A new direct method for calculation of coherent memory functions (MFs) entering the Nakajima-Zwanzig (or GME) equation is presented for rigid molecular chains with natural boundary conditions. The method is illustrated on the chains with three and five molecules and various kinds of imperfections. Obtained results imply a necessity of a more careful interpretation of experimental data (e.g. diffusivity).

1. INTRODUCTION

In our previous paper [1] (henceforth referred to as I) we were dealing with the derivation of the memory function (MF) (I.7) which is the kernel of the Nakajima-Zwanzig integral equation (I.1) for density operator. Our method for solving this problem is worth as a starting point for different perturbation expansions and theoretical treatments of the initial conditions in (I.1) as well as properties of symmetry of the memory function.

To avoid lengthy numerical calculations of determinants for large matrices and to avoid an indefiniteness in the condition (I.25) for number of poles, used in the expression (I.18) for the MF, we suggest for special cases another method based on the direct inversion of superoperator expressions.

In section 2 a basis of this new technique is given. In section 3 we solve some examples for linear finite chain. The discussion given in section 4 shows some physical consequences.

2. THE "σ-MATRIX" TECHNIQUE — MFs

As in I, after the completing the definition of the MF as zero for negative times, (see (I.7))\(^1\)

\[ w(t) = -\theta(t) \mathcal{D} \mathcal{L} e^{-\imath \mathcal{Q} z} Q \mathcal{L} \mathcal{D} \]

we are able to define the Fourier transform

\[ w(z) = \int_{-\infty}^{+\infty} w(t) e^{\imath z t} \, dt, \quad \text{Im} \, z \geq 0. \]

\(^1\) We use the usual convention \(\hbar = 1\).
After a straightforward calculation we arrive at

\[ w(z) = -i \mathcal{D} \mathcal{L} [\mathcal{Q}(z - \mathcal{L}) \mathcal{Q}]^{-1} \mathcal{D} \mathcal{L}. \]

Up to now we have used only the principal properties of projection superoperators

\[ \mathcal{D} + \mathcal{Q} = 1, \quad \mathcal{D} \cdot \mathcal{Q} = 0. \]

The projection superoperator \( \mathcal{D} \) decomposes the density operator \( \rho \) into the relevant part \( -\mathcal{D} \rho \) and irrelevant part \( -\mathcal{Q} \rho \). In the absence of phonons (or other kind of a bath) we take the following form of \( \mathcal{D} \) [2]

\[ \mathcal{D} = \sum_m |m\rangle \langle m| \langle |m\rangle \langle m|, \ldots \]

where \( \{|m\rangle\} \) is the complete orthonormal set of Wannier-like functions, \( m = 1, 2, \ldots, N \) is the site index. For the notation see [2].

Let us concentrate our attention on a linear finite chain with Hamiltonian \( \mathcal{H} \)

\[ \mathcal{H}_{ii} = \epsilon_i \quad \text{for} \quad i = 1, \ldots, N \]
\[ \mathcal{H}_{ik} = \mathcal{H}_{ki} = J_i \quad \text{for} \quad i = k - 1 \]
\[ \mathcal{H}_{ik} = 0 \quad \text{otherwise}. \]

The matrix \( Q(z - \mathcal{L}) \mathcal{Q} \) which is to be inverted is a four-index quantity (tetradix). Owing to the properties of \( Q \), we need only off-diagonal elements of the Hermitian tetradix

\[ (Q \mathcal{L} \mathcal{Q})_{i_1 i_2 k_1 k_2} = \sigma_{i_1 i_2, k_1 k_2} = \sigma(i_1 i_2, k_1 k_2) \]

\( i_1 \neq i_2 \) as well as \( k_1 \neq k_2 \). For every such pair of combinations of indices \( i_1 \neq i_2, i_1, i_2 = 1, \ldots, N \) it is worth introducing a single index \( I = 1, 2, \ldots, N(N - 1) \).

Before explaining the basic trick on which the present work relies, we introduce some notations. Let us denote the lower (upper) half of the set \( 1, 2, \ldots, N(N - 1) \) by \( \mathcal{J}_L (\mathcal{J}_U) \), i.e.

\[ \mathcal{J}_L = 1, \ldots, \frac{N(N - 1)}{2}, \quad \mathcal{J}_U = \frac{N(N - 1)}{2} + 1, \ldots, N(N - 1). \]

To pairs \((i_1 i_2)\) with \( i_1 < i_2 \) we ascribe the values of \( I \) from \( \mathcal{J}_L \) in an arbitrary manner. For pairs with \( i_1 > i_2 \) we assume \( I \) from \( \mathcal{J}_U \) ascribed in such a way that

\[ i_1(I) = i_2(I - I_0), \quad i_2(I) = i_1(I - I_0) \]

\( I \in \mathcal{J}_U, \quad (I - I_0) \in \mathcal{J}_L, \quad I_0 = \frac{N(N - 1)}{2} \).

As an example, for three sites and ascription \( I = 1, 2, 3 \) for \((i_1 i_2) = (12), (13)\) and \((23)\), the values of \( I = 4, 5, 6 \) correspond to \((i_1 i_2) = (21), (31)\) and \((32)\), respectively.