Relation between the Mori-Green-Kubo formulae and their Boltzmann approximation for electronic transport coefficients

Relation between the Mori–Green–Kubo formulae and their Boltzmann approximation for electronic transport coefficients†

Marcel Ausloos

International Center for Theoretical Solid State Physics, Belgium; Université de Liège, Institut de Physique, B5, 4000 Sart-Tilman/Liège 1, Belgium

Abstract. The generalised Langevin equation of motion for dynamic variables is used in order to derive general expressions for *electronic* transport coefficients in the vicinity of a critical point. All kinetic coefficients are treated on an equal footing, in the absence of an applied magnetic field. The derivation is model independent, although cubic symmetry is assumed. Such expressions are related to the more usual Boltzmann expressions by introducing a matrix of relaxation times. The Seebeck coefficient or thermoelectric power is given some special emphasis because it cannot be defined in terms of a single relaxation time. The Mott formula is however recovered in terms of a general kernel $\sigma(E)$.

1. Introduction

In order to take into account coupling between fluctuations of various fluxes near a critical point, it is usual to start from the generalised Langevin equation of Brownian motion (Mori 1965) which is in fact an identity, when the fluctuation dissipation theorem is used to define the memory function $\Phi(t)$ in terms of the appropriate correlation function. Such an approach dates back to the landmark paper of Zwanzig (1965) on the response function, and to the application of the response function theory of dielectric relaxation by Cole (1965). Such pioneering works induced by the intriguing singularities of transport coefficients in liquids still retain their powerful impact when applied to solid state physics.

Kawasaki (1970) has developed an elegant formalism based on such an identity in order to construct a kinetic equation to describe the slowed-down motion of the system near a critical point. He has illustrated the theory by working out the behaviour of singular transport coefficients of, for example, magnetic insulators, near the critical point T_c.

Electronic transport coefficients are not singular near a critical point. The theory thus has to be adapted in order to describe the effect of criticality on such coefficients, hence to describe the behaviour of their temperature derivative which is indeed singular.

The Mori–Kawasaki kinetic equation leads to a concise form for any transport coefficients. In the case treated here, the approach leads to a generalisation of the Green–Kubo formula for the electrical resistivity (Green 1956, Kubo 1966) and the

---

other electronic coefficients. Such formulae will be given in § 2. They do not seem to have been presented before as globally as here. Such formulae have to be rewritten in a more appropriate form in order to take into account explicitly the occurrence of various characteristic time and length scales near the critical point. The Mori identity has to be used again to derive such a new form. However the final expressions do not appear as simple as the familiar ones based on the Boltzmann equation.

Mori's intention has been to present a kinetic equation including the description of dynamic variables' fluctuations. In so doing, some connection between the Boltzmann regime (the characteristic length being of the order of the mean free path) and the classical hydrodynamic regime (the characteristic length is macroscopic, like the sample dimension) is supposed to be made near a critical point. It has never been shown that such a connection indeed exists for the electronic transport coefficients. It is appropriate to show it in our new general expressions.

Similarly, the connection between the Boltzmann equation approach and the *mean field reduction* of Mori–Kawasaki-like formulae for electronic transport coefficients is far from obvious (Edwards 1958). Indeed Thouless (1976) has recently been intrigued by such a relation. He has been able to derive the standard Boltzmann expression for the *electrical conductivity* starting from the Green–Kubo formula in the case of a disordered system, when the electron mean free path is large.

Our calculation shows the same connection, although we will be more general since we start from general (and cumbersome) expressions for the electronic transport coefficients, expressed in terms of correlation functions between (time derivatives of) various current operators. We will not only describe the connection in the case of the electrical resistivity, but also for the other transport coefficients of interest, i.e. the thermal conductivity and the Seebeck (and hence for the Peltier) coefficient. The latter does not have a simple Boltzmann expression except that given by Mott (1936). However, the latter is known to have some drawbacks in particular in the vicinity of a critical point.

It is therefore of interest to be more explicit than usual concerning such a thermoelectric coefficient. Its hybrid nature will be emphasised. We will however leave a detailed study of the Seebeck coefficient (in magnetic metals near T_c) until the generalisation (or interpretation) of the Mott formula near a critical point.

The equivalence of the generalised Langevin equation and the generalised master equation of Nakajima (1958) and Zwanzig (1960) has been proved recently by Grabert (1977). Our work therefore contributes further to understanding the connection between various approaches to the description of dynamic critical phenomena (see also Enz 1976). Notice that our work, like that quoted here, is restricted to 'linearised' equations. In order to go beyond such a restriction, it might be interesting to follow the pioneering work of Ueyama (1975) on the same subject.

Finally, let us point out that the Green–Kubo formula for the electrical conductivity in classical plasmas has been investigated by Balescu (1961, 1963). He has derived a general formula for the time-dependent electric current which connects the time dependence of the current to the singularities of the resolvent of Liouville's operator of a classical system. It has permitted direct contact with the general theory of approach to equilibrium developed by Prigogine and co-workers (e.g. Prigogine and Résibois 1961, Résibois 1964), and indicated the by now classical framework for a diagram expansion of transport coefficients.

Our work is quite similar, and goes beyond the mean-field-like formalism of the Green–Kubo linear response theory. Therefore like Balescu, one can infer from his

proof and our work that electronic transport coefficients can always be calculated from a Markoffian Boltzmann-like equation even in the vicinity of a critical point where that equation does not describe properly the approach to the stationary state. This result can be regarded as a general justification of the traditional method of calculating and expressing non-singular transport coefficients and interpreting their behaviour near a critical point in terms of the same quantities ('physical parameters') away from the critical region.

Section 2 contains some tedious, but necessary rewriting of well known expressions of the Mori formalism, in order to recall the notation. The Mori identity can be found at various places in the literature (Kawasaki 1970, Zwanzig 1976, Grabert 1977). Therefore we have attempted to be as concise as possible (§ 2.1) and have left for appendix 1 the explicit derivation of Onsager kinetic coefficient matrix elements in terms of the correlation function between the time derivative of the electrical and thermal currents. Some physical aspect is however integrated into § 2.2, where we indicate what is the 'dominant' correlation function for the various matrix elements of the Onsager tensor. In so doing we prepare the 'Boltzmann connection'. In § 3 we estimate such a 'dominant' term.

Section 4 contains the equivalence demonstration. The transport coefficients are rewritten under a form which *a priori* introduces matrix elements having the dimension of a time inverse. Such elements are identified with usual Boltzmann relaxation times for the electrical and thermal transport coefficients. The Seebeck coefficient describing the interplay between thermal force and electric effect has a hybrid form which is discussed.

Away from the critical point (i.e. in the mean-field region) the connection between Mori and Boltzmann descriptions is easily illustrated in the metallic limit ($kT \ll E_F$).

We conclude in § 5 with some remarks on the universality of critical exponents as predicted for these kinetic coefficients.

2. The Mori formalism

2.1. *Expressions for Onsager kinetic coefficients*

Since the Mori identity plays a major role in this work, it is appropriate to rewrite it in order to explain the notation. For a set of dynamical variables $\boldsymbol{A}$ (arranged in a column matrix), the generalised Langevin equation reads

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{A}(t) = \mathrm{i}\boldsymbol{\Omega} \cdot \boldsymbol{A}(t) - \int_0^t \boldsymbol{\Phi}(s) \cdot \boldsymbol{A}(t-s)\,\mathrm{d}s + \boldsymbol{F}(t) \tag{1}$$

where the first moment frequency matrix is a dyadic

$$\boldsymbol{\Omega} = -\mathrm{i}(\dot{\boldsymbol{A}}, \boldsymbol{A}^+) \cdot (\boldsymbol{A}, \boldsymbol{A}^+)^{-1} \tag{2}$$

and $\boldsymbol{A}^+$ is the (row matrix) composed of elements A_j^+, which is the Hermitian conjugate operator of A_j. The scalar product (F, G) is defined by

$$(F, G) = \beta^{-1} \int_0^\beta \mathrm{d}\lambda \langle \mathrm{e}^{\lambda H} F\, \mathrm{e}^{-\lambda H} G \rangle \tag{3}$$

where $\langle \ldots \rangle$ denotes the average over a canonical distribution with the whole Hamiltonian H, and $\beta = 1/kT$.

The matrix $\clubsuit(s)$ represents the memory function which describes the dissipation. It is related to the random force $F(t)$ by the fluctuation dissipation theorem (Kubo 1966):

$$\clubsuit(t) = (F(t), F^+(0)) \cdot (A, A^+)^{-1}. \tag{4}$$

In order that equation (1) be an identity, the random force has to be defined by

$$F(t) = \exp[t(1 - P)\mathrm{i}L](1 - P)\dot{A} \tag{5}$$

$$PA = (A, A^+)(A, A^+)^{-1}A \tag{6}$$

where P is obviously a projection operator acting upon a quantum operator A such that $\langle A \rangle = 0$. Zwanzig (1976) has clearly described the reason for such a definition, which is simply stated here.

Let us assume that there is a particular wavevector q for the problem, and decompose all quantities into their q-component. In such a case, Mori (1965) has shown that the Onsager kinetic coefficients L_{ij} relating linearly the dynamic variables

$$A = (A_1^x, A_1^y, A_1^z, A_2^x, \ldots) = (A_i)$$

to the generalised thermodynamic forces $X = (X_j)$ by

$$A_i = L_{ij}X_j, \qquad i, j = 1, 2 \tag{7}$$

are given by

$$L_{ij}^{\mu\nu} = \lim_{s \to 0} \lim_{q \to 0} \beta \int_0^\infty \mathrm{d}t \, \mathrm{e}^{-st}(A_{i,-q}^\mu(t), A_{j,-q}^{\nu*}(0)) \qquad \mu, \nu = x, y, z \tag{8}$$

where A^* is the complex conjugate of A.

In our case, A_1 and A_2 are respectively the electric current $(-eJ_N)$ and the thermal current (J_Q), which have quantum mechanical expressions

$$A_1 = (-\hbar e/m) \sum_{q,\sigma} q a_{q\sigma}^+ a_{q\sigma} \tag{9}$$

$$A_2 = (\hbar/m) \sum_{q,\sigma} q(E_q - E_F) a_{q\sigma}^+ a_{q\sigma}. \tag{10}$$

Whence the transport coefficients (the electrical conductivity σ, the thermal conductivity κ, the Seebeck coefficient S) are respectively given by

$$\sigma = L_{11}, \tag{11a}$$

$$\kappa = (L_{22} - L_{21}L_{11}^{-1}L_{12})T^{-1}, \tag{11b}$$

$$S = L_{11}^{-1}L_{12}T^{-1}. \tag{11c}$$

These expressions define the transport coefficients in terms of correlation functions of the electrical and thermal current operators between fluctuating states.

In the theory of irreversible processes, it is more appropriate to rewrite the transport coefficients in terms of the correlation functions of the time derivative of the two currents. In so doing, one takes into account the occurrence of different critical slowing down times (and lengths) for the various dissipative modes (currents).

One can easily show (see appendix 1) that the Onsager coefficients' matrix elements L_{ij} which appear in the right-hand side of (11) are given by

$$\beta(L^{-1})^{\mu\nu} = \{(A_q, A_q^+)^{-1}[\varphi_q - \mathrm{i}\Omega_q]\}^{\mu\nu} \tag{12}$$

where

$$\varphi_q = \int_0^\infty \Phi_q(s)\,\mathrm{d}s \tag{13}$$

contains the 'memory' of the fluctuating currents.

2.2. Expressions for the transport coefficients

It may be proved on the one hand that nó diffusion collective mode arises near T_c. Indeed, Ω is odd under time reversal in the absence of an applied magnetic field. Furthermore, since the critical behaviour only arises in the temperature derivative of the transport coefficients, it is sufficient to consider that the scattering mechanism of electrons by the order parameter fluctuations is a 'small' perturbation. The Hamiltonian H can be written as $H = H_0 + H_1$, where H_0 contains the driving mechanism for the critical behaviour. In modern language, H_1 could contribute to renormalised singularities or crossover phenomena of static properties.

For the non-critical transport properties, a given choice of H_1 will lead to specific critical exponents for the temperature derivative of the transport coefficients. Although we do not need an explicit form of H_1, one can imagine that it is Kasuya's H_{s-d} interaction Hamiltonian (Kasuya 1956). In such a case, it has been discussed elsewhere that one can linearise the above expressions for the electrical resistivity, and calculate its value in a first-order Born approximation in H_1 (Binder and Stauffer 1976, Ausloos 1976).

The linearisation is primarily important to simplify $F(t)$ after the expansion of the exponential factor in equation (5). Furthermore the non-linear contribution of $P\dot{A}$ is neglected with respect to the $\dot{A}$ term. This is based on the (reasonable) assumption that PA varies much more slowly than A, and can thus be considered as a constant on the time scale relative to the electronic mean free path. Notice also that $\langle PA \rangle = 0$ under time reversal[†].

Following such a linearisation procedure, it is a matter of trivial algebra to express φ_q in equation (12) in a form involving the time-dependent non-equilibrium correlation function between the time derivative $\dot{A}$ of the currents, namely

$$\beta \mathbf{L}^{-1} = (A, A^+)^{-1} \operatorname{Re} \int_0^\infty \mathrm{d}t (\dot{A}(t), \dot{A}^+(0)) \cdot (A, A^+)^{-1}. \tag{14}$$

The explicit inverse of $\mathbf{L}^{-1}$ is

$$\begin{pmatrix} L_{11} + L_{11}^{-1}L_{12}F^{-1}L_{21}L_{11}^{-1} & -L_{11}^{-1}L_{12}F^{-1} \\ -F^{-1}L_{21}L_{11}^{-1} & F^{-1} \end{pmatrix} \tag{15}$$

where $F = L_{22} - L_{21}L_{11}^{-1}L_{12}$ assuming that L_{11}^{-1} exists.

It is relatively cumbersome to carry through the following work if one expresses $(L_{ij})^{-1}$ in terms of a product of three matrices as in (14), each containing 36 elements.

Notice that two matrices involve static correlation functions only, i.e. $(A, A^+)^{-1}$. It is here assumed that such a quantity is a diagonal matrix, and the following notations are introduced

$$A_{ij}^{\mu\nu} = (A_i^\mu, A_j^{+\nu}) \tag{16}$$

[†] The definition of $\dot{A}$ is as usual $\dot{A} = \mathrm{i}L_1 A$, where L_1 is the perturbed Liouville operator, i.e. $\mathrm{i}L_1 A = (\mathrm{i}/h)[H_1, A]$.

with

$$A_{ij} = A_{ij}^{\mu\nu}\delta_{\mu\nu}.$$

We also define

$$Z = A_{11}A_{22} - A_{12}A_{21} \tag{17}$$

and

$$a_{ij}^{\mu\nu} = \mathrm{Re} \int_0^\infty \mathrm{d}t (\dot{A}_i^\mu(t), \dot{A}_j^{\nu+}(0)). \tag{18}$$

Because the second term of the element $(L^{-1})_{11}$ can be neglected (appendix 2), the final useful expressions for the transport coefficients become

$$\rho = \beta^{-1}Z^{-1}(\underline{A_{22}a_{11}A_{22}} - A_{21}a_{12}A_{22} - A_{22}a_{21}A_{12} + A_{12}a_{22}A_{21})Z^{-1} \tag{19a}$$

$$\kappa^{-1} = T\beta^{-1}Z^{-1}(A_{21}a_{11}A_{12} - A_{11}a_{12}A_{21} - A_{12}a_{21}A_{11} + \underline{A_{11}a_{22}A_{11}})Z^{-1} \tag{19b}$$

$$-S\kappa^{-1} = \beta^{-1}Z^{-1}(\underline{A_{22}a_{12}A_{11}} - A_{12}a_{22}A_{11} - \underline{A_{22}a_{11}A_{12}} + A_{12}a_{21}A_{12})Z^{-1}. \tag{19c}$$

The terms underlined are shown in the next section to involve the dominant contribution, hence the most relevant correlation function.

3. Leading contribution

Although equations (19) are the most important expressions, they do not immediately appear to be similar to the more familiar expressions derived from the relaxation time approximation of the Boltzmann equation, like

$$\rho = (m/ne^2)\tau_{\mathrm{el}}^{-1} \tag{20a}$$

or

$$\kappa = (n\pi^2/3m\beta^2 T)\tau_{\mathrm{th}}^{-1}. \tag{20b}$$

In § 4, it will be shown how the set of relaxation times entering expressions like (20) can be interpreted in terms of the $(\dot{A}(t), \dot{A}^+(0))$. However, let us calculate first the A_{ij}'s in a free-electron approximation (in such a case A_{ij} is truly diagonal). One has

$$A_{11} = (ne^2)/(m\beta) \tag{21a}$$

$$A_{12} = A_{21} = -e\sqrt{(2mE_\mathrm{F})}/(3\beta^3) \tag{21b}$$

$$A_{22} = (2/9)\sqrt{(2mE_\mathrm{F}^3)}/\beta^3. \tag{21c}$$

In order to estimate the relative order of magnitude of the a_{ij}'s one considers that kT_c is much smaller than E_F, which implies that a 'low-temperature' expansion is reasonable. Define the kernel $K_{ij}(t)$ such that

$$K_{ij}(t) = \mathrm{Re}(\dot{A}_i(t), \dot{A}_j^+(0)). \tag{22}$$

The identity

$$f(H) = \int \mathrm{d}E\, f(E)\delta(E - H) \tag{23}$$

can be used to write

$$a_{ij} = \int_0^\infty dt \int dE \, f(E) \delta(E-H) K_{ij}(t; E) \tag{24}$$

where

$$K_{ij}(t; E) = \int d\lambda \, \mathrm{Tr} \, e^{\lambda H} A_i(t) \, e^{-\lambda H} A_j^+(0) \delta(E-H). \tag{25}$$

The time integral can in practice be evaluated first. The remaining expression can then be considered as an energy derivative of some new kernel. After integration by parts, one obtains

$$a_{ij} = -\int dE \, \frac{\partial f(E)}{\partial E} G_{ij}(E) \tag{26}$$

with

$$G_{ij}(E) = \int^E d\mu \int dt \, K_{ij}(t; \mu). \tag{27}$$

Such an expression has so general a form that it does not require the precise form of $G_{ij}(E)$. It is valid beyond the Born approximation. In fact it has been implicitly used in a multiple scattering description of conduction processes in disordered systems (Levin *et al* 1970). In our case, we can notice useful relationships between different G_{ij}'s,

$$G_{12}(E) = -\frac{1}{e}(E - E_F)G_{11}(E) \tag{28a}$$

$$G_{22}(E) = \frac{1}{e^2}(E - E_F)^2 G_{11}(E). \tag{28b}$$

These expressions are immediate because the Fourier components of the heat current J_U and number current density J_N are related by

$$J_{U,q} = E_q J_{N,q}. \tag{29}$$

There is clearly no need to impose a free-electron assumption on the E_q spectrum in order to recover (28).

The next step consists in taking the low-temperature expansion of each a_{ij} according to the standard expansion of the Fermi distribution function $f(E)$. One obtains at once, e.g.

$$a_{11} = G_{11}(E_F) + \tfrac{1}{6}\pi^2 \beta^{-2} G_{11}^{(2)}(E_F) + O((\beta E_F)^{-4}) \tag{30}$$

and similarly for a_{12} and a_{22}, where the notation

$$G_{ij}^{(k)}(E_F) = \left[\frac{\partial^k}{\partial E^k} G_{ij}(E)\right]_{E_F} \tag{31}$$

has been introduced.

After evaluating such derivatives from (28), and substituting them into the definition (19) of the transport coefficients, one notices that due to the smallness of $1/\beta E_F$, the terms underlined in (19) are the main contributors.

After this work was completed, we found that simple relations as (28) have also been envisaged by Mjolsness and Visscher (1972) in a quite different context (plasma physics). In particular, if one of the currents vanishes, as imposed by experimental conditions, such authors have observed that Onsager coefficients are related by simple relations. Such a work indicates that if, for example, equation (29) holds the Wiedemann–Franz law follows easily. We have observed elsewhere a generalisation of such a statement to critical dynamics phenomena and indicated that it implies universal critical exponents. (Ausloos 1977).

4. Relaxation time 'approximation'

It is easily observed that when the memory function behaves like $\exp(-t/\tau)$ the relaxation time approximation (with constant τ) is recovered. However, the true nature of the relaxation time can only be found if it receives some interpretation and is not considered as a free parameter. We indicate here how the notion of relaxation time for electronic transport coefficients in equation (20) can still be used near a critical point in this formalism.

A matrix Γ is defined by

$$a_{ij} = A_{il}\Gamma_{lj} \tag{32}$$

in which each A_{ij} is supposed to be diagonal as in § 2. Furthermore they are proportional to the unit matrix if they are evaluated in a free-electron approximation as here. Thus equation (19) can be rewritten

$$\rho = \beta^{-1}Z^{-2}A_{11}A_{22}^2(\Gamma_{11} - A_{21}\Gamma_{12}A_{22}^{-1})(1 - X) \tag{33a}$$

$$\kappa^{-1} = T\beta^{-1}Z^{-2}A_{22}A_{11}^2(\Gamma_{22} - A_{12}\Gamma_{21}A_{11}^{-1})(1 - X) \tag{33b}$$

$$-S\kappa^{-1} = \beta^{-1}Z^{-2}A_{11}A_{22}A_{12}(A_{11}\Gamma_{12}A_{12}^{-1} - \Gamma_{11})(1 - X) \tag{33c}$$

where

$$X = A_{12}A_{21}/A_{11}A_{22} \tag{34}$$

which is a small quantity according to relations obtained in (21). Since $Z = A_{11}A_{22}(1 - X) - A_{11}A_{22}$, one has

$$\rho = \frac{m}{ne^2}\Gamma_{11}\left(1 - \frac{A_{21}}{A_{22}}\Gamma_{11}^{-1}\Gamma_{12}\right) \tag{35a}$$

$$\kappa^{-1} = \frac{3m}{n\pi^2 k_B^2 T}\Gamma_{22}\left(1 - \frac{A_{12}}{A_{11}}\Gamma_{22}^{-1}\Gamma_{21}\right). \tag{35b}$$

It is evident that Γ_1 and Γ_{22} both have the dimension of $(\text{time})^{-1}$. By comparison with the simple minded formulae like (19) one can thus identify

$$(\tau^{-1})_{11} \text{ with } (A_{22}\Gamma_{11} - A_{21}\Gamma_{12})A_{22}^{-1} \tag{36a}$$

and

$$(\tau^{-1})_{22} \text{ with } (A_{11}\Gamma_{22} - A_{12}\Gamma_{21})A_{11}^{-1} \tag{36b}$$

where τ^{-1} is a matrix having for elements the inverse relaxation time of the transport

coefficients. It is useful to notice that

$$A_{21}\Gamma_{12} \ll A_{22}\Gamma_{11} \tag{37a}$$

$$A_{12}\Gamma_{21} \ll A_{11}\Gamma_{22} \tag{37b}$$

by comparing (19) and (35). Such a case corresponds to the usual definition of the relaxation time orginating from, e.g., the (electrical current–electrical current) correlation function in the Kubo formula, i.e.

$$(\tau^{-1})_{11} = A_{11}^{-1} \lim_{s \to 0} \mathrm{Re} \int_0^\infty \mathrm{d}t \, \mathrm{e}^{-st} (\dot{A}_1^\mu(t), \dot{A}_1^{\nu*}(0)) \tag{38}$$

and similarly for the thermal conductivity. Hence, the Boltzmann relaxation time finds some expected definition.

The Seebeck coefficient requires some further writing. One obtains after substituting (32) into (19c)

$$ST = (A_{11}\Gamma_{12} - A_{12}\Gamma_{11})(A_{12}\Gamma_{21} - A_{11}\Gamma_{22})^{-1}$$

$$= \left(1 - \frac{A_{11}}{A_{12}}\Gamma_{12}\Gamma_{11}^{-1}\right)\left(\frac{A_{12}\Gamma_{11}}{A_{11}\Gamma_{22}}\right)\left(1 - \frac{A_{12}}{A_{11}}\Gamma_{21}\Gamma_{22}^{-1}\right)^{-1}. \tag{39}$$

Such a lengthy definition reflects the hybrid nature of the property, and the impossibility of defining a relaxation time to which S (or S^{-1}) would be proportional. Notice that *ratios* of inverse relaxation times appear. This, in some sense, draws more attention to the 'static' nature of S, i.e. the electronic entropy (Kelvin has indeed referred to S as the specific heat of electricity). However, another well known formula for S is that given by Mott (1936) where the electronic diffusion process is more apparent

$$S = \frac{\pi k^2 T}{3e} \left[\frac{\partial \ln \sigma(E)}{\partial E}\right]_{E_F} \tag{40}$$

where $\sigma(E)$ is the electrical conductivity of the material evaluated at the energy level E.

The complicated nature of (39) also indicates why the behaviour of such a coefficient in the vicinity of a critical point has been interpreted along two different lines, one called the 'transport entropy' model (Tang *et al* 1971), the other reflecting better the kinetic nature of S (Thomas *et al* 1972, Zorič *et al* 1973). Such different interpretations of S can be reconciled as follows. It is possible to write S as a sum of two contributions. Let us first notice that according to the above inequalities (37) and relations (30)–(31), one has

$$A_{11}a_{22} \simeq A_{22}a_{11} \simeq G_{11}(E_F) \tag{41}$$

and

$$a_{12} \simeq -e\left[\frac{\mathrm{d}}{\mathrm{d}E} \ln G_{11}(E)\right]_{E_F} a_{22}. \tag{42}$$

From (19), one has

$$-\beta S\kappa^{-1} = \frac{A_{12}}{A_{11}A_{22}}\left(\frac{a_{12}}{A_{12}} - \frac{a_{11}}{A_{11}} - \frac{a_{22}}{A_{22}}\right) \tag{43}$$

with

$$\beta\kappa^{-1} \simeq Ta_{22}/A_{22}^2 \tag{44}$$

which is correct up to $(kT/E_F)^2$. Whence some trivial algebra leads to

$$S = (2A_{12}/TA_{11})(1 - A_{22}a_{12}/2A_{12}a_{22})$$
$$= -\frac{\pi^2 k^2 T}{eE_F}\left[1 - \frac{E_F}{3}\frac{\mathrm{d}}{\mathrm{d}E}\ln G_{11}(E)\right]_{E_F}. \tag{45}$$

The first term is nothing other than the electronic specific heat contribution (Tang *et al* 1971), while the second term arises from the electronic scattering process, and is a generalisation of the Mott formula (40). The latter is exactly recovered if one approximates ρ as given in (19) by

$$\rho = \beta^{-1}a_{11}/A_{11}^2. \tag{36}$$

We must conclude this section by emphasising the usefulness of relations like (28) and the necessity of being able to express integrals in a_{ij}'s as energy integrals (27) before any further calculation.

5. Conclusion

Starting from the appropriate generalised Langevin equation of motion, electronic transport coefficients have received a general form near second-order phase transitions. They have been expressed in terms of correlation functions between the time derivative of the electrical and the thermal currents. These expressions are somewhat awkward and do not appear to resemble those written in the Boltzmann relaxation time approximation.

It has been possible on the one hand to simplify the formulae in the low-temperature degenerate electron gas limit. On the other hand, by introducing *a priori* a matrix of relaxation time, it has been possible to identify the Boltzmann relaxation time in terms of the previous correlation functions. The interpretation of such relaxation times is rather simple for the electrical resistivity and the thermal conductivity. In the former case, the relaxation time arises from electrical current—electrical current (time derivative) correlation function—while it arises from the corresponding correlation function for the thermal current in the latter case.

For the Seebeck coefficient however, one cannot define *one* relaxation time. It has been possible to show that a 'ratio of relaxation times' enters the definition. Therefore, the 'transport entropy model' based on a simple relation between static quantities (entropy and specific heat) can be now understood. However, if one pursues the analysis further, one can observe that the scattering contribution can also be presented as done by Mott. Both contributions are thus not equivalent but are complementary. Both terms must certainly be examined in the vicinity of a critical point.

Finally let us notice that the kernels $G_{ij}(E)$ are functionals of the appropriate susceptibility. Therefore when taking the temperature derivative of the transport coefficients, it can be easily predicted that a universal critical exponent has to be found, irrespective of an elastic scattering condition.

Acknowledgments

Appendix 1

It is usual to assume that $F_q(t)$ is very rapidly fluctuating with time. Because of the scalar product in (4), $\Phi(t)$ tends rapidly to zero. Therefore one can consider that a fast loss of memory occurs such that one can successively write

$$\int_0^t \boldsymbol{\Phi}_q(s) \cdot \boldsymbol{A}_q(t-s)\,\mathrm{d}s \simeq \int_0^\infty \boldsymbol{\Phi}_q(s)\,\mathrm{d}s\,\boldsymbol{A}_q(t) = \varphi_q\boldsymbol{A}_q(t). \tag{A1}$$

One can take the non-equilibrium average of the generalised Langevin equation written for the q component of the dynamic variable (currents A_i). The average of $F_q(t)$ vanishes. Furthermore, the average of the dynamic variable can be regarded as classical number. The Mori identity is thus easily rewritten and integrated to give

$$\boldsymbol{A}_q(t) = \boldsymbol{A}_q(0)\exp(\mathrm{i}\boldsymbol{\Omega}_q - \varphi_q)t. \tag{A2}$$

It is sufficient to take the scalar product of (A2) with respect to $\boldsymbol{A}_q^+(0)$, and integrate once again the resulting correlation function over t in order to obtain

$$\int_0^\infty (\boldsymbol{a}_q(t), \boldsymbol{A}_q^+(0))\,\mathrm{d}t = (\varphi_q - \mathrm{i}\boldsymbol{\Omega}_q)^{-1}(\boldsymbol{A}_q, \boldsymbol{A}_q^+) \tag{A3}$$

which readily shows that the right-hand side is nothing other than Mori form of the Onsager kinetic coefficients as defined in (8). In so doing one has obtained a concise expression for the electronic transport coefficients near a critical point.

Appendix 2

It is shown that the second term of the coefficient $(L^{-1})_{11}$ in (15) can be neglected in the case of metallic conduction.

Indeed if L_{21}^{-1} is not singular (as expected), $F^{-1}L_{21}L_{11}^{-1}$ is identical to $(L_{11}L_{21}^{-1}L_{22} - L_{12})^{-1}$ hence $F = T\kappa$. Therefore

$$L_{11}^{-1}L_{12}F^{-1} = S\kappa^{-1}. \tag{A4}$$

The second term of $(L^{-1})_{11}$ is thus of the order of $S\kappa^{-1}L_{21}L_{11}^{-1}$ or S^2T.

The Ioffe number (Wisniewski *et al* 1976) is defined for an isotropic system, but it can be considered as a tensor of elements $T(\sigma S^2\kappa^{-1})_{\mu\nu}$. If the elements of S^2 are thus smaller than a quantity about equal to the Lorenz number, the second term of $(L^{-1})_{11}$ can thus be neglected. Such is the case in metals.

References

Ausloos M 1976 *J. Phys. F: Metal Phys.* **6** 1723–30
—— 1977 *Solid St. Commun.* **21** 373–5

Balescu R 1961 *Physica* **27** 693
—— 1963 *Statististical Mechanics of Charged Particles* (London: Interscience) pp 268–74
Binder K and Stauffer D 1976 *Z. Phys.* B **24** 407
Cole R. H 1965 *J. Chem. Phys.* **42** 637
Edwards S F 1958 *Phil. Mag.* **3** 1020
Enz C P 1976 *Critical Phenomena* eds J Brey and R B Jones (Berlin: Springer) pp 80–110
Grabert H 1977 *Z. Phys.* B **26** 79–83
Green M S 1956 *J. Chem. Phys.* **25** 836–55
Kasuya T 1956 *Prog. Theor. Phys.* **16** 58
Kawasaki K 1970 *Ann. Phys., NY* **61** 1–56
Kubo R 1966 *Rep. Prog. Phys.* **29** 255
Levin K, Velicky B and Ehrenreich H 1970 *Phys. Rev.* B **2** 9387
Mjolsness R C and Visscher W M 1972 *Phys. Fluids* **15** 1854
Mori H 1965 *Prog. Theor. Phys.* **33** 423
Mott N F 1936 *Proc. R. Soc.* A **156** 368
Nakajima S 1958 *Prog. Theor. Phys.* **20** 948
Prigogine I and Résibois P 1961 *Physica* **27** 629
Résibois P 1964 *J. Chem. Phys.* **41** 2979
Tang S H, Craig P P and Kitchens T A 1971 *Phys. Rev. Lett.* **27** 593
Thomas G A, Levin K and Parks R D 1972 *Phys. Rev. Lett.* **29** 1321
Thouless D J 1976 *Phil. Mag.* **32** 877–9
Ueyama H 1975 *Physica* A **80** 98–104
Wisniewski S, Staniszewski B and Szymanik R 1976 *Thermodynamics of Nonequilibrium Processes* (Boston: Riedel) p 165
Zwanzig R W 1960 *J. Chem. Phys.* **33** 1338
—— 1965 *J. Chem. Phys.* **43** 714
—— 1976 *Molecular Fluids* eds R Balian and G Weill (London: Gordon and Breach) pp 1–3
Zorič I, Thomas G A and Parks R D 1973 *Phys. Rev. Lett.* **30** 22