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Generalised constitutive equations for glassy systems

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Abstract. For the model of a simple classical many-particle system generalised constitutive equations are derived which express fluctuations of arbitrary variables in terms of those for density, currents and temperature. In particular the microscopic expression for the dynamic specific heat is found. The generalised hydrodynamic equations for undercooled liquids and glasses are obtained as a special application of the theory.

1. Introduction

Recently heat spectroscopy was invented as a new technique to analyse structural relaxation in glassy materials (Birge and Nagel 1985, Birge 1986). The experimental results have been analysed with the aid of a temperature diffusion equation which was generalised phenomenologically by introduction of a complex specific heat $c_p(\omega) = c'_p(\omega) + ic''_p(\omega)$ depending on frequency ω . In this paper we want to derive the representation of $c_p(\omega)$ in terms of microscopic concepts. The calculations will be done for a model of a classical system of structureless particles. More generally, the proper microscopic formulation of generalised constitutive equations for arbitrary variables will be given. As a byproduct of the calculations generalised linear hydrodynamic equations will be obtained, which are valid for a description of long-wavelength fluctuations of density, currents and temperature in undercooled liquids and glasses. The latter were derived before by Bengtzelius and Sjögren (1986) on the basis of the kinetic equation approach towards hydrodynamics (Forster 1974, Mazenko 1974). The generalised hydrodynamic equations imply the experimentally relevant constitutive equations which connect for example stresses and velocity gradients. In this way all but two coefficients can be identified. The exceptions are the dynamic specific heat $c(\omega)$ and the heat conduction kernel $\lambda(\omega)$. The former connects energy with temperature fluctuations and the latter energy currents with temperature gradients. The relevant constitutive equations do not follow from the work of Bengtzelius and Sjögren (1986), since that work does not deal with energy or energy current fluctuations.

Generalisations of linearised hydrodynamic equations for simple fluids have been derived rigorously by Kadanoff and Martin (1963). The essence of their approach is the generalisation of the three transport coefficients, shear viscosity η , bulk viscosity ζ and thermal conductivity λ , to kernels depending on frequency ω and wavevector q . Ignoring in their equations for reasons of simplicity the coupling between heat and density fluctuations and neglecting the q dependence of the kernels, one gets those equations

for viscoelastic motion which have long been used for the analysis of sound experiments in glassy materials (Litovitz and Davis 1965). The same procedure does not lead to the concept of a dynamic specific heat, however. This was one reason for Oxtoby (1986) to argue that the mentioned heat spectroscopy data should rather be interpreted solely in terms of a frequency-dependent thermal conductivity $\lambda(\omega)$. He supported his reasoning by solving a special model for energy relaxation. His results imply in particular that Birge (1986) was not quite correct in relating $c_p(\omega)$ to enthalpy fluctuations. On the other hand, Oxtoby's results are not definitive enough to decide whether his objections against the dynamic specific heat concept really refer to a controversy or merely to a question of semantics. Let us mention also that the generalised heat conduction equation has been combined recently with the viscoelastic equations (Jäckle 1986); this work requires further phenomenological assumptions and contains various imprecise concepts like internal thermodynamic variables, thermometer temperature or frequency-dependent entropy. The following calculations clarify the indicated open questions. In particular the formulae provide a strict justification for Kramers–Kronig relations for all the introduced functions and for stability conditions like $c_p''(\omega)/\omega \geq 0$.

2. Preliminaries

In this section the necessary notations and standard results will be listed. We want to consider a grand canonical ensemble of classical particles within a volume V , specified by temperature T and chemical potential μ . Particle density, energy density and pressure are denoted respectively by n , u and p . The particle mass is abbreviated by m and the pair potential by $v(r)$. The Hamiltonian determines the averages $\langle \ \rangle$ as well as the evolution of dynamic variables A, B, \dots in time t . The set of dynamic variables is considered as a metric vector space with scalar product $(A|B) = \langle A^*B \rangle / k_B T$. The time evolution then is a unitary mapping generated by the Hermitian Liouvillian \mathcal{L} : $A(t) = \exp(i\mathcal{L}t)A$. The time-dependent X – Y correlator is introduced by $\Phi_{XY}(t) = (X(t)|Y)$. It is more convenient to characterise the dynamics by Laplace transforms for complex frequency z , defined by $F(z) = \pm i \int \Theta(\pm t) \exp(izt) F(t) dt$, $\text{Im } z \leq 0$. Off the real axis these functions are holomorphic, but across it they may be discontinuous: $F(\omega \pm i0) = F'(\omega) \pm iF''(\omega)$. The discontinuity $F''(\omega)$ is called the spectrum and it determines $F'(\omega)$ by a Kramers–Kronig relation. The correlator $\Phi_{XY}(z)$ is given as a Liouvillian resolvent matrix element, equation (A13).

The distinguished variables to be used are the fluctuations for wavevector \mathbf{q} of density $\rho(\mathbf{q})$, current density $j_\alpha(\mathbf{q})$, $\alpha = x, y, z$, and temperature $T(\mathbf{q})$. They can be written as

$$X(\mathbf{q}) = \sum_n x^n(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}^n) \quad (1)$$

where n labels the particles. Particle position and velocity will be denoted by \mathbf{r}^n , \mathbf{v}^n . For the mentioned cases one gets respectively: $x_\rho^n = 1$, $x_\alpha^n = v_\alpha^n$, $x_T^n = [m(v^n)^2 - 3k_B T] / 3k_B n$. For a classical system the temperature is given as $\langle m(v^n)^2 \rangle / 3k_B$. In order to calculate the fluctuations $T(\mathbf{q})$ one has to subtract that part due to density fluctuations. All variables can be measured mechanically. As instrument one can imagine in principle the analysis of a nuclear transition line. Intensity, linear and quadratic Doppler shift determine respectively density, velocity and temperature. Obviously, $T(\mathbf{q}) = Q_\rho E^K(\mathbf{q}) (2/3k_B n)$. Here $E^K(\mathbf{q})$ denotes the kinetic energy fluctuations and is given by equation (1) with $x^n = 1/2m(v^n)^2$. $Q_\rho = 1 - P_\rho$ with $P_\rho = |\rho(\mathbf{q})|(\rho(\mathbf{q}))^{-1}(\rho(\mathbf{q}))|$ denotes the projector perpendicular to density fluctuations of wavevector \mathbf{q} . To simplify

the notations we will often drop the momentum variable and write e.g. $P_\rho = |\rho\rangle(\rho|\rho)^{-1}(\rho|$ instead of the full expression. The specified five variables are pairwise orthogonal and the normalisations are given by:

$$(\rho(\mathbf{q})|\rho(\mathbf{q})) = NS(\mathbf{q})/Tk_B \tag{2a}$$

$$(j_\alpha(\mathbf{q})|j_\beta(\mathbf{q})) = N\delta_{\alpha\beta}/m \tag{2b}$$

$$(T(\mathbf{q})|T(\mathbf{q})) = NT2/(3n^2k_B). \tag{2c}$$

Here N is the particle number and $S(\mathbf{q})$ denotes the structure factor; $|\mathbf{q}| = q$. We will also need the total energy fluctuations, which are the sum of kinetic and potential parts: $E(\mathbf{q}) = E^K(\mathbf{q}) + E^P(\mathbf{q})$. The latter reads explicitly:

$$E^P(\mathbf{q}) = \frac{1}{2} \sum_{n \neq m} v(\mathbf{r}_n - \mathbf{r}_m) \exp(i\mathbf{q} \cdot \mathbf{r}_n). \tag{3}$$

The heat fluctuations $\varepsilon(\mathbf{q})$ are that part of the energy fluctuations which are not produced by density fluctuations:

$$\varepsilon(\mathbf{q}) = Q_\rho E(\mathbf{q}). \tag{4}$$

There are the fundamental conservation laws for particle number, momentum and energy:

$$\mathcal{L}\rho(\mathbf{q}) = q_\beta j_\beta(\mathbf{q}) \tag{5a}$$

$$\mathcal{L}j_\alpha(\mathbf{q}) = q_\beta \tau_{\alpha\beta}(\mathbf{q})/m \tag{5b}$$

$$\mathcal{L}E(\mathbf{q}) = q_\beta j_\beta^e(\mathbf{q}). \tag{5c}$$

Splitting the energy into kinetic and potential ones, equations (5a, c) yield the time derivative of the temperature fluctuations:

$$\mathcal{L}T(\mathbf{q}) = [q_\beta j_\beta^e(\mathbf{q}) - q_\beta j_\beta(\mathbf{q})(\rho(\mathbf{q})|E(\mathbf{q})) / (\rho(\mathbf{q})|\rho(\mathbf{q})) - \mathcal{L}Q_\rho E^P(\mathbf{q})] / (2/3k_B n). \tag{5d}$$

The energy current j^e can be written as equation (1). There are three contributions to x^n : one depends on v^n only; one is given by potential terms and depends on the positions only; and a third one depends on velocities and positions. The stress tensor τ is symmetric. There are two contributions to equation (1): a kinetic part with $x^n = mv_\alpha^n v_\beta^n$ and a potential part depending on the positions only. One splits τ into irreducible tensors:

$$\tau_{\alpha\beta}(\mathbf{q}) = \tau_{\alpha\beta}^s(\mathbf{q}) + \delta_{\alpha\beta} p(\mathbf{q}) \tag{6a}$$

$$p(\mathbf{q}) = \frac{1}{3} \tau_{\alpha\alpha}(\mathbf{q}). \tag{6b}$$

The virial theorem identifies $p(\mathbf{q})$ as pressure fluctuations. The kinetic part of the pressure fluctuations is given by the kinetic energy, $p^K = E^K 2/3$, and the potential part reads:

$$p^P(\mathbf{q}) = \frac{1}{6} \sum_{n \neq m} v'(\mathbf{r}_n - \mathbf{r}_m) |\mathbf{r}_n - \mathbf{r}_m| \{1 - \exp[i\mathbf{q} \cdot (\mathbf{r}_n - \mathbf{r}_m)]\} [i\mathbf{q} \cdot (\mathbf{r}_n - \mathbf{r}_m)]^{-1} \exp(i\mathbf{q} \cdot \mathbf{r}_n). \tag{7}$$

All the variables introduced like $p(\mathbf{q})$, $\rho(\mathbf{q})$ or $j_\alpha^e(\mathbf{q})$, $j_\alpha(\mathbf{q})$ are Fourier transforms of Hermitian densities with time inversion parity +1 or -1 respectively. We will use these in the following without mentioning that the scalar products of two such variables with different parity, like $(p(\mathbf{q})|j_\alpha(\mathbf{q}))$, vanish.

Suppose that the equilibrium ensemble is altered by enforcing potential fluctuations

$\delta\mu(\mathbf{q})$, velocity fluctuations $v_\alpha(\mathbf{q})$ and temperature fluctuations $\delta T(\mathbf{q})$. Then the expectation value of X^* is changed in linear approximation by $\langle\delta X^*\rangle = [(X|\rho)\delta\mu^* + (X|j_\alpha)m/nv_\alpha^* + (X|E)\delta T^*/T]/V$. Applying this to $X = \rho$ and eliminating $\delta\mu^*$ in terms of $\langle\delta\rho^*\rangle$ one gets for the thermodynamic variation of the X density:

$$\langle\delta X(\mathbf{q})^*\rangle^{\text{th}} = X_\rho^{\text{th}}(\mathbf{q})\langle\delta\rho(\mathbf{q})^*\rangle + X_\alpha^{\text{th}}(\mathbf{q})v_\alpha(\mathbf{q})^* + X_T^{\text{th}}(\mathbf{q})\delta T(\mathbf{q})^*. \quad (8)$$

Here the thermodynamic coefficients for density, velocity and temperature are given by:

$$X_\rho^{\text{th}}(\mathbf{q}) = (X(\mathbf{q})|\rho(\mathbf{q}))k_B T/NS(\mathbf{q}) \quad (9a)$$

$$X_\alpha^{\text{th}}(\mathbf{q}) = (X(\mathbf{q})|j_\alpha(\mathbf{q}))m/N \quad (9b)$$

$$X_T^{\text{th}}(\mathbf{q}) = (X(\mathbf{q})|\varepsilon(\mathbf{q}))/TV. \quad (9c)$$

Let us note those special cases which will be needed later. The density coefficient of the pressure can be reformulated with equations (2b), (5a, b) and (6):

$$q_\alpha q_\beta (\tau_{\alpha\beta}|\rho)/q^2 = (p|\rho) = q_\alpha (\mathcal{L}j_\alpha|\rho)m/q^2 = (j_\alpha|j_\beta)m q_\alpha q_\beta/q^2 = N.$$

Hence

$$p_\rho^{\text{th}}(\mathbf{q}) = k_B T/S(\mathbf{q}) = [K + O((qr_0)^2)]/n. \quad (10a)$$

In liquids and glasses one can assume absence of long-range order, i.e. spatial correlations like $\langle\rho(\mathbf{r})\rho(\mathbf{r}')\rangle$ decay on the scale given by the inter-particle distance $r_0 \propto 1/n^{1/3}$. In this paper only fluctuations of macroscopic wavelength $2\pi/q$ are considered. Therefore Fourier transforms of correlations like $S(\mathbf{q})$ can be replaced by their homogeneous limit like $S(\mathbf{q} \rightarrow 0)$. The corrections are of order qr_0 , unless symmetry requires even higher orders of this small parameter. Such correction will be ignored here and throughout the following. In equation (9a) the $q = 0$ limit is given by the isothermal bulk modulus: $K = -[V\partial p/\partial V]_T$. Similarly one can write for the temperature coefficient

$$p_T^{\text{th}}(\mathbf{q}) = \beta + O((qr_0)^2) \quad (10b)$$

where $\beta = [\partial p/\partial T]_V$ is the tension coefficient. In the same fashion one obtains for the energy derivations:

$$E_\rho^{\text{th}}(\mathbf{q}) = [\partial u/\partial n] + O((qr_0)^2) \quad (10c)$$

$$E_T^{\text{th}}(\mathbf{q}) = c + O((qr_0)^2). \quad (10d)$$

Here c denotes the isochore heat capacity per unit volume. To evaluate the velocity coefficients of the energy current one can reformulate with equations (5b, c) and (6):

$$\begin{aligned} m q_\alpha q_\beta (j_\beta^*|j_\alpha)/q^2 &= m q_\alpha (\mathcal{L}E|j_\alpha)/q^2 = (E|\tau_{\alpha\beta})q_\alpha q_\beta/q^2 = (E|p) = (\varepsilon|p) \\ &+ (E|\rho)(\rho|\rho)^{-1}(\rho|p). \end{aligned}$$

One can either substitute the explicit expression for j° and work out the left-hand side with the aid of the virial theorem, or one discusses the right-hand side with the aid of equations (9a, b, c). As a result one finds:

$$(j_\beta^*|j_\alpha)^{\text{th}}(\mathbf{q}) = \delta_{\alpha\beta}[h + O((qr_0)^2)] \quad (10e)$$

where $h = (u + p)/n$ is the enthalpy per particle. Further details can be found in the books by Boon and Yip (1980) or Hansen and McDonald (1986).

3. Generalised constitutive equations

Equations (8)–(10) are relevant for the interpretation of experiments only if the system relaxes from the perturbed equilibrium state to the equilibrium with a timescale τ which is much shorter than the timescale τ_{ex} characterising the imposed variations of $\delta\rho$, v and δT . In glassy materials τ can be of macroscopic size. Therefore the mentioned results have to be generalised such that no assumption on the magnitude of τ/τ_{ex} is required. This will be done by studying the free relaxation of the system starting with well defined initial conditions. Let us begin by considering r distinguishable independent variables A_i , $i = 1, \dots, r$. The initial state will be an equilibrium one specified by the altered Hamiltonian $H - Y$. Here Y is defined in terms of r conjugate fields α^j : $Y = A_j \alpha^j$. The notations are explained in connection with equation (A8). In linear approximation with respect to the fields the deviation from equilibrium of some variable X^* at time $t = 0$ is given by $\langle \delta X^* \rangle(t = 0) = (X|Y) = (X|A_j)\alpha^j$. In particular one finds for the initial conditions of the distinguishable variables

$$\langle \delta A_i^* \rangle(t = 0) = \alpha_i. \tag{11a}$$

The free motion of variable X^* for $t \geq 0$ for small α_i is given by the X - Y correlator $\langle \delta X^* \rangle(t) = \Phi_{XY}(t)$. However, we will describe the dynamics by Laplace transforms $\langle \delta X^* \rangle(z)$ as explained at the beginning of § 2: $\langle \delta X^* \rangle(z) = \Phi_{XY}(z)$. In particular the $r \times r$ matrix correlator $\Phi_{ij}(z) = \Phi_{A_i A_j}(z)$ then expresses the distinguished variables in terms of their initial values:

$$\langle \delta A_i^* \rangle(z) = \Phi_{ij}(z)\alpha^j. \tag{11b}$$

The preceding formulae are the well known basis of the theory of correlation functions (Kubo 1957, Forster 1975). To obtain a formula for the general quantity $\langle \delta X^* \rangle(z)$ we shall reformulate the X - Y correlator with the aid of equation (A14). This expression simplifies, since $QY = 0$ implies $R'(z)Y = 0$. Eliminating $(A^j|Y) = \alpha^j$ with equation (11b) one gets

$$\langle \delta X^* \rangle(z) = X^i(z)\langle \delta A_i^* \rangle(z) \tag{12a}$$

$$X^i(z) = (X|A^i) - (X|R'(z)|LA^i). \tag{12b}$$

As a result the quantity $\langle \delta X^* \rangle(z)$ is expressed in terms of $\langle \delta A_i^* \rangle(z)$. These quantities are measurable in principle and they are determined by the Liouvillian resolvent, equations (A10) and (A13). The coefficients $X^i(z)$ connecting the arbitrary variable with the set of r distinguished ones are composed of the thermodynamic derivative $(X|A^i)$ and of a frequency-dependent renormalisation. The latter is determined by the reduced resolvent, equation (A11). The mathematical properties of the coefficients $X^i(z)$ follow from those of resolvent matrix elements. $X^i(z)$ is holomorphic for $\text{Im } z \neq 0$, and this ensures causality of the X - A_i relation. Writing $X^i(\omega \pm i0) = X^i(\omega) \pm X''^i(\omega)$, the reactive part $X^i(\omega) - (X|A^i)$ is connected with the dissipative one $X''^i(\omega)$ via Kramers-Kronig relations. There is the large frequency asymptotics $X^i(z) = (X|A^i) + (X|Q|LA^i)/z + O(1/z^2)$, and so on.

Formulae (12) will be specialised now by choosing as distinguished variables the five hydrodynamic fluctuations for density, current and temperature:

$$\begin{aligned} \langle \delta X(\mathbf{q})^* \rangle(z) &= X_\rho(\mathbf{q}, z)\langle \delta \rho(\mathbf{q})^* \rangle(z) + X_\alpha(\mathbf{q}, z)\langle j_\alpha(\mathbf{q})^* \rangle(z) \\ &+ X_T(\mathbf{q}, z)\langle \delta T(\mathbf{q})^* \rangle(z). \end{aligned} \tag{13}$$

To get the expressions for the coefficients one has to remember that $g_{i \neq j} = 0$ and use the

diagonal metric coefficients from equations (2). Since $QL\rho = Q\mathbf{q} \cdot \mathbf{j} = 0$, there is no renormalisation of the density coefficient:

$$X_\rho(\mathbf{q}, z) = X_\rho^{\text{th}}(\mathbf{q}). \quad (14a)$$

The renormalisation of the velocity coefficients can be reformulated with equation (5b):

$$X_\alpha(\mathbf{q}, z) = X_\alpha^{\text{th}}(\mathbf{q}) - q_\beta (X(\mathbf{q})|R'(z)|\tau_{\alpha\beta}(\mathbf{q}))/N. \quad (14b)$$

For the energy coefficient one finds from equation (5d):

$$X_T(\mathbf{q}, z) = X_T^{\text{th}}(\mathbf{q}) + [z(X(\mathbf{q})|R'(z)|E^P(\mathbf{q})) - q_\beta (X(\mathbf{q})|R'(z)|j_\beta^*(\mathbf{q}))]/VT. \quad (14c)$$

Here $Q_\rho E = QE$, $Qj = 0$ and the equation of motion for the reduced resolvent, equation (A11), was used:

$$R'(z)L' = L'R'(z) = Q + zR'(z). \quad (15)$$

Equation (13) is the desired generalised linear constitutive equation; it replaces equation (8) for motion on an arbitrary timescale. Equations (14) are the corresponding generalisations for the coefficients, replacing equations (9).

The next task is the discussion of the long-wavelength limit of the various coefficients like e.g. of $F(\mathbf{q}, z) = (\varepsilon(\mathbf{q})|R'(z)|p(\mathbf{q}))$. If $F(\mathbf{q}, z)$ were defined with the complete resolvent $R(z)$ instead of with the reduced one $R'(z)$, a meaningful small- q expansion could not be performed. The conservation laws, equations (5), show that L exhibits eigenstates for wavevector q whose eigenvalues vanish for $q \rightarrow 0$. As a result $F(\mathbf{q}, z)$ is singular in the hydrodynamic limit. Operator L' , equation (A11), does not have these eigenvectors; projector Q eliminates $\rho(\mathbf{q})$, $j_\alpha(\mathbf{q})$ and a vector $T(\mathbf{q})$ which has a large component parallel to $E(\mathbf{q})$. Thus the typical hydrodynamic singularities are eliminated in reduced Liouvillian matrix elements like $F(\mathbf{q}, z)$ (Forster 1975). However, it is not possible to write in analogy to equation (10a) $F(\mathbf{q}, z) = F(\mathbf{q} = 0, z) + O(q^y)$ with $y = 2$. Product modes composed of pairs of hydrodynamic excitations like $\varepsilon(\mathbf{q} - \mathbf{k})j_\alpha(\mathbf{k})$ lead to non-analytic small- q behaviour implying e.g. $y = \frac{1}{2}$. These are the well known long-time singularities (Pomeau and Resibois 1975). We shall not enter a deeper discussion of this problem. Rather we will assume without detailed proof that $y > 0$, so that a long-wavelength expansion of quantities like $F(\mathbf{q}, z)$ is possible. Only the leading terms will be noted in the following and the $O(q^y)$ will not be indicated. As a result we shall find constitutive equations which share with the hydrodynamic ones the restriction to the small q limit, but which generalise the classical theory in the sense that no restrictions on the frequency is imposed. Notice also that only linearised constitutive or hydrodynamic equations are considered in this paper, so that the general linear response formalism could be applied. If one wanted to extend the theory to non-linear cases one would need additional assumptions like e.g. the one on a local thermal equilibrium. Let us consider various cases one after the other.

4. Generalised hydrodynamic constitutive equations

4.1. Dynamic specific heat and heat relaxation kernel

The constitutive equation for long-wavelength energy fluctuations is obtained by substituting $X(\mathbf{q}) = E(\mathbf{q})$ in equations (13) and (14):

$$\langle \delta E(\mathbf{q})^* \rangle(z) = (\partial u / \partial n) \langle \delta \rho(\mathbf{q})^* \rangle(z) + c(z) \langle \delta T(\mathbf{q})^* \rangle(z) \quad (16a)$$

$$c(z) = c + z(E^P(\mathbf{q})|R'(z)|E^P(\mathbf{q}))/TV \quad q \rightarrow 0. \quad (16b)$$

Here equations (10c, d) were used to express the thermodynamic derivatives in equations (14a, c). Because $QE(\mathbf{q}) = QE^P(\mathbf{q})$ the total energy could be replaced by the potential contribution in equation (16b). Equation (16a) identifies $c(z)$ as the isochore dynamic specific heat. If the potential energy fluctuations are ergodic variables, the reduced resolvent matrix element in equation (16c) does not exhibit a $(1/z)$ singularity. In this case the static limit of the dynamic specific heat reduces to the corresponding thermodynamic derivative: $c(z \rightarrow 0) = c$. In addition to the general analytic properties of $c(z)$ one finds that $c''(\omega)/\omega$ is an even non-negative function of frequency.

The other quantity relevant for the interpretation of energy transport experiments is the energy current density. Because of rotational invariance the quantities $(j_\gamma^c|R'(z)|\tau_{\alpha\beta})$ and $F(\mathbf{q}) = (j_\gamma^c|R'(z)|E^P)/VT$ vanish for $q = 0$. Using equation (10e) one finds

$$\langle j^c(\mathbf{q}^*)(z) \rangle = h\langle \mathbf{j}(\mathbf{q}^*)(z) \rangle - \lambda(z)\mathbf{q}\langle \delta T(\mathbf{q}^*)(z) \rangle \quad (17a)$$

$$\lambda(z) = \frac{1}{3}((j_\alpha^c(\mathbf{q})|R'(z)|j_\alpha^c(\mathbf{q}))/TV) \quad q \rightarrow 0. \quad (17b)$$

The general properties of resolvent matrix elements imply $\lambda''(\omega)$ to be an even non-negative function of frequency. Restricting frequencies z to such small values that $\lambda(z)$ can be treated as constant, equation (17a) reduces to the standard hydrodynamic constitutive equation with

$$\lambda = \lambda''(\omega = 0) = -i\lambda(z = i0) \quad (17c)$$

denoting the thermal conductivity. So $\lambda(z)$ replaces $i\lambda$ by a generalised kernel. Let us point out that equation (17a) does not provide a systematic expansion correct in linear order in q . Because of rotational invariance one gets $F(\mathbf{q}) = O(qr_0)$, and so the neglected first renormalisation term in equation (14c) yields a correction $\tilde{\lambda}(z) \sim F(q)/q$ to $\lambda(z)$. This term describes the transfer of energy over microscopic distances due to the non-zero potential range. This term is neglected, since qr_0 is so small for the wavevector range under study.

4.2. Dynamic tension coefficient and volume relaxation kernel

To derive the constitutive equation for the pressure one has to substitute $X(\mathbf{q}) = p(\mathbf{q})$ into equations (13) and (14). The density coefficient $p_\rho(\mathbf{q} \rightarrow 0, z)$ is given by the bulk modulus K via equations (14a) and (10b). Because of rotational symmetry the leading small- q contribution to the $p_\alpha(\mathbf{q}, z)$ renormalisation in equation (14b) is due to the scalar part of the stress tensor, equations (6). The thermodynamic derivative in equation (14c) is given by the tension coefficient β from equation (10b), and only the first renormalisation term contributes in the $q \rightarrow 0$ limit. Since $Qp(\mathbf{q}) = Qp^P(\mathbf{q})$ one finds the results:

$$\langle \delta p(\mathbf{q}^*)(z) \rangle = K\langle \delta \rho(\mathbf{q}^*)(z) \rangle - (1/n)K_v(z)\langle \mathbf{q} \cdot \mathbf{j}(\mathbf{q}^*)(z) \rangle + \beta(z)\langle \delta T(\mathbf{q}^*)(z) \rangle \quad (18a)$$

$$K_v(z) = (p^P(\mathbf{q})|R'(z)|p^P(\mathbf{q}))/V \quad q \rightarrow 0 \quad (18b)$$

$$\beta(z) = \beta + z(p^P(\mathbf{q})|R'(z)|E^P(\mathbf{q}))/TV \quad q \rightarrow 0. \quad (18c)$$

If there are no density fluctuations, $\langle \delta \rho \rangle = \langle \delta \dot{\rho} \rangle = 0$, coefficient $\beta(z)$ is the coefficient of proportionality between pressure and temperature fluctuations. It generalises the

thermodynamic tension coefficient β to a dynamic quantity. If E^P or p^P are ergodic so that $\langle p^P | R'(z) | E^P \rangle$ does not have a $(1/z)$ pole, the dynamic coefficient reduces to the thermodynamic one in the static limit $\beta(z \rightarrow 0) = \beta$. Coefficient $K_v(z)$ determines pressure changes due to volume variation velocities. The usual considerations show that $K_v''(\omega)$ is an even non-negative function of ω . Since $p^P(\mathbf{q})$ and $E^P(\mathbf{q})$ are Fourier transforms of Hermitian variables of equal time inversion symmetry $\beta''(\omega)/\omega$ is an even real function of ω . The role of E and p can be interchanged in the definitions of β and $\beta(z)$.

4.3. Shear relaxation kernel

If $X(\mathbf{q}) = \tau_{\gamma\delta}^s(\mathbf{q})$ is substituted one finds that $X_\rho(\mathbf{q}, z)$ and $X_T(\mathbf{q}, z)$ vanish like $(r_0 q)^2$ in the long-wavelength limit because of rotational symmetry. For the same reason the scalar part of $\tau_{\alpha\beta}(\mathbf{q})$ contributes in equation (14b) only terms of type $q_\beta O((r_0 q)^2)$. As a result the constitutive equation (13) reads in leading order

$$\langle \delta \tau_{\gamma\delta}^s \rangle(z) = -(\tau_{\gamma\delta}^s | R'(z) | \tau_{\alpha\beta}^s)(q_\beta j_\alpha - \delta_{\alpha\beta} \mathbf{q} \cdot \mathbf{j}/3).$$

The coefficients of the fourth-rank tensor can all be expressed in terms of one. As a result one gets

$$\langle \tau_{\alpha\beta}^s(\mathbf{q})^* \rangle(z) = -(1/n) K_s(z) [q_\alpha \langle j_\beta(\mathbf{q})^* \rangle(z) + q_\beta \langle j_\alpha(\mathbf{q})^* \rangle(z) - \frac{2}{3} \delta_{\alpha\beta} \langle \mathbf{q} \cdot \mathbf{j}(\mathbf{q})^* \rangle(z)] \quad (19a)$$

$$K_s(z) = (\tau_{xz}(\mathbf{q}) | R'(z) | \tau_{xz}(\mathbf{q})) / V \quad \mathbf{q} = (0, 0, q) \quad q \rightarrow 0. \quad (19b)$$

Again $K_s''(\omega)$ is an even non-negative function of frequency ω . If the shear is ergodic, the constitutive equation (19a) reduces to the Navier–Stokes equation result with

$$\eta = K_s''(\omega = 0) = -i K_s(z = i0) \quad (20)$$

denoting the shear viscosity. So $K(z)$ generalises $i\eta$ to a frequency-dependent kernel.

5. Generalised hydrodynamic equations

Some experiments can be analysed with the formulated constitutive equations. For example in an ordinary calorimetric measurement a homogeneous energy variation $\langle \delta E(\mathbf{q} = 0)^* \rangle(z)$ is enforced by light absorption and the temperature change $\langle \delta T(\mathbf{q} = 0)^* \rangle(z)$ is observed by some thermometer coupling to the particles' kinetic energy. Essentially, the result of the experiment is connected to the theory via $c(z)$ in equations (16). However, in other experiments the system is disturbed by manipulations of boundary conditions. This is the case for the quoted heat spectroscopy (Birge and Nagel 1985) as well as for sound reflection measurements (Litovitz and Davis 1965). To deal with these situations one has to know the equations of motion for the distinguished variables. Again the standard hydrodynamic equations have to be generalised such that no *ad hoc* restrictions for the frequencies are imposed. Within our approach the desired results are obtained from special constitutive equations. Let us first remember the elementary identity for Laplace transforms: $z \langle A_j^* \rangle(z) + \langle A_j^* \rangle(t=0) = \langle (-\dot{A})^* \rangle(z)$. Since $-i\dot{A}_j = LA_j$ one gets the equation of motion $z \langle A_j^* \rangle(z) - \langle (LA_j)^* \rangle(z) = -\langle A_j^* \rangle(t=0)$. Now one can use the r constitutive equations (12a) for $X = LA_j$, $j = 1, \dots, r$:

$$\langle (LA_j)^* \rangle(z) = N_j^i(z) \langle \delta A_i^* \rangle(z). \quad (21a)$$

The equations of motion then read

$$[z\delta_j^i - N_j^i(z)]\langle\delta A_i^*\rangle(z) = -\langle\delta A_j^*\rangle(t=0). \quad (21b)$$

With equations (11) one finds the equation for the matrix correlator of the distinguished variables, equation (A10),

$$[z\delta_j^i - N_j^i(z)]\Phi_i^K(z) = -\delta_j^K. \quad (21c)$$

The preceding three equations are pairwise equivalent. From equation (12b) one notices $N_j^i(z) = (LA_j|A^i) - (LA_j|R'(z)|LA^i)$ and so the results correspond to one of the Frobenius formulae, equation (A3) or (A12). The equations (21) are the Zwanzig–Mori equations which express time derivatives or correlators in terms of memory kernels (Forster 1975).

Because of rotational invariance the current correlator can be represented in terms of two independent functions:

$$\Phi_{\alpha\beta}(\mathbf{q}, z) = (j_\alpha(\mathbf{q})|R(z)|j_\beta(\mathbf{q})) = (q_\alpha q_\beta/q^2)\Phi_l(\mathbf{q}, z) + [\delta_{\alpha\beta} - (q_\alpha q_\beta/q^2)]\Phi_t(\mathbf{q}, z).$$

Here $\Phi_l(\mathbf{q}, z)$ is the correlator of the longitudinal currents, $\Phi_l(\mathbf{q}, z) = (j_l(\mathbf{q})|R(z)|j_l(\mathbf{q}))$, where $j_l(\mathbf{q}) = \mathbf{j}(\mathbf{q}) \cdot \mathbf{q}/q$. Choosing $\mathbf{q} = (0, 0, q)$ the transverse current correlator is given by $\Phi_t(\mathbf{q}, z) = \Phi_{xx}(\mathbf{q}, z) = \Phi_{yy}(\mathbf{q}, z)$. There is no mixing between transverse currents and any of the other hydrodynamic modes, and so the corresponding expression (21c) reduces to a scalar equation. From equations (5b), (6a), (18a) and (19a) one finds the specialisation of equation (21a):

$$\langle(Lj_x(\mathbf{q})^*)\rangle(z) \cdot m = q\langle\tau_{xz}^s(\mathbf{q})^*\rangle(z) = -K_s(z)q^2\langle j_x(\mathbf{q})^*\rangle(z).$$

As a result the transverse correlator is determined by the shear relaxation kernel. It has the form of a generalised diffusion propagator:

$$[z + q^2K_s(z)/nm]\Phi_t(\mathbf{q}, z) = -N/m. \quad (22)$$

The three longitudinal vectors $A_1(\mathbf{q}) = \rho(\mathbf{q})$, $A_2(\mathbf{q}) = j_l(\mathbf{q})$, $A_3(\mathbf{q}) = T(\mathbf{q})$ are coupled and equation (21c) is a 3×3 matrix identity. The task is the determination of N_j^i from the three constitutive equations (21a). The first of them is trivial, since the continuity equation (5a) yields

$$\langle(L\rho(\mathbf{q})^*)\rangle(z) = q\langle j_l(\mathbf{q})^*\rangle(z). \quad (23)$$

The second one is obtained by combining the constitutive equations (18a) and (19a) with the momentum conservation law $Lj_z m/q = \tau_{zz} = \tau_{zz}^s + p$, equations (5b) and (6):

$$\langle(Lj_l(\mathbf{q})^*)\rangle(z) = (qK/m)\langle\delta\rho(\mathbf{q})^*\rangle(z) - q^2K_l(z)/(nm)\langle j_l(\mathbf{q})^*\rangle(z) + q\beta(z)/m\langle\delta T(\mathbf{q})^*\rangle(z). \quad (24a)$$

Here the longitudinal relaxation kernel was introduced:

$$K_l(z) = K_v(z) + \frac{1}{3}K_s(z). \quad (24b)$$

To derive the remaining third constitutive relation from equation (5d) one uses result (17a) for the energy current and the discussion preceding equation (10e) in order to write $(\rho|E)/(\rho|\rho) = h - (\varepsilon|p)/N$. Hence with definition (10b) for β one obtains

$$\langle j_l^e(\mathbf{q})^*\rangle(z) - \langle j_l(\mathbf{q})^*\rangle(z)(\rho|E)/(\rho|\rho) = (T\beta/n)\langle j_l(\mathbf{q})^*\rangle(z) - q\lambda(z)\langle\delta T(\mathbf{q})^*\rangle(z). \quad (25a)$$

To deal with the last term in equation (5d) one has to work out the constitutive equation for $X = LQ_\rho E^P = LQE^P$. Variable X has odd time inversion symmetry and this implies in particular $X_\rho(z) = 0$ in equation (14a). Because of equation (15) one can write $\langle X|R'(z)|A \rangle = \langle E^P|Q|A \rangle + z\langle E^P|R'(z)|A \rangle$. Hence one derives for equation (14b):

$$NX_z = (Q_\rho E^P|Lj_z)m - q[(E^P|Q_\rho|\tau_{zz}) + z(E^P|R'(z)|\tau_{zz})] = -qz(E^P|R'(z)|\tau_{zz}).$$

In leading order in q only the scalar part of the stress tensor contributes because of rotational symmetry. From equations (6) one finds $X_z = -qz(E^P|R'(z)|p^P)/N$. Equation (14c) yields in leading order for small q :

$$X_T = [z(E^P|Q_\rho|E^P) + z^2(E^P|R'(z)|E^P)]/VT.$$

Remembering equation (16b) one summarises the formulae to

$$\begin{aligned} \langle (LQ_\rho E^P(\mathbf{q}))^* \rangle(z) &= -qz(E^P(\mathbf{q})|R'(z)|p^P(\mathbf{q}))\langle j_i(\mathbf{q})^* \rangle(z) \\ &+ z[c(z) - 3k_B n/2]\langle \delta T(\mathbf{q})^* \rangle(z). \end{aligned} \tag{25b}$$

Combining the preceding two equations with equation (18c) one arrives at the desired result:

$$\begin{aligned} \langle (LT(\mathbf{q}))^* \rangle(z) &= [2T\beta(z)/3k_B n^2]q\langle j_i(\mathbf{q})^* \rangle(z) + z\langle \delta T(\mathbf{q})^* \rangle(z) \\ &- [zc(z) + q^2\lambda(z)][2/(3k_B n)]\langle \delta T(\mathbf{q})^* \rangle(z). \end{aligned} \tag{26}$$

Results (23), (24) and (26) are one way to note the closed set of equations of motion for long-wavelength longitudinal fluctuations. Notice that all the four coefficients $K_i(z)$, $\lambda(z)$, $\beta(z)$ and $c(z)$ in these equations have been analysed in § 4. According to equation (21a) one can read off matrix $N_j^i(z)$ and note the result in the form of the negative inverse correlator $-\Phi_i^K(z)$, equation (21c):

$$[z\delta_j^i - N_j^i(z)]: \begin{bmatrix} z & -q & 0 \\ -qK/m & z + q^2K_1(z)/nm & -q\beta(z)/m \\ 0 & -q\beta(z)(2T/3k_B n^2) & [zc(z) + \lambda(z)q^2](2/3k_B n) \end{bmatrix}. \tag{27}$$

This formula generalises to arbitrary frequencies the known hydrodynamic matrix (Hansen and McDonald 1986).

For the discussion of boundary-value problems it is more useful to transform from fluctuations to densities as function of position \mathbf{r} and write the result in the form of equation (21b). According to equation (1) the Fourier transform is used with convention $X(\mathbf{q}) = \int d^3r \exp(i\mathbf{q} \cdot \mathbf{r})X(\mathbf{r})$. To simplify the notation let us write $\langle X(\mathbf{r}) \rangle(z) = X(\mathbf{r}, z)$, $\langle X(\mathbf{r}) \rangle(t=0) = X_0(\mathbf{r})$. Then the continuity equation (23) reads

$$-i[z\rho(\mathbf{r}, z) + \rho_0(\mathbf{r})] + \text{div } \mathbf{j}(\mathbf{r}, z) = 0. \tag{28}$$

The momentum conservation law is obtained by combining equations (22) and (24):

$$\begin{aligned} -i[z\mathbf{j}(\mathbf{r}, z) + \mathbf{j}_0(\mathbf{r})]m + K \text{grad } \rho(\mathbf{r}, z) + \beta(z) \text{grad } T(\mathbf{r}, z) \\ = -iK_s(z)\Delta \mathbf{j}(\mathbf{r}, z)/n - i[K_v(z) + \frac{1}{3}K_s(z)] \text{grad div } \mathbf{j}(\mathbf{r}, z)/n. \end{aligned} \tag{29}$$

The equation for temperature variations follows from equation (26):

$$-i[zc(z)T(\mathbf{r}, z) + \frac{2}{3}k_B nT_0(\mathbf{r})] + i\lambda(z)\Delta T(\mathbf{r}, z) = -\beta(z) \text{div } \mathbf{j}(\mathbf{r}, z)/n. \tag{30}$$

The results are identical to those one would obtain by Laplace transformation of the ordinary hydrodynamic equations of simple classical fluids. This holds with the reservation that in place of the transport coefficients η , ζ , λ there appear the kernels $-iK_s(z)$, $-iK_v(z)$, $-i\lambda(z)$, and instead of the thermodynamic derivatives there occur the corresponding dynamic generalisations $\beta(z)$ and $c(z)$. As a result one can take over all the known results of the classical theory as for example the transformation to isobaric conditions or the formulae for sound reflectivity coefficients; one merely has to replace the material constants by the corresponding complex functions of frequency. The situation is quite analogous to electrodynamics of simple media; there one gets the relevant equations for long-wavelength fields from the phenomenological ones by replacing the dielectric constant by a frequency-dependent function. Notice that the preceding equations describe the dynamics for $t \geq 0$ as follows from the specified very special prehistory for $t \leq 0$: $\langle \delta A_i^* \rangle(t) = \exp(\epsilon t \alpha_i)$, $\epsilon \rightarrow +0$ (Kubo 1957). Formulae for the more general case of an arbitrary prehistory can be derived from the obtained dynamic susceptibilities, and they are more involved (Jäckle and Frisch 1986).

6. Conclusions

The preceding analysis focused on the fluctuations of the temperature T rather than on those of the energy E . It might be worth while to explain why in glassy systems this procedure is to be preferred compared to a direct generalisation of the standard approach towards hydrodynamics. For the sake of simplicity let us ignore the coupling between temperature and density fluctuations. Let us remember the experimental fact that slow structural relaxation is the most outstanding feature of glassy dynamics. This means that many spectra like the one for density fluctuations $\Phi''(q, \omega)$ or for the specific heat $c''(\omega)/\omega$ exhibit a low-frequency resonance whose width $1/\tau$ decreases strongly with decreasing temperature. Below the calorimetric glass transition temperature the corresponding relaxation time τ becomes macroscopic. Let us simplify the reasoning by considering an idealised glass state where $1/\tau = 0$. Then the structural relaxation resonance is idealised by an elastic peak: $\Phi''(q, \omega) = \pi\delta(\omega)\Delta(q)$ or $c''(\omega)/\omega = \pi\delta(\omega)\Delta_c$ for $\omega \approx 0$. The corresponding fluctuations do not relax to zero, they arrest spontaneously; the variables exhibit non-ergodic dynamics for this idealised situation (Kubo 1957). Equivalently, the correlators develop a non-ergodicity pole: $\Phi:(q, z) = -\Delta(q)/z + \text{regular terms}$. The appearance of such poles is equivalent to the existence of similar poles in properly defined relaxation kernels. For the density fluctuations this is the longitudinal current relaxation kernel (Götze 1981), which reduces to $K_l(z)$ in the long-wavelength limit. Similarly, the possibility for the idealised glass to sustain static shear, i.e. the validity of Hooke's law for the static stress-strain relation for shear, is equivalent to the existence of a non-ergodicity pole for the transverse current relaxation kernel, which reduces to $K_s(z)$ for small wavevectors (Bengtzelius and Sjögren 1986). It is also an experimental fact that heat conduction of high-temperature glasses is not drastically different from that of the corresponding crystals or from that of the liquid state at some elevated temperature. Indeed, there is no obvious reason why structural arrest in a densely packed system should have a strong effect on the exchange of kinetic energy between the vibrating atoms. Hence long-wavelength temperature fluctuations will propagate as described by an ordinary diffusion equation. This is equivalent to kernel $\lambda(z)$ in equation (30) being a smooth function of frequency. So within our formalism normal variables like $\lambda(z)$ are well

separated from those exhibiting structural relaxation resonances like $K_i(z)$ or $c(z)$; and the latter are related most transparently to the resonances of the correlators. On the other hand, the correlator for the heat fluctuations $\Phi^e(q, z) = (\varepsilon(q)|R(z)|\varepsilon(q))$, which is a basic quantity within the usual hydrodynamic theory (Forster 1975), does not have a simple form for glassy systems. In the idealised glass state it exhibits a non-ergodicity pole, since arrest of density fluctuations implies that for potential energy fluctuations. In addition it has to exhibit a diffusion pole as a result of the temperature propagation process. Hence for small frequencies and wavevectors one finds $\Phi^e(q, z) = -(\Delta_e/z) - a/(z + i\lambda q^2)$. If one forces this result into one relaxation kernel $\kappa(q, z)$, $\Phi^e(q, z) \propto -1/[z + \kappa(q, z)q^2]$ (Kadanoff and Martin 1963), the latter becomes a complicated singular function of q . It is impossible to describe simultaneously structural arrest and diffusion by a simple expression for a single kernel $\kappa(q, z)$. The proper way to find formulae for quantities like $\Phi^e(q, z)$ is the derivation of a constitutive equation and then the substitution of the simple results for the correlators of ρ , j , T . More explicitly, substitution of $X = Y = \varepsilon(q)$ into equation (A14) expresses $\Phi^e(q, z)$ as a linear combination of the hydrodynamic correlators $\Phi_{ij}(q, z)$ with coefficients evaluated in § 4.

More theoretical support for our approach comes from the recently developed microscopic theory for undercooled liquids and glasses (Bengtzelius *et al* 1984, Götze and Sjögren 1987b). Within that theory density fluctuations $\rho(\mathbf{q})$ and density pair excitations $\rho(\mathbf{q} - \mathbf{k})\rho(\mathbf{k})$ are the essential variables. They exhibit slowing down of the motion for all wavevectors \mathbf{q} and \mathbf{k} , in particular for wavevectors representing short-range correlations $q \sim k \sim 1/r_0$, because of non-linear interaction effects. As a result all such variables exhibit structural relaxation peaks, or non-ergodicity poles if the idealised glass is considered, which have an overlap with the mentioned modes. For the generalised hydrodynamic equations this is the case for the variables entering $c(z)$, $\beta(z)$, $K_s(z)$ and $K_v(z)$. The derived microscopic formulae are a most convenient starting point for their approximate evaluation within the microscopic theory. On the basis of that theory one can conclude without any further detailed work that the spectra of the mentioned quantities exhibit the well known stretching phenomenon, and that the strongly temperature-dependent scale τ is universal for all the variables (Götze 1987, Götze and Sjögren 1987a). The mode-coupling contributions to $\lambda(z)$ in equation (17b) are proportional to squares of the decay amplitudes $(j^e(\mathbf{q})|A)$, where A are products of density fluctuations. Since A and j^e have different time inversion symmetries, the amplitudes vanish. Therefore $\lambda(z)$ does not exhibit a structural relaxation peak. The heat fluctuations $\varepsilon(\mathbf{q})$ have one part which is a superposition of pair modes. Every term in this superposition becomes slow in glassy systems. The other part, the temperature fluctuations, is perpendicular to the single and multiple density modes. It becomes slow only for small wavevectors because of the energy conservation law. The constitutive equations automatically separate the two quite different contributions mentioned. So the essential point of this paper is the proper separation of those modes which become almost non-ergodic only in glassy systems, from those which become slow for small wavevectors in all systems because of conservation laws.

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Appendix

A general expression for resolvent matrix elements in terms of the reduced resolvent will be derived. The desired result is a reformulation of well known Frobenius' formulae (Gantmacher 1986) for the inversion of a block matrix:

$$M = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \tag{A1}$$

$$M^{-1} = \begin{pmatrix} K^{-1} & -K^{-1}BD^{-1} \\ -D^{-1}CK^{-1} & D^{-1} + D^{-1}CK^{-1}BD^{-1} \end{pmatrix} \tag{A2}$$

$$K = A - BD^{-1}C. \tag{A3}$$

Here A , B , C and D are matrices of type $r \times r$, $r \times s$, $s \times r$ and $s \times s$ respectively. To write equation (A2) in a more condensed form let us define the following four block matrices:

$$K' = \begin{pmatrix} K^{-1} & 0 \\ 0 & 0 \end{pmatrix} \quad D' = \begin{pmatrix} 0 & 0 \\ 0 & D^{-1} \end{pmatrix} \tag{A4}$$

$$P = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad Q = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}. \tag{A5}$$

Then equation (A3) can be written in the equivalent fashion:

$$P(M - MD'M)PK'P = P. \tag{A6}$$

Furthermore

$$M^{-1} = D' - (P - D'M)K'(MD' - P). \tag{A7}$$

Let us consider the block matrices as linear mappings in an $(r + s)$ -dimensional unitary vector space. Let $A_i, i = 1, \dots, r$, be a basis of the subspace onto which operator P projects. The $r \times r$ metric matrix will be denoted by g_{ij} and the usual conventions like $g^{ij}g_{ij} = \delta^{ij}$, $A^i = g^{ij}A_j$ will be applied. One gets:

$$(A_i|A_j) = g_{ij} \quad P = |A^i)(A_i| \quad Q = 1 - P. \tag{A8}$$

For complex z let $M = L - z$ for some operator L . Then $R(z) = M^{-1}$ is the resolvent of L :

$$R(z) = (L - z)^{-1}. \tag{A9}$$

Block matrix K' is given by the r^2 matrix elements of the resolvent formed with the specified basis:

$$\Phi_{ij}(z) = (A_i|R(z)|A_j). \tag{A10}$$

Equation (A6) expresses this matrix in terms of the reduced resolvent $D' = R'(z)$, where

$$R'(z) = Q(L' - z)Q \quad L' = QLQ. \tag{A11}$$

Since $QP = 0$, one gets $QMP = QLP$, $PMQ = PLQ$ and therefore

$$[z\delta_i^j - (A_i|L|A^j) + (A_i|LR'(z)L|A^j)]\Phi_j^i(z) = -\delta_i^j. \tag{A12}$$

To express the general resolvent matrix element

$$\Phi_{XY}(z) = (X|R(z)|Y) \quad (\text{A13})$$

in terms of the reduced resolvent one evaluates $(X|M^{-1}|Y)$ from equation (A7):

$$\Phi_{XY}(z) = (X|R'(z)|Y) - [(X|A^i) - (X|R'(z)L|A^i)]\Phi_{ij}[(A^j|LR'(z)|Y) - (A^j|Y)]. \quad (\text{A14})$$

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