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Properties of the kinetic memory function in classical fluids[*]

Dieter Forster

The James Franck Institute and The Department of Physics, The University of Chicago, Chicago, Illinois 60637

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The kinetic theory of gases and liquids is discussed in terms of the phase-space density $f(\vec{r}\vec{p}t)$ and its autocorrelation function. Associated with the latter is the memory function $\Sigma^{(c)}(\vec{k}z)$ troduced in an earlier paper. Here, we analyze those properties of $\Sigma^{(c)}$, for a classical system of structureless interacting particles, which can be obtained without approximation. Apart from symmetry- and stability-related properties, and those that express the conservation laws, we give microscopic derivations of (i) a new sum rule for $\Sigma^{(c)}(\vec{k}z)$ which involves only the static-pair-correlation function and (ii) two new relations between $\Sigma^{(c)}$ and thermodynamic derivatives, namely the specific heat c_v and the pressure derivative $(\partial p/\partial T)_n$. These exact relations, if fulfilled by an approximate model for $\Sigma^{(c)}$, guarantee that the approach to equilibrium is described in a thermodynamically and dynamically consistent manner. It is also shown how, for such a model, the transport coefficients are obtained.

I. INTRODUCTION

The difficulty in setting up a microscopic theory of the collective dynamics in classical liquids[1] is that there is no apparent small parameter in terms of which one could do perturbation theory. In contrast to low-temperature solids and quantum liquids, there are no weakly coupled elementary excitations. In contrast to the Boltzmann gases, there is no "kinetic" region in which all that matters are two-particle collisions, so that, in a gas, the dynamics essentially reduces to a two-body problem. If one is to describe dynamical fluctuations in a liquid in the region of wave vector $\vec{k}$ and frequency ω which is accessible—say, to inelastic neutron scattering—one faces the full complexity of a highly correlated many-body problem. In order to make any progress at all under these circumstances it is important that one have a formal framework into which can be incorporated, in a unified manner, what knowledge one has of the dynamics.

There are, in particular, two regions in $\vec{k}$, ω about which we have some firm theoretical knowledge. Fluctuations which vary slowly in space and time (small k and ω) are described by the Navier-Stokes equations of hydrodynamics.[2] And at very high frequeneies, we can extract information from the application of sum rules.[3] It is the purpose of this paper to present results that pertain to either one of these limiting regions, in a form which suggests a procedure that allows one to rationally interpolate between them.

There is one simplifying feature of liquid dynamics that makes these results pertinent and the procedure promising: the intermediate region of unknown dynamics is relatively small. Because the mean free path is only of the order of the potential range, hydrodynamics is a theory valid to much shorter distances and times than it is in a rare gas. For example, neutron scattering and molecular dynamics experiments[4] at liquid density contain evidence of the onset of sound propagation already at wavelengths of several angstroms.

As in the conventional kinetic theory of gases, we describe the dynamics in terms of equations of motion for the one-particle phase-space density $f(\vec{r}\vec{p}t)$. If such a theory is to be applicable to liquids, it must correct the traditional Boltzmann equation in several important respects. Important among these, the theory must be reversible and memory retaining at short times. At long times, the theory must render proper recognition of the potential contributions to stress tensor and energy density if it is to yield the hydrodynamic limit correctly. In an earlier paper,[5] we presented such an equation and discussed techniques for its analysis, for the particularly simple case of a weakly coupled fluid. Mazenko[6] has extended the equation to include hard-core interactions in gases.

Much of the technique used in Forster-Martin (FM), however, was more generally applicable. In this paper, we shall extend certain aspects of our earlier treatment to classical systems of spinless particles with short-range interaction of arbitrary strength and any density. In particular, I shall present a number of useful properties of the dynamical memory function $\Sigma^{(c)}(\vec{k}z)$ which can be derived from first principles. We will not discuss specific approximations here but hope to do so in a future publication. I believe, and hope to convince the reader, that our formalism presents a vehicle particularly suited to perform, in a systematic way, practical calculations which are guaranteed to correctly render at least all of those features of the dynamics of which we have some knowledge.

In one respect, this formulation is less ambitious than conventional kinetic theory: we are only interested in small fluctuations about thermal equilibrium. Therefore, we can discuss the dynamics in terms of the equilibrium-averaged autocorrelation function

$$
\begin{aligned}
S(\vec{r}-\vec{r}\,', t-t'; \vec{\xi}\vec{\xi}\,')
&= \int \frac{d\vec{k}}{(2\pi)^3} \int \frac{d\omega}{2\pi}\, S'(\vec{k}\omega; \vec{\xi}\vec{\xi}\,') e^{i\vec{k}(\vec{r}-\vec{r}\,')-i\omega(t-t')} \\
&= (m v_0)^6 \langle [f(\vec{r}\vec{p}t) - \langle f(\vec{r}\vec{p}t)\rangle_{eq}] \\
&\quad \times [f(\vec{r}\,'\vec{p}\,'t') - \langle f(\vec{r}\,'\vec{p}\,'t')\rangle_{eq}]\rangle_{eq}, \qquad (1.1)
\end{aligned}
$$

where the one-particle density "operator" is given by

$$f(\vec{r}\vec{p}t) = \sum_{\alpha} \delta(\vec{r} - \vec{r}^{\,\alpha}(t))\delta(\vec{p} - \vec{p}^{\,\alpha}(t)). \qquad (1.2)$$

$\vec{r}^{\,\alpha}(t)$ and $\vec{p}^{\,\alpha}(t)$ are the position and momentum of the αth particle at time t. $\vec{\xi}$ is a dimensionless momentum variable,

$$\vec{\xi} = \vec{p}/m v_0, \quad v_0^2 = (m\beta)^{-1},$$

where m is the particle mass and $\beta^{-1} = k_B T$ so that v_0 is the thermal velocity.

The function $S(\vec{r}t; \vec{\xi}\vec{\xi}\,')$ or its Fourier transform is all that is needed to understand a wide variety of scattering and computer dynamics experiments. For example, by integrating over the momentum variables we obtain the dynamical liquid-structure factor

$$
\begin{aligned}
S'(k\omega) &= \int d\vec{\xi} \int d\vec{\xi}\,' S'(\vec{k}\omega; \vec{\xi}\vec{\xi}\,') \\
&= \int d(\vec{r}-\vec{r}\,') \int_{-\infty}^{\infty} d(t-t') \\
&\quad \times e^{-i\vec{k}(\vec{r}-\vec{r}\,')+i\omega(t-t')} \\
&\quad \times [\langle n(\vec{r}t)n(\vec{r}\,'t')\rangle_{eq} - n^2], \qquad (1.3)
\end{aligned}
$$

which is measured in neutron and light scattering experiments. The momentum density correlation function and other important properties of the system are similarly obtained.

As usual, it is convenient to define the complex fluctuation function

$$S(\vec{k}z; \vec{\xi}\vec{\xi}\,') = \int \frac{d\omega}{2\pi} \frac{S'(\vec{k}\omega; \vec{\xi}\vec{\xi}\,')}{\omega - z}, \qquad (1.4)$$

which is analytic for $\mathrm{Im}z \neq 0$. For $\mathrm{Im}z > 0$, it is the Laplace transform of $S(\vec{k}, t; \vec{\xi}\vec{\xi}\,')$:

$$S(\vec{k}z; \vec{\xi}\vec{\xi}\,') = i \int_0^{\infty} dt\, e^{izt} S(\vec{k}, t; \vec{\xi}\vec{\xi}\,'). \qquad (1.5)$$

Since $S'(\vec{k}\omega; \vec{\xi}\vec{\xi}\,')$ is real, it can be obtained from $S(\vec{k}z; \vec{\xi}\vec{\xi}\,')$ by

$$S'(\vec{k}\omega; \vec{\xi}\vec{\xi}\,') = 2\,\mathrm{Im}\,S(\vec{k}z; \vec{\xi}\vec{\xi}\,')|_{z=\omega+i0}. \qquad (1.6)$$

Systematic procedures for calculating the matrix $S(\vec{k}z, \vec{\xi}\vec{\xi}\,')$, with indices $\vec{\xi}$ and $\vec{\xi}\,'$, must take proper account of the secular effects of collisions. Since excitations in the system appear in $S(\vec{k}z)$ in the form of resonance denominators, such procedures are always based upon approximations to its inverse. For this reason, we have in FM introduced a matrix $\Sigma(\vec{k}z)$ which is formally akin to the memory functions, or self-energy operators, used in a variety of contexts. $\Sigma(\vec{k}z)$ is defined by an equation of motion which is also basic to the present paper, namely

$$
\begin{aligned}
(z - v_0\vec{k}\cdot\vec{\xi})S(\vec{k}z; \vec{\xi}\vec{\xi}\,') - \Sigma(\vec{k}z; \vec{\xi}\bar{\vec{\xi}}\,')S(\vec{k}z, \bar{\vec{\xi}}\vec{\xi}\,') \\
= -S^0(\vec{k}; \vec{\xi}\vec{\xi}\,'), \qquad (1.7a)
\end{aligned}
$$

where

$$S^0(\vec{k}; \vec{\xi}\vec{\xi}\,') \equiv S(\vec{k}, t=0; \vec{\xi}\vec{\xi}\,'), \qquad (1.7b)$$

and where, here and throughout this paper, an integration $\int d\bar{\vec{\xi}}$ over the barred variable is implied.

In FM, we discussed, and to a certain extent solved, the approximation to Eq. (1.7a) which is obtained by calculating $\Sigma(\vec{k}z)$ to second order in the interaction strength. We demonstrated there that even in this simple approximation, Eq. (1.7a) leads to physically sensible results for a weakly coupled fluid. Of course, Eq. (1.7a) itself is completely rigorous, and indeed little more than a definition of the mass operator $\Sigma(\vec{k}z)$. Derivations have also been given by Akcasu and Duderstadt[7] whose approach is similar to the one presented here, by Lebowitz, Percus, and Sykes[8] who started from the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy for distribution functions, and by others.

The subjects of our present discussion, then, are the general properties of, or requirements upon, the matrix $\Sigma(\vec{k}z; \vec{\xi}\vec{\xi}\,')$ and thus the kinetic equation (1.7a), for arbitrary interaction strength λ and density n. Some of these properties have been previously obtained; they are included here for completeness. Other results, in particular those that concern the hydrodynamic limit, are new, to our knowledge. Also new is an additional sum rule which is useful because it is surprisingly simple. Since it is possible that some readers will be more interested in the general properties of $\Sigma(\vec{k}z)$ than in the details of their derivation, we shall present our results first; an attempt has been made to make Sec. II independently comprehensible. Details of derivation and proof are deferred to later sections.

We begin Sec. II by listing the symmetries of $\Sigma(\vec{k}z)$ (II A) including one which guarantees detailed balance. In II B we discuss a positivity property which is necessary, though not sufficient, to guarantee the dynamical stability of the system. The proper behavior at short times is guaranteed if $\Sigma(\vec{k}z)$ fulfills a series of sum rules, the first two of which are listed in II C. In II D we discuss the conservation laws in the context of this formulation. At long times for small z, the behavior of $\Sigma(\vec{k}z)$ must be such as to lead to local equilibrium and proper hydrodynamic behavior. This requirement results in a few new and interesting relations which connect matrix elements of $\Sigma(\vec{k}z)$ and thermodynamic derivatives. These relations, which guarantee in particular that the speed of sound is the Laplace one, $(dp/dmn)_s^{1/2}$, are exhibited in II E.

In Sec. III we shall show that these requirements upon $\Sigma(\vec{k}z)$ do indeed, in conjunction with Eq. (1.7a), lead to the modes of linearized hydrodynamics,[5, 6] and we give expressions for the transport coefficients. The technique used is the one introduced in FM, and we can thus be brief. It is similar to a method developed independently by Résibois.[9] In Sec. IV we shall give a microscopic expression for $\Sigma(\vec{k}z)$ in terms of projectors in Liouville space, previously obtained by Akcasu and Duderstadt.[7] This expression is essentially equivalent to a characterization of $\Sigma(\vec{k}z)$ by a class of irreducible diagrams. We shall then use this expression to prove the results claimed in Sec. II. An Appendix gives some details concerning the derivation of the sum rules.

Before embarking upon the discussion, we would like to separate $\Sigma(\vec{k}z)$ into two physically distinct parts, namely

$$\Sigma(\vec{k}z,\vec{\xi}\,\vec{\xi}')=\Sigma^{(s)}(\vec{k},\vec{\xi})+\Sigma^{(c)}(\vec{k}z,\vec{\xi}\,\vec{\xi}'), \tag{1.8}$$

where $\Sigma^{(c)}(\vec{k}z)$ vanishes as $z\to\infty$. The "static" part $\Sigma^{(s)}$ is rigorously given by the equation already displayed in FM,

$$\Sigma^{(s)}(\vec{k},\vec{\xi})=-nc(k)v_0(\vec{k}\cdot\vec{\xi})\phi(\xi), \tag{1.9}$$

where n is the particle density, and $\phi(\xi)$ is the Maxwellian velocity distribution

$$\phi(\xi)=(2\pi)^{-3/2}e^{-\xi^2/2}. \tag{1.10}$$

$\Sigma^{(s)}(\vec{k},\vec{\xi})$ accounts for the mean field on one particle owing to all the others; it is the equivalent of the Hartree-Fock self-energy in the quantum-mechanical theory.[10] $\Sigma^{(s)}(\vec{k},\vec{\xi})$ has the form of the linearized Vlasov operator, but with $-\beta v(r)$ replaced by the direct-correlation function $c(r)$. If we were to omit $\Sigma^{(c)}(\vec{k}z)$ from (1.7a) and (1.8), we would have a collisionless equation for $S(\vec{k}z)$ which can be solved exactly,[8] and is correct for very short times.

The influence of collisions and their memory effects are contained in $\Sigma^{(c)}(\vec{k}z)$. It is the properties of this part with which we will be mostly concerned. It is easy to see that $\Sigma^{(c)}(\vec{k}z)$ is analytic in z for $\mathrm{Im}z\neq 0$.[11] Since it vanishes as $z\to\infty$, we can write it in spectral form as

$$\Sigma^{(c)}(\vec{k}z,\vec{\xi}\,\vec{\xi}')=-\int\frac{d\omega}{2\pi}\,\frac{\Gamma(\vec{k}\omega,\vec{\xi}\,\vec{\xi}')}{\omega-z}. \tag{1.11a}$$

$\Gamma(\vec{k}\omega;\vec{\xi}\vec{\xi}')$ can be called a "damping matrix"; it can be shown to be real so that

$$\Gamma(\vec{k}\omega;\vec{\xi}\,\vec{\xi}')=-2\mathrm{Im}\,\Sigma^{(c)}(\vec{k}z;\vec{\xi}\,\vec{\xi}')|_{z=\omega+i0}. \tag{1.11b}$$

Let us also define the collision kernel

$$K(\vec{k},t-t';\vec{\xi}\,\vec{\xi}')=\int\frac{d\omega}{2\pi}\,e^{-i\omega(t-t')}\Gamma(\vec{k}\omega;\vec{\xi}\,\vec{\xi}'). \tag{1.12}$$

For $t\geqslant 0$, Eq. (1.7a) can then be written in the perhaps more intuitive form

$$\begin{aligned}[\partial_t+iv_0(\vec{k}\cdot\vec{\xi})]S(\vec{k}t,\vec{\xi}\,\vec{\xi}')+i\Sigma^{(s)}(\vec{k},\vec{\xi})\,S(\vec{k}t,\vec{\xi}\,\vec{\xi}')\\=-\int_0^t d\tau K(\vec{k},t-\tau;\vec{\xi}\,\bar{\vec{\xi}})\,S(\vec{k},\tau;\bar{\vec{\xi}}\,\vec{\xi}').\end{aligned} \tag{1.13}$$

Because of the connection between fluctuations and linear response, Eq. (1.13) can be understood as a non-Markovian, nonlocal kinetic equation for the singlet distribution function $\delta\langle f(\vec{r}\vec{\xi}t)\rangle_{\text{non eq}}\sim S(\vec{r}t;\vec{\xi}\,\vec{\xi}')$, for an initial state which is slightly displaced from equilibrium, and characterized by the momentum variable $\vec{\xi}'$. Note that as it stands, Eq. (1.13) is valid for all times, not just long times. Indeed, the fluctuation-dissipation theorem determines even the correct initial condition to (1.13). The theorem states that[3]

$$\begin{aligned}\partial_t S(\vec{r},t;\vec{\xi}\,\vec{\xi}')|_{t=0}&=\beta^{-1}(mv_0)^6\langle[f(\vec{r}\vec{p}0),f(\vec{0}\vec{p}'0)]_{\mathrm{PB}}\rangle\\&=-nv_0(\vec{\xi}\cdot\vec{\nabla})\phi(\xi)\delta(\vec{\xi}-\vec{\xi}')\delta(\vec{r}),\end{aligned} \tag{1.14}$$

where $[\,,\,]_{\mathrm{PB}}$ indicates the classical Poisson bracket. Together with (1.9) and (1.13), taken at $t=0$, where rhs vanishes, this determines $S^0(k)$ of (1.7b) to be

$$\begin{aligned}(1/n)S^0(k,\vec{\xi}\,\vec{\xi}')=\phi(\xi)\delta(\vec{\xi}-\vec{\xi}')\\+\phi(\xi)nh(k)\phi(\xi'),\end{aligned} \tag{1.15}$$

where

$$h(k)=c(k)[1-nc(k)]^{-1} \qquad (1.16)$$

is the Fourier transform of $h(r)=g(r)-1$, where $g(r)$ is the pair-correlation function. Obviously, it is easier to derive $S^0(k)$ first and then $\Sigma^{(s)}(k)$ from it. However, as in FM we wish to stress the viewpoint that systematic approximations ought to start by calculating $\Sigma(\vec{k}z)$ in some fashion, and then $S(\vec{k}z)$ from it by using (1.7a) and (1.14). This procedure should result in an approximation to $S(\vec{k}z)$ which is statically and dynamically consistent.

Finally, note that because of (1.15), Eq. (1.7a) can also be written in the equivalent but more symmetric form

$$[z-v_0(\vec{k}\cdot\vec{\xi})]S(\vec{k}z;\vec{\xi}\vec{\xi}')-\Sigma(\vec{k}z;\vec{\xi}\bar{\vec{\xi}})S(\vec{k}z;\bar{\vec{\xi}}\vec{\xi}')$$
$$=-n\phi(\xi)\delta(\vec{\xi}-\vec{\xi}'), \qquad (1.17)$$

where

$$\Sigma(\vec{k}z;\vec{\xi}\vec{\xi}')=\Sigma^{(s)}(\vec{k}z;\vec{\xi}\vec{\xi}')+\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}') \qquad (1.18)$$

with $\Sigma^{(c)}$ unchanged, but

$$\Sigma^{(s)}(\vec{k}z,\vec{\xi}\vec{\xi}')=nc(k)\phi(\xi)[z-v_0\vec{k}(\vec{\xi}+\vec{\xi}')]. \qquad (1.19)$$

This form is somewhat more useful, particularly for the discussion of symmetry and stability. To establish the equivalence of (1.7a) and (1.17) one makes use of particle conservation, see Eq. (2.13a) below.

II. GENERAL PROPERTIES OF $\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')$

In this section we will list all the general properties we are aware of for the nonlocal collision operator $\Sigma^{(c)}(\vec{k}z)$ or its spectral weight $\Gamma(\vec{k}\omega)$. Some of these, such as the symmetries and positivity listed in II A and II B, are generally known; they are included for the convenience of the reader. Proofs, where necessary, are given later. We shall sometimes refer to these properties as "requirements": they should be fulfilled by any approximate kinetic model if it is to correctly render all known features of the dynamics. At present, no such models seem to exist except for gases, but we hope to present a calculation of this type in a future publication. Of course, the $\Sigma^{(c)}$ for a weakly coupled fluid discussed in FM, has all the properties stated here, to order $(\beta v)^2$ where applicable, as does Mazenko's[6] low-density memory function.

Throughout Secs. II and III, we shall again use a convenient bracket notation for integrals in momentum space. The scalar product of two functions $\varphi(\vec{\xi})$, $\psi(\vec{\xi})$ is denoted by

$$\langle\varphi|\psi\rangle\equiv\int d\vec{\xi}\,\varphi^*(\vec{\xi})\phi(\vec{\xi})\psi(\vec{\xi}). \qquad (2.1a)$$

This product has the usual properties. We also define the "matrix elements" of $M(\vec{\xi}\vec{\xi}')$ by

$$\langle\varphi|M|\psi\rangle\equiv\int d\vec{\xi}\int d\vec{\xi}'\,\varphi^*(\vec{\xi})M(\vec{\xi}\vec{\xi}')$$
$$\times\phi(\xi')\psi(\vec{\xi}'). \qquad (2.1b)$$

A. Symmetries

We consider a fluid system which is invariant under translations, rotations, parity, and time reversal. The corresponding symmetry properties of $S'(\vec{k}\omega;\vec{\xi}\vec{\xi}')$ are easy to derive; they are given in FM. These properties are guaranteed if $\Gamma(\vec{k}\omega;\vec{\xi}\vec{\xi}')\phi(\xi')$ is (a) real, (b) even under $\vec{k}$, $\omega\to-\vec{k}$, $-\omega$, (c) symmetric with respect to $\vec{\xi}\leftrightarrow\vec{\xi}'$, (d) invariant under rotations-reflections. Rotational invariance and parity imply that $\Gamma(\vec{k}\omega;\vec{\xi}\vec{\xi}')$ depends only on the six scalar combinations of $\vec{\xi}$, $\vec{\xi}'$, and $\vec{k}$. Equivalently, we require that

$$\Sigma^{(c)}(\vec{k}z;\,)=-\Sigma^{(c)}(-\vec{k},-z;\,)=[\Sigma^{(c)}(\vec{k},z^*)]^*, \qquad (2.2a)$$

$$\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')\phi(\vec{\xi}')=\Sigma^{(c)}(\vec{k}z;\vec{\xi}'\vec{\xi})\phi(\xi). \qquad (2.2b)$$

(2.2b) is the property which establishes detailed balance. Because of conditions (a)–(d), $\Gamma(\vec{k}\omega)$ is Hermitian, and its left and right eigenfunctions are identical.[12]

B. Positivity

The damping matrix $\Gamma(\vec{k}\omega;\vec{\xi}\vec{\xi}')$ is positive (semi-) definite in the sense that

$$\int d\vec{\xi}\int d\vec{\xi}'\Psi^*(\vec{\xi})\Gamma(\vec{k}\omega;\vec{\xi}\vec{\xi}')\phi(\xi')\Psi(\vec{\xi}')$$
$$\equiv\langle\Psi|\Gamma(\vec{k}\omega)|\Psi\rangle\geq 0, \qquad (2.3)$$

for arbitrary functions $\Psi(\vec{\xi})$, and all $\vec{k}$, ω. In FM, (2.3) was explicitly shown to hold for weak potentials. That it is generally true can be easily shown, e.g., from Eq. (4.15) below. From (2.3), we immediately conclude that everywhere in the upper half of the complex z plane, the imaginary part of $-\Sigma^{(c)}(\vec{k}z)$ is positive,

$$\langle\Psi|-\mathrm{Im}\,\Sigma^{(c)}(\vec{k}z)|\Psi\rangle\geq 0 \quad \text{if } \mathrm{Im}\,z>0. \qquad (2.4)$$

In the lower-half z plane, it is negative. For arbitrary $\vec{k}$, ω, (2.3) and (2.4) vanish only if $\Psi(\vec{\xi})=1$.

Equation (2.4) is connected with the dynamical stability of the system. If (2.3) and (2.4) are satisfied, the correlation matrix $S(\vec{k}z)$ will have no singularities on the physical z plane, or its inverse $S^{-1}(\vec{k}z)$ will have no zeros, provided that in addition

$$1-nc(k)\geq 0 \quad \text{for all } k. \qquad (2.5)$$

All the poles of $S(\vec{k}z)$ appear then on a second sheet in the z plane, reached by analytic continuation through the branch cut along the real axis. These poles represent decaying modes. If, however, either (2.4) or (2.5) were to break down, in some approximation, a pair of poles would appear on the physical sheet and raise havoc.

We note that (2.3) and (2.5) guarantee stability only with respect to infinitesimal disturbances. For example, if a van der Waals gas below its critical point is undercooled, it will remain stable in this sense, i.e., locally stable, until the inflexion point is reached where $1-nc(k)=0$ at $k=0$. For T below this point, (2.5) is violated, the system becomes locally unstable with respect to density fluctuations, and the gas liquefies. Of course, the phase transition will normally happen at a somewhat higher temperature at which the system is globally unstable even though (2.3) and (2.5) continue to hold. Equations (2.3) and (2.5) are therefore a necessary, but not a sufficient, condition of stability.

C. Sum rules

We noted that $\Sigma^{(c)}(\vec{k}z)$ vanishes as $z\to\infty$. The coefficients of an asymptotic expansion in powers of $1/z$ are given by sum rules. Since these coefficients also establish an expansion of $K(\vec{k}, t)$ of Eq. (1.13) in powers of t, they determine the dynamics for short-time differences. The first of these moments, which has already been given in FM, is

$$\begin{aligned}\int \frac{d\omega}{2\pi}\,\Gamma(\vec{k}\omega;\, \vec{\xi}\,\vec{\xi}\,')\,\phi(\xi') &= \lim_{z\to\infty} z\Sigma^{(c)}(\vec{k}z;\, \vec{\xi}\,\vec{\xi}\,')\,\phi(\xi') \\ &\equiv \Sigma_\infty^{(c)}(\vec{k};\, \vec{\xi}\,\vec{\xi}\,')\,\phi(\xi') \\ &= \frac{n}{m}\int d\vec{r}\, g(r)\, v_{ij}(\vec{r})\,\partial_i\partial_j'\,\phi(\xi)\,\delta(\vec{\xi}-\vec{\xi}\,') \\ &\quad -\frac{n}{m}\int dr\,\cos(\vec{k}\cdot\vec{r}) \\ &\quad \times[g(r)v_{ij}(\vec{r})+\beta^{-1}c_{ij}(\vec{r})]\,\partial_i\partial_j'\,\phi(\xi)\,\phi(\xi'), \end{aligned}\tag{2.6}$$

where $v(r)$ is the pair potential, $v_{ij}(\vec{r})=\nabla_i\nabla_j v(r)$, etc., and $\partial_i = \partial/\partial\xi_i$.

Notice an interesting property of the matrix $\Sigma_\infty^{(c)}(\vec{k})$ defined by (2.6). As $k\to 0$, it is of the form

$$\Sigma_\infty^{(c)}(0;\, \vec{\xi}\,\vec{\xi}\,') = \nu^2[A_s(\vec{\xi}, \vec{\xi}\,') - \phi(\xi)(\vec{\xi}\cdot\vec{\xi}\,')]\,, \tag{2.7}$$

where ν is the friction constant first obtained by Kirkwood *et al.*[13]:

$$\nu^2 = (n/3m)\int d\vec{r}\, g(r)\,\nabla^2 v(r)\,. \tag{2.8}$$

A_s is an operator well known in the theory of Brownian motion and the Fokker-Planck equation,[14]

$$A_s(\vec{\xi}, \vec{\xi}\,') = -\vec{\partial}\,(\vec{\partial}+\vec{\xi}\,)\,\delta(\vec{\xi}-\vec{\xi}\,')\,. \tag{2.9}$$

The eigenvectors of this operator are the Hermite polynomial tensors. If we were to replace $\Sigma^{(c)}(\vec{k}z;\, \vec{\xi}\,\vec{\xi}\,')$ in Eq. (1.7a) by $\Sigma_\infty^{(c)}(\vec{k},\, \vec{\xi}\,\vec{\xi}\,')$, we would obtain a kinetic equation of the Fokker-Planck type which can be solved exactly.[15] There is, however, a serious deficiency to that equation: it conserves particle number and momentum, but it violates energy conservation.

The derivation of additional sum rules is straightforward in principle although the amount of algebra involved keeps one from doing it. We have, nonetheless, obtained a notably simple expression for the next sum rule which, remarkably, is also completely determined by the static pair correlation function. It is given by (see Appendix)

$$\begin{aligned}\int \frac{d\omega}{2\pi}\,\omega\Gamma(\vec{k}\omega;\, \vec{\xi}\,\vec{\xi}\,')\,\phi(\xi') &\equiv \Sigma_1^{(c)}(\vec{k},\, \vec{\xi}\,\vec{\xi}\,')\,\phi(\xi') \\ &= (nv_0/m)\int d\vec{r}\, g(r)\, v_{ij}(\vec{r})\,\partial_i\partial_j'(\vec{k}\cdot\vec{\xi}\,) \\ &\quad \times \phi(\xi)\,\delta(\vec{\xi}-\vec{\xi}\,') + (nv_0/m) \\ &\quad [A_{ijk}(\vec{k})\partial_k + A_{jik}(\vec{k})\partial_k']\,\partial_i\partial_j'\,\phi(\xi)\,\phi(\xi'), \end{aligned}\tag{2.10a}$$

where

$$A_{ijk}(\vec{k}) = \int d\vec{r}\,\sin(\vec{k}\cdot\vec{r})\, g_i(\vec{r})\, v_{jk}(\vec{r})\,. \tag{2.10b}$$

This expression is still sufficiently simple so that it can be useful to restrict a realistic kinetic model. Additional sum rules, however, become increasingly complicated as to their momentum dependence, and since they involve triple and higher static correlation functions about which little is accurately known, their practical usefulness is doubtful. The two sum rules given here each summarizes, of course, many sum rules that one obtains in a description by a finite number of variables. It may be worth pointing out, therefore, that traditional applications of sum rules, in theories which have used "generalized hydrodynamics" procedures,[4] have not exhausted the content of even Eq. (2.6).

In a system of hard spheres, the sum rules fail. Their failure is associated with the fact that in a discontinuous potential, a particle can change its momentum instantaneously. Correspondingly, there is an essentially infinite frequency in the system. In this case, it is no longer true that $\Sigma^{(c)}(\vec{k}z)$

vanishes as $z\to\infty$. Indeed, for a low density system of hard spheres Mazenko *et al.*[16] have shown that $\Sigma^{(c)}(\vec{k}z)$ is, in fact, frequency independent.

D. Conservation laws

The existence of hydrodynamics is intimately tied to the conservation laws for particle number, momentum, and energy, and thus to the behavior of $\Sigma^{(c)}(\vec{k}z)$ in the region of small k and z. In FM, Sec. III, we showed how the conservation laws are represented within a kinetic equation of the form (1.7a). Since much of that discussion was quite general, not restricted to a weak potential, we shall be brief here.

The crucial property is the following: Let us define the matrix

$$K(\vec{\xi},\vec{\xi}')=\lim_{z\to i0}\lim_{k\to 0} i\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')\,. \tag{2.11}$$

From (2.2) one concludes that $K(\vec{\xi},\vec{\xi}')\phi(\xi')$ is real, and symmetric. Moreover, in Sec. IV we will show that, at any density and interaction strength,

$$\int d\vec{\xi}\{1,\xi,\xi^2\}K(\vec{\xi},\vec{\xi}')=0\,. \tag{2.12}$$

$K(\vec{\xi},\vec{\xi}')$ has therefore the properties of the local (in both space and time) collision operator of a linearized Boltzmann-like equation: If we were to replace $\Sigma(\vec{k}z)$ in Eq. (1.7a) by K we would have a Markovian kinetic equation which conserves the particle number, momentum, and kinetic energy.

According to (2.12), $K(\vec{\xi},\vec{\xi}')$ has five eigenstates with eigenvalue zero. Since there is no additional local conservation law in a simple liquid, we require moreover that all other eigenvalues of $K(\vec{\xi},\vec{\xi}')$ are nonzero and in fact positive as a consequence of (2.4). (property A).

In a rare gas, the third Eq. (2.12) is an immediate expression of kinetic energy conservation. That the equation also holds at arbitrary density is not trivial, and requires proof (see Sec. IV B).

In dense fluids, it is the total energy which is conserved, of course, not the kinetic energy, and there are potential contributions to stress tensor and energy current. As in FM, the requisite properties of $\Sigma^{(c)}(\vec{k}z)$ can be written in the following form:

$$\int d\vec{\xi}\,\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')=0\,, \tag{2.13a}$$

$$\int d\vec{\xi}\,\xi_i\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')=v_0k_jT_{ij}(\vec{k}z;\vec{\xi}')\,, \tag{2.13b}$$

$$\int d\vec{\xi}(\tfrac{1}{2}\xi^2)\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')=-zE(\vec{k}z;\vec{\xi}')+v_0\vec{k}\cdot\vec{J}^{\epsilon}(\vec{k}z;\vec{\xi}')\,, \tag{2.13c}$$

where the functions $T_{ij}, E,$ and J_i^{ϵ} have definite limits as $k\to 0$ and $z\to i0$. In other words, we require that the following functions be finite, well-behaved functions in $\vec{\xi}$ space:

$$T_{ij}(\vec{\xi}')=v_0^{-1}\lim_{z\to i0}\lim_{k\to 0}\frac{\partial}{\partial k_j}\int d\vec{\xi}\,\xi_i\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')\,, \tag{2.14a}$$

$$E(\xi')=-\lim_{z\to i0}\lim_{k\to 0}\frac{\partial}{\partial z}\int d\vec{\xi}\,\tfrac{1}{2}\xi^2\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')\,, \tag{2.14b}$$

$$J_i^{\epsilon}(\vec{\xi}')=v_0^{-1}\lim_{z\to i0}\lim_{k\to 0}\frac{\partial}{\partial k_i}\int d\vec{\xi}\,\tfrac{1}{2}\xi^2\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')\,. \tag{2.14c}$$

From (2.2) it is easy to see that all three (or four, actually) functions are real.

Clearly, (2.13) and (2.14) impose a somewhat stronger restriction on $\Sigma^{(c)}(\vec{k}z)$ than does (2.12), in that a degree of analyticity near vanishing $\vec{k}$ and z is required.[17] While this "analyticity", i.e., (2.15) is exceedingly difficult to prove—we have not rigorously done so—it is certainly a very plausible consequence of the local character of the conserved densities. Hydrodynamics will only result, or the transport coefficients will only be finite, if the limits in (2.14) exist.

The connection of Eqs. (2.13) with the continuity equations is obvious. Consider momentum conservation. Since the momentum density [rather, its correlation function with $f(\vec{r}'\vec{\xi}'t')$] is given by

$$g_i(\vec{k}z;\vec{\xi}')=mv_0\int d\vec{\xi}\,\xi_iS(\vec{k}z;\vec{\xi}\vec{\xi}')\,, \tag{2.15}$$

Eqs. (1.7) and (2.13b) lead to a continuity equation of the form

$$zg_i(\vec{k}z;\vec{\xi}')-k_j\tau_{ij}(\vec{k}z;\vec{\xi}')=-g_i(\vec{k};\vec{\xi}')\,, \tag{2.16}$$

where the initial value is, correctly, given by

$$g_i(\vec{k};\vec{\xi}')=-mnv_0\xi_i'\phi(\xi')\,, \tag{2.17}$$

and the stress tensor (correlation function) by

$$\tau_{ij}(\vec{k}z;\vec{\xi}')=mv_0^2\int d\vec{\xi}[\xi_i\xi_j-nc(k)\delta_{ij}+T_{ij}(\vec{k}z;\vec{\xi})]S(\vec{k}z;\vec{\xi}\vec{\xi}')\,. \tag{2.18}$$

$T_{ij}(\vec{k}z;\vec{\xi}')$ therefore incorporates collisional contributions to the stress tensor. The functions $E(\vec{k}z;\vec{\xi})$ and $\vec{J}^{\epsilon}(\vec{k}z;\vec{\xi})$ similarly represent potential contributions to the energy and energy current densities. Note, incidentally, that in a simple liquid the microscopic stress tensor is symmetric so that

$$T_{ij}(\vec{k}z;\,\vec{\xi})=T_{ji}(\vec{k}z;\,\vec{\xi})\,. \tag{2.19}$$

As usual, this property guarantees angular momentum conservation.

E. Local equilibrium requirements

At long times, a many-particle system will establish local equilibrium, as a result of many conserving collisions. In this region, the dynamics will be dominated by the five hydrodynamic modes: two propagating sound waves and three diffusive modes describing the transport of heat and of transverse momentum. These modes are dynamical in origin; their properties are chiefly determined by properties of the collision operator $\Sigma^{(c)}(\vec{k}z)$. On the other hand, if hydrodynamics is correct these modes are characterized by certain thermodynamic derivatives: the speed of sound is $c=(dp/dmn)_s^{1/2}$, and the coupling of sound and heat is determined by the specific-heat ratio c_p/c_v. Information about these parameters must be buried in properties of $\Sigma^{(c)}(\vec{k}z)$.

It is true, of course, that full information about the thermodynamics is also contained in the mean-field part $\Sigma^{(s)}(\vec{k})$ of the mass operator, notably in the direct correlation function $c(k)$. As was discussed in FM, this imposes a problem of consistency of $\Sigma^{(s)}$ and $\Sigma^{(c)}$ for all those approximations which aim at a proper description of the hydrodynamic limit. The equations which we are about to write down should be helpful in achieving this consistency of statics and dynamics.

The crucial properties are two statements about matrix elements of $\Sigma^{(c)}(\vec{k}z)$ which we will prove in Sec. IV C. These statements are

$$\left(\frac{dp}{dT}\right)_n=nk_B\left[1+\frac{1}{v_0}\left(\frac{3}{2}\right)^{1/2}\lim_{z\to i0}\lim_{k\to 0}\frac{1}{k_3}\times\langle\xi_3|\Sigma^{(c)}(\vec{k}z)|\epsilon\rangle\right] \tag{2.20}$$

and

$$mc_v=\tfrac{3}{2}k_B\left[1-\lim_{z\to i0}\lim_{k\to 0}\frac{\partial}{\partial z}\langle\epsilon|\Sigma^{(c)}(\vec{k},z)|\epsilon\rangle\right], \tag{2.21}$$

where $\epsilon(\xi)=(\xi^2-3)/\sqrt{6}$ is the kinetic-energy "state", and mc_v the specific heat per particle at constant volume,

$$mnc_v=\frac{T}{V}\left(\frac{dS}{dT}\right)_n.$$

It is clear why the two statements (2.20) and (2.21) are necessary. If we were to omit $\Sigma^{(c)}(\vec{k},z)$ from Eq. (1.7a), we would derive the familiar collisionless sound mode with the isothermal speed since

$$\left(\frac{dp}{dmn}\right)_T=v_0^2\lim_{k\to 0}[1-nc(k)]\,. \tag{2.22}$$

The collision operator $\Sigma^{(c)}(\vec{k},z)$ couples energy and density fluctuations and converts this to the correct isentropic speed since

$$c^2=\left(\frac{dp}{dmn}\right)_S=\left(\frac{dp}{dmn}\right)_T+\frac{T}{(mn)^2c_v}\left(\frac{dp}{dT}\right)_n^2.$$

In terms of the functions defined in Eqs. (2.14), we can write (2.20) and (2.21) in the form

$$\begin{aligned}\left(\frac{dp}{dT}\right)_n&=nk_B(1+\langle T_{33}|\tfrac{1}{2}\xi^2\rangle)\\&=nk_B(1+\langle J_3^\epsilon|\xi_3\rangle)\,,\end{aligned} \tag{2.23}$$

and

$$mc_v=k_B(\tfrac{3}{2}+\langle E|\tfrac{1}{2}\xi^2\rangle)\,. \tag{2.24}$$

The second line of Eq. (2.23) can be understood as an expression of Galileian invariance.

This concludes our presentation of the general properties of, or requirement upon, the collision operator $\Sigma^{(c)}(\vec{k},z)$. In Sec. III, we shall show that in the collision-dominated regime of small k and z, these properties lead to the correct hydrodynamic behavior, and we will deduce rigorous expressions for the transport coefficients in terms of $\Sigma^{(c)}(\vec{k},z)$.

III. HYDRODYNAMIC MODES

The experiments which one normally performs on liquids, measure properties which are obtained by contracting the matrix $S(\vec{k}z;\,\vec{\xi}\,\vec{\xi}')$ in momentum space. Most importantly, the complex density-density fluctuation function

$$g_{nn}(kz)=\int d\vec{\xi}\int d\vec{\xi}'\,S(\vec{k}z;\,\vec{\xi}\,\vec{\xi}')\,, \tag{3.1}$$

whose imaginary part, for $z=\omega+i0$, is $\frac{1}{2}$ times the dynamical liquid-structure factor $S'(k,\omega)$ defined in (1.3); the momentum-density fluctuation function

$$\begin{aligned}g_{ij}(\vec{k},z)&=(mv_0)^2\int d\vec{\xi}\int d\vec{\xi}'\,\xi_i S(\vec{k}z;\,\vec{\xi}\,\vec{\xi}')\xi_j'\\&=i\int_0^\infty dt\,e^{izt}\int d\vec{r}\,e^{-i\vec{k}\vec{r}}\langle g_i(\vec{r}t)g_j(00)\rangle\,,\end{aligned} \tag{3.2}$$

where $g_i(\vec{r}t)$ is the microscopic momentum density, and the second line of Eq. (3.2) holds only for $\mathrm{Im}z>0$.

For small wave numbers k and frequencies z, these functions can be calculated from the linearized Navier-Stokes equations of hydrodynamics. Let us first write down the resulting rigorous limiting expressions, discussed in detail by Kadanoff and Martin.[2] The transverse part of the momentum-density fluctuation function, $g_t(kz) \equiv g_{xx}(kz)$ (for $\vec{k}$ in z direction) is dominated by the shear diffusion pole,

$$g_t(kz) = \frac{-mn\beta^{-1}}{z + ik^2\eta/mn}, \quad \mathrm{Im}\, z > 0 \tag{3.3}$$

where η is the shear viscosity. The longitudinal modes of attenuated sound propagation and heat diffusion both contribute to $g_{nn}(kz)$, in the form

$$g_{nn}(kz) = -n\beta^{-1}\left(\frac{dn}{dp}\right)_T \left(\frac{1 - c_v/c_p}{z + ik^2 D_T} + \frac{c_v}{c_p} \times \frac{z + ik^2[\Gamma + D_T(c_p - c_v)/c_v]}{z^2 - c^2k^2 + izk^2\Gamma}\right), \tag{3.4}$$

where mc_p and mc_v are the specific heats per atom at constant pressure and volume,

$$mnc_p = \frac{T}{V}\left(\frac{dS}{dT}\right)_p, \quad mnc_v = \frac{T}{V}\left(\frac{dS}{dT}\right)_n, \tag{3.5}$$

c is the isentropic sound velocity,

$$c^2 = \left(\frac{dp}{dmn}\right)_S = \frac{c_p}{c_v}\left(\frac{dp}{dmn}\right)_T, \tag{3.6}$$

and the damping constants are given by

$$D_T = \frac{\kappa}{mnc_p}, \Gamma = \frac{\frac{4}{3}\eta + \zeta}{mn} + D_T\left(\frac{c_p}{c_v} - 1\right), \tag{3.7}$$

in terms of the heat conductivity κ, and the shear and bulk viscosities η and ζ.

For a normal liquid, Eqs. (3.3) and (3.4) are rigorous for small k and z. They must therefore be compatible with our fundamental kinetic equation (1.7a). In this section, we shall show that this is indeed the case. In deriving (3.3) and (3.4) from (1.7a) we will obtain rigorous expressions for the transport coefficients κ, η, and ζ in terms of the collision operator $\Sigma^{(c)}(\vec{k}z)$.

It will be apparent that our derivation relies *only* on the properties of $\Sigma^{(c)}(\vec{k}z)$ stated in Sec. II. This being so, our results will not only apply to the rigorous kinetic equation—hardly the most interesting case—but to any approximate model whose collision operator $\Sigma^{(c)}_{\mathrm{appr}}(\vec{k}z)$ is in line with Sec. II.

Following the procedure already used in FM, we define the matrix

$$G_{\mu\nu}(\vec{k}z) = \langle \varphi_\mu | [z - \omega^0(\vec{k}) - \Sigma(\vec{k}z)]^{-1} | \varphi_\nu \rangle , \tag{3.8}$$

where

$$\omega^0(\vec{k}; \vec{\xi}\vec{\xi}') \equiv v_0(\vec{k}\cdot\vec{\xi})\delta(\vec{\xi} - \vec{\xi}') . \tag{3.9}$$

$G_{\mu\nu}(\vec{k}z)$ is the formal solution of the kinetic equation (1.7a), projected onto the five "hydrodynamic" variables,

$$\{\varphi_\mu(\vec{\xi})\} = \{n(\vec{\xi}); g_l(\vec{\xi}); \epsilon(\vec{\xi}); g_t(\vec{\xi}); g_t'(\vec{\xi})\} = \{1; \xi_3; (\xi^2 - 3)/\sqrt{6}; \xi_1; \xi_2\} . \tag{3.10}$$

Clearly,

$$g_{nn}(kz) = \frac{-n}{1 - nc(k)} G_{11}(kz) , \tag{3.11a}$$

and

$$g_t(kz) = -nm\beta^{-1} G_{44}(kz) . \tag{3.11b}$$

From these two functions, all thermodynamic and transport coefficients can be obtained. To do so, we have to isolate the hydrodynamic singularities in $G_{\mu\nu}(\vec{k}z)$, which is accomplished by use of the projection operator in $\vec{\xi}$ space,

$$P = \sum_{\nu=1}^{5} | \varphi_\nu \rangle \langle \varphi_\nu | \equiv 1 - Q , \tag{3.12}$$

which projects onto the subspace where K [see Eqs. (2.11) and (2.12)] vanishes: $PK = KP = 0$. It is then easy to see that (3.8) becomes

$$[z\delta_{\mu\sigma} - \Omega_{\mu\sigma}(\vec{k}z)]G_{\sigma\nu}(\vec{k}z) = \delta_{\mu\nu} , \tag{3.13}$$

where

$$\Omega(\vec{k}z) = \Omega''(\vec{k}z) + \Omega'(\vec{k}z) , \tag{3.14a}$$

$$\Omega''_{\mu\nu}(\vec{k}z) = \langle \varphi_\mu | \tilde{\Sigma}(\vec{k}z) | \varphi_\nu \rangle , \tag{3.14b}$$

$$\Omega'_{\mu\nu}(\vec{k}z) = \langle \varphi_\mu | \tilde{\Sigma}(\vec{k}z) Q [z - Q\tilde{\Sigma}(\vec{k}z)Q]^{-1} \times Q\tilde{\Sigma}(\vec{k}z) | \varphi_\nu \rangle , \tag{3.14c}$$

and $\tilde{\Sigma}(\vec{k}z) \equiv \omega^0(\vec{k}) + \Sigma(\vec{k}z)$. For any theory which has property A the operator $Q(z - Q\tilde{\Sigma}Q)^{-1}Q$ is nonsingular for small k, z, and $\Omega(\vec{k}z)$ can therefore be expanded in terms of $\vec{k}$ and z.

A. Transverse modes

On the basis of the properties stated in Sec. I, such an expansion is easily accomplished. We first note that because of rotational symmetry, (2.2), longitudinal ($\mu = 1, 2, 3$) and transverse ($\mu = 4, 5$) modes are not coupled. The tranverse contributions to $\Omega(\vec{k}z)$ are at least of order k^2, and to this order are given by ($\Omega_{44} = \Omega_{55} = \Omega_t$; $\Omega_{45} = 0$)

$$\Omega_t(kz) = -ik^2(\eta'' + \eta')/mn , \tag{3.15}$$

where

$$\frac{\eta''}{mn} = \tfrac{1}{2} \lim_{\omega\to 0} \lim_{k\to 0} \frac{1}{k^2} \langle \xi_1 | \Gamma(\vec{k}\omega) | \xi_1 \rangle , \tag{3.16a}$$

and

$$\eta'/mn = v_0^2 \langle \xi_1\xi_3 + T_{13} | QK^{-1}Q | \xi_1\xi_3 + T_{13} \rangle . \tag{3.16b}$$

As a consequence of Eq. (2.4), both η' and η'' are positive. The transverse momentum density fluctuation function, $g_t(kz)$, is therefore given, to hydrodynamic order,[18] by the expression (3.3) where the shear viscosity is

$$\eta = \eta' + \eta'' . \tag{3.16c}$$

The separation of transport coefficients into two contributions, which might be called "direct"(η'') and "indirect"(η') is characteristic for the kinetic-theory approach. In FM, we found this separation for the more explicitly tractable weakly coupled fluid. It is noteworthy that both contributions are positive.

B. Longitudinal modes

The expansion of the longitudinal part ($\mu, \nu = 1, 2, 3$) of $\Omega_{\mu\nu}(\vec{k}z)$ proceeds in an analogous fashion. First-order contributions, i.e, those linear in $\vec{k}$ and z, stem from (3.14b) only. It is here where the properties (2.20) and (2.21) of $\Sigma^{(c)}(\vec{k}z)$ enter—due to these relations, $\Omega_{\mu\nu}(\vec{k}z)$ is entirely thermodynamic to first order. It is given by $v_0 k \Omega^{[1]}_{\mu\nu}(x)$ with $x = z/v_0 k$, where

$$\Omega^{[1]}_{\mu\nu} = \begin{pmatrix} 0 & 1 & 0 \\ 1 - nc(0) & 0 & \left(\frac{2}{3}\right)^{1/2} \left(\frac{dp}{dT}\right)_n \Big/ nk_B \\ 0 & \left(\frac{2}{3}\right)^{1/2} \left(\frac{dp}{dT}\right)_n \Big/ nk_B & x(1 - \frac{2}{3} mc_v/k_B) \end{pmatrix} . \tag{3.17}$$

If this contribution to $\Omega_{\mu\nu}(\vec{k}z)$ is inserted into (3.13), one obtains a pair of propagating sound modes with $z = \pm ck$ where c is the hydrodynamically correct adiabatic sound speed of Eq. (3.6).

To second order in k and z, making liberal use of symmetry, we get

$$\Omega_{\mu\nu}(\vec{k}, z) = v_0 k \Omega^{[1]}_{\mu\nu}(x) + (v_0 k)^2 \Omega^{[2]}_{\mu\nu}(x) , \tag{3.18}$$

where $\Omega^{[2]}_{\mu\nu}(x)$ is of the form

$$\Omega^{[2]}_{\mu\nu}(x) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -i\gamma_{22} & ix\gamma_{23} \\ 0 & ix\gamma_{23} & -i\gamma_{33} - ix^2 \cdot \bar{\gamma}_{33} \end{pmatrix} . \tag{3.19}$$

Because of Eq. (2.4), the three coefficients γ_{22}, γ_{33}, and $\bar{\gamma}_{33}$ are positive and γ_{23} is real. Each of these coefficients consists of two additive terms, one each from (3.14b) and (3.14c); they determine the transport coefficients. If one inserts (3.17)–(3.19) into (3.13) and solves the resulting equation for $g_{nn}(kz)$, one obtains precisely the hydrodynamic expression[19] (3.4), with the following identification of transport coefficients:

heat conductivity:

$$\kappa = \kappa' + \kappa'' , \tag{3.20a}$$

$$\frac{\kappa''}{nk_B} = \frac{1}{2} \lim_{k \to 0} \lim_{\omega \to 0} \frac{1}{k^2} \langle \tfrac{1}{2}\xi^2 | \Gamma(\vec{k}\omega) | \tfrac{1}{2}\xi^2 \rangle , \tag{3.20b}$$

$$\kappa'/nk_B = v_0^2 \langle \tfrac{1}{2}\xi_3(\xi^2 - 3) + J_3^\epsilon | QK^{-1}Q | \times \tfrac{1}{2}\xi_3(\xi^2 - 3) + J_3^\epsilon \rangle ; \tag{3.20c}$$

bulk viscosity:

$$\zeta = \zeta' + \zeta'' , \tag{3.21a}$$

$$\frac{\frac{4}{3}\eta'' + \zeta''}{mn} = \frac{1}{2} \lim_{\omega \to 0} \lim_{k \to 0} \frac{1}{k^2} \times \left\langle \xi_3 + \alpha \left(\frac{v_0 k}{\omega}\right) \frac{\xi^2}{2} \middle| \Gamma(\vec{k}\omega) \middle| \xi_3 + \alpha \left(\frac{v_0 k}{\omega}\right) \frac{\xi^2}{2} \right\rangle , \tag{3.21b}$$

$$\zeta'/mn = v_0^2 \langle T - \alpha E | QK^{-1}Q | T - \alpha E \rangle , \tag{3.21c}$$

where

$$T(\xi) = \frac{1}{3} \sum_{i=1}^{3} [\xi_i^2 + T_{ii}(00; \xi)] \tag{3.22}$$

is the scalar part of the "stress tensor," and

$$\alpha = \frac{1}{mnc_v} \left(\frac{dp}{dT}\right)_n = \left(\frac{dp}{d\epsilon}\right)_n \tag{3.23}$$

is the thermodynamic derivative of the pressure with respect to the energy density, at constant volume. This gives Eq. (3.21c) a transparent interpretation: If we identify T and E, respectively, with the potential contributions to stress tensor (pressure) and energy density, then the primed part of the bulk viscosity is due to fluctuations of the quantity

$$\delta T - \left(\frac{dp}{d\epsilon}\right)_n \delta E \sim \delta p|_\epsilon , \tag{3.24}$$

describing stress-tensor fluctuations which take place at constant energy density, allowing, however, for the collisional transfer of kinetic into potential energy.

An equally transparent interpretation cannot be easily given, at the kinetic-theory level, to the "direct" contribution to the longitudinal diffusivity, $D_l'' = (\frac{4}{3}\eta'' + \zeta'')/mn$. For example, while it is clear from (3.21b) and (2.3) that D_l'' is positive—a stability requirement—it is not apparent that ζ'' itself is positive. That is, nevertheless, true. We defer discussion to Sec. IV D where ζ'' will be given a form as physically transparent as that of ζ' in Eq. (3.21c).

This concludes our discussion of the hydrodynamic limit of the kinetic equation (1.7a). It is clear that our derivation relies only on the general properties of $\Sigma(\vec{k}z)$ stated in Sec. II (excluding II C). Any kinetic model of the form (1.7a) but with some approximate kernel $\Sigma^{(c)}(\vec{k}z)$, will therefore lead to results in agreement with the predictions of the Navier-Stokes equations so long as the approximate kernel satisfies the properties of Sec. II.

IV. MICROSCOPIC FORMULATION AND PROOFS

In this section, we will give a microscopic expression, simple only in appearance, for the collision operator $\Sigma^{(c)}(\vec{k}z)$. This expression, Eq. (4.16) below, has been earlier derived by Akcasu and Duderstadt[7] along similar lines. The reader who is aware of the insolubility of even the classical three-body problem will not expect us to calculate, for an infinite system, $\Sigma^{(c)}(\vec{k}z)$ explicitly although manageable approximations, appropriate mainly for gases, can be given.[5-7] Our expression for $\Sigma^{(c)}(\vec{k}z)$ is therefore quite formal; however, the reader will be pleased to see that it is just manageable enough to provide some further insight into the separation of the dynamical many-body problem accomplished by Eq. (1.7a). And, importantly, manageable enough to supply microscopic proofs of all the properties of $\Sigma^{(c)}(\vec{k}z)$ states in Sec. II.

The reader is cautioned not to confuse the bracket notation (and projectors) for thermal averages used in Sec. IV, with the one for momentum integrals used in Secs. II and III, nor the projector $\tilde{Q}$ used here, with Q used in Secs. II and III.

A. Formal microscopic expression for $\Sigma^{(c)}(\vec{k}z;\vec{p}\vec{p}\,')$

An expression for $\Sigma^{(c)}$ can be obtained by application of Mori's[20] projector scheme to the correlation function $S(\vec{r}t, \vec{p}\vec{p}\,')$. This scheme begins with the recognition that a matrix $S_{\lambda\kappa}(t)$ of correlation functions of dynamical variables $A_\lambda(t)$ can be written in the form (taking $\langle A_\lambda\rangle = 0$),

$$S_{\lambda\kappa}(t) = \langle A_\lambda(t) A_\kappa(0)\rangle_{\text{eq}} = \langle A_\lambda | e^{-iLt} | A_\kappa\rangle , \tag{4.1}$$

or for the Laplace transform, defined as in (1.5),

$$S_{\lambda\kappa}(z) = \langle A_\lambda | \frac{-1}{z-L} | A_\kappa\rangle . \tag{4.2}$$

Here L is the Liouville operator, defined by $\partial_t A_\lambda(t) = iLA_\lambda(t)$, and the brackets indicate thermal averages according to

$$\langle A | B\rangle \equiv \langle A^* B\rangle_{\text{eq}} . \tag{4.3}$$

Defining the projection operator

$$\tilde{P} = \sum_{\lambda,\kappa} |A_\lambda\rangle\, (S^0)^{-1}_{\lambda\kappa} \langle A_\kappa | \equiv 1 - \tilde{Q} , \tag{4.4}$$

where $S^0_{\lambda\kappa} = \langle A_\lambda | A_\kappa\rangle = S_{\lambda\kappa}\ (t=0)$, and using the operator identity

$$\frac{1}{z - L\tilde{Q} - L\tilde{P}} = \frac{1}{z - L\tilde{Q}} + \frac{1}{z - L\tilde{Q}}\, L\tilde{P}\, \frac{1}{z-L} ,$$

one easily casts (4.2) into the "equation of motion" form,

$$[z\delta_{\lambda\sigma} - \Omega_{\lambda\sigma} - \Sigma^{(c)}_{\lambda\sigma}(z)] S_{\sigma\kappa}(z) = -S^0_{\lambda\kappa} , \tag{4.5a}$$

with the identification

$$\Omega_\lambda = i\langle \dot{A}_\lambda A_\sigma\rangle (S^0)^{-1}_{\sigma\kappa} , \tag{4.5b}$$

$$\Sigma^{(c)}_{\lambda\kappa}(z) = \langle \dot{A}_\lambda | \tilde{Q}\, \frac{1}{z - \tilde{Q}L\tilde{Q}}\, \tilde{Q} | \dot{A}_\sigma\rangle\, (S^0)^{-1}_{\sigma\kappa} . \tag{4.5c}$$

This scheme is easily applied[7] to our correlation "matrix"

$$S(\vec{r}\vec{p}, \vec{r}\,'\vec{p}\,'; z) = \langle f(\vec{r}\vec{p}) | \frac{-1}{z-L} | f(\vec{r}\,'\vec{p}\,')\rangle , \tag{4.6}$$

where Σ_ν is replaced by $\int d\vec{p} \int d\vec{r}$ where appropriate. In this section, we find it more convenient to use physical momenta $\vec{p}$ instead of $\vec{\xi} = \vec{p}/mv_0$ used before. To unclutter the equations, we shall also omit vector arrows over $\vec{r}$ and $\vec{p}$ where these appear as arguments. Since

$$\langle f(rp)\rangle = n\phi(p) = n(mv_0)^{-3} (2\pi)^{-3/2}\, e^{-\beta(p^2/2m)} \tag{4.7}$$

is independent of $\vec{r}$, one conveniently accounts for the requirement "$\langle A_\lambda\rangle = 0$" by interpreting, for spatial Fourier transforms, all $k=0$ values as $\lim k \to 0$.

We first note that the Liouville operator L, microscopically given by

$$iL = \sum_\alpha \frac{\vec{p}^{\,\alpha} \cdot \vec{\nabla}^\alpha}{m} - \frac{1}{2} \sum_{\alpha\neq\beta} \vec{\nabla} v(r^\alpha - r^\beta) \cdot (\vec{\partial}^\alpha - \vec{\partial}^\beta) , \tag{4.8}$$

where $\vec{\nabla}^\alpha = \partial/\partial\vec{r}^{\,\alpha}$ and $\vec{\partial}^\alpha = \partial/\partial\vec{p}^{\,\alpha}$, can also be written, in our case, in the more convenient field form

$$iL = \int d\vec{\mathrm{r}}\, d\vec{\mathrm{p}} \left[-\frac{\vec{\mathrm{p}}\vec{\nabla}}{m} + \int d\vec{\bar{\mathrm{r}}}\vec{\nabla} v(r-\bar{r})n(\bar{r}) \cdot \vec{\partial} \right] \times f(rp)\,\frac{\delta}{\delta f(rp)}, \tag{4.9}$$

since the field $f(rpt)$ is canonical, obeying the closed equation of motion

$$\partial_t f(rpt) = -\frac{\vec{\mathrm{p}} \cdot \vec{\nabla}}{m} f(rpt) + [\vec{\nabla} v(r-\bar{r}) \cdot \vec{\partial} n(\bar{r}t)] \times f(rpt)\,. \tag{4.10}$$

Here and henceforth, an integral over barred variables is implied. Further, the equilibrium correlation function

$$S^0(rp, r'p') = n\phi(p)\delta(p-p')\delta(r-r') + n^2 h(r-r')\phi(p)\phi(p') \tag{4.11}$$

has the simple inverse

$$(S^0)^{-1}(rp, r'p') = [n\phi(p)]^{-1}\delta(p-p') \times \delta(r-r') - c(r-r')\,. \tag{4.12}$$

Therefore, the projector (4.3) is of the form

$$\begin{aligned}\tilde{P} &= 1 - \tilde{Q}\\ &= |f(\bar{r}\bar{p})\rangle\!\rangle (S^0)^{-1}(\bar{r}\bar{p}, \bar{r}'\bar{p}')\langle\!\langle f(\bar{r}'\bar{p}')|\\ &= |f(\bar{r}\bar{p})\rangle\!\rangle [n\phi(\bar{p})]^{-1}\langle\!\langle f(\bar{r}\bar{p})|\\ &\quad - |n(\bar{r})\rangle\!\rangle c(\bar{r}\bar{r}')\langle\!\langle n(\bar{r}')|\,.\end{aligned} \tag{4.13}$$

Mori's general equation (4.5) thus becomes ("1" $\equiv \vec{\mathrm{r}}, \vec{\mathrm{p}}$)

$$\left(z + i\frac{\vec{\mathrm{p}} \cdot \vec{\nabla}}{m}\right) S(11'; z) - in\phi(p)\frac{\vec{\mathrm{p}} \cdot \vec{\nabla}}{m} c(r-\bar{r})S(\bar{1}1'; z) - \Sigma^{(c)}(1\bar{1}; z)S(\bar{1}1'; z) = -S^0(11')\,, \tag{4.14}$$

where we have calculated and inserted the matrix Ω of (4.5b), obtaining the result (1.9) trivially. Equation (4.14) is, of course, the spatial Fourier transform of Eq. (1.7a). To obtain $\Sigma^{(c)}$, we notice that in applying (4.12) and (4.13) to (4.5c), the last term of (4.12) gives no contribution. Namely,

$$\tilde{Q}|\dot{f}(\bar{r}\bar{p})\rangle\!\rangle\, c(\bar{r}r') = \tilde{Q}|\dot{n}(\bar{r})\rangle\!\rangle\, c(\bar{r}r') = \tilde{Q}|\vec{\mathrm{g}}(\bar{r})\rangle\!\rangle\, \vec{\bar{\nabla}} c(\bar{r}r')/m\,, \tag{4.15}$$

which uses particle conservation. However, $\vec{\mathrm{g}}(r) = \int d\vec{\mathrm{p}}\,\vec{\mathrm{p}} f(rp)$ is entirely within the $\tilde{P}$ subspace, and thus the $\tilde{Q}$ operator demolishes this term. We therefore obtain

$$n\Sigma^{(c)}(rp, r'p'; z)\phi(p') = \langle\!\langle \dot{f}(rp)|\tilde{Q}\,\frac{1}{z - \tilde{Q}L\tilde{Q}}\,\tilde{Q}|\dot{f}(r'p')\rangle\!\rangle\,, \tag{4.16}$$

which is the desired expression. [There is a scale factor $(mv_0)^3$ relating $\Sigma(\xi\xi')$ and $\Sigma(pp')$.] $\Sigma^{(c)}(kz; pp')\phi(p')$ is the spatial Fourier transform of (4.16). Equation (4.16), while formal, clearly indicates the physical separation that is accomplished by Eq. (4.14) or (1.7a). $\tilde{Q}$ is a projector which discriminates against all one-particle properties. These are contained in (4.14) explicitly, in the kinematic streaming term and the mean-field term [$\Sigma^{(s)}$ of Eq. (1.8)]. By (4.16), $\Sigma^{(c)}$ is a force correlation function which admits, in its dynamics, only two- (and more-) particle-correlated processes. In the language of diagrammatic field theory, one would call $\Sigma^{(c)}$ "one-particle irreducible." In a rare gas, two-particle collisions are the only ones that have to be accounted for, and these are local and essentially instantaneous. Consequently, for all but the highest frequencies, $\Sigma^{(c)}(kz)$ is independent of k and z. In a liquid, collisions involving more than two particles are important, and since they are not separable into individual completed collision events the dependence of $\Sigma^{(c)}(kz)$ on $\vec{\mathrm{k}}$ as well as on z will become important. However, it still seems a promising route to treat these processes in an approximate and summary fashion, e.g., by using an interpolation model for $\Sigma^{(c)}(kz)$.

The symmetry properties of Sec. II A follow easily from (4.16). The positivity of Γ, Sec. II B, can be also easily deduced. We defer discussion of the sum rules to the Appendix, and proceed here to demonstrate the hydrodynamic properties of Secs. II D and E.

B. Conservation laws

Because of *particle conservation*,

$$\int d\vec{\mathrm{p}}\dot{f}(rp) = \dot{n}(r) = -\frac{\vec{\nabla} \cdot \vec{\mathrm{g}}(r)}{m} = -\frac{\vec{\nabla}\int d\vec{\mathrm{p}}\,\vec{\mathrm{p}} f(rp)}{m}, \tag{4.17}$$

it is clear that

$$\int d\vec{\mathrm{p}}\langle\!\langle \dot{f}(rp)|\tilde{Q} = 0\,,$$

so that (2.13a) is satisfied. If we use the equation of motion (4.10), we find this verified since

$$n\Sigma^{(c)}(rp, r'p'; z)\phi(p') = \partial_i\partial_j'[\nabla_i v(r-\bar{r})][\nabla_j v(r'-\bar{r}')]\langle\;\rangle, \tag{4.18}$$

$$\langle\;\rangle = \langle\!\langle f(rp)n(\bar{r})|\tilde{Q}(z - \tilde{Q}L\tilde{Q})^{-1}\tilde{Q}|f(r'p')n(\bar{r}')\rangle\!\rangle\,.$$

This general structure of $\Sigma^{(c)}(kz)$ was also found in both sum rules of IIC, of course.

Microscopic *momentum conservation*

$$\int d\vec{\mathrm{p}}\, p_i \dot{f}(rp) = \dot{g}_i(r) = -\nabla_j \tau_{ij}(r) \tag{4.19}$$

then entails the second result, Eq. (2.13b), with

$$T_{ij}(r-r', z; \xi')\phi(\xi') = -(im^2 v_0/n)\langle \tau_{ij}(r)|\tilde{Q}(z-\tilde{Q}L\tilde{Q})^{-1}\tilde{Q}|\dot{f}(r'p')\rangle\!\rangle\,. \tag{4.20}$$

Since the microscopic stress tensor $\tau_{ij}(r)$ is symmetric, so is T_{ij}. And unless something peculiar happens, such as spontaneous symmetry breaking (and not likely then), $T_{ij}(r-r';\,)$ will be a local quantity, with a Fourier transform which is finite as $k\to 0$ as asserted after Eqs. (2.14).

To prove *energy conservation* in the form (2.12) or (2.13c) is a little more involved since the microscopic conservation law

$$\partial_t \epsilon(rt) = \partial_t \epsilon^{\mathrm{kin}}(rt) + \partial_t \epsilon^{\mathrm{pot}}(rt) = -\vec{\nabla}\cdot\vec{j}^{\,\epsilon}(rt) \tag{4.21}$$

involves the microscopic potential energy

$$\epsilon^{\mathrm{pot}}(r) = \tfrac{1}{2}\sum_{\alpha\neq\beta}\delta(r-r^\alpha)v(r^\alpha - r^\beta)\,, \tag{4.22}$$

(at $t=0$) which cannot be expressed as a simple integral over the one-particle observable, $f(rp)$. We begin by noticing that

$$\langle \epsilon^{\mathrm{pot}}(r)|f(r'p')\rangle\!\rangle = \langle \epsilon^{\mathrm{pot}}(r)|n(r')\rangle\!\rangle\,\phi(p')\,, \tag{4.23}$$

since classically, momentum averages can be taken independently, and $\epsilon^{\mathrm{pot}}(r)$ depends only on position variables r^α. With the projector as given in (4.13), we find therefore that

$$\langle \epsilon^{\mathrm{pot}}(r)|\tilde{P}L\tilde{Q} \sim \langle n(r)|L\tilde{Q} = 0\,. \tag{4.24}$$

This result and (4.21) lead to

$$n\int d\vec{\mathrm{p}}\,\frac{p^2}{2m}\Sigma^{(c)}(rp, r'p'; z)\phi(p') = i\langle \epsilon^{\mathrm{pot}}(r)|\tilde{Q}L\tilde{Q}(z-\tilde{Q}L\tilde{Q})^{-1}\tilde{Q}|\dot{f}(r'p')\rangle\!\rangle + \vec{\nabla}\cdots\,, \tag{4.25}$$

except for a gradient term resulting from the energy current in (4.21), whose contribution vanishes as $k\to 0$.

Now further

$$\lim_{z\to i0}\tilde{Q}L\tilde{Q}(z-\tilde{Q}L\tilde{Q})^{-1} = -\tilde{Q}\,. \tag{4.26}$$

It is then easy to show, using a property similar to (4.23), that the Fourier transform of

$$\langle \epsilon^{\mathrm{pot}}(r)|\tilde{Q}|\dot{f}(r'p')\rangle\!\rangle\,(k)\to 0$$

vanishes as $k\to 0$, proving the last Eq. (2.12) and, assuming a moderate amount of analyticity, (2.13c). Expressions for the functions E and $\vec{J}^{\epsilon}$ of (2.13c) can be given but they are not very illuminating.

C. Local-equilibrium properties

1. *Specific heat*

To prove (2.21), we apply once more the argument which lead to (4.25), and obtain

$$n\int d\vec{\mathrm{p}}\int d\vec{\mathrm{p}}'\,\frac{p^2}{2m}\Sigma^{(c)}(rp, r'p'; z)\frac{p'^2}{2m}\phi(p') = \langle \epsilon^{\mathrm{pot}}(r)|\tilde{Q}L\tilde{Q}(z-\tilde{Q}L\tilde{Q})^{-1}\tilde{Q}L\tilde{Q}|\epsilon^{\mathrm{pot}}(r')\rangle\!\rangle \tag{4.27}$$

except for a gradient term which vanishes as $k\to 0$. Thus, since

$$\lim_{z\to i0}\tilde{Q}L\tilde{Q}(z-\tilde{Q}L\tilde{Q})^{-2}\tilde{Q}L\tilde{Q} = \tilde{Q}\,, \tag{4.28}$$

we obtain [spatial Fourier transformation is indicated by $\langle\;\rangle(k)$]

$$\begin{aligned}\lim_{z\to 0,\, k\to i0} -n\frac{\partial}{\partial z}\int\int \frac{p^2}{2m}\Sigma^{(c)}(kz; pp')\phi(p')\frac{p'^2}{2m} &= \langle \epsilon^{\mathrm{pot}}(r)|\tilde{Q}|\epsilon^{\mathrm{pot}}(r)\rangle\!\rangle \quad (k\to 0)\\ &= [\chi_{\epsilon^{\mathrm{pot}},\epsilon^{\mathrm{pot}}}(k) - \chi_{\epsilon^{\mathrm{pot}},n}(k)\chi_{nn}^{-1}(k)\chi_{n\epsilon^{\mathrm{pot}}}(k)]_{k\to 0}\,,\end{aligned} \tag{4.29}$$

where we have used (4.13) and (4.23), and the notation

$$\chi_{A,B}(\vec{\mathrm{k}}) = \int d(\vec{\mathrm{r}}-\vec{\mathrm{r}}')\,e^{-i\vec{\mathrm{k}}\cdot(\vec{\mathrm{r}}-\vec{\mathrm{r}}')} \times[\langle A(\vec{\mathrm{r}})B(\vec{\mathrm{r}}')\rangle\!\rangle - \langle A\rangle\langle B\rangle]\,. \tag{4.30}$$

Now the specific heat is given by

$$\begin{aligned} mnc_v &= -k_B\beta^2\left(\frac{\partial\epsilon}{\partial\beta}\right)_n \\ &= -k_B\beta^2\left[\left(\frac{\partial\epsilon}{\partial\beta}\right)_\mu - \left(\frac{\partial\epsilon}{\partial\mu}\right)_\beta\left(\frac{\partial n}{\partial\beta}\right)_\mu \Big/ \left(\frac{\partial n}{\partial\mu}\right)_\beta\right],\end{aligned} \tag{4.31a}$$

or

$$mnc_v = k_B\beta^2[\chi_{\epsilon\epsilon}(k) - \chi_{\epsilon n}(k)\chi_{nn}^{-1}(k)\chi_{n\epsilon}(k)]_{k\to 0}\,, \tag{4.31b}$$

where ϵ is the total energy density. With the help of (4.23) and the relations which follow from (4.11),

$$\chi_{nn}(k) = \tfrac{2}{3}\beta\chi_{\epsilon^{\mathrm{kin}}n}(k) = \tfrac{4}{9}\beta^2\chi_{\epsilon^{\mathrm{kin}}\epsilon^{\mathrm{kin}}}(k) - \tfrac{2}{3}n\,, \tag{4.32}$$

we obtain the desired result

$$mc_v - \tfrac{3}{2}k_B = -k_B\beta^2 \frac{\partial}{\partial z} \int\int \frac{p^2}{2m}\Sigma^{(c)}(k, z; pp') \times\frac{p'^2}{2m}\phi(p')|_{k\to 0,\, z\to i0}, \tag{4.33}$$

which is Eq. (2.21).

2. *Pressure derivative*

Equation (2.20) is proved in a similar manner. Proceeding as before, one finds first that (omitting gradient terms which vanish as $k\to 0$)

$$\begin{aligned}\lim_{k\to 0,\, z\to i0} \frac{n}{k}\int\int p_3\Sigma^{(c)}(kz; pp')\phi(p')\frac{p'^2}{2m} &= \langle \tau_{33}|\tilde{Q}|\epsilon^{\text{pot}}\rangle \quad (k\to 0)\\ &= [\chi_{\tau\,\epsilon^{\text{pot}}}(k) - \chi_{\tau\, n}(k)\chi_{nn}^{-1}(k)\chi_{n\epsilon^{\text{pot}}}(k)]_{k\to 0}\,.\end{aligned} \tag{4.34}$$

The potential part of the stress tensor, τ^{pot}, is again independent of particle momenta so that

$$\langle \tau_{33}^{\text{pot}}(r)|\epsilon^{\text{kin}}(r')\rangle = \tfrac{3}{2}\beta^{-1}\langle \tau_{33}^{\text{pot}}(r)|n(r')\rangle\ , \tag{4.35}$$

and with the thermodynamic relation

$$\left(\frac{dp}{dT}\right)_n = k_B\beta^2[\chi_{\tau\,\epsilon}(k) - \chi_{\tau\, n}(k)\chi_{nn}^{-1}(k)\,\chi_{n\epsilon}(k)]_{k\to 0}, \tag{4.36}$$

one obtains Eq. (2.20).

This completes our microscopic proofs of properties exhibited in Sec. II.

D. Bulk viscosity–direct part

In (3.21b), the "direct" bulk viscosity was left in a somewhat inelegant form, which, in particular, left unverified the claim that $\zeta''>0$. This can be remedied by an examination of the microscopic counterpart of (3.21b).

For the shear viscosity, calculating (3.16a) from the microscopic memory function (4.16) and using momentum conservation, we find that

$$\eta'' = \beta \lim_{\epsilon\to 0}\langle \tau_{13}(r)|\tilde{R}(\epsilon)|\tau_{13}(r')\rangle \quad (k\to 0), \tag{4.37}$$

where

$$\tilde{R}(\epsilon) = \tilde{Q}(\epsilon + \tilde{Q}iL\tilde{Q})^{-1}\tilde{Q} \tag{4.38}$$

is a scalar positive operator so that $\eta''>0$ as seen already in (3.16a). Equation (4.37) is, of course, reminiscent of a Kubo relation.

Now if we decompose the stress tensor $\tau_{ij}(r)$ into its irreducible parts,

$$\tau_{ij}(\vec{r}) = \hat{\tau}_{ij}(\vec{r}) + \delta_{ij}\tau(\vec{r}), \tag{4.39}$$

where $\text{tr}\,\hat{\tau}=0$, then as $k\to 0$, there is no coupling between $\hat{\tau}$ and τ, nor between $\hat{\tau}$ and the potential energy ϵ^{pot}. Writing Eq. (3.21b), too, in microscopic form we can therefore separate out the shear viscosity contribution, and obtain this expression for the "direct" part of the bulk viscosity:

$$\zeta'' = \beta \lim_{\epsilon\to 0}\langle \tau(r) - \alpha\epsilon^{\text{pot}}(r)|\tilde{R}(\epsilon)|\,\tau(r') - \alpha\epsilon^{\text{pot}}(r')\rangle \quad (k\to 0), \tag{4.40}$$

where $\alpha = (\partial p/\partial\epsilon)_n$ as in (3.21c). This expression shows that $\zeta''>0$, and is strongly reminiscent of the one obtained for ζ' in (3.21c). Because of the projectors $\tilde{Q}$ in (4.38), ϵ^{pot} in (4.40) can be replaced by the total energy density ϵ.

V. SUMMARY AND DISCUSSION

We have discussed, and proved where necessary, a list of general properties of the collision operator which determines a kinetic theory of fluctuations in gases and liquids. By themselves, these properties are far from constituting a full theory of liquid dynamics. They do, however, provide a useful set of checks to which any such theory will have to submit. Moreover, the sum rules given, in particular, are sufficiently explicit to provide welcome guidelines in the search for realistic models.

We have, at present, little to say about how to further narrow down such models. In line with remarks made in the Introduction, it is suggestive to attempt an extension of the interpolation procedure of Chung and Yip[4] to kinetic theory as phrased here. In so doing, we have found it convenient to extend the present formalism slightly, and include among the explicitly treated variables, one two-particle property, namely the potential energy, in addition to variables summarized in $f(\vec{r}\vec{p}t)$. We hope to present results of this calculation in the near future.

The ultimate goal, of course, is an explicit if approximate microscopic calculation of $\Sigma^{(c)}(\vec{k}z)$. It is possible that the renormalized-expansion formalism, recently proposed by Martin *et al.*[21] for classical theories of this type and applied by them to the turbulence problem, will be a useful tool here. It is also very likely that the idea due to Rice and Allnatt[22] of separating the pair potential into a hard core and a soft tail, and treating the latter by perturbation theory, will be of great help.

Note added in manuscript. After this work was completed, I learned of recent work[23] by G. F. Mazenko who has independently obtained some of the results presented here. In particular, Mazenko also obtained my Eqs. (2.20) and (2.21), and his expressions for the transport coefficients can be shown to be equivalent to mine. I thank G. Mazenko for the ensuing helpful correspondence.

APPENDIX: SUM RULES

We comment here on the derivation of the sum rule (2.10a). It is most conveniently obtained from Eq. (4.16). If one expands

$$\Sigma^{(c)}(z)=\frac{1}{z}\Sigma^{\infty}+\frac{1}{z^2}\Sigma_1+\frac{1}{z^3}+\cdots , \tag{A1}$$

then from (4.16)

$$n\Sigma_1(11')\phi(1')=\langle \dot{f}(1)\,|\,\tilde{Q}L\tilde{Q}\,|\,\dot{f}(1')\rangle . \tag{A2}$$

Because of the operator $\tilde{Q}$, if one inserts $\dot{f}(1)$ from Eq. (4.10), only the potential term in (4.10) contributes so that

$$n\Sigma_1(11')\phi(1')=\partial_i\partial_j' v_i(r\bar{r})v_i(r'\bar{\bar{r}}) \times\langle f(1)n(\bar{r})\,|\,\tilde{Q}L\tilde{Q}\,|\,f(1')n(\bar{\bar{r}})\rangle . \tag{A3}$$

To evaluate this expression, we use (i) a static property:

$$\begin{aligned}-\beta v_i(r\bar{r})\langle f(1)n(\bar{r})f(1')\rangle &=\nabla_i[\langle f(1)f(1')\rangle-\langle f(1)\rangle\delta(11')]\\ &=n^2\varphi(p)\phi(p')g_i(rr') ,\end{aligned} \tag{A4}$$

which is easily derived, in a canonical ensemble. Because of this equation, which represents a rigorous (and well-known) relation between the pair and triplet correlation functions, one can in fact omit the $\tilde{Q}$ operators in (A3). To evaluate the remainder, we use (ii) the fluctuation-dissipation theorem:

$$\langle A\,|\,L\,|\,B\rangle=i\langle \dot{A}\,|\,B\rangle=i\beta^{-1}\langle[A,B]_{\mathrm{PB}}\rangle \tag{A5}$$

and (iii) the Poisson bracket

$$[f(1),f(1')]_{\mathrm{PB}}=(\vec{\nabla}\,\vec{\partial}'-\vec{\nabla}'\vec{\partial})f(1)\delta(11') . \tag{A6}$$

Equation (A3) is then easily evaluated, and leads to the result given in Eq. (2.10a).

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[1] For general background, see, e.g., S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Wiley, New York, 1965); I. Prigogine, *Non-Equilibrium Statistical Mechanics* (Wiley, New York, 1963); B. J. Berne and D. Forster, Annu. Rev. Phys. Chem. 22, 563 (1971).

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[17] In particular, it is necessary, as will become clear in Sec. III, that $\langle\varphi_\mu|\Sigma^{(c)}(\vec{k}z|\varphi_\nu\rangle$ can be expanded to second order in k and z.

[18] As usual, we mean by this that functions like $g_t(kz)$ are obtained as a sum of single-pole contributions where the poles are calculated to order k^2, and the residues to order k.

[19] If (3.17)–(3.19) are taken literally, one also obtains an additional pole at $z=i2mc_v/(3\bar{\gamma}_{33}k_B)$, i.e., on the forbidden physical sheet. This pole is spurious, resulting from the Taylor expansion of $\Omega(\vec{k}z)$. Moreover, it occurs in $g_{nn}(kz)$ with vanishing strength as $k\to 0$.

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