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Fully renormalized kinetic theory. III. Density fluctuations

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The fully renormalized kinetic theory (FRKT) previously discussed by the author in the case of self-diffusion is extended to the case of density fluctuations. In the theory techniques are developed for calculating classical phase-space time-dependent correlation functions. The method centers around the development of an exact expression for the memory function associated with the phase-space-correlation function. This exact expression is written in a compact and symmetric form that is convenient for making approximations. It is shown explicitly how one can make contact with the Boltzmann-Enskog approximation for the memory function which is valid for moderate densities, as well as the ring terms which lead to the much-discussed $t^{-2/3}$ long-time behavior. The most striking difference between self-diffusion and the case of density fluctuation arises in the region of the critical point. It is shown in the theory how to make contact with the mode-mode coupling results of Kawasaki. From a formal point of view the development of the FRKT is carried forward three important steps in this paper. It is shown how to relate the memory function to the two-particle source function in a more powerful and direct method than the projection-operator approach developed in FRKT I. After a simple rearrangement, the memory function is written in a far more symmetric form than in FRKT I, and finally it is shown how the ideas of connectedness and cumulants can be successfully introduced into the theory.

I. INTRODUCTION

In a previous set of papers[1,2] a new theory was developed for treating dynamical processes involving a tagged particle in a classical monatomic fluid. In this paper this theory will be applied to the case of density fluctuations in a monatomic classical fluid. It will be shown that the basic ideas developed in FRKT I can be extended and more fully developed. Before discussing any extensions and improvements on FRKT I it is worthwhile summarizing the basic ideas developed there.

It is assumed from the beginning that most of the interesting dynamical properties of a fluid can be expressed in terms of time-dependent equilibrium averaged correlation functions.[3] While this assumption may restrict the analysis to physical systems where linear-response theory[4] is valid or scattering experiments where Born approximation is valid,[3] this restrictiveness is balanced by the definiteness of the problem posed. There is also the incentive that these correlation functions are calculated in computer molecular dynamics.[5]

The main ideas in the FRKT are renormalization of collisional effects through the use of memory functions and the expression of the memory function associated with the phase-space density correlation function in terms of an effective two-body problem. One builds in from the very beginning the ideas from renormalization theory that one should consistently try to replace bare interactions with effective interactions. The advantage of introducing an effective two-body problem is that approximations can be made from a physical point of view.

One of the main requirements for the theory is that it make contact with a good zeroth-order approximation. This requires reduction of the N-body problem to an effective few-body problem and it is well known that the Boltzmann-Enskog theory[6] provides such a zeroth-order approximation for classical short-ranged fluids. It was shown in I how one can make contact with the Boltzmann-Enskog theory in a straightforward and natural way. This is discussed further in this paper. The *main* purpose of the present theory is to develop convenient and physical methods for finding corrections to the zeroth-order theory.

The basic formalism for expressing these ideas mathematically were developed in FRKT I. First one must settle on the basic correlation function to be calculated. It is convenient for physical and mathematical reasons to work with the phase-space correlation function. Realizing that this correlation function possesses a resonant structure in the hydrodynamical regime, one switches one's attention from the correlation function itself to the associated memory function which is defined to be that function which gives the effect of the other $N-1$ particles on a free streaming particle. One then uses the basic equations of motion satisfied by the phase-space density correlation function to obtain an exact equation for the memory function. These expressions for the memory function are in terms of higher-order correlation functions which enter because of the hierarchic nature of the equations of motion. One then runs into a rather tricky technical point at this stage in the development. This was treated under the heading "plateau-value" problem in FRKT I. This problem, stated simply, is that the memory function is given as the difference between two functions each of which is "more complicated" than their difference. In more mathematical language the memory function is given in terms of a doubly connected correlation function. The difficulty is in combining two correlation functions that are not doubly connected to obtain a compact expression for this doubly connected function. A large number of authors[7] have dealt with this problem in treating the theory of transport coefficients which requires knowledge of the memory function only for small wave numbers. Only fairly recently, with the development of projection-operator techniques,[8] has there been progress in understanding the behavior of memory functions for all wave numbers.

In FRKT I an alternate approach to the plateau-value problem was presented. The idea was to express the two contributing pieces to the memory function in terms of an effective two-body problem and then use projection operators that act in this two-body space to combine these two pieces. In I this combination was carried out with the resulting compact expression (I.4.28). The analysis in this paper will be carried several important steps further than the development in I.

The major difference between the analysis in FRKT I and the analysis here relates to the method used to obtain expressions for the doubly connected quantity G in terms of the two-particle source M. In FRKT I projection operators were used to relate G and M. The theory of density fluctuations was initially developed[9] using essentially the same projection-operators techniques developed in I. It was found that the resulting projection-operator expression for the memory function could be considerably simplified compared to the expression (I.4.28). It was found that the effects of the projection operators, as they appear in (I.4.28), could be evaluated explicitly such that the final expression for the memory function contains no further reference to the projection operator. Therefore, the resulting equations for the memory function turn out to be ensemble independent in the thermodynamical limit and independent of the choice of the projection operator. Since the memory function can eventually be written in a compact form that is independent of the initial choice of the projection operator, one suspects that the same result can be derived without introducing projection operators. In Sec. IV of this paper a more direct method is presented for relating the memory function to the two-particle source M.

A second important new step taken in this paper will be to show how the memory function can be written in a far more symmetric form than in I. This eliminates the formal awkwardness in going from Eqs. (I.4.28) to (I.4.38) and all of the resulting equations become much more symmetric.

The third main new ingredient is the introduction and the use of cumulants[10] and the separation of correlation functions into their connected and disconnected parts. Such a separation is very important in those cases where the fields in an average can become statistically independent. In such cases the disconnected part of the correlation function dominates the connected contribution. Such effects have been observed in recent light-scattering experiments.[11] Using these ideas of connectedness and the fact that effective interactions may be very long-ranged near the critical point it is very easy to make contact, using the FRKT, with the mode-mode coupling theories[12] that have been successful near the critical point. Of course the FRKT also tells one how the transport coefficients behave as one approaches the critical point. This is because the theory includes the microscopic as well as the hydrodynamical or collective couplings in the system.

These new ideas should also be introduced back into the theory of self-diffusion. It should be pointed out that these more powerful techniques are more necessary in the case of density fluctuations which is more complicated than the case of self-diffusion. This complexity arises in the case of density fluctuations because of the more involved static contributions. This is manifested in the critical behavior that shows up in the dynamics structure factor $S_{nn}(k, \omega)$ but which is absent in an analysis of $S_s(k, \omega)$.[13] A further complexity in the analysis of S_{nn} comes from the coupled modes that appear in the hydrodynamical regime.

One of the major results of the present theory is an understanding of the competition between the microscopic or localized events and collective effects in determining the memory function. The microscopic effects or interactions between bare particles serves as a local or zeroth-order approximation. These events are characterized by two-particle collisions and give rise to the Boltzmann-Enskog contributions and these terms dominate for very low densities.[14-17] For moderate densities the microscopic and collective effects compete and lead to things like the long-time tails discussed in FRKT II. One expects that the cooperative effects dominate near a phase transition, while the microscopic effects provide the "background." It is, of course, a great advantage of the FRKT that the static-correlation functions are treated as input. This is especially true near the phase transition where there has been great recent progress in calculating the static-correlation functions.[18] These theories can then be taken over as input to the FRKT.

One of the reasons one can understand such a diverse range of phenomena is because the FRKT does not single out any expansion parameter until very far along into the theory. Thus exact static-correlation functions appear in the theory and no resummations of the "most divergent" terms is necessary since there has been no expansion. The "divergences" of the density expansion of transport coefficients[19] is easily understood within this theory since it can be seen that a direct density expansion of the memory function involves an internal expansion of a time-correlation function in a power series in the density. Because of the resonant nature of the time correlation function such an expansion is not admissable.

Since the density cannot be used as a systematic expansion parameter,[20] one must introduce a new expansion parameter. This is a very old problem in the theory of fluids, and there has not been much progress. In the theory developed here one introduces a four-point fully-connected "vertex." This vertex appears naturally in the theory and seems to be a natural expansion parameter. It will be shown in Sec. VI that if one expands to lowest order in the vertex, then one has an approximation that includes the Boltzmann-Enskog theory, the ring terms,[21] and the mode-mode coupling terms which have been successful in describing critical phenomena. Unfortunately a direct calculation of the vertex is quite involved and it has not yet been possible to show that the contributions from these terms are small. The attitude here is to ignore the vertex and see that one is led to reasonable agreement with experiment. For those who are not so optimistic there is a short discussion of how one can go about calculating the vertex function.

It is hopefully clear from the preceeding remarks that the FRKT is a rather flexible and general framework within to discuss dynamical problems. The theory is complementary to the field theoretical work done in calculating static phenomena, it should be applicable to quantum as well as classical systems, and it is rather easy to extend the formalism to the case of multicomponent systems.[22] The theory also provides a bridge between the sucessful applications of kinetic theory to the calculation of transport coefficients and the more phenomenological generalized hydrodynamical theories.[23] The theory therefore possesses a unifying quality.

In Sec. II the basic definitions in the formalism are introduced. In Sec. III these definitions are used together with the basic equations of motion to obtain equations for the memory function in terms of four-point correlation functions. In Sec. IV the two pieces that contribute to the memory function are combined in a compact expression for the memory function. A detailed analysis of the various components in this expression for the memory function is carried out in Sec. V. It is also at this state that the powerful ideas related to connectedness and cumulants are introduced and used to advantage. These properties are used in Sec. VI to develop an iteration scheme that allows one to identify the Boltzmann-Enskog contribution, the ring terms discussed in FRKT II (suitably generalized) and the mode-mode coupling terms important near the critical point. It is then shown in Sec. VII how the memory-function formalism can be used in the hydrodynamical regime. Explicit expressions for the transport coefficients (shear viscosity, thermal conductivity, and sound-damping coefficients) are obtained in terms of the memory function and as a special case the thermal conductibility is investigated near the critical point. Section VIII is devoted to a brief discussion of results and work remaining.

II. BASIC DEFINITIONS

In this section the various notations and definitions needed in the description of time-dependent phase-space correlation functions are introduced.

A. System

The system of interest in this paper will be a classical single-component monatomic fluid. This fluid contains N particles of mass m enclosed in a volume Ω. The system is assumed to be in equilibrium at temperature $T=(k_B\beta)^{-1}$ and, if $\vec{r}_i$ and $\vec{p}_i$ are the phase-space coordinates of the ith particle in the system, then the Hamiltonian for the system is

$$H=\sum_{i=1}^{N}\frac{p_i^2}{2m}+\frac{1}{2}\sum_{i\neq j=1}^{N}V(\vec{r}_i-\vec{r}_j), \qquad (2.1)$$

where it is assumed that one has a pair-wise additive central potential.

B. Fundamental fields

It is quite useful to introduce a set of fields that allow one to carry out the classical equivalent of second quantization. All of the microscopic variables of interest can be expressed in terms of the fundamental fields

$$f(1)=\sum_{i=1}^{N}\delta(1-q_i), \tag{2.2}$$

$$\begin{aligned} g(1\bar{1})&=\sum_{i\neq j=1}^{N}\delta(1-q_i)\delta(\bar{1}-q_j)\\ &=f(1)f(\bar{1})-\delta(1\bar{1})f(1), \end{aligned}\tag{2.3}$$

$$\begin{aligned} h(1\bar{1}\bar{1}')&=\sum_{i\neq j\neq k=1}^{N}\delta(1-q_i)\delta(\bar{1}-q_j)\delta(\bar{1}'-q_k)\\ &=f(1)g(\bar{1}\bar{1}')-\delta(1\bar{1}')g(\bar{1}\bar{1}')-\delta(\bar{1}\bar{1}')g(1\bar{1}'), \end{aligned}\tag{2.4}$$

where $1=(\vec{r}_1,\vec{p}_1)$, etc. denote the phase coordinates of an external variable and $q_i=(\vec{r}_i,\vec{p}_i)$, the phase coordinates of particle i, is an internal variable.[24]

C. Thermodynamic averages of the fields

Since one may be interested in considering equilibrium averages in either the canonical or the grand canonical ensembles, it is useful to leave open the specification of the ensemble with the condition that $\langle N\rangle=N$ in the canonical ensemble. The equilibrium density is given by

$$n=\langle N\rangle/\Omega. \tag{2.5}$$

Before calculating the averages of the fundamental fields it is useful to introduce the definition,

$$\omega_0(12\cdots s)=\Big\langle\sum_{i_1\neq i_2\neq\cdots\neq i_s=1}^{N}\delta(1-q_{i_1})\delta(2-q_{i_2})\cdots\delta(s-q_{i_s})\Big\rangle \tag{2.6}$$

$$=n^sf_0(p_1)f_0(p_2)\cdots f_0(p_s)g(\vec{r}_1,\vec{r}_2,\cdots\vec{r}_s), \tag{2.7}$$

where[25]

$$n^sg(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_s)=\Big\langle\sum_{i_1\neq i_2\neq\cdots\neq i_s=1}^{N}\delta(\vec{r}_1-\vec{r}_{i_1})\delta(\vec{r}_2-\vec{r}_{i_2})\cdots\delta(\vec{r}_s-\vec{r}_{i_s})\Big\rangle \tag{2.8}$$

is the s-particle static distribution function, and

$$f_0(p)=(\beta/2\pi m)^{3/2}e^{-\beta p^2/2M} \tag{2.9}$$

is the Maxwell distribution. One of the great simplifications of working with classical systems is that the momentum dependence of the static-correlation functions can be evaluated explicitly. We have then, using (2.6) and (2.7), that

$$\langle f(1)\rangle=\omega_0(1)=nf_0(p_1), \tag{2.10}$$

$$\langle g(1\bar{1})\rangle=\omega_0(1\bar{1})=n^2f_0(p_1)f_0(p_{\bar{1}})g(\vec{r}_1-\vec{r}_{\bar{1}}), \tag{2.11}$$

where $g(\vec{r}_1-\vec{r}_{\bar{1}})$ is the pair-distribution function. Clearly the average of $h(1\bar{1}\bar{1}')$ will be related to the triplet distribution function $g(\vec{r}_1,\vec{r}_{\bar{1}},\vec{r}_{\bar{1}'})$.

D. Static correlations between fields

It will be necessary to know various averages between these fields at equal times. In particular one will need to know the connected correlation functions or cumulants

$$K(12\cdots s)=\langle f(1)f(2)\cdots f(s)\rangle_c, \tag{2.12}$$

where a cumulant for an arbitrary product of fields is defined by Kubo.[10] One is particularly interested in the two-point cumulant[26]

$$K(12)=\langle f(1)f(2)\rangle_c=\langle\delta f(1)\delta f(2)\rangle\equiv\tilde{C}(12), \tag{2.13}$$

where the fluctuation of a field A is defined by $\delta A=A-\langle A\rangle$. Because of the simple momentum dependence in classical systems one can write,

$$\tilde{C}(12)=\delta(12)\,nf_0(p_1)+n^2f_0(p_1)f_0(p_2)h(\vec{r}_1-\vec{r}_2), \tag{2.14}$$

where

$$h(\vec{r}_1-\vec{r}_2)=g(\vec{r}_1-\vec{r}_2)-1. \tag{2.15}$$

If one integrates (2.14) over $\vec{p}_1$ and $\vec{p}_2$ one obtains the structure factor times the density,

$$\begin{aligned} n\tilde{S}(\vec{r}_1-\vec{r}_2)&=n\delta(\vec{r}_1-\vec{r}_2)+n^2h(\vec{r}_1-\vec{r}_2)\\ &=\int d^3p_1\,d^3p_2\,\tilde{C}(12). \end{aligned}\tag{2.16}$$

A related quantity of interest is the direct correlation function C_D that is defined in terms of the Fourier transform of h as

$$C_D(k)=h(k)[1+nh(k)]^{-1}. \tag{2.17}$$

One also needs the three-point correlation function

$$\tilde{C}(1\bar{1};\,2)=\langle\delta f(2)\delta g(1\bar{1})\rangle \tag{2.18}$$

and the four-point correlation function

$$\tilde{C}(1\bar{1};\,2\bar{2})=\langle\delta g(1\bar{1})\delta g(2\bar{2})\rangle \tag{2.19}$$

whose counterpart $\langle g_sg_s\rangle$ played an important role in FRKT I [see Eq. (I.2.12)]. Here one can see how the case of density fluctuations is more complicated than the case of self-diffusion because of the more complicated static correlations.

It will be very important to consider the cluster properties of these higher-order correlation functions. Using the definition for the cumulants,[10] one can easily express the three-point function as

$$\tilde{C}(1\bar{1};\,2)=K(1\bar{1}2)+K(\bar{1})K(12)+K(1)K(\bar{1}2)-\delta(1\bar{1})K(12). \tag{2.20}$$

One sees that $\tilde{C}(1\bar{1};\,2)$ has two disconnected pieces (portions which are nonzero when a field variable becomes statistically independent of the other field variables). A detailed analysis of $\tilde{C}(1\bar{1};\,2\bar{2})$ shows that it contains many disconnected pieces. This leads to the undesirable feature[27] that $\tilde{C}(1\bar{1};\,2\bar{2})$ does not possess a matrix inverse in the sense that there is no function $\tilde{C}^{-1}$ such that

$$\tilde{C}^{-1}(1\bar{1};\,3\bar{3})\tilde{C}(3\bar{3};\,2\bar{2})=\tfrac{1}{2}[\delta(12)\delta(\bar{1}\bar{2})+\delta(1\bar{2})\delta(\bar{1}2)]$$

[where repeated internal indices (like 3 and $\bar{3}$ above) imply an integration over that variable in the above equation and in the remainder of the paper]. It will therefore be useful to investigate a new four-point correlation function,

$$\tilde{G}(1\bar{1};\,2\bar{2})=\tilde{C}(1\bar{1};\,2\bar{2})-\tilde{C}(1\bar{1};\,3)\tilde{C}^{-1}(34)\tilde{C}(4;\,2\bar{2}). \tag{2.21}$$

A simple analysis shows that the disconnected part of $\tilde{G}$ is given by

$$\tilde{G}_D(1\bar{1};\,2\bar{2})=\tilde{C}(12)\tilde{C}(\bar{1}\bar{2})+\tilde{C}(1\bar{2})\tilde{C}(\bar{1}2), \tag{2.22}$$

and the connected part by

$$\tilde{G}_c(1\bar{1};\,2\bar{2})=K(1\bar{1}2\bar{2})-K(1\bar{1}3)K^{-1}(34)K(42\bar{2}). \tag{2.23}$$

If any of the particles associated with 1, $\bar{1}$, 2 or $\bar{2}$ becomes spatially independent of the other particles, then $\tilde{G}_c$ vanishes. For moderate densities one can approximate $\tilde{G}_c$ as

$$\tilde{G}_c(1\bar{1};\,2\bar{2})\approx[\delta(12)\delta(\bar{1}\bar{2})+\delta(1\bar{2})\delta(\bar{1}2)]\times\omega_0(1)\,\omega_0(\bar{1})\,h(\vec{r}_1-\vec{r}_{\bar{1}}) \tag{2.24}$$

which is a very simple two-body result. It will be of great importance that one can define a matrix inverse of $\tilde{G}$ such that

$$\tilde{G}^{-1}(1\bar{1};\,3\bar{3})\,\tilde{G}(3\bar{3};\,2\bar{2})=\tfrac{1}{2}[\delta(12)\delta(\bar{1}\bar{2})+\delta(\bar{1}2)\delta(1\bar{2})]. \tag{2.25}$$

E. Time-dependent correlation functions

A basic quantity in the discussion will be the time-dependent phase-space-correlation function

$$C(12,t-t')=\langle\delta f(1,t)\,\delta f(2,t')\rangle, \tag{2.26}$$

where the fundamental fields are displaced in time. One is also interested in the Fourier transform of this quantity,

$$C(12,\omega)=\int_{-\infty}^{+\infty}d(t-t')\,e^{+i\omega(t-t')}C(12,t-t') \tag{2.27}$$

and the Laplace transform

$$C(12)=-i\int_{0}^{+\infty}d(t-t')\,e^{+iz(t-t')}C(12,t-t')=\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\,\frac{C(12,\omega)}{z-\omega}, \tag{2.28}$$

where in (2.28) $\mathrm{Im}\,z>0$. The correlation function depends only on the time difference $t-t'$ because the equilibrium system is time translationally invariant. ω will always be a real frequency and z a complex frequency. Following the analysis in Sec. II C in I one can introduce Koopman's operator[28] to obtain

$$C(12)=\langle\delta f(2)[z+L]^{-1}\delta f(1)\rangle, \tag{2.29}$$

where L is the Liouville operator defined by (I.2.18). In the following it will also be useful to introduce the correlation functions

$$C(1\bar{1};\,2)=\langle\delta f(2)[z+L]^{-1}\delta g(1\bar{1})\rangle, \tag{2.30}$$

$$C(1\bar{1};\,2\bar{2})=\langle\delta g(2\bar{2})[z+L]^{-1}\delta g(1\bar{1})\rangle, \tag{2.31}$$

and

$$C(1\bar{1}\bar{1}';\,2\bar{2})=\langle\delta g(2\bar{2})[z+L]^{-1}\delta h(1\bar{1}\bar{1}')\rangle \tag{2.32}$$

which are the dynamical counterparts of the static functions introduced in Sec. II D.

III. EQUATIONS OF MOTION

A. Hierarchy

As in FRKT I the fundamental equations are the equations of motion satisfied by the correlation functions in Laplace transform space. These equations follow once one has proven the identities

$$Lf(1)=-L_0(1)f(1)-\int d\bar{1}\,L_I(1\bar{1})\,g(1\bar{1}) \tag{3.1}$$

and

$$Lg(1\bar{1})=-L(1\bar{1})\,g(1\bar{1})-\int d\bar{1}\,\sigma(1\bar{1}\bar{1}')\,h(1\bar{1}\bar{1}'), \tag{3.2}$$

where

$$L_0(1)=-i\,\vec{p}_1\cdot\nabla_{r_1}/m \tag{3.3}$$

is the single-particle Liouville operator,

$$L_I(1\bar{1}) = i\nabla_{r_1} V(\vec{r}_1 - \vec{r}_{\bar{1}}) \cdot (\nabla_{p_1} - \nabla_{p_{\bar{1}}}) \tag{3.4}$$

is the interaction part of the two-particle Liouville operator,

$$\begin{aligned} L(1\bar{1}) &= L_0(1) + L_0(\bar{1}) + L_I(1\bar{1}) \\ &= L_0(1\bar{1}) + L_I(1\bar{1}) \end{aligned} \tag{3.5}$$

is the two-particle Liouville operator, and

$$\sigma(1\bar{1}\bar{1}') = L_I(1\bar{1}') + L_I(\bar{1}\bar{1}'). \tag{3.6}$$

It should be noted, since $\langle Lf(1)\rangle = \langle Lg(1\bar{1})\rangle = 0$, that one can replace f, g, and h in (3.1) and (3.2) by the corresponding fluctuating quantities. After using Eq. (I.3.5) one can then easily obtain the equations of motion

$$[z - L_0(1)]C(12) - \int d\bar{1} L_I(1\bar{1}) C(1\bar{1};\, 2) = \tilde{C}(12), \tag{3.7}$$

$$[z + L_0(2)]C(12) + \int d\bar{2} L_I(2\bar{2}) C(1;\, 2\bar{2}) = \tilde{C}(12); \tag{3.8}$$

and

$$[z + L_0(2)]C(1\bar{1};\, 2) + \int d\bar{2} L_I(2\bar{2}) C(1\bar{1};\, 2\bar{2}) = \tilde{C}(1\bar{1};\, 2), \tag{3.9}$$

$$[z - L(1\bar{1})]C(1\bar{1};\, 2) - \int d\bar{1}' \sigma(1\bar{1}\bar{1}') C(1\bar{1}\bar{1}';\, 2) = \tilde{C}(1\bar{1};\, 2), \tag{3.10}$$

$$[z - L(1\bar{1})]C(1\bar{1};\, 2\bar{2}) - \int d\bar{1}' \sigma(1\bar{1}\bar{1}') C(1\bar{1}\bar{1}';\, 2\bar{2}) = \tilde{C}(1\bar{1};\, 2\bar{2}). \tag{3.11}$$

B. Renormalization of collisional effects

The general ideas concerning renormalization were discussed in I and preceding papers by the author.[14-16] The main point is that one wants to make approximations for quantities which do not contain a resonant structure. Since one knows that the correlation function $C(12)$ is resonant for long time and distances (in the hydrodynamical regime) one should shift one's attention to the quantities that describe the placement and width of these hydrodynamical poles. It is now well established that the phase-space memory function defined by the generalized kinetic equation[29]

$$[z - L_0(1)]C(12) - \varphi(13)C(32) = \tilde{C}(12) \tag{3.12}$$

controls the location and width of these poles. This kinetic equation is also valid outside the hydrodynamic regime. Since one expects the memory function φ to be more susceptible to approximation than the correlation function itself, one should focus attention on φ since the correlation function can then be calculated from the kinetic equation.

The memory function has the physical interpretation of a nonlocal, non-Markovian external source modifying the propagation, described by $z - L_0(1)$, of a single free-streaming particle. Consequently, the memory function describes the effect of the other $N-1$ particles on a chosen particle. It was similar reasoning which led Boltzmann to the Boltzmann equation and the author[15] has shown that to lowest order in the density and in the limit of long times and distances φ reduces to i times the linearized Boltzmann collision operator. The kinetic equation (3.12) is then essentially the linearized Boltzmann equation.

The program for investigating the memory function will follow that developed in Sec. III B in I. One notes on comparing (3.12) to (3.7) that the memory function satisfies the equation

$$\varphi(13)C(32) = \int d\bar{1}\, L_I(1\bar{1}) C(1\bar{1};\, 2). \tag{3.13}$$

Then, as in I, one can apply the operator $z + L_0(2)$ to (3.13), and after using (3.8), (3.9), and (3.13), one finds an explicit expression for the memory function,

$$\varphi(13)\tilde{C}(32) = \varphi^{(s)}(13)\tilde{C}(32) + \varphi^{(c)}(13)\tilde{C}(32), \tag{3.14}$$

where the static (z-independent) part of the memory function is given by

$$\varphi^{(s)}(13)\tilde{C}(32) = \int d\bar{1}\, L_I(1\bar{1}) \tilde{C}(1\bar{1};\, 2) \tag{3.15}$$

and the collisional part is given by

$$\varphi^{(c)}(13)\tilde{C}(32) = -\int d\bar{1}\, d\bar{2}\, L_I(1\bar{1}) L_I(2\bar{2}) G(1\bar{1};\, 2\bar{2}), \tag{3.16}$$

where

$$G(1\bar{1};\, 2\bar{2}) = C(1\bar{1};\, 2\bar{2}) - C(1\bar{1};\, 3) C^{-1}(34) C(4;\, 2\bar{2}). \tag{3.17}$$

In the case of self-diffusion the static term vanished. In the case of density fluctuation one finds that $\varphi^{(s)}$ plays an important role in both the hydrodynamical regime and in the high frequency and wave-number regime where $\varphi^{(s)}$ serves as an effective mean field term. $\varphi^{(s)}$ will be evaluated more explicitly in Sec. VI A.

It should be noted that G, defined by Eq. (3.17), is the dynamical (z-dependent) generalization of the static-correlation function $\tilde{G}$ defined by Eq. (2.21). The connection between these quantities will be made clearer in Sec. IV.

IV. CORRELATION FUNCTION $G(1\bar{1};2\bar{2})$

A. Introduction

In I the next step in the analysis was to assume that the correlation function $C(1\bar{1};\,2\bar{2})$ satisfies a kinetic equation [see Eq. (I.3.17)]. It is convenient to depart from this approach for three reasons. First one notes that it is really the correlation function $G(1\bar{1};\,2\bar{2})$ that appears in the expression for the memory function. If one assumes that $C(1\bar{1};\,2\bar{2})$ satisfies a kinetic equation of the form of (I.3.17) and goes through the complete projection-operator analysis one eventually finds an expression for $G(1\bar{1};\,2\bar{2})$ with the simple interpretation that G also satisfies a kinetic equation like (I.3.17). Rather than go through the projection-operator analysis it is more direct to assume that G satisfies a kinetic equation and then determine the corresponding memory functions. A second reason for shifting one's attention from C to G is related to the poor connectedness properties of C and its static value $\tilde{C}$. As was pointed out in Sec. II one cannot define a matrix inverse for $\tilde{C}$. This leads to complications when one comes to expressions like (I.3.19), where one has an unknown function multiplied by $\tilde{C}$. While one can eventually develop methods for solving for the unknown (one cannot simply matrix multiply by $\tilde{C}^{-1}$ since it does not exist), one never encounters these difficulties if one works with the correlation function $G(1\bar{1};\,2\bar{2})$.

The final reason for developing a new technique (besides the fact it is more direct) is that one would like to remove some of the restrictions involved in the projection-operator technique. These restrictions involved the use of relations like

$$C(1\bar{1};\,2)=\int\frac{d\bar{2}}{(N-1)}\,C(1\bar{1};\,2\bar{2})$$

which are ensemble dependent and must be established before taking the thermodynamic limit. The method used here is ensemble independent and all of the manipulations can be carried out after the thermodynamic limit has been taken.

B. Equation of motion for G

One can derive an equation of motion for G, as defined by Eq. (3.17), by using the equations of motion satisfied by $C(1\bar{1};\,2\bar{2})$ and $C(1\bar{1};\,3)$ given by (3.10) and (3.11). One has then that

$$[z-L(1\bar{1})]\,G(1\bar{1};\,2\bar{2})=\tilde{C}(1\bar{1};\,2\bar{2})-\tilde{C}(1\bar{1};\,3)C^{-1}(34)C(4;\,2\bar{2})$$
$$+\int d\bar{1}'\,\sigma(1\bar{1}\bar{1}')[C(1\bar{1}\bar{1}';\,2\bar{2})\;-C(1\bar{1}\bar{1}';\,3)C^{-1}(34)C(4;\,2\bar{2})]. \tag{4.1}$$

This can be put into a more convenient form if one notes that

$$C^{-1}(34)=\tilde{C}^{-1}(35)[z-L_0(5)]\,\delta(54)-\tilde{C}^{-1}(35)\,\varphi(54). \tag{4.2}$$

Then, after using the transpose of (3.9), one has

$$C^{-1}(34)C(4;\,2\bar{2})=\tilde{C}^{-1}(34)\left[\tilde{C}(4;\,2\bar{2})+\int d\bar{4}\,L_I(4\bar{4})C(4\bar{4};\,2\bar{2})-\varphi(45)C(5;\,2\bar{2})\right]. \tag{4.3}$$

But if one eliminates $C(4\bar{4};\,2\bar{2})$ in (4.3) using (3.17) and then uses (3.13) one finds

$$C^{-1}(34)C(4;\,2\bar{2})=\tilde{C}^{-1}(34)\tilde{C}(4;\,2\bar{2})+\tilde{C}^{-1}(34)\int d\bar{4}\,L_I(4\bar{4})\,G(4\bar{4};\,2\bar{2}). \tag{4.4}$$

Putting (4.4) back into (4.1) gives

$$[z-L(1\bar{1})]\,G(1\bar{1};\,2\bar{2})+\tilde{C}(1\bar{1};\,3)\tilde{C}^{-1}(34)\int d\bar{4}\,L_I(4\bar{4})\,G(4\bar{4};\,2\bar{2})$$
$$-\int d\bar{1}'\,\sigma(1\bar{1}\bar{1}')[C(1\bar{1}\bar{1}';\,2\bar{2})-C(1\bar{1}\bar{1}';\,3)C^{-1}(34)C(4;\,2\bar{2})]=\tilde{G}(1\bar{1};\,2\bar{2}); \tag{4.5}$$

similarly

$$[z+L(2\bar{2})]\,G(1\bar{1};\,2\bar{2})-\tilde{C}(2\bar{2};\,3)\tilde{C}^{-1}(34)\int d\bar{4}\,L_I(4\bar{4})\,G(1\bar{1};\,4\bar{4})$$
$$+\int d\bar{2}'\,\sigma(2\bar{2}\bar{2}')[C(1\bar{1};\,2\bar{2}\bar{2}')-C(1\bar{1};\,4)C^{-1}(45)C(5;\,2\bar{2}\bar{2}')]=\tilde{G}(1\bar{1};\,2\bar{2}). \tag{4.6}$$

C. Memory-function equations for G

One can now proceed very much as for $C(12)$ and assume that G satisfies the kinetic equations

$$[z-L(1\bar{1})]\,G(1\bar{1};\,2\bar{2})-V(1\bar{1};\,3\bar{3})\,G(3\bar{3};\,2\bar{2})=\tilde{G}(1\bar{1};\,2\bar{2}), \tag{4.7}$$

$$[z+L(2\bar{2})]\,G(1\bar{1};\,2\bar{2})-G(1\bar{1};\,3\bar{3})\,V^{T}(3\bar{3};\,2\bar{2})=\tilde{G}(1\bar{1};\,2\bar{2}), \tag{4.8}$$

where V and V^T are now “two-particle” memory functions. One immediately sees on comparing (4.5) through (4.8) that

$$\begin{aligned}V(1\bar{1};\,3\bar{3})\,G(3\bar{3};\,2\bar{2})=&-\tilde{C}(1\bar{1};\,3)\,\tilde{C}^{-1}(34)\int d\bar{4}\,L_I(4\bar{4})\,G(4\bar{4};\,2\bar{2})\\&+\int d\bar{1}'\,\sigma(1\bar{1}\bar{1}')[C(1\bar{1}\bar{1}';\,2\bar{2})-C(1\bar{1}\bar{1}';\,3)\,C^{-1}(34)\,C(4;\,2\bar{2})]\end{aligned} \tag{4.9}$$

and

$$\begin{aligned}G(1\bar{1};\,3\bar{3})\,V^{T}(3\bar{3};\,2\bar{2})=&\,\tilde{C}(2\bar{2};\,3)\,\tilde{C}^{-1}(34)\int d\bar{4}\,L_I(4\bar{4})\,G(1\bar{1};\,4\bar{4})\\&-\int d\bar{2}'\,\sigma(2\bar{2}\bar{2}')[C(1\bar{1};\,2\bar{2}\bar{2}')-C(1\bar{1};\,4)\,C^{-1}(43)\,C(3;\,2\bar{2}\bar{2}')]\,.\end{aligned} \tag{4.10}$$

One can now use essentially the same trick used in going from (3.13) to (3.16) and operate to the right on (4.9) with $[z+L(2\bar{2})]$. It is easy to see that this leads to the result

$$\begin{aligned}V(1\bar{1};\,3\bar{3})\,\tilde{G}(3\bar{3};\,2\bar{2})=&\int d\bar{1}'\,d\bar{2}'\,\sigma(1\bar{1}\bar{1}')\sigma(2\bar{2}\bar{2}')[C(1\bar{1}\bar{1}';\,2\bar{2}\bar{2}')-C(1\bar{1}\bar{1}';\,3)\,C^{-1}(34)\,C(4;\,2\bar{2}\bar{2}')]\\&+\int d\bar{1}'\,\sigma(1\bar{1}\bar{1}')[\tilde{C}(1\bar{1}\bar{1}';\,2\bar{2})-C(1\bar{1}\bar{1}';\,3)\,C^{-1}(34)\,\tilde{C}(4;\,2\bar{2})]-V(1\bar{1};3\bar{3})G(3\bar{3};4\bar{4})V^{T}(4\bar{4};2\bar{2})\\&-\tilde{C}(1\bar{1};\,3)\,\tilde{C}^{-1}(34)\int d\bar{3}\,L_I(3\bar{3})[\tilde{G}(3\bar{3};2\bar{2})+G(3\bar{3};4\bar{4})\,V^{T}(4\bar{4};2\bar{2})]\,.\end{aligned} \tag{4.11}$$

One can use the same types of arguments used in deriving (4.4) to obtain

$$\begin{aligned}C(1\bar{1}\bar{1}';3)\,C^{-1}(34)\,\tilde{C}(4;2\bar{2})=&\,\tilde{C}(1\bar{1}\bar{1}';3)\,\tilde{C}^{-1}(34)\,\tilde{C}(4;2\bar{2})\\&-\tilde{C}(2\bar{2};3)\,\tilde{C}^{-1}(34)\int d\bar{4}\,L_I(4\bar{4})[C(1\bar{1}\bar{1}';4\bar{4})-C(1\bar{1}\bar{1}';3)\,C^{-1}(35)\,C(5;4\bar{4})].\end{aligned} \tag{4.12}$$

One can then put (4.12) back into (4.11), use (4.9) and (4.10) to eliminate V and V^T and cancel a large number of terms to obtain

$$V(1\bar{1};2\bar{2})=U(1\bar{1};2\bar{2})+M(1\bar{1};\,2\bar{2}), \tag{4.13}$$

where the static or z-independent part of V is given by

$$\begin{aligned}U(1\bar{1};3\bar{3})\,\tilde{G}(3\bar{3};2\bar{2})=&\int d\bar{1}'\,\sigma(1\bar{1}\bar{1}')[\tilde{C}(1\bar{1}\bar{1}';2\bar{2})-\tilde{C}(1\bar{1}\bar{1}';3)\,\tilde{C}^{-1}(34)\,\tilde{C}(4;2\bar{2})]\\&-\tilde{C}(1\bar{1};3)\,\tilde{C}^{-1}(34)\int d\bar{4}\,L_I(4\bar{4})\,\tilde{G}(4\bar{4};2\bar{2}),\end{aligned} \tag{4.14}$$

while the z-dependent part of V is given by

$$M(1\bar{1};3\bar{3})\,\tilde{G}(3\bar{3};2\bar{2})=-\int d\bar{1}'\,d\bar{2}'\,\sigma(1\bar{1}\bar{1}')\sigma(2\bar{2}\bar{2}')\,G(1\bar{1}\bar{1}';2\bar{2}\bar{2}') \tag{4.15}$$

and

$$\begin{aligned}G(1\bar{1}\bar{1}';2\bar{2}\bar{2}')=&\,C(1\bar{1}\bar{1}';2\bar{2}\bar{2}')-C(1\bar{1}\bar{1}';3)\,C^{-1}(34)\,C(4;2\bar{2}\bar{2}')\\&-[C(1\bar{1}\bar{1}';5\bar{5})-C(1\bar{1}\bar{1}';3)\,C^{-1}(34)\,C(4;5\bar{5})]\,G^{-1}(5\bar{5};6\bar{6})\\&\times[C(6\bar{6};2\bar{2}\bar{2}')-C(6\bar{6};7)\,C^{-1}(78)\,C(8;2\bar{2}\bar{2}')]\,.\end{aligned} \tag{4.16}$$

It should be noted that these are actually integral equations for U and M, but, since $\tilde{G}^{-1}$ exists, one can in principle invert these equations. It will be seen in Sec. V that this is in general unnecessary.

D. Relation between φ, U, and M

The next step in the analysis is to introduce a linear vector space spanned by the complete and orthonormal set of vectors

$$\langle 1\bar{1}|2\bar{2}\rangle = \tfrac{1}{2}[\delta(12)\delta(\bar{1}\bar{2}) + \delta(1\bar{2})\delta(\bar{1}2)], \tag{4.17}$$

$$1 = \int d1\, d\bar{1}\, |1\bar{1}\rangle\langle 1\bar{1}|. \tag{4.18}$$

It should be noted that in the case of density fluctuations that one must symmetrize with respect to the two end indices since the correlation functions, like $G(1\bar{1};2\bar{2})$, are symmetric under the interchange of 1 and $\bar{1}$. One can then define various operators in this vector space by, for example,

$$G(1\bar{1};2\bar{2}) = \langle 1\bar{1}|G(z)|2\bar{2}\rangle. \tag{4.19}$$

It will also be useful to introduce the transpose of an operator A by

$$\langle 1\bar{1}|A^T|2\bar{2}\rangle = \langle 2\bar{2}|A|1\bar{1}\rangle. \tag{4.20}$$

Using these definitions and the completeness of the "states," one can write the kinetic equation for $G(z)$ in the operator form

$$[z - L - U - M(z)]G(z) = \tilde{G} \tag{4.21}$$

which one can formally invert to find

$$G(1\bar{1};2\bar{2}) = \langle 1\bar{1}|[z - L - U - M(z)]^{-1}\tilde{G}|2\bar{2}\rangle. \tag{4.22}$$

One can then put this expression back into (3.16) to obtain for the memory function

$$\varphi^{(c)}(13)\tilde{C}(32) = -\int d\bar{1}\, d\bar{2}\, L_I(1\bar{1})L_I(2\bar{2}) \times \langle 1\bar{1}|[z - L - U - M(z)]^{-1}\tilde{G}|2\bar{2}\rangle. \tag{4.23}$$

This expression for the memory function should be compared with Eq. (I.4.28). There are no longer any factors $N-1$ or the volume present. $\varphi^{(c)}$ is an intensive quantity. One easily sees therefore that this expression is ensemble independent and valid in the thermodynamic limit.

V. DISCUSSION OF QUANTITIES CONTRIBUTING TO THE MEMORY FUNCTION

A. Symmetrization

Equation (4.23) is not entirely satisfactory since it is not symmetric with respect to the appearance of $\tilde{G}$. This is intimately related to the fact that the quantity one really knows is $V\tilde{G}$ [see (4.14) and (4.15)] not V itself. Equation (4.23) can be written in a more symmetric form by noting the following rearrangements.

First one defines an operator D by

$$G = \tilde{G}D \tag{5.1}$$

and then substitutes for G, using (5.1), in (4.21) to obtain

$$[(z - L)\tilde{G} - U\tilde{G} - M(z)\tilde{G}]D = \tilde{G}. \tag{5.2}$$

This equation can be inverted to give

$$D = [(z - L)\tilde{G} - U\tilde{G} - M(z)\tilde{G}]^{-1}\tilde{G}. \tag{5.3}$$

If one then multiplies this by $\tilde{G}$, one has a symmetrized expression for G

$$G = \tilde{G}[(z - L)\tilde{G} - U\tilde{G} - M(z)\tilde{G}]^{-1}\tilde{G}. \tag{5.4}$$

This last rearrangement is another departure from the approach taken in FRKT I, but will prove extremely useful in developing iterated expressions for the memory function.

It is immediately clear from this symmetrized expression for $G(z)$ that a new four-point function

$$\bar{G}(1\bar{1};2\bar{2}) = \langle 1\bar{1}|[z\tilde{G} - W - \Gamma(z)]^{-1}|2\bar{2}\rangle, \tag{5.5}$$

where

$$\langle 1\bar{1}|W|2\bar{2}\rangle = L(1\bar{1})\tilde{G}(1\bar{1};2\bar{2}) + U(1\bar{1};3\bar{3})\tilde{G}(3\bar{3};2\bar{2}) \tag{5.6}$$

and

$$\langle 1\bar{1}|\Gamma(z)|2\bar{2}\rangle = M(1\bar{1};3\bar{3})\tilde{G}(3\bar{3};2\bar{2}), \tag{5.7}$$

will enter the analysis. The introduction of $\bar{G}$ has the added advantage that the associated memory functions W and $\Gamma(z)$ are given directly by (4.14) and (4.15). The memory function can now be written in the symmetric form

$$\varphi^{(c)}(13)\tilde{C}(32) = -\mathfrak{v}(1;3\bar{3})\bar{G}(3\bar{3};4\bar{4})\mathfrak{v}(2;4\bar{4}), \tag{5.8}$$

where the "end-point" vertices are defined

$$\mathfrak{v}(1;3\bar{3}) = \int d\bar{1}\, L_I(1\bar{1})\tilde{G}(1\bar{1};3\bar{3}). \tag{5.9}$$

B. End-point vertices

The end-point vertices multiplying the new propagator $\bar{G}$ and given by Eq. (5.9) are completely determined by the static properties of the system. In evaluating the form of $\mathfrak{v}$ more explicitly (and as will be needed in discussing W) it is very useful to develop a technique for handling static-correlation functions of the form $\langle A(1)f(2)\cdots f(n)\rangle_c$ where

$$A(1) \equiv \int d\bar{1}\, L_I(1\bar{1})\,\delta g(1\bar{1}). \tag{5.10}$$

The evaluation of these correlation functions in terms of cumulants is discussed in Appendix A. Since $\mathfrak{v}$ can be expressed in terms of the set $\langle A(1)f(2)\cdots f(n)\rangle_c$, one can use the results in Appendix A to obtain $\mathfrak{v} = \mathfrak{v}_1 + \mathfrak{v}_2$ where

$$\mathcal{V}_1(1;2\bar{2}) = -\omega_0(2\bar{2})\tilde{L}_I(2\bar{2})[\delta(12)+\delta(1\bar{2})] \tag{5.11}$$

with

$$\tilde{L}_I(2\bar{2}) = i\beta^{-1}[\nabla_{r_2}\ln g(\vec{r}_2-\vec{r}_{\bar{2}})]\cdot(\nabla_{p_2}-\nabla_{p_{\bar{2}}}), \tag{5.12}$$

and

$$\mathcal{V}_2(1;2\bar{2}) = i\frac{\vec{p}_1\cdot\nabla_{r_1}}{m}\omega_0(1)\,\omega_0(\bar{2})\,\omega_0(2) \times\tilde{S}^{-1}(\vec{r}_1-\vec{r}_3)B(\vec{r}_3;\vec{r}_2\vec{r}_{\bar{2}}), \tag{5.13}$$

where $\tilde{S}^{-1}$ is the inverse structure factor, and

$$B(\vec{r}_3;\vec{r}_2\vec{r}_{\bar{2}}) = g(\vec{r}_3,\vec{r}_2,\vec{r}_{\bar{2}}) - g(\vec{r}_2-\vec{r}_{\bar{2}}) \times[h(\vec{r}_2-\vec{r}_3)+h(\vec{r}_{\bar{2}}-\vec{r}_3)+1]\ . \tag{5.14}$$

Note that B is connected with respect to its three arguments. Considering first $\mathcal{V}_1$, one sees that the quantity $\tilde{L}_I$ appeared in the theory of self-diffusion [see Eq. (I.5.4)]. It is clear that this is a renormalized two-particle Liouville interaction operator since the force $-\nabla_r V(r)$ is replaced by the "mean" force.[30] In the case of self-diffusion one finds the end-point vertex (I.5.3),

$$\mathcal{V}_{\mathrm{SD}}(1;2\bar{2}) = -\omega_0(2\bar{2})\tilde{L}_I(2\bar{2})\delta(12). \tag{5.15}$$

This corresponds to the first piece in (5.11). The second term in (5.11) comes from the "exchange" process that does not occur when one tags a single particle. It is even more interesting that the piece $\mathcal{V}_2$ is absent from the self-diffusion case. It should also be noted that in I the manipulations in the last section were not carried out. Consequently the expressions in I were not symmetric with respect to the appearance of $\tilde{L}_I$. This asymmetry in the theory has now been removed.

One now wants to focus on $\mathcal{V}_2$. The analysis is conveniently carried out in terms of the Fourier transform over the $\vec{r}_1$ index

$$\begin{aligned}\mathcal{V}_2(\vec{k}\vec{p}_1,2\bar{2}) &= \int d^3r_1\, e^{-i\vec{k}\cdot\vec{r}_1}\mathcal{V}_2(1;2\bar{2})\\ &= -(\vec{k}\cdot\vec{p}_1/m)\,\omega_0(1)\,\omega_0(2)\,\omega_0(\bar{2})\\ &\quad\times\tilde{S}^{-1}(\vec{k})B_k(\vec{r}_2,\vec{r}_{\bar{2}}),\end{aligned} \tag{5.16}$$

where

$$B_k(\vec{r}_2,\vec{r}_{\bar{2}}) = \int d^3r_3\, e^{-i\vec{k}\cdot\vec{r}_3}B(\vec{r}_3;\vec{r}_2,\vec{r}_{\bar{2}}). \tag{5.17}$$

One can see from (5.16) that $\mathcal{V}_2$ vanishes as $k\to 0$ and couples only to the longitudinal current matrix element since it is proportional to $\vec{k}\cdot\vec{p}_1 f_0(p_1)$. It is interesting to note that in the long-wavelength limit B_k, which depends on three-particle static-correlation functions, can be expressed in terms of a two-body quantity since[31]

$$\lim_{k\to 0} B_k(\vec{r}_2,\vec{r}_{\bar{2}}) = \left(\frac{\partial}{\partial n}h(\vec{r}_2-\vec{r}_{\bar{2}})\right)_\beta . \tag{5.18}$$

These end-point vertices multiply the propagator $\bar{G}$. Since one eventually has to approximate $\bar{G}$ one needs to know what range of arguments are permitted by the end-point vertices. Consider first $\mathcal{V}_1$. It should be clear from (5.12) that the quantity $\nabla_{r_1} g(\vec{r}_1-\vec{r}_{\bar{1}})$ controls the range of spatial variation needed in approximating $\bar{G}(1\bar{1};2\bar{2})$. This quantity breaks naturally into two pieces. If one writes[32]

$$g(r) = e^{-\beta V(r)}\tilde{g}(r) \equiv g_0(r)\tilde{g}(r), \tag{5.19}$$

then the gradient of $\tilde{g}$ and g_0 will lead to very different spatial dependences if the potential is short ranged.[33]

The gradient of g_0 will be very sharply peaked for short-ranged potentials since $\nabla_r g_0(r)$ has a very large maximum near some point $|r|\sim r_0$ where r_0 is an effective hard-sphere diameter. Consequently, the term $\tilde{g}(r)\nabla_r g_0(r)$ can be approximated by $\tilde{g}(r_0)\hat{r}_i\delta(r-r_0)$ plus corrections that can be computed by expanding g_0 about its effective hard-sphere[34] value. Thus one sees that this part of $\mathcal{V}_1$ restricts the argument of $\bar{G}(1\bar{1};2\bar{2})$ such that $|\vec{r}_1-\vec{r}_{\bar{1}}|\approx r_0$ which constrains the "two" particles to be very close together. Thus it is appropriate to define the "local" or short-ranged part of the end-point vertex $\mathcal{V}_s$, by replacing $\ln g$ with $\ln g_0$ in Eq. (5.12).

One can now contrast the spatial behavior of $\mathcal{V}_s$ with that part of $\mathcal{V}_1$ where $\ln g$ is replaced with $\ln\tilde{g}$. The question centers about the spatial dependence of $\tilde{g}(r)$. This can be understood from two simple examples. First consider the low-density value of $\tilde{g}(r)$. It is not difficult to show that to first order in the density[35] and for hard spheres that

$$\nabla_{r_i}\tilde{g}(r) = \hat{r}_i(\pi/3)nr_0^2[1-(r/2r_0)^2]\Theta(2r_0-r),$$

where $\theta(x)=1$ for $x>0$ and is zero otherwise. This function is not sharply peaked, but varies smoothly from $\frac{1}{4}\pi nr_0^2$ at $r=r_0$ (the factor of g_0 constrains the product to be zero for $r<r_0$) to zero at $r=2r_0$ and vanishes for $r>2r_0$. Thus the quantity $g_0(r)\nabla_r\tilde{g}(r)$ has a much longer range than $\tilde{g}(r)\nabla_r g_0(r)$ even in the most restricted case of low densities and hard spheres. If one does not have hard spheres then the range of $\nabla_r g(r)$ will extend beyond $2r_0$, and for high densities the range increases as more shells of neighbors are included in the calculation.[35] As one approaches the critical point these effects are enhanced. Because critical phenomena involve cooperative long-range effects there is little effect on the factor $\tilde{g}(r)\nabla_r g_0(r)$. This term remains short ranged and well localized, but the term

$g_0(r)\nabla_r \tilde{g}(r)$ becomes very long ranged. For r greater than a few molecular diameters one has $g_0(r)\nabla_r \tilde{g}(r) \approx \nabla_r g(r)$, since the potential is approximately zero in this region and therefore $g_0(r)=1$. Near the liquid-gas critical point the structure factor has the approximate Ornstein-Zernike[36] form

$$\tilde{S}(\vec{r}) = \delta(\vec{r}) + n(g(r)-1) \approx e^{-r/\xi}/r, \qquad (5.20)$$

where ξ is the correlation length that becomes infinite at the critical point. Therefore one has for large r that

$$g_0(r)\nabla_r g(r) \approx \hat{r} e^{-r/\xi}/r^2$$

which is very long ranged. It should be noted from (5.13) that $\mathcal{V}_2$ is also a long-ranged quantity and it is therefore convenient to define the long-ranged part of the end-point vertex $\mathcal{V}_L$ as the sum of $\mathcal{V}_2$ and the part of $\mathcal{V}_1$ where $\ln g$ is replaced by $\ln \tilde{g}$.

C. Analysis of W

Having obtained some understanding of how one treats the static quantity $\mathcal{V}$ one can move on to the more complicated quantity W defined by (5.6). This equation, taken with (4.14), is not very illuminating as it stands. To gain insight into the structure of W it is useful to break W into its connected and disconnected pieces and to display its momentum dependence explicitly using the results from Appendix A. One finds after a great deal of algebra that $W = W_D + W_C$ where,

$$\langle 1\bar{1}|W_D|2\bar{2}\rangle = (1+P_{1\bar{1}})(1+P_{2\bar{2}})[\delta(\bar{1}\bar{2}) + \omega_0(\bar{2})h(\vec{r}_{\bar{1}} - \vec{r}_{\bar{2}})]\,\omega_0(2)\,\omega_0(\bar{2})L_0(1)\delta(12), \qquad (5.21)$$

$$\langle 1\bar{1}|W_c|2\bar{2}\rangle = (1+P_{1\bar{1}})(1+P_{2\bar{2}})[-i\beta^{-1}\nabla_{r_1}F(1;\bar{1}\bar{2})\cdot\nabla_{p_1} + F(1;\bar{1}\bar{2})L_0(1)]\,\delta(12), \qquad (5.22)$$

where P_{ij} interchanges i and j when it operates on a function of i and j,

$$F(1;\bar{1}\bar{2}) = \omega_0(1)\,\omega_0(\bar{1})\{\delta(\bar{1}\bar{2})h(\vec{r}_1 - \vec{r}_{\bar{1}}) + \omega_0(\bar{2})[\sigma(\vec{r}_1, \vec{r}_{\bar{1}}, \vec{r}_{\bar{2}}) - h(\vec{r}_1 - \vec{r}_{\bar{1}})h(\vec{r}_1 - \vec{r}_{\bar{2}})]\} \qquad (5.23)$$

and[37]

$$\sigma(\vec{r}_1, \vec{r}_2, \vec{r}_3) = g(\vec{r}_1, \vec{r}_2, \vec{r}_3) - h(\vec{r}_1 - \vec{r}_2) - h(\vec{r}_1 - \vec{r}_3) - h(\vec{r}_2 - \vec{r}_3) - 1. \qquad (5.24)$$

This is a rather simple result. One can see from this result that W satisfies the symmetry condition

$$\langle 1\bar{1}|W|2\bar{2}\rangle = -\langle 2\bar{2}|W|1\bar{1}\rangle. \qquad (5.25)$$

It can be seen that W_c has a structure similar to that of $\mathcal{V}$ with the major difference that it contains an additional index. For moderate densities it is reasonable to approximate W by[38]

$$\langle 1\bar{1}|W|2\bar{2}\rangle \simeq \omega_0(1\bar{1})[L_0(1\bar{1}) + \tilde{L}_I(1\bar{1})]\,2\langle 1\bar{1}|2\bar{2}\rangle \qquad (5.26)$$

and the previous discussion about $\nabla_r g(r)$ is still applicable. The above approximation should be quite good if $\vec{r}_1$ is very close to $\vec{r}_{\bar{1}}$ because of the sharply peaked behavior of $\nabla_{r_1} g(\vec{r}_1 - \vec{r}_{\bar{1}})$ for $\vec{r}_1$ very near $\vec{r}_{\bar{1}}$. It then follows that in the low-density limit that[39]

$$\lim_{n\to 0}\langle 1\bar{1}|W|2\bar{2}\rangle = \omega_0(1\bar{1})\,L(1\bar{1})\,2\langle 1\bar{1}|2\bar{2}\rangle, \qquad (5.27)$$

where L is just the two-particle Liouville operator.

D. Investigation of $\Gamma(z)$

The frequency-dependent part of the "four-point" memory function is defined by Eqs. (5.7) and (4.15). There are a few simple properties that follow from Eq. (4.15). First one can see that Γ satisfies the conservation of particles conditions

$$\int d^3p_1\, d^3p_{\bar{1}}\, \Gamma(1\bar{1};2\bar{2}) = \int d^3p_2\, d^3p_{\bar{2}}\, \Gamma(1\bar{1};2\bar{2}) = 0. \qquad (5.28)$$

It is not so obvious that Γ satisfies the symmetry condition $\Gamma(z) = -\Gamma^T(-z)$. This symmetry property for $\Gamma(z)$ is analogous to the symmetry property, Eq. (5.25), satisfied by W. This symmetry property follows from the general result

$$\langle A[z+L]^{-1}B\rangle = \langle B[z-L]^{-1}A\rangle \qquad (5.29)$$

or $C_{AB}(z) = -C_{BA}(-z)$ which depends on the commutation of the Liouville operator with the canonical distribution function. This commutation relation is very sensitive to approximations since, for example, the Liouville operator for an $N-1$ particle system does not commute with the Hamiltonian for a corresponding N particle system. Since commutation relations between L and the canonical distribution also leads to a symmetry relation for the memory function (see Sec. VI) one must be careful in treating those quantities that contribute to the memory function to preserve these symmetries.

In order to make further progress one needs to separate out the disconnected part of Γ. The cumulant analysis of $\Gamma(z)$ is similar to that for W except that one must first go from Laplace transform space into time space, perform the cumulant analysis, and go back to Laplace transform space. One finds that the disconnected part of Γ is given by

$$\begin{aligned}\Gamma_D(1\bar{1};2\bar{2}) = &-F(1\bar{1};2\bar{2}) - \Delta(1\bar{1};3\bar{3})\\ &\times G_D^{-1}(3\bar{3};4\bar{4})\Delta^T(4\bar{4};2\bar{2}),\end{aligned} \tag{5.30}$$

where

$$\begin{aligned}F(1\bar{1};2\bar{2}) = &(1+P_{1\bar{1}})(1+P_{2\bar{2}})(-i)\int_0^{+\infty} dt\, e^{+izt}\\ &\times[C(12,t)\langle A(\bar{1},t)A(\bar{2})\rangle_c\\ &+\langle f(1,t)A(\bar{2})\rangle_c\langle A(\bar{1},t)f(2)\rangle_c],\end{aligned} \tag{5.31}$$

$$\begin{aligned}\Delta(1\bar{1};2\bar{2}) &= (1+P_{1\bar{1}})q_z(1\bar{1};2\bar{2})\\ &= -\Delta^T(2\bar{2};1\bar{1};-z),\end{aligned} \tag{5.32}$$

$$\begin{aligned}q_z(1\bar{1};3\bar{3}) &= (1+P_{3\bar{3}})(-i)\int_0^{+\infty} dt\, e^{+izt}\\ &\quad\times\langle A(\bar{1},t)f(3)\rangle_c C(1\bar{3},t)\\ &= -q^T_{-z}(3\bar{3};1\bar{1}),\end{aligned} \tag{5.33}$$

and G_D^{-1} is the inverse for the disconnected part of G defined by

$$G_D^{-1}(1\bar{1};3\bar{3})G_D(3\bar{3};2\bar{2}) = \langle 1\bar{1}|2\bar{2}\rangle, \tag{5.34}$$

where the disconnected part of G is given by

$$G_D(1\bar{1};2\bar{2}) = -i\int_0^{+\infty} dt\, e^{+izt}G_D(1\bar{1};2\bar{2};t) \tag{5.35}$$

and

$$G_D(1\bar{1};2\bar{2};t) = C(12,t)C(\bar{1}\bar{2},t)+C(1\bar{2},t)C(\bar{1}2,t). \tag{5.36}$$

The connected part of Γ is given by

$$\begin{aligned}\langle 1\bar{1}|\Gamma_c(z)|2\bar{2}\rangle = &-(1+P_{1\bar{1}})(1+P_{2\bar{2}})[\langle f(1)A(\bar{1});f(2)A(\bar{2})\rangle_c^z - \langle f(1)A(\bar{1});f(5)\rangle_c^z C^{-1}(56)\langle f(6);f(2)f(\bar{2})\rangle_c^z\\ &-Q_z(1\bar{1};3\bar{3})G^{-1}(3\bar{3};6\bar{6})Q_z^T(6\bar{6};2\bar{2})+q_z(1\bar{1};3\bar{3})G_D^{-1}(3\bar{3};6\bar{6})q_z^T(6\bar{6};2\bar{2})],\end{aligned} \tag{5.37}$$

where

$$\begin{aligned}Q_z(1\bar{1};3\bar{3}) &= q_z(1\bar{1};3\bar{3})+\langle f(1)A(\bar{1});f(3)f(\bar{3})\rangle_c^z - \langle f(1)A(\bar{1});f(5)\rangle_c^z C^{-1}(54)\langle f(4);f(3)f(\bar{3})\rangle_c^z\\ &= -Q^T_{-z}(3\bar{3};1\bar{1}),\end{aligned} \tag{5.38}$$

and it is convenient to introduce the notation

$$\langle A;B\rangle^z = -i\int_0^{+\infty} dt\, e^{+izt}\langle A(t)B\rangle. \tag{5.39}$$

One of the reasons for splitting of the disconnected parts of W and Γ is that W_D and Γ_D serve as the memory functions for G_D. This can be seen as follows. Consider the case where $\tilde{G}$ and W are replaced by their disconnected pieces and Γ is set equal to zero. This leads to the approximation for $\bar{G}$

$$\bar{G}\approx\bar{G}' = (z\tilde{G}_D - W_D)^{-1}. \tag{5.40}$$

This, in turn, leads to the approximation for G given by $G' = \tilde{G}_D\bar{G}'\tilde{G}_D$. One can evaluate G' more explicitly by noting that W_D can be written

$$\langle 1\bar{1}|W_D|2\bar{2}\rangle = \{[L_0(1)\delta(13)+\varphi^{(s)}(13)\delta(\bar{1}\bar{3})]+[L_0(\bar{1})\delta(\bar{1}\bar{3})+\varphi^{(s)}(\bar{1}\bar{3})]\}\tilde{G}_D(3\bar{3};2\bar{2}). \tag{5.41}$$

After operating on (5.40) from the left by $[z\tilde{G}_D - W_D]$ and multiplying from the right by $\tilde{G}_D$, one finds

$$[z-L_0(1\bar{1})]G'(1\bar{1};2\bar{2}) - [\varphi^{(s)}(13)\delta(\bar{1}\bar{3})+\varphi^{(s)}(\bar{1}\bar{3})\delta(13)]G'(3\bar{3};2\bar{2}) = \tilde{G}_D(1\bar{1};2\bar{2}). \tag{5.42}$$

The solution of this equation is

$$G'(1\bar{1};2\bar{2}) = -i\int_0^{+\infty} d(t_1-t_2)\,e^{+iz(t_1-t_2)}[C_0(12,t_1-t_2)C_0(\bar{1}\bar{2},t_1-t_2)+C_0(1\bar{2},t_1-t_2)C_0(\bar{1}2,t_1-t_2)], \tag{5.43}$$

where the C_0's satisfy the equation[40]

$$[z-L_0(1)]C_0(12)-\varphi^{(s)}(13)C_0(32)=\tilde{C}(12). \quad (5.44)$$

If one now defines

$$\overline{G}_D=[z\tilde{G}_D-W_D-\Gamma_D(z)]^{-1}, \quad (5.45)$$

then one can show, following the analysis of $\overline{G}'$, that $G_D=\tilde{G}_D\overline{G}_D\tilde{G}_D$ where G_D is given by Eq. (5.35). Thus one can separate out the connected and disconnected parts of G in terms of the connected and disconnected parts of $\tilde{G}$, W, and Γ. This will be very important in dealing with long-ranged phenomena.

The basic structure of Γ_D is not obvious from (5.30). It is not difficult to convince oneself that Γ_D must be somehow connected to the disconnected approximation discussed for $M\tilde{C}$ in FRKT II.[41] Establishment of the connection is instructive and leads to some insight into the structure of the theory. The general expression for Γ_D can be made more transparent by noting the following identities. After using (3.13), (3.16), and (3.17) one finds

$$\langle A(\bar{1});A(\bar{2})\rangle_c^z=-\varphi^{(c)}(\bar{1}3)\tilde{C}(32)+\varphi(13)C(34)\varphi^T(4\bar{2}) \quad (5.46)$$

and

$$\langle A(\bar{1});f(2)\rangle_c^z=\varphi(\bar{1}3)C(32). \quad (5.47)$$

If one puts these expressions into (5.31) and (5.32) one obtains a rather complicated expression for Γ_D. One sees, however, that there is considerable simplification if one assumes that φ is Markovian,

$$\varphi(12,t-t')\cong i\varphi_0(12)\delta(t-t'). \quad (5.48)$$

This was one of the essential properties of the low-density hard-sphere memory function used in deriving the "disconnected approximation" in FRKT II. Putting this assumption into (5.46) and (5.47) and then into (5.31) one obtains the simple results

$$F(1\bar{1};2\bar{2})=(1+P_{1\bar{1}})(1+P_{2\bar{2}})[-\varphi_0^{(c)}(13)\tilde{C}(32)\tilde{C}(\bar{1}\bar{2})+\varphi_0(13)G_D(3\bar{1};4\bar{2})\varphi_0^T(42)] \quad (5.49)$$

and from (5.32)

$$\Delta(1\bar{1};2\bar{2})=(1+P_{1\bar{1}})\varphi_0(13)G_D(\bar{1}3;2\bar{2}). \quad (5.50)$$

The disconnected part of $\Gamma(z)$ is then found, after some cancellations to be given by the simple result

$$\Gamma_D^0(1\bar{1};2\bar{2})=(1+P_{1\bar{1}})(1+P_{2\bar{2}})\times\varphi_0^{(c)}(13)\tilde{C}(32)\tilde{C}(\bar{1}\bar{2}). \quad (5.51)$$

This is clearly just the result derived in FRKT II except for the symmetrization and the appearance of two "density" memory functions.

The expression for $\Gamma_c(z)$ given by (5.37) is rather formidable. It consists basically of a connected four-point time-dependent correlation function. The reader may also note that (5.37) is similar to (3.17) in that there are subtractions from the first term. One might therefore guess that there are "plateau-value" like difficulties in dealing with (5.37). If one takes the approach developed to treat (3.17) seriously in this respect, then one might try to write (5.37) in terms of an effective three-body problem and introduce new "three-body" memory functions. A preliminary analysis indicates that such an approach is practical for treating Γ_c, although things at the three-body level are quite complicated. There are "local" contributions from connected three-body collisions which are controlled by the classical Faddeev equations (see FRKT II) and there are longer-ranged contributions from three- and higher-mode contributions as well as contributions from products of two- and four-point correlation functions. A detailed analysis has not yet been attempted.

The approach taken in Sec. VI of this paper is that one can expand the memory function in powers of $\Gamma_c(z)$. The validity of this procedure at present can only be appraised after comparison with experiment. It seems from the analysis presented in Sec. VI that the lowest-order approximation where $\Gamma_c(z)$ is ignored completely is in qualitative agreement with experiment. One expects, however, if the theory is pursued far enough, that one will have to compute corrections due to terms linear in $\Gamma_c(z)$.

It is worthwhile to note here that $\Gamma_c(z)$ is of third order in n (compared to n^2 in G and W) and vanishes as z^{-1} for large z. One suspects that $\Gamma_c(z)$ is important only for long times (small z) and high densities.

VI. PROPERTIES OF φ

A. Discussion of $\varphi^{(s)}$

The static part of the memory function is defined by (3.15). Clearly $\varphi^{(s)}(13)\tilde{C}(32)$ is equal to $\langle A(1)f(2)\rangle_c$ and can therefore be evaluated using the results from Appendix A. One finds, after multiplying from the right by $\tilde{C}^{-1}$ and Fourier transforming, that

$$\varphi^{(s)}(\vec{k},\vec{p}_1\,\vec{p}_2)=-\frac{\vec{k}\cdot\vec{p}_1}{m}nf_0(p_1)C_D(k), \quad (6.1)$$

where $C_D(k)$ is the direct-correlation function. Note that $\varphi^{(s)}$ is independent of $\vec{p}_2$. If one sets

$\varphi^{(c)}=0$ one can solve the kinetic equation exactly.[42] This approximation corresponds to a generalized random-phase approximation or a linearized Vlasov approximation where the bare potential is replaced by $-\beta^{-1}C_D(k)$.

B. Collisional term–general discussion

One can read off a number of properties of the collisional part of the memory function from (4.23) or (5.8). One first observes that Eq. (5.8) only gives one an expression for $\varphi^{(c)}$ times $\tilde{C}$ and is therefore an integral equation for $\varphi^{(c)}$. Fortunately this integral equation can be solved simply due to the simple momentum dependence of $\tilde{C}(12)$. One finds that

$$\varphi^{(c)}(13)\tilde{C}(32)=\varphi^{(c)}(12)nf_0(p_2). \tag{6.2}$$

One of the most obvious properties of $\varphi^{(c)}$ is the large-z behavior. Since W is independent of z and Γ goes as $1/z$ for large z (see 4.16) one has immediately

$$\lim_{z\to\infty} z\varphi^{(c)}(12)nf_0(p_2)$$

$$=-\int d\bar{1}\,d\bar{2}\,L_I(1\bar{1})L_I(2\bar{2})\tilde{G}(1\bar{1};2\bar{2}). \tag{6.3}$$

It is simply a matter of equilibrium manipulations to show that (6.3) can be expressed in terms of the pair-correlation function and the direct-correlation function.[43]

Forster and Martin[44] have analyzed the various symmetry properties satisfied by $C(12)$ and $\varphi^{(c)}$. Here it will suffice to point out that on using (5.29) in (3.16) that

$$\varphi^{(c)}(12)f_0(p_2)=-\varphi^{(c)}(21;-z)f_0(p_1) \tag{6.4}$$

which is analogous to the symmetry relation satisfied by $\Gamma(z)$ given above (5.29).

C. Discussion of iteration scheme

One can now move on to analyze the ways in which one can approximate the propagator $\bar{G}$ defined by (5.5). It is hoped that a reasonable approximation for $\bar{G}$ will lead to a quite good expression for the memory function. This hope is produced by the knowledge that $\bar{G}$ must be integrated over to obtain φ and one knows that approximations to integrands can lead to good approximations for the integral. One also would like to know the correction to any such approximation, therefore one would like to develop an exact iteration scheme for $\bar{G}$ such that the first iterate is a good approximation. Because of the complexity of $\bar{G}$ there is probably no simple iteration of $\bar{G}$ that is valid for all of its various spatial and momentum arguments. However, there are two basic ideas that one can use in setting up an iteration approach. The hope is that one can combine these ideas to obtain a sort of mixed perturbation scheme.

It is traditional in many-body theory to express all of the higher-order correlation functions in terms of a product of lower-order correlation functions. This is at the root of the recent classical perturbation theory approach developed by Martin, Rose, and Siggia.[45] One of the main motivating physical principles is that a correlation function can always be written as a sum of connected and disconnected parts. A main input in the normal perturbation theories is that the connected part of the correlation function is proportional to some interaction and is therefore a perturbation of the disconnected part. This is, in many cases, quite reasonable since one knows that if the various spatial indices of the correlation functions are well separated, then the correlation function is given by the disconnected approximation. However there is a situation where a factorization is a very poor approximation. This was clearly pointed out by Martin and Schwinger[46] in their derivation of the T-matrix approximation in the theory of quantum systems. If one has, for example, that $\bar{G}$ is multiplied by the short-ranged part of the end-point vertex, $\int d3\,d3'\,\mathcal{V}_s \times(1;33')\bar{G}(33';4\bar{4})$, and $\mathcal{V}_s$ is nonzero only for $\vec{r}_3$ and very near to $\vec{r}_{3'}$, then it is a very poor approximation to represent $\bar{G}$ by the factorized form $\bar{G}=\bar{G}_D$. This approximation mutilates the behavior of G for $\vec{r}_3$ near $\vec{r}_{3'}$ which is the important region. If $\bar{G}$ is confined to the region $\vec{r}_3=\vec{r}_{3'}$ then one suspects that its inverse is dominated by the terms $L(1\bar{1})$ in W_c which are very large in this region. It seems reasonable that one can ignore $\Gamma_c(1\bar{1};2\bar{2})$ compared to $L(1\bar{1})\langle 1\bar{1}|2\bar{2}\rangle$ when $\vec{r}_1\approx\vec{r}_{\bar{1}}$ because of the large peak in $L(1\bar{1})$. One also expects that $\Gamma_c(z)$ will be small in this region because the "initial" or end-states processes in $\Gamma(z)$ do not originate with 1 and $\bar{1}$ interacting. The end process in $\Gamma(z)$ is where 1 or $\bar{1}$ interact with a third particle. This initial process is then followed by a sequence of three-particle collisions. It thus seems reasonable to write $\mathcal{V}_s\bar{G}\approx\mathcal{V}_s\bar{G}_s$ where[47]

$$\bar{G}_s=(z\tilde{G}-W)^{-1} \tag{6.5}$$

is a generalization of the two-particle propagator $(z-L)^{-1}$. If one chose to iterate strictly in terms of $\bar{G}_s$ then one would start to generate something similar to the binary collision expansion developed by Zwanzig.[48] One would be emphasizing the two-particle nature of the processes. This would contradict the statement made earlier that no one method of iterating $\bar{G}$ is valid everywhere. In fact one finds situations where $\bar{G}$ is not constrained to be in the region $\vec{r}_3$ near $\vec{r}_{3'}$. Thus one is interested in the region where the interaction between particles 3 and 3′ is small. If one used the approximation for $\bar{G}$ in terms of $\bar{G}_s$ in the region where $\vec{r}_3$ is well separated from $\vec{r}_{3'}$ then $\bar{G}_s$ will reduce to a product of two-free-particle propagators since L will be approximately L_0 in this region. Thus this approximation is inferior to the disconnected approximation which says that the particles are independent but are not free since they are interacting with the rest of the medium. Thus one should have a product of full two-point propagators in this region. This is clearly superior to working with free propagators. It is just this point which leads the workers on the density expansion for transport coefficients to spurious divergences. They did not renormalize their propagators.

The iteration rules $\mathcal{V}_s\bar{G} \approx \mathcal{V}_s\bar{G}_s$ and $\mathcal{V}_L\bar{G} \approx \mathcal{V}_L\bar{G}_D$ are not quite sufficient since there will occur cross terms like $\mathcal{V}_L\bar{G}\mathcal{V}_s$ and the simple rules are ambiguous. One has to choose between the two. It seems more reasonable to choose $\mathcal{V}_L\bar{G}\mathcal{V}_s \approx \mathcal{V}_L\bar{G}_s\mathcal{V}_s$ for two reasons. The first reason is that $\mathcal{V}_s$ has a very strong localizing effect and is large in that region. At the same time one expects that $\bar{G}_s$ is compensatingly small such that the product is well defined for hard spheres. This effect was called "shielding" in FRKT I. The approximation $\mathcal{V}_L\bar{G}\mathcal{V}_s = \mathcal{V}_L\bar{G}_s\mathcal{V}_s$ is also superior in that it preserves the low-density and large-z properties exactly. The approximation $\mathcal{V}_L\bar{G}\mathcal{V}_s = \mathcal{V}_L\bar{G}_D\mathcal{V}_s$ does not satisfy these properties.

In summary then it seems reasonable to iterate $\bar{G}$ in terms of $\bar{G}_s$ in those cases where $\bar{G}$ is confined to a small interaction region, while using $\bar{G}_D$ as a first iterate for $\bar{G}$ in all other regions. One should note that by choosing either $\bar{G} = \bar{G}_s$ or $\bar{G} = \bar{G}_D$ as the appropriate iterate, one is consistently assuming that $\Gamma_c(z)$ is small. Thus this scheme allows one to develop systematic approximations as a power series in $\Gamma_c(z)$. It is the author's belief that this rearrangement gives one an intuitive feel for the types of processes that contribute to the memory function. It will also be shown how one can make contact with many of the previous results derived for short-ranged classical systems.

One now wants to use these ideas to iterate the expression for the memory function. The first step in the rearrangement is to separate out those terms in $\bar{G}$ explicitly of order $\Gamma_c(z)$. One first notes that $\bar{G}$ satisfies the integral equation

$$\bar{G} = \bar{G}_D + \bar{G}_D I_c(z)\bar{G}, \tag{6.6}$$

where

$$I_c(z) = I_c^0(z) + \Gamma_c(z) \tag{6.7}$$

and

$$I_c^0(z) = W_c - z\tilde{G}_c. \tag{6.8}$$

If one completely ignores $\Gamma_c(z)$ then $\bar{G}$ is given to "zeroth" order by

$$\bar{G}^0 = \bar{G}_D + \bar{G}_D I_c^0(z)\bar{G}^0 \tag{6.9}$$

and the connected part satisfies

$$\bar{G}_c^0 = \bar{G}_D I_c^0(z)\bar{G}_D + \bar{G}_D I_c^0(z)\bar{G}_c^0. \tag{6.10}$$

Similarly the connected part of $\bar{G}$ satisfies

$$\bar{G}_c = \bar{G}_D I_c(z)\bar{G}_D + \bar{G}_D I_c(z)\bar{G}_c. \tag{6.11}$$

Then if one defines $\bar{G}_c^1$ by

$$\bar{G}_c = \bar{G}_c^0 + \bar{G}_c^1, \tag{6.12}$$

one finds easily that $\bar{G}_c^1$ satisfies the equation

$$\bar{G}_c^1 = \bar{G}_D\Gamma_c(z)\bar{G}_D + \bar{G}_D\Gamma_c(z)\bar{G}_c^1 \tag{6.13}$$

and so $\bar{G}_c^1$ is clearly of order $\Gamma_c(z)$. The memory function can then be written

$$-\varphi^{(c)} = \mathcal{V}\bar{G}^0\mathcal{V} + \mathcal{V}\bar{G}_c^1\mathcal{V}. \tag{6.14}$$

Henceforth the term proportional to $\bar{G}_c^1$ will be dropped and the analysis will focus on the approximation

$$-\varphi_1^{(c)} = \mathcal{V}\bar{G}^0\mathcal{V}. \tag{6.15}$$

In dealing with (6.15) one needs a few properties of $\bar{G}^0$. Starting with (6.9) one can easily see that

$$[\bar{G}_D^{-1} - I_c(z)]\bar{G}^0 = 1, \tag{6.16}$$

where

$$\bar{G}_D^{-1} = \bar{G}_D^{0-1} - \Gamma_D \tag{6.17}$$

and

$$\bar{G}_D^{0-1} = z\tilde{G}_D - W_D. \tag{6.18}$$

One has from (6.5) and (6.16)

$$\bar{G}_D^{-1} - I_c^0(z) = \bar{G}_s^{-1} - \Gamma_D, \tag{6.19}$$

so $\bar{G}^0$ satisfies the alternate integral equation

$$\bar{G}^0 = \bar{G}_s + \bar{G}_s\Gamma_D\bar{G}^0 = \bar{G}_s + \bar{G}_s\Gamma_D\bar{G}_s + \bar{G}_s\Gamma_D\bar{G}^0\Gamma_D\bar{G}_s. \tag{6.20}$$

One can then use the "iteration rules" with (6.9) and (6.20) to obtain

$$\varphi_1^{(c)} = \varphi_{11}^{(c)} + \varphi_{12}^{(c)}, \tag{6.21}$$

where

$$\begin{aligned}-\varphi_{11}^{(c)} = {} & \mathcal{V}_s(\bar{G}_s + \bar{G}_s\Gamma_D\bar{G}_s + \bar{G}_s\Gamma_D\bar{G}_D\Gamma_D\bar{G}_s)\mathcal{V}_s \\ & + \mathcal{V}_L(\bar{G}_s + \bar{G}_D\Gamma_D\bar{G}_s)\mathcal{V}_s + \mathcal{V}_s(\bar{G}_s + \bar{G}_s\Gamma_D\bar{G}_D)\mathcal{V}_L \\ & + \mathcal{V}_L\bar{G}_D\mathcal{V}_L\end{aligned} \tag{6.22}$$

and

$$-\varphi_{12}^{(c)} = \mathcal{V}_s\overline{G}_s\Gamma_D\overline{G}_c^0\Gamma_D\overline{G}_s\mathcal{V}_s + \mathcal{V}_L\overline{G}_c^0\Gamma_D\overline{G}_s\mathcal{V}_s + \mathcal{V}_s\overline{G}_s\Gamma_D\overline{G}_c^0\mathcal{V}_L + \mathcal{V}_L\overline{G}_c^0\mathcal{V}_L . \tag{6.23}$$

Clearly $\varphi_{12}^{(c)}$ is linear in $\overline{G}_c^0$ which is in turn proportional to $I_c^0(z)$. For the time being it is convenient to focus on $\varphi_{11}^{(c)}$. Later one can come back and investigate the relative importance of $\varphi_{12}^{(c)}$.

One can considerably simplify $\varphi_{11}^{(c)}$ by noting the identity

$$\Gamma_D + \Gamma_D\overline{G}_D\Gamma_D = \overline{G}_D^{0-1}(\overline{G}_D - \overline{G}_D^0)\overline{G}_D^{0-1} . \tag{6.24}$$

Using (6.24) in (6.22) one has

$$-\varphi_{11}^{(c)} = \mathcal{V}_s\overline{G}_s\mathcal{V}_s + \mathcal{V}_s\overline{G}_s\overline{G}_D^{0-1}(\overline{G}_D - \overline{G}_D^0)\overline{G}_D^{0-1}\overline{G}_s\mathcal{V}_s + \mathcal{V}_L\overline{G}_D\overline{G}_D^{0-1}\overline{G}_s\mathcal{V}_s + \mathcal{V}_s\overline{G}_s\overline{G}_D^{0-1}\overline{G}_D\mathcal{V}_L + \mathcal{V}_L\overline{G}_D\mathcal{V}_L \tag{6.25}$$

and, after defining the generalized classical T matrices (see Appendix B)

$$T = \mathcal{V}_s\overline{G}_s\overline{G}_D^{0-1} \tag{6.26}$$

and

$$T^\dagger = \overline{G}_D^{0-1}\overline{G}_s\mathcal{V}_s , \tag{6.27}$$

one can write

$$-\varphi_{11}^{(c)} = \mathcal{V}_s\overline{G}_s\mathcal{V}_s + (T + \mathcal{V}_L)\overline{G}_D(T^\dagger + \mathcal{V}_L) - T\overline{G}_D^0 T^\dagger . \tag{6.28}$$

$\varphi_{11}^{(c)}$ is the memory function one should probably look at in zeroth-order theory. The first term $\mathcal{V}_s\overline{G}_s\mathcal{V}_s$ can be interpreted as a generalized Boltzmann-Enskog term and will be discussed further below. The second group of terms are mode-mode coupling terms. If one sets $\mathcal{V}_L = 0$ then these terms reduce to $T(\overline{G}_D - \overline{G}_0)T^\dagger$ which one can recognize almost immediately as including the ring terms discussed in FRKT II. This can be easily seen from Eq. (II.4.12). It is satisfying that this result can be obtained from general considerations thus supporting the physical arguments given in Sec. II of FRKT II. It was pointed out in this paper in the discussion of $\Gamma_D(z)$ that the "disconnected approximation" discussed in FRKT II was based on a Markovian assumption for $\varphi^{(c)}$ that is valid only for low-density hard-sphere systems. In the present formulation no such assumptions are necessary and one has the added benefit that the exact correlation functions appear in the ring expression. Thus there have been a large number of resummations beyond the ordinary ring resummations. This will, of course, have immediate consequences concerning the long-time behavior in the system. For example the previous kinetic theories dealing with the long time tails have found that the autocorrelation functions for long times can be written [see Eq. (II.6.1)]

$$V(s) \sim \alpha s^{-3/2} , \tag{6.29}$$

where

$$\alpha \approx (D_E + v_E)^{-3/2} , \tag{6.30}$$

and the subscript E indicates that the transport coefficients are the Enskog values. One expects on looking at (6.25) that the transport coefficients in (6.30) will be replaced by their full values. This was the prediction of the semiphenomenological hydrodynamical theories.[49] There are however other modifications in α that must be discussed and will be deferred to a separate analysis.

If one sets $T = 0$ in the mode-coupling term then one has a contribution $\mathcal{V}_L\overline{G}_D\mathcal{V}_L$. This term is intimately connected with the mode-mode coupling approximations developed by Kawasaki[12] and Kadanoff and Swift.[12] The connection between these results will be developed further in Sec. VII.

One might ask whether there are regions where the T terms might predominate over $\mathcal{V}_L$ and visa versa. One is, of course, prejudiced by one's knowledge that the T's have led to reasonable agreement in discussing long-time behavior away from the critical point and the $\mathcal{V}_L$ terms, as will be shown in Sec. VII, lead to good agreement with experiment near the critical point. One can see why T and $\mathcal{V}_L$ play different roles by estimating their relative "size" via the ratio $(T \sim \mathcal{V}_s)$:

$$\frac{\mathcal{V}_L}{\mathcal{V}_s} \approx \frac{\int d^3r\,[\hat{r}\cdot\nabla_r\tilde{g}(r)]\,e^{-\beta V(r)}}{\int d^3r\,\tilde{g}(r)\,\hat{r}\cdot\nabla_r e^{-\beta V(r)}} . \tag{6.31}$$

This ratio can be evaluated explicitly in the case of hard spheres and to lowest order in the density to find $\mathcal{V}_L/\mathcal{V}_s \sim \frac{47}{60}\pi n r_0^3$. Consequently the long-ranged part of the end-point vertex is negligible compared to the short-ranged part for low densities. If however one is near the critical point where $\tilde{g}(r)$ is given by Eq. (5.20), then one can show that (6.31) can be evaluated to give $\mathcal{V}_L/\mathcal{V}_s \sim \xi/r_0$. Consequently, $\mathcal{V}_L$ dominates near the critical point where ξ goes to infinity. This argument alone would indicate that $\mathcal{V}_L\overline{G}_D\mathcal{V}_L$ is important near the critical point.

These last arguments also allow one to estimate the relative importance of φ_{12}. Away from the critical point one expects that the terms proportional to $\mathcal{V}_L$ are less important than those proportional to $\mathcal{V}_s$, so one can approximate

$$-\varphi_{12}^{(c)} \approx \mathcal{V}_s\overline{G}_s\Gamma_D\overline{G}_c^0\Gamma_D\overline{G}_s\mathcal{V}_s . \tag{6.32}$$

On comparing this with $\mathcal{V}_s\overline{G}_s\mathcal{V}_s$ one sees that $\varphi_{12}/\varphi_{11}$ vanishes for short times and is first order in the density for low densities. This term probably leads to observable quantitative changes in $\mathcal{V}_s\overline{G}_s\mathcal{V}_s$ only for rather dense systems and for long times. These statements should however be investigated further.[50]

If one is near the critical point then $\mathcal{V}_L >> \mathcal{V}_s$ and one suspects that $-\varphi_{12}^{(c)} \approx \mathcal{V}_L\overline{G}_c^0\mathcal{V}_L$ which should be compared with $-\varphi_{11}^{(c)} \approx \mathcal{V}_L\overline{G}_D\mathcal{V}_L$. One expects that $\varphi_{12}^{(c)}$ is much smaller than $\varphi_{11}^{(c)}$ because one expects that $\overline{G}_D$ is longer-ranged than $\overline{G}_c^0$. This is a reasonable assumption in light of recent work[51] which indicates that the static two-point correlation functions have a range longer or equal to the range of the higher order cumulants. It therefore seems reasonable to concentrate on $\varphi_{11}^{(c)}$ first. Eventually, of course, one is free to come back and investigate these other terms further.

In summary, since the first term in $\varphi_{11}^{(c)}$ leads to the Boltzmann-Enskog term and the other terms in $\varphi_{11}^{(c)}$ include the mode-mode terms that explain both the long-time phenomena in liquids and the divergence of transport coefficients near the critical point,[52] it seems reasonable to approximate the memory function by $\varphi_{11}^{(c)}$ since it explains the qualitative features of a fluid over a wide range of thermodynamic states.

D. Boltzmann-Enskog approximation

All of the information in the Enskog-Boltzmann approximation plus some corrections are given by the leading term in Eq. (6.28). One has, putting in the indices,

$$\varphi_0^{(c)}(12)\,nf_0(p_2) = -\mathcal{V}_s(1;3\overline{3})\langle 3\overline{3}|[z\tilde{G} - W]^{-1}|4\overline{4}\rangle\mathcal{V}_s(2;4\overline{4}). \tag{6.33}$$

The Boltzmann-Enskog approximation for $\varphi^{(c)}$ follows from two basic approximations. First one keeps only the "diagonal" terms that contribute to $\tilde{G}$ and W. From (2.24) one has

$$\tilde{G}(1\overline{1};2\overline{2}) = \omega_0(1\overline{1})\,2\langle 1\overline{1}|2\overline{2}\rangle + O(n^3) \tag{6.34}$$

and from (5.26)

$$W(1\overline{1};2\overline{2}) = \omega_0(1\overline{1})\,\tilde{L}(1\overline{1})\,2\langle 1\overline{1}|2\overline{2}\rangle + O(n^3), \tag{6.35}$$

where

$$\tilde{L}(1\overline{1}) = L_0(1\overline{1}) + \tilde{L}_I(1\overline{1}) \tag{6.36}$$

and $\tilde{L}_I(1\overline{1})$ is given by (5.12). Thus this approximation is exact to lowest order in the density and represents a selective resummation of static contributions to higher orders in the density. The terms neglected would give corrections from processes where the two dynamically interacting particles are statically correlated with a third particle in the system. One expects these terms to be small for low densities. After using Eq. (5.11) with these approximations one has

$$\varphi_0^{(c)}(12)\,nf_0(p_2) = -\int d3\,d\overline{3}\,d4\,d\overline{4}\,\omega_0(3\overline{3})\,\{\tilde{L}_I(3\overline{3})[\delta(13)+\delta(1\overline{3})]\}\,\frac{1}{\omega_0(3\overline{3})}\,[z-\tilde{L}(3\overline{3})]^{-1}$$
$$\times\,(\tfrac{1}{2})\langle 3\overline{3}|4\overline{4}\rangle\,\omega_0(4\overline{4})\,\tilde{L}_I(4\overline{4})[\delta(24)+\delta(2\overline{4})]. \tag{6.37}$$

The second basic approximation is that $\tilde{L}_I$ is very sharply peaked near the point where the collision occurs. Therefore one can write

$$\omega_0(4\overline{4})\,\tilde{L}_I(4\overline{4}) \simeq \tilde{g}(r_0)\,\overline{\omega}_0(4\overline{4})\,\tilde{L}_I(4\overline{4}), \tag{6.38}$$

where

$$\overline{\omega}_0(4\overline{4}) = \omega_0(p_4)\,\omega_0(p_{\overline{4}})\,e^{-\beta V(\vec{r}_4-\vec{r}_{\overline{4}})}. \tag{6.39}$$

Similarly, since the integrand is restricted to the point where $\vec{r}_3$ is very near $\vec{r}_{\overline{3}}$ one can replace $\tilde{L}(3\overline{3})$ by $L(3\overline{3})$ which means neglecting $\nabla_{r_3}\ln\tilde{g}(\vec{r}_3-\vec{r}_{\overline{3}})$ compared with $\nabla_{r_3}[-\beta V(r_3-r_3)]$. This should be quite a good approximation. Putting this approximation back into (6.37) one has what will be referred to as the generalized Enskog memory function[53]

$$\varphi_E^{(c)}(12)\,nf_0(p_2) = -\tfrac{1}{2}\tilde{g}(r_0)\int d3\,d\overline{3}\,\{L_I(3\overline{3})[\delta(13)+\delta(1\overline{3})]\}\,[z-L(3\overline{3})]^{-1}\omega_0(p_3)\,\omega_0(p_{\overline{3}})$$
$$\times\,e^{-\beta V(\vec{r}_3-\vec{r}_{\overline{3}})}L_I(3\overline{3})[\delta(24)+\delta(2\overline{4})]. \tag{6.40}$$

It is not difficult to show that this result is simply $\tilde{g}(r_0)$ times the low-density memory function found previously by the author. Consequently in the limit of low densities the approximations made above are exact as may easily be checked [note $\tilde{g}(r_0)=1$ to lowest order in the density]. It is also quite interesting that in the case of hard spheres this result gives the exact instantaneous value for the memory function,[54]

$$\lim_{z\to\infty} \varphi^{(c)}_{\mathrm{HS}}(12) = \varphi^{(c)}_{E,\mathrm{HS}}(12). \tag{6.41}$$

Recently van Leeuween and Konijnendijk have shown[55] that this memory function gives the Enskog values for the various transport coefficients. Equation (6.40) should also be very useful in the case where one has a more realistic potential.[56]

VII. HYDRODYNAMICS

A. Predictions of hydrodynamics

In the previous sections the analysis has focused on the calculation of frequency- and wave-number-dependent correlation functions over the entire range of frequencies and wave numbers. Consider now the hydrodynamical region of small frequencies and wave numbers where only the "modes" of the system associated with conserved variables[57] will survive. Thus one expects that the correlation functions can be calculated in this hydrodynamical region through the use of the Navier-Stokes equations which express the conservation laws. Kadanoff and Martin[55] have carried out such a computation and found that density-density correlation function is given in the hydrodynamical regime by

$$S_{nn}(\vec{k},z) = mnV_0^2\left(\frac{\partial n}{\partial P}\right)_T \left(\frac{1-C_v/C_p}{z+ik^2D_T} + \frac{C_v}{C_p}\,\frac{z+ik^2[\Gamma + D_T(C_p-C_v)/C_v]}{z^2-C_0^2k^2+izk^2\Gamma}\right) \tag{7.1}$$

while the transverse current-current correlation function is given by

$$S_t(\vec{k},z) = \frac{n(mV_0)^2}{z+ik^2\eta/mn}, \tag{7.2}$$

where C_v and C_p are the specific heats, C_0 is the adiabatic speed of sound, D_T is the thermal diffusion coefficient, Γ is the sound damping coefficient, and η is the shear viscosity. D_T is related to the thermal conductivity λ by

$$D_T = \lambda/mnC_p, \tag{7.3}$$

and Γ is related to η, λ, and the bulk viscosity ζ by

$$\Gamma = \frac{\frac{4}{3}\eta+\zeta}{mn} + D_T(C_p/C_v - 1). \tag{7.4}$$

It is clear that the transverse case is considerably simpler than the longitudinal case. This is because there is only one collective mode and the shear viscosity can easily be identified as the limit

$$\eta^{-1} = \lim_{k\to 0}\frac{ik^2}{mn}\lim_{z\to 0}\frac{1}{n(mV_0)^2}S_t(\vec{k},z). \tag{7.5}$$

In the longitudinal case the analysis is more complicated. This is, of course, because there are two modes and one must separate them. One finds, after a little algebra, that λ and Γ can be calculated from

$$\lambda^{-1} = i\left[mnV_0^2\left(\frac{\partial n}{\partial P}\right)_T mn(C_p-C_v)\right]^{-1} \times \lim_{k\to 0}\lim_{z\to 0}[k^2S_{nn}(\vec{k},z)] \tag{7.6}$$

and

$$\Gamma^{-1} = i\left[mnV_0^2\left(\frac{\partial n}{\partial P}\right)_T \frac{C_v}{C_p}\right]^{-1} \times \lim_{k\to 0}[k^2S_{nn}(\vec{k},C_0k)]. \tag{7.7}$$

One now wants to use these expressions to obtain an equation for η, λ, and Γ in terms of the memory function. This analysis will be carried out using the projection operator formalism of Forster and Martin (FM).[44,15]

B. Hydrodynamical projection operators

In setting up the formalism for extracting the hydrodynamical limit it is useful to introduce dimensionless momentum variables

$$\vec{\xi} = \vec{p}/mV_0, \tag{7.8}$$

where $mV_0^2 = \beta^{-1}$. It is also useful to introduce the dimensionless weight function

$$W_0(\xi) = (2\pi)^{-3/2}e^{-\xi^2/2}. \tag{7.9}$$

One then wants to introduce a bracket notation for integrals in momentum space. The scalar product for two functions $H(\vec{\xi})$ and $G(\vec{\xi})$ is denoted by

$$\langle H|G\rangle = \int d^3\xi\, H^*(\vec{\xi})W_0(\xi)G(\vec{\xi}). \tag{7.10}$$

The matrix elements of some "operator" $R(\vec{\xi},\vec{\xi}')$ are defined by

$$\langle H|R|G\rangle = \int d^3\xi\, d^3\xi'\, H^*(\vec{\xi})R(\vec{\xi}\;\vec{\xi}')W_0(\xi')G(\vec{\xi}'). \tag{7.11}$$

The hydrodynamical states $H_\mu(\vec{\xi})$, are defined by

$$H_1(\vec{\xi}) = n(\vec{\xi}) = 1, \tag{7.12}$$

$$H_2(\vec{\xi}) = g_l(\vec{\xi}) = \xi_3, \tag{7.13}$$

$$H_3(\vec{\xi}) = \epsilon(\vec{\xi}) = (1/\sqrt{6})(\xi^2 - 3), \tag{7.14}$$

$$H_4(\vec{\xi}) = g_t(\vec{\xi}) = \xi_1, \tag{7.15}$$

$$H_5(\vec{\xi}) = g_t'(\vec{\xi}) = \xi_2, \tag{7.16}$$

where the wave vector $\vec{k}$ is taken in the 3 direction so that H_μ, with $\mu = 1, 2$, and 3, are longitudinal modes and H_μ, with $\mu = 4, 5$, are transverse modes. These five states can be understood as part of a complete orthonormal set $\{H_i(\vec{\xi})\}$. One does not have to specify the form of these functions for $i > 5$ at this point.

It is now quite useful to introduce the projection operator P that projects onto the five hydrodynamical states,

$$P = \sum_{i=1}^{5} |H_i\rangle\langle H_i| \equiv 1 - Q. \tag{7.17}$$

Using an operator notation one can then formally solve the kinetic equation for C to obtain for the transverse-current correlation function

$$S_t(\vec{k}, z) = n(mV_0)^2[z - D_t(\vec{k}, z)]^{-1}, \tag{7.18}$$

where

$$D_t(\vec{k}, z) = \langle g_t|\overline{\varphi}|g_t\rangle + \langle g_t|\overline{\varphi}Q[z - Q\overline{\varphi}Q]^{-1}Q\overline{\varphi}|g_t\rangle, \tag{7.19}$$

$$\overline{\varphi}(\vec{k}, z) = z^0(k) + \varphi(\vec{k}, z), \tag{7.20}$$

and the operator $z^0(k)$ has the explicit form

$$\langle\vec{\xi}|z^0(k)|\vec{\xi}'\rangle = V_0\vec{k}\cdot\vec{\xi}\,\delta(\vec{\xi} - \vec{\xi}').$$

If one compares this Eq. (7.18) with (7.2) from hydrodynamics one sees that the shear viscosity is given by

$$\eta = \lim_{z\to i0^+}\lim_{k\to 0}(imn/k^2)D_t(\vec{k}, z). \tag{7.21}$$

In the case of the longitudinal modes the density, longitudinal momentum and energy correlation functions are coupled. Because of this coupling, FM considered the matrix correlation function

$$G_{ij}(\vec{k}, z) = \langle i|[z - z^0(k) - \varphi(\vec{k}, z)]|j\rangle, \tag{7.22}$$

where $i, j = 1, 2, 3$ are the three longitudinal states n, g_l, and ϵ. One should note that

$$S_{nn}(\vec{k}, z) = n\tilde{S}(k)G_{11}(\vec{k}, z). \tag{7.23}$$

FM show, in complete analogy to the transverse case, that one can write

$$\sum_{j=1}^{3}[z\delta_{ij} - D_{ij}(\vec{k}, z)]G_{jk}(\vec{k}, z) = \delta_{ik}, \tag{7.24}$$

where

$$D_{ij}(\vec{k}, z) = \langle i|\overline{\varphi}|j\rangle + \langle i|\overline{\varphi}Q[z - Q\overline{\varphi}Q]^{-1}Q\overline{\varphi}|j\rangle \tag{7.25}$$

and

$$\langle i|\varphi^{(s)}(k)|j\rangle = -nC_D(k)kV_0\delta_{i,2}\delta_{j,1}\,. \tag{7.26}$$

C. Shear viscosity

One now needs to compute various matrix elements of the memory function in the limit of small k and z. These matrix elements will be needed in evaluating D_t and D_{ij}.

In the case of the transverse excitations, where there are no coupled modes, one can calculate the matrix elements appearing in (7.19) rather directly.

One first notes that one can write

$$\langle g_t|\varphi^{(c)}(\vec{k}, z)|\vec{p}_2\rangle = kV_0\langle T_t(\vec{k}, z)|\vec{p}_2\rangle, \tag{7.27}$$

where $\langle T_t(\vec{k}, z)|\vec{p}_2\rangle$ has a finite limit as $\vec{k}$ and z go to zero. This can be most easily seen from (3.16) and the result

$$\int d1\,d\overline{1}\,p_1^i\,e^{-i\vec{k}\cdot\vec{r}_1}L_I(1\overline{1})G(1\overline{1};2\overline{2}) = -\int d1\,d\overline{1}\,2j_0\left(\frac{\vec{k}\cdot(\vec{r}_1 - \vec{r}_{\overline{1}})}{2}\right)\sum_{j=1}^{3}k_j T_{ij}(\vec{r}_1 - \vec{r}_{\overline{1}})G(1\overline{1};2\overline{2}), \tag{7.28}$$

where $T_{ij}(\vec{r}) = r_i r_j |r|^{-1}(d/dr)V(r)$ and $j_0(x) = (\sin x)/x$. In the transverse case one has then

$$\langle T_t(\vec{k}, z)|\vec{p}_2\rangle = -\frac{\beta}{2n}\int\frac{d1\,d\overline{1}\,d2\,d\overline{2}}{\Omega}\,e^{+i\vec{k}\cdot\vec{r}_2}j_0\left(\frac{\vec{k}\cdot(\vec{r}_1 - \vec{r}_{\overline{1}})}{2}\right)T_{13}(\vec{r}_1 - \vec{r}_{\overline{1}})L_I(2\overline{2})G(1\overline{1};2\overline{2}). \tag{7.29}$$

One has immediately then that

$$\langle g_t|\overline{\varphi}|g_t\rangle = \langle g_t|\varphi^{(c)}(\vec{k}, z)|g_t\rangle = (kV_0)^2\Phi_t(\vec{k}, z), \tag{7.30}$$

where

$$\Phi_t(\vec{k}, z) = -\frac{\beta^2}{4n}\int\frac{d1\,d\overline{1}\,d2\,d\overline{2}}{\Omega}\,j_0\left(\frac{\vec{k}\cdot(\vec{r}_1 - \vec{r}_{\overline{1}})}{2}\right)j_0\left(\frac{\vec{k}\cdot(\vec{r}_2 - \vec{r}_{\overline{2}})}{2}\right)T_{13}(\vec{r}_1 - \vec{r}_{\overline{1}})T_{13}(\vec{r}_2 - \vec{r}_{\overline{2}})G(1\overline{1};2\overline{2}) \tag{7.31}$$

and it follows that $\Phi_t(0) = \Phi_t(0, i0^+)$ is given by

$$\Phi_t(0)=\lim_{z\to i0^+}\left(-\frac{\beta^2}{4n}\right)\int\frac{d1\,d\bar{1}\,d2\,d\bar{2}}{\Omega}\,T_{13}(\vec{r}_1-\vec{r}_{\bar{1}})\,T_{13}(\vec{r}_2-\vec{r}_{\bar{2}})\,G(1\bar{1};2\bar{2}). \tag{7.32}$$

Combining these results, one obtains

$$\eta=imnV_0^2\{\Phi_t(0)+\langle(\xi_1\xi_3+T_t(0))|Q[-Q(iK)Q]^{-1}Q|(\xi_1'\,\xi_3'+T_t(0))\rangle\}, \tag{7.33}$$

where

$$iK\equiv\lim_{z\to i0^+}\lim_{k\to 0}\bar{\varphi}(\vec{k},z), \tag{7.34}$$

$$\langle T_t(0)|=\lim_{z\to i0^+}\lim_{k\to 0}\langle T_t(\vec{k},z)|, \tag{7.35}$$

and

$$\langle\xi_1\xi_3|=\frac{1}{kV_0}\langle g_t|z^0(k). \tag{7.36}$$

Thus a calculation of the shear viscosity reduces to a calculation of

$$\Phi_t(0)=\lim_{z\to i0^+}\lim_{k\to 0}\frac{1}{(kV_0)^2}\langle g_t|\varphi^{(c)}(\vec{k},z)|g_t\rangle \tag{7.37}$$

and

$$\langle T_t(0)|\vec{\xi}'\rangle=\lim_{z\to i0^+}\lim_{k\to 0}\frac{1}{kV_0}\langle g_t|\varphi^{(c)}(\vec{k},z)|\vec{\xi}'\rangle \tag{7.38}$$

together with the determination of the eigenspectrum of the operator $QiKQ$.

D. Thermal conductivity and sound attenuation coefficient

The analysis of the shear viscosity is considerably more direct than the calculation of the thermal conductivity and the sound attenuation coefficient. This is primarily because of the coupled modes and the fact that one of them is a traveling mode. In the case of the transverse modes one found that

$$D_t(\vec{k},z)=(kV_0)^2M_t(\vec{k},z),$$

where M_t had a finite limit as k and z go to zero, given essentially by (7.33). In that case M_t is determined by Φ_t, T_t, and K. In the case of longitudinal excitations the D's have the more general form

$$D_{\mu\nu}(\vec{k},z)=kV_0\hat{\omega}_{\mu\nu}(z)+(kV_0)^2M_{\mu\nu}(\vec{k},z), \tag{7.39}$$

where the $\hat{\omega}$'s and M's must be determined in terms of matrix elements of the memory function.

It is now convenient to note that if μ is one of the conserved states then one can write

$$\langle\mu|\varphi^{(c)}(\vec{k},z)|\vec{\xi}'\rangle=kV_0\langle T_{\mu,k}(\vec{k},z)|\vec{\xi}'\rangle+z\langle T_{\mu,z}(\vec{k},z)|\vec{\xi}'\rangle \tag{7.40}$$

in analogy with (7.27). One also has, expanding to second-order in k and z,

$$\langle\mu|\varphi^{(c)}(\vec{k},z)|\nu\rangle=kV_0\Phi^{(1)}_{\mu\nu,k}+z\Phi^{(1)}_{\mu\nu,z}+(kV_0)^2\Phi^{(2)}_{\mu\nu,k}+kV_0z\Phi^{(2)}_{\mu\nu,kz}+z^2\Phi^{(2)}_{\mu\nu,z}. \tag{7.41}$$

The T's and Φ's can be unambiguously identified with various small k and z limits of matrix elements of $\varphi^{(c)}$.

One can show using symmetry arguments that all of the $T_{\mu,k}$ are nonzero except $T_{1,k}$ and the only nonzero $T_{\mu,z}$ is

$$\langle T_{3,z}|\vec{p}_2\rangle=\lim_{z\to i0^+}(\tfrac{2}{3})^{1/2}\frac{\beta^2}{n}\int\frac{d1\,d\bar{1}\,d\bar{2}\,d^3r_2}{\Omega}\times V(\vec{r}_1-\vec{r}_{\bar{1}})L_I(2\bar{2})G(1\bar{1};2\bar{2}). \tag{7.42}$$

It will be shown that all of the $\Phi^{(1)}$ can be evaluated explicitly in terms of thermodynamic derivatives. The $\Phi^{(2)}$ contributions cannot be evaluated explicitly, as with Φ_t, since they depend on the dynamics of the system. One can show however that many of the $\Phi^{(2)}$'s are zero due to symmetry requirements. This follows from the condition

$$\varphi^{(c)}(-\vec{k},-\vec{p}-\vec{p}',z)=\varphi^{(c)}(\vec{k},\vec{p}\vec{p}',z). \tag{7.43}$$

Consequently, one can easily show that the matrix elements $\Phi^{(1)}_{22,k}$, $\Phi^{(2)}_{22,kz}$, $\Phi^{(2)}_{23,k}$, $\Phi^{(1)}_{33,k}$, and $\Phi^{(2)}_{33,kz}$ all vanish. A number of other terms vanish because they are explicitly proportional to k and vanish as k goes to zero. These vanishing elements include $\Phi^{(1)}_{22,z}$, $\Phi^{(2)}_{22,z}$, $\Phi^{(1)}_{23,z}$, and $\Phi^{(2)}_{23,z}$. The nonvanishing second-order matrix elements are $\Phi^{(2)}_{22,k}$, $\Phi^{(2)}_{23,kz}$, $\Phi^{(2)}_{32,kz}$, $\Phi^{(2)}_{33,z}$, and $\Phi^{(2)}_{33,k}$. The nonzero first-order matrix elements have been evaluated in Appendix C. One finds

$$\Phi^{(1)}_{23,k}=-(\tfrac{2}{3})^{1/2}\frac{\beta^2}{n}\left[\left(\frac{\partial P}{\partial\beta}\right)_n+\frac{n}{\beta^2}\right], \tag{7.44}$$

where P is the equilibrium pressure, and

$$\Phi^{(1)}_{33,z}=\frac{2}{3}\,\frac{\beta^2}{n}\left[\left(\frac{\partial\epsilon}{\partial\beta}\right)_n+\frac{3}{2}\,\frac{n}{\beta^2}\right], \tag{7.45}$$

where ϵ is the equilibrium energy density. It is very easy to show that all of the $\langle\mu|z^0(k)|\nu\rangle$ are zero except,

$$\langle 1|z^0(k)|2\rangle=kV_0=\langle 2|z^0(k)|1\rangle, \tag{7.46}$$

$$\langle 2|z^0(k)|3\rangle=(\tfrac{2}{3})^{1/2}kV_0=\langle 3|z^0(k)|2\rangle. \tag{7.47}$$

Combining all of these results one finds

$$\hat{\omega}_{\mu\nu}(x)=\begin{bmatrix} 0 & 1 & 0 \\ 1-nC_D(0) & 0 & -(\tfrac{2}{3})^{1/2}\dfrac{\beta^2}{n}\left(\dfrac{\partial P}{\partial\beta}\right)_n \\ 0 & -(\tfrac{2}{3})^{1/2}\dfrac{\beta^2}{n}\left(\dfrac{\partial P}{\partial\beta}\right)_n & \left[1+\dfrac{2}{3}\,\dfrac{\beta^2}{n}\left(\dfrac{\partial\epsilon}{\partial\beta}\right)_n\right]x \end{bmatrix}, \tag{7.48}$$

$$M_{1\nu}=M_{\mu 1}=0, \tag{7.49}$$

$$M_{23}(x)=x\Phi^{(2)}_{23,z}+\langle(\xi_3^2+T_{2,k})|Q[Q(-iK)Q]^{-1}Q|(\xi_3'\epsilon(\xi')+T_{3,k}+xT_{3,z})\rangle, \tag{7.50}$$

$$M_{32}(x)=x\Phi^{(2)}_{32,z}+\langle(\xi_3\epsilon(\xi)+T_{3,k}+xT_{3,z})|Q[Q(-iK)Q]^{-1}Q|(\xi_3'^2+T_{2,k})\rangle, \tag{7.51}$$

$$M_{22}(x)=\Phi^{(2)}_{22,k}+\langle(\xi_3^2+T_{2,k})|Q[Q(-iK)Q]^{-1}Q|(\xi_3'^2+T_{2,k})\rangle \tag{7.52}$$

$$M_{33}(x)=\Phi^{(2)}_{33,k}+x^2\Phi^{(2)}_{33,z}+\langle(\xi_3\epsilon(\xi)+T_{3,k}+xT_{3,z})|Q[Q(-iK)Q]^{-1}Q|(\xi_3'\epsilon(\xi')+T_{3,k}+xT_{3,z})\rangle. \tag{7.53}$$

where $x=z/kV_0$.

One can further reduce these expressions for the M's by noting the symmetry properties of the T's as $\vec{\xi}\to-\vec{\xi}$. These results will not be needed here.

One can now use the above results in a direct calculation of G_{11}. Starting with (7.24) one easily finds that

$$G_{11}(\vec{k},z)=[\det(z-D(\vec{k},z))]^{-1}$$
$$\times[(z-D_{22})(z-D_{33})-D_{23}D_{32}], \tag{7.54}$$

where the D's are given for small k and z by (7.39). In the analysis here one is most interested in finding the thermal conductivity and the sound attenuation coefficient. One sees from (7.6) and (7.23) that the thermal conductivity can be obtained from

$$\lim_{k\to 0}\lim_{z\to 0} k^2 G_{11}(\vec{k},z).$$

From (7.54) one easily finds to lowest order in k

$$G_{11}(\vec{k},0)=-\frac{\hat{\omega}_{23}\hat{\omega}_{32}}{(kV_0)^2\hat{\omega}_{12}\hat{\omega}_{21}M_{33}(0)}. \tag{7.55}$$

Then, using (7.29), one has from (7.6) that

$$\lambda^{-1}=n\tilde{S}(0)\left[imnV_0^2\left(\frac{\partial n}{\partial P}\right)_T mn(C_p-C_v)V_0^2\right]^{-1}$$
$$\times\frac{\hat{\omega}_{23}\hat{\omega}_{32}}{\hat{\omega}_{12}\hat{\omega}_{21}M_{33}(0)}. \tag{7.56}$$

After noting that $\tilde{S}(0)=(\delta n/\delta P)_T k_B T$ and using the explicit expressions for the $\hat{\omega}$'s given by (7.48), one obtains

$$\lambda=\frac{3}{2}\,\frac{n(C_p-C_v)}{(\beta^2/n)(\partial P/\partial\beta)_n^2(\partial n/\partial P)_T}\,[i\Phi^{(2)}_{33,k}+i\langle\xi_3\epsilon(\xi)+T_{3,k}|Q(Q(-iK)Q)^{-1}Q|(\xi_3'\epsilon(\xi')+T_{3,k})\rangle]. \tag{7.57}$$

This is an exact expression for the thermal conductivity in terms of the memory function.

There is a new element that enters into the calculation of Γ. One can see from (7.7) that one must set $z=C_0k$ where C_0 is the location of the sound mode. Therefore, before one can find an expression for Γ, one must determine C_0 in terms of the $\hat{\omega}$'s. Comparing (7.7) and (7.54) one sees that C_0 is defined by the condition

$$\det[kC_0-kV_0\hat{\omega}(x)]=0, \tag{7.58}$$

which is just the equation determining the undamped collective modes in the system. One finds that this determinental equation can be written

$$\left(\frac{C_0}{V_0}\right)^2=\hat{\omega}_{21}\hat{\omega}_{12}+\frac{\hat{\omega}_{23}\hat{\omega}_{32}}{1-\hat{\omega}_{33}(x)/x}. \tag{7.59}$$

Putting in the explicit expressions for the $\hat{\omega}$'s from (7.48), one easily finds that

$$\left(\frac{C_0}{V_0}\right)^2=m\beta\left(\frac{\partial P}{\partial(mn)}\right)_\beta-\frac{\beta^2}{n}\left(\frac{\partial P}{\partial\beta}\right)_n^2\bigg/\left(\frac{\partial\epsilon}{\partial\beta}\right)_n. \tag{7.60}$$

It is then a simple matter of thermodynamics to show that this can be written

$$C_0^2=\left(\frac{\partial P}{\partial(mn)}\right)_s \tag{7.61}$$

which is just the adiabatic speed of sound.

In calculating the sound-absorption coefficient, one then needs to find $G_{11}(\vec{k}, kC_0)$. One finds after some algebra that

$$G_{11}(\vec{k}, kC_0) = -\frac{C[C-\hat{\omega}_{33}(C)] - \hat{\omega}_{23}\hat{\omega}_{32}}{(kV_0)^2\Delta}, \tag{7.62}$$

where

$$\Delta = M_{33}(C)(C^2 - \hat{\omega}_{21}\hat{\omega}_{12}) + C[C - \hat{\omega}_{33}(C)]M_{22} + C[\hat{\omega}_{23}M_{32}(C) + \hat{\omega}_{32}M_{23}(C)]. \tag{7.63}$$

and $C = C_0/V_0$. Combining (7.62) with (7.7), one finds after a few rearrangements and use of the identity

$$\left(\frac{\partial\epsilon}{\partial\beta}\right)_n = -\frac{mn}{\beta^2 k_B}C_v \tag{7.64}$$

that

$$\Gamma = \tfrac{3}{2}V_0^2\left(1 - \frac{C_v}{C_p}\right)\left(\frac{n}{k_B}\right)^2\left(\frac{\partial P}{\partial T}\right)^{-2}\Delta. \tag{7.65}$$

This is an explicit expression for the sound attenuation coefficient in terms of the memory function and thermodynamic quantities. One can, of course, further reduce Δ, but this will not be carried out here.

E. Mode-mode coupling contribution to λ

A nontrivial example of the usefulness of these expressions involves the calculation of the thermal conductivity near the critical point. The analysis here will be rather rough since this calculation will be described in detail in another paper.

One can show that near the critical point the main contribution to the thermal conductivity in (7.57) is given by the $\mathcal{V}_L G_D \mathcal{V}_L$ contribution to $\Phi^{(2)}_{33,k}$. One has then

$$\lambda_c \sim \frac{3}{2}\,\frac{n(C_p - C_v)}{(\beta^2/n)^2(\partial P/\partial\beta)_n^2(\partial n/\partial P)_T}\,i\Phi^{(2)}_{33,k}. \tag{7.66}$$

It is not difficult to show, in the case where $\varphi^{(c)} = -\mathcal{V}_L\overline{G}\mathcal{V}_L$, that

$$\Phi^{(2)}_{33,k} = \frac{-2i\beta^{-2}}{gV_0^2 n(mV_0)^2}\int_0^{+\infty}dt\int\frac{d^3\bar{k}}{(2\pi)^3}\,Q(\bar{k},t), \tag{7.67}$$

where

$$Q(\bar{k},t) = M^2(\bar{k})S_{nn}(\bar{k},t)[S_l(\bar{k},t) + 2S_t(\bar{k},t)] + M(\bar{k})\left(\frac{d}{d\bar{k}}M(\bar{k})\right)\bar{k}S_{nn}(\bar{k},t)S_l(\bar{k},t) - \bar{k}^2 S_l(\bar{k},t)\left[M(\bar{k})\frac{d}{d\bar{k}}M(\bar{k})\frac{d}{d\bar{k}}S_{nn}(\bar{k},t) + \left(\frac{dM(\bar{k})}{d\bar{k}}\right)^2 S_{nn}(\bar{k},t) + \tfrac{1}{2}M(\bar{k})\left(\frac{d^2}{d\bar{k}^2}M(\bar{k})\right)S_{nn}(\bar{k},t)\right] \tag{7.68}$$

and

$$M(k) = [1 - nC_D(k)]\left(\tilde{h}(k) + ik^{-2}\int d^3r\,e^{-i\vec{k}\cdot\vec{r}}F(r)\vec{k}\cdot\nabla_r\tilde{g}(r)\right), \tag{7.69}$$

$$\tilde{h}(k) = \int d^3r\,e^{-i\vec{k}\cdot\vec{r}}[\tilde{g}(r) - 1], \tag{7.70}$$

$F(r)$ is the Mayer function and S_l is the longitudinal current correlation function. If one is very near the critical point, one can make a large number of simplifications. First one notes that it is the small-$\bar{k}$ behavior that is important in the integral for $\Phi^{(2)}_{33}$.[59] One therefore sees because of explicit powers of $\bar{k}$ that one can approximate

$$Q(\bar{k},t) \approx M^2(\bar{k})S_{nn}(\bar{k},t)[S_l(\bar{k},t) + 2S_t(\bar{k},t)]. \tag{7.71}$$

One also knows that for small $\bar{k}$ that $S(\bar{k})$ diverges at the critical point, therefore $1 - nC_D(k)$ must vanish. This seems to indicate that $M(0)$ vanishes at the critical point, but closer analysis shows that

$$\tilde{h}(0) \approx h(0) \tag{7.72}$$

and

$$[1 - nC_D(0)]h(0) = C_D(0) = 1/n, \tag{7.73}$$

so at the critical point and for small $\bar{k}$

$$M(0) = 1/n. \tag{7.74}$$

Putting these results back into the integral for $\Phi^{(2)}_{33}$, assuming only small values of $\bar{k}$ contribute, one has

$$\Phi^{(2)}_{33,k} = -\frac{2i\beta^{-2}}{gV_0^2 n^3(mV_0)^2}\int_0^{+\infty}dt\int\frac{d^3\bar{k}}{(2\pi)^3} \times S_{nn}(\bar{k},t)[S_l(\bar{k},t) + 2S_t(\bar{k},t)]. \tag{7.75}$$

This expression can be evaluated more explicitly if (since $\bar{k}$ is small) one assumes S_{nn}, S_t, and S_l are given by their hydrodynamical time dependences,

$$S_{nn}(\bar{k},t) = n\tilde{S}(\bar{k})[(1 - C_p/C_v)e^{-\bar{k}^2 D_T t} + (C_v/C_p)\cos(C_0\bar{k}t)e^{-\bar{k}^2\Gamma t/2}], \tag{7.76}$$

$$S_t(\bar{k},t) = ne^{-\bar{k}^2\nu t}, \tag{7.77}$$

where $\nu = \eta/mn$. S_t can be expressed in terms of a second time derivative of S_{nn}. One can show that the coupling between S_{nn} and S_t leads to no divergences in Φ_{33} near the critical point. One should therefore focus on the S_{nn}-S_t coupling.
If one notes that $C_v/C_p \ll 1$ near the critical point, then

$$\Phi^{(2)}_{33,k} = -\frac{4i\beta^{-2}}{gnV_0^2(mV_0)^2}\int_0^{+\infty} dt \int \frac{d^3\bar{k}}{(2\pi)^3} \times \tilde{S}(\bar{k})\, e^{-\bar{k}^2(D_T+\nu)t}. \tag{7.78}$$

The time integration can then be done explicitly to obtain

$$\Phi^{(2)}_{33,k} = -\frac{4i\beta^{-2}}{gnV_0^2(mV_0)^2}\,\frac{1}{(D_T+\nu)}\int \frac{d^3\bar{k}}{(2\pi)^3}\,\frac{\tilde{S}(\bar{k})}{\bar{k}^2}. \tag{7.79}$$

One can now evaluate the $\bar{k}$ integration explicitly if one uses the Ornstein-Zernike form

$$\tilde{S}(k) = k_B T\left(\frac{\partial n}{\partial P}\right)_T \frac{\xi^{-2}}{k^2+\xi^{-2}}. \tag{7.80}$$

One then obtains the result

$$\Phi^{(2)}_{33,k} = -\frac{ik_BT}{g\pi n}\,\frac{\xi^{-1}}{(D_T+\nu)}\left(\frac{\partial n}{\partial P}\right)_T. \tag{7.81}$$

Putting this result back into (7.66) gives

$$\lambda_c \sim \frac{k_BT(C_p-C_v)}{6\pi\xi\,(D_T+\nu)}\left[\left(\frac{\partial P}{\partial\beta}\right)_n^2\left(\frac{\beta^2}{n}\right)^2\right]^{-1}. \tag{7.82}$$

If one further notes that for a van der Waals equation of state the term in brackets can be approximated by 1, that near the critical point $C_p \gg C_v$, and that $\nu \gg D_T$, then one has the Kawasaki[60] result

$$\lambda_c \sim (k_BT/6\pi\xi\eta)\, mnC_p. \tag{7.83}$$

The reader should realize that there have been a large number of approximations in going from (7.67) to (7.83). Many of these approximations are quite good, while others must be discussed further.[61] This will be discussed in detail elsewhere.

VIII. DISCUSSION

The FRKT, as developed in this paper, gives one a practical, microscopic method for calculating the dynamical properties in classical, equilibrium systems. It has been shown how one can make contact with the Boltzmann-Enskog approximation for low densities and the ring terms for high densities. Thus one regains some of the major results from kinetic theory. However, because the FRKT treats the static properties of the system in a natural way, the theory is also practical near the critical point, and the relationship with the mode-mode coupling theories has been discussed.

There are many more details of the theory that remain to be worked out. Many of these are of a computational nature. It would, for example, be quite interesting if some matrix elements of the low-density memory function could be worked out explicitly for the case of a Lennard-Jones-type potential. Much of the analysis centers around more complete evaluation of the mode-mode coupling terms appearing in Eq. (6.28) and in a better understanding of the properties of Γ_c (why one seems to be able to neglect it), and further study of the static corrections to transport coefficients as would arise in finding corrections to approximations like (6.34). There appear, however, no conceptual obstacles in carrying out such investigations.

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APPENDIX A: ANALYSIS OF THE QUANTITIES $\langle A(1)f(2)\cdots f(n)\rangle_c$

To facilitate this analysis one introduces a source function

$$\mathcal{S}(\eta) = \exp\int d1\,\eta(1)f(1), \tag{A1}$$

where $\eta(1)$ can be considered as an external potential. Then for example

$$W(\eta) \equiv \ln\langle \mathcal{S}(\eta)\rangle \tag{A2}$$

is essentially the partition function in the presence of the external one body potential $\eta(1)$. W is also the generating function for the cumulants for the fields f,

$$K(12\ldots s) = \left(\frac{\delta}{\delta\eta(1)}\,\frac{\delta}{\delta\eta(2)}\cdots\frac{\delta}{\delta\eta(s)}\,W\right)_{\eta=0}. \tag{A3}$$

Next one defines the quantity

$$\langle A(1)\rangle_\eta = \langle A(1)\,\mathcal{S}(\eta)\rangle\langle\mathcal{S}(\eta)\rangle^{-1}. \tag{A4}$$

It is immediately clear that

$$\langle A(1)f(2)\cdots f(n)\rangle_{c,\eta}=\frac{\delta}{\delta\eta(2)}\cdots\frac{\delta}{\delta\eta(n)}\langle A(1)\rangle_\eta. \tag{A5}$$

Consequently, if one wants to evaluate $\langle A(1)f(2)\cdots f(n)\rangle_c$ then one needs an expression for $\langle A(1)\rangle_\eta$. This can be accomplished directly. Working, for convenience, in the canonical ensemble

$$\langle A(1)\rangle_\eta=-\langle\mathcal{S}(\eta)\rangle^{-1}\langle(L_I f(1))\mathcal{S}(\eta)\rangle \tag{A6}$$

$$=-\langle\mathcal{S}(\eta)\rangle^{-1}z^{-1}\int(dq)_N\,e^{-\beta H_N}\,\mathcal{S}(\eta)\,L_I f(1) \tag{A7}$$

$$=-i\langle\mathcal{S}(\eta)\rangle^{-1}z^{-1}\left(-\nabla^l_{p_1}\int(dq)_N\,\mathcal{S}(\eta)\sum_{i=1}^{N}\nabla^l_{r_i}(-\beta^{-1}e^{-\beta H_N})\,\delta(1-q_i)\right). \tag{A8}$$

After integrating by parts,

$$\langle A(1)\rangle_\eta=i\langle\mathcal{S}(\eta)\rangle^{-1}\beta^{-1}\,\nabla^l_{p_1}\left\langle\sum_{i=1}^{N}\nabla^l_{r_i}[\delta(1-q_i)\mathcal{S}(\eta)]\right\rangle \tag{A9}$$

$$=i\beta^{-1}\nabla^l_{p_1}\left(-\nabla^l_{r_1}\langle f(1)\rangle_\eta+\langle\mathcal{S}(\eta)\rangle^{-1}\left\langle\sum_{i=1}^{N}\delta(1-q_i)\nabla^l_{r_i}\mathcal{S}(\eta)\right\rangle\right), \tag{A10}$$

but

$$\nabla_{r_i}\mathcal{S}(\eta)=\mathcal{S}(\eta)\int d1'\,\eta(1')\nabla_{r_i}f(1')$$

$$=\mathcal{S}(\eta)\nabla_{r_i}\eta(r_i);$$

so one finds eventually

$$\langle A(1)\rangle_\eta=i\beta^{-1}\nabla^l_{r_1}\{-\nabla^l_{r_1}\langle f(1)\rangle_\eta+\langle f(1)\rangle_\eta\nabla_{r_1}\eta(1)\} \tag{A11}$$

which is very useful since the potential no longer appears explicitly. One can now evaluate the cumulants of interest by taking functional derivatives and using (A3).

APPENDIX B: LOW-DENSITY LIMIT FOR T

One now wants to know the relationship of the generalized T matrix defined by (6.26) to the usual classical T matrix introduced by Zwanzig.[33] This connection can be seen by evaluating T to lowest order in the density. One must first evaluate $\mathcal{V}_s\overline{G}_s\overline{G}^{0-1}_D$ to lowest order in the density.

It is easy to see from (5.11) that

$$\mathcal{V}^0(1;2\bar{2})=-\omega_0(2\bar{2})\,L_I(2\bar{2})[\delta(12)+\delta(1\bar{2})]. \tag{B1}$$

Similarly from (2.24) and (5.26) one has

$$\tilde{G}^0(1\bar{1};2\bar{2})=\omega_0(1\bar{1})\,2\langle 1\bar{1}|2\bar{2}\rangle, \tag{B2}$$

$$\langle 1\bar{1}|W^0|2\bar{2}\rangle=\omega_0(1\bar{1})\,L(1\bar{1})\,2\langle 1\bar{1}|2\bar{2}\rangle, \tag{B3}$$

so that

$$\langle 1\bar{1}|\overline{G}^0|2\bar{2}\rangle=\frac{1}{\omega_0(1\bar{1})}[z-L(1\bar{1})]^{-1}\,2\langle 1\bar{1}|2\bar{2}\rangle. \tag{B4}$$

Similarly one finds from (6.18) that

$$\langle 1\bar{1}|\overline{G}^{0-1}_D|2\bar{2}\rangle=[z-L_0(1\bar{1})]\;2\langle 1\bar{1}|2\bar{2}\rangle\,\omega_0(1)\,\omega_0(\bar{1}). \tag{B5}$$

One has then that

$$\langle 1|T^0|2\bar{2}\rangle=\mathcal{V}^0(1;3\bar{3})\,\overline{G}^0_s(3\bar{3};4\bar{4})\,\overline{G}^{0-1}_D(4\bar{4};2\bar{2}) \tag{B6}$$

$$=4\int d3\,L_I(13)[z-L(13)]^{-1}[z-L_0(3\bar{3})]$$

$$\times\langle 3\bar{3}|2\bar{2}\rangle\,\omega_0(2)\,\omega_0(\bar{2}). \tag{B7}$$

And since the classical T matrix is defined by

$$t(12)\equiv L_I(12)[z-L(12)]^{-1}[z-L_0(12)], \tag{B8}$$

one has

$$\langle 1|T^0|2\bar{2}\rangle=4\int d3\,t(13)\langle 13|2\bar{2}\rangle\,\omega_0(2)\,\omega_0(\bar{2}). \tag{B9}$$

APPENDIX C: CALCULATION OF $\Phi^{(1)}_{23,k}$ AND $\Phi^{(1)}_{33,z}$

The first matrix element to be evaluated is

$$\Phi^{(1)}_{23,k}=\lim_{k\to 0}\frac{1}{kV_0}\lim_{z\to i0^+}\langle 2|\varphi^{(c)}(\vec{k},z)|3\rangle. \tag{C1}$$

One can then use (7.29) and take the small-k and -z limit to obtain

$$\Phi^{(1)}_{23,k}=\lim_{k\to 0}\frac{1}{kV_0}\lim_{z\to i0^+}\frac{kV_0}{6}\left(\tfrac{2}{3}\right)^{1/2}\frac{\beta^2}{n}$$

$$\times\int\frac{d1\,d\bar{1}\,d2\,d\bar{2}}{\Omega}\,T_{33}(\vec{r}_1-\vec{r}_{\bar{1}})$$

$$\times(-\tfrac{1}{2})\,V(\vec{r}_2-\vec{r}_{\bar{2}})\,L_0(2\bar{2})\,G(1\bar{1};2\bar{2}). \tag{C2}$$

It is then convenient to use the transpose of (4.22) to represent G so that

$$\Phi^{(1)}_{23,k}=\lim_{k\to 0}\lim_{z\to i0^+}\left(-\frac{1}{12}\right)(\tfrac{2}{3})^{1/2}\frac{\beta^2}{n}\int\frac{d1\,d\bar{1}\,d2\,d\bar{2}}{\Omega}\,T_{33}(\vec{r}_1-\vec{r}_{\bar{1}})\langle 1\bar{1}|\tilde{G}[z+L^T+U^T+M^T(-z)]^{-1}L_0^T|2\bar{2}\rangle . \tag{C3}$$

One can then use the operator identity $[A+B]^{-1}B=1-[A+B]^{-1}A$ to obtain

$$\Phi^{(1)}_{23,k}=\lim_{k\to 0}\lim_{z\to i0^+}\left(\frac{-\sqrt{2}\,\beta^2}{12\sqrt{3}\,n}\right)\int\frac{d1\,d\bar{1}\,d2\,d\bar{2}}{\Omega}\,T_{33}(\vec{r}_1-\vec{r}_{\bar{1}})V(\vec{r}_2-\vec{r}_{\bar{2}})\langle 1\bar{1}|\{\tilde{G}-G(z)[z+L_I^T+U^T+M^T(-z)]\}|2\bar{2}\rangle . \tag{C4}$$

One can easily show that

$$\int d^3p_2\,d^3p_{\bar{2}}\,(L_I^T+U^T+M^T(-z))|2\bar{2}\rangle=0.$$

So one has, after letting $z\to i0^+$

$$\Phi^{(1)}_{23,k}=\lim_{k\to 0}\left(\frac{-\beta^2\sqrt{2}}{12\sqrt{3}\,n}\right)\int\frac{d1\,d\bar{1}\,d2\,d\bar{2}}{\Omega}\times T_{33}(\vec{r}_1-\vec{r}_{\bar{1}})V(\vec{r}_2-\vec{r}_{\bar{2}})\tilde{G}(1\bar{1};2\bar{2}). \tag{C5}$$

One now has a strictly thermodynamical problem. If one eliminates $\tilde{G}$ by using (2.21) and introduces the potential-energy fluctuation

$$\delta V_k=\frac{1}{2}\int\frac{d1\,d\bar{1}}{\Omega^{1/2}}\,e^{+i\vec{k}\cdot\vec{r}_1}\delta g(1\bar{1})V(\vec{r}_1-\vec{r}_{\bar{1}}),$$

one easily sees that

$$\Phi^{(1)}_{23,k}=\lim_{k\to 0}(\tfrac{2}{3})^{1/2}\frac{\beta^2}{n}[\langle\delta V_kP^I_{-k}\rangle-\langle\delta V_kn_{-k}\rangle\langle n_kn_{-k}\rangle\langle n_kP^I_{-k}\rangle], \tag{C6}$$

where

$$P^I_{-k}=-\frac{1}{6}\int\frac{d2\,d\bar{2}}{\Omega^{1/2}}\,g(2\bar{2})T_{33}(\vec{r}_2-\vec{r}_{\bar{2}})e^{-i\vec{k}\cdot\vec{r}_2} \tag{C7}$$

is the potential-energy contribution to the pressure-operator fluctuation and n_k is the Fourier transform of the density. It should be observed that one can replace δV_k by V_k since the average term $\langle V_k\rangle$ does not contribute in the limit $k\to 0$. If one substitutes $V_k=E_k-K_k$, where K_k is the kinetic-energy density and E_k the energy density, into (C6) one finds, after some cancellation, that

$$\Phi^{(1)}_{23,k}=\lim_{k\to 0}(\tfrac{2}{3})^{1/2}\frac{\beta^2}{n}[\langle E_kP^I_{-k}\rangle-\langle E_kn_{-k}\rangle\langle n_kn_{-k}\rangle^{-1}\langle n_kP^I_{-k}\rangle]. \tag{C8}$$

Following Schofield,[62] one writes the energy density

$$E_k=en_k+ne_k \tag{C9}$$

where e, the mean energy per particle, equals $\langle E_0\rangle/n$ and

$$e_k=n^{-1}\sum_{i=1}^{N}\left[\frac{1}{2}\left(\frac{p_i^2}{m}+\sum_{i\neq j}V(\vec{r}_i-\vec{r}_j)\right)-e\right]e^{-i\vec{k}\cdot\vec{r}_i} \tag{C10}$$

is the fluctuation in the energy per particle. Then after substituting for E_k in terms of e_k, one finds that the term en_k does not contribute and

$$\Phi^{(1)}_{23,k}=\lim_{k\to 0}(\tfrac{2}{3})^{1/2}\beta^2[\langle e_kP^I_{-k}\rangle-\langle e_kn_{-k}\rangle\langle n_kn_{-k}\rangle^{-1}\langle n_kP^I_{-k}\rangle]. \tag{C11}$$

Since Schofield[63] has shown that

$$\left(\frac{\partial e}{\partial n}\right)_\beta=\lim_{k\to 0}\frac{\langle e_kn_{-k}\rangle}{\langle n_kn_{-k}\rangle}, \tag{C12}$$

one has

$$\Phi^{(1)}_{23,k}=\lim_{k\to 0}(\tfrac{2}{3})^{1/2}\beta^2\left[\langle e_kP^I_{-k}\rangle-\left(\frac{\partial e}{\partial n}\right)_\beta\langle n_kP^I_{-k}\rangle\right]. \tag{C13}$$

Schofield[64] has further shown that this expression can be reduced to

$$\Phi^{(1)}_{23,k}=-(\tfrac{2}{3})^{1/2}\frac{\beta^2}{n}\left(\frac{\partial P^I}{\partial\beta}\right)_n, \tag{C14}$$

where P^I is the potential contribution to the equilibrium pressure. Since the full pressure is given by $P=n\beta^{-1}+P^I$, one has

$$\Phi^{(1)}_{23,k}=-(\tfrac{2}{3})^{1/2}\frac{\beta^2}{n}\left[n\beta^{-2}+\left(\frac{\partial P}{\partial\beta}\right)_n\right]. \tag{C15}$$

The matrix element $\Phi^{(1)}_{33,z}$ can be evaluated in a manner very similar to that used in evaluating $\Phi^{(1)}_{23,z}$. The major difference is that P^I_{-k} is replaced by V_{-k} and one obtains the simple result

$$\Phi^{(1)}_{33,z}=\lim_{z\to i0^+}\frac{1}{z}\lim_{k\to 0}\langle 3|\varphi^{(c)}(\vec{k},z)|3\rangle=\frac{2}{3}\frac{\beta^2}{n}\left[\left(\frac{\partial\epsilon}{\partial\beta}\right)_n+\frac{3}{2}n\beta^{-2}\right]. \tag{C16}$$

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[1] G. F. Mazenko, Phys. Rev. A 7, 209 (1973). This paper (FRKT I) will be referred to as I and equations from this paper will be labeled (I...).

[2] G. F. Mazenko, Phys. Rev. A 7, 222 (1973). This paper (FRKT II) will be referred to as II and equations from this paper will be labeled (II...).

[3] P. C. Martin, in *Many-Body Physics*, edited by C. DeWitt and R. Balian (Gordon and Breach, New York, 1968).

[4] R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).

[5] See for example: B. J. Adler, D. M. Gass, and T. E. Wainwright, J. Chem. Phy. 53, 3813 (1970); A. Rahman, Phys. Rev. 136, A405 (1964); D. Levesque and L. Verlet, Phys. Rev. A 2, 2514 (1970); D. Levesque, L. Verlet, and J. Kurkijarvi, Phys. Rev. A 7, 1690 (1973).

[6] G. E. Uhlenbeck and G. W. Ford, *Lectures in Statistical Mechanics* (American Mathematical Society, Providence, R.I., 1963); S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Cases*, 3rd ed. (Cambridge U. P., London, 1970); H. L. Frisch and E. McLaughlin, J. Chem. Phys. 55, 3706 (1971); B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. 53, 3813 (1970) and earlier articles; H. J. M. Hanley, R. D. McCarty, and J. V. Sengers, J. Chem. Phys. 50, 857 (1969). H. J. M. Hanley, R. D. McCarty, and E. G. D. Cohen, Physica 60, 322 (1972).

[7] J. G. Kirkwood, J. Chem. Phys. 14, 180 (1946); R. Zwanzig, J. Chem. Phys. 40, 2527 (1964); P. C. Martin in *Statistical Mechanics of Equilibrium and Non-Equilibrium*, edited by J. Meixner (North-Holland, Amsterdam, 1965); R. Kubo, in *Many-Body Theory*, Part I, edited by R. Kubo (Benjamin, New York, 1966); K. Kawasaki, Phys. Rev. 150, 291 (1966).

[8] H. Mori, Progr. Theor. Phys. (Kyoto) 33, 423 (1965); R. Zwanzig, Phys. Rev. 124, 983 (1961); V. M. Kenkre, Phys. Rev. A 7, 772 (1973); V. M. Kenkre and M. Dresden, Phys. Rev. A 6, 769 (1972); M. H. Ernst, in *Lectures in Theoretical Physics*, edited by W. E. Brittin (Gordon and Breach, New York, 1967), Vol. 9C.

[9] G. F. Mazenko, Internal Report, Dept. of Nuclear Engineering, Massachusetts Institute of Technology, 1973 (unpublished).

[10] R. Kubo, J. Phys. Soc. Japan 17, 1100 (1962).

[11] P. Tartaglia and S. H. Chen, J. Chem. Phys. 58, 4389 (1973); J. Swift, Ann. Phys. (N.Y.) 75, 1 (1973); V. Korenman, Phys. Rev. A 2, 449 (1970).

[12] K. Kawasaki, Ann. Phys. (N.Y.) 61, 1 (1970); L. P. Kadanoff and J. Swift, Phys. Rev. 166, 89 (1968); R. Zwanzig, University of Maryland Institute for Fluid Dynamics and Applied Mathematics Technical Report No. 3N-695, 1971 (unpublished). R. A. Ferrell, Phys. Rev. Lett. 24, 1169 (1970).

[13] This difference is most easily seen from the equal-time values of S_{nn} and S_s. S_{nn} is given at equal times by $n\tilde{S}(k)$ where $\tilde{S}(k)$ is the structure factor which diverges at the critical point as k goes to zero. The initial values of S_s is just n independent of any other details of the thermodynamic state.

[14] G. F. Mazenko, Phys. Rev. A 3, 2121 (1971).

[15] G. F. Mazenko, Phys. Rev. A 5, 2545 (1972).

[16] G. F. Mazenko, T. Y. C. Wei, and S. Yip, Phys. Rev. A 6, 1981 (1972).

[17] C. D. Boley, Phys. Rev. A 5, 986 (1972).

[18] K. G. Wilson, Phys. Rev. B 4, 3174 (1971); K. G. Wilson, and M. E. Fisher, Phys. Rev. Lett. 28, 240 (1972); K. G. Wilson, Phys. Rev. Lett. 28, 548 (1972); E. Brezin, D. J. Wallace, and K. G. Wilson, Phys. Rev. Lett. 29, 591 (1972). E. Brezin and D. J. Wallace, Phys. Rev. B 7, 1967 (1973); and a literature that grows daily.

[19] The basic ideas of modern kinetic theory up to the time of the "divergence" of the transport coefficients are reviewed by M. H. Ernst, L. K. Haines, and J. R. Dorfman, Rev. Mod. Phys. 41, 296 (1969). More details are given in *Lectures in Theoretical Physics*, edited by W. E. Brittin (Gordon and Breach, New York, 1967), Vol. 9C. More recent developments are included in works of J. R. Dorfman and E. G. D. Cohen, Phys. Rev. Lett. 25, 1257 (1970); Phys. Rev. A 6, 2247 (1972); Y. Pomeau, Phys. Rev. A 3, 1174 (1971); J. Dufty, Phys. Rev. A 5, 2247 (1972).

[20] One can expand the memory function up to order n^2 before one encounters difficulties. Very recently C. D. Boley and R. C. Desai [Phys. Rev. A 7, 1700 (1973); 7, 2192 (1973)] have extended the author's low-density memory-function theory (Ref. 15) to the next order in the density. In this work they show the relationship of the memory-function theory to the Bogoliubov theory [see for example N. N. Boboliubov, in *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck (North-Holland, Amsterdam, 1962), Vol. I] and where it breaks down. They also compare the predictions of their second-order memory function with the generalized Boltzmann equations developed by S. T. Choh and G. E. Uhlenbeck, *The Kinetic Theory of Phenomena in Dense Gases*, Navy Theoretical Physics, Contract No. Nour. 1224 (15), 1958; M. S. Green, Chem. Phys. 25, 836 (1956); E. G. D. Cohen, J. Math. Phys. 4, 183 (1963); and K. Kawasaki and I. Oppenheim, Phys. Rev. 136, A1519 (1964). They find agreement between the theories in the calculation of the first density correction for the shear viscosity.

[21] See in particular the articles by Dorfman and Cohen in Ref. 19.

[22] J. Castrosana, G. F. Mazenko, and S. Yip (unpublished).

[23] B. J. Berne, J. P. Boon, and S. A. Rice, J. Chem. Phys. 45, 1086 (1966); C. H. Chung and S. Yip, Phys. Rev. 182, 323 (1969).

[24] See footnote 35 in FRKT I.

[25] P. A. Egelstaff, *An Introduction to the Liquid State* (Academic, London, 1967), see Chap. 2.

[26] The two-point static correlation function is important enough to warrent its own symbol $\tilde{C}(12)$. The two symbols $\tilde{C}(12)$ and $K(12)$ will be used interchangeably depending on context.

[27] This point was not properly appreciated in I. See, for example, Eq. (II. E. 2). The author wishes to thank Dr. C. D. Boley for pointing out these difficulties.

[28] R. Zwanzig, Phys. Rev. 144, 170 (1966).

[29] A. Z. Akcasu and J. J. Duderstadt, Phys. Rev. 188, 479 (1969); R. C. Desai, Phys. Rev. A 3, 320 (1971); D. Forster and P. C. Martin, Phys. Rev. A 2, 1575 (1970); P. Ortelova and M. Nelkin, Phys. Rev. 181, 429 (1969); Phys. Rev. A 2, 187 (1970); J. L. Lebowitz,

J. K. Percus, and J. Sykes, Phys. Rev. 188, 487 (1960); L. Blum and J. L. Lebowitz, Phys. Rev. 185, 273 (1969).

[30] See p. 53 in Ref. 25.

[31] One needs to use the identity given by Eq. (A8) in P. Schofield, Proc. Phys. Soc. 88, 149 (1966).

[32] Such a separation is quite natural as can be seen from the Mayer expansion. See, for example, G. Shell, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964).

[33] Here is the first place where the short-ranged nature of the potential plays a role. If the potential has a long-ranged part and a short-ranged part, then one may want to make the separation $g_0 = g_0^s g_0^L$ where g_0^L contains the long-range part of the interaction. This separation will not be carried out here for simplicity, but it is this type of effect that underlies the van der Waals-gas approach to this problem investigated by P. Resibois, J. Piasecki, and Y. Pomeau, Phys. Rev. Lett. 28, 882 (1972). Such terms also give rise to the Fokker-Planck terms discussed by Forster and Martin (see Ref. 29) using the memory-function formalism and were included by Rice and Allnat (see Ref. 82) in their kinetic treatment of transport coefficients. If short-ranged forces are not involved, e.g., in treating a plasma, then the approximations one makes, starting from Eq. (6.23) will be quite different. See, for example, E. J. Linneburr and J. J. Duderstadt, Phys. Fluids (to be published).

[34] It is precisely this idea that is exploited by Anderson, Chandler, and Weeks in developing their theory of dense fluids. J. D. Weeks, D. Chandler, and H. C. Anderson, J. Chem. Phys. 54, 5237 (1971); H. C. Anderson, J. D. Weeks, and D. Chandler, Phys. Rev. A 4, 1597 (1971).

[35] B. R. A. Nijboer and L. Van Hove, Phys. Rev. 85, 777 (1952).

[36] See, for example, H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford U. P., New York, 1971), p. 104.

[37] One should note that $\sigma(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ is the three-particle generalization of $h(\vec{r}_1 - \vec{r}_2)$ and appears naturally in the theory in several places.

[38] It seems reasonable in treating these static quantities to break them into their "natural" two-, three-, and four-body parts [see in this regard Eq. (5.2) for $\tilde{G}$] and treat the three- and four-body contributions as perturbations on the two-body results.

[39] This is the statement that corresponds to the fact that $\mathfrak{L}$ introduced in I reduces to L in the low-density limit.

[40] See, for example, the first part of Sec. IV in FRKT II for a similar calculation.

[41] See Eq. (II.2.11).

[42] M. Nelkin and S. Ranganathan, Phys. Rev. 164, 222 (1967); R. Zwanzig, Phys. Rev. 144, 170 (1966).

[43] See Eq. (3.4) in Ref. 15.

[44] D. Forster, Ph.D. thesis (Harvard University, 1969) (unpublished); D. Forster and P. C. Martin, Phys. Rev. A 2, 1575 (1970).

[45] P. Martin, E. Siggia, and H. Rose, Phys. Rev. A 8, 423 (1973).

[46] P. C. Martin and J. Schwinger, Phys. Rev. 115, 1342 (1959).

[47] One may also question why one chooses $\bar{G}_s$ in terms of the full $z\tilde{G}$ and W as opposed to the choice

$$\bar{G}_0 = (z\tilde{G}_0 - L\tilde{G}_0)$$

where $\tilde{G}_0$ is the part of G proportional to $\langle 1\bar{1} | 2\bar{2} \rangle$. This is somewhat arbitrary, but the choice of $\tilde{G}_s$ given by (6.19) leads to a more compact splitting up of terms and it seems reasonable to keep the various connected parts of W together and separate $\Gamma(z)$ since they have a very different physical origin. This also seems reasonable since one expects that

$$\mathfrak{V} s \bar{G} s \approx \mathfrak{V} s \bar{G}_0$$

plus small corrections that one can calculate. Thus in evaluating $\bar{G}_s$ one will develop an iteration scheme for it in terms of $\bar{G}_0$. One might also wonder why one does not exclude the disconnected part of W in defining $\bar{G}_s$. The reason is that this would not lead to the correct low-density limit for $\bar{G}$ and this limit is quite important in making contact with the Boltzmann-Enskog term.

[48] R. Zwanzig, Phys. Rev. 129, 486 (1963).

[49] M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuween, Phys. Rev. Lett. 25, 1254 (1970); Phys. Rev. A 4, 2055 (1971); Y. Pomeau, Phys. Rev. A 5, 2569 (1972); Y. Pomeau, Phys. Rev. A 7, 1134 (1973); P. Resibois (private communication).

[50] Included in these terms will be the repeated ring terms discussed by M. H. Ernst and J. R. Dorfman [Physica 61, 157 (1972)]. In this paper the authors have studied the effects of the regular ring terms on the hydrodynamic modes. They found a dispersion relation that is nonanalytic in k. At low densities (STP) the ratio of the $k^{5/2}$ term to k^2 is of order $(n^3)^2 k^{1/2} \times 10^{-7}$ which is outside the range of experimental detection. The effect will be considerably larger at liquid-like densities, but the quantitative effect has been evaluated only to lowest order in the density. [See also M. H. Ernst and J. R. Dorfman, Phys. Lett. A 38, 269 (1972)].

[51] J. L. Lebowitz (private communication).

[52] Comparison with experiment is given by J. V. Sengers, in *Critical Phenomena*, edited by M. S. Green (Academic, New York, 1971).

[53] This statement is not completely concise and requires a discussion of the Enskog theory as it would appear in the memory-function formalism. A good discussion of this point is given by J. Sykes, J. Stat. Phys. (to be published). He starts with the conventional Enskog equation for the singlet distribution function with the prescription due to E. P. Gross and W. Wisnivesky [Phys. Fluids 11, 1387 (1968)] that the function $\chi(\vec{r})$ appearing in Enskog's equation be evaluated as

$$\chi(r) = \tilde{g}(r_0)\big|_{n = n(\vec{r}, t)}.$$

Sykes then linearizes the resulting equation about equilibrium and finds that the resulting memory function has a collisional part given by (6.70) (in the hard-sphere limit) and hence the identification with Enskog, but he finds that the Enskog equation leads to a $\varphi(s)$ where $C_D(k)$ is replaced by

$$V(k) = [C_D(0) - \tilde{g}(r_0) C_D^0(0)] C_D^0(\tfrac{1}{2}k) / C_D^0(0) + \tilde{g}(r_0) C_D^0(k)$$

with

$$C_D^0(k) = \lim_{k \to 0} C_D(0).$$

Note $V(k) = C_D(k)$ to lowest order in the density and to lowest order in k. With this background one sees that in the case of hard spheres (6.40) is equivalent to the collisional part of the memory function in the Boltzmann-Enskog theory. Equation (6.40) is a generalized Enskog result because it is also applicable to more realistic potentials if one interprets the r_0 that appears in $\tilde{g}$ as an effective hard-sphere diameter.

[54] The result was apparently first obtained by J. L. Lebowitz, J. K. Percus, and J. Sykes, Phys. Rev. 188, 487 (1960). Since this relation is exact for short times the hard-sphere expression for (6.70) (see Ref. 22) is called by some the "short-time" approximation. Similar equations have been found recently by other authors using different methods: H. H. U. Konijnendijk and J. M. J. van Leeuween, Physica 64, 342 (1973); H. van Beijeren and M. H. Ernst (print prior to publication).

[55] See the article by Konijnendijk and van Leeuween in Ref. 54 and the article by Sykes in Ref. 53.

[56] In this case r_0 should be defined as the value of r where $dg_0(r)/dr$ has a maximum.

[57] The discussion here is limited to simple fluids. In the case of liquid crystals, etc., one may have other modes with long lifetimes. [see P. C. Martin, O. Parodi, and P. S. Pershan, Phys. Rev. A 6, 2401 (1972)].

[58] L. P. Kadanoff and P. C. Martin, Ann. Phys. (N.Y.) 24, 419 (1963).

[59] One of the most crucial ideas in discussing critical phenomena is the idea that correlations can extend over very long distances. It is therefore the small wave numbers that contain the important collective information [see for example L. P. Kadanoff *et al.*, Rev. Mod. Phys. 39, 615 (1967)].

[60] J. V. Sengers, Ber. Bunsenges. Physik. Chem. 76, 234 (1972).

[61] To get an idea of the corrections needed one should see B. Chu, S. P. Lee, and W. Tscharnuter, Phys. Rev. A 7, 353 (1973); K. Kawasaki and S. M. Lo, Phys. Rev. Lett. 29, 48 (1972).

[62] P. Schofield, Proc. Phys. Soc. 88, 149 (1966).

[63] See Eq. (37) in Ref. 62.

[64] See Eq. (47) in Ref. 62.