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Nonequilibrium statistical mechanics of a dense fluid

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A theory is constructed for the nonequilibrium statistical mechanics of a many-particle system, including effects of multiparticle correlations. The particular system studied is a dense monatomic fluid, whose atoms interact by pairwise central forces. The nonequilibrium fluid possesses coupled position and momentum correlations, of which the two-particle correlations are treated explicitly, while three- and more-particle correlations are included in a mean-field approximation. A truncated gradient expansion is applied, representing the condition that the one- and two-particle probability densities vary by a relatively small amount under translation through a distance not larger than the correlation length. New concepts which are used in the theoretical construction include the following: a localized nonequilibrium potential of mean force; a nonequilibrium h function and the corresponding h currents; and interaction integrals, which are the counterpart of Boltzmann's collision integral, and which are based on effective two-particle interactions that conserve particle number, momentum, and a statistically appropriate energy. The resulting theory consists of two coupled evolution equations, one for the one-particle probability density, and one for the two-particle correlation function. The evolution equations satisfy the continuum equations for conservation of particles, of momentum, and of energy; the evolution equations also satisfy an h theorem, whose source function is a Lyapunov functional, and whose equilibrium solution gives the correct equilibrium values for the one-particle probability density and the two-particle correlation function. The simplified theory that results from neglecting two-particle momentum correlations is also presented.

I. INTRODUCTION AND SUMMARY

At the present time, the most successful theory for describing the statistical-mechanical evolution of a nonequilibrium system is that due to Boltzmann.[1] Boltzmann constructed an irreversible evolution equation for the one-particle ensemble-probability density; the irreversibility arises from the collision integral, which is a statistical representation of two-particle scattering processes. The Boltzmann equation applies to dilute gases in arbitrary nonequilibrium states. Because it governs the approach to equilibrium, as a special case, the Boltzmann equation determines the transport coefficients in the irreversible-thermodynamic regime, and it also determines the equilibrium value of the one-particle momentum distribution.

The Boltzmann equation does not account for interparticle correlations, which are important in a dense system. Much research has been devoted to the problem of extending Boltzmann's theory to dense gases and to liquids. Perhaps the best-known theory is that of Enskog, which dates from 1922, and which is discussed by Hirschfelder, Curtiss, and Byrd,[2] and by Chapman and Cowling.[3] Enskog applied the Boltzmann equation to a system of hard spheres. He modified the collision integral to account for excluded volume, i.e., the fact that the sphere diameter need not be small compared to the mean free path, and in calculating momentum and energy fluxes, he also included *collisional transfer* of flux. The Enskog theory is developed for near-equilibrium situations, and it gives the density dependence of viscosity and thermal conductivity at a given temperature, in terms of properties of the dilute-gas phase at the same temperature. The modified Enskog theory is a practical adaptation of the Enskog theory, which expresses transport coefficients of real fluids in terms of equation-of-state data for the fluid, together with transport coefficients of the dilute gas phase. Hanley, McCarty, and Cohen[4] have carried out extensive comparisons of the Enskog and modified Enskog theories with experiment for argon, oxygen, and parahydrogen. For the shear viscosity and thermal conductivity, Hanley, McCarty, and Cohen[4] found reasonable agreement between the modified Enskog theory and experiment, for densities generally not exceeding twice the critical density.

A systematic procedure for extending the Boltzmann equation to higher densities was presented by Bogoliubov in 1946.[5] The key to Bogoliubov's method is the so-called *functional assumption*: he assumes that the multiparticle probability densities, insofar as their time dependences are concerned, are functionals only of the one-particle probability density. He then shows how to construct an evolution equation for the one-particle probability density, i.e., a generalized Boltzmann equation, as an expansion in powers of the density. A detailed study of the Bogoliubov theory in general, and of its approach to equilibrium in particular, was reported by Cohen.[6] In the first order in density, which corresponds to three-particle collision terms, the generalized Boltzmann equation yields corrections to the Boltzmann results for shear viscosity and thermal conductivity. However, in second order in density, i.e., at the level of four-particle collisions, the Bogoliubov expressions for the multiparticle probability densities, as well as the corresponding contributions to the transport coefficients, are all infinite.[6] The origin of these divergences is the increasing phase-space volume associated with n-particle collisions, as n increases. As an alternate method to obtain a density expansion of the general nonequilibrium theory, Cohen[7,8] developed a technique based on a cluster expansion of the probability densities. The same divergence problems also appear in this technique, and lead to the conclusion that the general theory is not analytic in density.[7,8] While the n-particle collision analysis becomes complicated, some partial resummations were achieved by Cohen. In a review article covering density expansions of transport coefficients, as obtained from time-correlation functions in a moderately dense gas, Ernst, Haines, and Dorfman[9] also conclude that all density expansions diverge, in particular that n-particle terms do not exist for $n \geq 4$ in three dimensions.

A different approach to the nonequilibrium statistical mechanics of many-particle systems was investigated by Kirkwood.[10] For the multiparticle probability densities, which are ensemble averages, Kirkwood introduces a further *time average,* over a coarse-graining time interval τ. He then constructs, as a series in τ, and to zeroth-order in this series, a Langevin equation for the motion of a single particle in the fluctuating force field due to its neighboring particles. When τ is sufficiently long that this coarse-grained force is uncorrelated in successive times t and $t+\tau$, then the single particle exhibits Brownian motion. With this condition on τ, and for near-equilibrium situations (where temperature is defined), Kirkwood constructs generalized Fokker-Planck equations for the hierarchy of coarse-grained multiparticle probability densities. A significant modification of this theory was constructed by Rice and Allnatt, and is described in detail by Rice and Gray.[11] In the Rice-Allnatt theory, the short-range repulsion between particles is represented by a hard-sphere model; it is then assumed that, in the coarse-graining time interval τ, there is one rigid-core encounter between a pair of particles, followed by erratic motion in the fluctuating force field of neighbors, and that dynamical events occurring in successive τ intervals are uncorrelated. The Rice-Allnatt equations apply to near-equilibrium situations, and they express the evolution of the one-particle probability density and the two-particle correlation function. A brief comparison of the Rice-Allnatt theory with experiment is given by Hanley, McCarty, and Cohen.[4]

In the present paper we report the results of an effort to construct a new theory of nonequilibrium statistical mechanics of a classical dense fluid. The guiding principle in this development has been to follow, insofar as possible, the logic of Boltzmann.[1] Discussion of a few specific points will help clarify the relation of the present work to those works mentioned above. First, in consideration of time coarse graining so as to achieve Brownian motion, we note that τ must be long enough to lose correlations in the one-particle mean force, but in order to obtain meaningful evolution equations for the coarse-grained probability densities, τ must be short on the time scale of this evolution. Conditions under which such a τ exists for a dense fluid poses a difficult problem; we will avoid this problem by working with the ensemble probability densities, as continuous functions of time, as did Boltzmann. Second, with reference to hard-sphere models, it is remarkable how well the generalized Enskog theory can account for transport coefficients in dense systems.[4] Ultimately, however, hard spheres cannot accurately represent the interacting atoms in a dense fluid, and so we will consider a system of particles interacting by pairwise central forces. Externally applied forces are neglected for simplicity. Third, we will not try to make a density expansion of the theory, but will go immediately to the dense regime, where a particle is in continuous interaction with a number of neighboring particles, and where the concepts of collisions and mean free paths are not useful. Our picture of a nonequilibrium dense fluid is based in turn upon our picture of an ***equilibrium*** dense fluid, which was also developed in conjunction with this work. In particular, the entropy of an equilibrium dense fluid is expressed as an expansion in irreducible multiparticle correlations,[12] and neglecting terms beyond two-particle correlations produces an effective two-particle formulation of the free energy of an equilibrium fluid. For a nonequilibrium dense fluid as well, we will construct an effective two-particle theory, in which two-particle correlations are treated explicitly, and higher-order correlations appear only in a mean-field approximation. Fourth, it is desirable to construct a theory which is not limited to near-equilibrium situations, but is valid for arbitrary nonequilibrium states. This aim is achieved, up to one significant limitation: in order to obtain a particle-interchange symmetry, which is useful in constructing an h theorem, the entire theory is subjected to a truncated gradient expansion, representing the notion that, under translation through a distance of order or less than the correlation length, there is only a relatively small change in the one- and two-particle probability densities. This approximation is appropriate near equilibrium, it might in fact be valid for a wide range of situations, but it is probably not of universal validty. Finally, since the h theorem is an essential part of Boltzmann's theory,[1] we consider it essential that our dense-fluid theory should also possess an h theorem. While no h theorem has been proven for the above-mentioned theories (see Refs. 2—11), Résibois[13] has constructed a modified Enskog equation (not related to the modified Enskog theory[4]) which *does* support an h theorem. The modified Enskog equation is based on a hard-sphere correlation function which is different from Enskog's original function, and the h theorem holds for the total system with periodic boundary conditions.[13] In the present work, our desire to achieve a *local h* theorem, in the spirit of Boltzmann's h theorem, has exerted a strong influence on the theoretical development.

Sections II—V describe the present theoretical development, wherein several new physical concepts are introduced. First we construct the localized two-particle potential of mean force which operates in a nonequilibrium fluid. This allows us to extract, from the multiparticle correlation hierarchy [the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy], a system of equations based on effective two-particle interactions. A nonequilibrium h function is constructed, including effects of two-particle correlations, and the corresponding h currents are also constructed. Interaction integrals are then defined, based on effective two-particle interactions which conserve the number of particles, the momentum, and the statistically appropriate energy, namely, the two-particle energy whose potential is the potential of mean force. The potential of mean force enters the evolution equations only through the interaction integrals, and in this role the potential of mean force is approximated by neglecting its momentum dependence, and its angular dependence. Finally, two-particle correlations which do not contribute to the macroscopic equations for conservation of particles, of momentum, and of energy, are removed from the BBGKY equations, and these parts are replaced by appropriate interaction integrals. The interaction integrals account for irreversibility in the fluid evolution.

The one-particle probability density at position $\mathbf{r}$, momentum $\mathbf{p}$, and time t is $f^{(1)}(\mathbf{r},\mathbf{p},t)$. The two-particle correlation function is $g^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)$. A major source of complication of the theory is the momentum dependence of $g^{(2)}$. We are not able to eliminate this momentum dependence, but by physical arguments we can reduce it to the single vector $\mathbf{p}_1+\mathbf{p}_2$, as embodied in a reduced correlation function $\gamma^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1+\mathbf{p}_2,t)$. The main result of the present paper is a pair of coupled evolution equations for $f^{(1)}$ and $\gamma^{(2)}$, Eqs. (92) and (98). Each of these equations contains four classes of terms: a time derivative, drift terms, force terms, and interaction integrals. Upon appropriate averaging, the evolution equations yield correct equations for conservation of particles, of linear momentum, and of energy. With the aid of an auxiliary integral condition, Eq. (105), the evolution equations also yield an h theorem. Finally, at equilibrium, the evolution equations lead to the correct values of the one-particle probability density, and the two-particle correlation function. The reader will find an occasional mention of a near-equilibrium property of the present theory; this near-equilibrium expansion will be the subject of a forthcoming paper. If we are willing to neglect the momentum dependence of $\gamma^{(2)}$, a much simplified theory results, and this is presented in Sec. V E.

II. A STUDY OF THE BBGKY EQUATIONS

A. Basic concepts

To clarify our basic concepts, it is helpful to first define a mechanical system which represents a nonequilibrium fluid. The system contains N like particles in a volume V. The volume is a constant regular shape, e.g., a sphere or a cube, and no particles flow across the surface, so that N is constant. At any time t the particle positions and momenta are respectively $\mathbf{r}_\kappa$ and $\mathbf{p}_\kappa$, and $\kappa=1,2,\ldots,N$. The Hamiltonian is $\mathcal{H}_N$,

$$\mathcal{H}_N=\sum_{\kappa=1}^{N}\frac{\mathbf{p}_\kappa^2}{2m}+\tfrac{1}{2}\sum_{\kappa,\lambda=1}^{N}\phi_{\kappa\lambda}\,, \tag{1}$$

where m is the particle mass and $\phi_{\kappa\lambda}=\phi(\,|\mathbf{r}_\kappa-\mathbf{r}_\lambda|\,)$, with $\phi_{\kappa\kappa}=0$. The system phase point moves in accordance with Liouville's equation. Components of the total linear and angular momentum are taken to be zero for convenience.

We now consider an ensemble of mechanical systems, each one as described above, and specifically each one having the same V, except that the ensemble contains a distribution of particle numbers N. The phases of the mechanical systems constitute a fine dust of points distributed over phase space. The ensemble probability that there is one particle in $d\mathbf{r}_1d\mathbf{p}_1$, one particle in $d\mathbf{r}_2d\mathbf{p}_2$, etc., and one particle in $d\mathbf{r}_nd\mathbf{p}_n$, at time t, is

$$f^{(n)}(\mathbf{r}_1,\mathbf{p}_1,\ldots,\mathbf{r}_n,\mathbf{p}_n,t)d\mathbf{r}_1d\mathbf{p}_1\cdots d\mathbf{r}_n\,d\mathbf{p}_n\;.$$

This probability has dimension 1, and represents indistinguishable particles. The corresponding probability *density* is $f^{(n)}(\mathbf{r}_1,\mathbf{p}_1,\ldots,\mathbf{r}_n,\mathbf{p}_n,t)$. We will use properties of the $f^{(n)}$ for small n, since specific attention is limited to $n\leq 3$ in the present work. Hence the $f^{(n)}$ are evaluated in the interior of the mechanical systems, and are independent of surface effects; also the $f^{(n)}$ will depend on the mean particle number $\bar{N}$. We assume the existence of a finite correlation length l_c, which is of the order of the range of the two-particle potential $\phi(\,|\mathbf{r}|\,)$, and beyond which particle-particle correlations vanish. Two particles are "distant" when their separation is greater than l_c, and a function of $\mathbf{r}_1,\mathbf{r}_2$ is "local" if it vanishes for $|\mathbf{r}_1-\mathbf{r}_2|>l_c$. Our assumption of a finite l_c implies that, when $\mathbf{r}_n$ is distant from $\mathbf{r}_1,\ldots,\mathbf{r}_{n-1}$, then

$$f^{(n)}(\mathbf{r}_1,\mathbf{p}_1,\ldots,\mathbf{r}_n,\mathbf{p}_n,t)=f^{(1)}(\mathbf{r}_n,\mathbf{p}_n,t)f^{(n-1)}(\mathbf{r}_1,\mathbf{p}_1,\ldots,\mathbf{r}_{n-1},\mathbf{p}_{n-1},t)\;.$$

For $n=2$, it follows

$$f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)-f^{(1)}(\mathbf{r}_1,\mathbf{p}_1,t)f^{(1)}(\mathbf{r}_2,\mathbf{p}_2,t)$$

is a local function.

Equations of motion for the probability densities are constructed from the Liouville equation, and are called the BBGKY hierarchy (see, e.g., Kreuzer,[14] McQuarrie,[15] and Hansen and McDonald[16]). The equation for $f^{(n)}$ is

$$\left[\frac{\partial}{\partial t}+\sum_{\kappa=1}^{n}\left[\frac{\mathbf{p}_\kappa}{m}\cdot\frac{\partial}{\partial\mathbf{r}}-\sum_{\lambda=1}^{n}\frac{\partial\phi_{\kappa\lambda}}{\partial\mathbf{r}_\kappa}\cdot\frac{\partial}{\partial\mathbf{p}_\kappa}\right]\right]f^{(n)}(\mathbf{r}_1,\mathbf{p}_1,\ldots,\mathbf{r}_n,\mathbf{p}_n,t)$$
$$=\sum_{\kappa=1}^{n}\int\int\frac{\partial\phi_{\kappa,n+1}}{\partial\mathbf{r}_\kappa}\cdot\frac{\partial}{\partial\mathbf{p}_\kappa}f^{(n+1)}(\mathbf{r}_1,\mathbf{p}_1,\ldots,\mathbf{r}_{n+1},\mathbf{p}_{n+1},t)d\mathbf{r}_{n+1}d\mathbf{p}_{n+1}\;. \tag{2}$$

This hierarchy will be the starting point for our construction of the evolution equations for a nonequilibrium fluid.

A useful property of the probability densities is that they vanish at the surface of V, since particles do not cross the surface, and they vanish at infinite momenta, so that physically meaningful momentum averages exist. Hence for any function $Q(\mathbf{r}_1,\mathbf{p}_1,t)$, such that $\int f^{(n)}Q\,d\mathbf{r}_1$ and $\int f^{(n)}Q\,d\mathbf{p}_1$ exist,

$$\int \nabla_{\mathbf{r}_1}[f^{(n)}(\mathbf{r}_1,\mathbf{p}_1,\ldots,\mathbf{r}_n,\mathbf{p}_n,t)Q(\mathbf{r}_1,\mathbf{p}_1,t)]d\mathbf{r}_1=0\,, \tag{3}$$

$$\int \nabla_{\mathbf{p}_1}[f^{(n)}(\mathbf{r}_1,\mathbf{p}_1,\ldots,\mathbf{r}_n,\mathbf{p}_n,t)Q(\mathbf{r}_1,\mathbf{p}_1,t)]d\mathbf{p}_1=0\,. \tag{4}$$

B. Nonequilibrium potential of mean force

It is convenient to factor $f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)$, thus defining the two-particle correlation function $g^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)$, a conditional probability,

$$f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)=f^{(1)}(\mathbf{r}_1,\mathbf{p}_1,t)f^{(1)}(\mathbf{r}_2,\mathbf{p}_2,t)g^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)\,. \tag{5}$$

$g^{(2)}$ is symmetric in particles, is non-negative, and $g^{(2)}-1$ is a local function. We next define $\mathbf{K}(\mathbf{r}_1,\mathbf{p}_1,t)$ as the mean force on a particle at $\mathbf{r}_1,\mathbf{p}_1,t$, given that there *is* a particle at $\mathbf{r}_1,\mathbf{p}_1,t$,

$$f^{(1)}(\mathbf{r}_1,\mathbf{p}_1,t)\mathbf{K}(\mathbf{r}_1,\mathbf{p}_1,t)=-\int\int[\nabla_{\mathbf{r}_1}\phi(|\mathbf{r}_1-\mathbf{r}_2|)]\times f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)d\mathbf{p}_2d\mathbf{r}_2\,, \tag{6}$$

or

$$\mathbf{K}(\mathbf{r}_1,\mathbf{p}_1,t)=-\int\int[\nabla_{\mathbf{r}_1}\phi(|\mathbf{r}_1-\mathbf{r}_2|)]f^{(1)}(\mathbf{r}_2,\mathbf{p}_2,t)\times g^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)d\mathbf{p}_2d\mathbf{r}_2\,. \tag{7}$$

The BBGKY equation for $n=1$ can then be written

$$\left[\frac{\partial}{\partial t}+\frac{\mathbf{p}_1}{m}\cdot\nabla_{\mathbf{r}_1}\right]f^{(1)}(\mathbf{r}_1,\mathbf{p}_1,t)+\nabla_{\mathbf{p}_1}\cdot f^{(1)}(\mathbf{r}_1,\mathbf{p}_1,t)\mathbf{K}(\mathbf{r}_1,\mathbf{p}_1,t)=0\,. \tag{8}$$

A nonlocal two-particle potential of mean force, $W^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)$, is defined by

$$\begin{aligned}[\nabla_{\mathbf{r}_1}W^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)]f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)&=[\nabla_{\mathbf{r}_1}\phi(|\mathbf{r}_1-\mathbf{r}_2|)]f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)\\&\quad+\int\int[\nabla_{\mathbf{r}_1}\phi(|\mathbf{r}_1-\mathbf{r}_3|)]\times f^{(3)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,\mathbf{r}_3,\mathbf{p}_3,t)d\mathbf{p}_3d\mathbf{r}_3\,.\end{aligned} \tag{9}$$

The interpretation of this equation is given that there are particles at $\mathbf{r}_1,\mathbf{p}_1,t$ and at $\mathbf{r}_2,\mathbf{p}_2,t$, then $-\nabla_{\mathbf{r}_1}W^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)$ is the mean force on the particle at $\mathbf{r}_1,\mathbf{p}_1,t$. When $\mathbf{r}_1$ and $\mathbf{r}_2$ are distant, then $\phi(|\mathbf{r}_1-\mathbf{r}_2|)=0$, and the right side of (9) reduces to

$$-f^{(1)}(\mathbf{r}_1,\mathbf{p}_1,t)f^{(1)}(\mathbf{r}_2,\mathbf{p}_2,t)\mathbf{K}(\mathbf{r}_1,\mathbf{p}_1,t)\,.$$

We can subtract this quantity from (9), to construct a local potential of mean force. But there are other functions which have the same distant limit as the above expression, for example,

$$-f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)\mathbf{K}(\mathbf{r}_1,\mathbf{p}_1,t)\,.$$

We choose to subtract this last quantity from the right side of (9), to define the local potential of mean force $w^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)$,

$$\begin{aligned}[\nabla_{\mathbf{r}_1}w^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)]f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)&=[\nabla_{\mathbf{r}_1}\phi(|\mathbf{r}_1-\mathbf{r}_2|)]f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)\\&\quad+\int\int[\nabla_{\mathbf{r}_1}\phi(|\mathbf{r}_1-\mathbf{r}_3|)][f^{(3)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,\mathbf{r}_3,\mathbf{p}_3,t)-f^{(1)}(\mathbf{r}_2,\mathbf{p}_2,t)g^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_3,\mathbf{p}_3,t)]d\mathbf{r}_3d\mathbf{p}_3\,.\end{aligned} \tag{10}$$

Hence $\nabla_{\mathbf{r}_1}w^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)$ is local, because the one-particle mean force $\mathbf{K}(\mathbf{r}_1,\mathbf{p}_1,t)$ has been subtracted out at large distances, and the energy zero is to be chosen so that $w^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)$ is also local.

The BBGKY equation for $n=2$ can be expressed in terms of $w^{(2)}$, as follows:

$$\begin{aligned}\left[\frac{\partial}{\partial t}+\frac{\mathbf{p}_1}{m}\cdot\nabla_{\mathbf{r}_1}+\frac{\mathbf{p}_2}{m}\cdot\nabla_{\mathbf{r}_2}\right]f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)&=\nabla_{\mathbf{p}_1}\cdot\{[\nabla_{\mathbf{r}_1}w^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)-\mathbf{K}(\mathbf{r}_1,\mathbf{p}_1,t)]f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)\}\\&\quad+\nabla_{\mathbf{p}_2}\cdot\{[\nabla_{\mathbf{r}_2}w^{(2)}(\mathbf{r}_2,\mathbf{p}_2,\mathbf{r}_1,\mathbf{p}_1,t)-\mathbf{K}(\mathbf{r}_2,\mathbf{p}_2,t)]f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)\}\,.\end{aligned} \tag{11}$$

This equation has the appearance of a closed two-particle equation, because the three-particle terms are hidden in the local $w^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)$. We have thus taken the first step toward construction of a local two-particle evolution equation. Note when $\mathbf{r}_1$ and $\mathbf{r}_2$ are distant, only the $\mathbf{K}$ terms remain on the right side, and (11) reduces to the one-particle equation (8), applied to the product function $f^{(1)}(\mathbf{r}_1,\mathbf{p}_1,t)f^{(1)}(\mathbf{r}_2,\mathbf{p}_2,t)$.

C. The conservation equations

A key requirement for any system of evolution equations is that they must conserve mass, momentum, and energy. These conservation laws are satisfied by the BBGKY equations, since the BBGKY equations represent classical Hamiltonian dynamics. This was shown in detail for the case of two-particle central forces by Irving and

Kirkwood;[17] the same results in a different notation appear in Kreuzer.[14] We begin by listing the one- and two-particle contributions to the mechanical densities and currents in the fluid.

Expressions for the particle density, the fluid velocity, and the energy density are obvious at sight. The particle density at $\mathbf{r},t$ is $\rho(\mathbf{r},t)$

$$\rho(\mathbf{r},t)=\int f^{(1)}(\mathbf{r},\mathbf{p},t)d\mathbf{p}\;. \tag{12}$$

The fluid velocity is $\mathbf{v}(\mathbf{r},t)$

$$\rho(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)=\int \frac{\mathbf{p}}{m}f^{(1)}(\mathbf{r},\mathbf{p},t)d\mathbf{p}\;. \tag{13}$$

The center-of-mass energy per particle $\epsilon(\mathbf{r},t)$ is the sum of a one-particle term (kinetic energy) and a two-particle term (potential energy),

$$\epsilon(\mathbf{r},t)=\epsilon^{(1)}(\mathbf{r},t)+\epsilon^{(2)}(\mathbf{r},t)\;, \tag{14}$$

$$\rho(\mathbf{r},t)\epsilon^{(1)}(\mathbf{r},t)=\int \frac{[\mathbf{p}-m\mathbf{v}(\mathbf{r},t)]^2}{2m}f^{(1)}(\mathbf{r},\mathbf{p},t)d\mathbf{p}\;, \tag{15}$$

$$\rho(\mathbf{r}_1,t)\epsilon^{(2)}(\mathbf{r}_1,t)=\tfrac{1}{2}\int\int\int \phi(|\mathbf{r}_1-\mathbf{r}_2|)\times f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)d\mathbf{p}_1\,d\mathbf{p}_2\,d\mathbf{r}_2\;. \tag{16}$$

Expressions for the pressure tensor $\mathbf{P}(\mathbf{r},t)$, and the energy current $\mathbf{J}(\mathbf{r},t)$, are not completely obvious; these are the quantities which appear in the conservation laws, as constructed from the BBGKY equations, as Irving and Kirkwood[17] have shown. For the pressure,

$$\mathbf{P}(\mathbf{r},t)=\mathbf{P}^{(1)}(\mathbf{r},t)+\mathbf{P}^{(2)}(\mathbf{r},t)\;, \tag{17}$$

where $\mathbf{P}^{(1)}$ is a momentum-flux tensor,

$$\mathbf{P}^{(1)}(\mathbf{r},t)=\int \frac{[\mathbf{p}-m\mathbf{v}(\mathbf{r},t)][\mathbf{p}-m\mathbf{v}(\mathbf{r},t)]}{2m}f^{(1)}(\mathbf{r},\mathbf{p},t)d\mathbf{p}\;; \tag{18}$$

and $\mathbf{P}^{(2)}$ is a two-particle—force tensor,

$$\mathbf{P}^{(2)}(\mathbf{r},t)=-\tfrac{1}{2}\int_0^1 d\lambda\int\int\int \frac{\mathbf{s}\mathbf{s}}{|\mathbf{s}|}\phi'(|\mathbf{s}|)f^{(2)}(\mathbf{r}+(1-\lambda)\mathbf{s},\mathbf{p}_1,\mathbf{r}-\lambda\mathbf{s},\mathbf{p}_2,t)d\mathbf{p}_1\,d\mathbf{p}_2\,d\mathbf{s}\;. \tag{19}$$

Here $\mathbf{s}$ arises from the substitution $\mathbf{s}=\mathbf{r}_2-\mathbf{r}_1$, and $\phi'(|\mathbf{s}|)$ is defined by

$$\nabla_{\mathbf{s}}\phi(|\mathbf{s}|)=\frac{\mathbf{s}}{|\mathbf{s}|}\phi'(|\mathbf{s}|)\;. \tag{20}$$

Note both $\mathbf{P}^{(1)}$ and $\mathbf{P}^{(2)}$ are symmetric. Also, for comparison with our previous work on lattice dynamics,[18,19] and on continuum mechanics,[20] the pressure tensor is *minus* the stress tensor. The energy current contains a one-particle term and two distinct two-particle terms,

$$\mathbf{J}(\mathbf{r},t)=\mathbf{J}^{(1)}(\mathbf{r},t)+\mathbf{J}^{(2a)}(\mathbf{r},t)+\mathbf{J}^{(2b)}(\mathbf{r},t)\;. \tag{21}$$

$\mathbf{J}^{(1)}$ is the kinetic energy drift current,

$$\mathbf{J}^{(1)}(\mathbf{r},t)=\int \frac{[\mathbf{p}-m\mathbf{v}(\mathbf{r},t)]}{m}\,\frac{[\mathbf{p}-m\mathbf{v}(\mathbf{r},t)]^2}{2m}f^{(1)}(\mathbf{r},\mathbf{p},t)d\mathbf{p}\;; \tag{22}$$

$J^{(2a)}$ is a two-particle-work current,

$$\mathbf{J}^{(2a)}(\mathbf{r},t)=-\tfrac{1}{4}\int_0^1 d\lambda\int\int\int \phi'(|\mathbf{s}|)\frac{\mathbf{s}\mathbf{s}}{|\mathbf{s}|}\cdot\frac{[\mathbf{p}_1+\mathbf{p}_2-2m\mathbf{v}(\mathbf{r},t)]}{m}f^{(2)}(\mathbf{r}+(1-\lambda)\mathbf{s},\mathbf{p}_1,\mathbf{r}-\lambda\mathbf{s},\mathbf{p}_2,t)d\mathbf{p}_1d\mathbf{p}_2d\mathbf{s}\;; \tag{23}$$

and $\mathbf{J}^{(2b)}$ is the potential energy drift current,

$$\mathbf{J}^{(2b)}(\mathbf{r}_1,t)=\tfrac{1}{2}\int\int\int \frac{[\mathbf{p}_1-m\mathbf{v}(\mathbf{r}_1,t)]}{m}\phi(|\mathbf{r}_1-\mathbf{r}_2|)\times f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)d\mathbf{p}_1\,d\mathbf{p}_2\,d\mathbf{r}_2\;. \tag{24}$$

The basis of continuum mechanics is the set of field equations which express conservation of mass, momentum, and energy at all times and locations within a continuous material. Prager[21] has a fine monograph on the subject; the example of fluids is treated by Landau and Lifshitz;[22] and dissipative plastic flow is treated by the author.[20] The conservation laws are obtained from the BBGKY equations (8) and (11) in the following way. Integrate (8) over $d\mathbf{p}_1$ to obtain the equation for conservation of particles,

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t}+\nabla_{\mathbf{r}}\cdot\rho(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)=0\;. \tag{25}$$

Multiply (8) by $\mathbf{p}_1/m$ and integrate over $d\mathbf{p}_1$ to obtain the equation for conservation of linear momentum,

$$m\frac{\partial\rho(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)}{\partial t}+\nabla_{\mathbf{r}}\cdot[\mathbf{P}(\mathbf{r},t)+m\rho(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)]=0\;. \tag{26}$$

Multiply (8) by $(2m)^{-1}[\mathbf{p}_1-m\mathbf{v}(\mathbf{r}_1,t)]^2$ and integrate over $d\mathbf{p}_1$, multiply (11) by $\frac{1}{2}\phi(|\mathbf{r}_1-\mathbf{r}_2|)$ and integrate over

$d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{r}_2$, and add these to get the equation for conservation of energy,

$$\frac{\partial\rho(\mathbf{r},t)\epsilon(\mathbf{r},t)}{\partial t}+\nabla_{\mathbf{r}}\cdot[\rho(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)\epsilon(\mathbf{r},t)+\mathbf{J}(\mathbf{r},t)] + \mathbf{P}(\mathbf{r},t):\nabla_{\mathbf{r}}\mathbf{v}(\mathbf{r},t)=0 \,. \qquad (27)$$

It is of interest to observe certain contributions in the preceding calculations. The one-particle mean force $\mathbf{K}$, in Eq. (8), contributes nothing to particle conservation (since forces do not change particle number), and it contributes $\nabla_{\mathbf{r}}\cdot\mathbf{P}(\mathbf{r},t)$ to momentum conservation. In energy conservation, the term in $\mathbf{K}$ from (8) mixes with the left-side contribution from (11) to produce $\nabla_{\mathbf{r}}\cdot\mathbf{J}^{(2a)}(\mathbf{r},t)+\mathbf{P}^{(2)}(\mathbf{r},t):\nabla_{\mathbf{r}}\mathbf{v}(\mathbf{r},t)$. The right side of (11) contributes nothing to the conservation laws.

D. Equilibrium limits

We consider global equilibrium, denoted by a subscript 0, in which the fluid properties are independent of position and time. Dependences of the probability densities reduce to the following:

$$f_0^{(1)}(\mathbf{r},\mathbf{p},t)=f_0^{(1)}(|\mathbf{p}|) \,, \qquad (28)$$

$$g_0^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)=g_0^{(2)}(|\mathbf{r}_1-\mathbf{r}_2|) \,, \qquad (29)$$

where $f_0^{(1)}(|\mathbf{p}|)$ is the Boltzmann function, and $g_0^{(2)}(|\mathbf{r}|)$ is the radial distribution function. Specifically, with k_B = Boltzmann's constant, T is the temperature, and $\beta=(k_BT)^{-1}$,

$$f_0^{(1)}(|\mathbf{p}|)=\rho_0(\beta/2\pi m)^{3/2}\exp(-\beta\mathbf{p}^2/2m) \,, \qquad (30)$$

and

$$\rho_0=\bar{N}/V=\int f_0^{(1)}(|\mathbf{p}|)d\mathbf{p} \,. \qquad (31)$$

The spatial integral on the right of (6) or (7) vanishes by symmetry, so that

$$\mathbf{K}_0(\mathbf{r},\mathbf{p},t)=\mathbf{0} \,. \qquad (32)$$

The local potential of mean force, Eq. (10), reduces to

$$\nabla_{\mathbf{r}_1}w_0^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)=\nabla_{\mathbf{r}_1}w_0^{(2)}(|\mathbf{r}_1-\mathbf{r}_2|) \,, \qquad (33)$$

where

$$\nabla_{\mathbf{r}_1}w_0^{(2)}(|\mathbf{r}_1-\mathbf{r}_2|) = \nabla_{\mathbf{r}_1}\phi(|\mathbf{r}_1-\mathbf{r}_2|) + \frac{\rho_0\int[\nabla_{\mathbf{r}_1}\phi(|\mathbf{r}_1-\mathbf{r}_3|)]g_0^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)d\mathbf{r}_3}{g_0^{(2)}(|\mathbf{r}_1-\mathbf{r}_2|)} \,. \qquad (34)$$

When we use the equilibrium definition of $w_0^{(2)}$, namely,

$$g_0^{(2)}(|\mathbf{r}_1-\mathbf{r}_2|)=\exp[-\beta w_0^{(2)}(|\mathbf{r}_1-\mathbf{r}_2|)] \,, \qquad (35)$$

then (34) is the correct expression for $w_0^{(2)}$ (see, e.g., Ref. 16, p. 44).

Let us now evaluate the first two BBGKY equations in equilibrium. Since the time and position derivatives of $f_0^{(1)}(|\mathbf{p}|)$ vanish, and since $\mathbf{K}_0=0$, the one-particle equation (8) vanishes term by term. In contrast, Eq. (11) does not vanish term by term, but reduces to

$$\left[\frac{\mathbf{p}_1}{m}\cdot\nabla_{\mathbf{r}_1}+\frac{\mathbf{p}_2}{m}\cdot\nabla_{\mathbf{r}_2}\right]f_0^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2) = [\nabla_{\mathbf{r}_1}w_0^{(2)}(|\mathbf{r}_1-\mathbf{r}_2|)]\cdot(\nabla_{\mathbf{p}_1}-\nabla_{\mathbf{p}_2})f_0^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2) \,. \qquad (36)$$

The left side is composed of drift terms, and the right side consists of two-particle mean-force terms. From (30) and (35), it follows that the two sides of (36) are identically equal; this equilibrium cancellation of drift and force terms is a manifestation of detailed balance.

III. NONEQUILIBRIUM MOMENTUM CORRELATIONS

A. Truncated gradient expansion

At this point it is convenient to introduce the variables $\mathbf{r}$ for the center position of two particles, and $\mathbf{s}$ for their separation,

$$\mathbf{r}=\tfrac{1}{2}(\mathbf{r}_1+\mathbf{r}_2) \,, \qquad \mathbf{s}=(\mathbf{r}_2-\mathbf{r}_1) \,. \qquad (37)$$

Then $\nabla_{\mathbf{r}_1}=\frac{1}{2}\nabla_{\mathbf{r}}-\nabla_{\mathbf{s}}$, and $\nabla_{\mathbf{r}_2}=\frac{1}{2}\nabla_{\mathbf{r}}+\nabla_{\mathbf{s}}$. The momentum variables are also changed, to achieve notational simplification,

$$\mathbf{p}=\mathbf{p}_1 \,, \qquad \mathbf{p}'=\mathbf{p}_2 \,, \qquad \mathbf{q}=\mathbf{p}+\mathbf{p}' \,. \qquad (38)$$

When using the new variables, the order of position and momentum variables will be changed, as in the example

$$f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)=f^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t) \,. \qquad (39)$$

The particle symmetry of $f^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$, and of $g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$, means these functions are invariant under interchange of $\mathbf{s},\mathbf{p},\mathbf{p}'$ with $-\mathbf{s},\mathbf{p}',\mathbf{p}$. A useful property of any local function $Q(\mathbf{r},\mathbf{s},t)$ is

$$\int \nabla_{\mathbf{s}}Q(\mathbf{r},\mathbf{s},t)d\mathbf{s}=0 \,. \qquad (40)$$

Now, in a nonequilibrium fluid, to the extent that multiparticle correlations are important, there must be some restrictions on gradients of the probability densities. For example, under a translation of $\mathbf{r}$ by a distance of order or less than the correlation length l_c, at a given time, the function $f^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$ should change by a relatively small amount. In other words, $\mathbf{s}\cdot\nabla_{\mathbf{r}}f^{(2)}$ should be small compared to $f^{(2)}$, for $|\mathbf{s}|\lesssim l_c$. This condition should hold separately for the factors of $f^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$, namely, $f^{(1)}(\mathbf{r},\mathbf{p},t)$ and $g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$. With this concept, $f^{(2)}$ has the following gradient expansion, restricted to $|\mathbf{s}|\lesssim l_c$,

$$f^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t) = f^{(1)}(\mathbf{r},\mathbf{p},t)f^{(1)}(\mathbf{r},\mathbf{p}',t)g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t) + \tfrac{1}{2}\mathbf{s}\cdot\mathbf{A}(\mathbf{r},\mathbf{p},\mathbf{p}',t)g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)+\cdots \,, \qquad (41)$$

where

$$\mathbf{A}(\mathbf{r},\mathbf{p},\mathbf{p}',t)=f^{(1)}(\mathbf{r},\mathbf{p},t)\nabla_r f^{(1)}(\mathbf{r},\mathbf{p}',t) -f^{(1)}(\mathbf{r},\mathbf{p}',t)\nabla_r f^{(1)}(\mathbf{r},\mathbf{p},t)\ . \tag{42}$$

Note that while (41) for $f^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$ is restricted to $|\mathbf{s}|\lesssim l_c$, the two-particle correlation function $g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$ is still defined for all $\mathbf{s}$, and still has the distant value 1, so that $g^{(2)}-1$ is a local function of $\mathbf{s}$.

Expansions in the spirit of (41) are assumed to converge rapidly. This is not to say that gradients are small in an absolute sense, but rather that statistically meaningful correlations cannot extend across significant variations in the probability densities, so that the correlation length l_c ought to be small compared to the distance over which $f^{(1)}$ and $g^{(2)}$ change appreciably. With this in mind, the second step in constructing local evolution equations for a dense fluid is to apply the gradient expansion to the BBGKY equations. In doing this, the expansion of each theoretical expression will be truncated after the lowest contributing order. This constitutes a slight *redefinition* of theoretical functions, and allows us to construct a theory which satisfies the conservation laws and the h theorem *exactly*, and not merely in a certain order of an expansion. Since we cannot argue that this procedure has universal validity, the truncated gradient expansion constitutes a limitation of the present theory.

We consider first the mechanical densities and currents, defined in Sec. II C. The one-particle densities and currents are not affected by the gradient expansion. The truncated two-particle contributions are much simpler than the originals. With the abbreviation

$$f_a^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)=f^{(1)}(\mathbf{r},\mathbf{p},t)f^{(1)}(\mathbf{r},\mathbf{p}',t)g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)\ , \tag{43}$$

the two-particle densities and currents are

$$\rho(\mathbf{r},t)\epsilon^{(2)}(\mathbf{r},t)=\tfrac{1}{2}\int\int\int \phi(|\mathbf{s}|)f_a^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)d\mathbf{p}\,d\mathbf{p}'d\mathbf{s}\ , \tag{44}$$

$$\mathbf{P}^{(2)}(\mathbf{r},t) =-\tfrac{1}{2}\int\int\int \phi'(|\mathbf{s}|)\frac{\mathbf{s}\mathbf{s}}{|\mathbf{s}|}f_a^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)d\mathbf{p}\,d\mathbf{p}'d\mathbf{s}\ , \tag{45}$$

$$\mathbf{J}^{(2a)}(\mathbf{r},t)=-\tfrac{1}{2}\int\int\int \phi'(|\mathbf{s}|)\frac{\mathbf{s}\mathbf{s}}{|\mathbf{s}|}\cdot\left[\frac{\mathbf{p}+\mathbf{p}'}{2m}-\mathbf{v}(\mathbf{r},t)\right] \times f_a^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)d\mathbf{p}\,d\mathbf{p}'\,d\mathbf{s}\ , \tag{46}$$

$$\mathbf{J}^{(2b)}(\mathbf{r},t)=\tfrac{1}{2}\int\int\int \phi(|\mathbf{s}|)\left[\frac{\mathbf{p}+\mathbf{p}'}{2m}-\mathbf{v}(\mathbf{r},t)\right] \times f_a^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)d\mathbf{p}\,d\mathbf{p}'\,d\mathbf{s}\ . \tag{47}$$

An important point is that the truncated gradient expansion is capable of representing all these mechanical quantities in zeroth order, i.e., none of the above expressions vanishes in a general nonequilibrium fluid. A further property of these expressions, not present in the original definitions of Sec. II C, is that the integrands are symmetric in particles. This invariance of integrands under interchange of particles is a property of importance when it comes to constructing an h theorem.

B. Reduced correlation function

The question of the momentum dependence of $g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$, i.e., what $\mathbf{p},\mathbf{p}'$ dependence should $g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$ actually possess, is difficult. In fact, this question can be avoided, because the momentum dependence of $g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$ which enters the two-particle densities and currents, according to Eqs. (44)–(47), is limited to the single vector $\mathbf{q}=\mathbf{p}+\mathbf{p}'$. To reflect this situation, we will introduce a reduced two-particle correlation function $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$. First $B(\mathbf{r},\mathbf{q},t)$ is defined by

$$B(\mathbf{r},\mathbf{q},t)=\int\int f^{(1)}(\mathbf{r},\mathbf{p},t)f^{(1)}(\mathbf{r},\mathbf{p}',t)\delta(\mathbf{p}+\mathbf{p}'-\mathbf{q})d\mathbf{p}\,d\mathbf{p}'\ . \tag{48}$$

Integral properties of $B(\mathbf{r},\mathbf{q},t)$, which follow from the integrals (12) and (13) of $f^{(1)}(\mathbf{r},\mathbf{p},t)$, are

$$\int B(\mathbf{r},\mathbf{q},t)d\mathbf{q}=\rho^2(\mathbf{r},t)\ , \tag{49}$$

$$\int\left[\frac{\mathbf{q}}{2m}-\mathbf{v}(\mathbf{r},t)\right]B(\mathbf{r},\mathbf{q},t)d\mathbf{q}=0\ . \tag{50}$$

Now $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ is defined by

$$B(\mathbf{r},\mathbf{q},t)\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t) =\int\int f^{(1)}(\mathbf{r},\mathbf{p},t)f^{(1)}(\mathbf{r},\mathbf{p}',t) \times g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)\delta(\mathbf{p}+\mathbf{p}'-\mathbf{q})d\mathbf{p}\,d\mathbf{p}'\ . \tag{51}$$

Properties of $\gamma^{(2)}$ are $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)=\gamma^{(2)}(\mathbf{r},-\mathbf{s},\mathbf{q},t)$, $\gamma^{(2)}-1$ is a local function of $\mathbf{s}$, and $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ has the equilibrium limit $g_0^{(2)}(|\mathbf{s}|)$, as defined in Sec. II D.

The two-particle densities and currents, Eqs. (44)–(47), are expressed in terms of $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ as follows:

$$\rho(\mathbf{r},t)\epsilon^{(2)}(\mathbf{r},t)=\tfrac{1}{2}\int\int \phi(|\mathbf{s}|)B(\mathbf{r},\mathbf{q},t)\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}\,d\mathbf{s}\ , \tag{52}$$

$$\mathbf{P}^{(2)}(\mathbf{r},t)=-\tfrac{1}{2}\int\int \phi'(|\mathbf{s}|)\frac{\mathbf{s}\mathbf{s}}{|\mathbf{s}|}B(\mathbf{r},\mathbf{q},t) \times\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}\,d\mathbf{s}\ , \tag{53}$$

$$\mathbf{J}^{(2a)}(\mathbf{r},t)=-\tfrac{1}{2}\int\int \phi'(|\mathbf{s}|)\frac{\mathbf{s}\mathbf{s}}{|\mathbf{s}|}\cdot\left[\frac{\mathbf{q}}{2m}-\mathbf{v}(\mathbf{r},t)\right] \times B(\mathbf{r},\mathbf{q},t)\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}\,d\mathbf{s}\ , \tag{54}$$

$$\mathbf{J}^{(2b)}(\mathbf{r},t)=\tfrac{1}{2}\int\int \phi(|\mathbf{s}|)\left[\frac{\mathbf{q}}{2m}-\mathbf{v}(\mathbf{r},t)\right]B(\mathbf{r},\mathbf{q},t) \times\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}\,d\mathbf{s}\ . \tag{55}$$

Since these expressions represent all the significant mechanical densities and currents, then $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ is the physically significant part of $g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$. We therefore want to construct the entire theory in terms of $\gamma^{(2)}$, instead of $g^{(2)}$.

The third step in our construction is to separate the $\gamma^{(2)}$ terms in the BBGKY equations. This is done in the following way: $g^{(2)}$ is replaced by $\gamma^{(2)}+(g^{(2)}-\gamma^{(2)})$, terms in $(g^{(2)}-\gamma^{(2)})$ only are put on the right sides, and the left sides are evaluated in the truncated gradient expansion. The left side of the one-particle equation retains the appearance of (8), where now $\mathbf{K}(\mathbf{r},\mathbf{p},t)$ is given by

$$\begin{aligned} f^{(1)}(\mathbf{r},\mathbf{p},t)\mathbf{K}(\mathbf{r},\mathbf{p},t) &= \nabla_{\mathbf{r}}\cdot\tfrac{1}{2}\int\int\phi'(|\mathbf{s}|)\frac{\mathbf{ss}}{|\mathbf{s}|}f^{(1)}(\mathbf{r},\mathbf{p},t)f^{(1)}(\mathbf{r},\mathbf{q}-\mathbf{p},t) \\ &\qquad\times\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}\,d\mathbf{s} \\ &\quad+\tfrac{1}{2}\int\int\phi'(|\mathbf{s}|)\frac{\mathbf{ss}}{|\mathbf{s}|}\cdot\mathbf{A}(\mathbf{r},\mathbf{p},\mathbf{q}-\mathbf{p},t) \\ &\qquad\times\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}\,d\mathbf{s}\ . \end{aligned} \tag{56}$$

Hence in the truncated gradient expansion, all contributions to the one-particle mean force $\mathbf{K}(\mathbf{r},\mathbf{p},t)$ are of order $\nabla_{\mathbf{r}}$; such terms, of course, vanish in equilibrium.

In the two-particle BBGKY equation (11), the potential of mean force $w^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$ appears in a driving term. We will not try to evaluate this term, but will merely represent it by a function $\mathscr{W}$, whose form will be expressed in Sec. III C. For the remainder of Eq. (11), all $\gamma^{(2)}$ terms are collected on the left side, the truncated gradient expansion is applied, and the result is multiplied by $\delta(\mathbf{p}+\mathbf{p}'-\mathbf{q})$ and integrated over $d\mathbf{p}\,d\mathbf{p}'$. The left side of the two-particle equation, comprising the time derivative and all drift and force terms, is then

$$\begin{aligned} &\left[\frac{\partial}{\partial t}+\frac{\mathbf{q}}{2m}\cdot\nabla_{\mathbf{r}}\right]B(\mathbf{r},\mathbf{q},t)\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t) \\ &\qquad+\mathbf{C}(\mathbf{r},\mathbf{q},\mathrm{t}):\nabla_{\mathbf{s}}\mathbf{s}\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},\mathrm{t}) \\ &\qquad+\nabla_{\mathbf{q}}\cdot\mathbf{D}(\mathbf{r},\mathbf{q},t)\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)+\mathscr{W}(\mathbf{r},\mathbf{s},\mathbf{q},t)\ , \end{aligned} \tag{57}$$

where $B(\mathbf{r},\mathbf{q},t)$ is defined in (48), the nonsymmetric tensor $\mathbf{C}(\mathbf{r},\mathbf{q},t)$ is given by

$$\mathbf{C}(\mathbf{r},\mathbf{q},t)=\int[\nabla_{\mathbf{r}}f^{(1)}(\mathbf{r},\mathbf{p},t)]\left[\frac{2\mathbf{p}-\mathbf{q}}{m}\right]f^{(1)}(\mathbf{r},\mathbf{q}-\mathbf{p},t)d\mathbf{p}\ , \tag{58}$$

and the vector $\mathbf{D}(\mathbf{r},\mathbf{q},t)$ is given by

$$\mathbf{D}(\mathbf{r},\mathbf{q},t)=2\int f^{(1)}(\mathbf{r},\mathbf{p},t)f^{(1)}(\mathbf{r},\mathbf{q}-\mathbf{p},t)\mathbf{K}(\mathbf{r},\mathbf{p},t)d\mathbf{p}\ . \tag{59}$$

The function $\mathscr{W}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ is local, and from its origin in the $w^{(2)}$ terms in Eq. (11), it must satisfy

$$\int\mathscr{W}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}=0\ . \tag{60}$$

Now every term in (57) is linear in $\partial/\partial t$ or in $\nabla_{\mathbf{r}}$, including $\mathscr{W}$, so every term vanishes in equilibrium. The nonzero equilibrium terms of the original BBGKY equation, as displayed in Eq. (36), were taken out by the momentum integrations. This is a proper result, since the nonzero rates of change which identically cancel in equilibrium, will appear in the irreversible parts.

C. The potential-of-mean-force term

Let us separate $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ into two contributions. The first is the momentum-averaged correlation function $\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)$, defined by

$$\begin{aligned} \rho^2(\mathbf{r},t)\Gamma^{(2)}(\mathbf{r},\mathbf{s},t) &= \int\int f^{(1)}(\mathbf{r},\mathbf{p},t)f^{(1)}(\mathbf{r},\mathbf{p}',t)g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)d\mathbf{p}\,d\mathbf{p}'\ , \end{aligned} \tag{61}$$

or in view of the definition (51) of $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$,

$$\rho^2(\mathbf{r},t)\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)=\int B(\mathbf{r},\mathbf{q},t)\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}\ . \tag{62}$$

The $\mathbf{q}$-dependent part of $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ is then $\delta\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ defined by

$$\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)=\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)+\delta\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)\ . \tag{63}$$

From these definitions it follows

$$\int B(\mathbf{r},\mathbf{q},t)\delta\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}=0\ . \tag{64}$$

Significant properties of the constituents of $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ are $\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)-1$ and $\delta\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ are local functions; $\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)\geq 0$, and $\delta\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ is of indefinite sign; and in equilibrium $\Gamma_0^{(2)}(\mathbf{r},\mathbf{s},t)=g_0^{(2)}(|\mathbf{s}|)$, and $\delta\gamma_0^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)=0$. Because of the integral conditions (49) and (50), the two-particle densities $\rho\epsilon^{(2)}$ and $\mathbf{P}^{(2)}$ depend only on $\Gamma^{(2)}$, while the two-particle energy currents $\mathbf{J}^{(2a)}$ and $\mathbf{J}^{(2b)}$ depend only on $\delta\gamma^{(2)}$.

The expression (57) is the left side of the equation for $\mathbf{B}(\mathbf{r},\mathbf{q},t)\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$. This can be integrated over $d\mathbf{q}$ to find, with the help of (25) for conservation of particles, the left side of the equation for $\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)$,

$$\begin{aligned} &\rho^2(\mathbf{r},t)\left[\frac{\partial}{\partial t}+\mathbf{v}(\mathbf{r},t)\cdot\nabla_{\mathbf{r}}+\mathbf{s}\cdot\nabla_{\mathbf{r}}\mathbf{v}(\mathbf{r},t)\cdot\nabla_{\mathbf{s}}\right]\Gamma^{(2)}(\mathbf{r},\mathbf{s},t) \\ &\qquad+\nabla_{\mathbf{r}}\cdot\int\left[\frac{\mathbf{q}}{2m}-\mathbf{v}(\mathbf{r},t)\right]B(\mathbf{r},\mathbf{q},t)\delta\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}+\int\mathbf{C}(\mathbf{r},\mathbf{q},t):\nabla_{\mathbf{s}}\mathbf{s}\delta\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}\ . \end{aligned} \tag{65}$$

This result, together with (57) and (8), gives the left side of the equation for $\delta\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$, in which the terms not linear in $\delta\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ are

$$\mathscr{W}(\mathbf{r},\mathbf{s},\mathbf{q},t)+\mathbf{B}(\mathbf{r},\mathbf{q},t)\left[\frac{\mathbf{q}}{2m}-\mathbf{v}(\mathbf{r},t)\right]\cdot\nabla_r\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)+\mathbf{s}\cdot[\mathbf{C}(\mathbf{r},\mathbf{q},t)-B(\mathbf{r},\mathbf{q},t)\nabla_r\mathbf{v}(\mathbf{r},t)]\cdot\nabla_s\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)\ . \tag{66}$$

Here $\mathscr{W}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ represents the force term arising from $w^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$, while the terms in $\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)$ are drift terms. These force and drift terms are not independent, since the potential-of-mean force depends on momenta; in fact, we will assume that the effect of $\mathscr{W}$ is merely to modify the drift terms in (66). Hence (66) represents the net of force and drift terms arising from the momentum-averaged correlations $\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)$, and contributing to the evolution of the momentum correlations $\delta\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$. The role we assign to $\mathscr{W}$ is to cancel the center-of-mass drift of particle pairs, represented by the $\nabla_r\Gamma^{(2)}$ term in (66), and to cancel the *central component* of the drift of particle pairs with respect to the center of mass, represented by the $\nabla_s\Gamma^{(2)}$ term in (66),

$$\begin{aligned}\mathscr{W}&(\mathbf{r},\mathbf{s},\mathbf{q},t)\\ &=-B(\mathbf{r},\mathbf{q},t)\left[\frac{\mathbf{q}}{2m}-\mathbf{v}(\mathbf{r},t)\right]\cdot\nabla_r\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)\\ &\quad-[\mathrm{Tr}\mathbf{C}(\mathbf{r},\mathbf{q},t)-B(\mathbf{r},\mathbf{q},t)\nabla_r\cdot\mathbf{v}(\mathbf{r},t)]\mathbf{s}\cdot\nabla_s\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)\ .\end{aligned}\tag{67}$$

This expression is local, and satisfies the integral condition (60).

D. The h function

For an equilibrium dense fluid, we have recently proposed an entropy expression which includes the effects of multiparticle correlations.[12] That expression will now be extended to a nonequilibrium fluid, to define $h(\mathbf{r},t)$, the h quantity per particle. The one-particle contribution is of the Boltzmann form,

$$\rho(\mathbf{r},t)h^{(1)}(\mathbf{r},t)=\int f^{(1)}(\mathbf{r},\mathbf{p},t)\ln h^3 f^{(1)}(\mathbf{r},\mathbf{p},t)d\mathbf{p}\ . \tag{68}$$

By extension of the equilibrium result, the two-particle contribution is of the form

$$\tfrac{1}{2}\int\int\int f^{(1)}(\mathbf{r},\mathbf{p},t)f^{(1)}(\mathbf{r},\mathbf{p}',t)g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)\times\ln g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)d\mathbf{p}\,d\mathbf{p}'\,d\mathbf{s}\ .$$

However, since we are constructing a theory based on $\gamma^{(2)}$, we will replace $g^{(2)}$ with $\gamma^{(2)}$ in the above expression, to obtain

$$\rho(\mathbf{r},t)h^{(2)}(\mathbf{r},t)=\tfrac{1}{2}\int\int B(\mathbf{r},\mathbf{q},t)\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)\times\ln\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}\,d\mathbf{s}\ . \tag{69}$$

Because the correlation function appears as the argument of a logarithm, the step of replacing $g^{(2)}$ by $\gamma^{(2)}$ is profound; this choice will exert a strong influence on construction of the irreversible parts. Finally, since the series $h^{(1)}+h^{(2)}+\cdots$ is assumed to converge rapidly, and since we want to construct a closed two-particle theory, we will omit higher-order correlation contributions and write

$$h(\mathbf{r},t)=h^{(1)}(\mathbf{r},t)+h^{(2)}(\mathbf{r},t)\ . \tag{70}$$

In equilibrium, $h^{(1)}$ and $h^{(2)}$ reduce to one- and two-particle contributions to the total system entropy S, as follows:

$$\begin{aligned}h_0^{(1)}&=-S^{(1)}/\bar{N}k_B\ ,\\ h_0^{(2)}&=-S^{(2)}/\bar{N}k_B\ .\end{aligned}\tag{71}$$

Contributions to the h current, $\mathbf{I}(\mathbf{r},t)$, can be constructed by analogy to the energy current $\mathbf{J}(\mathbf{r},t)$. $\mathbf{J}^{(1)}(\mathbf{r},t)$ is given by (22), and is merely a drift, relative to the center of mass, of the one-particle energy $(\mathbf{p}-m\mathbf{v})^2/2m$, so $\mathbf{I}^{(1)}(\mathbf{r},t)$ should be the corresponding drift of $\ln h^3 f^{(1)}$,

$$\mathbf{I}^{(1)}(\mathbf{r},t)=\int\frac{\mathbf{p}-m\mathbf{v}(\mathbf{r},t)}{m}[\ln h^3 f^{(1)}(\mathbf{r},\mathbf{p},t)]f^{(1)}(\mathbf{r},\mathbf{p},t)d\mathbf{p}\ . \tag{72}$$

$\mathbf{J}^{(2)}(\mathbf{r},t)$ has two contributions, listed in (54) and (55). The simple contribution is $\mathbf{J}^{(2b)}(\mathbf{r},t)$, which is merely a drift, relative to the center of mass, of the two-particle energy $\frac{1}{2}\phi(\,|\mathbf{s}|\,)$, so $\mathbf{I}^{(2b)}(\mathbf{r},t)$ should be the corresponding drift of $\frac{1}{2}\ln\gamma^{(2)}$,

$$\mathbf{I}^{(2b)}(\mathbf{r},t)=\tfrac{1}{2}\int\int\ln\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)\left[\frac{\mathbf{q}}{2m}-\mathbf{v}(\mathbf{r},t)\right]\times B(\mathbf{r},\mathbf{q},t)\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}\,d\mathbf{s}\ . \tag{73}$$

$\mathbf{J}^{(2a)}(\mathbf{r},t)$ can be constructed from its physical basis, as follows. The rate of increase of kinetic energy density at $(\mathbf{r}-\frac{1}{2}\mathbf{s},\mathbf{p})$, due to the particle density at $(\mathbf{r}+\frac{1}{2}\mathbf{s},\mathbf{p}')$, is

$$j(\mathbf{r}-\tfrac{1}{2}\mathbf{s},\mathbf{p})=\nabla_s\phi(\,|\mathbf{s}|\,)\cdot\left[\nabla_p\frac{[\mathbf{p}-m\mathbf{v}(\mathbf{r}-\frac{1}{2}\mathbf{s},t)]^2}{2m}\right]\times f^{(2)}(\mathbf{r}-\tfrac{1}{2}\mathbf{s},\mathbf{p},\mathbf{r}+\tfrac{1}{2}\mathbf{s},\mathbf{p}',t)\ ,$$

the rate of increase of kinetic energy density at $(\mathbf{r}+\frac{1}{2}\mathbf{s},\mathbf{p}')$, due to the particle density at $(\mathbf{r}-\frac{1}{2}\mathbf{s},\mathbf{p})$, is

$$j(\mathbf{r}+\tfrac{1}{2}\mathbf{s},\mathbf{p}')=-\nabla_s\phi(\,|\mathbf{s}|\,)\cdot\left[\nabla_{p'}\frac{[\mathbf{p}'-m\mathbf{v}(\mathbf{r}+\frac{1}{2}\mathbf{s},t)]^2}{2m}\right]\times f^{(2)}(\mathbf{r}-\tfrac{1}{2}\mathbf{s},\mathbf{p},\mathbf{r}+\tfrac{1}{2}\mathbf{s},\mathbf{p}',t)\ ,$$

and $\mathbf{s}$ times the difference of these quantities is a current. In fact, if we write the total of this current,

$$\tfrac{1}{4}\int\int\int\mathbf{s}[j(\mathbf{r}+\tfrac{1}{2}\mathbf{s},\mathbf{p}')-j(\mathbf{r}-\tfrac{1}{2}\mathbf{s},\mathbf{p})]d\mathbf{p}\,d\mathbf{p}'d\mathbf{s}\ ,$$

and then apply the truncated gradient expansion, the result is exaclty $\mathbf{J}^{(2a)}(\mathbf{r},t)$ as given by (54). Now the analogous expression for $\mathbf{I}^{(2a)}(\mathbf{r},t)$ is

$$-\tfrac{1}{4}\int\int\int \mathbf{s}\nabla_{\mathbf{s}}\phi(|\mathbf{s}|)\cdot[\nabla_{\mathbf{p}}\ln h^3 f^{(1)}(\mathbf{r},\mathbf{p},t)+\nabla_{\mathbf{p}'}\ln h^3 f^{(1)}(\mathbf{r},\mathbf{p}',t)]\,f^2(\mathbf{r}-\tfrac{1}{2}\mathbf{s},\mathbf{p},\mathbf{r}+\tfrac{1}{2}\mathbf{s},\mathbf{p}',t)\,d\mathbf{p}\,d\mathbf{p}'\,d\mathbf{s}\ .$$

Applying the truncated gradient expansion, and introducing the definition (51) of $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$, leads to the result

$$\mathbf{I}^{(2a)}(\mathbf{r},t)=\tfrac{1}{2}\int\int B(\mathbf{r},\mathbf{q},t)\phi'(|\mathbf{s}|)\frac{\mathbf{s}\mathbf{s}}{|\mathbf{s}|}\cdot\nabla_{\mathbf{q}}\times\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)\,d\mathbf{q}\,d\mathbf{s}\ . \tag{74}$$

The total h current is finally

$$\mathbf{I}(\mathbf{r},t)=\mathbf{I}^{(1)}(\mathbf{r},t)+\mathbf{I}^{(2a)}(\mathbf{r},t)+\mathbf{I}^{(2b)}(\mathbf{r},t)\ . \tag{75}$$

IV. THE INTERACTION INTEGRALS

A. Transition rates

The nature of a dense fluid, which is in contrast to the nature of a gas, is that a particle in a fluid is in continuous interaction with a large number of other particles, where the "large number" is of order 10. This in true in equilibrium or in nonequilibrium. The interactions of fluid particles are not a sum of *independent* two-particle interactions, but are rather a sum of *statistically correlated* two-particle interactions. The problem at hand is to represent the effect of such interactions in the evolution of a nonequilibrium fluid, in an effective two-particle formulation. This will be done by defining transition rates, and then by constructing the interaction integrals.

The potential of mean force will appear explicitly in the transition rates. In this function we assume that a momentum-independent central potential is appropriate. We could construct a momentum- and angle-average of $w^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$, but in fact we will merely represent the potential as $w^{(2)}(\mathbf{r},|\mathbf{s}|,t)$, a local function. It may be noted that this limitation is strictly correct in a near-equilibrium situation, where $w^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$ becomes $w_0^{(2)}(|\mathbf{s}|)$, a known equilibrium function.

At a given $\mathbf{r},t$ in an equilibrium or nonequilibrium fluid, there are effective two-particle interactions in which $(\mathbf{s},\mathbf{p},\mathbf{p}')$ goes to $(\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')$. For a given phase-space volume element $d\hat{\mathbf{p}}\,d\hat{\mathbf{p}}'\,d\hat{\mathbf{s}}$, the transition rate is

$$\mathcal{X}(\mathbf{s},\mathbf{p},\mathbf{p}'\,|\,\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')\,d\hat{\mathbf{p}}\,d\hat{\mathbf{p}}'\,d\hat{\mathbf{s}}\ .$$

The dependence of $\mathcal{X}$ on $\mathbf{r},t$ is suppressed for abbreviation. The important properties of $\mathcal{X}$ are (a)—(d) of the following list:

$$\text{(a) } \mathcal{X}(\mathbf{s},\mathbf{p},\mathbf{p}'\,|\,\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')\geq 0\ . \tag{76}$$

(b) $\mathcal{X}$ contains two δ functions as factors. These δ functions express conservation of linear momentum,

$$\delta(\mathbf{p}+\mathbf{p}'-\hat{\mathbf{p}}-\hat{\mathbf{p}}'),\ \text{or}\ \delta(\mathbf{q}-\hat{\mathbf{q}})\ , \tag{77}$$

and conservation of the "energy of mean force,"

$$\delta(\omega-\hat{\omega})\ , \tag{78}$$

where

$$\omega(\mathbf{r},\mathbf{s}\,|\,\mathbf{p}\,|,|\,\mathbf{p}'\,|,t)=\frac{\mathbf{p}^2}{2m}+\frac{\mathbf{p}'^2}{2m}+w^{(2)}(\mathbf{r},|\,\mathbf{s}\,|,t)\ . \tag{79}$$

Aside from the δ functions noted here, $\mathcal{X}$ is presumably a smooth function of its variables. The requirement for conservation of the energy of mean force is the key to an effective two-particle formulation of statistically correlated interactions.

$$\text{(c) } \mathcal{X}(\mathbf{s},\mathbf{p},\mathbf{p}'\,|\,\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')\text{is local in } \mathbf{s},\hat{\mathbf{s}}\ . \tag{80}$$

Note there *are* nonlocal transitions, involving two distant particles, but these particles are not correlated *with one another.* Hence the transition rate for correlated two-particle interactions has to be a local function.

(d) $\mathcal{X}$ satisfies the following three symmetries:

$$\begin{aligned}&\mathcal{X}(\mathbf{s},\mathbf{p},\mathbf{p}'\,|\,\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')=\mathcal{X}(\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}'\,|\,\mathbf{s},\mathbf{p},\mathbf{p}')\ ,\\ &\mathcal{X}(\mathbf{s},\mathbf{p},\mathbf{p}'\,|\,\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')=\mathcal{X}(-\mathbf{s},\mathbf{p},\mathbf{p}'\,|\,-\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')\ ,\\ &\mathcal{X}(\mathbf{s},\mathbf{p},\mathbf{p}'\,|\,\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')=\mathcal{X}(\mathbf{s},\mathbf{p}',\mathbf{p}\,|\,\hat{\mathbf{s}},\hat{\mathbf{p}}',\hat{\mathbf{p}})\ .\end{aligned} \tag{81}$$

The first of these is a statement of detailed balance. The second two are sufficient conditions to obtain required symmetries of the interaction integral, as discussed following equation (84) below.

Let us return momentarily to the two-particle probability density $f^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$, defined before the gradient expansion is applied. In an equilibrium or nonequilibrium fluid, the total rate of change of $f^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$, due to effective two-particle interactions in which $(\mathbf{s},\mathbf{p},\mathbf{p}')\to(\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')$, and in which $(\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')\to(\mathbf{s},\mathbf{p},\mathbf{p}')$, is

$$\int\int\int [f^{(2)}(\mathbf{r},\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}',t)-f^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)]\times\mathcal{X}(\mathbf{s},\mathbf{p},\mathbf{p}'\,|\,\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')\,d\hat{\mathbf{p}}\,d\hat{\mathbf{p}}'\,d\hat{\mathbf{s}}\ .$$

Because $\mathcal{X}$ is local in $\mathbf{s},\hat{\mathbf{s}}$, only the local part of $f^{(2)}$ enters this expression. After the truncated gradient expansion, and the replacement of $g^{(2)}$ with $\gamma^{(2)}$, the significant two-particle density is

$$f_c^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)=f^{(1)}(\mathbf{r},\mathbf{p},t)f^{(1)}(\mathbf{r},\mathbf{p}',t)\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p}+\mathbf{p}',t)\ . \tag{82}$$

The total rate of change of *this* quantity is $F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$, given by

$$F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)=\int\int\int [f_c^{(2)}(\mathbf{r},\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}',t)-f_c^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)]\times\mathcal{X}(\mathbf{s},\mathbf{p},\mathbf{p}'\,|\,\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')\,d\hat{\mathbf{p}}\,d\hat{\mathbf{p}}'d\hat{\mathbf{s}}\ . \tag{83}$$

$F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$ is our primary interaction integral. All other interaction integrals will be defined in terms of $F^{(2)}$. For example, the rate of change of $f^{(1)}(\mathbf{r},\mathbf{p},t)$, due to the same effective two-particle interactions, is $F^{(1)}(\mathbf{r},\mathbf{p},t)$, where

$$F^{(1)}(\mathbf{r},\mathbf{p},t)=\int\int F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)\,d\mathbf{p}'\,d\mathbf{s}\ . \tag{84}$$

Since $F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}'t)$ is the rate of change of the quantity (82), then $F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$ must be invariant under the interchange of $\mathbf{s}$ with $-\mathbf{s}$, and also under the interchange of $\mathbf{p}$ with $\mathbf{p}'$. These invariances will frequently be used in manipulating integrals containing $F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$, integrals which will appear in the conservation laws and in the h theorem. Sufficient (but not necessary) conditions to ensure these invariances are the last two symmetries of $\mathcal{X}$ listed in (81).

B. Interaction invariants

A function $\psi(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$ which is unchanged through transitions induced by the effective two-particle interaction is an interaction invariant, and satisfies the equation

$$\int\int\int F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)\psi(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)d\mathbf{p}\,d\mathbf{p}'\,d\mathbf{s}=0\ . \tag{85}$$

Because of the first symmetry of $\mathcal{X}$ listed in (81), and because of the δ-function factors of $\mathcal{X}$, there are three interaction invariants:

$$\begin{aligned}&\psi=1\ ,\\ &\psi=\mathbf{p}+\mathbf{p}'\ ,\\ &\psi=\omega(\mathbf{r},\mathbf{s},|\mathbf{p}|,|\mathbf{p}'|,t)\ .\end{aligned} \tag{86}$$

The integral condition (85), for each interaction invariant, can be expressed with the help of $F^{(1)}(\mathbf{r},\mathbf{p},t)$, as follows:

$$\int F^{(1)}(\mathbf{r},\mathbf{p},t)d\mathbf{p}=0\ , \tag{87}$$

$$\int \mathbf{p}F^{(1)}(\mathbf{r},\mathbf{p},t)d\mathbf{p}=0\ , \tag{88}$$

$$\begin{aligned}\int \frac{\mathbf{p}^2}{2m}F^{(1)}(\mathbf{r},\mathbf{p},t)d\mathbf{p}&\\ +\tfrac{1}{2}\int\int\int w^{(2)}(\mathbf{r},|\mathbf{s}|,t)&\\ \times F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)d\mathbf{p}\,d\mathbf{p}'\,d\mathbf{s}&=0\ .\end{aligned} \tag{89}$$

While the interactions conserve the energy of mean force microscopically, i.e., within the process of each effective two-particle interaction, the interactions must also conserve total energy macroscopically, i.e., in the mean. This can be expressed as a single integral condition on $\mathcal{X}$,

$$\begin{aligned}\int \frac{\mathbf{p}^2}{2m}F^{(1)}(\mathbf{r},\mathbf{p},t)d\mathbf{p}&\\ +\tfrac{1}{2}\int\int\int \phi(|\mathbf{s}|)F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)d\mathbf{p}\,d\mathbf{p}'\,d\mathbf{s}&=0\ .\end{aligned} \tag{90}$$

In view of (89), this equation can be replaced by

$$\begin{aligned}\int\int\int [\phi(|\mathbf{s}|)-w^{(2)}(\mathbf{r},|\mathbf{s}|,t)]&\\ \times F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)d\mathbf{p}\,d\mathbf{p}'\,d\mathbf{s}&=0\ .\end{aligned} \tag{91}$$

There is a significant contrast between the present theory and Boltzmann's. In Boltzmann's theory there is no energy of mean force, the collision invariants are 1, $\mathbf{p}+\mathbf{p}'$, and $(\mathbf{p}^2/2m)+(\mathbf{p}'^2/2m)$, and the energy invariance of the collisions guarantees macroscopic energy conservation as well.

V. COMPLETE EVOLUTION EQUATIONS

A. One- and two-particle equations

It is helpful at this point to summarize our philosophy for the construction of the evolution equations. Starting with the BBGKY equations, the first step was to introduce the potential of mean force $w^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$, and the second step was to apply the truncated gradient expansion. At this point, the BBGKY equations retain their original physical content. The third step was to gather terms in $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ on the left sides of the equations, and the fourth step was to reconstruct the potential-of-mean-force term on the left side of the two-particle equation. The last step will be to replace the right sides by irreversible terms, in the form of interaction integrals. This step converts the equations to irreversible evolution equations, and significantly alters their physical content. In the final form of the evolution equations, the quantities $w^{(2)}(\mathbf{r},|\mathbf{s}|,t)$ and $\mathcal{X}(\mathbf{s},\mathbf{p},\mathbf{p}'\,|\,\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')$ are considered known functions, in the same way the scattering cross section is supposed to be a known input function for the Boltzmann equation.

The left side of the one-particle equation is given by (8). Since this is an equation for $\partial f^{(1)}/\partial t$, the interaction integral should be the rate of change of $f^{(1)}$ due to effective two-particle interactions, namely, $F^{(1)}$ of Eq. (84). Hence the one-particle evolution equation has an appearance similar to the Boltzmann equation,

$$\begin{aligned}\left[\frac{\partial}{\partial t}+\frac{\mathbf{p}}{m}\cdot\nabla_{\mathbf{r}}\right]&f^{(1)}(\mathbf{r},\mathbf{p},t)\\ &+\nabla_{\mathbf{p}}\cdot f^{(1)}(\mathbf{r},\mathbf{p},t)\mathbf{K}(\mathbf{r},\mathbf{p},t)=F^{(1)}(\mathbf{r},\mathbf{p},t)\ ,\end{aligned} \tag{92}$$

where $\mathbf{K}(\mathbf{r},\mathbf{p},t)$ is the one-particle mean force, and is given by Eq. (56).

The equation for the product function $f^{(1)}(\mathbf{r},\mathbf{p},t)f^{(1)}(\mathbf{r},\mathbf{p}',t)$ follows at once from Eq. (92). When the equation for $f^{(1)}(\mathbf{r},\mathbf{p},t)f^{(1)}(\mathbf{r},\mathbf{p}',t)$ is multiplied by $\delta(\mathbf{p}+\mathbf{p}'-\mathbf{q})$, and integrated over $d\mathbf{p}\,d\mathbf{p}'$, the following result is obtained:

$$\begin{aligned}\left[\frac{\partial}{\partial t}+\frac{\mathbf{q}}{2m}\cdot\nabla_{\mathbf{r}}\right]&B(\mathbf{r},\mathbf{q},t)\\ &+\mathrm{Tr}\mathbf{C}(\mathbf{r},\mathbf{q},t)+\nabla_{\mathbf{q}}\cdot\mathbf{D}(\mathbf{r},\mathbf{q},t)=X(\mathbf{r},\mathbf{q},t)\ ,\end{aligned} \tag{93}$$

where

$$\begin{aligned}X(\mathbf{r},\mathbf{q},t)=\int\int [&f^{(1)}(\mathbf{r},\mathbf{p},t)F^{(1)}(\mathbf{r},\mathbf{p}',t)\\ &+f^{(1)}(\mathbf{r},\mathbf{p}',t)F^{(1)}(\mathbf{r},\mathbf{p},t)]\\ &\times\delta(\mathbf{p}+\mathbf{p}'-\mathbf{q})d\mathbf{p}\,d\mathbf{p}'\ .\end{aligned} \tag{94}$$

Equation (93) will help us in constructing the two-particle-evolution equation. Also, because of (87) and (88), $X(\mathbf{r},\mathbf{q},t)$ satisfies the integral conditions

$$\int X(\mathbf{r},\mathbf{q},t)d\mathbf{q}=0\ , \tag{95}$$

$$\int \mathbf{q}X(\mathbf{r},\mathbf{q},t)d\mathbf{q}=0\ . \tag{96}$$

The interaction-integral contribution to

$(\partial/\partial t)f^{(1)}(\mathbf{r},\mathbf{p},t)f^{(1)}(\mathbf{r},\mathbf{p}',t)\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p}+\mathbf{p}',t)$, due to effective interactions between the two particles at $\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t$, is $F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$. There is a further interaction-integral contribution to this time derivative, a contribution containing $f^{(1)}(\mathbf{r},\mathbf{p},t)F^{(1)}(\mathbf{r},\mathbf{p}',t)+f^{(1)}(\mathbf{r},\mathbf{p}',t)F^{(1)}(\mathbf{r},\mathbf{p},t)$, due to interactions of *one* of these particles with *other* particles. These two interaction-integral contributions are to be multiplied by $\delta(\mathbf{p}+\mathbf{p}'-\mathbf{q})$, and integrated over $d\mathbf{p}\,d\mathbf{p}'$, to obtain the corresponding contributions to $(\partial/\partial t)B(\mathbf{r},\mathbf{q},t)\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$. Hence the first contribution is $G^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$,

$$G^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)=\int\int F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)\delta(\mathbf{p}+\mathbf{p}'-\mathbf{q})d\mathbf{p}\,d\mathbf{p}'\ , \tag{97}$$

and the second contribution contains $X(\mathbf{r},\mathbf{q},t)$, according to (94). We write the second contribution in the form $[\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)+\sigma(\mathbf{r},\mathbf{s},t)]X(\mathbf{r},\mathbf{q},t)$, where $\sigma(\mathbf{r},\mathbf{s},t)$ is a local function of $\mathbf{s}$; this form has the correct distant limit, and also has the property that $\sigma(\mathbf{r},\mathbf{s},t)=0$ in a near-equilibrium situation. Then the two-particle evolution equation, whose left side is the expression (57), becomes

$$\left[\frac{\partial}{\partial t}+\frac{\mathbf{q}}{2m}\cdot\nabla_{\mathbf{r}}\right]B(\mathbf{r},\mathbf{q},t)\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)+\mathbf{C}(\mathbf{r},\mathbf{q},t):\nabla_{\mathbf{s}}\mathbf{s}\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)+\nabla_{\mathbf{q}}\cdot\mathbf{D}(\mathbf{r},\mathbf{q},t)\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)+\mathscr{W}(\mathbf{r},\mathbf{s},\mathbf{q},t)$$
$$=G^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)+[\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)+\sigma(\mathbf{r},\mathbf{s},t)]X(\mathbf{r},\mathbf{q},t)\ . \tag{98}$$

The local function $\sigma(\mathbf{r},\mathbf{s},t)$ is arbitrary except for a single integral condition, namely, the condition required to achieve an h theorem, as discussed in Sec. IV C. An important property of $G^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$, representing the fact that $\delta(\mathbf{p}+\mathbf{p}'-\mathbf{q})$ is an interaction invariant, is

$$\int G^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{s}=0\ . \tag{99}$$

It is useful at this point to remark on the "normalization" of the correlation function. From its definition by Eq. (61), or by (62), $\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)$ is the total pair-correlation function at $\mathbf{r},\mathbf{s},t$, averaged over all particle momenta. In a nonequilibrium dense fluid, we expect $\Gamma^{(2)}$ to satisfy the normalization

$$\rho(\mathbf{r},t)\int[\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)-1]d\mathbf{s}=-1+\alpha(\mathbf{r},t)\ , \tag{100}$$

where $\alpha(\mathbf{r},t)$ results from density fluctuations, and $\alpha(\mathbf{r},t)$ is small compared to 1. For many applications, it will be an acceptable approximation to set $\alpha=0$; our evolution equations are consistent with this approximation, providing the following condition on $\delta\gamma^{(2)}$ is satisfied:

$$\int\int\left[\frac{\mathbf{q}}{2m}-\mathbf{v}(\mathbf{r},t)\right]B(\mathbf{r},\mathbf{q},t)\delta\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}\,d\mathbf{s}=0\ . \tag{101}$$

On the other hand, one may wish to impose a normalization on every $\mathbf{q}$ component of $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$, as, for example,

$$\int B(\mathbf{r},\mathbf{q},t)[\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)-1]d\mathbf{s}=-\rho(\mathbf{r},t)\ . \tag{102}$$

In this case (101) is automatically satisfied, and our evolution equations are consistent with (102) if

$$\int\sigma(\mathbf{r},\mathbf{s},t)d\mathbf{s}=0\ . \tag{103}$$

B. The conservation laws

Consider the distant evaluation of (98). When $|\mathbf{s}|>l_c$, $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)=1$, $G^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)=0$, and Eq. (98) reduces to Eq. (93). This is a necessary property of the two-particle evolution equation: at any $\mathbf{r},t$ in the evolution of a nonequilibrium fluid, the distant value of $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ is 1, and this distant value must remain 1 under evolution according to the two-particle equation. Equation (98) is nonlocal, because it has terms which do not vanish when $|\mathbf{s}|>l_c$. By subtracting (93) from (98), the following local form of the two-particle evolution equation is constructed:

$$B(\mathbf{r},\mathbf{q},t)\left[\frac{\partial}{\partial t}+\frac{\mathbf{q}}{2m}\cdot\nabla_{\mathbf{r}}\right]\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)+\tilde{\mathbf{C}}(\mathbf{r},\mathbf{q},t):\mathbf{s}\nabla_{\mathbf{s}}\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)+\mathbf{D}(\mathbf{r},\mathbf{q},t)\cdot\nabla_{\mathbf{q}}\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)+\mathscr{W}(\mathbf{r},\mathbf{s},\mathbf{q},t)$$
$$=G^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)+[\sigma(\mathbf{r},\mathbf{s},t)-\delta\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)]X(\mathbf{r},\mathbf{q},t)\ , \tag{104}$$

where $\tilde{\mathbf{C}}$ is the transpose of $\mathbf{C}$. Every term of (104) is local in $\mathbf{s}$; hence, for example, this equation can be integrated over $d\mathbf{s}$, term by term.

Equations for conservation of particles, momentum, and energy are (25), (26), and (27), respectively. The one-particle densities and currents are given by (12), (13), (15), (18), and (22), and the two-particle densities and currents are given in final form by (52)–(55). The coupled one- and two-particle evolution equations, (92) and (98), now satisfy identically the three mechanical conservation laws. The one-particle equation alone is used to prove conservation of particles, and conservation of linear momentum. For energy conservation, the one-particle equation determines mean kinetic energy, and the two-particle equation determines mean potential energy. Hence only the *local part* of (98) is significant in the conservation laws, since (98) is multiplied by the local function $\phi(|\mathbf{s}|)$ to construct the mean potential energy. Also in energy conservation, there is a term

$$\tfrac{1}{2}\int\int \phi'(|\mathbf{s}|)\frac{\mathbf{s}\mathbf{s}}{|\mathbf{s}|}:\mathbf{C}(\mathbf{r},\mathbf{q},t)\delta\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}\,d\mathbf{s}$$

on the left side of the kinetic energy equation. This is the *sum* of two forcing terms, based on the *j* quantities defined below Eq. (73), and the entire term is exactly cancelled by an opposite change of mean potential energy, which arises from the $\mathbf{C}(\mathbf{r},\mathbf{q},t)$ term in (98). Finally, because of the interaction-invariant conditions (87) and (88), and the energy condition (90), the interaction integrals contribute nothing to the conservation laws.

C. The *h* theorem

The integral condition which is required to obtain an *h* theorem is

$$\int\int \{\ln\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)[\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)X(\mathbf{r},\mathbf{q},t)+\sigma(\mathbf{r},\mathbf{s},t)X(\mathbf{r},\mathbf{q},t)-\mathscr{W}(\mathbf{r},\mathbf{s},\mathbf{q},t)]-\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)X(\mathbf{r},\mathbf{q},t)\}d\mathbf{q}\,d\mathbf{s}=0\ . \tag{105}$$

If the integral on $d\mathbf{q}$ is carried out, the resulting $\mathbf{s}$ integrand is local in $\mathbf{s}$, term by term. Hence (105) is a condition on the local function $\sigma(\mathbf{r},\mathbf{s},t)$, which is otherwise arbitrary. For example, a solution is

$$\sigma(\mathbf{r},\mathbf{s},t)=\hat{\sigma}(\mathbf{r},t)\nabla_s\cdot\mathbf{s}[\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)-1]\ ,$$

where $\hat{\sigma}(\mathbf{r},t)$ is uniquely determined by (105). Given a solution for $\sigma(\mathbf{r},\mathbf{s},t)$, we can add a local function $\delta\sigma(\mathbf{r},\mathbf{s},t)$, provided $\delta\sigma$ makes no contribution to (105). Then the term $\delta\sigma X$ in the two-particle equation (98) contributes zero to the conservation laws, and to the *h* theorem, and to the evolution of $\mathbf{P}(\mathbf{r},t)$ and $\mathbf{J}(\mathbf{r},t)$. The term $\delta\sigma X$ does contribute to the evolution of the *h* current $\mathbf{I}(\mathbf{r},t)$, but the nonequilibrium $h(\mathbf{r},t)$ is not unique; in fact, there are whole classes of functions which will serve as bases for an *h* theorem, and only the equilibrium limit of $h(\mathbf{r},t)$ has physical significance. Since $\sigma(\mathbf{r},\mathbf{s},t)$ does not influence the equilibrium limit of $h(\mathbf{r},t)$, as determined by our evolution equations, we assume that the arbitrariness of $\sigma(\mathbf{r},\mathbf{s},t)$ is of no physical consequence.

The *h*-function density is given in (68)—(70), and the *h* currents are given in (72)—(75). The evolution equations (92) and (98) are used to calculate the evolution of $\rho h^{(1)}+\rho h^{(2)}$, with the following result:

$$\frac{\partial\rho(\mathbf{r},t)h(\mathbf{r},t)}{\partial t}+\nabla_r\cdot[\rho(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)h(\mathbf{r},t)+\mathbf{I}(\mathbf{r},t)]=\Sigma(\mathbf{r},t)\ , \tag{106}$$

where the source term $\Sigma(\mathbf{r},t)$ is

$$\Sigma(\mathbf{r},t)=\int F^{(1)}(\mathbf{r},\mathbf{p},t)\ln h^3 f^{(1)}(\mathbf{r},\mathbf{p},t)d\mathbf{p} +\tfrac{1}{2}\int\int G^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)\ln\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)d\mathbf{q}\,d\mathbf{s}\ . \tag{107}$$

The $\mathbf{s}$ integrand in (107) is a local function. In fact, just as in the proof of energy conservation, only the *local part* of the two-particle evolution equation is significant in the *h* theorem. Let us examine the terms which contribute to $\partial\rho h/\partial t$. First, the one-particle mean force $\mathbf{K}(\mathbf{r},\mathbf{p},t)$ does not contribute to $\partial\rho h^{(1)}/\partial t$, so this force is reversible, even though it is momentum dependent. Second, in (98), the terms in $\mathbf{C}(\mathbf{r},\mathbf{q},t)$ and $\mathbf{D}(\mathbf{r},\mathbf{q},t)$ give zero contribution to $\partial\rho h^{(2)}/\partial t$. Contributions to $\partial\rho h^{(2)}/\partial t$ from $\mathscr{W}(\mathbf{r},\mathbf{s},\mathbf{q},t)$, and from $X(\mathbf{r},\mathbf{q},t)$, are set zero by the integral condition (105). In a near-equilibrium situation, the contribution from $\mathscr{W}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ vanishes by symmetry, leading to the result $\sigma(\mathbf{r},\mathbf{s},t)=0$ near equilibrium.

The *h*-theorem source term is always negative or zero. This can be shown by using the definitions of Sec. IV to rewrite $\Sigma(\mathbf{r},t)$, first in the intermediate form

$$\Sigma(\mathbf{r},t)=\tfrac{1}{2}\int\int\int [\ln h^3 f^{(1)}(\mathbf{r},\mathbf{p},t)+\ln h^3 f^{(1)}(\mathbf{r},\mathbf{p}',t) +\ln\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p}+\mathbf{p}',t)] \times F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)d\mathbf{p}\,d\mathbf{p}'\,d\mathbf{s}\ , \tag{108}$$

and then in the form of a Lyapunov functional,

$$\Sigma(\mathbf{r},t)=-\tfrac{1}{4}\int\cdots\int [f_c^{(2)}(\mathbf{r},\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}',t)-f_c^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)][\ln h^6 f_c^{(2)}(\mathbf{r},\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}',t)-\ln h^6 f_c^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)] \times\mathcal{X}(\mathbf{s},\mathbf{p},\mathbf{p}'\,|\,\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')d\hat{\mathbf{p}}\,d\hat{\mathbf{p}}'\,d\hat{\mathbf{s}}\,d\mathbf{p}\,d\mathbf{p}'\,d\mathbf{s}\ , \tag{109}$$

where $f_c^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$ is defined by (82). Including the minus sign in front, the integrand is (109) is ≤ 0 everywhere, i.e., for all values of the integration variables. Hence the integral vanishes only when the integrand vanishes everywhere. We have the following interesting situation: through the interaction integrals in the one- and two-particle evolution equations, the effective two-particle interactions, which depend on $w^{(2)}(\mathbf{r},|\mathbf{s}|,t)$, drive the probability densities $f^{(1)}(\mathbf{r},\mathbf{p},t)$ and $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p}+\mathbf{p}',t)$ toward "equilibrium." Simultaneously, $w^{(2)}(\mathbf{r},|\mathbf{s}|,t)$ changes as the system evolves. Presumably $w^{(2)}(\mathbf{r},|\mathbf{s}|,t)$, in a general nonequilibrium fluid, contains some sense of local equilibrium, and attempts to "lead the way" in this self-consistent evolutionary process. Again in a near equilibrium situation, this concept *does* take place, and in a natural way.

D. Equilibrium solution

Regarding the expression (109) for $\Sigma(\mathbf{r},t)$, it is conceivable that there are phase points for which the integrand vanishes, so that $\Sigma(\mathbf{r},t)=0$ for some $\mathbf{r},t$, yet the fluid is not in equilibrium. Such points do not correspond to a steady solution of the evolution equations, hence are only transient points in the fluid evolution. At equilibrium, however, the evolution equations vanish term by term, and so do the equations which express the conservation laws and the h theorem. In particular, $\Sigma(\mathbf{r},t)=0$ at equilibrium.

To examine this equilibrium condition, it is convenient to imagine an expansion near equilibrium, where subscript 0 denotes equilibrium, and subscript 1 denotes a first-order nonequilibrium quantity. Then $F_0^{(2)}=0$, and $F_1^{(2)}$ contains only the equilibrium transition rate $\chi_0(\mathbf{s},\mathbf{p},\mathbf{p}'\,|\,\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')$. Equation (108) in lowest order is

$$\Sigma_1=\tfrac{1}{2}\int\int\int[\ln h^3 f_0^{(1)}(\mathbf{p})+\ln h^3 f_0^{(1)}(\mathbf{p}')+\ln\gamma_0^{(2)}(\mathbf{s},\mathbf{p}+\mathbf{p}')]\times F_1^{(2)}(\mathbf{s},\mathbf{p},\mathbf{p}')d\mathbf{p}\,d\mathbf{p}'\,d\mathbf{s}\;, \tag{110}$$

where we are considering global equilibrium, in which there is no $\mathbf{r},t$ dependence. Σ_1 vanishes only when the square brackets containing logarithm functions is a combination of the interaction invariants contained in $F_1^{(2)}(\mathbf{s},\mathbf{p},\mathbf{p}')$, which means

$$\ln h^3 f_0^{(1)}(\mathbf{p})+\ln h^3 f_0^{(1)}(\mathbf{p}')+\ln\gamma_0^{(2)}(\mathbf{s},\mathbf{p}+\mathbf{p}') = a+\mathbf{b}\cdot(\mathbf{p}+\mathbf{p}')+c\left[\frac{\mathbf{p}^2}{2m}+\frac{\mathbf{p}'^2}{2m}+w_0^{(2)}(|\mathbf{s}|)\right] + \text{terms in}(\mathbf{p}+\mathbf{p}')^n,\quad n=2,3,\ldots,$$

where $a,\mathbf{b},c$ are strict constants. Since $\ln\gamma_0^{(2)}(\mathbf{s},\mathbf{p}+\mathbf{p}')$ is a local function, and since the terms in $(\mathbf{p}+\mathbf{p}')^n$ on the right side are nonlocal, then $\gamma_0^{(2)}$ cannot depend on $\mathbf{p}+\mathbf{p}'$, and the right-side terms in $(\mathbf{p}+\mathbf{p}')^n$ must vanish. It then follows

$$\ln h^3 f_0^{(1)}(\mathbf{p})=\tfrac{1}{2}a+\mathbf{b}\cdot\mathbf{p}+c\left[\frac{\mathbf{p}^2}{2m}\right], \tag{111}$$

$$\ln\gamma_0^{(2)}(\mathbf{s})=cw_0^{(2)}(|\mathbf{s}|)\;. \tag{112}$$

Now the initial properties of the nonequilibrium fluid, which are conserved in the evolution, are the total number of particles, the total momentum, and the total energy. These represent unique equilibrium values of the particle density ρ_0, the center-of-mass velocity $\mathbf{v}_0$, and the temperature β, thus fixing the constants $a,\mathbf{b},c$, and giving finally

$$f_0^{(1)}(\mathbf{p})=\rho_0(\beta/2\pi m)^{3/2}\exp[-\beta(\mathbf{p}-m\mathbf{v}_0)^2/2m]\;, \tag{113}$$

$$\gamma_0^{(2)}(\mathbf{s})=g_0^{(2)}(|\mathbf{s}|)=\exp[-\beta w_0^{(2)}(|\mathbf{s}|)]\;. \tag{114}$$

In equilibrium, χ_0 does not vanish, and transitions do not cease, but the interaction integrals nevertheless vanish, by detailed balance. The primary interaction integral $F_0^{(2)}(\mathbf{s},\mathbf{p},\mathbf{p}')$, from Eq. (83), vanishes because

$$f_0^{(1)}(\hat{\mathbf{p}})f_0^{(1)}(\hat{\mathbf{p}}')\gamma_0^{(2)}(\hat{\mathbf{s}})=f_0^{(1)}(\mathbf{p})f_0^{(1)}(\mathbf{p}')\gamma_0^{(2)}(\mathbf{s})\;. \tag{115}$$

Also the equilibrium comparison between h_0 and the entropy per particle, $S/\overline{N}$, is given by (71), so that $S/\overline{N}$ contain terms in addition to $-k_B(h_0^{(1)}+h_0^{(2)})$, namely, the higher-order terms $S^{(3)}/\overline{N},\ldots,$ which are presumably very small.

E. On neglecting momentum correlations

Suppose we reconstruct our arguments through Eqs. (44)–(47), which give the two-particle densities and currents in the truncated gradient expansion. At this point suppose we are prepared to neglect the two-particle energy currents, $\mathbf{J}^{(2a)}$ and $\mathbf{J}^{(2b)}$, at least for a given nonequilibrium-fluid calculation. Then $\mathbf{J}^{(2)}=\mathbf{0}$, and explicit momentum dependence of $g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$ does not appear in any mechanical density or current. The theory can be developed exactly as before, with $\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)$ replacing $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$. The one-particle densities and currents remain unchanged, but the two-particle contributions simplify to the following list:

$$\rho(\mathbf{r},t)\epsilon^{(2)}(\mathbf{r},t)=\tfrac{1}{2}\rho^2(\mathbf{r},t)\int\phi(|\mathbf{s}|)\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)d\mathbf{s}\;, \tag{116}$$

$$\mathbf{P}^{(2)}(\mathbf{r},t)=-\tfrac{1}{2}\rho^2(\mathbf{r},t)\int\phi'(|\mathbf{s}|)\frac{\mathbf{s}\mathbf{s}}{|\mathbf{s}|}\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)d\mathbf{s}\;, \tag{117}$$

$$\rho(\mathbf{r},t)h^{(2)}(\mathbf{r},t)=\tfrac{1}{2}\rho^2(\mathbf{r},t)\int\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)\ln\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)d\mathbf{s}\;, \tag{118}$$

$$\mathbf{J}^{(2)}(\mathbf{r},t)=\mathbf{I}^{(2)}(\mathbf{r},t)=0\;. \tag{119}$$

The primary interaction integral is now written

$$F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t) = \int\int[f^{(1)}(\mathbf{r},\hat{\mathbf{p}},t)f^{(1)}(\mathbf{r},\hat{\mathbf{p}}',t)\Gamma^{(2)}(\mathbf{r},\hat{\mathbf{s}},t) - f^{(1)}(\mathbf{r},\mathbf{p},t)f^{(1)}(\mathbf{r},\mathbf{p}',t)\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)] \times\chi(\mathbf{s},\mathbf{p},\mathbf{p}'\,|\,\hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')d\hat{\mathbf{p}}\,d\hat{\mathbf{p}}'d\hat{\mathbf{s}}\;. \tag{120}$$

Integrals of $F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$ which will now appear in the evolution equations are $F^{(1)}(\mathbf{r},\mathbf{p},t)$, the same as before,

$$F^{(1)}(\mathbf{r},\mathbf{p},t)=\int\int F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)d\mathbf{p}'\,d\mathbf{s}\;, \tag{121}$$

and $G^{(2)}(\mathbf{r},\mathbf{s},t)$, defined by

$$G^{(2)}(\mathbf{r},\mathbf{s},t)=\int\int F^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)d\mathbf{p}\,d\mathbf{p}'\;. \tag{122}$$

The transition rate χ has the same properties as listed in Sec. IV A, the interaction invariants still lead to the integral conditions (87)–(89), and conservation of total energy by the interactions is still expressed by (90).

Now in the one-particle evolution equation, the one-particle mean force $\mathbf{K}(\mathbf{r},\mathbf{p},t)$ becomes the momentum-independent force $\mathbf{L}(\mathbf{r},t)$,

$$\left[\frac{\partial}{\partial t}+\frac{\mathbf{p}}{m}\cdot\nabla_{\mathbf{r}}\right]f^{(1)}(\mathbf{r},\mathbf{p},t) + \mathbf{L}(\mathbf{r},t)\cdot\nabla_{\mathbf{p}}f^{(1)}(\mathbf{r},\mathbf{p},t)=F^{(1)}(\mathbf{r},\mathbf{p},t)\;, \tag{123}$$

where

$$\rho(\mathbf{r},t)\mathbf{L}(\mathbf{r},t) = -\nabla_r \cdot \mathbf{P}^{(2)}(\mathbf{r},t) \; . \tag{124}$$

The two-particle evolution equation (98) can be integrated over $d\mathbf{q}$, to give the equation for $\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)$,

$$\rho^2(\mathbf{r},t) \left[\frac{\partial}{\partial t} + \mathbf{v}(\mathbf{r},t)\cdot\nabla_r + \mathbf{s}\cdot\nabla_r \mathbf{v}(\mathbf{r},t)\cdot\nabla_s \right] \times \Gamma^{(2)}(\mathbf{r},\mathbf{s},t) = G^{(2)}(\mathbf{r},\mathbf{s},t) \; . \tag{125}$$

This equation is local in $\mathbf{s}$, and compared to (98) or (104) for $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$, this equation is very simple. The left side of (125) contains only the time-derivative and drift terms, and $\mathscr{W}(\mathbf{r},\mathbf{s},\mathbf{q},t)$ and $\mathscr{X}(\mathbf{r},\mathbf{q},t)$ no longer appear in the two-particle equation. The coupled equations (123) and (125) provide an *apparent* separation of the $\mathbf{p}$ dependence, and the $\mathbf{s}$ dependence, in the evolution of a nonequilibrium fluid; in fact these dependences remain coupled only within the transition rate function $\mathscr{X}(\mathbf{s},\mathbf{p},\mathbf{p}' \mid \hat{\mathbf{s}},\hat{\mathbf{p}},\hat{\mathbf{p}}')$. Finally, with the densities and currents given in Eqs. (116)–(119), plus the standard one-particle expressions, Eqs. (123) and (125) satisfy the conservation laws *and* the h theorem, without the need for an auxiliary h-theorem condition.

The philosophical basis for the above approximation is, *if* we can neglect $\mathbf{J}^{(2)}(\mathbf{r},t)$ for all $\mathbf{r},t$, then $\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)$ is the physically significant part of $g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$, and it makes sense to construct the entire theory in terms of $\Gamma^{(2)}(\mathbf{r},\mathbf{s},t)$ instead of $g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$. It remains to be learned under what conditions $\mathbf{J}^{(2)}(\mathbf{r},t)=0$ is a physically acceptable approximation. In any case, however, this approximation has simplicity and elegance to recommend it.

A final observation can be made, regarding the general theory *with* momentum correlations. In the theoretical development, the original correlation function $g^{(2)}(\mathbf{r},\mathbf{s},\mathbf{p},\mathbf{p}',t)$ was replaced by one with less information, namely $\gamma^{(2)}(\mathbf{r},\mathbf{s},\mathbf{q},t)$. The fact that the resulting two-particle equation (98) contains arbitrariness, in the function $\sigma(\mathbf{r},\mathbf{s},t)$, suggests that a *further reduced* correlation function may yet be found, in terms of which the two-particle equation will be unique. This is precisely what happens when momentum correlations are completely neglected, as the analysis of Sec. V E shows.

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