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Continued-Fraction Description of Collective Motion in Simple Fluids*

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In this paper a many-variable form of the Mori continued-fraction technique is employed to investigate the relaxation function of simple liquids. A general relationship between a truncated-continued-fraction expression and the Zwanzig and Nossal variational result for the relaxation function is presented. In addition, a specific example of this relationship is explored to show the connection between the eigenvalues found from high-frequency hydrodynamic equations and those obtained from a variational method. The structure of the relaxation function in the low-wave-vector limit is examined in considerable detail, and some comments are made concerning the applicability of the variational method in the low-wave-vector and high-frequency regime.

I. INTRODUCTION

Recently there has been considerable interest in the description of irreversible processes in simple liquids. Much of the stimulus for research in this area has been provided by the molecular dynamics[1-3] calculations of correlation functions and numerous neutron and light scattering experiments performed on simple liquids.[4-6] The memory function method of Zwanzig[7] and Mori[8] has proved an extremely useful formalism to interpret the results of these experiments. The basic attractiveness of a description of simple fluids in terms of collective excitations prompted the suggestion by Zwanzig[9] that one could construct collective modes by a variational solution of the Liouville equation. Subsequent work by Nossal and Zwanzig[10] indicated how the use of basis functions constructed from the conserved variables was able to provide microscopic analogues of the modes obtained by the use of linearized hydrodynamic equations. In addition, attempts were made to construct the microscopic analogues of high-frequency hydrodynamic modes by including the time derivatives of the conserved variables in the basis set for the variational calculation.[11,12] The question of whether such modes have physical significance has been the subject of several recent investigations.[13-15] Even if the lifetimes of these modes are too short to have physical significance, a variational procedure can, in principle, provide a convenient mathematical basis for the calculation of the conserved variable correlation functions.

In this article we wish to discuss several aspects of the variational solution to the Liouville equation in terms of Mori's continued-fraction expansion for correlation functions.[16] In Sec. II the matrix of the conserved variable correlation functions is calculated by a variational procedure equivalent to that of Zwanzig and Nossal, and the result is found to correspond to a particular truncation of the continued-fraction expression. In addition, the use of an extended set of variables in the framework of the generalized Langevin equation is discussed in terms of the continued-fraction expression and compared to the variational approach. In Sec. III we consider the low-$\vec{k}$ (wave vector) limit of the equations explicitly in order to obtain some information about the description of simple fluids in terms of high-frequency long-wavelength collective modes. The paper is concluded with a brief discussion in Sec. IV.

II. GENERAL DISCUSSION

A. Relation between Variational Approach and Continued-Fraction Method

In this section several aspects of the description of simple fluids in terms of collective excitations are discussed. It is illustrated how this topic can be most easily described in terms of Mori's continued-fraction representation of correlation functions. In this section and Sec. III it is shown that this formalism is especially convenient when one wishes to define the frequencies and wave vectors which are of interest.

Since in this paper we wish to explore the low-$\vec{k}$ limit of the equations which are obtained, the set of conserved variables takes on a fundamental significance. In this limit, these variables are strongly coupled and have similar time dependence. Consequently, these variables are always treated as a unit, and thus the Mori formalism will yield matrix equations involving the hydrodynamic variables. (Although Mori's formulation in Ref. 16 was

in matrix language, to our knowledge, the continued-fraction technique has not been applied to fluids utilizing a set of variables.)

One of the aims of this section is to point out the relation between the variational procedure of Zwanzig and Nossal and the continued-fraction expansion. Zwanzig and Nossal pointed out that perhaps the most straightforward way of constructing the collective coordinates, which can then be used to evaluate the pertinent correlation functions, is to calculate the approximate eigenfunctions of the Liouville operator by a variational technique. The trial functions which they use are constructed from the spatial Fourier transforms of the number, momentum, and energy densities and the time derivatives of the latter two quantities. This approach can easily be shown to correspond to a particular truncation of the continued-fraction expansion. As an example, the matrix of conserved variable correlation functions is calculated by employing a particular truncation scheme. It is shown that the resulting matrix equation is equivalent to the one obtained by a variational approach with trial functions constructed from the conserved variables and their time derivatives. Furthermore, it is shown that this is in general not equivalent to the use of high-frequency hydrodynamic equations proposed by Nossal. This fact will be indicated in this section, and discussed in more detail in Sec. III, which will deal with the small-$\vec{k}$ limit.

Finally, the general question of the choice of variables is discussed. It is demonstrated that extending the set of variables to include the time derivatives of those variables already in the chosen set is equivalent to a truncation of the continued-fraction expansion of the original set one level deeper. Since one would have to go to infinite order in the expansion to compensate for the neglect of one of the conserved variables, it is important that none of these variables be omitted in the original set. Since this section and Sec. III will utilize the symbols introduced by Mori, we begin with a brief review of his results and notation.

If one selects a set of variables $\{n_k, \vec{g}_k, e_k\}$, the spatial Fourier transforms of the number density being n_k, the momentum density being $\vec{g}_k$, and the energy density being e_k, and denotes this collection of variables by the vector $\underline{A}$,

$$\underline{A} = \begin{pmatrix} n_k \\ \vec{g}_k \\ e_k \end{pmatrix} , \tag{2.1}$$

Mori's expression for the corresponding relaxation matrix can be written[17]

$$\underline{\Xi}_0(z) = \langle \underline{A}(z)\underline{A}^\dagger \rangle \langle \underline{A}\,\underline{A}^\dagger \rangle^{-1} \tag{2.2}$$

$$= \left[z\underline{I} - i\underline{\omega}_0 + \begin{pmatrix} 0 & 0 \\ \underline{\Xi}_1(z) & \end{pmatrix} \underline{\Delta}_1^2 \right]^{-1} . \tag{2.3}$$

In this and the subsequent equations $\underline{A}(z)$ is used to denote the Laplace transform of $\underline{A}(t)$ while $\underline{A} \equiv \underline{A}(t=0)$ and $\underline{A}^\dagger$ is the adjoint of $\underline{A}$. The continued-fraction representation of $\underline{\Xi}_0(z)$ is obtained when $\underline{\Xi}_1(z)$ is expanded as

$$\underline{\Xi}_1(z) = \cfrac{1}{z\underline{I} - i\underline{\omega}_1 + \cfrac{1}{z\underline{I} - i\underline{\omega}_2 + \underline{\Delta}_2^2 \ddots \cfrac{1}{z\underline{I} - i\underline{\omega}_n + \underline{\Xi}_{n+1}(z)\underline{\Delta}_{n+1}^2} \underline{\Delta}_n^2}} , \tag{2.4}$$

where

$$i\underline{\omega}_j = \langle \dot{\underline{f}}_j \underline{f}_j^\dagger \rangle \langle \underline{f}_j \underline{f}_j^\dagger \rangle^{-1} , \tag{2.5a}$$

$$\underline{\Delta}_j^2 = \langle \underline{f}_j \underline{f}_j^\dagger \rangle \langle \underline{f}_{j-1} \underline{f}_{j-1}^\dagger \rangle^{-1} \quad (j \geq 2) , \tag{2.5b}$$

$$\underline{\Xi}_j(z) = \langle \underline{f}_j(z) \underline{f}_j^\dagger \rangle \langle \underline{f}_j \underline{f}_j^\dagger \rangle^{-1} . \tag{2.5c}$$

The matrix $\underline{\Delta}_1^2$ is defined by

$$\underline{\Delta}_1^2 = \langle \underline{f}_1 (0 \underline{f}_1^\dagger) \rangle \langle \underline{A}\,\underline{A}^\dagger \rangle^{-1} . \tag{2.6}$$

The random forces $\underline{f}_j$ and their time derivatives are defined by

$$\underline{f}_0 = \underline{A} , \tag{2.7a}$$

$$\begin{pmatrix} 0 \\ \underline{f}_1 \end{pmatrix} = iL_1 \underline{A} , \tag{2.7b}$$

$$\underline{f}_j = iL_j \underline{f}_{j-1} \quad (j \geq 2) , \tag{2.7c}$$

$$\dot{\underline{f}}_j = iL_j \underline{f}_j , \tag{2.7d}$$

where

$$L_j = (1 - P_{j-1}) L_{j-1} , \quad L_0 = L \tag{2.8}$$

and P_j is the projector onto $\underline{f}_j$. As mentioned earlier the variational procedure described by Zwanzig and Nossal employs trial functions constructed from the set $\{n_k, \vec{g}_k, e_k, \dot{\vec{g}}_k, \dot{e}_k\}$ and subsets of this set. One could of course include higher-order time derivatives as well, and in our

notation the basis vectors including these higher-order time derivatives would consist of the set $\{\underline{A}, \dot{\underline{A}}, \ddot{\underline{A}}, \ldots\}$. Since a linear transformation of the basis vectors will not affect the eigenvalues or $\underline{\Xi}_0(z)$ found by the variational method, we can just as well construct the trial functions from a new set of basis vectors formed by Schmidt orthogonalization of the vector of conserved variables and its time derivatives. This new set of basis vectors is just the set of random forces introduced by Mori, $\{\underline{f}_0, \underline{f}_1, \underline{f}_2, \ldots\}$.[18] Note that although $\underline{A}$ is a three-dimensional column vector, $\underline{f}_i$ $(i \geq 1)$ is a two-dimensional column vector.

We now consider the calculation of the matrix of conserved variable correlation functions by a variational solution of the Liouville equation which employs the random forces as basis vectors.[19] The Laplace transform of the Liouville equation for the vector of conserved variables can be written

$$\underline{A} = (z - iL)\,\underline{A}(z) \,. \tag{2.9}$$

The nth approximation to $\underline{A}(z)$ can be written

$$\underline{A}^{(n)}(z) = \sum_{i=0}^{n} \underline{a}_i^{(n)}(z)\,\underline{f}_i \,, \tag{2.10}$$

where the coefficient matrixes $\underline{a}_0^{(n)}(z)$ and $\underline{a}_i^{(n)}(z)$ $(i \geq 1)$ have dimensionalities 3×3 and 3×2, respectively. Substitution of (2.10) into (2.9) and the multiplication of the resulting equation by $\underline{f}_j^{\dagger}\langle \underline{f}_j \underline{f}_j^{\dagger}\rangle^{-1}$ from the left-hand side followed by an equilibrium canonical average leads to the set of coupled equations for the coefficient matrices:

$$\langle \underline{A}\underline{f}_j^{\dagger}\rangle\langle \underline{f}_j \underline{f}_j^{\dagger}\rangle^{-1} = \sum_{i=0}^{n} \underline{a}_i^{(n)}(z)\{z\langle \underline{f}_i \underline{f}_j^{\dagger}\rangle\langle \underline{f}_j \underline{f}_j^{\dagger}\rangle^{-1} - \langle (iL\underline{f}_i)\underline{f}_j^{\dagger}\rangle\langle \underline{f}_j \underline{f}_j^{\dagger}\rangle^{-1}\} \quad (j = 0, 1, 2, \ldots, n) \,. \tag{2.11}$$

The orthogonality properties of the random forces and the definitions in Eq. (2.5) can be used to simplify the matrix elements. For $i, j \neq 0$, we have

$$\langle (iL\underline{f}_i)\underline{f}_j^{\dagger}\rangle\langle \underline{f}_j \underline{f}_j^{\dagger}\rangle^{-1} = \begin{cases} \underline{I}\,\delta_{i+1,j} \,, & j > i \\ i\underline{\omega}_i \,, & i = j \\ -\underline{\Delta}_i^2\,\delta_{i,j+1} \,, & j < i \end{cases} \tag{2.12}$$

and

$$\langle (iL\underline{f}_0)\underline{f}_j^{\dagger}\rangle\langle \underline{f}_j \underline{f}_j^{\dagger}\rangle^{-1} = \begin{pmatrix} 0 & 0 \\ \underline{I}\delta_{1j} \end{pmatrix} \,, \tag{2.13}$$

$$\langle (iL\underline{f}_i)\underline{f}_0^{\dagger}\rangle\langle \underline{f}_0 \underline{f}_0^{\dagger}\rangle^{-1} = -\underline{\Delta}_1^2\,\delta_{i1} \,. \tag{2.14}$$

Equation (2.11) can now be written

$$(\underline{I}\,\underline{0}\,\underline{0}\cdots\underline{0}) = [\underline{a}_0^{(n)}(z)\underline{a}_1^{(n)}(z)\cdots\underline{a}_n^{(n)}(z)]\,\underline{R} \,, \tag{2.15a}$$

with[20]

$$\underline{R} = \begin{pmatrix} (z\underline{I} - i\underline{\omega}_0) & \begin{pmatrix} 0 & 0 \\ -\underline{I} \end{pmatrix} & \underline{0} & \cdots & \underline{0} \\ \underline{\Delta}_1^2 & (z\underline{I} - i\underline{\omega}_1) & -\underline{I} & \cdots & \vdots \\ \underline{0} & \underline{\Delta}_2^2 & (z\underline{I} - i\underline{\omega}_2) & \cdots & \underline{0} \\ \vdots & \vdots & \vdots & & -\underline{I} \\ \underline{0} & \underline{0} & \underline{0} & \cdots & \underline{\Delta}_n^2 \quad (z\underline{I} - i\underline{\omega}_n) \end{pmatrix} \,. \tag{2.15b}$$

From Eqs. (2.10) and (2.15) the nth approximation to $\underline{\Xi}_0(z)$ can be obtained:

$$\underline{\Xi}_0^{(n)}(z) = \underline{a}_0^{(n)}(z) = \left[z\underline{I} - i\underline{\omega}_0 + \begin{pmatrix} 0 & 0 \\ \underline{\Xi}_1^{(n)}(z) \end{pmatrix} \underline{\Delta}_1^2\right]^{-1} \,, \tag{2.16}$$

with

$$\underline{\Xi}_1^{(n)}(z) = \cfrac{1}{z\underline{I} - i\underline{\omega}_1 + \cfrac{1}{z\underline{I} - i\underline{\omega}_2}\,\underline{\Delta}_2^2 + \ddots \cfrac{1}{z\underline{I} - i\underline{\omega}_n}\,\underline{\Delta}_n^2} \,. \tag{2.17}$$

This result corresponds to a particular truncation of Eq. (2.4), and allows one to associate a particular truncation of the continued-fraction expansion with a particular variational solution of the Liouville equation.

In order to illustrate these equations we now specialize the above results and indicate how the continued-fraction expansion leads to both the high-frequency hydrodynamic results and the variational results obtained by Nossal. To facilitate a direct comparison with some of Nossal's results, we restrict the set of variables under consideration to the longitudinal component of the momentum density and the energy density:

$$\underline{A} = \begin{pmatrix} d_k \\ e_k \end{pmatrix} = V \begin{pmatrix} A_3 \\ A_5 \end{pmatrix}, \tag{2.18}$$

with

$$d_k = \sum_j \frac{\vec{k}\cdot\vec{p}_j}{k} e^{-i\vec{k}\cdot\vec{r}_j} , \tag{2.19a}$$

$$e_k = \sum_j \frac{p_j^2}{2m} e^{-i\vec{k}\cdot\vec{r}_j} + \tfrac{1}{2}\sum_{j\neq l}\sum v(r_{lj}) e^{-i\vec{k}\cdot\vec{r}_j} , \tag{2.19b}$$

where V is the volume and A_3 and A_5 are defined by Nossal[11] (indicated by N in equation numbers) in Eqs. (N 1. 9) and (N 3. 4), respectively. For this set of variables Eq. (2. 3) is altered somewhat. Since we now have a linearly independent set of variables, only square matrices appear:

$$\underline{\Xi}_0(z) = [z\underline{I} - i\underline{\omega}_0 + \underline{\Xi}_1(z)\underline{\Delta}_1^2]^{-1} . \tag{2.20}$$

The dispersion relations obtained from Eq. (2. 20) when the time dependence of $\underline{\Xi}_1(t)$ is ignored [$\underline{\Xi}_1(z) = z^{-1}\underline{I}$] are identical to those obtained from high-frequency hydrodynamic equations when density fluctuations are neglected (N 3. 14). This may be easily shown by using the definitions introduced by Nossal [Eq. (N 3. 8)]; the matrices in Eq. (2. 20) can be written

$$i\underline{\omega}_0 = \begin{pmatrix} 0 & i\tilde{U}/B \\ i\tilde{U}/W & 0 \end{pmatrix}, \tag{2.21}$$

$$i\underline{\omega}_1 = \begin{pmatrix} 0 & \\ i\,\dfrac{Y - \tilde{U}\,\bar{X}/W - (Z - \tilde{U}^2/W)\tilde{U}/B}{(\bar{X} - \tilde{U}^2/B)} & \end{pmatrix}$$

$$i\,\frac{Y - \tilde{U}\bar{X}/W - (Z - \tilde{U}^2/W)\tilde{U}/B}{(Z - \tilde{U}^2/W)} \quad 0 \Bigg) . \tag{2.25}$$

$$\underline{\Delta}_1^2 = \begin{pmatrix} \dfrac{\bar{X}}{W} - \dfrac{\tilde{U}^2}{WB} & 0 \\ 0 & \dfrac{Z}{B} - \dfrac{\tilde{U}^2}{WB} \end{pmatrix} . \tag{2.22}$$

The dispersion relations are found to be

$$2z_\pm^2 = -\left(\frac{\bar{X}}{W} + \frac{Z}{B} - \frac{\tilde{U}^2}{WB}\right) \pm \left[\left(\frac{\bar{X}}{W} + \frac{Z}{B} - \frac{\tilde{U}^2}{WB}\right)^2 - 4\left(\frac{\bar{X}}{W} - \frac{\tilde{U}^2}{WB}\right)\left(\frac{Z}{B} - \frac{\tilde{U}^2}{WB}\right)\right]^{1/2} , \tag{2.23}$$

which is identical to Eq. (N 3. 14).

We now consider a variational solution to the Liouville equation where the trial function is constructed from the set of variables in Eq. (2. 18) and their time derivatives. Using the procedure outlined earlier, one finds

$$\underline{\Xi}_0(z) = \frac{1}{z\underline{I} - i\underline{\omega}_0 + (z\underline{I} - i\underline{\omega}_1)^{-1}\underline{\Delta}_1^2} , \tag{2.24}$$

where

The dispersion relation can be calculated from the condition

$$z^4 + z^2(Z\bar{X}^2 B - Z\bar{X}\tilde{U}^2 - 2\tilde{U}Y\bar{X}B + \tilde{U}^3 Y + Z^2\bar{X}W - 2\tilde{U}YWZ + Y^2BW)/H + (\tilde{U}^2Y^2 - 2\tilde{U}Y\bar{X}Z + Z^2\bar{X}^2)/H = 0 \tag{2.26a}$$

with

$$H = WZB\bar{X} - \tilde{U}^2B\bar{X} - \tilde{U}^2WZ + \tilde{U}^4 , \tag{2.26b}$$

and the result agrees with Nossal's Eq. (N 3. 17). It is clear that the approximations used for $\underline{\Xi}_1(z)$ in arriving at the high-frequency hydrodynamic results and the variational results are very different. As mentioned earlier, in order to obtain high-frequency hydrodynamics, $\underline{\Xi}_1(t)$ was replaced by its initial value

$$\underline{\Xi}_1 = \underline{I} . \tag{2.27}$$

Equation (2. 24), on the other hand, is equivalent to an exponential expression for this correlation function

$$\underline{\Xi}_1(t) = e^{+i\underline{\omega}_1 t} . \tag{2.28}$$

The first result corresponds to a very short time approximation while the latter result corresponds to a much longer time approximation.

The above considerations show that the eigenvalues obtained via the variational equation are not equivalent to those found from the high-frequency hydrodynamic equations ignoring density fluctuations. However, they would be equivalent if the correlation function

$$Y \equiv \langle (L^3 A_3) A_5^* \rangle \tag{2.29}$$

were equal to $(\bar{X}/W - \tilde{U}^2/WB + Z/B)\tilde{U}$ as conjectured by Nossal. This form for Y implies $i\underline{\omega}_1 = \underline{0}$. It appears however that this identification is not cor-

rect.[21] Similar conclusions can be drawn when the full set of conserved variables [Eq. (2.1)] is used. Since the calculations are somewhat lengthy and most of the necessary results have been given by Nossal, we will not present these calculations here. The important feature to note both in the simple two-variable case with $\underline{A}^T = (d_k, e_k)$ and the result for the full set of conserved variables is that $i\underline{\omega}_1$ is not zero, which causes the variational procedure to yield results which are different from high-frequency hydrodynamics. For large enough z the variational results will certainly reduce to the high-frequency hydrodynamic results. However, if one is interested in the behavior of $\underline{\Xi}_0(z)$ in the vicinity of its poles, then the results are not equivalent and do not become equivalent even when $\vec{k}$ is small (see Sec. III).

In an earlier paper, Nossal and Zwanzig[10] found a genuine equivalence between high-frequency hydrodynamics with neglect of thermal conductivity and a variational solution constructed from the set $\{n_k, \vec{g}_k, \vec{g}_k\}$. The equivalence in this case is easy to understand. If we let $\underline{A}$ in Eq. (2.2) be given by

$$\underline{A} = \begin{pmatrix} n_k \\ \vec{g}_k \end{pmatrix} , \tag{2.30}$$

the corresponding random force is one dimensional (see Ref. 17) and is given by

$$\vec{f}_1 = \vec{g}_k - \frac{i\vec{k}}{m} \cdot \frac{\langle \vec{g}_k \vec{g}_{-k} \rangle}{\langle n_k n_{-k} \rangle} n_k . \tag{2.31}$$

Since the random force is one dimensional, $i\omega_1 = 0$ (this matrix can only contain off-diagonal elements because of symmetry), and Eq. (2.16) for this set of variables reduces to

$$\underline{\Xi}_0(z) = \left[z\underline{I} - i\underline{\omega}_0 + \begin{pmatrix} 0 & \\ z^{-1} & \end{pmatrix} \underline{\Delta}_1^2 \right]^{-1} , \tag{2.32}$$

which is equivalent to use of a high-frequency limit for $\underline{\Xi}_1(z)$. The equivalence does not, of course, hold when higher-order time derivatives are included as can be seen from an examination of Eq. (2.17) (set $i\omega_n = 0$ for this one-variable case). This point will be discussed further in Sec. III. Once the random forces become multidimensional the results become qualitatively different even at the level of including only first-order time derivatives in the basis set. Since $i\omega_n \neq 0$, the relaxation function is being studied over a larger frequency region than is appropriate to high-frequency hydrodynamics.

B. Choice of Variables

Recently Akcasu and Daniels[22] have presented a multidimensional analysis of fluctuations in a simple fluid. Their analysis is actually closely related to the variational solution and the comparison of these approaches is best made via the continued-fraction expansion. The calculation used an extended set of variables equivalent to $\{n_k, g_k, e_k, \vec{g}_k, \dot{e}_k\}$ in Mori's generalized Langevin equation. From the previous discussion it is clear that this set is equivalent to

$$\underline{A}' = \begin{pmatrix} \underline{A} \\ \underline{f}_1 \end{pmatrix} . \tag{2.33}$$

The relaxation matrix $\underline{\Xi}_0'(z)$ was calculated from

$$\underline{\Xi}_0'(z) = \frac{1}{z\underline{I}' - i\underline{\omega}_0' + \underline{\phi}'(z)} , \tag{2.34}$$

with the aid of a Markov approximation for $\underline{\phi}'(z)$. The primed quantities have definitions similar to those in Eqs. (2.2) and (2.5a) with $\underline{A}$ replaced by $\underline{A}'$. The damping matrix $\underline{\phi}'(z)$ is defined by

$$\underline{\phi}'(z) = \langle \underline{f}_1'(z) \underline{f}_1'^{\dagger} \rangle \langle \underline{A}' \underline{A}'^{\dagger} \rangle^{-1} , \tag{2.35}$$

where $\underline{f}_1'$ is the random force corresponding to $\underline{A}'$,

$$\underline{f}' = iL_1' \underline{A}' = i(1 - P_0')L\underline{A}' , \tag{2.36}$$

and P_0' is the projector onto $\underline{A}'$. Once again we can consider an extension of this set of variables:

$$\underline{A}' = \begin{pmatrix} \underline{A} \\ \underline{f}_1 \\ \vdots \\ \underline{f}_n \end{pmatrix} . \tag{2.37}$$

In this basis the relaxation matrix $\underline{\Xi}_0'(z)$ is block diagonal with elements $\underline{\Xi}_i(z)\,\delta_{ij}$, the matrix $z\underline{I}' - i\underline{\omega}_0'$ is identical to $\underline{R}$ in Eq. (2.15b), and the damping matrix has the form

$$\underline{\varphi}'(z) = \begin{pmatrix} \underline{0} & \cdots & \underline{0} \\ \vdots & \ddots & \vdots \\ \underline{0} & \cdots & \underline{0} \\ \underline{0} \cdots & \underline{0} & \underline{\Xi}_{n+1}(z) \quad \underline{\Delta}_{n+1}^2 \end{pmatrix} . \tag{2.38}$$

If these expressions for the matrices along with Eq. (2.34) are used to solve for $\underline{\Xi}_0(z)$, we obtain Eq. (2.3) with $\underline{\Xi}_1(z)$ replaced by Eq. (2.4).

From the above considerations it is apparent that if one starts with the vector of variables $\underline{A}$ and makes a Markov truncation on the continued-fraction expansion at the level $n+1$, this procedure is equivalent to starting with the set $\underline{A}'$ [Eq. (2.37)] and truncating at the first level. One should note that a variational procedure starting with the set of variables $\underline{A}'$ would yield an identical result for the relaxation matrix, but with the damping matrix absent. As is well known, the level at which one truncates determines the frequency regime of the

relaxation function one is probing. For example, at very low frequencies one should use $\underline{A}$ (i.e., n_k, $\vec{g}_k$, e_k) and truncate at the first level to obtain the relaxation via the ordinary linearized hydrodynamic equations. In essence, this says the group of variables contained in $\underline{A}$ have similar decay times which are much longer than those associated with all the $\underline{f}_n$, with $n \geq 1$. In a higher-frequency regime, one is investigating the time decay of $\underline{A}$ on the time scale of some $\underline{f}_n$, say $\underline{f}_1$. In this event, one could start with the vector

$$\begin{pmatrix} \underline{A} \\ \underline{f}_1 \end{pmatrix}$$

and truncate after the first level, or equivalently choose $\underline{A}$ and truncate at the second level. The expression obtained for the relaxation function would also reduce to the correct limiting form for small z. At this point, though, one should note that the use of the set

$$\begin{pmatrix} \underline{A} \\ \dot{\underline{A}} \end{pmatrix} \text{ rather than } \begin{pmatrix} \underline{A} \\ \underline{f}_1 \end{pmatrix}$$

would yield the low-z result, but only after the application of considerable manipulations, since $\dot{\underline{A}}(t)$ contains a slowly decaying component.

III. LOW-$\vec{k}$ LIMIT

In Sec. II we did not consider the $\vec{k}$ dependence of the relaxation function, or of the correlation functions in terms of which it is expressed. Although the results of Sec. II are valid for arbitrary values of $\vec{k}$, we will now investigate the structure of $\underline{\Xi}_0(z)$ in the limit of small wave vectors. The motivation for such a study is twofold. First, we wish to point out that even in the low-$\vec{k}$ limit the calculation of $\underline{\Xi}_0(z)$ using high-frequency hydrodynamic equations and the calculation employing the variational method are not equivalent. The discussion will, of course, exclude the special cases mentioned in Sec. II where an equivalence does exist. Second, we will discuss the applicability of the variational method for small $\vec{k}$. Also, since the variational results are qualitatively altered when time derivatives beyond the first order are included in the calculation, we illustrate this behavior in the low-$\vec{k}$ limit by treating explicitly the examples described in Sec. IIA.

As a preliminary to this discussion we begin by noting the $\vec{k}$ dependence of the matrices which appear in the continued-fraction expansion. The leading $\vec{k}$ dependence of these matrices is given by

$$\begin{aligned} i\underline{\omega}_n &= i\underline{\omega}_n^{[1]} k + \cdots , \\ \underline{\Delta}_1^2 &= \underline{\Delta}_1^{[2]} k^2 + \cdots , \\ \underline{\Delta}_n^2 &= \underline{\Delta}_n^{[0]} + \cdots , \quad n \geq 2 \end{aligned} \tag{3.1}$$

where the superscript on the $\vec{k}$-independent matrices in the right-hand side of Eq. (3.1) signifies the power of k multiplying the matrix. These results can be justified by using the fact that the time derivatives of conserved variables are proportional to k, and that any correlation function of an odd-rank tensor is odd in $\vec{k}$ while the correlation function of an even-rank tensor is even in $\vec{k}$.[23]

It is now an easy task to show that the dispersion relations obtained by the variational method using the set of variables $\{\underline{A}, \underline{f}_1\}$,

$$\det \left[z\underline{I} - i\underline{\omega}_0 + \begin{pmatrix} 0 & 0 \\ (z\underline{I} - i\underline{\omega}_1)^{-1} & \end{pmatrix} \underline{\Delta}_1^2 \right] = 0 , \tag{3.2}$$

do not reduce to those obtained from high-frequency hydrodynamic equations,

$$\det \left[z\underline{I} - i\underline{\omega}_0 + \frac{1}{z} \begin{pmatrix} 0 & 0 \\ \underline{I} & \end{pmatrix} \underline{\Delta}_1^2 \right] = 0 , \tag{3.3}$$

in the low-$\vec{k}$ limit. The dispersion relations to any order in $\vec{k}$ can be evaluated by writing

$$z = \sum_n \alpha_n k^n , \tag{3.4}$$

substituting Eqs. (3.1) and (3.4) into Eqs. (3.2) and (3.3), and equating the coefficients of each power of k separately to zero. Both Eq. (3.2) and Eq. (3.3) yield $z \sim O(k)$. The corresponding α_1 coefficients are given by the above equations with each matrix replaced by its leading $\vec{k}$-independent matrix. Because $i\underline{\omega}_1 \sim O(k)$, it is not eliminated in this limit. A specific illustration of this result is provided by the example which was worked out in Sec. IIA where $\underline{A}^T = (d_k, e_k)$ [compare Eqs. (2.23) and (2.26) to lowest order in k]. This result might seem surprising since it is certainly true that[24]

$$\lim_{\vec{k} \to 0} \frac{1}{k^2} \begin{pmatrix} 0 & 0 \\ (z\underline{I} - i\underline{\omega}_1)^{-1} & \end{pmatrix} \underline{\Delta}_1^2 = \frac{1}{z} \begin{pmatrix} 0 & 0 \\ \underline{I} & \end{pmatrix} \underline{\Delta}_1^{[2]} . \tag{3.5}$$

Therefore, to order k^2,

$$\begin{pmatrix} 0 & 0 \\ \underline{\Xi}_1^{(1)}(z) & \end{pmatrix} \quad \text{and} \quad \frac{1}{z} \begin{pmatrix} 0 & 0 \\ \underline{I} & \end{pmatrix} \underline{\Delta}_1^2$$

are identical, and it would appear that one could $\vec{k}$ order

$$\begin{pmatrix} 0 & 0 \\ \underline{\Xi}_1^{(1)}(z) & \end{pmatrix} \underline{\Delta}_1^2$$

and the results of the variational method and high-frequency hydrodynamics would agree for small $\vec{k}$. However, it is easy to show that if the variational method is used to compute the relaxation function and if one is interested in values of z near the poles of $\underline{\Xi}_0(z)$, then the matrix

$$\begin{pmatrix} 0 & 0 \\ \underline{\Xi}_1^{(1)}(z) & \end{pmatrix} \underline{\Delta}_1^2$$

cannot be $\vec{k}$ ordered. Using Eq. (3.1) we can write

$$\begin{pmatrix} 0 & 0 \\ \underline{\Xi}_1^{(1)}(z) & \end{pmatrix} \underline{\Delta}_1^2 = \begin{pmatrix} 0 & 0 \\ \underline{I} & \end{pmatrix} \underline{\Delta}_1^{[2]} \frac{k^2}{z} + \begin{pmatrix} 0 & 0 \\ i\underline{\omega}_1^{[1]} & \end{pmatrix} \underline{\Delta}_1^{[2]} \frac{k^3}{z^2} + \cdots \tag{3.6}$$

In the region where the dispersion relations hold $z \sim O(k)$, the series in Eq. (3.6) cannot be truncated and hence the matrix cannot be $\vec{k}$ ordered in general.

Selwyn and Oppenheim[25] have recently shown that for small $\vec{k}$ one is able to obtain an expression for $\underline{\Xi}_0(z)$ by $\vec{k}$ ordering the matrix

$$\begin{pmatrix} 0 & 0 \\ \underline{\Xi}_1(z) & \end{pmatrix} \underline{\Delta}_1^2 .$$

The statements of the previous paragraph are not in contradiction with their results. The inability to $\vec{k}$ order

$$\begin{pmatrix} 0 & 0 \\ \underline{\Xi}_1^{(1)}(z) & \end{pmatrix} \underline{\Delta}_1^2$$

in this case is a direct result of the neglect of the damping term. One can consider Eqs. (2.16) and (2.17) with $n=1$ as being obtained from the procedure outlined in Sec. II B with use of Eq. (2.33) and a Markov approximation for the damping matrix,

$$\underline{\Xi}_0(z) = \frac{1}{z\underline{I} - i\underline{\omega}_0 + \begin{pmatrix} 0 & 0 \\ [z\underline{I} - i\underline{\omega}_1 + \underline{\phi}_2(0)]^{-1} & \end{pmatrix} \underline{\Delta}_1^2}, \tag{3.7}$$

with the added condition that the damping matrix,

$$\underline{\phi}_2(0) = \lim_{z\to 0,\, \vec{k}\to 0} \underline{\Xi}_2(z)\underline{\Delta}_2^2 ,$$

be small compared to $i\underline{\omega}_1$ and hence may be neglected. While it is true that this condition may be satisfied for large $\vec{k}$, for simple fluids $\underline{\phi}_2(0)$ must be large compared to $i\underline{\omega}_1$ when $\vec{k}$ is small. This can be seen by using the definition of $\underline{\Xi}_2(z)$ in Eq. (2.5c) and the results in Eq. (3.1). One may readily show that the diagonal elements of this matrix are of $O(k^0)$ while the off-diagonal elements are of $O(k)$. Since $i\underline{\omega}_1$ is of $O(k)$, it is clear that for small $\vec{k}$ one cannot neglect the damping term in comparison to $i\underline{\omega}_1$. Thus we conclude that the variational procedure may be of use in finding the poles of the relaxation function only in a high-$\vec{k}$ regime, i.e., higher than the k^2 region appropriate to hydrodynamics. [One should note that in defining the Markov approximation after Eq. (3.7) we have implicitly ignored the off-diagonal elements of the damping matrix. If one is interested in the roots of the dispersion equation to order k^3, these elements must be retained. Since, however, in what follows we will present dispersion relations correct to only order k^2, this definition will suffice.] Once damping is included the frequency region which one is describing is also changed; then Eq. (3.7) can be written as

$$\underline{\Xi}_0(z) = \frac{1}{z\underline{I} - i\underline{\omega}_0 + \begin{pmatrix} 0 & 0 \\ \{z\underline{I} - i\underline{\omega}_1 + [\underline{\Xi}_1^{[0]}(0)]^{-1}\}^{-1} & \end{pmatrix} \underline{\Delta}_1^2} \tag{3.8}$$

with the aid of the identity

$$\underline{\Xi}_1^{[0]}(0) = \lim_{z\to 0,\, \vec{k}\to 0} \underline{\Xi}_1(z) = \underline{\phi}_2^{-1}(0). \tag{3.9}$$

Hence, $\underline{\Xi}_1(t)$ can be formally written as

$$\underline{\Xi}_1(t) = \exp(-[\underline{\Xi}_1^{[0]}(0)]^{-1} + i\underline{\omega}_1)t \tag{3.10}$$

and is now a decaying function. This behavior should be contrasted with that in Eq. (2.28) for the case where damping is neglected. If we compute the poles of $\underline{\Xi}_0(z)$, given by Eq. (3.8), only two propagating modes are found while the remaining poles are real and $O(k^0)$. It is instructive to compare the poles of $\underline{\Xi}_0(z)$ at high z when damping is included to those with neglect of damping for the two-variable case treated earlier, $\underline{A}^T = (d_k, e_k)$. When damping is included, the dispersion relations can be calculated from

$$\det\{z^2\underline{\Xi}_1^{[0]}(0) + z[\underline{I} - \underline{\Xi}_1^{[0]}(0)(i\underline{\omega}_1 + i\underline{\omega}_0)] - i\underline{\omega}_0 + \underline{\Xi}_1^{[0]}(0)(i\underline{\omega}_1 i\underline{\omega}_0 + \underline{\Delta}_1^2)\} = 0 \tag{3.11}$$

with the aid of Eq. (3.4). To low order in $\vec{k}$ the results are

$$z_{1,2} = \pm ik\left[\frac{(e_0+p)}{m n_0}\left(\frac{\partial p}{\partial e_0}\right)_{n_0}\right]^{1/2}$$

$$-\tfrac{1}{2}k^2\left[\frac{\frac{4}{3}\eta^*+\zeta^*}{mn_0}+\kappa\left(\frac{\partial T}{\partial e_0}\right)_{n_0}\right]+O(k^3)\,,$$

$$z_3=-\left(\frac{K_\infty-K_0+\frac{4}{3}G_\infty}{\frac{4}{3}\eta^*+\zeta^*}\right)+O(k^2)\,,$$

$$z_4=-(\theta_\infty-\theta_0)/\kappa+O(k^2)\,. \tag{3.12}$$

In these equations, T is the temperature, m is the mass, p is the pressure, and e_0 and n_0 are the equilibrium energy and number densities, respectively. The bulk moduli are defined by

$$K_\infty-K_0+\tfrac{4}{3}G_\infty=\frac{\beta}{V}\lim_{\vec{k}\to 0}\frac{1}{k^2}\langle f_{11}f_{11}^\dagger\rangle \tag{3.13a}$$

and

$$\theta_\infty-\theta_0=\frac{\beta}{VT}\lim_{\vec{k}\to 0}\frac{1}{k^2}\langle f_{12}f_{12}^\dagger\rangle \tag{3.13b}$$

while the transport coefficients are defined by

$$\tfrac{4}{3}\eta^*+\zeta^*=\frac{\beta}{V}\lim_{z\to 0}\lim_{\vec{k}\to 0}\frac{1}{k^2}\langle f_{11}(z)f_{11}^\dagger\rangle \tag{3.14a}$$

and

$$\kappa=\frac{\beta}{VT}\lim_{z\to 0}\lim_{\vec{k}\to 0}\frac{1}{k^2}\langle f_{12}(z)f_{12}^\dagger\rangle\,, \tag{3.14b}$$

where f_{11} and f_{12} are the components of $\underline{f}_1$, $\beta=1/k_BT$, and V is the volume. Note that the starred transport coefficients defined by these equations differ from the usual shear-viscosity and bulk-viscosity coefficients because of the subtractive fluxes in the definition of the random force f_{11}. The definitions of the bulk moduli are the same as those given by Nossal.[11] These results should be compared with Eq. (2.26a) where four propagating modes were obtained. Hence, we see that if additional modes exist at high z and low $\vec{k}$ they are nonpropagating and correspond to microscopic relaxation processes. The truncation at this level just corresponds to the use of exponentially relaxing transport coefficients and is a commonly used procedure.

When the variational method is carried to higher order by including derivatives of the conserved variables beyond the first, the relaxation spectrum of $\underline{\Xi}_0(z)$ is qualitatively altered. This is because higher-order $\underline{\Delta}_n^2$ matrices ($n\geq 2$) which are of $O(k^0)$ now appear [see Eqs. (2.16) and (2.17)]. Once again we will use as an example the case $\underline{A}^T=(d_k,\ e_k)$. Setting $n=2$ in Eq. (2.17), the dispersion relations for this case can be calculated from

$$\det\{[(z\underline{I}-i\underline{\omega}_2)(z\underline{I}-i\underline{\omega}_1)+\underline{\Delta}_2^2]$$

$$\times(z\underline{I}-i\underline{\omega}_0)+(z\underline{I}-i\underline{\omega}_2)\,\underline{\Delta}_1^2\}=0. \tag{3.15}$$

Using Eq. (3.4) we find to lowest order in $\vec{k}$

$$z_{1,2}=\pm ik\left[\frac{(e_0+p)}{mn_0}\left(\frac{\partial p}{\partial e_0}\right)_{n_0}\right]^{1/2}+O(k^3)\,,$$

$$z_{3,4}=\pm i[(\underline{\Delta}_2^{[0]})_{11}]^{1/2}+O(k^2)\,, \tag{3.16}$$

$$z_{5,6}=\pm i\,[(\underline{\Delta}_2^{[0]})_{22}]^{1/2}+O(k^2)\,.$$

Hence, when higher-order time derivatives are included the number of propagating modes which are proportional to $\vec{k}$ changes from 4 [Eq. (2.26a)] to 2. The remaining roots are imaginary and $\vec{k}$ independent in lowest order. A comparison of these results with Eq. (3.12) shows that even at this order the variational method is not appropriate for the description of $\underline{\Xi}_0(z)$ at high z and low $\vec{k}$. Although the roots which are proportional to $\vec{k}$ might appear to agree, note that the coefficient of k^2 in $z_{1,2}$ in Eq. (3.16) is zero while the corresponding coefficient in Eq. (3.12) is not. In addition, damped microscopic modes similar to those in Eq. (3.12) are not obtained.

IV. SUMMARY

It has been demonstrated that using a many-variable form of the Mori continued-fraction technique one is able to gain some insight into the nature of the relaxation function with emphasis placed on the low-$\vec{k}$ regime. In addition, several interrelationships between seemingly different approaches have been provided. First, a general connection between the continued-fraction expression for the relaxation function and the form obtained by a variational procedure was established. This connection was used to demonstrate that the eigenvalues derived from the variational procedure with the use of the variables

$$\begin{pmatrix}\underline{A}\\ \underline{f}_1\end{pmatrix}$$

are not equivalent to those found from high-frequency hydrodynamic equations. Furthermore, it was shown that these eigenvalues do not become equivalent in the low-$\vec{k}$ limit. The question of the choice of the starting set of variables used to calculate the relaxation function was discussed. While it was clear that neglect of the higher-order time derivatives in the original set could easily be compensated for by a finite higher-order truncation the neglect of one of the conserved variables requires that the expansion be carried to all orders.

Finally, the inappropriateness of the variational technique in the low-$\vec{k}$ regime was demonstrated.

By utilizing the exact relationship between the variational technique and a high-frequency truncation of the Mori continued fraction, and a further comparison between this latter truncation and the corresponding Markov one, it was possible to demonstrate the necessity of retaining the damping term in the low-$\vec{k}$ region. This conclusion, of course, was reached only if one is interested in describing $\underline{\Xi}_0(z)$ in the vicinity of the hydrodynamic poles.

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[17]Since $\dot{n}_k = -(i\vec{k}/m)\cdot\vec{g}_k$, the random force associated with this variable is zero. Consequently, there are only two independent random forces associated with $\underline{A}$. In order to avoid singular matrices in the definitions of $\underline{\Xi}_n(z)$, $i\underline{\omega}_n$, and $\underline{\Delta}_n^2$, we chose to write $\underline{\Delta}_1^2$ as a rectangular matrix (2×3 if correlation functions involving $\vec{g}_k$ are treated as one element). Note that the product

$$\begin{pmatrix} 0 & 0 \\ \underline{\Xi}_1(z) \end{pmatrix} \underline{\Delta}_1^2$$

is now 3×3 with $\underline{\Xi}_1(z)$ a 2×2 matrix.

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[19]The procedure described below resembles that used by F. Lado [Phys. Rev. A 2, 1467 (1970)] in his discussion of the calculation of the density autocorrelation function by the memory function method of Zwanzig. The procedure we employ in our study of the Zwanzig-Nossal variational results utilizes sets of variables. This difference is crucial to the subsequent discussion.

[20]The matrix $z\underline{I} - i\underline{\omega}_0$ which is the 1-1 element of the supermatrix $\underline{R}$ has dimensionality 3×3; the remaining matrices in the first row are all 3×2. The remaining matrices in the first column are 2×3. All of the other elements of $\underline{R}$ are 2×2 matrices.

[21]An inconsistency can easily be shown by evaluating Eq. (2.29) for Y and $(\overline{X}/W - \tilde{U}^2/WB + Z/B)\tilde{U}$ for an ideal gas. We find $Y = -21$ and $(\overline{X}/W - \tilde{U}^2/WB + Z/B)\tilde{U} = -\frac{55}{3}$ in units of $(N/V^2)\ (k^3/2m^4)\ (mkT)^3$.

[22]A. Z. Akcasu and E. Daniels, Phys. Rev. A 2, 962 (1970).

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[24]A reduction of this sort is not obtained when the variational method is carried out to a higher order, e.g.,

$$\lim_{k\to 0} \underline{\Xi}_1^{(2)}(z) = \frac{1}{z + \underline{\Delta}_2^{[0]}/z} \quad .$$

[25]Selwyn and Oppenheim (Ref. 23) actually $\vec{k}$ order the matrix

$$\underline{M}(\vec{k}, z) = i\underline{\omega}_0 + \begin{pmatrix} 0 & 0 \\ \underline{\Xi}_1(z) \end{pmatrix} \underline{\Delta}_1^2 .$$