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On the conductivity of topologically disordered systems

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Abstract. An exact analysis is presented for the configurationally averaged two-body Green function of a random tight-binding model characterized by topological (e.g. positional) disorder. A general consistency relation is found between one-body and two-body Green functions, thus providing a unique and consistent way of extracting the contribution of the two-body function to the conductivity, whenever the averaged one-body Green function is available from a given approximate theory. In the effective-medium approximation the conductivity problem reduces to the sum of a ladder series for the two-body function, or alternatively to the solution of a simple one-dimensional integral equation. For illustration some numerical calculations are reported for the random hard-sphere approximation: a comparison with other single-site calculations clearly shows the important role played by a proper inclusion of the structural properties and by the internal consistency of the theory.

1. Introduction

During recent years a new interest has emerged in developing self-consistent tight-binding schemes for the densities of states (DOSs) of liquid metals [1–8]. Such theories are quite general and may be extended to any system characterized by quenched liquid-like disorder such as alloys and doped semiconductors. The first attempt to extract some transport properties from a tight-binding model came from the pioneering work of Matsubara and Toyozawa [9] (MT) on the conductivity of impurity band semiconductors. That calculation provided the basis for several theories which have been proposed [10] for evaluating electronic or transport properties of a topologically (e.g. positionally) disordered system.

Recently, Logan and Winn [4] developed an exact diagrammatic description of the averaged Green functions, in analogy to liquid-state graph methods, thus showing [6] the equivalence between the effective-medium approximation (EMA) of Roth [11–14] and the single-superchain approximation (SSCA) proposed by Wertheim [15] in the context of classical dielectric theory. Moreover they have shown that, for a simple choice of the pair distribution function, the EMA is equivalent to the mean-spherical approximation of liquid-state theory for the pair distribution function of a classical liquid [16]. Analytical solutions of this problem are available, and may be extended to the electronic context, thus giving rise to new analytically tractable approaches to the study of DOSs and transport in the presence of topological disorder.

In this context it would be desirable to develop an analytically tractable theory for the conductivity, starting from the averaged two-body Green function which would be required together with the one-body function. It is generally believed [6] that in the limit of weak disorder (the Boltzmann regime) the two-body Green function could be approximated by a product of two one-body functions, thus breaking the average. However, on proceeding

in such a manner one finds that the resulting two-body function is not consistent with the approximations adopted in evaluating the one-body function [17, 18].

In this paper, in the framework of the exact diagrammatic description developed by Logan and Winn [4], we show the existence of a general consistency relation between two-body and one-body averaged Green functions. Such a relation provides a unique and consistent way of extracting the contribution of the two-body function to the DC conductivity, if the one-body function is available from a given approximate theory. In the low-density limit this method could be the starting point for a consistent evaluation of the conductivity in the context of some non-single-site theory, while in the high-density regime it could be employed for a systematic and consistent study of the conductivity in the framework of single-site theories. To our knowledge the best of these theories is the EMA which is believed [8, 17] to be the most natural extension of the coherent-potential approximation for diagonal (e.g. substitutional) disorder to the case of topological disorder. At the SSCA/EMA level our conductivity problem is reduced to the solution of a simple one-dimensional integral equation, and the formal result of Itoh *et al* [18] is recovered. As shown by Winn and Logan [6], for some simple choice of the pair distribution function, the analogy with the mean-spherical approximation of liquid-state theory may be employed in order to obtain an analytically tractable theory, and for illustration some numerical calculations are presented in the random-hard-sphere approximation.

Section 2 is devoted to a general survey of the perturbative expansions for the averaged one-body and two-body Green functions in the presence of topological disorder. The static conductivity is written in terms of an averaged two-body function whose exact expansion is discussed together with the general topological reduction and renormalization of the contributing diagrams. In section 3 a general proof is given for the topological equivalence of the diagrams contributing to the one-body and two-body functions, thus recovering a general consistency relation between such functions. For illustration, the method is shown to yield analytically tractable theories for the conductivity in the opposite limits of low and high density. In the low-density regime the conductivity problem is addressed in the simple Elyutin model [19], which provides an interesting example of an analytical non-single-site approximation. Then, in the high-density regime, single-site theories are taken into consideration. In section 4 the conductivity problem is developed at the SSCA/EMA level, giving rise to a ladder expansion for the two-body function. Finally in section 5 some numerical results are presented in the random-hard-sphere approximation, and are compared to other single-site calculations.

2. Topological disorder: averages and perturbative expansions

In order to describe the electronic properties, a disordered system is commonly represented by a random ensemble of N localized Wannier states filled with N_e electrons. The filling fraction $y = N_e/N$ may differ from unity in the presence of doping. Transport is allowed via a non-zero matrix element of the Hamiltonian connecting different states. Ignoring the presence of spin and of any interaction among the electrons we can write the simple one-particle tight-binding Hamiltonian as

$$\hat{H} = \sum_{i \neq j} V_{ij} C_i^+ C_j \quad (1)$$

where C_i , C_i^+ are annihilation and creation operators for an electron on the local site i , with a centre-of-mass position \mathbf{R}_i , and the sums run over the N sites. The transfer-matrix element $V_{ij} = V(\mathbf{R}_i, \mathbf{R}_j)$ is supposed to depend only on the coordinates of the sites i, j .

For any given configuration the Green function is defined by

$$G_{ij}(z) = \langle 0 | C_i \frac{1}{z - \hat{H}} C_j^+ | 0 \rangle \quad (2)$$

where $|0\rangle$ is the vacuum and z is a complex variable. G_{ij} satisfies the equation of motion

$$zG_{ij}(z) = \delta_{ij} + \sum_{k \neq i} V_{ik} G_{kj}(z) \quad (3)$$

which may be expanded to give the locator series.

Diagonal and off-diagonal configurational averages are defined by

$$G(z) = \langle G_{ii}(z) \rangle \quad (4a)$$

$$G(z, \mathbf{R} - \mathbf{R}') = \frac{1}{\rho^2} \left\langle \sum_{i \neq j} G_{ij}(z) \delta^3(\mathbf{R}_i - \mathbf{R}) \delta^3(\mathbf{R}_j - \mathbf{R}') \right\rangle \quad (4b)$$

where ρ is the density of sites. Performing an averaging of equation (3) we find

$$zG(z) = 1 + \rho \int d^3 \mathbf{R}' G(z, \mathbf{R} - \mathbf{R}') V(\mathbf{R}' - \mathbf{R}). \quad (5)$$

An exact analysis of the averaged one-body Green functions has been developed by Logan and Winn [4] starting from equations (4) and (5), and using the methods of liquid-state graph theory.

The averaged Green function $G(z)$ satisfies the exact relations

$$zG(z) = 1 + \rho [G(z)]^2 \int d(2) H(1, 2) V(2, 1) \quad (6)$$

$$H(1, 2) = C(1, 2) + \rho G(z) \int d(3) H(1, 3) C(3, 2) \quad (7)$$

where $i = 1, 2, \dots$ is shorthand for \mathbf{R}_i , and $d(i) \equiv d^3 \mathbf{R}_i$. The function $H(1, 2)$ is related to the averaged off-diagonal Green function

$$G(z, 12) = G(z) H(1, 2) G(z). \quad (8)$$

$H(1, 2)$ and $C(1, 2)$ have a diagrammatical representation in terms of s -site diagrams consisting of a path of V_{ij} bonds connecting the s sites from 1 to 2, with additional connectors coming from the s -particle structural distribution functions $g_s(1, 2, \dots, s)$. The number of stages associated with each path may be larger than s since the path can touch any site several times. The perturbative expansion of $H(1, 2)$ is basically a renormalized version of the locator expansion of equation (3). $H(1, 2)$ is the sum of all of the diagrams with end sites labelled 1 and 2, a factor ρ for each internal site, a factor $G(z)$ for each internal stage, and no one-articulation points. Equation (7) relates $H(1, 2)$ to the irreducible part $C(1, 2)$ which is the sum of all of the diagrams that lack both one-articulation and one-chain bridge points. All of the centre-of-mass position vectors \mathbf{R}_i for the internal sites are integrated over. The topological reduction of diagrams is illustrated in figure 1.

Both $H(1, 2)$ and $C(1, 2)$ are functions of z , the dependence being implicit in the $G(z)$ -dependence. Equation (7), which is exact, has been referred to as the analogous Ornstein-Zernike (OZ) equation [4].

A self-energy is defined as

$$S(z) = \rho G(z) \int d(2) H(1, 2) V(2, 1) \quad (9)$$

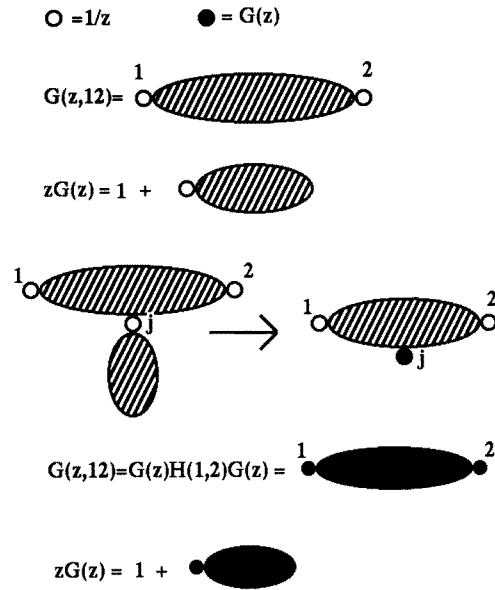


Figure 1. Topological reductions of one-body diagrams. The hatched areas represent the sums of all of the unrenormalized diagrams with the same fixed end points 1, 2 (the second row) or with coincident end points (the third row). All one-articulated parts may be eliminated by multiplying by $zG(z)$ at each stage, thus substituting $G(z)$ for $1/z$ as shown in the fourth row. The filled regions in the fifth and sixth rows represent the sums of all of the renormalized diagrams (=free of one-articulation points).

and from equation (6) the diagonal Green function reads

$$G(z) = \frac{1}{z - S(z)}. \quad (10)$$

The OZ equation can be solved only if a closure relation is available, and in practice some approximation must be invoked in order to get a closed expression for such a relation.

The problem of calculating the static conductivity for a topologically disordered assembly of local electronic states has been studied by several authors [9, 17, 18, 20], making use of different kinds of approximation. Our central interest is in the static conductivity tensor which reads according to Kubo [21]

$$\sigma = \lim_{s \rightarrow 0^+} \int_0^\infty dt \int_0^\beta d\lambda e^{-st} \langle \mathbf{J}(-i\hbar\lambda) \cdot \mathbf{J}(t) \rangle \quad (11)$$

where \mathbf{J} is the current density vector and $\beta = 1/K_B T$. The current-current averaged correlation function can be written in terms of Green functions yielding [9]

$$\sigma = -\frac{\pi e^2}{\hbar} \left\langle \sum_{i \neq j} \sum_{k \neq l} \int dE \mathbf{R}_{ij} \cdot \mathbf{R}_{kl} V_{ij} V_{kl} d_{li}(E) d_{jk}(E) \left(-\frac{df(E)}{dE} \right) \right\rangle \quad (12)$$

where $f(E)$ is the Fermi distribution, $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ and $d_{ij}(E) = -(1/\pi) \text{Im} G_{ij}(E + i0)$.

For a random distribution of the sites, the conductivity tensor should be isotropic; taking into account the spin degeneracy the scalar conductivity reads

$$\sigma = \frac{2\pi e^2}{3\hbar} \int dE M(E) \left(-\frac{df(E)}{dE} \right) \quad (13)$$

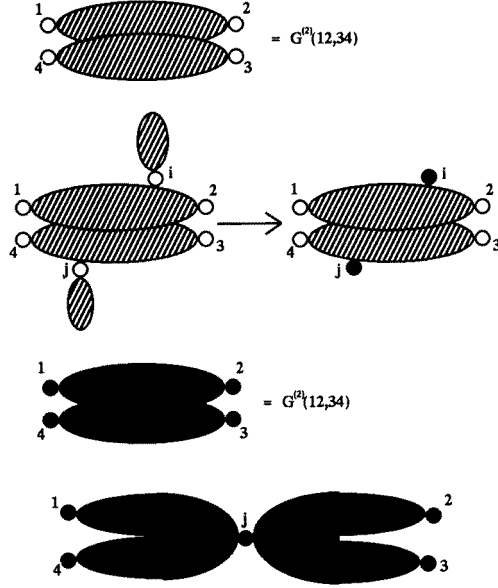


Figure 2. Topological reductions of two-body diagrams. In the first row the overlapping hatched areas represent the sums of all of the unrenormalized diagrams contributing to $G(12, 34)$. The overlap may be due to the intersection of the paths on some common site or, even when the paths are disconnected, to the structural connectors between the sites. As shown in the second row, the same renormalization procedure as was adopted for the one-body function allows one to eliminate the one-articulated parts with the only exception of overlapping one-articulated parts whose articulation point belongs to both of the paths. In the third row, the overlapping filled areas represent the renormalized diagrams. These are free of one-articulation points with the only exception of the intersection points between the paths. The subclass of renormalized diagrams with at least a bridge point is shown in the fourth row.

where

$$M(E) = \frac{1}{2\pi^2} \operatorname{Re} [A(E^+, E^+) - A(E^+, E^-)] \quad E^\pm = E \pm i0 \quad (14)$$

with

$$A(z, z') = \left\langle \sum_{i \neq j} \sum_{k \neq l} (\mathbf{W}_{ij} \cdot \mathbf{W}_{kl}) G_{jk,li}^{(2)}(z, z') \right\rangle \quad (15)$$

and with the notation $\mathbf{W}_{ij} = \mathbf{R}_{ij} V_{ij}$. Here $G_{ij,kl}^{(2)}(z, z') = G_{ij}(z)G_{kl}(z')$ is the two-body function which factorizes in the present single-particle description.

The averaged two-body function is introduced in analogy to the one-body case (4):

$$\begin{aligned} G^{(2)}(z, 12; z', 34) &= \frac{1}{\rho^4} \left\langle \sum_{ij} \sum_{kl} G_{jk}(z) G_{li}(z') \right. \\ &\quad \left. \times \delta^3(\mathbf{R}_j - \mathbf{R}_1) \delta^3(\mathbf{R}_k - \mathbf{R}_2) \delta^3(\mathbf{R}_l - \mathbf{R}_3) \delta^3(\mathbf{R}_i - \mathbf{R}_4) \right\rangle. \end{aligned} \quad (16)$$

This definition incorporates both diagonal and off-diagonal parts since no restrictions are imposed to the indices. Equation (15) now reads

$$A(z, z') = \rho^4 \int d(1) d(2) d(3) d(4) G^{(2)}(z, 12; z', 34) (\mathbf{W}(4, 1) \cdot \mathbf{W}(2, 3)) \quad (17)$$

with the obvious notation $\mathbf{W}(1, 2) = V(1, 2)\mathbf{R}_{12}$. Notice that the restriction on indices in equation (15) requires the constraints $1 \neq 4$ and $2 \neq 3$ for the integration variables of equation (17). However, the formal elimination of a single point from the integration domain has no practical relevance unless the two-body function had a singular behaviour

$$G^{(2)}(12, 34) \sim \text{regular part} + \delta^3(\mathbf{R}_1 - \mathbf{R}_4).$$

This is indeed the case, since from equation (16) for $i = j$ a contribution arises that is proportional to a delta function. Such a contribution must be omitted in order to reproduce equation (15) with the proper restrictions on indices. This basically means that the two-body function $G^{(2)}(12, 34)$ in equation (17) must be simply evaluated for $1 \neq 4$ and $2 \neq 3$.

An exact expansion of the averaged two-body Green function follows from equation (16) in analogy to the one-body expansion previously discussed. Thus substituting $G^{(2)}(z, 12; z', 34)$ for $G(z, 12)$ in the exact analysis of Logan and Winn [4], and retaining almost all of the details unchanged, we are able to represent the two-body function in terms of double-chain diagrams. In fact the only relevant difference arises from the presence of two one-body Green functions inside the average in equation (16), so the product of the respective locator expansions gives rise to diagrams connected by two different chains of V_{ij} -bonds. The generic s -site diagram contributing to $G^{(2)}(z, 12; z', 34)$ has four end points labelled 1, 2, 3 and 4; it consists of two paths of $V(ij)$ -connectors through the s sites and respectively from 1 to 2 and from 3 to 4. Additional connectors come from the s -particle structural distribution function $g_s(1, 2, \dots, s)$.

Even the topological reduction of the diagrams remains almost unchanged in passing from the one-body to the two-body analysis, thus allowing for the elimination of all of the one-articulated parts (as shown in figure 2) with the only exception of overlapping one-articulated parts whose articulation point belongs to both the paths. That is, the sum of all of the possible decorating one-articulated parts amounts to $zG(z)$ at each stage. Thus any renormalized diagram is free of one-articulation points (with the above-mentioned exception of the intersection points between the paths), and the factors $G(z)$, $G(z')$ are associated respectively with each stage of the first and of the second path. A factor ρ is then associated with any internal site, and all of the internal coordinates are integrated over.

In order to evaluate the conductivity we may neglect a class of diagrams whose contribution to the integral in equation (17) is exactly zero. In fact the diagrams for $G^{(2)}(12, 34)$ containing at least a bridge point are even with respect to the inversion of the end-point coordinates $1 \leftrightarrow 4$ or $2 \leftrightarrow 3$. (By bridge point we mean a point where the diagram may be cut into two pieces, one containing the end points 1, 4, and the other containing the end points 2, 3.) Since the vectors \mathbf{W} are obviously odd with respect to the interchange of their extremities, we may neglect the whole class of diagrams containing such bridge points. We will denote by $\bar{G}^{(2)}$ the relevant part of $G^{(2)}$, i.e. the part contributing to the conductivity, given by the sum of all of the renormalized diagrams which are free of bridge points, with $1 \neq 4$ and $2 \neq 3$.

3. Exact consistency relations and the variational approach

In this section we show the existence of a topological equivalence between the class of diagrams contributing to the two-body function $G^{(2)}$ and the class of diagrams contributing

to the one-body function $G(z, 12)$. For any diagram contributing to the two-body function $G^{(2)}(z, 12; z, 34)$ we obtain a diagram for the one-body function $G(z, 14)$ by just connecting together the end points 2, 3 with a $V(2, 3)$ -factor and integrating over the corresponding position vectors. Conversely by deleting a $V(i, j)$ -connector in a diagram for $G(z, 14)$ we obtain a diagram for $G^{(2)}(z, 1i; z, j4)$. Moreover all of the double-path diagrams contributing to the two-body function are obtained by deleting a $V(i, j)$ -connector in any possible position from the diagrams contributing to the one-body function. A similar topological equivalence was first employed by Itoh *et al* [18] at the EMA level. However, we observe that such correspondence is completely general and follows from the exact expansions of the Green functions discussed above. In other words we have a consistent prescription for extending all of the approximations adopted in the description of the structural properties from the one-body to the two-body function.

The topological equivalence gives rise to an exact consistency relation which is of general validity. In order to prove it, we start by generalizing the definition (2) for the Green function in an operatorial notation:

$$(z - \hat{H})\hat{G} = \hat{I}. \quad (18)$$

For the following discussion \hat{H} is any Hamiltonian, and the matrix elements

$$H_{ij} = \langle i | \hat{H} | j \rangle \quad (19)$$

are taken between an arbitrary basis set of states $\{|i\rangle\}$. Differentiating equation (18) with respect to H_{kl} we obtain

$$-\frac{\partial \hat{H}}{\partial H_{kl}} \hat{G} + (z - \hat{H}) \frac{\partial \hat{G}}{\partial H_{kl}} = 0 \quad (20)$$

where in the derivative $\partial/\partial H_{kl}$ the conjugated term H_{lk} is kept fixed. We introduce the operator $\hat{O}^{(kl)}$ whose matrix elements are

$$\hat{O}_{ij}^{(kl)} = \delta_{ik}\delta_{jl} = \left(\frac{\partial \hat{H}}{\partial H_{kl}} \right)_{ij} \quad (21)$$

and, with such notation, equation (20) reads

$$-\hat{O}^{(kl)} \hat{G} + (z - \hat{H}) \frac{\partial \hat{G}}{\partial H_{kl}} = 0. \quad (22)$$

Then, by multiplying by \hat{G} ,

$$\frac{\partial \hat{G}}{\partial H_{kl}} = \hat{G} \hat{O}^{(kl)} \hat{G}. \quad (23)$$

This last relation can be seen as a generalized Ward identity: for the special case where $k = l$

$$\sum_k \frac{\partial \hat{G}}{\partial H_{kk}} = \hat{G} \hat{G}. \quad (24)$$

Thus, from the definition (18),

$$\frac{\partial \hat{G}}{\partial z} = -\sum_k \frac{\partial \hat{G}}{\partial H_{kk}} \quad (25)$$

which together with equation (24) gives the usual Ward identity

$$\frac{\partial \hat{G}}{\partial z} = -\hat{G} \hat{G}. \quad (26)$$

The off-diagonal contribution ($k \neq l$) of equation (23) in its explicit matrix representation reads

$$\frac{\partial G_{ij}}{\partial H_{kl}} = G_{ik} G_{lj}. \quad (27)$$

If \hat{H} does not contain any interaction term, then the right-hand side of this relation is the two-body Green function. Equation (27) translates the above-discussed topological equivalence between the diagrams contributing to one-body and two-body functions, since in the representation of the local sites $H_{kl} = V(k, l)$. We notice that in the derivative the conjugated term $V(l, k)$ is kept fixed; otherwise the inverted term $G_{il} G_{kj}$ must be added to the right-hand side of equation (27).

Regarding the off-diagonal matrix element as a two-point function

$$V(k, l) = V(\mathbf{R}_k, \mathbf{R}_l) \quad (28)$$

we are allowed to write for a generic functional $F[V]$

$$\begin{aligned} & \frac{\delta F[V(\mathbf{R}_1, \mathbf{R}_2)]}{\delta V(\mathbf{S}_1, \mathbf{S}_2)} \\ &= \lim_{\epsilon \rightarrow 0} \frac{F[V(\mathbf{R}_1, \mathbf{R}_2) + \epsilon \delta^3(\mathbf{R}_1 - \mathbf{S}_1) \delta^3(\mathbf{R}_2 - \mathbf{S}_2)] - F[V(\mathbf{R}_1, \mathbf{R}_2)]}{\epsilon} \end{aligned} \quad (29)$$

and

$$\frac{\delta V(k, l)}{\delta V(i, j)} = \delta^3(ik) \delta^3(jl). \quad (30)$$

Provided that the one-body averaged Green function (4b) is known as a functional $G(1, 2; V)$ of the generic off-diagonal matrix element of the Hamiltonian, the functional derivative follows:

$$\frac{\delta G(1, 2; V)}{\delta V(3, 4)} = \frac{1}{\rho^2} \left\langle \sum_{i \neq j} \frac{\delta G_{ij}(z)}{\delta V(3, 4)} \delta^3(1i) \delta^3(2j) \right\rangle \quad (31)$$

where we have made use of the fact that the function $V(3, 4)$ does not depend on the chosen configuration. The functional derivative of G_{ij} is

$$\frac{\delta G_{ij}(z)}{\delta V(3, 4)} = \sum_{k \neq l} \frac{\partial G_{ij}(z)}{\partial H_{kl}} \frac{\delta V(k, l)}{\delta V(3, 4)} \quad (32)$$

where of course in the derivative $\partial/\partial H_{kl}$ the conjugated term H_{lk} is kept fixed since the indices k, l are summed over. Inserting equation (32) and (30) in equation (31):

$$\frac{\delta G(1, 2; V)}{\delta V(3, 4)} = \frac{1}{\rho^2} \left\langle \sum_{i \neq j} \sum_{k \neq l} \left(\frac{\partial G_{ij}(z)}{\partial H_{kl}} \right) \delta^3(1i) \delta^3(2j) \delta^3(3k) \delta^3(4l) \right\rangle. \quad (33)$$

Then finally, making use of the off-diagonal identity (27) and of the definition (16), we obtain for $3 \neq 4$ and $1 \neq 2$

$$\frac{\delta G(1, 2; V)}{\delta V(3, 4)} = \rho^2 G^{(2)}(1, 3; 4, 2) \quad (34)$$

which is an exact consistency relation for consistency between one-body and two-body functions. However, we must notice that such a functional derivative is not easily evaluated in general. In fact, in the most common case, $V(i, j) = V(\mathbf{R}_i - \mathbf{R}_j)$ and $G(i, j)$ is known

as a functional of $V(\mathbf{R}) = V(-\mathbf{R}) \equiv V^*(\mathbf{R})$. Then the functional derivative with respect to V contains two contributions:

$$\frac{\delta G}{\delta V} = \left(\frac{\delta G}{\delta V} \right)_{V^*} + \left(\frac{\delta G}{\delta V^*} \right)_V = \rho^2 [G^{(2)}(12, 34) + G^{(2)}(13, 24)] \quad (35)$$

and the symmetrized two-body Green function on the right-hand side does not play any role in the conductivity problem, where the antisymmetrized part is relevant.

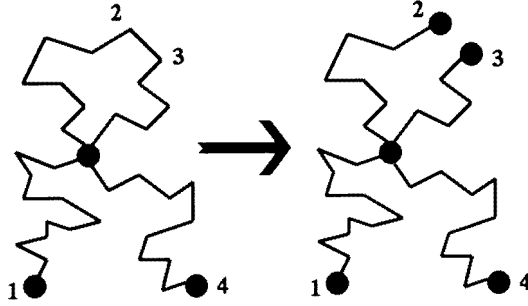


Figure 3. The variational derivative with respect to V of a one-body diagram is obtained by deleting a V -connector in any possible position, thus yielding a double-path diagram. If the deleted V -connector were inside a one-articulated part then the diagram arising would have at least a bridge point in the articulation point. The figure illustrates such a correspondence in the simple case of a chain diagram.

Going back to the conductivity problem, the consistency relation (34) simplifies when dealing with the relevant part $\tilde{G}^{(2)}$ of the two-body function. In fact, inserting equation (8), the relation (34) reads

$$\rho^2 \tilde{G}^{(2)}(z, 12; z, 34) = [G(z)]^2 \frac{\delta H(1, 4)}{\delta V(2, 3)} \quad (36)$$

since any variational derivative of $G(z)$ adds diagrams which contain at least one bridge point, and as previously discussed this class of diagrams does not contribute to the conductivity for symmetry reasons. In order to prove such an assertion we observe that the off-diagonal one-body function $G(z, 12)$ depends on z implicitly through the function $G(z)$, since a factor $zG(z)$ has been added at some stage of the renormalized diagrams to take into account all of the decorating one-articulated parts. Taking the variational derivative of the factor $zG(z)$ with respect to V is equivalent to opening the single path of any one-body diagram inside a one-articulated part. The double-path diagram which arises has a bridge point in the one-articulation point of the corresponding one-body diagram, as illustrated in figure 3. Thus we may neglect the functional dependence of $G(z)$ on V in the functional derivative of $G(z, 12)$, when we are interested in the relevant part $\tilde{G}^{(2)}$ of the two-body function.

Equation (36) is very general since no special assumptions or approximations have been employed in its derivation. Such a variational consistency relation is all we need in order to address the conductivity problem through equation (17), provided that the one-body Green function is available as a functional of the off-diagonal matrix element V .

In order to illustrate the method, we show that an analytically tractable theory emerges in both of the opposite limits of high and low density, starting from corresponding approximations for the one-body Green function: respectively, single-site theories at high density and the Elyutin (see [19, 4]) expansion at low density.

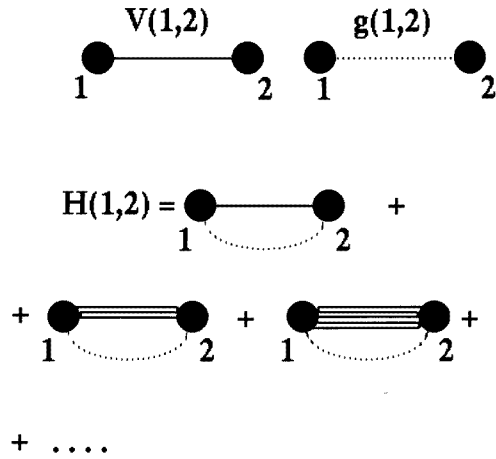


Figure 4. Two-site diagrams contributing to the one-body function $H(1,2)$ in the Elyutin approximation.

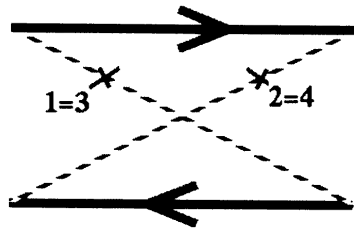


Figure 5. The off-diagonal part, equation (43), of the averaged two-body Green function according to the conventional diagrammatic description; here the arrows represent off-diagonal Green functions, and the crosses refer to scattering processes.

3.1. Low density

The model proposed by Elyutin (see [19, 4]), in the low-density limit, is the simplest example of a non-single-site theory, and basically contains only the leading terms in an expansion in powers of the density ρ . The generic renormalized s -site diagram contributing to the one-body Green function has a factor ρ^{s-2} since any site contributes with a factor ρ except for at the end points of the diagram. Thus the leading term in powers of ρ is given by the sum of all of the diagrams with $s = 2$. Such diagrams are shown in figure 4. Neglecting higher powers of ρ , from equation (7) $H(1,2) \approx C(1,2)$, and the irreducible part $C(1,2)$ is given by the expansion in terms of such diagrams lacking in internal sites ($s = 2$):

$$H(1,2) \approx C(1,2) = g_2(1,2) [V(1,2) + V(1,2)G(z)V(2,1)G(z)V(1,2) + \dots] \tag{37}$$

where the only structural connector $g_2(1,2)$ is the pair distribution function. The series is readily summed and insertion in equation (8) yields

$$G(1,2) = \left[\frac{g_2(1,2)V(1,2)G(z)^2}{1 - G(z)^2V(1,2)V(2,1)} \right]. \tag{38}$$

In the present derivation the matrix elements $V(1, 2)$ and $V(2, 1)$ are regarded as independent quantities in order to evaluate the functional derivative occurring in equation (34). As previously discussed this point is crucial if one is to obtain the correct response function.

The self-energy, equation (9), reads

$$S(z) = \rho \int d^3 \mathbf{R}_{12} \frac{g_2(1, 2) |V(1, 2)|^2}{z - S(z) - |V(1, 2)|^2 / (z - S(z))}. \quad (39)$$

This self-consistency equation is equivalent to the renormalized perturbation series for the self-energy truncated at the second-order term [4, 22]. (Such a procedure is exact for a Cayley tree and in fact, taking into account all of the decorating parts, all of the diagrams retained have the topology of a Cayley tree with a connectivity ranging from 0 to ∞ at any site [4, 19].)

The variational derivative of equation (38) yields according to equation (36)

$$\begin{aligned} \rho^2 \bar{G}^{(2)}(z, 12; z, 34) \\ = \frac{G(z)^2 g_2(1, 4)}{[1 - G(z)^2 |V(1, 4)|^2]^2} \delta(12) \delta(34) \\ + \frac{G(z)^4 g_2(1, 4) V(1, 4)^2}{[1 - G(z)^2 |V(1, 4)|^2]^2} \delta(24) \delta(13). \end{aligned} \quad (40)$$

The first term on the right-hand side can be seen as the product

$$g_2(1, 4) \left[\frac{G(z)}{1 - G(z)^2 |V(1, 4)|^2} \delta(12) \right] \left[\frac{G(z)}{1 - G(z)^2 |V(1, 4)|^2} \delta(34) \right] \quad (41)$$

where the terms in square brackets represent the sums of all of the two-site contributions to the diagonal Green function:

$$\left[\frac{G(z)}{1 - G(z)^2 |V(1, 4)|^2} \right] = G(z) + G(z) V(1, 4) G(z) V(4, 1) G(z) + \dots \quad (42)$$

The product of such terms in equation (41) is easily interpreted as the diagonal-diagonal part of the averaged two-body Green function, which does not reduce to the mere product of two diagonal-averaged Green functions in the present theory.

The second term on the right-hand side of equation (40) can be interpreted as the product of two off-diagonal Green functions:

$$G(1, 2) G(3, 4) \left[\frac{\delta(13) \delta(24)}{g_2(1, 2)} \right] \quad (43)$$

according to equation (38), and apart from the factor in brackets which forces the extremes to coincide and avoids a double presence of the pair distribution function. As shown in figure 5 this term belongs to the class of *maximally crossed* [23, 24] diagrams (in the conventional diagrammatic description) which play an important role at low density, giving rise to a decreasing of the conductivity and eventually to a metal-insulator transition due to the localization of states. We will show that such a term gives a negative contribution to the total conductivity of the system.

Denoting by α and β the diagonal and off-diagonal contributions respectively:

$$\alpha(z, \mathbf{R}) = \left[\frac{G(z)}{1 - G(z)^2 |V(\mathbf{R})|^2} \right] \quad (44a)$$

$$\beta(z, \mathbf{R}) = \left[\frac{G(z)^2 |V(\mathbf{R})|}{1 - G(z)^2 |V(\mathbf{R})|^2} \right] \quad (44b)$$

where we finally assume $V(1, 2) \equiv V(\mathbf{R}_1 - \mathbf{R}_2)$, and then inserting equation (40) in equation (17):

$$A(z, z') = \rho^2 \int d^3\mathbf{R} R^2 |V(\mathbf{R})|^2 g_2(\mathbf{R}) [\beta(z, \mathbf{R})\beta(z', \mathbf{R}) - \alpha(z, \mathbf{R})\alpha(z', \mathbf{R})]. \quad (45)$$

Then according to equations (13) and (14), at $T = 0$, the conductivity follows as

$$\sigma = \frac{2e^2}{3\pi\hbar} \rho^2 \int d^3\mathbf{R} R^2 |V(\mathbf{R})|^2 g_2(\mathbf{R}) \left[(\text{Im} \alpha(E_f, \mathbf{R}))^2 - (\text{Im} \beta(E_f, \mathbf{R}))^2 \right] \quad (46)$$

where E_f is the Fermi energy. This is the leading term in an expansion of the conductivity in powers of ρ , and it incorporates the contribution of all of the two-site diagrams for the averaged two-body Green function. As anticipated we notice the opposite sign of the contributions due to the functions α and β , e.g. diagonal and off-diagonal parts of the averaged two-body Green function. In fact the diagram of figure 5 (off-diagonal) gives rise to the product of two β -functions in equation (45) and thus to a negative contribution to the conductivity in equation (46).

It is worth noticing that for the special case where $g_2(R) = 1$, $V(R) = V_0/R^3$, the solution of the self-consistency equation (39) yields [4] a constant self-energy $S(E^+) = i\gamma$, where $\gamma = (2\pi^2/3)\rho V_0$. In such a case the integral in equation (46) can be analytically evaluated:

$$\sigma = 2 \left(\frac{2\pi}{3} \right)^3 \frac{e^2}{\hbar} V_0^{8/3} \rho^3 \frac{\sin(5\theta/3)}{E_f(E_f^2 + \gamma^2)^{5/6}} \quad (47)$$

where $\theta = \arctan(E_f/\gamma)$. However, even more realistic approximations, for both the pair distribution function g_2 and the Hamiltonian matrix element $V(R)$, may be explored in this low-density limit.

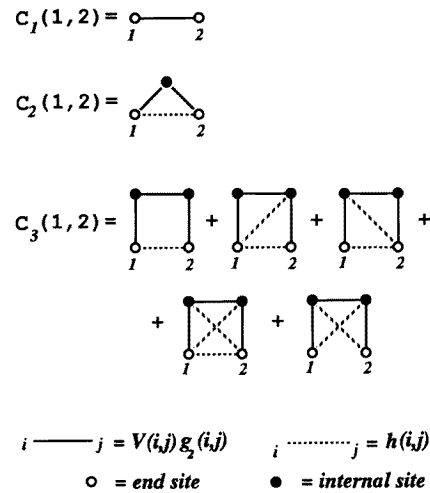


Figure 6. First-, second- and third-order diagrams contributing to $C(1, 2)$ in the single-site approximation.

3.2. High density

A single-site theory consists [4] in an approximate summation of the diagrams contributing to $C(1, 2)$: only single-site diagrams are retained, i.e. the class of diagrams with a one-to-one correspondence between sites and stages in the path. Moreover the structural connectors

$g_s(1, 2, \dots, s)$ are approximated by the Kirkwood expansion [25]

$$g_s(1, 2, \dots, s) = \prod_{i=1}^{s-1} \prod_{j=1+1}^s [h(ij) + 1] \tag{48}$$

where the direct short-range connector is $h(ij) = g_2(ij) - 1$. A generic s -site diagram contributing to $C(1, 2)$ consists of a simple s -point chain together with a sufficient number of h -connectors to render the diagram irreducible. First-, second- and third-order diagrams contributing to $C(1, 2)$ are shown in figure 6. A single-site theory is expected to be quite reliable at high density; however, it is not an exactly soluble theory and further approximations are required in order to close the OZ equation (7).

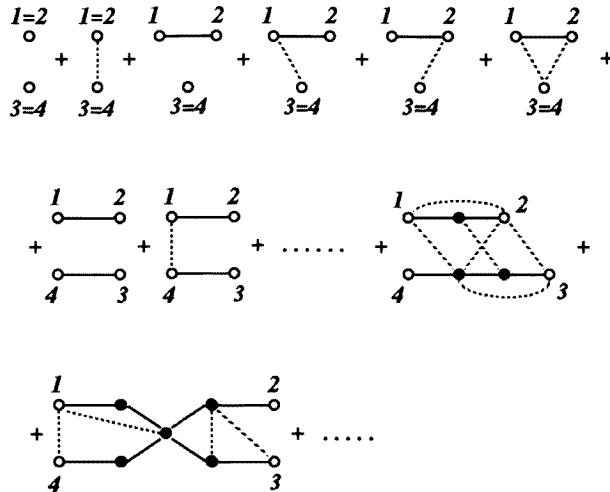


Figure 7. Some typical single-site double-chain diagrams contributing to $G^{(2)}(z, 12; z', 34)$. The meaning of the notation is the same as in figure 6.

For a generic single-site theory, after renormalization, all of the retained diagrams for $H(1, 2)$ are open-chain diagrams, with each bond $V(i, j)$ occurring only once. Thus in such a case the functional derivative in equation (36) is trivial. In terms of diagrams it consists in deleting a V -bond inside each open-chain diagram contributing to H , in any possible position, thus yielding a series of double-chain diagrams for the two-body function. Some typical single-site diagrams contributing to the two-body function are reported in figure 7, and consist of a double chain of $[V(i, j)g_2(ij)]$ -bonds. Now for each chain a one-to-one correspondence holds between sites touched and chain points. A factor ρ is associated with any internal site, a factor $G(z)$ for any point of the first chain, and a factor $G(z')$ for any point of the second chain. Both of the chains must be free of one-articulation points. Additional connectors come from the expansion (48) of the structural distribution function $g_s(1, 2, \dots, s)$ in terms of the short-ranged $h(ij)$. These connect sites belonging to the same chain to sites belonging to different chains. All of the centre-of-mass position vectors \mathbf{R}_i for the internal sites are integrated over. As shown in figure 7, the expansion of $G^{(2)}$ contains both diagonal and off-diagonal contributions. In principle the chains could touch each other at some sites, as shown in the last diagram of figure 7; however, such diagrams have at least a bridge point and do not contribute to $\bar{G}^{(2)}$. As already discussed, in the variational derivative of equation (36) the function $G(z)$ may be regarded as a constant,

since its contribution to the derivative would give a sum of terms with at least a bridge point. For any single-site theory, regarding $G(z)$ as a constant, the functional derivative of H always yields two disjoint open chains, since all of the single-site diagrams for H are open-chain diagrams.

The simplest single-site approximation was proposed by Matsubara and Toyozawa [9] (MT) in their calculation of the conductivity for impurity band semiconductors. It consists in neglecting any structural deviation from the perfectly random system by imposing

$$g_s(1, 2, \dots, s) = 1 \quad (49)$$

and in retaining only the first term in the diagram expansion of $C(1, 2)$, i.e. $C(1, 2) \approx V(1, 2)$, which is reasonable at high density. All of the single-site theories reduce to the MT limit in the case of a perfectly random system (when equation (49) holds).

A generic single-site theory is basically defined by the OZ equation (7) implemented via a closure relation. Fourier transforming equation (7) we formally solve it as

$$H(k) = \frac{C(k)}{1 - \rho G(z)C(k)}. \quad (50)$$

In the limit of a perfectly random system $g_2(R) = 1$, and then $C(k) = C_1(k) = V(k)$ and $H(k)$ reduces to the MT result [9]

$$H_{MT}(k) = \frac{V(k)}{1 - \rho G(z)V(k)}. \quad (51)$$

Inserting equation (36) in equation (17) we find

$$A(z, z) = [\rho G(z)]^2 \int d(1) d(2) d(3) d(4) \frac{\delta H(1, 4)}{\delta V(2, 3)} \mathbf{W}(4, 1) \cdot \mathbf{W}(2, 3) \quad (52)$$

and in order to make some progress towards the evaluation of this integral we introduce the Fourier transforms

$$\mathbf{W}(\mathbf{R}) = \int \frac{d^3 \mathbf{k}}{(2\pi)^3} e^{-i\mathbf{k} \cdot \mathbf{R}} \mathbf{W}(\mathbf{k}) \quad (53a)$$

$$\Gamma(\mathbf{k}, \mathbf{q}) = \int d(2) d(3) d(4) e^{i\mathbf{k} \cdot \mathbf{R}_{14}} e^{i\mathbf{q} \cdot \mathbf{R}_{23}} \frac{\delta H(1, 4)}{\delta V(2, 3)}. \quad (53b)$$

Then considering that

$$\Gamma(\mathbf{k}, \mathbf{q}) = \int d(2) d(3) e^{i\mathbf{q} \cdot \mathbf{R}_{23}} \frac{\delta H(\mathbf{k})}{\delta V(2, 3)} = (2\pi)^3 \frac{\delta H(\mathbf{k})}{\delta V(\mathbf{q})} \quad (54)$$

and substituting in equation (52) we obtain

$$A(z, z) = [\rho G(z)]^2 \int \frac{d^3 \mathbf{k} d^3 \mathbf{q}}{(2\pi)^3} \left[\frac{dV(\mathbf{k})}{d\mathbf{k}} \frac{dV(\mathbf{q})}{d\mathbf{q}} \right] \frac{\delta H(\mathbf{k})}{\delta V(\mathbf{q})}. \quad (55)$$

Inserting equation (50) in equation (54), the two-body function Γ follows as

$$\Gamma(\mathbf{k}, \mathbf{q}) = \frac{(2\pi)^3}{[1 - \rho G(z)C(k)]^2} \frac{\delta C(k)}{\delta V(q)} \quad (56)$$

and finally equation (55) reads

$$A(z, z) = [\rho G(z)]^2 \int \frac{d^3 \mathbf{k} d^3 \mathbf{q}}{(2\pi)^3} \frac{\delta C(k)/\delta V(q)}{[1 - \rho G(z)C(k)]^2} \left[\frac{dV(\mathbf{k})}{d\mathbf{k}} \frac{dV(\mathbf{q})}{d\mathbf{q}} \right]. \quad (57)$$

In the MT limit $\delta C(k)/\delta V(q) = \delta^3(\mathbf{k} - \mathbf{q})$ and we recover the known expression [9]

$$A(z, z) = \rho^2 \int \frac{d^3 \mathbf{k}}{(2\pi)^3} \left[\frac{G(z)}{1 - \rho G(z)V(k)} \right]^2 \left| \frac{dV(\mathbf{k})}{d\mathbf{k}} \right|^2. \quad (58)$$

We observe that the term in square brackets can be written as $[G(z) + \rho G(z)^2 H_{MT}(k)]$ which is the Fourier transform of a generalized one-body Green function $[G(z) \delta^3(\mathbf{R}) + \rho G(z, \mathbf{R})]$. Then in the MT limit the averaged two-body Green function factorizes into the product of two one-body functions, and this approximation is consistent with the approximations made for the evaluation of the one-body function [17]. In the language of diagrams, since all of the connectors $h(ij) = g_2(ij) - 1 = 0$, the chains are disconnected in all of the diagrams retained, and the two-body function factorizes. As shown by Itoh and Watabe [17] this result is exact, due to the vanishing contribution of the vertex corrections, even in the Ishida–Yonezawa approximation [26]. The same conclusion is achieved in the coherent-potential approximation for the case of diagonal disorder [27]. However, this means that such theories furnish a trivial answer to the conductivity problem. For instance it is well known that the DOS and the averaged one-body Green function are continuous across the mobility edge. In principle $G^{(2)}$ contains information on the extent of the states, while the one-body function loses such information in the averaging process. The presence of the functional derivative in equation (57) ensures that in general even for a single-site theory, which does not contain any localization effect, $G^{(2)}$ contains more information than the one-body function, provided that non-trivial approximations are adopted for the structural properties. In other words the approximation of factorizing the two-body function is not always consistent with a single-site theory, and this is the case for the SSCA/EMA, as we will see in the next section.

4. The SSCA/EMA and the ladder expansion

In our knowledge, the best single-site theory which can be exactly solved is the SSCA, originally suggested by Wertheim [15] in the context of classical dielectric theory, and then developed by Winn and Logan [6] who showed its equivalence to the EMA of Roth [11–14] and—for a particular choice of the pair distribution function g_2 —to the mean-spherical approximation of liquid-state theory [28]. The SSCA consists [6] in neglecting all of the diagrams with crossing h -connectors (for instance the fourth and fifth diagrams contributing to C_3 in figure 6). As shown by Winn and Logan [6], the SSCA is equivalent to the following closure relation:

$$g_2(1, 2)C(1, 2) = g_2(1, 2)V(1, 2) + h(1, 2)H(1, 2) \quad (59)$$

which allows for a solution of the OZ equation (7). $G(z)$ is then self-consistently determined through equation (6). This approximation is somewhat arbitrary but it allows for a soluble theory which is analytical for some choices of the functions $V(ij)$, $g_2(ij)$, and includes important structural corrections that are neglected in other single-site theories. Moreover the SSCA reproduces the results of numerical simulations remarkably well [7].

If $g_2(\mathbf{R})$ is approximated by a simple step function

$$g_2(R) = \theta(R - a) \quad (60)$$

then the SSCA/EMA is formally equivalent to the mean-spherical approximation of liquid-state theory. This problem has well known solutions for some classes of $V(R)$ -functions.

The basis for a systematic study of the transport properties at the EMA level [29] was given by the independent work of Roth and Singh [20] and Itoh *et al* [18]. Such results are easily recovered by the functional method developed in the previous section: the functional derivative appearing in equation (57) can be evaluated by use of the SSCA closure condition

(59) for the OZ equation. Taking the Fourier transform of the closure condition (59):

$$\int g_2(\mathbf{q} - \mathbf{k})C(k) d^3\mathbf{k} = \int g_2(\mathbf{q} - \mathbf{k})V(k) d^3\mathbf{k} + \int h(\mathbf{q} - \mathbf{k})H(\mathbf{k}) d^3\mathbf{k} \quad (61)$$

and differentiating with respect to δV , and then observing that $g_2(\mathbf{k}) = (2\pi)^3 \delta^3(\mathbf{k}) + h(\mathbf{k})$, we obtain with the aid of equation (56)

$$\Gamma(\mathbf{k}, \mathbf{q}) = g_2(\mathbf{k} - \mathbf{q}) + \int \frac{d^3\mathbf{p}}{(2\pi)^3} g_2(\mathbf{k} - \mathbf{p}) [1 - \gamma^2(p)] \Gamma(\mathbf{p}, \mathbf{q}) \quad (62)$$

where $G(z)/\gamma(k) = G(z)/[1 - \rho G(z)C(k)] = [G(z) + \rho G(z)^2 H(k)]$ is the Fourier transform of a generalized averaged one-body Green function ($G(z) \delta^3(\mathbf{R}) + \rho G(z, \mathbf{R})$). The solution of this integral equation is a two-body function Γ which turns out to be consistent with the one-body function evaluated at the SSCA/EMA level. The function Γ is formally equivalent to the propagator of a particle moving in \mathbf{k} -space in the presence of the potential $1 - \gamma^2(k)$, and with a free propagator $g_2(\mathbf{k})$. When $g_2(\mathbf{R})$ is approximated by the step function (60) then $[g_2(\mathbf{R})]^2 = g_2(\mathbf{R})$ and $g_2(\mathbf{k})$ satisfies

$$\int g_2(\mathbf{k} - \mathbf{q})g_2(\mathbf{q} - \mathbf{p}) d^3\mathbf{q} = g_2(\mathbf{k} - \mathbf{p}) \quad (63)$$

which is typical of a free propagator. A simplified version of equation (62) could be written by approximating the pair function g_2 with its random-limit value $g_2(\mathbf{k}) \approx (2\pi)^3 \delta^3(\mathbf{k})$; the equation can be solved giving $\Gamma(\mathbf{k}, \mathbf{q}) = \delta^3(\mathbf{k} - \mathbf{q})/\gamma^2(k)$ which basically is again the square of the one-body function. We should have predicted this result by observing that in such an approximation we are neglecting all of the $h(i, j)$ -factors connecting one chain to the other, while we are retaining their contributions inside each chain. The averaged two-body function factorizes but this is not a consistent approximation, since different strategies have been adopted for the calculation of one-body and two-body functions.

The calculation of the conductivity follows from the solution of the integral equation (62) for the two-body function Γ . The physical content of this equation is readily understood by iterating in order to obtain a perturbative expansion in terms of the connectors h . We introduce the following operatorial notation: $\hat{\Gamma} = \Gamma(\mathbf{k}, \mathbf{q})$, $\hat{g} = g_2(\mathbf{k} - \mathbf{q})$, $\hat{h} = h(\mathbf{k} - \mathbf{q})$ and $\hat{I} = (2\pi)^3 \delta^3(\mathbf{k} - \mathbf{q})$. The operatorial product is understood as

$$\hat{\Gamma} f \hat{g} = \int \frac{d^3\mathbf{p}}{(2\pi)^3} \Gamma(\mathbf{k} \cdot \mathbf{p}) f(\mathbf{p}) g_2(\mathbf{p} - \mathbf{q}) \quad (64)$$

for any generic function $f(\mathbf{p})$. With the substitution $\hat{g} = \hat{I} + \hat{h}$ equation (62) becomes

$$\hat{\Gamma} = \hat{I} + \hat{h} + (1 - \gamma^2)\hat{\Gamma} + \hat{h}(1 - \gamma^2)\hat{\Gamma}. \quad (65)$$

This can be rearranged as

$$\hat{\Gamma} = \frac{1}{\gamma^2} \hat{I} + \frac{1}{\gamma^2} \hat{h} + \frac{1}{\gamma^2} \hat{h}(1 - \gamma^2)\hat{\Gamma}. \quad (66)$$

Then iterating,

$$\begin{aligned} \hat{\Gamma} &= \frac{1}{\gamma^2} \hat{I} + \frac{1}{\gamma^2} \hat{h} + \frac{1}{\gamma^2} \hat{h}(1 - \gamma^2) \frac{1}{\gamma^2} + \frac{1}{\gamma^2} \hat{h}(1 - \gamma^2) \frac{1}{\gamma^2} \hat{h} \\ &\quad + \frac{1}{\gamma^2} \hat{h}(1 - \gamma^2) \frac{1}{\gamma^2} \hat{h}(1 - \gamma^2) \frac{1}{\gamma^2} + \dots \end{aligned} \quad (67)$$

and after some cancellation we finally obtain

$$\hat{\Gamma} = \frac{1}{\gamma^2} \hat{I} + \frac{1}{\gamma^2} \hat{h} \frac{1}{\gamma^2} + \frac{1}{\gamma^2} \hat{h} \left[\frac{1}{\gamma^2} - 1 \right] \hat{h} \frac{1}{\gamma^2} + \frac{1}{\gamma^2} \hat{h} \left[\frac{1}{\gamma^2} - 1 \right] \hat{h} \left[\frac{1}{\gamma^2} - 1 \right] \hat{h} \frac{1}{\gamma^2} + \dots \tag{68}$$

Alternatively this expansion can be rewritten as

$$\hat{\Gamma} = \frac{1}{\gamma^2} \hat{I} + \frac{1}{\gamma^2} \hat{T} \frac{1}{\gamma^2} \tag{69}$$

where \hat{T} is given by

$$\hat{T} = \hat{h} + \hat{h} \left[\frac{1}{\gamma^2} - 1 \right] \hat{h} + \hat{h} \left[\frac{1}{\gamma^2} - 1 \right] \hat{h} \left[\frac{1}{\gamma^2} - 1 \right] \hat{h} + \dots \tag{70}$$

and can be formally summed as

$$\hat{T} = \hat{h} + \hat{h} \left[\frac{1}{\gamma^2} - 1 \right] \hat{T}. \tag{71}$$

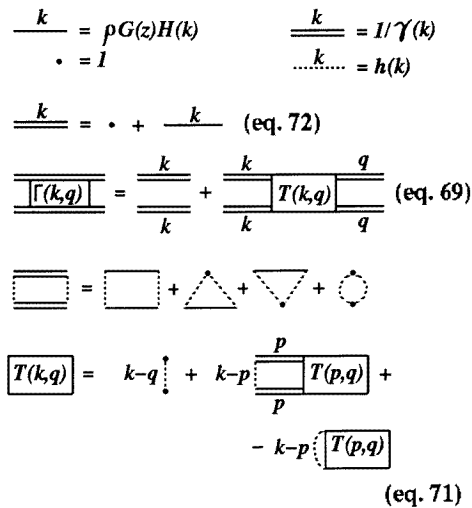


Figure 8. Diagrammatic representations of some of the equations of the text.

These expansions have a simple graphical interpretation in terms of k -space double-chain diagrams. In figure 8 the propagator

$$1/\gamma(k) = 1 + \rho G(z)H(k) \tag{72}$$

is represented by a double line. A simple line represents the renormalized transfer element $\rho G(z)H(k)$, while the short-ranged connectors h are represented as dotted lines. Any internal variable is integrated over and a factor $1/(2\pi)^3$ must be added for any integration. Equations (69), (71) and (72) are displayed in figure 8. As shown in the same figure the term $\hat{h}(1/\gamma^2)\hat{h}$ contains the spurious addendum h^2 which is correctly cancelled to any order by the (-1) correction appearing in the $(1/\gamma^2 - 1)$ factors. As shown in figure 9 the series (68) for $\Gamma(k, q)$ has the shape of a ladder expansion (apart from the (-1) corrections), with two chains joined by all of the possible h -connectors. Some first-order contributions are shown explicitly in terms of the transfer element $\rho G(z)H(k)$ (a

$$\begin{aligned}
 \overline{\overline{\Gamma(\mathbf{k}, \mathbf{q})}} &= \overline{\overline{\frac{\mathbf{k}}{k}}} + \overline{\overline{\frac{\mathbf{k} \quad \mathbf{q}}{k \quad q}}} + \\
 &+ \left[\overline{\overline{\frac{\mathbf{k} \quad \mathbf{p} \quad \mathbf{q}}{k \quad p \quad q}}} - \overline{\overline{\frac{\mathbf{k} \quad \mathbf{q}}{k \quad q}}} \right] + \dots \\
 \\
 \overline{\overline{\Gamma}} &= \overline{\overline{|\quad}} + \overline{\overline{|\quad}} + \overline{\overline{|\quad}} + \overline{\overline{|\quad}} + \\
 &+ \overline{\overline{|\quad}} + \overline{\overline{|\quad}} + \overline{\overline{|\quad}} + \dots
 \end{aligned}$$

Figure 9. A diagrammatic representation of the ladder expansion (68). Some first-order contributions are shown explicitly in terms of the renormalized transfer element $\rho G(z)H(k)$ (single lines). The meaning of the notation is the same as in figure 8.

single line). We observe that this is a renormalized transfer element which sums all of the contributions from intra-chain h -connectors at the SSCA/EMA level. Consistently with such an approximation we are neglecting all of the double-chain diagrams with crossing h -connectors. The approximation of factorizing the averaged two-body Green function as the product of two one-body functions is equivalent to retaining only the first diagram of the expansion (68), or alternatively to setting $\hat{T} = 0$ in equation (69). We stress once more that such broken average (BA) approximation is not consistent with the SSCA since all of the chain-to-chain h -connectors are explicitly neglected while retaining the intra-chain ones. However, the BA approximation becomes exact in the MT limit since then all of the h -connectors vanish, but we expect that the contribution coming from higher-order terms would become more and more important as the density increases, in a system made of real impenetrable ions. This is illustrated in the next section where some numerical calculations are presented in the random-hard-sphere approximation.

This diagrammatic analysis of the ladder expansion is of some utility for generalizing equation (55) to the case of $A(z, z')$ with $z \neq z'$. In fact the calculation of the conductivity requires the knowledge of the function A for conjugated values of the variables. By inspection of the diagrams in figure 9 we observe that such a generalization is immediately obtained by substituting z' for z in all of the factors associated with one of the two chains. Since the z -dependence is implicit in the dependence on $G(z)$ and $\gamma(k)$, we only need to replace γ^2 with $\gamma\gamma'$ where $\gamma'(k) = 1 - \rho G(z')C'(k)$ and $C'(k)$ is the irreducible C -function evaluated at $z = z'$. The integral equation (62) then reads

$$\Gamma(\mathbf{k}, \mathbf{q}) = g_2(\mathbf{k} - \mathbf{p}) + \int \frac{d^3 \mathbf{p}}{(2\pi)^3} g_2(\mathbf{k} - \mathbf{p}) [1 - \gamma(p)\gamma'(p)] \Gamma(\mathbf{p}, \mathbf{q}) \quad (73)$$

and the $A(z, z')$ -function is given by

$$A(z, z') = \rho^2 G(z)G(z') \int \frac{d^3 \mathbf{k} \, d^3 \mathbf{q}}{(2\pi)^6} \left[\frac{dV(\mathbf{k})}{d\mathbf{k}} \frac{dV(\mathbf{q})}{d\mathbf{q}} \right] \Gamma(\mathbf{k}, \mathbf{q}). \quad (74)$$

This is all that we need for the evaluation of the conductivity through equation (13) and (14), provided that we are able to solve the integral equation (73).

For successive numerical work on the conductivity it would be convenient to rearrange the problem in order to obtain a one-dimensional integral equation. This can be easily done

for a generic isotropic system: let us introduce the vectorial function

$$\chi(\mathbf{k}) = \int \frac{d^3\mathbf{q}}{(2\pi)^3} \Gamma(\mathbf{k}, \mathbf{q}) \frac{dV(q)}{dq} \frac{\mathbf{q}}{q}. \quad (75)$$

In terms of χ the function $A(z, z')$ is written as

$$A(z, z') = \rho^2 G(z)G(z') \int \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{dV(k)}{dk} \frac{\mathbf{k}}{k} \cdot \chi(\mathbf{k}). \quad (76)$$

Since we are assuming that the system is isotropic, rotational invariance ensures that $\Gamma(\mathbf{k}, \mathbf{q}) \equiv \Gamma(k, q, \mathbf{k} \cdot \mathbf{q})$. The integration in the definition (75) of χ can be carried out in a (q_x, q_y, q_z) -frame with the q_z -axis parallel to the \mathbf{k} -vector. In such a frame the x, y -components of χ vanish identically for symmetry reasons and thus the vectorial function χ is parallel to the \mathbf{k} -vector:

$$\frac{\mathbf{k}}{k} \cdot \chi(\mathbf{k}) = |\chi(\mathbf{k})| = \chi(k). \quad (77)$$

Moreover, since the angles are integrated over in equation (75), the scalar function $\chi(k)$ depends only on the modulus k and equation (76) becomes

$$A(z, z') = \rho^2 G(z)G(z') \frac{1}{2\pi^2} \int_0^{+\infty} k^2 dk \frac{dV(k)}{dk} \chi(k). \quad (78)$$

Now let us multiply all of the terms in the integral equation (73) by the factor

$$\frac{1}{(2\pi)^3} \frac{\mathbf{k} \cdot \mathbf{q}}{kq} \frac{dV(q)}{dq}$$

and integrate over the variable q :

$$\begin{aligned} \chi(k) &= \int \frac{d^3\mathbf{q}}{(2\pi)^3} \frac{\mathbf{k} \cdot \mathbf{q}}{kq} \frac{dV(q)}{dq} g_2(\mathbf{k} - \mathbf{q}) \\ &\quad + \int \frac{d^3\mathbf{p}}{(2\pi)^3} g_2(\mathbf{k} - \mathbf{p}) [1 - \gamma(p)\gamma'(p)] \frac{\mathbf{k}}{k} \cdot \chi(p). \end{aligned} \quad (79)$$

The vector $\chi(p)$ is obviously parallel to \mathbf{p} , and we can write $\chi(p) = (\mathbf{p}/p)\chi(p)$, so equation (79) becomes

$$\psi(k) = \phi(k) + \int_0^{+\infty} \frac{p^2 dp}{(2\pi)^2} f(k, p) \left[\frac{1}{\gamma(p)\gamma'(p)} - 1 \right] \psi(p) \quad (80)$$

where $\psi(k) = \chi(k)\gamma(k)\gamma'(k)$ and the function $f(k, p)$ is defined as

$$f(k, p) = \int_{-1}^{+1} d\left(\frac{\mathbf{k} \cdot \mathbf{p}}{kp}\right) h(\mathbf{k} - \mathbf{p}) \frac{\mathbf{k} \cdot \mathbf{p}}{kp}. \quad (81)$$

The free term $\phi(k)$ follows from the first integral of equation (79):

$$\phi(k) = \frac{\mathbf{k}}{k} \int \frac{d^3\mathbf{q}}{(2\pi)^3} \frac{dV(q)}{dq} g_2(\mathbf{k} - \mathbf{q}) = \frac{\mathbf{k}}{k} \frac{d}{d\mathbf{k}} \int d^3\mathbf{R} [V(R)g_2(R)] e^{-i\mathbf{k} \cdot \mathbf{R}} = \frac{d}{dk} U(k) \quad (82)$$

where $U(k)$ is the Fourier transform of the product $V(R)g_2(R)$. We notice that equation (80) is equivalent to the integral equation proposed by Itoh *et al* [18] for the vertex function in the EMA. Such an equation can easily be solved numerically if the analytical form of the one-body Green function is known together with the short-ranged connector h and the pair distribution function g_2 .

The great advantage of using an SSCA formalism consists in the ‘privilege’ of being able to make use of some analogies with liquid-state theory. Equation (7) is analogous to the OZ equation [4] and exact solutions are available for some classes of closure conditions; then the existence of an analytically tractable theory for the one-body Green function renders the integral equation (80) for the conductivity easily solvable numerically, even for a real high-density liquid with non-trivial structural properties.

5. Numerical results

In this section we present some numerical results at the SSCA/EMA level in the random-hard-sphere approximation, for a Yukawa transfer-matrix element. In this approximation the pair distribution function $g_2(R)$ is approximated by the step function (60), as is reasonable for small values of the packing fraction $\eta = (4\pi/3)\rho(a/2)^3$. This choice is not reliable for large values of the packing fraction since the structure factor goes negative for $\eta > 0.125$. Numerical simulations have shown [7] that, even for unphysical values of η , this random-hard-sphere approximation produces a DOS which is basically correct except for the states close to the upper band edge which are more sensitive to the local structure. Further problems arise in the calculation of the conductivity which is strongly related to the behaviour of the off-diagonal Green function, since such behaviour becomes unphysical for η larger than 0.125. We notice that the occurrence of such difficulties is a sign of a correct sensitivity to the structural properties, and that the SSCA/EMA by itself would be very accurate if the $g_2(R)$ -function were exact. On the other hand the random-hard-sphere approximation of equation (60) is correct in the low-density limit and provides an analytical solution which is reliable for an intermediate range of densities.

With such a choice for the pair distribution function, the problem is formally equivalent [6] to solving the OZ equation of the mean-spherical approximation for a simple hard-sphere fluid. An analytical solution of this problem is available for a wide class of $V(R)$ -functions, and the one-body Green function has been explicitly evaluated by Winn and Logan [6] in the case of a Yukawa transfer-matrix element:

$$V(R) = -\frac{V_0}{R} e^{-\alpha R} \quad (83)$$

which is appropriate for describing important physical processes such as electronic transport in liquid metals or in doped semiconductors. In the following part of the paper we will make use of natural units, taking $1/\alpha$ and αV_0 respectively as the length and energy units. The conductivity is reported in adimensional form, with units of $e^2\alpha/\hbar$.

The evaluation of the free term $\phi(k)$, in the integral equation (80), is straightforward, and follows from the insertion of the Yukawa transfer-matrix element (83) in equation (82):

$$\phi(k) = \frac{4\pi e^{-a}}{(1+k^2)} \left[\left(3 + a(1+k^2) + \frac{1}{k^2} \right) \sin(ka) + \left((2-a)k - \frac{a}{k} \right) \cos(ka) \right]. \quad (84)$$

The Fourier transform of the short-ranged connector h is readily obtained from equation (60):

$$h(k) = -\frac{4\pi}{k^3} [\sin(ka) - (ka) \cos(ka)] \quad (85)$$

and the function $f(k, p)$ follows via the simple integration of (81):

$$f(k, p) = \frac{4\pi a^3}{(ka)(pa)} \left[2 \frac{\sin(ka) \sin(pa)}{ka} \frac{1}{pa} + -\frac{\sin(ka+pa)}{ka+pa} - \frac{\sin(ka-pa)}{ka-pa} \right]. \quad (86)$$

The irreducible function $C(R)$ must satisfy the OZ equation (7) with the SSCA/EMA closure condition (59) which becomes, for a random-hard-sphere pair function (60),

$$\begin{cases} C(R) = V(R) & \text{if } R \geq a \\ H(R) = 0 & \text{otherwise.} \end{cases} \quad (87)$$

This problem has been discussed by several authors [30–33], and the solution is the simple expression

$$C(R) = \begin{cases} -S \frac{1 - e^{-R}}{R} + S^2 \frac{\cosh(R) - 1}{2R} & \text{if } R < a \\ V(R) & \text{if } R > a \end{cases} \quad (88)$$

where the self-energy $S = S(z)$, as defined in equation (9), satisfies the quartic equations

$$u_0^2(S) = \frac{\pi}{2} \rho G(z) \left[S(z) + \frac{1}{2} S(z)^2 \right] \quad (89a)$$

$$u_0(S) = \pi \rho G(z) \left[S(1 - e^{-a}) - S^2 \frac{\cosh(a) - 1}{2} - e^{-a} \right]. \quad (89b)$$

Of course the averaged Green function $G(z)$ must be self-consistently determined by use of equation (10).

Finally, the Fourier transform $C(k)$ is easily recovered from equation (88):

$$\rho G(z) C(k) = 4 \left[2u_0^2 \frac{\cos(ka) - 1}{k^2(1 + k^2)} + u_0 \frac{\cos(ka)}{1 + k^2} - \left(\frac{\partial u_0}{\partial a} \right) \frac{\sin(ka)}{k(1 + k^2)} \right] \quad (90)$$

which thus completely defines the kernel of the integral equation (80).

The one-body off-diagonal Green function $G(R)$ follows from its Fourier transform $G^2(z)C(k)/\gamma(k)$. We observe that the long-range behaviour of $G(R)$ is determined by the presence of a complex pole in the Fourier transform for $k = k_0(E) + i/\lambda(E)$ with $z = E + i0^+$. For large values of R the function $G(R)$ behaves as $\exp(ik_0R) \exp(-R/\lambda)/R$ and then λ is a sort of *coherence length*. λ has an important role in the conductivity problem, and must be finite for physical reasons since otherwise for $\lambda \rightarrow \infty$ the function $G(R)$ would lose its exponentially decreasing factor. In this random-hard-sphere approximation, whenever the packing fraction η exceeds the value 0.125, the structure factor goes negative, and for larger values of η the pole of $1/\gamma(k)$ crosses the real axis at a critical value of $E = E_c$ in the low-energy tail of the band. For $E = E_c$, we have $\lambda \rightarrow \infty$ and the corresponding $G(R)$ -function assumes an unphysical behaviour. Both the self-energy and the averaged diagonal Green function $G^+(E)$ are continuous functions at $E = E_c$, since the integral in equation (9) is still convergent for the presence of the transfer-matrix element $V(R)$. As a consequence the calculation of an averaged DOS is not affected by any inconsistency even for large values of the packing fraction. We cannot say the same for the conductivity: in the BA approximation we obtain a divergent result due to the presence of a second-order pole in equation (74); at the SSCA/EMA level the sum of all of the divergent terms in the ladder expansion (68) gives rise to a finite answer for the conductivity, but still a discontinuous jump of the first derivative occurs at $E = E_c$. We expect that such inconsistencies will emerge only in the low-energy tail of the band because these deep states are more affected by an incorrect evaluation of the short-range structural properties. Even when the packing fraction exceeds 0.125, this approximation is still reliable for $E \gg E_c$.

In figures 10 and 11 we report the conductivity versus the occupation number N_{occ} of the band: $N_{occ} = y/2$ where y is the filling fraction $y = N_e/N$ as defined in section 2. The results are compared to the simple BA approximation which coincides with the

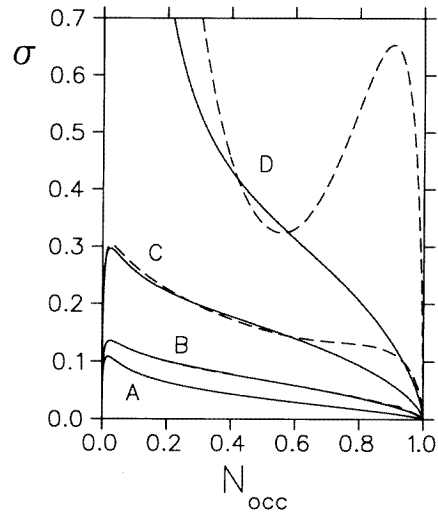


Figure 10. The conductivity σ versus the occupation number N_{occ} , at a fixed density $\rho = 1.0$, and for: (A) $a = 0.05$ ($\eta = 6 \times 10^{-5}$); (B) $a = 0.25$ ($\eta = 0.008$); (C) $a = 0.5$ ($\eta = 0.065$); (D) $a = 0.75$ ($\eta = 0.22$). The broken lines are the corresponding results in the BA approximation.

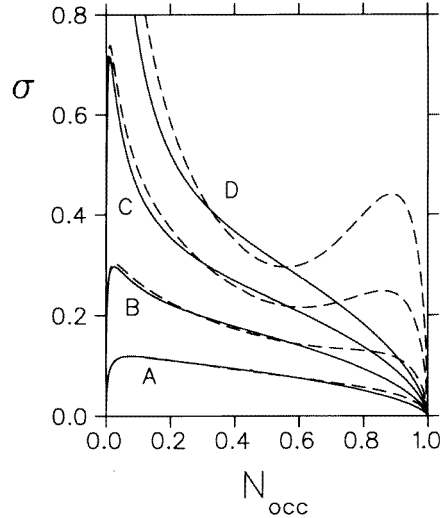


Figure 11. The conductivity σ versus the occupation number N_{occ} , for a fixed hard-core radius $a = 0.5$, and for: (A) $\rho = 0.5$ ($\eta = 0.033$); (B) $\rho = 1.0$ ($\eta = 0.065$); (C) $\rho = 1.5$ ($\eta = 0.1$); (D) $\rho = 2.0$ ($\eta = 0.13$). The broken lines are the corresponding results in the BA approximation.

SSCA/EMA in the MT limit ($a \rightarrow 0$) or for a small enough density to render the packing fraction negligible. The temperature T is fixed at $T = 0$, but any generalization to $T \neq 0$ is straightforward, and follows from the simple integration (13) over the proper Fermi distribution. In figure 10 the conductivity is shown for several values of the hard-core radius a , at a fixed density $\rho = 1$. The lower curve, for $a = 0.05$ and a corresponding packing fraction $\eta = 6 \times 10^{-5}$, is basically the MT limit of a perfectly random system. We observe that the inclusion of a hard core in the pair distribution function produces strong changes in the conductivity. This large increase of the conductivity with a could be expected, since the existence of a hard core reduces the averaged value of the transfer-matrix element, thus giving rise to a narrower band and to a larger DOS. We still observe a large mobility in the low-energy tail compared to the small mobility of the upper band edge. In figure 11 the conductivity is reported for several values of the density ρ , at a fixed value of the hard-core radius $a = 0.5$. The BA approximation is excellent in the lower half of the band, say for $N_{occ} < 0.5$, and for moderate values of the density, since the low-energy mobility peak becomes divergent for $\eta > 0.125$. In the upper half of the band the presence of the hard cores gives rise to a very large DOS, which must be compensated by a consistent sum of terms contributing to the two-body Green function. In the BA approximation such a compensation cannot take place since the presence of the hard cores is partially neglected in the evaluation of the two-body Green function. As a consequence the conductivity is overestimated for the high-energy states. As shown in figures 10 and 11 the consistent sum of all of the diagrams at the SSCA/EMA level removes the anomalous high-energy mobility peak, in agreement with the numerical calculations of Itoh and Watabe [34]. It is remarkable that, even in this simple structural approximation, the internal consistency of the theory plays an important role for a correct evaluation of the transport properties. We observe that even the BA approximation contains some hard-core corrections, but these are not consistently

described and the lack of consistency could give rise to uncontrollable errors. As shown in figures 10 and 11, even in the hard-core approximation the internal consistency of the theory—as guaranteed by equation (36)—cannot be ruled out and, especially in the high-density domain, any further improvement in the description of the structural properties can be achieved only through a fully consistent theory.

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References

- [1] Stratt R M and Xu B C 1989 *Phys. Rev. Lett.* **62** 1675
- [2] Stratt R M 1990 *Annu. Rev. Phys. Chem.* **41**
- [3] Xu B C and Stratt R M 1989 *J. Chem. Phys.* **91** 5613
- [4] Logan D E and Winn M D 1988 *J. Phys. C: Solid State Phys.* **21** 5773
- [5] Bush I J, Logan D E, Madden P A and Winn M D 1989 *J. Phys.: Condens. Matter* **1** 2551
- [6] Winn M D and Logan D E 1989 *J. Phys.: Condens. Matter* **1** 1753
- [7] Bush I J, Logan D E, Madden P A and Winn M D 1989 *J. Phys.: Condens. Matter* **1** 8735
- [8] Strnadl C F and Kahl G 1993 *J. Phys.: Condens. Matter* **5** 6801
- [9] Matsubara T and Toyozawa Y 1961 *Prog. Theor. Phys.* **26** 739
- [10] Watabe M 1977 *Liquid Metals 1976 (Inst. Phys. Conf. Ser. 30)* (Bristol: Institute of Physics Publishing) pp 288–304
- [11] Roth L M 1974 *J. Physique Coll.* **35** C4 317
- [12] Roth L M 1974 *Phys. Rev. B* **9** 2476
- [13] Roth L M 1975 *Phys. Rev. B* **11** 3769
- [14] Roth L M 1976 *J. Phys. F: Met. Phys.* **6** 2267
- [15] Wertheim M S 1973 *Mol. Phys.* **25** 211
- [16] Lebowitz J L and Percus J K 1966 *Phys. Rev.* **144** 251
- [17] Itoh M and Watabe M 1978 *J. Phys. F: Met. Phys.* **8** 1725
- [18] Itoh M, Niizeki K and Watabe M 1981 *J. Phys. F: Met. Phys.* **11** 1605
- [19] Elyutin P V 1981 *J. Phys. C: Solid State Phys.* **14** 1435
- [20] Roth L M and Singh V A 1982 *Phys. Rev. B* **25** 2522
- [21] Kubo R 1957 *J. Phys. Soc. Japan* **12** 570
- [22] Feenberg E 1948 *Phys. Rev.* **74** 206
- [23] Lee P A and Ramakrishnan T V 1985 *Rev. Mod. Phys.* **57** 287
- [24] Vollhardt D and Wölfle P 1980 *Phys. Rev. B* **22** 4666
- [25] Kirkwood J G 1935 *J. Chem. Phys.* **3** 300
- [26] Ishida Y and Yonezawa F 1973 *Prog. Theor. Phys.* **49** 731
- [27] Elliott R J, Krumhansl J A and Leath P L 1974 *Rev. Mod. Phys.* **46** 465
- [28] Hansen J P and McDonald I R 1986 *Theory of Simple Liquids* (New York: Academic)
- [29] Itoh M, Beck H and Fresard R 1989 *J. Phys.: Condens. Matter* **1** 6381; 1990 *J. Phys.: Condens. Matter* **2** 2687
- [30] Waisman E 1973 *Mol. Phys.* **25** 45
- [31] Høye J S and Stell G 1976 *Mol. Phys.* **32** 195
- [32] Høye J S, Stell G and Waisman E 1976 *Mol. Phys.* **32** 209
- [33] Smith E R 1979 *Mol. Phys.* **38** 823
- [34] Itoh M and Watabe M 1984 *J. Phys. F: Met. Phys.* **14** 1847