Journal of Statistical Physics, Vol. 13, No. 1, 1975

Modified One-Body Memory Function for Classical Fluids

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Received December 15, 1974

A microscopic theory applicable to simple classical fluids, particularly in the hydrodynamic regime, is presented. A simple isomorphic transformation of the space of one-body additive phase-space functions is considered whose distinguishing feature is that the total energy density is contained in the new space. A projection operator formalism for this subspace has certain desirable properties for the study of the hydrodynamic regime. It is shown that, for a broad class of approximations, one obtains a prediction for the VanHove structure factor $S(k, \omega)$ that has the correct hydrodynamic structure and in which the only quantities that are approximated are the dissipative transport coefficients; all thermodynamic quantities appearing in the expression are rendered exactly. In particular, a weak coupling approximation is made on the memory function, and results are compared with the analogous theory of Forster and Martin. Agreement is found for the dissipative transport coefficients to lowest nontrivial order in the coupling. On the other hand, thermodynamic quantities are accurately predicted only to second order by Forster and Martin, whereas in the present theory they are exact.

KEY WORDS: Memory function; weak coupling hydrodynamics.

1. INTRODUCTION

In this paper we will investigate an application of the projection operator formalism of Zwanzig(1) and Mori(2) to the study of the hydrodynamic

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Research supported in part by the National Science Foundation under contract No. NSF GH35691.

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behavior of simple classical fluids. We are essentially modifying the procedure introduced by Forster and Martin(3) to study the dynamical behavior of a weakly coupled fluid, and further developed for the general system by Forster(4) and by Mazenko.(5)

Forster and Martin (FM hereafter) introduced an approximation scheme based on the smallness of the potential at all distances, which allows one to make contact with the linearized equations of hydrodynamics, starting from microscopic first principles. It was shown by Akcasu and Duderstadt(6) that the FM kinetic equation can be simply derived in the projection operator language. The projection subspace in that case is the space S_1 of one-body additive functions, spanned by

$$|N(\mathbf{pk})\rangle = \sum_{\alpha} [\exp(i\mathbf{k}\cdot\mathbf{q}_\alpha)]\, \delta(\mathbf{p} - \mathbf{p}_\alpha) \tag{1}$$

The FM theory can then be viewed as an approximation to the associated memory function that is accurate to second order in the potential.

We will show that by introducing a new subspace S_M, which contains the total energy density, this approach can be modified so as to afford an exact treatment of the subspace of single hydrodynamic excitations. In so doing, we obtain a prediction for the dynamic structure factor $S(k, \omega)$ that has the correct hydrodynamic structure and in which the only quantities that are approximated are the dissipative transport coefficients; i.e., in contrast to FM, all thermodynamic quantities are rendered exactly. Furthermore, the predictions for the transport coefficients of the weakly coupled fluid are in agreement with those of FM. The ability to confine the approximation to the dissipative part of the theory is not restricted to the weak coupling approximation; we demonstrate that a broad class of approximations also have this property.

The paper is organized as follows. Section 2 introduces notation and briefly reviews the projection operator formalism. The modified subspace of phase space functions is introduced in Section 3 and the associated memory functions are discussed. In Section 4 we consider a class of approximations for the memory function that lead to predictions for the density and momentum correlation functions that are in exact agreement with linearized hydrodynamics. The weak coupling approximation is considered in Section 5 and the results are compared with those of FM. Finally, Section 6 is a summary and discussion.

2. MEMORY OPERATOR FORMALISM

We consider a system of N identical particles interacting classically via a central potential $V(r)$. We let Γ_t be a point in phase space evolving via

Newton's laws. We represent an arbitrary function $A(\Gamma_t)$ as a vector $|A(t)\rangle$ in the space of phase space functions. Canonical ensemble averages over initial conditions are then represented as inner products over the Gibbs distribution $\Phi(\Gamma_0)$:

$$\langle A|B\rangle = \int d\Gamma_0\, A^*(\Gamma_0)B(\Gamma_0)\Phi(\Gamma_0) \tag{2}$$

The complex Laplace-transformed resolvent operator G for the Liouville equation satisfies

$$(iz + L)G = -1 \tag{3}$$

where L is the (anti-Hermitian) Liouville operator. If P is the projection operator onto some subspace S of phase space functions and $Q = 1 - P$, then PGP satisfies$^{(1,2,7)}$

$$(iz + PLP + M)PGP = -P \tag{4}$$

where the memory operator is

$$M = -PLQ(iz + QLQ)^{-1}QLP \tag{5}$$

This description is useful for time-dependent correlation functions of the form

$$\tilde{c}_{AB}(t) = \langle A(0)|B(t)\rangle \tag{6}$$

because the Laplace transform is given by

$$c_{AB}(z) = \int_0^\infty dt\, e^{izt}\tilde{c}_{AB}(t) = \langle A(0)|PGP|B(0)\rangle \tag{7}$$

if $|A\rangle$ and $|B\rangle$ are both in S. In particular, the complex density and momentum correlation functions are of this form:

$$g_{nn}(\mathbf{k}z) = i\Omega^{-1}\langle\rho_{\mathbf{k}}|G|\rho_{\mathbf{k}}\rangle \tag{8}$$

$$g_t(\mathbf{k}z) = i\Omega^{-1}\langle j_x|G|j_x\rangle \tag{9}$$

where $\mathbf{k}$ is along the z axis, Ω is the volume of the system, and

$$\rho_k = \sum_\alpha \exp(i\mathbf{k}\cdot\mathbf{q}_\alpha) \tag{10}$$

$$j_x = \sum_\alpha p_{x\alpha} \exp(i\mathbf{k}\cdot\mathbf{q}_\alpha) \tag{11}$$

3. THE MODIFIED SUBSPACE

For the weakly coupled system the subspace S_1 defined in (1) is a useful choice because the associated memory function M_1 is $O(\lambda^2)$, where λ measures the strength of the potential at all distances. This means that we can replace L in the denominator by L_0, the free particle Liouville operator, generating errors only of $O(\lambda^3)$. It is also important that $|\rho_k\rangle$ and $|\mathbf{j}\rangle$ are contained in S_1, so the theory yields predictions for $g_{nn}(\mathbf{k}z)$ and $g_t(\mathbf{k}z)$.

One disadvantage of this choice, however, is that the total energy density

$$|E_k\rangle = |T_k\rangle + |V_k\rangle \tag{12}$$

$$T_k(\Gamma_t) = \sum_{\alpha} (p_\alpha{}^2/2m)\exp(i\mathbf{k}\cdot\mathbf{q}_\alpha) \tag{13}$$

$$V_k(\Gamma_t) = \tfrac{1}{2} \sum_{\alpha \neq \beta} V(\mathbf{q}_\alpha \mathbf{q}_\beta)\exp(i\mathbf{k}\cdot\mathbf{q}_\alpha) \tag{14}$$

is not contained in S_1, because $|V_k\rangle$ is not. This is not an insuperable difficulty, as demonstrated by FM. However, as we shall see, there are distinct benefits to be gained by any theory that has the property that all five densities of conserved quantities are contained in S. We will considere here a simple modification of the subspace S_1 that ensures this property without affecting the more useful properties of S_1.

We first choose a new basis in S_1. We construct the following set of functions of p, which are orthonormal with the Maxwellian weight function $\phi(p)$:

$$R_{lmn}(\mathbf{p}) = y_{lm}(\theta, \phi) r_{nl}(u) \tag{15}$$

where the y_{lm} are normalized spherical harmonics and $u^2 = \beta p^2/2m$. The r_{nl} are a set of polynomials that are orthonormal on $(0 < r < \infty)$ with the weight function $p^2\phi(p)$. Following Gross and Jackson,(8) we use

$$r_{nl} = \left[\frac{2n!\,\pi^{3/2}}{\Gamma(n + l + \frac{3}{2})}\right]^{1/2} u^l L_n^{l+1/2} \tag{16}$$

where L_n are Laguerre–Sonine polynomials.(15) These functions satisfy

$$\int_0^\infty dp\, p^2\phi(p) r_{nl}(u) r_{n'l}(u) = \delta_{n,n'} \tag{17}$$

which ensures that

$$\int d\mathbf{p}\, \phi(p) R_{lmn}(\mathbf{p}) R_{l'm'n'}(\mathbf{p}) = \delta_{l,l'}\delta_{m,m'}\delta_{n,n'} \tag{18}$$

It is useful to point out that the first five R_{lmn} are simply related to the functions used by FM, which are associated with the five densities of conserved quantities. Letting $\alpha^2 = \beta m^{-1}$,

$$\psi_1(\mathbf{p}) = 1 = R_{000} \tag{19a}$$

$$\psi_2(\mathbf{p}) = \alpha p_z = R_{110} \tag{19b}$$

$$\psi_3(\mathbf{p}) = (\alpha^2 p^2 - 3)/\sqrt{6} = R_{002} \tag{19c}$$

$$\psi_4(\mathbf{p}) = \alpha p_x = (R_{110} - R_{1-10})/\sqrt{2} \tag{19d}$$

$$\psi_5(\mathbf{p}) = \alpha p_y = (R_{110} + R_{1-10})/\sqrt{2} \tag{19e}$$

We now express the p dependence of $|N(\mathbf{pk})\rangle$ in terms of these functions:

$$|N(\mathbf{pk})\rangle = \sum_{lmn} |E_{lmn}(\mathbf{k})\rangle \phi(p) R_{lmn}(\mathbf{p}) \tag{20}$$

$$|E_{lmn}(\mathbf{k})\rangle = \int d\mathbf{p}\, R^{*}_{lmn}(\mathbf{p}) |N(\mathbf{pk})\rangle \tag{21}$$

The new subspace S_M is obtained by modifying one of the E_{lmn} to include the potential energy. We define

$$|D_{002}(\mathbf{k})\rangle = |E_{002}(\mathbf{k})\rangle - \beta\sqrt{\tfrac{2}{3}}\, |V_k\rangle \tag{22}$$

This has the effect of coupling the kinetic to the potential energy inextricably, without changing the dimensionality of the subspace. We then define

$$|D_{lmn}\rangle = |E_{lmn}\rangle; \qquad (lmn) \neq (002) \tag{23}$$

and consider the functions

$$|D(\mathbf{pk})\rangle = \sum_{lmn} R_{lmn}(\mathbf{p}) |E_{lmn}(\mathbf{k})\rangle \tag{24}$$

We define the modified subspace S_M to be spanned by the set $|D(\mathbf{pk})\rangle$. All of the densities of microscopically conserved quantities are contained in S_M. In particular the total energy density is

$$|E_k\rangle = \int dp\, (p^2/2m) |D(\mathbf{pk})\rangle \tag{25}$$

while the momentum and number densities are

$$|\mathbf{j}_k\rangle = \int d\mathbf{p}\, |D(\mathbf{pk})\rangle \mathbf{p} \tag{26}$$

$$|\rho_k\rangle = \int dp\, |D(\mathbf{pk})\rangle \tag{27}$$

The projection operator onto the subspace of S_M associated with wave vector $\mathbf{k}$ is defined by

$$P_M(\mathbf{k}) = \Omega^{-1} \int d\mathbf{p}\, d\mathbf{p}'\, |D(\mathbf{pk})\rangle\langle D(\mathbf{p}'\mathbf{k})| W(\mathbf{k}; \mathbf{pp}') \tag{28}$$

where W is the inversion kernel satisfying

$$\Omega^{-1} \int d\mathbf{p}'\, W(\mathbf{k}; \mathbf{pp}') \langle D(\mathbf{p}'\mathbf{k})\, | D(\mathbf{p}''\mathbf{k})\rangle = \delta(\mathbf{p} - \mathbf{p}'') \tag{29}$$

This can be solved exactly. We give the resulting expression for $W(\mathbf{k}; \mathbf{pp}')$ in Appendix A.

The evolution of the phase space operator $P_M G P_M$ is specified completely by its matrix elements in the basis $|D(\mathbf{pk})\rangle$:

$$S_M(\mathbf{k}z;\, \mathbf{pp}') = i\Omega^{-1}\langle D(\mathbf{pk})|G|D(\mathbf{p}'\mathbf{k})\rangle \tag{30}$$

We can then write the matrix realization of Eq. (5):

$$\begin{aligned} zS_M(\mathbf{k}z;\, \mathbf{pp}') &- \int d\mathbf{p}''\, \mathscr{L}_M(\mathbf{k};\, \mathbf{pp}'')S_M(\mathbf{k}z;\, \mathbf{p}''\mathbf{p}') \\ &- \int d\mathbf{p}''\, \mathscr{M}_M(\mathbf{k}z;\, \mathbf{pp}'')S_M(\mathbf{k}z;\, \mathbf{p}''\mathbf{p}') = -(1/\Omega)\langle D(\mathbf{pk})|D(\mathbf{p}'\mathbf{k})\rangle \end{aligned} \tag{31}$$

where

$$\begin{aligned} \begin{Bmatrix} \mathscr{L}_M(\mathbf{k};\, \mathbf{pp}'') \\ \mathscr{M}_M(\mathbf{k}z;\, \mathbf{pp}'') \end{Bmatrix} &= (1/\Omega)\int d\mathbf{p}_1\, \langle D(\mathbf{pk})| \begin{Bmatrix} iL \\ iM_M(z) \end{Bmatrix} \\ &\qquad \times |D(\mathbf{p}_1\mathbf{k})\rangle W(\mathbf{k};\, \mathbf{p}_1\mathbf{p}'')\rangle \end{aligned} \tag{32}$$

Note that (31) is not a "generalized kinetic equation" in the sense of a closed equation for the evolution of the singlet distribution. $|N(\mathbf{pk})\rangle$ cannot be obtained from $|D(\mathbf{pk})\rangle$ with a z-independent kernel.

4. HYDRODYNAMIC ANALYSIS; GENERAL FEATURES

Before we introduce any concrete approximations, it is of interest to investigate a number of properties of the theory that are approximation-independent; i.e., they are consequences only of the fact that we can find $\mathscr{L}_M$ and $W(\mathbf{k};\, \mathbf{pp}')$ exactly. In the following analysis the function $\mathscr{M}(\mathbf{k}z;\, \mathbf{pp}')$ is to be interpreted as either the exact operator, or the result of some approximation to $\langle D(\mathbf{pk})|M_M|D(\mathbf{p}'\mathbf{k})\rangle$ in conjunction with the exact $W(\mathbf{k}z;\, \mathbf{pp}')$. We include only the class of approximations that satisfy a few rather elementary properties, which will be pointed out in the course of the analysis.

We first introduce a convenient notation for inner products over dp:

$$\begin{aligned} \psi_i(\mathbf{p}) &= (\mathbf{p}|i) \\ (A|B) &= \int d\mathbf{p}\, \phi(p)A^*(\mathbf{p})B(\mathbf{p}) \\ (A|T|B) &= \int d\mathbf{p}\, d\mathbf{p}'\, \phi(p)T(\mathbf{pp}')A(\mathbf{p})B(\mathbf{p}')\phi(\mathbf{p}') \end{aligned} \tag{33}$$

The orthonormality of the $\psi_i(\mathbf{p})$ then appears as

$$(i|j) = \delta_{ij} \tag{34}$$

but the associated phase space functions

$$|i\rangle = \int d\mathbf{p}\, \psi_i(\mathbf{p})|D(\mathbf{pk})\rangle \tag{35}$$

are neither orthogonal nor normalized.

The feature that distinguishes the present theory from that of FM is that we now have all five conservation laws in their rigorous form:

$$(i|\mathscr{M}_M(0z)|\mathbf{p}') = 0, \qquad i = 1,\ldots, 5 \tag{36}$$

In the FM theory, because only the kinetic energy is contained in S_1, the corresponding equation is, for $i = 3$,

$$(3|\mathscr{M}_1(0z)|\mathbf{p}) = zE(z\mathbf{p}) \tag{37}$$

where $E(z\mathbf{p})$ is a function associated with the potential energy density. This is the source of most of the calculational differences between the two theories.

In the hydrodynamic regime we are principally interested in the motion of

$$G_{ij} \equiv (i|S_M(\mathbf{k}z)|j) \tag{38}$$

Using a p-space projection operator

$$q = 1 - \sum |i)(i| \tag{39}$$

we can construct a memory function equation for G_{ij}:

$$\Omega[z\delta_{i,l} - (i\mathscr{L}_M|l) - W_{il}(\mathbf{k}z)]G_{lj} = -\langle i|j\rangle \tag{40}$$

$$W = W' + W'' \tag{41}$$

$$W''_{ij} = (i|\mathscr{M}_M(\mathbf{k}z)|j) \tag{42}$$

$$W''_{ij}(\mathbf{k}z) = (i|[\mathscr{L}_M + \mathscr{M}_M]q\frac{1}{z - q(\mathscr{L}_M + \mathscr{M}_M)q}q[\mathscr{L}_M + \mathscr{M}_M]|j) \tag{43}$$

To investigate the hydrodynamic regime, we will expand W_{ij} to second order in k [treating z as $O(k)$ or smaller]. All other matrix elements can be evaluated exactly. We will then be able to solve (40) and identify transport coefficients by comparison with the corresponding equation obtained from hydrodynamics. This is essentially the procedure introduced by FM.

In the remainder of this section we will assume we are dealing with an approximation to $\langle D(\mathbf{pk})|M_M|D(\mathbf{p}'\mathbf{k})\rangle$ that has the following properties:

$$W_{ij} = O(k^2) \tag{44a}$$

$$\langle i|M_M|4\rangle = \langle 4|M_M|i\rangle = 0 \tag{44b}$$

$$\left.\begin{array}{l}(1 - \mathbb{P}_0)\\(1 - \mathbb{P}_x)\\(1 - \mathbb{P}_y)\end{array}\right\}\langle D(\mathbf{pk})|M_M|D(\mathbf{p}'\mathbf{k})\rangle = 0 \tag{44c}$$

The $\mathbb{P}$'s represent reflections of $\mathbf{k}$, $\mathbf{p}$, and $\mathbf{p}'$ through the origin, the ZY plane, and the ZX plane, respectively. Properties (44b) and (44c) are easily seen to be true for the exact memory function. Property (44a) is plausible for the exact theory [cf. Eq. (36)], but it is not easily proved. It will be apparent from the subsequent analysis that it is equivalent to the assertion that the hydrodynamic description is valid. It can also be shown to be essentially equivalent to "property A" of Forster.(4) In the following we will demonstrate that any theory with property (44a) will predict sound propagation with the exact adiabatic sound speed as predicted from fluctuation analysis.(9) As an example, the mode-coupling memory function of Kadanoff and Swift(14) for critical transport coefficients has property (44a). We will present another example in Section 5.

Before writing the explicit form of W_{ij} to second order in k, we introduce a lemma relating the two different kinds of inner products. If J is any phase space operator, and we define

$$(\mathbf{p}|J|\mathbf{p}') \equiv \int d\mathbf{p}_1 \, \langle D(\mathbf{pk})|J|D(\mathbf{p}_1\mathbf{k})\rangle W(\mathbf{k}; \mathbf{pp}') \tag{45}$$

then it is not difficult to show (see Appendix A) that

$$\langle D(\mathbf{pk})|J|m\rangle = (\mathbf{p}|J|i)\langle i|m\rangle\Omega^{-1} \tag{46}$$

In particular we note that the integral operators $\mathscr{M}_M$ and $\mathscr{L}_M$ are related to M_M and L in this manner. We now define

$$(i|\mathscr{L}_M|j) + W_{ij} = R_{ij} + O(k^3) \tag{47}$$

As a consequence of (45) and (47) we find the explicit form for the uncoupled transverse submatrix ($i, j = 4, 5$)

$$R_{ij} = \begin{pmatrix} ik^2d & 0 \\ 0 & ik^2d \end{pmatrix} \tag{48}$$

and longitudinal submatrix ($i, j = 1, 2, 3$)

$$R_{ij} = \begin{pmatrix} 0 & k\mathscr{L}_{12} & 0 \\ k\mathscr{L}_{21} - ikzb\mu_1 & ik^2a & k\mathscr{L}_{23} + ikzb\mu_2 \\ -ik^2c\mu_1 & k\mathscr{L}_{32} + ikzb & ik^2c \end{pmatrix} \tag{49}$$

The quantities a, b, c, and d are independent of k and z, and we have introduced

$$\mu_1 = \langle 5|4\rangle/\langle 4|4\rangle \tag{50}$$

$$\mu_2 = (\Omega/\langle 4|4\rangle)\det(\Omega^{-1}\langle i|m\rangle) \tag{51}$$

and $k\mathscr{L}_{ij} = (i|\mathscr{L}_M|j)$. This is the form, to $O(k^2)$, of any theory based on an approximation for $\langle D(\mathbf{pk})|M_M|D(\mathbf{p}'\mathbf{k})\rangle$ that satisfies (45), in conjunction with the exact $\mathscr{L}_M(\mathbf{k}; \mathbf{pp}')$ and $W(\mathbf{k}; \mathbf{pp}')$

4.1. First-Order k Calculation: Sound Velocity

The identification of the eigenvalues of Eq. (50) proceeds by solving

$$\det\{(i|\mathscr{L}_M|j) - z\delta_{i,j}\} = 0 \tag{52}$$

An explicit calculation is not necessary, however, because we can use the lemma (46) to show that this is equivalent to

$$\det\{z\langle j|k\rangle - \langle j|iL|k\rangle\} = 0 \tag{53}$$

which is the secular equation obtained when one diagonalizes the Liouville operator in the five-dimensional space of the densities of conserved quantities. As shown by Nossal and Zwanzig,(13) the five eigenvalues and eigenvectors are exactly those associated with nondissipative linearized hydrodynamics. In particular,

$$z_1 = -z_2 = C_0 k, \qquad z_{3,4,5} = 0 \tag{54}$$

where

$$C_0^2 = m^{-1}(\partial P/\partial \rho_0)_s \tag{55}$$

is the adiabatic sound speed, as predicted by equilibrium fluctuation analysis.(9) That we obtain the exact sound speed is not surprising, since, by (44a), our theory is exact to first order in k. In contrast, the FM theory has an $O(k)$ contribution from the memory function, so that the sound speed predicted is only as accurate as the choice of the memory function.

4.2. Second-Order k Calculation: Transport Coefficients

Now G_{ij} satisfies, to second order in k,

$$(z\delta_{ij} - R_{ij})G_{jk} = -\Omega^{-1}\langle i|k\rangle \tag{56}$$

We need a solution correct to second order in k and z that can be compared with conventional results obtained from the linearized equations of hydrodynamics. The $O(k^2)$ corrections to the eigenvalues (54) can be written

$$z_{1,2} = \pm C_0 k - \tfrac{1}{2} i\bar{\Gamma}k^2 \tag{57a}$$

$$z_3 = -ik^2 D_t \tag{57b}$$

$$z_{4,5} = -(m\rho_0)^{-1}\bar{\eta}k^2 \tag{57c}$$

where

$$\bar{\eta} = -m\rho_0 d \tag{58}$$

$$D_t = -(\rho_0\Omega/\beta\langle 4|4\rangle)C_0^{-2}c \equiv -\mu_3 c \tag{59}$$

and the sound attenuation coefficient can be written in the conventional form of a longitudinal and a transverse contribution:

$$\bar{\Gamma} = \bar{D}_L + \bar{D}_t(\mu_3^{-1} - 1) \tag{60}$$

$$\bar{D}_L = -a - b(\mathscr{L}_{32} + \mu_2\mathscr{L}_{23} - \mu_1\mathscr{L}_{12}) \tag{61}$$

To make complete the identification with the conventional decomposition of Γ, we would expect

$$\mu_3 = c_v/c_p \tag{62}$$

But in fact this is true, because

$$(\Omega\rho_0)^{-1}m\beta\langle 4|4\rangle = m\beta(1 + \rho_0 G_k) = m(\partial\rho_0/\partial P)_T \tag{63}$$

(in the $k \to 0$ limit), so that μ_3 is the ratio of the isothermal to the adiabatic compressibilities. We thus identify

$$\bar{D}_L = (\tfrac{4}{3}\bar{\eta} + \bar{\zeta})(m\rho_0)^{-1} \tag{64}$$

In the conventional hydrodynamic analysis,(10,11) one locates the poles and writes G_{ij} as a sum of terms each of which is singular at only one pole. We shall now do the same thing for G_{11} and G_{44}, identifying the numerator of each term by calculating the residue of the Cramer's rule solution of (55). We find

$$\begin{aligned} G_{11}(kz) = g_{nn}(kz) = -S(k)\Bigg\{&\left(1 - \frac{c_v}{c_p}\right)(z + ik^2\bar{D}_t)^{-1} \\ &+ \sum_{+,-} \frac{1}{2}\frac{c_v}{c_p}\, \frac{1 \pm ik^2C_0^{-1}[\frac{1}{2}\bar{\Gamma} - \bar{D}_t(1 - c_p/c_v)]}{z \mp C_0k + ik^2\bar{\Gamma}/2}\Bigg\} \end{aligned} \tag{65}$$

$$G_{44}(kz) = \beta m^{-1}g_t(kz) = -p_0\left(z + \frac{ik^2\bar{\eta}}{m\rho_0}\right)^{-1} \tag{66}$$

where $S(k)$ is the static structure factor. This is in exact agreement with the results obtained from linearized hydrodynamics.(10,11) Furthermore, the only quantities that are sensitive to the approximation are $\bar{\eta}$, $\bar{\Gamma}$, and $\bar{D}_t$. All thermodynamic quantities are rendered exactly, as long as the approximation used is in the class specified by properties (45). In contrast, FM obtain expressions that are of the same form as (65) and (66), but the quantities c_0, c_p/c_v, and $S(k)$ are given by expressions that are correct only to second order in the potential.

5. THE WEAK COUPLING APPROXIMATION

5.1. The Memory Function

In this section a simple approximation, based on the assumption that the potential is small [$O(\lambda)$] at all distances, will be investigated. An explicit evaluation of the memory function to second order in λ will be possible. When applied to the space S_1, this procedure leads to the FM theory.

If we separate L into its free particle and interaction parts, $L = L_0 + L_i$, the important property is that

$$[L_0, P_M] = O(\lambda) \tag{67}$$

This can be verified from Eqs. (22), (24), and (A.1). The consequence is that $P_M L_0 Q_M$ is also $O(\lambda)$, so that M_M is $O(\lambda^2)$. We can then neglect the interaction term in the denominator of M_M at the expense of $O(\lambda^3)$ errors. Since the spectrum of L_0 is known, we can then calculate the memory function to lowest order. Defining

$$M_M(\mathbf{k}z; \mathbf{pp}') = \Omega^{-1}\langle D(\mathbf{pk})|M_M|D(\mathbf{p}'\mathbf{k})\rangle \tag{68}$$

we find four contributions, corresponding to the two parts of each vertex, $P_M L Q_M$:

$$M_M(\mathbf{k}z; \mathbf{pp}') = \sum_{\alpha,\beta=1,2} M_{\alpha\beta}(\mathbf{k}z; \mathbf{pp}') \tag{69}$$

where

$$\begin{aligned} iM_{11} = {} & \rho_0{}^2\Omega^{-1} \sum_{\mathbf{k}'} V(\mathbf{k}')^2 \mathbf{k}'\cdot\frac{\partial}{\partial \mathbf{p}'}\, \mathbf{k}'\cdot\frac{\partial}{\partial \mathbf{p}} \\ & \times \int d\mathbf{p}_1 \frac{\phi(p_1)\phi(p)\,\delta(\mathbf{p} - \mathbf{p}')}{z + (\mathbf{k} - \mathbf{k}')\cdot\mathbf{p}/m + \mathbf{k}'\cdot\mathbf{p}_1/m} \\ & + \rho_0{}^2\Omega^{-1} \sum V(\mathbf{k}')V(\mathbf{k} - \mathbf{k}')\mathbf{k}'\cdot\frac{\partial}{\partial \mathbf{p}}\,(\mathbf{k} - \mathbf{k}')\cdot\frac{\partial}{\partial \mathbf{p}} \\ & \times \frac{\phi(p)\phi(p')}{z + (\mathbf{k} - \mathbf{k})\cdot\mathbf{p}'/m + \mathbf{k}'\cdot\mathbf{p}/m} \end{aligned} \tag{70a}$$

$$\begin{aligned} iM_{12}(\mathbf{k}z; \mathbf{pp}') = {} & \frac{\beta\rho_0{}^2}{m\sqrt{6}}\frac{1}{\Omega}\sum_{\mathbf{k}'}\int d\mathbf{p}_2\, \phi(p_2)\psi_3(\mathbf{p}') \\ & \cdot\Bigg\{\mathbf{k}'\cdot\frac{\partial}{\partial \mathbf{p}}\,[\mathbf{k}\cdot(\mathbf{p}' - \mathbf{p}) + \mathbf{k}\cdot(\mathbf{p} - \mathbf{p}_2)] \\ & \times \frac{[V(\mathbf{k}')^2 + V(\mathbf{k}')V(\mathbf{k} - \mathbf{k}')]\phi(p)\phi(p')}{z + \mathbf{k}\cdot\mathbf{p}/m + \mathbf{k}'\cdot(\mathbf{p}_2 - \mathbf{p})/m}\Bigg\} \end{aligned} \tag{70b}$$

$$iM_{21}(\mathbf{k}z; \mathbf{pp}') = iM_{12}(\mathbf{k}z; \mathbf{p}'\mathbf{p}) \tag{70c}$$

$$\begin{aligned} iM_{22}(\mathbf{k}z; \mathbf{p}'\mathbf{p}) = {} & \frac{\rho_0{}^2\beta^2}{6m}\frac{1}{\Omega}\sum_{k'}\int d\mathbf{p}_1\, d\mathbf{p}_2\, \phi(p_1)\phi(p_2)\psi_3(\mathbf{p})\psi_3(\mathbf{p}')\phi(p)\phi(p') \\ & \cdot[\mathbf{k}\cdot(\mathbf{p}' - \mathbf{p}_2) + \mathbf{k}'\cdot(\mathbf{p}_2 - \mathbf{p}_1)] \\ & \times [\mathbf{k}\cdot(\mathbf{p} - \mathbf{p}_2) + \mathbf{k}'\cdot(\mathbf{p}_2 - \mathbf{p}_1)] \\ & \times \frac{V(\mathbf{k}')^2 + V(\mathbf{k}')V(\mathbf{k} - \mathbf{k}')}{z + \mathbf{k}'\cdot(\mathbf{p}_1 - \mathbf{p}_2)/m + \mathbf{k}\cdot\mathbf{p}_2/m} \end{aligned} \tag{70d}$$

The first term, M_{11}, is the FM memory function. The remaining terms are all separable and somewhat easier to deal with. To calculate $\mathscr{M}_M(\mathbf{k}z; \mathbf{pp}')$ in this theory, we would use the exact $W(\mathbf{k}; \mathbf{pp}')$ in Eq. (28).

We first consider whether the approximate memory function satisfies the conservation laws (36). Taking $k = 0$, it is not hard to show that

$$(i|M_{\alpha\beta}(0z)|\mathbf{p}') = 0, \qquad i = 1, 2, 4, 5 \tag{71}$$

and

$$\begin{aligned} (3|M_{22}(0z)|\mathbf{p}) &= -(3|M_{12}(0z)|\mathbf{p}) \\ (3|M_{11}(0z)|\mathbf{p}) &= -(3|M_{21}(0z)|\mathbf{p}) \end{aligned} \tag{72}$$

so that the conservation laws are satisfied.

The low-(k, z) limit of M_M plays an important role in the analysis of the hydrodynamic regime. We let k become continuous and use the Plemelj prescription, finding

$$\lim_{k\to 0;\, z\to i0^+} M_M(\mathbf{k}z; \mathbf{pp}') = -iK(\mathbf{pp}') \tag{73}$$

where K is the linearized Fokker–Planck operator of Brout and Prigogine.(12) This is the same as the Markovian limit of the FM memory function.

We now will show that properties (44a)–(44c) hold. Properties (44b) and (44c) are obvious. To determine whether W_{ij} is $O(k^2)$, we consider first the part W'_{ij} defined in (43). As observed by FM, K is nonzero except on the five $\psi_i(\mathbf{p})$. Hence $qK^{-1}q$ is finite and W_{ij} is $O(k^2)$ because each vertex is $O(k)$. The second part, W''_{ij}, can be investigated by direct calculation. Each $M_{\alpha\beta}$ gives a first order in k contribution to $(2|M_{\alpha\beta}|3)$, but these cancel as in (72). All other matrix elements are second order, and we conclude that $W_{ij} = O(k^2)$ for the weak coupling memory function; the results of Section 4 then apply. In the FM theory, the term $(2|M_{11}|3)$ made a contribution to the sound speed which was correct at second order in λ, but not at third.

5.2. Transport Coefficients

What remains is to calculate the coefficients a, b, c, d for this theory. Many of the calculations are the same as those appearing in FM, so we will follow a similar notation and be brief. In imitation of (41), we write $a = a' + a''$, $b = b' + b''$, etc. To obtain the primed contributions, we will need the fluxes,

$$\begin{aligned} \lim(i|M_M(\mathbf{k}z)|\mathbf{p}') &= k_j T_{ij}(\mathbf{p}'), \qquad i = 2, 4, 5 \\ \lim(3|M_M(\mathbf{k}z)|\mathbf{p}') &= k_j J_j(\mathbf{p}') \end{aligned} \tag{74}$$

where the limit $k \to 0$, $z \to i\epsilon$ is taken. The contributions from M_{11} are the same as in the FM theory. We denote them as

$$T_{ij}^{11}(\mathbf{p}') = \tfrac{1}{4}\delta_{ij}E(\mathbf{p}') + \tilde{T}_{ij}(\mathbf{p}') \tag{75}$$

$$J_j^{11}(\mathbf{p}) = \frac{2\rho_0\beta}{m\sqrt{6}}\int \frac{d\mathbf{k}}{(2\pi)^3}\,\mathbf{k}'\cdot\frac{\partial}{\partial\mathbf{p}'}\,V(\mathbf{k}') \tag{76}$$

$$\cdot\int dp_1\left[V(\mathbf{k}')(\mathbf{p}_1 - \mathbf{p}')_j + \frac{\partial V}{\partial k_j{}'}\,\mathbf{k}'\cdot\mathbf{p}_1\right]\frac{\phi(p_1)\phi(p')}{i\epsilon + \mathbf{k}'\cdot(\mathbf{p}' - \mathbf{p}_1)}$$

$$E(\mathbf{p}) = 2(2\pi)^{-3}\int d\mathbf{k}\;V(\mathbf{k}')^2U_1(\mathbf{k}'\mathbf{p}) \tag{77}$$

$$\tilde{T}_{ij}(\mathbf{p}) = -(2\pi)^{-3}\int d\mathbf{k}'\,\frac{V(k')^2}{2}\,k_i{}'\,\frac{\partial}{\partial k_{j'}}\,U_1(\mathbf{k}'\mathbf{p}) \tag{78}$$

$$U_1(\mathbf{k}'\mathbf{p}) = -m\rho_0\alpha\int d\mathbf{p}_1\;\phi(p_1)\mathbf{k}'\cdot\frac{\partial}{\partial\mathbf{p}'}\,\frac{\phi(p')}{i\epsilon + \mathbf{k}'\cdot(\mathbf{p}_1 - \mathbf{p}')} \tag{79}$$

In addition, we have contributions from each of the other $M_{\alpha\beta}$. Of these, however, the only term that contributes to W'_{ij} is

$$T_{ij}^{21} = -\tfrac{1}{3}\delta_{ij}E(\mathbf{p}') \tag{80}$$

It should be noted that the other difference from the FM calculation is that the term $zE(\mathbf{p})$ is missing from the rhs of our (74). The effect of these two differences will be that the primed contributions to the actual transport coefficients are unchanged.

Including the contribution from $\mathscr{L}$, we find

$$\begin{aligned} a' &= -(\bar{\tau}_{33}|qK^{-1}q|\bar{\tau}_{33}) - (1/144)(E|qK^{-1}q|E) \\ b' &= 0, \qquad c' = -(j_3{}^e|qK^{-1}q|j_3{}^e), \qquad d' = -(\bar{\tau}_{13}|qK^{-1}q|\bar{\tau}_{13}) \end{aligned} \tag{81}$$

where

$$\tilde{T}_{ij}(p) = -\alpha^2m^{-1}(p_ip_j - \tfrac{1}{3}\delta_{ij}p^2) - \tilde{T}_{ij} \tag{82}$$

$$j_3{}^e = [(p^2p_2/6m)\alpha^4 - J_3^{11}(\mathbf{p})] \tag{83}$$

There are only two second-order contributions to W''_{ij} from the new parts of the memory function. They are

$$a''_{22} = \chi_2/9 \tag{84}$$

$$b''_{21} = m\alpha\chi_2/3\sqrt{6} = -b''_{11} \tag{85}$$

where

$$\chi_2 = \rho_0m\alpha^3\pi^{1/2}(2\pi)^{-3}\int dk'\;[V(k')^2/|k'|] \tag{86}$$

Again, we will find that the two new terms lead to cancelling contributions to the transport coefficients.

The remaining contributions are from M_{11} and also appear in the FM calculations. We have, finally,

$$\begin{aligned} a'' &= -\chi_3/20 - 7\chi_2/36, \qquad b'' = 0 \\ c'' &= -2\chi_2/9 - \chi_3/36, \qquad d'' = -\chi_3/60 \end{aligned} \tag{87}$$

where

$$\chi_3 = \rho_0 m\alpha^3\pi^{1/2}(2\pi)^{-3}\int dk'\, k'(\partial V/\partial k')^2 \tag{88}$$

The predictions for the transport coefficients are, from Eqs. (58)–(61), (64), (81), and (87), as follows:

Thermal conductivity:

$$\bar\kappa''(c_v)^{-1} = m\rho_0(8\chi_2 - \chi_3)/36, \qquad \bar\kappa'(c_v)^{-1} = m\rho_0({j_3}^e|qK^{-1}q|{j_3}^e) \tag{89}$$

Shear viscosity:

$$\bar\eta'' = m\rho_0\chi_3/60, \qquad \bar\eta' = m\rho_0(\bar\tau_{13}|qK^{-1}q|\bar\tau_{13}) \tag{90}$$

Bulk viscosity:

$$\bar\zeta'' = m\rho_0(\chi_3 - \chi_2)/36, \qquad \zeta'' = m\rho_0(E|qK^{-1}q|E)/144 \tag{91}$$

We have utilized FM's observation that

$$(\bar\tau_{33}|qK^{-1}q|\bar\tau_{33}) = \tfrac{4}{3}(\bar\tau_{13}|qK^{-1}q|\bar\tau_{13}) \tag{92}$$

These predictions are the same, to lowest order in λ, as those of the FM theory. (There are, however, some typographical errors in the final results given in the FM paper.)

6. DISCUSSION

We conclude that, at least to lowest order, the calculation of dissipative effects in a weakly coupled system is not sensitive to whether the exact conserved quantities are isolated in the subspace. This was also true for the nondissipative part of the theory, because FM did obtain the correct thermodynamics to second order in λ. This conclusion is supportive of the FM procedure in that it shows that no errors are generated to lowest order by possible residual hydrodynamic resonances in the memory function W_{ij} caused by the fact that the potential energy density has not been eliminated by q or Q. The question of whether the resulting transport coefficients are a good approximation (i.e., whether the FM weak coupling approximation procedure is valid in the hydrodynamic regime) has not been closely examined here. The scheme at least has the advantage of simplicity, and the predictions are sensible. For our purposes it serves to demonstrate that it is not necessary to have approximations for the reversible and irreversible parts of the dynamical behavior that are consistent with each other (e.g., that are the same order in a parametric expansion). The theory presented here has been shown to be capable of including exact thermodynamic quantities while making the same predictions as FM in the irreversible part of the theory.

APPENDIX A

To find the form of the inversion kernel $W(\mathbf{k};\mathbf{pp}')$, we first note that, from (22) and (24),

$$\langle D(\mathbf{pk})|D(\mathbf{p}'\mathbf{k})\rangle = \rho_0\delta(p-\mathbf{p}') + B_{ij}\psi_i(\mathbf{p})\psi_j(\mathbf{p}')\phi(p)\phi(p') \tag{A.1}$$

where

$$\begin{aligned} B_{11} &= \Omega^{-1}\langle\rho_k|\rho_k\rangle \\ B_{13} &= B_{31}^* = \Omega^{-1}\beta\sqrt{\tfrac{2}{3}}\,\langle\rho_k|V_k\rangle \\ B_{33} &= \tfrac{2}{3}\Omega^{-1}\beta\langle V_k|V_k\rangle \end{aligned} \tag{A.2}$$

and all the other B_{ij} are zero. The integral equation (29) is then degenerate and easily solved. We find

$$W(\mathbf{k};\mathbf{pp}') = [\delta(\mathbf{p}-\mathbf{p}')/\rho_0\phi(p)] - D_{ij}\psi_i(\mathbf{p})\psi_j(\mathbf{p}') \tag{A.3}$$

where

$$D_{ij} = \rho_0^{-1}\delta_{ij} - (\rho_0\delta + B)_{ij}^{-1} \tag{A.4}$$

The lemma (46) is seen by inserting (A.1) into (45) and using the orthonormality of the $\psi_i(\mathbf{p})$, which yields

$$\langle D(\mathbf{pk})|J|m\rangle = (\mathbf{p}|J|i)(\rho_0\delta_{im} + B_{im}) \tag{A.5}$$

The key observation is that

$$(\rho_0\delta_{im} + B_{im}) = \Omega^{-1}\langle i|m\rangle$$

which is true because B_{ij} contains all terms of $\langle i|j\rangle$ involving purely spatial correlations. This proves (46).

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