= D_{(6+j)2}(\mathbf{r}', \mathbf{r}) = kL_{ii} \nabla_j \delta(\mathbf{r} - \mathbf{r}'), \\ D_{33}(\mathbf{r}, \mathbf{r}') &= kL_{qq} \nabla \cdot \nabla' \delta(\mathbf{r} - \mathbf{r}') + 2kL \nabla \mathbf{v}(\mathbf{r}) : \overline{\nabla' \mathbf{v}(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}')} \\ &\quad + kL_v \nabla' \nabla : \mathbf{v}(\mathbf{r}) \mathbf{v}(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'), \\ D_{3(3+j)}(\mathbf{r}, \mathbf{r}') &= D_{(3+j)3}(\mathbf{r}', \mathbf{r}) \\ &= k(2L \nabla' \cdot \overline{\nabla \mathbf{v}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')} + L_v \nabla' \nabla \cdot \mathbf{v}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')), \quad (5.10) \\ D_{3(6+j)}(\mathbf{r}, \mathbf{r}') &= D_{(6+j)3}(\mathbf{r}', \mathbf{r}) = kL_{qi} \nabla_j \delta(\mathbf{r} - \mathbf{r}'), \\ D_{(3+j)(3+k)}(\mathbf{r}, \mathbf{r}') &= D_{(3+k)(3+j)}(\mathbf{r}', \mathbf{r}) \\ &= k \left(L \mathbf{U} \nabla \cdot \nabla' \delta(\mathbf{r} - \mathbf{r}') + \left(L_v + \frac{1}{3} L \right) \nabla \nabla' \delta(\mathbf{r} - \mathbf{r}') \right)_{jk}, \\ D_{(6+j)(6+k)}(\mathbf{r}, \mathbf{r}') &= D_{(6+k)(6+j)}(\mathbf{r}', \mathbf{r}) = kL_{ii} \delta_{jk} \delta(\mathbf{r} - \mathbf{r}'). \end{aligned}$$

To determine the derivatives of the logarithm of the equilibrium distribution, we write the entropy density as a function of our basic variables $\alpha(\mathbf{r})$ with the aid of eq. (2.12):

$$\begin{aligned}
 \overline{s_v(\mathbf{r})} &= s_v(u_v, \rho, \rho_e) \\
 &= s_v\left(e_v - \frac{1}{2} \frac{(\mathbf{g} - c^{-1} \mathbf{E} \wedge \mathbf{B})^2}{\rho} - \frac{1}{2} \mathbf{E}^2 - \frac{1}{2} \mathbf{B}^2, \rho, \rho_e\right). \quad (5.11)
 \end{aligned}$$

From eq. (5.11) and the Gibbs-equation (2.11), we now obtain for the derivatives of the equilibrium distribution (5.5), which are used in the evaluation of eq. (5.8),

$$\begin{aligned}
 \frac{\delta \ln P^{\text{eq}}}{\delta \alpha_2(\mathbf{r})} &= k^{-1} \frac{\delta S}{\delta \rho_e(\mathbf{r})} = -k^{-1} \frac{\mu_1(\mathbf{r}) - \mu_2(\mathbf{r})}{(z_1 - z_2) T(\mathbf{r})}, \\
 \frac{\delta \ln P^{\text{eq}}}{\delta \alpha_3(\mathbf{r})} &= k^{-1} \frac{\delta S}{\delta e_v(\mathbf{r})} = k^{-1} \frac{1}{T(\mathbf{r})}, \\
 \frac{\delta \ln P^{\text{eq}}}{\delta \alpha_{3+j}(\mathbf{r})} &= k^{-1} \frac{\delta S}{\delta g_j(\mathbf{r})} = -k^{-1} \frac{v_j(\mathbf{r})}{T(\mathbf{r})}, \\
 \frac{\delta \ln P^{\text{eq}}}{\delta \alpha_{6+j}(\mathbf{r})} &= k^{-1} \frac{\delta S}{\delta E_j(\mathbf{r})} = -k^{-1} \left(\frac{\mathbf{E}(\mathbf{r}) + c^{-1} \mathbf{v}(\mathbf{r}) \wedge \mathbf{B}(\mathbf{r})}{T(\mathbf{r})} \right)_j. \quad (5.12)
 \end{aligned}$$

Upon substitution of eqs. (5.9), (5.10) and (5.12) into eq. (5.8), one obtains the following equations for the systematic parts of the dissipative fluxes (In checking these formulae, it is important to realize that the gradient operators in the elements of D act on everything at their right):

$$\begin{aligned}
 F_2^{\text{irr}}(\mathbf{r}) &= -\nabla \cdot \mathbf{i}^s(\mathbf{r}) \\
 &= L_{ii} \left[\nabla^2 \left(\frac{\mu_1(\mathbf{r}) - \mu_2(\mathbf{r})}{(z_1 - z_2) T(\mathbf{r})} \right) - \nabla \cdot \left(\frac{\mathbf{E}(\mathbf{r}) + c^{-1} \mathbf{v}(\mathbf{r}) \wedge \mathbf{B}(\mathbf{r})}{T(\mathbf{r})} \right) \right] \\
 &\quad - L_{qi} \nabla^2 \frac{1}{T(\mathbf{r})}. \quad (5.13)
 \end{aligned}$$

$$\begin{aligned}
 F_3^{\text{irr}}(\mathbf{r}) &= -\nabla \cdot (\mathbf{H}^s(\mathbf{r}) \cdot \mathbf{v}(\mathbf{r}) + \mathbf{J}^s(\mathbf{r})) \\
 &= L_{qi} \nabla^2 \left[\frac{\mu_1(\mathbf{r}) - \mu_2(\mathbf{r})}{(z_1 - z_2) T(\mathbf{r})} \right] - L_{qa} \nabla^2 \frac{1}{T(\mathbf{r})} \\
 &\quad - 2L \nabla \cdot \left[\overline{\mathbf{v}(\mathbf{r}) \nabla \left(\frac{1}{T(\mathbf{r})} \right)} \cdot \mathbf{v}(\mathbf{r}) \right] - L_v \nabla \cdot \left[\mathbf{v}(\mathbf{r}) \mathbf{v} \cdot \nabla \left(\frac{1}{T(\mathbf{r})} \right) \right] \\
 &\quad + 2L \nabla \cdot \left[\overline{\nabla \left(\frac{\mathbf{v}(\mathbf{r})}{T(\mathbf{r})} \right)} \cdot \mathbf{v}(\mathbf{r}) \right] + L_v \nabla \cdot \left[\mathbf{v}(\mathbf{r}) \nabla \cdot \left(\frac{\mathbf{v}(\mathbf{r})}{T(\mathbf{r})} \right) \right] \\
 &\quad - L_{qa} \nabla \cdot \left[\frac{\mathbf{E}(\mathbf{r}) + c^{-1} \mathbf{v}(\mathbf{r}) \wedge \mathbf{B}(\mathbf{r})}{T(\mathbf{r})} \right]
 \end{aligned}$$

$$\begin{aligned}
 &= 2L\nabla \cdot \left[\frac{\overline{\nabla \mathbf{v}(\mathbf{r})} \cdot \mathbf{v}(\mathbf{r})}{T(\mathbf{r})} \right] + L_v \nabla \cdot \left[\frac{\nabla \cdot \mathbf{v}(\mathbf{r}) \mathbf{v}(\mathbf{r})}{T(\mathbf{r})} \right] \\
 &+ L_{qi} \nabla \cdot \left[\nabla \left\{ \frac{\mu_1(\mathbf{r}) - \mu_2(\mathbf{r})}{(z_1 - z_2)T(\mathbf{r})} \right\} - \left\{ \frac{\mathbf{E}(\mathbf{r}) + c^{-1} \mathbf{v}(\mathbf{r}) \wedge \mathbf{B}(\mathbf{r})}{T(\mathbf{r})} \right\} \right] \\
 &- L_{qq} \nabla \cdot \nabla \frac{1}{T(\mathbf{r})}, \tag{5.14}
 \end{aligned}$$

$$\begin{aligned}
 F_{3+j}^{\text{irr}}(\mathbf{r}) &= -(\nabla \cdot \mathbf{H}^s)_j \\
 &= -2L \left[\nabla \cdot \mathbf{v}(\mathbf{r}) \nabla \left(\frac{1}{T(\mathbf{r})} \right) \right]_j - L_v \nabla_j \left[\mathbf{v}(\mathbf{r}) \cdot \nabla \left(\frac{1}{T(\mathbf{r})} \right) \right] \\
 &+ 2L \left[\nabla \cdot \nabla \left(\frac{\mathbf{v}(\mathbf{r})}{T(\mathbf{r})} \right) \right]_j + L_v \nabla_j \left[\nabla \cdot \frac{\mathbf{v}(\mathbf{r})}{T(\mathbf{r})} \right] \\
 &= 2L \left[\nabla \cdot \frac{\overline{\nabla \mathbf{v}(\mathbf{r})}}{T(\mathbf{r})} \right]_j + L_v \nabla_j \left[\frac{\nabla \cdot \mathbf{v}(\mathbf{r})}{T(\mathbf{r})} \right], \tag{5.15}
 \end{aligned}$$

$$\begin{aligned}
 F_{6+j}^{\text{irr}}(\mathbf{r}) &= -i_j^s \\
 &= -L_{qi} \nabla_j \frac{1}{T(\mathbf{r})} + L_{ii} \left[\nabla \left(\frac{\mu_1(\mathbf{r}) - \mu_2(\mathbf{r})}{(z_1 - z_2)T(\mathbf{r})} \right) - \frac{\mathbf{E}(\mathbf{r}) + c^{-1} \mathbf{v}(\mathbf{r}) \wedge \mathbf{B}(\mathbf{r})}{T(\mathbf{r})} \right]_j. \tag{5.16}
 \end{aligned}$$

These equations lead to the following identification for \mathbf{H}^s , \mathbf{J}^s and i^s :

$$\mathbf{H}^s(\mathbf{r}) = -2L \frac{\overline{\nabla \mathbf{v}(\mathbf{r})}}{T(\mathbf{r})} - L_v \mathbf{U} \frac{\nabla \cdot \mathbf{v}(\mathbf{r})}{T(\mathbf{r})} \tag{5.17}$$

$$\mathbf{J}^s(\mathbf{r}) = L_{qq} \nabla \frac{1}{T(\mathbf{r})} - L_{qi} \left[\nabla \left(\frac{\mu_1(\mathbf{r}) - \mu_2(\mathbf{r})}{(z_1 - z_2)T(\mathbf{r})} \right) - \frac{\mathbf{E}(\mathbf{r}) + c^{-1} \mathbf{v}(\mathbf{r}) \wedge \mathbf{B}(\mathbf{r})}{T(\mathbf{r})} \right], \tag{5.18}$$

$$i^s(\mathbf{r}) = L_{qi} \nabla \frac{1}{T(\mathbf{r})} - L_{ii} \left[\nabla \left(\frac{\mu_1(\mathbf{r}) - \mu_2(\mathbf{r})}{(z_1 - z_2)T(\mathbf{r})} \right) - \frac{\mathbf{E}(\mathbf{r}) + c^{-1} \mathbf{v}(\mathbf{r}) \wedge \mathbf{B}(\mathbf{r})}{T(\mathbf{r})} \right]. \tag{5.19}$$

The expressions for the dissipative fluxes are of the same form as the laws that are derived in thermodynamics of irreversible processes on the basis of eq. (2.14)⁶). However, the above laws are less general than those found in thermodynamics of irreversible processes: in the present fluctuation theory the Onsager coefficients L , L_v , L_{qq} , L_{ii} and L_{qi} (i.e. the quantities which couple the fluxes and conjugate thermodynamic forces in the entropy production (2.14)) are constants which do not depend on the fluctuating fields, whereas in thermodynamics of irreversible processes these Onsager coefficients are allowed to depend on the state variables.

It should also be noted that in thermodynamics of irreversible processes, additional requirements (invariance of the terms in the entropy balance equation under a Galilei-transformation, the requirement that the entropy

production σ should vanish in equilibrium) are imposed in order to separate the convection and production terms in the entropy balance equation (2.13) in a unique way⁶). In the above fluctuation theory, these requirements are not explicitly imposed in order to obtain the laws (5.17)–(5.19).

The above analysis was confined to a system which is materially and energetically isolated, so that the equilibrium distribution (5.5) applies. However, the same expressions for Π^s , J^s and i^s are found upon substitution into eq. (5.8) of the appropriate equilibrium distributions for systems which can exchange energy and/or mass with a bath.

We finally remark that the discretization rules which were introduced in papers I and II have led without modification to unambiguous results also in the present case, in which it is impossible to characterize the state of the system by conserved variables alone. The reason is that the analysis of the terms in eq. (4.28) containing quantities which are not conserved, did not depend on the discretization rules explicitly (cf. the discussion after eq. (4.28)).

6. Linear response

In paper II, the fluctuation–dissipation theorems for the response of an uncharged one-component fluid to an external potential were derived. For the response of a charged binary fluid to an external electric field similar response formulae hold, the derivation of which completely parallels the analysis of paper II. Therefore, we only briefly indicate here the changes to be made in the latter analysis in order to arrive at Green–Kubo relations for the linear response to an external electric field.

In the presence of an external electric potential $\phi(\mathbf{r}, t)$, the field equations (2.3) and (2.4) become (the other equations, eqs. (2.1), (2.2), (2.5)–(2.10) and (3.1) remain unchanged)

$$\frac{\partial \mathbf{g}}{\partial t} = -\nabla \cdot (\mathbf{j}\mathbf{v} + p - \mathbf{T}) - \nabla \cdot \Pi - \rho_e \nabla \phi, \quad (6.1)$$

$$\frac{\partial e_v}{\partial t} = -\nabla \cdot \left\{ (e_v - \frac{1}{2}\mathbf{E}^2 - \frac{1}{2}\mathbf{B}^2 + p)\mathbf{v} + c\mathbf{E} \wedge \mathbf{B} \right\} - \nabla \cdot (\Pi \cdot \mathbf{v} + \mathbf{J}) - \rho_e \mathbf{v} \cdot \nabla \phi. \quad (6.2)$$

It should be noted that the total energy density is from now on given by $e_v + \rho_e \phi$; hence e_v is the total energy density minus the potential energy of the charge density. On the other hand, \mathbf{E} now denotes the total electric field, i.e. the sum of the external field and the field generated by the charges.

The presence of the external potential only adds two extra reversible terms

to eqs. (2.3) and (2.4). Accordingly, only the terms F^{rev} are changed in the Fokker–Planck equation. Therefore, we neglect for the moment the dissipative terms in the Fokker–Planck equation, and investigate the reversible terms in it in the continuum limit. In this case the distribution function $P(\{\alpha(r)\}, t)$ obeys the evolution equation

$$\frac{\partial P}{\partial t} = - \sum_{\beta} \int d\mathbf{r} \left(F_{\beta}^{\text{rev}}(\mathbf{r}) \frac{\delta}{\delta \alpha_{\beta}(\mathbf{r})} + F_{\beta}^{1,\text{rev}}(\mathbf{r}, t) \frac{\delta}{\delta \alpha_{\beta}(\mathbf{r})} \right) P, \quad (6.3)$$

where $F_{\beta}^{\text{rev}}(\mathbf{r})$, defined in eq. (5.3), contains the terms also present in the absence of the potential, while $F_{\beta}^{1,\text{rev}}(\mathbf{r}, t)$ is defined by

$$F_3^{1,\text{rev}}(\mathbf{r}, t) = - \rho_c(\mathbf{r}) \mathbf{v}(\mathbf{r}) \cdot \nabla \phi(\mathbf{r}, t), \quad (6.4)$$

$$F_{3+i}^{1,\text{rev}}(\mathbf{r}, t) = - \rho_c(\mathbf{r}) \nabla_j \phi(\mathbf{r}, t). \quad (6.5)$$

The other components of $F_{\beta}^{1,\text{rev}}$ are zero. One may now verify that

$$\begin{aligned} & - \sum_{\beta} \int d\mathbf{r} \left(F_{\beta}^{\text{rev}}(\mathbf{r}) \frac{\delta}{\delta \alpha_{\beta}(\mathbf{r})} + F_{\beta}^{1,\text{rev}}(\mathbf{r}, t) \frac{\delta}{\delta \alpha_{\beta}(\mathbf{r})} \right) \\ & \times \exp \left(- \frac{1}{kT_0} \int d\mathbf{r}' \left[e_v(\mathbf{r}') + \rho_c(\mathbf{r}') \phi(\mathbf{r}', t) - T_0 s_v(\mathbf{r}') \right] \right) = 0. \end{aligned} \quad (6.6)$$

By expanding this result up to linear order in ϕ , one obtains

$$\begin{aligned} & - \sum_{\beta} \int d\mathbf{r} F_{\beta}^{1,\text{rev}}(\mathbf{r}, t) \frac{\delta P^{\text{eq}}(\{\alpha(r)\})}{\delta \alpha_{\beta}(\mathbf{r})} \\ & = - \frac{1}{kT_0} \sum_{\beta} \int d\mathbf{r} F_{\beta}^{\text{rev}}(\mathbf{r}) \frac{\delta}{\delta \alpha_{\beta}(\mathbf{r})} \left(\int d\mathbf{r}' \rho_c(\mathbf{r}') \mathbf{v}(\mathbf{r}') \phi(\mathbf{r}', t) P^{\text{eq}}(\{\alpha(r)\}) \right) \\ & = \frac{1}{kT_0} \int d\mathbf{r} \phi(\mathbf{r}, t) \nabla \cdot \rho_c(\mathbf{r}) \mathbf{v}(\mathbf{r}) P^{\text{eq}}(\{\alpha(r)\}), \end{aligned} \quad (6.7)$$

where P^{eq} is the equilibrium distribution for a system in contact with a heat bath in the absence of an external potential

$$P^{\text{eq}} \sim \exp \left\{ - \frac{1}{kT_0} \int d\mathbf{r} (e_v(\mathbf{r}) - T_0 s_v(\mathbf{r})) \right\}. \quad (6.8)$$

Eq. (6.7) is the immediate analogue of eq. (6.12) of paper II. Comparison of these equations shows that the formal linear response analysis of the Fokker–Planck equation given in section 6 of paper II also applies to the response of the system to an electric potential provided that we change in all the formulae after eq. (II.6.12) the momentum density \mathbf{j} into the charge density current $\mathbf{j}_e \equiv \rho_c \mathbf{v}$ and the potential V into ϕ . If $\phi(\mathbf{r}, t) \rightarrow 0$ for $t \rightarrow -\infty$ and if the system initially was in equilibrium, the analysis of paper II consequently yields for

the linear response of the variables α (cf. eq. (II.6.24))

$$\begin{aligned}\Delta\langle\alpha_{\beta}(\mathbf{r}, t)\rangle &= \frac{1}{kT_0} \int_{-\infty}^t dt' \int d\mathbf{r}' \langle\alpha_{\beta}(\mathbf{r}, t)\nabla' \cdot \mathbf{j}_e(\mathbf{r}', t')\rangle_{\text{eq}} \phi(\mathbf{r}', t') \\ &= \frac{1}{kT_0} \int_{-\infty}^t dt' \int d\mathbf{r}' \langle\alpha_{\beta}(\mathbf{r}, t)\mathbf{j}_e(\mathbf{r}', t')\rangle_{\text{eq}} \cdot \boldsymbol{\epsilon}(\mathbf{r}', t').\end{aligned}\quad (6.9)$$

Here $\langle \cdot \rangle_{\text{eq}}$ denotes an equilibrium average in the system without an external potential and $\Delta\langle\alpha_{\beta}\rangle \equiv \langle\alpha_{\beta}\rangle - \langle\alpha_{\beta}\rangle_{\text{eq}}$, and $\boldsymbol{\epsilon}(\mathbf{r}, t) = -\nabla\phi(\mathbf{r}, t)$ is the applied electric field due to the external potential. Eq. (6.9) represents the fluctuation-dissipation theorem for the response to an external field.

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