Higher-order Einstein relations for nonlinear charge transport

S A Hope†, G Féat‡ and P T Landsberg

Department of Mathematics, University of Southampton, Southampton, UK

Abstract. Nonlinear terms in relations for current densities are treated macroscopically, semi-microscopically and microscopically. In the macroscopic treatment, terms in ϕ^2, E^2, $(\nabla n)^2$, $\nabla^2 n$ and $\boldsymbol{E} \cdot \nabla n$ are included, where ϕ is the electrostatic potential, n is the carrier concentration and E is the electric field. The power series expansion of the current density is valid for equilibrium and yields conductivity–diffusion type Einstein relations. In the semi-microscopic approach a perturbation theory for the density matrix is used, and Einstein relations are then derived by equating the average of the current density operator to zero. In the microscopic approach a Kubo formalism is developed, based on a local non-equilibrium distribution function due to Mori. This leads to Einstein relations via correlation functions and Liouville's equation. A set of such relations which emerge consistently from such a treatment is given.

1. Introduction

There are a number of distinct ways of approaching nonlinear transport phenomena. One can do so experimentally and phenomenologically, and this has been done extensively in the area of semiconductors. The charged particles are here often in strong electric fields and this gives rise to important phenomena: hot electrons, transfer effects, impact ionisation, etc. For reviews see for instance Barker *et al* (1980), Robbins (1980a, b), Urgell (1978). The dominant theoretical tool is the Boltzmann transport equation using appropriate scattering processes. However, in moderate fields linear transport theory has been extensively confirmed in both solids and gases (Miller 1974).

Leaving these physical effects on one side, we wish in this paper to explore the departure from the linear regime by using *general* macroscopic and microscopic methods without direct appeal to scattering mechanisms. Such an approach cannot be expected to yield explicit expressions for transport coefficients but, at best, relations between them. This is shown here by a macroscopic method (§ 2), a semi-microscopic method (§ 3) and a microscopic method (§ 4). The calculations to analyse nonlinear regimes are usually long and tedious, as has been known since Boltzmann's time and the two long papers on the 'distribution of velocities in a slightly non-uniform gas' by Burnett (1934, 1935). In order to avoid too much algebra and too many special cases, therefore, we focus attention on a system at uniform temperature and ask how the Einstein relation has to be modified. Even so, the argument tends to become complicated and nothing like full mathematical details can be given in §§ 3 and 4 of this paper.

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† Now at BP Research Centre, Sunbury-on-Thames.
‡ Now at the Department of Ship Science, University of Southampton, Southampton, UK.

But at least § 2 gives the flavour of the argument and is simple. We focus on the Einstein relation because of its use in experimentally active solid state areas and because of a long-standing interest in it (Landsberg 1952, Landsberg and Hope 1977, Féat 1981).

The electric, particle and heat currents

$$J = -\sigma \text{ grad } \phi, \qquad J_p = -D \text{ grad } n, \qquad J_h = -\lambda \text{ grad } T,$$

receive additional terms on the right-hand side in a nonlinear theory, the number depending on the approximation one wishes to make. Here we are concerned only with J and J_p. Powers of gradients, higher-order gradients and cross-terms between terms derived from ϕ and n are required, as reviewed by Ernst *et al* (1969) and recently considered by Mason and collaborators (Whealton and Mason 1974, Weinert and Mason 1980). We believe our approach to be different, since we allow for Fermi degeneracy, whereas Mason deals with classical gases (see also McDaniel and Mason 1973). Nonetheless, a comparison of the two approaches would be desirable. Also we base §§ 3 and 4 on fluctuation–dissipation theorems, which are not invoked by Weinert and Mason. In fact, it is simple to see how generalised Einstein relations can be obtained once one realises that the perturbations in the fluctuation–dissipation theorems can be taken to infinite order and that the lowest order is sufficient for the normal Einstein relation (Luttinger 1964, Korneev *et al* 1974). This consideration guides us in §§ 3 and 4.

To give the reader some idea of the interest in the Einstein relations in Fermi systems, we conclude with a few references to relevant papers in the semiconductor area: Butcher *et al* (1974), Choudhury *et al* (1976), Jain (1977), Ghatak *et al* (1980).

2. Macroscopic treatment

The average current density along the coordinate x_μ can normally be represented as a sum of transport terms. For a system at uniform temperature these terms are of three kinds: those depending on the electric field $E(r)$, those depending on the concentration gradient $\nabla n(r)$ of the charged particles considered, and mixed terms. Accordingly it will be supposed that

$$\langle J_\mu(r) \rangle = A_\mu + B_\mu + C_\mu \tag{2.1}$$

where

$$A_\mu \equiv \sigma_{\mu\nu}^{(1)} E_\nu + \sigma_{\mu\nu\lambda}^{(2)} \nabla_\nu E_\lambda + \sigma_{\mu\nu\delta}^{(3)} E_\nu E_\delta + \sigma_{\mu\nu\varepsilon\delta}^{(4)} E_\nu \nabla_\varepsilon E_\delta + \sigma_{\mu\nu\lambda\varepsilon\delta}^{(5)} \nabla_\nu E_\lambda \nabla_\varepsilon E_\delta + \ldots,$$

$$B_\mu \equiv -q D_{\mu\nu}^{(1)} \nabla_\nu n - q D_{\mu\nu\lambda}^{(2)} \nabla_\nu \nabla_\lambda n + q^2 D_{\mu\nu\gamma}^{(3)} \nabla_\nu n \nabla_\gamma n$$

$$\qquad + q^2 D_{\mu\nu\varepsilon\delta}^{(4)} \nabla_\nu n \nabla_\varepsilon \nabla_\delta n + q^2 D_{\mu\nu\lambda\varepsilon\delta}^{(5)} (\nabla_\nu \nabla_\lambda n)(\nabla_\varepsilon \nabla_\delta n) - \ldots, \tag{2.2}$$

$$C_\mu \equiv -q \Upsilon_{\mu\nu\delta}^{(1)} E_\nu \nabla_\delta n - q \Upsilon_{\mu\nu\varepsilon\delta}^{(2)} (\nabla_\nu E_\varepsilon)(\nabla_\delta n)$$

$$\qquad - q \Upsilon_{\mu\nu\varepsilon\delta}^{(3)} E_\nu \nabla_\varepsilon \nabla_\delta n - q \Upsilon_{\mu\nu\lambda\varepsilon\delta}^{(4)} (\nabla_\nu E_\lambda)(\nabla_\varepsilon \nabla_\delta n) + \ldots.$$

In the simplest (linear) theory only $\sigma^{(1)}$ and $D^{(1)}$ play a part. For stronger fields and/or concentration gradients the higher terms come successively into play. If the sample is not at a uniform temperature T additional sets of terms must be added to (2.1), namely those in ∇T, those in E and ∇T, those in ∇n and ∇T and possibly terms in E, ∇n and ∇T. However, these complications will not be pursued in this paper.

The electrochemical potential $\bar{\mu}$ is related to the chemical potential $\mu(r)$ and the electrostatic potential $\phi(r)$ by

$$\bar{\mu} = \mu(r) - |q|\phi(r). \tag{2.3}$$

Here q is the electric charge on the particles considered, and the sign convention is such that the electrochemical potential $\bar{\mu}$ increases upwards for electrons and other negatively charged particles (Landsberg and Hope 1977, Landsberg 1978). Using partial derivatives at constant T and V, one then has

$$\nabla_\nu n(r) = \frac{\partial n(r)}{\partial \mu(r)} \nabla_\nu \mu(r) = -|q|\frac{\partial n(r)}{\partial \mu(r)} E_\nu(r), \tag{2.4}$$

as $\bar{\mu}$ is spatially constant in thermal equilibrium. Similarly,

$$\nabla_\lambda \nabla_\nu n(r) = \frac{\partial^2 n(r)}{\partial \mu(r)^2} \nabla_\lambda \mu(r) \nabla_\nu \mu(r) + \frac{\partial n(r)}{\partial \mu(r)} \nabla_\lambda \nabla_\nu \mu(r)$$

$$= q^2 \frac{\partial^2 n(r)}{\partial \mu(r)^2} E_\lambda(r) E_\nu(r) - |q|\frac{\partial n(r)}{\partial \mu(r)} \nabla_\lambda E_\nu(r). \tag{2.5}$$

Substitution of (2.4) and (2.5) into (2.1) yields

$$\langle J_\mu(r) \rangle = A^{(1)}_{\mu\nu} E_\nu + A^{(2)}_{\mu\nu\lambda} \nabla_\nu E_\lambda + A^{(3)}_{\mu\nu\delta} E_\nu E_\delta + A^{(4)}_{\mu\nu\varepsilon\delta} E_\nu \nabla_\varepsilon E_\delta + A^{(5)}_{\mu\nu\lambda\varepsilon\delta} \nabla_\nu E_\lambda \nabla_\varepsilon E_\delta + \ldots \tag{2.6}$$

where, with $\partial n(r)/\partial\mu(r)$ written $\partial n/\partial\mu$ for brevity,

$$\mathbf{A}^{(1)} \equiv \boldsymbol{\sigma}^{(1)} + q|q|\mathbf{D}^{(1)} \, \partial n/\partial \mu \qquad \text{(2nd-order tensors),}$$

$$\mathbf{A}^{(2)} \equiv \boldsymbol{\sigma}^{(2)} + q|q|\mathbf{D}^{(2)} \, \partial n/\partial \mu$$

$$\left.\mathbf{A}^{(3)} \equiv \boldsymbol{\sigma}^{(3)} - q^3\mathbf{D}^{(2)}\frac{\partial^2 n}{\partial\mu^2} + q^4\mathbf{D}^{(3)}\left(\frac{\partial n}{\partial\mu}\right)^2 + q|q|\mathbf{Y}^{(1)}\frac{\partial n}{\partial\mu}\right\} \qquad \text{(3rd-order tensors),} \tag{2.7}$$

$$\mathbf{A}^{(4)} \equiv \boldsymbol{\sigma}^{(4)} + q^4\mathbf{D}^{(4)}\left(\frac{\partial n}{\partial\mu}\right)^2 + q|q|\mathbf{Y}^{(2)}\frac{\partial n}{\partial\mu} + q|q|\mathbf{Y}^{(3)}\frac{\partial n}{\partial\mu} \qquad \text{(4th-order tensors),}$$

$$\mathbf{A}^{(5)} \equiv \boldsymbol{\sigma}^{(5)} + q^4\mathbf{D}^{(5)}\left(\frac{\partial n}{\partial\mu}\right)^2 + q|q|\mathbf{Y}^{(4)}\frac{\partial n}{\partial\mu} \qquad \text{(5th-order tensors).}$$

A possible way of advancing to non-equilibrium situations from equilibrium (all at a uniform temperature for the system) is to bring in successive terms in (2.6) so that

$$\mathbf{A}^{(i)} = 0, \qquad i = 1, 2, 3, 4, 5, \ldots. \tag{2.8}$$

This assumes that terms in

$$E, \nabla E, E \cdot E, E \cdot \nabla E, \nabla E \cdot \nabla E$$

are all of different orders of magnitude, and this may be reasonable for a sufficiently slowly varying electrostatic potential. Thus $A^{(1)} = 0$ yields a usual generalised Einstein relation (Landsberg and Hope 1977, Landsberg 1978):

$$\boldsymbol{\sigma}^{(1)} = -q|q|(\partial n(r)/\partial \mu(r))\mathbf{D}^{(1)}. \tag{2.9}$$

For electrons $q = -|e|$, and $\sigma = |e|nv$, v being the mobility. Thus for a Maxwell–Boltzmann distribution one finds in the scalar case the usual result

$$|e|D^{(1)}/v = kT. \tag{2.10}$$

Thus (2.9) is a generalised Einstein relation. Indeed, $A^{(2)} = 0, \ldots, A^{(5)} = 0$ are generalisations of this procedure to the nonlinear regime. One finds

$$
\left.
\begin{aligned}
\boldsymbol{\sigma}^{(2)} &= -q|q|(\partial n(r)/\partial \mu(r))\mathbf{D}^{(2)}, \\
\boldsymbol{\sigma}^{(3)} &= -q|q|\frac{\partial n(r)}{\partial \mu(r)}\mathbf{Y}^{(1)} + q^3\frac{\partial^2 n(r)}{\partial \mu(r)^2}\mathbf{D}^{(2)} - q^4\left(\frac{\partial n(r)}{\partial \mu(r)}\right)^2\mathbf{D}^{(3)}, \\
\boldsymbol{\sigma}^{(4)} &= -q|q|\frac{\partial n(r)}{\partial \mu(r)}(\mathbf{Y}^{(2)} + \mathbf{Y}^{(3)}) - q^4\left(\frac{\partial n(r)}{\partial \mu(r)}\right)^2\mathbf{D}^{(4)}, \\
\boldsymbol{\sigma}^{(5)} &= -q|q|\frac{\partial n(r)}{\partial \mu(r)}\mathbf{Y}^{(4)} - q^4\left(\frac{\partial n(r)}{\partial \mu(r)}\right)^2\mathbf{D}^{(5)}.
\end{aligned}
\right\} \tag{2.11}
$$

In all cases we see that a conductivity tensor is related to a diffusion tensor, just as in the linear regime.

3. Semi-microscopic treatment

A semi-microscopic interpretation of the macroscopic results (2.11) can be based on a density matrix approach. The unperturbed system with Hamiltonian H is perturbed at $t = -\infty$ to another configuration with Hamiltonian H_T, and equilibrium averages are then calculated at a time $t = 0$. In this section only these averages will be treated, and where they refer to quantities considered in § 2, they will be assumed to be identical. Hence the approach is only semi-microscopic. The perturbation is regarded as due to an imposed electrostatic potential $\phi(r)$. This contributes a term

$$F = -|e|\sum_{j=1}^{N}\phi(r_j) = -|e|\int_V n(r)\phi(r)\,dr \equiv \varepsilon H^{(1)} \tag{3.1}$$

to H_T, where the particle density is

$$n(r) = \sum_1^N \delta(r - r_j), \tag{3.2}$$

and negatively charged particles are considered. We shall put

$$H - \mu N \equiv H^{(0)}, \qquad \exp[(\mu N - H_T)/kT] \equiv A(\beta), \tag{3.3}$$

so that the 'initial' and 'final' density matrices in grand canonical ensembles are respectively

$$\rho_0 = \exp(-\beta H^{(0)})/\Xi_0, \qquad \rho_T = A(\beta)/\Xi, \tag{3.4}$$

their traces being unity.

Following the method of Nakajima (1955) and others, we note from (3.1) and (3.3) that

$$A(\beta) = \exp[-\beta(H^{(0)} + \varepsilon H^{(1)})] \tag{3.5}$$

satisfies

$$A(\beta) = \exp(-\beta H^{(0)})\left(1 - \varepsilon \int_0^\beta d\lambda_1 \exp(\lambda_1 H^{(0)}) H^{(1)} A(\lambda_1)\right).$$

This has a well known iterative solution for $A(\beta)$ as an infinite sum of products of integrals of the type

$$\ldots \int_0^{\lambda_{n-1}} d\lambda_n \, H^{(1)}(-i\hbar\lambda_n) \int_0^{\lambda_n} d\lambda_{n+1} \, H^{(1)}(-i\hbar\lambda_{n+1}) \ldots$$

where

$$H^{(1)}(-i\hbar\lambda_n) \equiv \exp(\lambda_n H^{(0)}) H^{(1)} \exp(-\lambda_n H^{(0)}). \tag{3.6}$$

This leads after some manipulation to

$$\rho_T = \rho_0\left(1 - \int_0^\beta d\lambda_1 \, F(-i\hbar\lambda_1) + \int_0^\beta d\lambda_1 \, F(-i\hbar\lambda_1) \int_0^{\lambda_1} d\lambda_2 \, F(-i\hbar\lambda_2)\right) + \beta\rho_0\langle F\rangle_0$$

$$- \beta\rho_0\langle F\rangle_0 \int_0^\beta d\lambda_1 \, F(-i\hbar\lambda_1) - \tfrac{1}{2}\beta\rho_0 \int_0^\beta d\lambda_1 \, \langle F(-i\hbar\lambda_1)F\rangle_0 + \beta^2\rho_0\langle F\rangle_0^2$$

$$+ \ldots \tag{3.7}$$

where $F(-i\hbar\lambda_n)$ is defined as in (3.6),

$$\langle F\rangle_0 \equiv \mathrm{Tr}(\rho_0 F) \qquad \text{and} \qquad \langle F(-i\hbar\lambda)F\rangle_0 \equiv \mathrm{Tr}[\rho_0 F(-i\hbar\lambda)F]. \tag{3.8}$$

Thus averages for $t = -\infty$ are distinguished by a suffix zero. Higher terms in the perturbation denoted by ... will henceforth be omitted. The advantage of the present procedure is that insertion of the integral expression of (3.1) into (3.7) yields another seven-term expression which may be inserted into

$$\langle n(r)\rangle = \mathrm{Tr}[\rho_T n(r)]. \tag{3.9}$$

This expression, valid for spatial variations in $\phi(r)$ which are not too rapid (i.e. for electric fields which are small enough), is

$$\rho_T = \rho_0 + \rho_0|e| \int_0^\beta d\lambda_1 \int_V dr_1 \, \phi(r_1)[n(r_1, -i\hbar\lambda_1) - \langle n(r_1)\rangle_0]$$

$$+ \rho_0|e|^2 \int_0^\beta d\lambda_1 \int_0^{\lambda_1} d\lambda_2 \int_V dr_1 \int_V dr_2 \, \phi(r_1)\phi(r_2)n(r_1, -i\hbar\lambda_1)n(r_2, -i\hbar\lambda_2)$$

$$- \beta\rho_0|e|^2 \int_0^\beta d\lambda_1 \int_V dr_1 \int_V dr_2 \, \phi(r_1)\phi(r_2)n(r_1, -i\hbar\lambda_1)\langle n(r_2)\rangle_0$$

$$- \tfrac{1}{2}\beta\rho_0|e|^2 \int_0^\beta d\lambda_1 \int_V dr_1 \int_V dr_2 \, \phi(r_1)\phi(r_2)\langle n(r_1, -i\hbar\lambda_1)n(r_2)\rangle_0$$

$$+ \beta^2\rho_0|e|^2 \int_V dr_1 \int_V dr_2 \, \phi(r_1)\phi(r_2)\langle n(r_1)\rangle_0\langle n(r_2)\rangle_0 + \ldots. \tag{3.10}$$

Here V is the volume of the system as specified in a grand canonical ensemble.

In the result obtained by combining (3.9) and (3.10), it will be assumed that the equilibrium averages of correlations between particle density operators $n(r)$ (or other operators, e.g. $\dot{n}(r)$) remain unchanged when each of the operators entering the

correlation is translated by the same vector (r_0 say). This is the 'statistical homogeneity' assumption (Katz 1967, Luttinger 1964). One also needs the general results from the grand canonical ensemble

$$\left[\frac{\partial \langle N \rangle_0}{\partial \alpha}\right]_{\beta,V} = \langle (N - \langle N \rangle_0)^2 \rangle_0, \qquad \left[\frac{\partial^2 \langle N \rangle_0}{\partial \alpha^2}\right]_{\beta,V} = \langle (N - \langle N \rangle_0)^3 \rangle_0,$$

where the mean total number of particles is $\langle N \rangle_0$. After some manipulation one finds from (3.9) and (3.10) with $\alpha \equiv \mu/kT$

$$\langle n(r) \rangle = \frac{1}{V}\langle N \rangle_0 + \frac{\beta|e|}{V}\left[\frac{\partial \langle N \rangle_0}{\partial \alpha}\right]_{\beta,V}\phi(r) + \frac{\beta^2|e|^2}{2V}\left[\frac{\partial^2 \langle N \rangle_0}{\partial \alpha^2}\right]_{\beta,V}\phi^2(r). \tag{3.11}$$

This is an expansion of the expected form

$$\langle n(r) \rangle = n_0 + a_1\phi(r) + \tfrac{1}{2}a_2\phi^2(r) + \dots \qquad (n_0 \equiv \langle N \rangle_0/V) \tag{3.12}$$

where the coefficients a_1 and a_2 can now be identified. They are

$$a_1 = |e|(\partial n_0/\partial \mu)_{T,V}, \qquad a_2 = |e|^2(\partial^2 n_0/\partial \mu^2)_{T,V}. \tag{3.13}$$

One can now proceed as in § 2, by using (2.2) together with the consequences of (3.12):

$$\nabla_\gamma \langle n(r) \rangle = -[a_1 + a_2\phi(r)]E_\gamma(r), \tag{3.14}$$

$$\nabla_\beta \nabla_\gamma \langle n(r) \rangle = -[a_1 + a_2\phi(r)]\nabla_\beta E_\gamma(r) + a_2 E_\gamma(r)E_\beta(r). \tag{3.15}$$

Equating the coefficients of E_ν, $E_\nu E_\lambda$, etc, to zero as before, one finds

$$\sigma^{(1)} = \frac{|e|^2}{kT}\mathbf{D}^{(1)}\left[\frac{\partial \langle n(r) \rangle}{\partial \eta(r)}\right]_{T,V}, \tag{3.16}$$

$$\sigma^{(2)} = \frac{|e|^2}{kT}\mathbf{D}^{(2)}\left[\frac{\partial \langle n(r) \rangle}{\partial \eta(r)}\right]_{T,V}, \tag{3.17}$$

$$\sigma^{(3)} = \frac{e|e|^2}{(kT)^2}\mathbf{D}^{(2)}\left[\frac{\partial^2 \langle n(r) \rangle}{\partial \eta(r)^2}\right]_{T,V} - \frac{|e|^4}{(kT)^2}\mathbf{D}^{(3)}\left[\frac{\partial \langle n(r) \rangle}{\partial \eta(r)}\right]^2_{T,V} + \frac{|e|^2}{kT}Y^{(1)}\left[\frac{\partial \langle n(r) \rangle}{\partial \eta(r)}\right]_{T,V}. \tag{3.18}$$

These results agree with (2.11) provided the quantity $\eta(r)$ is correctly interpreted. It is an electrochemical potential divided by kT, but its sign depends on the sign of the charge of the current carriers and is measured from the energy of the 'band edge' A (relevant to electrons or holes in semiconductors, for example). It is introduced as η in equation (1.8) of Landsberg and Hope (1977) and as γ_j in equation (17.16) of Landsberg (1978). It is defined by

$$\eta = (e/|e|)(A - \bar{\mu})/kT \tag{3.19}$$

and is the quantity occurring in the Fermi–Dirac distribution

$$[\exp(x_c - \eta_c) + 1]^{-1}. \tag{3.20}$$

Here x_c is the kinetic energy of electrons divided by kT, $(E - E_c)/kT$, while $\eta_c = (\bar{\mu}_c - E_c)/kT$. For holes in a valence band one would have

$$[\exp(\eta_v - x_v) + 1]^{-1}. \tag{3.21}$$

The last two results (2.11), and higher-order results, could in principle be obtained by an extension of the method of this section.

It is important to note that the spatial dependence of the conductivity–diffusivity ratio defined via (3.16) is to be *directly* attributed to the spatial dependence of the applied electrostatic potential $\phi(r)$ given by (2.3). Using (3.16), (2.3) and (3.11)

$$\sigma^{(1)} = \frac{|e|^2}{kT} \mathbf{D}^{(1)} \left(\frac{\partial n_0}{\partial \mu} + \frac{\partial^2 n_0}{\partial \mu^2} \phi(r) \right). \tag{3.22}$$

The results (3.17) and (3.18) can likewise be expressed in terms of $\phi(r)$.

In the expansion (3.11) for the particle density operator terms of $O[\phi^3(r)]$ have been omitted. Thus (3.22) depends only linearly on the electrostatic potential. Based on (3.11), note that one might *propose* the generalised Maxwell–Boltzmann distribution

$$\langle n(r) \rangle = \exp[|e|\beta\Phi(r)]n_0 \tag{3.23}$$

with

$$\Phi(r) \equiv \phi(r)\partial/\partial\alpha \tag{3.24}$$

valid for Fermi degeneracy. The expansion (3.23) is rather novel and is to be compared with the non-degenerate Maxwell–Boltzmann distribution

$$\langle n(r) \rangle = \exp[|e|\beta\phi(r)]n_0. \tag{3.25}$$

4. A microscopic treatment

In this section we investigate an alternative approach to the problem which does not rely on setting the current density coefficients equal to zero for the generation of new Einstein relations. At the outset we treat the system from a non-equilibrium point of view, and our aim is to set up what is essentially a Kubo (1957) formalism; however, the interpretation is novel in the sense that it can produce all the field, diffusion and mixed contributions to the average current density—the usual Kubo theory examines the response to an external perturbation, and produces only the field-dependent terms. Liouville's equation is central to our framework; however, contrary to the approach of some authors, e.g. Kalashnikov (1971), we shall not modify the actual form of the equation by the addition of infinitesimal terms. This governing equation is fundamental, and instead of modifying it, we seek a justification of the inclusion of an effective interaction which would produce the required total current density.

It is well known that diffusion contributions arise as a result of the spatial variations of the chemical potential $\mu(r)$ (Gibbs 1906). Consider now a system of particles which is not in full equilibrium; we shall associate with it an interaction Hamiltonian $H_e^{(1)}$ say, corresponding to forces which are externally applied or may be present within the system as a result of concentration gradients, and an unperturbed Hamiltonian H. Suppose that although we are away from a full equilibrium situation, the particles are nevertheless in a state of *local* equilibrium. That is, the appropriate density matrix is given by

$$\rho_e = \frac{1}{\Xi_e} \exp\left[-\beta\left(H + H_e^{(1)} - \int \mu(r)n(r)\,dr \right) \right] \tag{4.1}$$

where

$$\Xi_e = \text{Tr} \exp\left[-\beta\left(H + H_e^{(1)} - \int \mu(r)n(r)\,dr \right) \right]. \tag{4.2}$$

This local distribution function was introduced by Mori (1958) and its properties have been examined by various authors, e.g. Zubarev (1974). Note that the inverse temperature β is usually a function of space also, since energy from an external field is distributed among the particles; for simplicity, we ignore the existence of temperature gradients in this paper, although the framework which follows could well be extended to take such energy transfers into account. Equation (4.1) may be derived from information theory (e.g. Katz 1967) using a constraint on the Fourier components of the particle number density. In setting up our interpretation we exploit an idea formulated by Bogolyubov (1962). When a system relaxes from any non-equilibrium state to a state of full equilibrium, this is carried out in two steps. First, local equilibrium is established *very rapidly* in small volume elements, and this is followed by a longer decay towards the grand canonical distribution. Essentially there are two relaxation times for the processes, τ_l and τ respectively, with $\tau_l \ll \tau$. The time τ depends on the total volume, whereas τ_l corresponds to equilibrium being set up in macroscopically small volumes which must nevertheless still contain many particles. Having established the rapid occurrence of local equilibrium, almost at the onset of relaxation for our purposes, we now make the following analogy which will then be implicit in our development of the appropriate Kubo formalism.

When a system has a local equilibrium density matrix of the type (4.1), it could be considered as being *formally* equivalent to a system described by full equilibrium parameters (constant chemical potential μ and total number of particles N) with a total Hamiltonian $H + H^{(1)}$ where $H^{(1)}$ represents only the *external* interaction. This equivalent system would then have a grand canonical distribution

$$\rho = (1/\Xi) \exp[-\beta(H + H^{(1)} - \mu N)] \tag{4.3}$$

where, as in (3.1),

$$H^{(1)} = q \int n(r)\phi(r) \, dr \tag{4.4}$$

and q is the charge on the particles. If we compare with (4.1), the analogy will be achieved if the effective Hamiltonian introduced earlier is given by

$$H_e^{(1)} = H^{(1)} + \int [\mu(r) - \mu] n(r) \, dr. \tag{4.5}$$

If we wish to define $H_e^{(1)}$ in a form similar to (4.4), we may do so by introducing an effective potential

$$\phi^{(e)}(r) = \phi(r) + [\mu(r) - \mu]/q \tag{4.6}$$

so that

$$H_e^{(1)}(r) = q \int n(r)\phi^{(e)}(r) \, dr$$

and the effective field is

$$E^{(e)}(r) = -\nabla\phi(r) - (1/q)\nabla\mu(r). \tag{4.7}$$

The calculation of an average current density now follows from Liouville's equation with the above arguments taken into account, i.e. we take our governing equation to be

$$\partial\rho/\partial t + i[H + H_e^{(1)} e^{st}, \rho] = 0 \tag{4.8}$$

with the boundary condition that at $t = -\infty$ ρ is given by

$$\rho_0 = (1/\Xi_0) \exp[-\beta(H - \mu N)] \tag{4.9}$$

with an effective interaction $H_e^{(1)}$; (4.9) is the boundary condition and s a small switching parameter. The usual Kubo formalism has been applied by many authors, including Luttinger (1964) who considered the standard Einstein solution as being derived from a phenomenological argument. In the linear case, it is well known that the average current density is then given by

$$\langle j_\mu(\mathbf{r}) \rangle = \int_{-\infty}^{t} \mathrm{d}t' \int_{0}^{\beta} \mathrm{d}\beta' \int \mathrm{d}\mathbf{r}' \langle j_\nu(\mathbf{r}', -\mathrm{i}\beta') j_\mu(\mathbf{r}, t-t') \rangle_0 E_\nu^{(e)}(\mathbf{r}') \, e^{st'} \tag{4.10}$$

where $\langle \ \rangle_0$ is an equilibrium ensemble expectation value (the trace involves ρ_0 as defined in (4.9)). If our generalised field is slowly varying in space, $\mathbf{E}^{(e)}(\mathbf{r}') \simeq \mathbf{E}^{(e)}(\mathbf{r})$ in the integrand of (4.10), we obtain

$$\langle j_\mu(\mathbf{r}) \rangle = \sigma_{\mu\nu}^{(1)} E_\nu(\mathbf{r}) - (\sigma_{\mu\nu}^{(1)}/q) \nabla_\nu \mu \tag{4.11}$$

where $\mathbf{E} = -\nabla \phi$ and $\sigma_{\mu\nu}^{(1)}$ is the correlation function which follows directly from (4.10) in the slow variation approximation. Comparing the second term of (4.11) with the phenomenological form of the diffusion current density, $-qD_{\mu\nu}^{(1)} \nabla_\nu n$, we obtain *directly* the Einstein relation for the linear case as

$$\frac{1}{q} \frac{\partial \mu}{\partial n} \sigma_{\mu\nu}^{(1)} \equiv q D_{\mu\nu}^{(1)}. \tag{4.12}$$

Considering now nonlinear dependences on the field, a conduction current, for instance, may be generalised to

$$\langle j_\mu(\mathbf{r}) \rangle_{\text{conduction}} = \sigma_{\mu\nu}^{(1)}(E) E_\nu(\mathbf{r}) \tag{4.13}$$

if the field is slowly varying, and $\boldsymbol{\sigma}^{(1)}$ may be regarded as a function of the electric field. Formally it turns out that the appropriate correlation function for $\boldsymbol{\sigma}^{(1)}(E)$ is very similar to that of the linear case. A closed expression for nonlinear response has been proposed by Tani (1964). The expectation value of any operator B (when the effective perturbation $H_e^{(1)} \, e^{s\tau}$ appropriate to our formulation is applied) has the form

$$\langle B \rangle_t - \langle B \rangle_0 = -\int_{-\infty}^{t} \mathrm{d}t' \int_{0}^{\beta} \mathrm{d}\beta' \langle \dot{H}_e^{(1)}(-\mathrm{i}\beta') B(t, t' | H + H_e^{(1)} \, e^{s\tau}) \rangle_0 \exp(st') \tag{4.14}$$

where in Tani's notation

$$B(t, t' | H + H_e^{(1)} \, e^{s\tau}) \equiv \exp\left(\mathrm{i} \int_{t'}^{t} (H + H_e^{(1)} \, e^{s\tau}) \, \mathrm{d}\tau\right) B \exp\left(-\mathrm{i} \int_{t'}^{t} (H + H_e^{(1)} \, e^{s\tau}) \, \mathrm{d}\tau\right) \tag{4.15}$$

and (4.14) is valid to all orders in the perturbation. It may be shown from an equation of continuity that

$$\dot{H}_e^{(1)} = -\int \mathrm{d}\mathbf{r} \, \mathbf{j}(\mathbf{r}) \cdot [\mathbf{E}(\mathbf{r}) - (1/q) \nabla \mu(\mathbf{r})]. \tag{4.16}$$

Substituting into (4.14), with B taken as a current density operator, and assuming slow spatial variations of E and $\nabla \mu$ yields

$$\langle j_\mu(\mathbf{r}) \rangle = \sigma_{\mu\nu}^{(G)}(E, \nabla \mu) E_\nu(\mathbf{r}) - \sigma_{\mu\nu}^{(G)}(E, \nabla \mu)(1/q) \nabla_\nu \mu \tag{4.17}$$

where the generalised correlation function is

$$\sigma_{\mu\nu}^{(G)} \equiv \lim_{s \to 0} \int_{-\infty}^{t} dt' \int_{0}^{\beta} d\beta' \int dr' \langle j_\nu(r', -i\beta')j_\mu(r, t, t'|H + H_e^{(1)} e^{s\tau})\rangle_0 \exp(st'). \qquad (4.18)$$

The simplest generalisation for $\langle j_\mu(r) \rangle$ is that of second order in the interaction, which corresponds to an evaluation of (4.15) to linear terms only. The latter may be expressed in terms of a commutator, the result being

$$B(t, t'|H + H_e^{(1)} e^{s\tau}) \simeq B(t - t') + \left[i \int_{t'}^{t} H_e^{(1)}(t'' - t') \exp(st'') dt'', B(t - t')\right]. \qquad (4.19)$$

One may now separate the field and chemical potential derivations in (4.18); thus

$$\sigma_{\mu\nu}^{(G)} \simeq \lim_{s \to 0} \left\{ \int_{-\infty}^{t} dt' \int_{0}^{\beta} d\beta' \int dr' \exp(st') \langle j_\nu(r', -i\beta')j_\mu(r, t - t')\rangle_0 \right.$$

$$\left. + \left\langle j_\nu(r', -i\beta')\left[i \int_{t'}^{t} H_e^{(1)}(t'' - t') \exp(st''), j_\mu(r, t - t')\right]\right\rangle_0 \right\}. \qquad (4.20)$$

The first term corresponds to $\sigma_{\mu\nu}^{(1)}$; the second may be split into an E-dependent and a $\nabla\mu$-dependent contribution. Introducing the polarisation operator

$$P(r) = q \sum_{j} \delta(r - r_j)r_j, \qquad (4.21)$$

we may write

$$H_e^{(1)} = -\int dr \left[E(r) - (1/q)\nabla\mu(r)\right] \cdot P(r). \qquad (4.22)$$

From (4.17), (4.20) and (4.22), the total current density in the slow variation approximation for the second-order case is then

$$\langle j_\mu(r) \rangle = \sigma_{\mu\nu}^{(1)}E_\gamma(r) + \sigma_{\mu\nu\delta}^{(3)}E_\delta(r)E_\nu(r) - (\sigma_{\mu\nu}^{(1)}/q)\nabla_\nu\mu$$

$$- (\sigma_{\mu\nu\delta}^{(3)}/q)(E_\delta\nabla_\nu\mu + E_\nu\nabla_\delta\mu) + \sigma_{\mu\nu\delta}^{(3)}(1/q^2)\nabla_\delta\mu\nabla_\nu\mu \qquad (4.23)$$

where

$$\sigma_{\mu\nu\delta}^{(3)} = \lim_{s \to 0} \left(\int_{0}^{t} dt' \int_{0}^{\beta} d\beta' \int dr' \exp(st') \right.$$

$$\left. \times \left\langle j_\nu(r', -i\beta')\left[-i \int_{t'}^{t} dt'' \int dr'' P_\delta(r'', t'' - t') \exp(st''), j_\mu(r, t - t')\right]\right\rangle_0 \right). \qquad (4.24)$$

Finally, if the effective field (4.9) is not slowly varying, we shall have further contributions to the current density. These are obtained from a Taylor expansion of $E^{(e)}(r')$. Equation (4.17) is modified to

$$\langle j_\mu(r) \rangle = \sigma_{\mu\nu}^{(G)}(E, \nabla\mu)\left(E_\nu(r) - \frac{1}{q}\nabla_\nu\mu\right) + \sigma_{\mu\nu\lambda}^{(\tilde{G})}\left(\nabla_\lambda E_\nu(r') - \frac{1}{q}\nabla_\lambda\nabla_\nu\mu(r')\right) \qquad (4.25)$$

where

$$\sigma_{\mu\nu\lambda}^{(\tilde{G})} \equiv \lim_{s \to 0} \left(\int_{-\infty}^{t} dt' \int_{0}^{\beta} d\beta' \int d\boldsymbol{r}' \langle j_{\nu}(\boldsymbol{r}', -i\beta') j_{\mu}(\boldsymbol{r}; t, t'|H+H_{e}^{(1)} e^{s\tau}) \rangle_{0} \exp(st')(r_{\lambda}' - r_{\lambda}) \right)$$

(4.26)

and we have retained only the simplest correction in the Taylor expansion. The latter is also applied in (4.22). Equation (4.20) now yields

$$\sigma_{\mu\nu}^{(G)} = \sigma_{\mu\nu}^{(1)} + \sigma_{\mu\nu\delta}^{(3)} E_{\delta} - \frac{1}{q} \sigma_{\mu\nu\delta} \nabla_{\delta}\mu + \beta_{\mu\nu\varepsilon\delta} \nabla_{\varepsilon} E_{\delta} - \frac{1}{q} \beta_{\mu\nu\varepsilon\delta} \nabla_{\varepsilon} \nabla_{\delta}\mu$$

(4.27)

where $\sigma^{(3)}$ is defined in (4.24) and

$$\beta_{\mu\nu\varepsilon\delta} = \lim_{s \to 0} \left(\int_{-\infty}^{t} dt' \int_{0}^{\beta} d\beta' \int d\boldsymbol{r}' \exp(st') \left\langle j_{\nu}(\boldsymbol{r}', -i\beta') \right. \right.$$

$$\times \left. \left. \left[-i \int_{t'}^{t} dt'' \int d\boldsymbol{r}'' \, (r_{\varepsilon}'' - r_{\varepsilon}) P_{\delta}(\boldsymbol{r}'', t'' - t') \exp(st''), j_{\mu}(\boldsymbol{r}, t - t') \right] \right\rangle_{0} \right). \quad (4.28)$$

The correlation function (4.26) may also be expressed as

$$\sigma_{\mu\nu\lambda}^{(\tilde{G})} = \lim_{s \to 0} \left(\int_{-\infty}^{t} dt' \int_{0}^{\beta} d\beta \int d\boldsymbol{r}' \exp(st') \langle j_{\nu}(\boldsymbol{r}', -i\beta') j_{\mu}(\boldsymbol{r}, t - t') \rangle_{0} (r_{\lambda}' - r_{\lambda}) \right.$$

$$\left. + \left\langle j_{\nu}(\boldsymbol{r}', -i\beta') \left[i \int_{t'}^{t} H_{e}^{(1)}(t'' - t') \exp(st'') \, dt'', j_{\mu}(\boldsymbol{r}, t - t') \right] \right\rangle_{0} (r_{\lambda}' - r_{\lambda}) \right)$$

(4.29)

which is analogous to (4.20). An expansion of E and ∇_{μ} in (4.22) is then used in (4.29), and yields

$$\sigma_{\mu\nu\lambda}^{(\tilde{G})} = \sigma_{\mu\nu\lambda}^{(2)} + \gamma_{\mu\nu\lambda\delta} E_{\delta} - (1/q) \gamma_{\mu\nu\lambda\delta} \nabla_{\delta}\mu + \sigma_{\mu\nu\lambda\varepsilon\delta}^{(5)} \nabla_{\varepsilon} E_{\delta} - (1/q) \sigma_{\mu\nu\lambda\varepsilon\delta}^{(5)} \nabla_{\varepsilon} \nabla_{\delta}\mu$$

(4.30)

where

$$\sigma_{\mu\nu\lambda}^{(2)} = \lim_{s \to 0} \left(\int_{-\infty}^{t} dt' \int_{0}^{\beta} d\beta' \int d\boldsymbol{r}' \exp(st') \langle j_{\nu}(\boldsymbol{r}', -i\beta') j_{\mu}(\boldsymbol{r}, t - t') \rangle_{0} (r_{\lambda}' - r_{\lambda}) \right),$$

(4.31)

$$\gamma_{\mu\nu\lambda\delta} = \lim_{s \to 0} \left(\int_{-\infty}^{t} dt' \int_{0}^{\beta} d\beta' \int d\boldsymbol{r}' \exp(st') \left\langle j_{\nu}(\boldsymbol{r}', -i\beta') \right. \right.$$

$$\times \left. \left. \left[-i \int_{t'}^{t} dt'' \int d\boldsymbol{r}'' \, P_{\delta}(\boldsymbol{r}'', t'' - t') \exp(st''), j_{\mu}(\boldsymbol{r}, t - t') \right] \right\rangle_{0} (r_{\lambda}' - r_{\lambda}) \right), \quad (4.32)$$

$$\sigma_{\mu\nu\lambda\varepsilon\delta}^{(5)} = \lim_{s \to 0} \left(\int_{-\infty}^{t} dt' \int_{0}^{\beta} d\beta' \int d\boldsymbol{r}' \exp(st') \left\langle j_{\nu}(\boldsymbol{r}', -i\beta') \right. \right.$$

$$\times \left. \left. \left[-i \int_{t'}^{t} dt'' \int d\boldsymbol{r}'' \, (r_{\varepsilon}'' - r_{\varepsilon}) P_{\delta}(\boldsymbol{r}'', t'' - t') \exp(st''), j_{\mu}(\boldsymbol{r}, t - t') \right] \right\rangle_{0} (r_{\lambda}' - r_{\lambda}) \right).$$

(4.33)

Collecting results (4.25), (4.27), (4.30) and defining

$$\sigma_{\mu\nu\varepsilon\delta}^{(4)} = \beta_{\mu\nu\varepsilon\delta} + \gamma_{\mu\delta\varepsilon\nu}$$

(4.34)

gives the final form for the total current density (all fields being evaluated at a point r)

$$\langle j_\mu(r)\rangle = \sigma^{(1)}_{\mu\nu}E_\nu + \sigma^{(2)}_{\mu\nu\lambda}\nabla_\lambda E_\nu + \sigma^{(3)}_{\mu\nu\delta}E_\delta E_\nu + \sigma^{(4)}_{\mu\nu\varepsilon\delta}E_\nu\nabla_\varepsilon E_\delta + \sigma^{(5)}_{\mu\nu\lambda\varepsilon\delta}(\nabla_\varepsilon E_\delta)\nabla_\lambda E_\nu - \sigma^{(1)}_{\mu\nu}\frac{1}{q}\nabla_\nu\mu$$

$$- \sigma^{(2)}_{\mu\nu\lambda}\frac{1}{q}\nabla_\lambda\nabla_\nu\mu + \sigma^{(3)}_{\mu\nu\delta}\left(\frac{1}{q^2}(\nabla_\delta\mu)\nabla_\nu\mu - \frac{1}{q}E_\delta\nabla_\nu\mu - \frac{1}{q}E_\nu\nabla_\delta\mu\right)$$

$$+ \sigma^{(4)}_{\mu\nu\varepsilon\delta}\left(\frac{1}{q^2}(\nabla_\varepsilon\nabla_\delta\mu)\nabla_\nu\mu - \frac{1}{q}(\nabla_\nu\mu)\nabla_\varepsilon E_\delta - \frac{1}{q}(\nabla_\varepsilon\nabla_\delta\mu)E_\nu\right)$$

$$+ \sigma^{(5)}_{\mu\nu\lambda\varepsilon\delta}\left(\frac{1}{q^2}(\nabla_\varepsilon\nabla_\delta\mu)(\nabla_\lambda\nabla_\nu\mu) - \frac{1}{q}(\nabla_\varepsilon\nabla_\delta\mu)\nabla_\lambda E_\nu - \frac{1}{q}(\nabla_\lambda\nabla_\nu\mu)\nabla_\varepsilon E_\delta\right).$$

$$(4.35)$$

The microscopic analysis of this section is an alternative approach which in principle generates a whole set of Einstein relations from a non-equilibrium point of view. The final expression for the total current density is necessarily quite complicated: the first five terms represent the conduction current density; the remaining terms are connected with diffusion contributions (involving derivatives of μ only) or mixed contributions (involving products of E, $\nabla\mu$ and their derivatives). If we note that

$$\nabla_\nu\mu = (\partial\mu/\partial n)\nabla_\nu n$$

and

$$\nabla_\lambda\nabla_\nu\mu = (\partial^2\mu/\partial n^2)\nabla_\lambda n\nabla_\nu n + (\partial\mu/\partial n)\nabla_\lambda\nabla_\nu n,$$

then the current density may be written in such a way that a direct comparison with the phenomenological form (2.2) can be made. One can then simply extract relations for the coefficients $\mathbf{D}$ in terms of the correlation functions σ to any order:

$$q^2\mathbf{D}^{(1)} = \boldsymbol{\sigma}^{(1)}\partial\mu/\partial n,$$

$$q^2\mathbf{D}^{(2)} = \boldsymbol{\sigma}^{(2)}\partial\mu/\partial n,$$

$$q^4\mathbf{D}^{(3)} = \boldsymbol{\sigma}^{(3)}(\partial\mu/\partial n)^2 - q\boldsymbol{\sigma}^{(2)}\partial\mu^2/\partial n^2,$$

$$q^2\mathbf{Y}^{(1)} = (\boldsymbol{\sigma}^{(3)} + \boldsymbol{\sigma}^{(3)\dagger})\partial\mu/\partial n,$$

$$q^4\mathbf{D}^{(4)} = \boldsymbol{\sigma}^{(4)}(\partial\mu/\partial n)^2,$$

$$q^2\mathbf{Y}^{(2)} = \boldsymbol{\sigma}^{(4)}\partial\mu/\partial n = q^2\mathbf{Y}^{(3)},$$

$$q^4\mathbf{D}^{(5)} = \boldsymbol{\sigma}^{(5)}(\partial\mu/\partial n)^2,$$

$$q^2\mathbf{Y}^{(4)} = (\boldsymbol{\sigma}^{(5)} + \boldsymbol{\sigma}^{(5)\dagger})\partial\mu/\partial n,$$

where $C^\dagger_{\alpha\nu\delta} \equiv \mathbf{C}_{\alpha\delta\nu}$ is the definition of the dagger symbol.

If one chooses q as negative and identifies $\boldsymbol{\sigma}^{(3)\dagger}$ and $\boldsymbol{\sigma}^{(5)\dagger}$ with $\boldsymbol{\sigma}^{(3)}$ and $\boldsymbol{\sigma}^{(5)}$ respectively, these results are consistent with (2.11) and (3.16)–(3.18), but contain more information.

5. Conclusion

In this paper it has been shown that one can obtain higher-order Einstein relations as they arise in nonlinear transport. Three sets of consistent relations have been obtained,

and it is clear that the whole procedure can be generalised to yet higher orders so as to cover the cases of stronger electric fields and concentration gradients. It can also be generalised to cover non-uniform temperatures—a situation which has been avoided here for simplicity.

It has been seen that the macroscopic and the semi-macroscopic methods depend on equating the total average current density to zero, whence Einstein relations are obtainable by comparing corresponding terms. The microscopic treatment, which was based on Liouville's equation, does not depend on this procedure. There are restrictions on the validity of this theory, however, since the analysis depends on a formal analogy between full and local equilibrium (discussed after equation (4.2)). The theory is not expected to be applicable until local equilibrium really is established in small volumes within the system. But, as noted earlier, the relevant relaxation time τ_1 is very small compared with the total time τ for relaxation of the whole system, and we would therefore anticipate that the procedure is correct over a wide time range.

In conclusion, we have established extensions to the nonlinear regimes from both macroscopic and microscopic points of view. Our framework is rather general, and we have included ideas based on the fundamental statistical mechanics of the problem, whilst avoiding complexities (Zubarev 1974) which occur in this field. This forms a complement to the published work mentioned in the Introduction and provides a firmer basis for generalised Einstein relations.

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