MAXIMIZATION OF ENTROPY, KINETIC EQUATIONS AND IRREVERSIBLE THERMODYNAMICS

John Karkheck

Department of Mechanical Engineering
State University of New York
Stony Brook, New York 11794

and

G. Stell

Departments of Mechanical Engineering and Chemistry
State University of New York
Stony Brook, New York 11794

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ABSTRACT

By an extension to the dense-fluid regime of a method first exploited by Lewis to obtain the Boltzmann equation, kinetic equations for one- and two-particle classical distribution functions are obtained. For the hard-sphere potential, the kinetic equation of the revised Enskog theory is obtained at the one-particle level, and a generalization of the theory of Livingston and Curtiss is obtained at the two-particle level. For a pair potential with hard-sphere core plus smooth attractive tail, a new mean-field kinetic equation is obtained on the one-particle level. In the Kac-tail limit the equation takes the form of an Enskog-Vlasov equation. The method, which is based upon the maximization of entropy, yields an explicit entropy functional in each case. Explicit demonstration of an H-theorem is made for the one-particle theories in a novel way that illustrates the roles of the reversible and irreversible part of the hard-sphere piece of the collision integral. The latter part leads to the classical form of entropy-production density as described by linear irreversible thermodynamics and so possesses many of the features of the Boltzmann collision integral. The former part introduces new elements into the entropy production term. It is noted that the kinetic coefficients of the revised Enskog theory exhibit Onsager reciprocity in the linear regime. Upon extension to the standard Enskog theory, in the linear regime, we construct an entropy production density and identify conjugate fluxes and forces and also kinetic coefficients which are shown to exhibit Onsager reciprocity. The standard theory is in disagreement, however, with the results of phenomenological irreversible thermodynamics for the conventional forms of fluxes and forces.

I. INTRODUCTION

The great advances made by Boltzmann[1] and Enskog[2] toward constructing a kinetic theory of dilute and dense classical fluids, respectively, were the products of brilliant intuition. Boltzmann's explicit construction of an entropy functional and demonstration of its monotonic increase in time (H-theorem) is a landmark in the program of relating microscopic dynamics and irreversible processes. Thus, aside from their value in describing hydrodynamic and transport processes, we have come to regard kinetic equations as a bridge between the microscopic domain and the realm of macroscopic irreversible processes.

Enskog's equation represents a generalization of the Boltzmann equation to the dense-fluid regime for the hard-sphere potential model. Construction of an explicit entropy functional has not yet been done for the original Enskog theory (herein referred to as standard Enskog theory -- SET) though a recent result[3] provides a prescription for constructing an entropy functional. An explicit entropy functional and irreversibility have been demonstrated for a revised version (RET).[4]

Investigations over the last three and a half decades have sought to elucidate the principles and assumptions inherent in these theories in order to establish systematic techniques for the construction of more general irreversible kinetic equations that are appropriate to dense gases and liquids. A logical starting point for the description of classical many-body dynamics has proven to be the BBGKY hierarchy,[5] which connects the evolution of an s-particle distribution function, F_s, to the distribution function for s+1 particles, F_{s+1}. Both objects are unknown. To determine F_s exactly, therefore, requires solution of the full many-body problem. Performance of this exceedingly difficult task would yield a huge amount of superfluous information, inasmuch as the physical quantities of greatest interest can be expressed in terms of the lowest-order distribution functions, typically $s = 1,2$. The approach is taken, therefore, to develop a closed set of approximate equations for the evolution of these lowest-order distribution functions.

Several schools of thought have arisen regarding methods that can be used to close the hierarchy. Most efforts have been aimed at the one-particle equation; not nearly as much effort has been devoted to the two-particle equation though it is the two-particle distribution function which contains the information of paramount interest to a description of the dense-fluid state.

Closure in a manner that yields irreversibility seems to require expression of F_s in terms of F_t, $s > t$, possibly in a non-local way in general. Bogoliubov[6] first introduced a scheme, which has been developed and expanded by many workers,[7] to describe the evolution of F_1 in terms of the dynamics of distinct groups of two particles (the Boltzmann term), three particles (the Choh-Uhlenbeck term), etc. The density of the fluid is regarded as the determinant of how many terms one should include. The main assumption in these approaches is in regard to the correlations among the particles of each group at some distant time in the past. Closure is had by assuming no correlation among particles in the far past when the members of a group are far apart and not interacting. Then F_s, s = 2,3,... is factorized into a product of F_1's at some time in the past. Thereby indirect dynamical correlations among members of a group through interaction with the remaining fluid are neglected. With the exception of the theory of Klimontovich [ref. 7c], theories of this kind have yet to be demonstrated as irreversible, or, to have an entropy functional. Moreover, they are not tractable at liquid densities.

Now Enskog's theory[8] extends only as far as the Boltzmann term in group dynamics but accommodates spatial correlation between the two colliding particles via the two-particle spatial correlation function of the dense uniform hard-sphere fluid at equilibrium. Van Beijeren and Ernst[9] have generalized this kinetic equation by using instead the correlation function appropriate to a nonuniform fluid at equilibrium. Resibois[4] has shown that this RET does indeed have an entropy functional and an H-theorem.

A natural basis for incorporation of the fluid structure, in general, is had by recourse to the two-particle equation. A Markovian kinetic equation is obtained[10] when the Kirkwood superposition approximation[11] (KSA) is applied to F_3 for closure. Alternatives to this have been considered[12] but neither an entropy functional nor irreversibility have been exhibited by such approaches.

Quite apart from the kinetic theory, the problem of the relationship of higher-order distribution functions to given ones of low order has been investigated from several points of view. Mayer[13] has characterized the ensemble which exhibits maximum entropy subject to a prescribed set of low-order distribution functions. An alternate analysis to this end was given subsequently by McLachlan and Harris[14] using Lagrange undetermined multipliers. A maximum "entropy" principle was used by Ramanathan, Dawson and Kruskal[15] to derive the KSA and higher-order generalizations.

Lewis[16] employed maximization of entropy subject to constraints to effect closure in a derivation of the Boltzmann equation. Here we extend Lewis' method into a form suitable to application to dense fluids. In particular, we recover the kinetic equation,[9] entropy functional and H-theorem[4] of the RET assuming a hard-sphere repulsive interparticle potential. By generalizing to a potential with hard-sphere core plus smooth attractive tail we obtain a mean-field kinetic equation, which is suited to liquid dynamics, such that the hard-sphere fluid structure serves as a reference structure for the attractive tail which appears linearly in the mean-field term. We show that this theory also has an entropy functional and an H-theorem. When the tail strength is set to zero, the RET is recovered, and when the Kac limit is taken on the tail, an equation of the Enskog-Vlasov type[17] is obtained. (A number of other nice formal properties and applications of this theory to liquid transport are described elsewhere.[18]) A new one-particle kinetic equation for the square-well potential is also obtained and an H-theorem is proven for it.

The method is also used to obtain a closed equation for F_2 for the hard-sphere potential. This new equation goes beyond that of Livingston and Curtiss[10] who applied the KSA to F_3 for closure. The new equation contains within F_3 a three-particle phase-space correlation function which manifests the possibility of long-range velocity correlations. The reversible part of this kinetic equation is shown to yield at equilibrium the correct two-particle member of the Yvon, Born, Green hierarchy.[19] An explicit form for the entropy functional is also obtained.

The maximum-entropy approach has great formal mathematical power, yet is conceptually simple. It is a compact systematic technique for deriving kinetic equations associated with entropy functionals as well as a formally closed BBGKY hierarchy. Moreover, its basic principle, the maximization of entropy, conceptually unifies equilibrium and nonequilibrium statistical mechanics. The existence of a physical mechanism for closure is not addressed in this approach. Rather, the method provides a mathematical framework whose relevance to the physical problem is best judged *a posteriori*.

In Section II the basic dynamical equation for the one-particle theories is derived and in Section III the statistical procedure for closure is set up. For completeness, a derivation of the Boltzmann equation is given in Section IV, following Lewis,[16] to illustrate the role of time smoothing. In Section V one-particle kinetic equations for dense fluids are derived and H-theorems proven, and in Section VI

a two-particle kinetic theory for the hard-sphere fluid is discussed. In Section VII properties of the RET hard-sphere theory in relation to irreversible thermodynamics are developed. A local entropy production density is constructed and forces and conjugate fluxes are identified. The kinetic coefficients are shown to exhibit Onsager reciprocity. (These formal results are shown to hold also for the SET, although the forces and conjugate fluxes do not both take the form expected on phenomenological grounds. Our general conclusion is that the RET is superior to the SET in regard to its relation to irreversible thermodynamics, although we differ in some specifics with van Beijeren and Ernst.[9]) A summarizing discussion follows in the last section.

II. THE DYNAMICAL EQUATION

The BBGKY hierarchy for the specific distribution functions F_s, in the thermodynamic limit and for pair interparticle interaction, is[5]

$$\frac{\partial}{\partial t} F_s + \{H_s, F_s\} = n \int dx_{s+1} \sum_{i=1}^{s} \frac{\partial}{\partial \vec{r}_i} \phi_{i\ s+1} \cdot \frac{\partial}{\partial \vec{p}_i} F_{s+1} \qquad (1)$$

where $H_s = \sum_{i=1}^{s} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i<j}^{s} \phi_{ij}$, $n = \frac{N}{V}$, $x = (\vec{r}, \vec{p})$ and the F_s are normalized so that $\int d^s x\, F_s = V^s$. For convenience we set $m = 1$ so that $\vec{p} = \vec{v}$. A formal solution of (1) in powers of n was obtained by Lewis:[20]

$$F_s(x^s, t+\tau) = \sum_{k=0}^{\infty} n^k \int dx_{s+1} \ldots dx_{s+k}$$

$$\times \sum_{j=0}^{k} \frac{(-1)^{k-j}}{j!(k-j)!} T_{-\tau}^{(j+s)} F_{k+s}(x^{k+s}, t) \qquad (2)$$

where $T_{-\tau}^{(j+s)} F_{k+s} = F_{k+s}(S_{-\tau}^{(j+s)} x^{j+s}, S_{-\tau}^{(1)} x_{j+s+1}, \ldots, S_{-\tau}^{(1)} x_{k+s}, t)$ and $S_{-\tau}^{(j)} = \exp \tau\{H_j, \ \}$. Equation (2) demonstrates that there are two parameters at our disposal, n and τ.

For s = 1, we obtain

$$F_1(x_1, t+\tau) - T_{-\tau}^{(1)} F_1(x_1, t) = n \int dx_2 \Big\{ T_{-\tau}^{(2)} F_2(x_1, x_2, t)$$

$$- T_{-\tau}^{(1)} F_2(x_1, x_2, t) \Big\} + n^2 \int dx_2 dx_3 \Big\{ \frac{1}{2} T_{-\tau}^{(3)} F_3(x^3, t)$$

$$- T_{-\tau}^{(2)} F_3(x^3, t) + \frac{1}{2} T_{-\tau}^{(1)} F_3(x^3, t) \Big\} + \ldots \qquad (3)$$

The integrands on the RHS do not vanish only when the particle configurations are such that the multiparticle streaming operators induce

interaction among the particles.

Replace x_1 by $S_\tau^{(1)} x_1$ in (3), which is an identity in x_1. The LHS of (3) becomes equal to $\int_0^\tau dr \frac{d}{dr} F_1(S_r^{(1)} x_1, t+r)$; the integrand of which is equal to $(\vec{v}_1 \cdot \nabla_1 + \frac{\partial}{\partial t}) F_1(S_r^{(1)} s_1, t+r)$. Now the LHS of (3) can be written

$$\tau(\vec{v}_1 \cdot \nabla_1 + \frac{\partial}{\partial t}) \overline{F}_1 , \qquad (4)$$

where

$$\overline{F}_1 = \frac{1}{\tau} \int_0^\tau dr\, F_1(S_r^{(1)} x_1, t+r) . \qquad (5)$$

The binary collision term on the RHS can be similarly transformed to

$$n \int dx_2 \Big\{ T_{-\tau}^{(2)} T_\tau^{(1)} F_2(x_1, x_2, t) - F_2(x_1, x_2, t) \Big\} . \qquad (6)$$

Similar forms can be obtained for the ternary and higher order terms on the RHS of (3), but inasmuch as any high order term is $O(n\tau\pi R_\phi^2 \overline{g})$ times the preceding term[6] (where R_ϕ is the range of the interparticle interaction and $\overline{g}$ is the mean relative speed of colliding particles) we will not be interested in the ternary and higher order terms in the sequel because we choose n or τ such that these terms will be very small. Combining (3) and (5) we obtain the result

$$\overline{F}_1(x_1, t) = F_1(x_1, t) + O\left(\frac{\tau}{\tau_m}\right) , \qquad (7)$$

where $\tau_m = (n\pi R_\phi^2 \overline{g})^{-1}$. Therefore the time-smoothed and unsmoothed one-particle distribution functions are approximately equal if $\tau << \tau_m$.

As we will see subsequently, the role of time smoothing is to establish a time scale which captures a complete collision. As utilized here time smoothing does not play a role per se in introducing irreversibility.

The dynamical equation of interest in the one-particle theories is comprised of (4), (6) and (7). In anticipation of later results we assume here that $\tau << \tau_m$ and also define the correlation function

$$g_2(x_1,x_2,t) = \frac{F_2(x_1,x_2,t)}{F_1(x_1,t)F_1(x_2,t)} \tag{8}$$

and introduce the notation

$$T_{-\tau}^{(2)}T_{\tau}^{(1)}F_2(x_1,x_2,t) \equiv F_2(x_1',x_2',t) \tag{9}$$

where x_1', x_2' are related to x_1, x_2 through the interparticle potential. Combining (4), (6), (7), (8) and (9) we obtain the leading order result

$$\left(\frac{\partial}{\partial t} + \vec{v}_1 \cdot \nabla_1\right)F_1(x_1,t) = \frac{n}{\tau}\int dx_2\{g_2(x_1',x_2',t)F_1(x_1',t)F_1(x_2',t) - g_2(x_1,x_2,t)F_1(x_1,t)F_1(x_2,t)\} \ . \tag{10}$$

III. THE CLOSURE PRINCIPLE

To simplify the formulae in this and following sections we replace the specific functions F_s by generic functions $f_s = n^s F_s$. The macroscopic fluid properties can be expressed in terms of f_1 and f_2,[21] and, in particular, knowledge of f_1 is sufficient to describe the state of a dilute gas. Generally, then, we assume that some low-order function f_s is known at time t. Closure can be had[13,14] by maximizing the statistical entropy functional S,[22]

$$S = -k\int d^Nx\, W_N \ln(W_N/\Gamma), \tag{11}$$

where $\int d^Nx\, W_N = 1$ and Γ is a measure on the phase space whose value is not pertinent to the following development so will be suppresssed, subject to constraints of symmetry and that all known information (f_s) is reproduced precisely by contraction of W_N. The latter means

$$f_s(x^s,t) = \frac{N!}{(N-s)!}\int d^{N-s}x\, W_N(x^N,t) \ . \tag{12}$$

Formally, we express this problem via the use of Lagrange multipliers[14] -- maximize the functional

$$I[D_N] = S[D_N] + k\gamma\left[1 - \int d^Nx\, E_N D_N\right] + k\int d^sx\, \lambda(x^s,t)f_s(x^s,t) - \frac{N!}{(N-s)!}k\int d^Nx\, \lambda(x^s,t)E_N D_N(x^N,t) \ . \tag{13}$$

Here for convenience we have split W_N into a product of factors, $E_N = E_N(\vec{r}^N)$ which is assumed to have a known form, and $D_N = D_N(x^N,t)$

which is not known in form and is the function to be varied in seeking the maximum of S. The Lagrange multiplier function λ is symmetric in all x_i, as are all f_s, so the last term in (13) may be written in the symmetric form

$$-k \sum_{i_1 \ldots i_s = 1}^{N\,\prime} \int d^N x\, \lambda(x_{i_1}, \ldots, x_{i_s}, t) E_N D_N$$

where the prime means no indices equal.

The operations $\partial I/\partial\gamma = 0$ and $\delta I/[\delta\lambda(x_0^N,t)] = 0$ yield the normalization conditions $1 = \int d^N x\, W_N$ and (12) respectively. The functional variation with respect to D_N yields

$$\frac{\delta I}{\delta D_N(x_0^N,t)} = -kE_N(\vec{r}_0^N)\Big[1 + \ell n E_N(\vec{r}_0^N) + \ell n D_N(x_0^N,t) + \gamma + \sum_{i_1 \ldots i_s = 1}^{N\,\prime} \lambda(x_{0i_1}, \ldots, x_{0i_s}, t)\Big] \,. \qquad (14)$$

Provided that $E_N(\vec{r}_0^N) \neq 0$, setting $\delta I/[\delta D_N(x_0^N,t)] = 0$ yields

$$\ell n E_N(\vec{r}_0^N) + \ell n D_N(x_0^N,T) = -\gamma - 1 - \sum_{i_1 \ldots i_s = 1}^{N\,\prime} \lambda(x_{0i_1}, \ldots, x_{0i_s}, t) \,. \qquad (15)$$

IV. DILUTE GAS AND THE BOLTZMANN EQUATION

Here $nv_0 << 1$ where $v_0 \sim$ volume of a particle. Set $s = 1$ and $E_N = 1$ and from (15) obtain

$$W_N(x^N,t) = e^{-1-\gamma} \prod_{i=1}^{N} e^{-\lambda(x_i,t)} = N^{-N} \prod_{i=1}^{N} f_1(x_i,t) \qquad (16)$$

so that, (through (8) in generic function language), obtain

$$g_2(x_1,x_2,t) = 1 \,. \qquad (17)$$

In terms of the generic functions, (10) now takes the form

$$\left(\frac{\partial}{\partial t} + v_1 \cdot \nabla_1\right) f_1(x_1,t) = \frac{1}{\tau}\int dx_2 \{f_1(x_1',t) f_1(x_2',t) - f_1(x_1,t) f_1(x_2,t)\} \,. \qquad (18)$$

The configurations for which the integrand of (18) does not vanish permit a collision to occur upon backward streaming by $T^{(2)}$ after free streaming of both particles by $T^{(1)}$ [cf (9)]. This situation is typified in Figure 1a, where $\vec{R}_0 = \vec{r}_2 - \vec{r}_1$, $\vec{g} = \vec{v}_2 - \vec{v}_1$ and $\vec{R}_\tau = \vec{R}_0 + \vec{g}\tau$. Given $\vec{r}_1$, $\vec{v}_1$, $\vec{v}_2$, τ then $\vec{r}_2$ must be so that:

(i) if $\vec{R}_0 \cdot \vec{g} \geq 0$, then $R_0 \leq R_\phi$, where R_ϕ is the range of the potential

(ii) if $\vec{R}_0 \cdot \vec{g} < 0$, then $R_\phi \geq (R_0^2 - \vec{R}_0 \cdot \vec{g}^2)^{1/2}$ and either $R_\tau \leq R_\phi$ or $\vec{R}_\tau \cdot \vec{g} > 0$ and $R_\tau > R_\phi$.

The volume of this region of contributing $\vec{r}_2$'s is of order $\pi\tau g R_\phi^2$

(neglecting end caps). As already mentioned the ternary and higher order collision terms will be negligible if

$$\tau \ll \tau_m = \frac{1}{n\bar{g}\pi R_\phi^2} .$$

Now regions A and C correspond to configurations which produce incomplete collisions in time τ and their total volume is $\frac{8}{3}\pi R_\phi^3$, which may be neglected if $\tau \gg \frac{8}{3}\frac{R_\phi}{\bar{g}} \sim \tau_c$, the duration of a collision. The physical domain of applicability of our ultimate result is then characterized by the relation

$$\tau_c \ll \tau \ll \tau_m . \qquad (19)$$

To the same order of approximation, based upon the first inequality of (19), we may write

$$\int_B d\vec{r}_2 = \int db\, bd\varepsilon \int_0^{\tau g} dz$$

where db bdε is the differential cross section for scattering which applies to both terms in the integrand of (18) due to microscopic reversibility which is naturally built-in by the presence of $T^{(2)}$. To complete the analysis we make a smoothness assumption:

$$f_1(\vec{r}+\vec{\Delta},\vec{v},t) \simeq f_1(\vec{r},\vec{v},t)$$

if $|\vec{\Delta}| \sim O(\tau\bar{g})$. Thereby, we obtain from (18) the Boltzmann equation

$$\left(\frac{\partial}{\partial t} + \vec{v}_1 \cdot \nabla_1\right) f_1(x_1,t) = \int d\vec{v}_2 \int db\, bd\varepsilon\, g\Big\{f_1(\vec{r}_1,\vec{v}_1',t)f_1(\vec{r}_1,\vec{v}_2',t) - f_1(x_1,t)f_1(\vec{r}_1,\vec{v}_2,t)\Big\} . \qquad (20)$$

To complete the picture, we obtain from (11) and (16) the dilute gas entropy functional

$$S_1^{dil} = kN\ell nN - k\int dx\, f_1(x,t)\ell n f_1(x,t) . \qquad (21)$$

It is straightforward to show[1] that $\frac{\partial}{\partial t} S_1^{dil} \geq 0$ using (20), equality holding if f_1 is the Maxwellian distribution. As a final note here, as shown already by Grad,[23] (20) follows as an exact result from (3) [given (17)] in the limit $n \to \infty$, $R_\phi \to 0$ such that $nR_\phi^3 = 0$, $nR_\phi^2 =$ constant. In our context this limit implies $\tau_c \to 0$, $\tau_m =$ constant, and permits taking $\tau \to 0^+$ while still capturing a complete collision and conforming to (19).

If instead of relation (19) we impose $\tau \to 0$, down through τ_c, onto (3) and use (8), (17), then we obtain the Vlasov equation

$$\left(\frac{\partial}{\partial t} + \vec{v}_1 \cdot \nabla_1\right) f_1(x_1,t) = \frac{\partial}{\partial \vec{v}_1} f_1(x_1,t) \cdot \int dx_2\, \nabla_1\phi_{12} f_1(x_2,t) , \qquad (22)$$

which is completely reversible.

V. DENSE GAS AND SIMPLE LIQUIDS

V.1. Kinetic Equations

Here $nv_0 \lesssim 1$ and for a general potential the strong inequality (19) cannot hold. To simplify matters we model the repulsive part of the potential by a hard-sphere repulsion. The duration of such a collision is $\tau_c = 0$ so that an inequality like (19) can be maintained while taking $\tau \to 0^+$. Also in this limit the ternary and higher order terms in (3) vanish and, from (7), $\overline{F}_1 = F_1$ holds exactly. In this framework we distinguish several cases.

A. Hard-sphere core, diameter σ, no attractive tail potential

The configurations which contribute to binary collisions are shown in Figure 1b. In terms of generic distribution functions, (10) becomes the exact result

$$\left(\frac{\partial}{\partial t} + \vec{v}_1 \cdot \nabla_1\right) f_1(x_1,t) = \sigma^2 \int d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\theta(\hat{\sigma}\cdot\vec{g})$$
$$\left\{g_2(\vec{r}_1,\vec{v}_1',\vec{r}_1+\sigma\hat{\sigma},\vec{v}_2',t) f_1(\vec{r}_1,\vec{v}_1',t) f_1(\vec{r}_1+\sigma\hat{\sigma},\vec{v}_2',t)\right.$$
$$\left. - g_2(\vec{r}_1,\vec{v}_1,\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t) f_1(\vec{r}_1,\vec{v}_1,t) f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t)\right\}, \qquad (23)$$

where $\theta(x)$ is the Heaviside function.

The $E_N = \Theta$, which is the overlap function

$$\Theta = 1 \quad \text{if } |\vec{r}_i - \vec{r}_j| > \sigma \quad \text{for every } i \neq j$$
$$\Theta = 0 \quad \text{if } |\vec{r}_i - \vec{r}_j| < \sigma \quad \text{for any pair } i,j \ .$$

In this case $E_N \ell n E_N = 0$ always, so, interpreting $\{x_0^N\}$ in (15) to yield $\Theta = 1$, when $s = 1$ (15) yields

$$D_N = e^{-\gamma-1} \prod_{i=1}^{N} e^{-\lambda(x_i,t)}$$

whereby

$$W_N = e^{-\gamma-1}\, \Theta \prod_{i=1}^{N} e^{-\lambda(x_i,t)} \ . \qquad (24)$$

This function is identical in form to the N-particle equilibrium distribution function for hard-sphere particles in an external field. In particular it renders

$$f_2(x_1,x_2,t) = g_2(\vec{r}_1,\vec{r}_2|n_1(t)) f_1(x_1,t) f_1(x_2,t) \qquad (25)$$

where $n_1(\vec{r}_1,t) = \int d\vec{v}_1 f_1(x_1,t)$ and g_2 is that functional of the density field which reduces to the equilibrium radial distribution function for the hard-sphere potential if the density n_1 is constant; g_2 has the same graphical structure as its uniform-system counterpart[24] except that each field point is weighted by the appropriate value of the number density field instead of a constant number density.

Insertion of (25) into (23) yields the kinetic equation of the revised Enskog theory[9]

$$\left(\frac{\partial}{\partial t} + \vec{v}_1 \cdot \nabla_1\right) f_1(\vec{r}_1,\vec{v}_1,t) = C_E(f_1,f_1)$$
$$\equiv \sigma^2 \int d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\theta(\hat{\sigma}\cdot\vec{g})$$
$$\left\{g_2(\vec{r}_1,\vec{r}_1+\sigma\hat{\sigma}|n_1(t)) f_1(\vec{r}_1,\vec{v}_1',t) f_1(\vec{r}_1+\sigma\hat{\sigma},\vec{v}_2',t) \right. -$$

$$- g_2(\vec{r}_1,\vec{r}_1-\sigma\hat{\sigma}|n_1(t))f_1(\vec{r}_1,\vec{v}_1,t)f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t)\Big\} \ . \qquad (26)$$

The only difference between (26) and Enskog's equation lies in the form of dependence of g_2 on density: in the original formulation g_2 was treated as a uniform-equilibrium function evaluated at the density at the point of contact. As far as the linear transport properties of the one-component hard-sphere fluid are concerned, the revised and standard Enskog theories are identical in prediction.[9] However, the revised theory appears to be superior when applied to hard-sphere mixtures; the standard-theory thermodynamic driving force for diffusion does not exhibit the form expected on phenomenological grounds[25] whereas the driving force of the revised theory does[9] (see Section VII).

B. Square-well potential

Any smooth potential can be approximated by a sequence of step functions with the result that "collisions" occur instantaneously and only at the discontinuities. The square-well potential

$$\begin{aligned} \phi(r) &= \infty \qquad & r < \sigma \\ &= -\varepsilon & \sigma < r < R\sigma \\ &= 0 & R\sigma < r \end{aligned} \qquad (27)$$

is the simplest such representation of a real potential. An exact dynamical equation for the potential (27), analogous to (23), follows from analysis similar to that above.[26] Closure of this equation is had by setting $E_N = \Theta$ which makes g_2, as in (25), dependent only upon

the hard-core repulsion. The square-well kinetic equation is obtained:

$$\begin{aligned}
\left(\frac{\partial}{\partial t} + \vec{v}_1 \cdot \nabla_1\right) f_1(x_1,t) &= \sigma^2 \int d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\theta(\hat{\sigma}\cdot\vec{g}) \\
&\Big\{ g_2(\vec{r}_1,\vec{r}_1+\sigma^+\hat{\sigma}|n) f_1(\vec{r}_1,\vec{v}_1',t) f_1(\vec{r}_1+\sigma\hat{\sigma},\vec{v}_2',t) \\
&\quad - g_2(\vec{r}_1,\vec{r}_1-\sigma^+\hat{\sigma}|n) f_1(x_1,t) f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t)\Big\} \\
&+ R^2\sigma^2 \int d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\theta(\hat{\sigma}\cdot\vec{g}) \\
&\Big\{ g_2(\vec{r}_1,\vec{r}_1+R\sigma^-\hat{\sigma}|n) f_1(\vec{r}_1,\vec{v}_1'',t) f_1(\vec{r}_1+R\sigma\hat{\sigma},\vec{v}_2'',t) \\
&\quad - g_2(\vec{r}_1,\vec{r}_1-R\sigma^+\hat{\sigma}|n) f_1(x_1,t) f_1(\vec{r}_1-R\sigma\hat{\sigma},\vec{v}_2,t)\Big\} \\
&+ R^2\sigma^2 \int d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\theta(\hat{\sigma}\cdot\vec{g} - \sqrt{4\varepsilon}) \\
&\Big\{ g_2(\vec{r}_1,\vec{r}_1-R\sigma^+\hat{\sigma}|n) f_1(\vec{r}_1,\vec{v}_1''',t) f_1(\vec{r}_1-R\sigma\hat{\sigma},\vec{v}_2''',t) \\
&\quad - g_2(\vec{r}_1,\vec{r}_1+R\sigma^-\hat{\sigma}|n) f_1(x_1,t) f_1(\vec{r}_1+R\sigma\hat{\sigma},\vec{v}_2,t)\Big\} \\
&+ R^2\sigma^2 \int d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\theta(\hat{\sigma}\cdot\vec{g})\theta(\sqrt{4\varepsilon} - \hat{\sigma}\cdot\vec{g}) \\
&\Big\{ g_2(\vec{r}_1,\vec{r}_1-R\sigma^-\hat{\sigma}|n) f_1(\vec{r}_1,\vec{v}_1',t) f_1(\vec{r}_1-R\sigma\hat{\sigma},\vec{v}_2',t) \\
&\quad - g_2(\vec{r}_1,\vec{r}_1+R\sigma^-\hat{\sigma}|n) f_1(x_1,t) f_1(\vec{r}_1+R\sigma\hat{\sigma},\vec{v}_2,t)\Big\} \ , \qquad (28)
\end{aligned}$$

where

$$\begin{aligned}
\vec{v}_1' - \vec{v}_1 &= \hat{\sigma}\hat{\sigma}\cdot\vec{g} \\
\vec{v}_1'' - \vec{v}_1 &= \tfrac{1}{2}\hat{\sigma}[\hat{\sigma}\cdot\vec{g} - \sqrt{(\hat{\sigma}\cdot\vec{g})^2 + 4\varepsilon}] \\
\vec{v}_1''' - \vec{v}_1 &= \tfrac{1}{2}\hat{\sigma}[\hat{\sigma}\cdot\vec{g} - \sqrt{(\hat{\sigma}\cdot\vec{g})^2 - 4\varepsilon}] \ . \qquad (29)
\end{aligned}$$

Though g_2 obtained from (25) is continuous for $|\vec{r}_2 - \vec{r}_1| > \sigma$, distinction is made in (28) between points just inside and just outside the well edge. This distinction is used in the subsequent discussion of irreversibility. This equation differs formally from that of Davis, Rice and Sengers (DRS)[27] in the pair correlation function g_2. These authors assume a form of f_2 like that of (25), but give g_2 an equilibrium form dependent upon the full square-well potential. Our (28) does not satisfy detailed balance at equilibrium, whereas DRS theory does.

C. Hard-core repulsion plus smooth attractive tail

In the limit $\tau \to 0^+$ we obtain from (3) and (8) in this case the exact equation

$$\left(\frac{\partial}{\partial t} + \vec{v}_1 \cdot \nabla_1\right) f_1(x,t) = \int dx_2 \frac{\partial \phi_{12}^{\text{tail}}}{\partial \vec{r}_1} \cdot \frac{\partial}{\partial \vec{v}_1} [g_2(x_1,x_2,t) f_1(x_1,t)] f_1(x_2,t)$$
$$+ \sigma^2 \int d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\theta(\hat{\sigma}\cdot\vec{g})$$
$$\Big\{ g_2(\vec{r}_1,\vec{v}_1',\vec{r}_1+\sigma^+\hat{\sigma},\vec{v}_2',t) f_1(\vec{r}_1,\vec{v}_1',t) f_1(\vec{r}_1+\sigma\hat{\sigma},\vec{v}_2',t)$$
$$- g_2(\vec{r}_1,\vec{v}_1,\vec{r}_1-\sigma^+\hat{\sigma},\vec{v}_2,t) f_1(\vec{r}_1,\vec{v}_1,t) f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t) \Big\} . \tag{30}$$

Recognizing that $\Theta = \prod_{i<j=2}^{N} \theta_{ij}$ may be interpreted as a product of Boltzmann factors for the hard-sphere potential suggests that a

way to generalize the Ansatz $W_N = \Theta D_N$ for more general potentials is to let $E_N = \prod_{i<j=2}^{N} e_{ij} \cdot \Theta$ such that $\ell n e_{ij} \propto \phi_{ij}^{\text{tail}}$.

Choosing again $\{x_0^N\}$ to correspond to a nonoverlap configuration, several cases of interest may be distinguished for (15).

1. At low density the mean particle separation is much greater than the range of the potential, so that $\ell n E_N$ is zero except on a set of relatively small measure [see discussion above Eq. (19)]. Then (16) is recovered.

2. When the potential has a weak long-range attractive tail, e.g., the Kac potential, each particle sits in a mean field produced by all the others which is sensibly the same for each particle, hence $\ell n E_N = O(N)$. Since also $\ell n D_N = O(N)$ by (15), at best we can say $E_N D_N = e^{-1-\gamma}\, \Theta \prod_{i=1}^{N} e^{-\lambda(x_i,t)}$ which implies g_2 given in (25), so that more general a priori factorization does not produce here a more general form of g_2.

3. When the potential has a short-ranged strong attractive tail, e.g., a Lennard-Jones type, the $\ell n e_{ij}$ is appreciable only among near neighbors so that $\ell n E_N = O(N)$ and is of order $\ell n D_N$. Again $E_N D_N = e^{-1-\gamma}\, \Theta \prod_{i=1}^{N} e^{-\lambda(x_i,t)}$ and g_2 as given by (25) follows.

At the one-particle level, this closure principle will give the dense fluid a hard-sphere structure at most, if the potential has a hard-core repulsion. There is no velocity correlation manifested in g_2 in any case. So, using for closure the result (25), we obtain from (30) in generic-function language the kinetic variational equation[18]

$$\left(\frac{\partial}{\partial t} + \vec{v}_1 \cdot \nabla_1\right) f_1(x_1,t) = \frac{\partial}{\partial \vec{v}_1} f_1(x_1,t) \cdot \int d\vec{r}_2 \left(\nabla_1 \phi_{12}^{tail}\right) n_1(\vec{r}_2,t)\, g_2(\vec{r}_1,\vec{r}_2|n_1(t)) + C_E(f_1,f_1) \; . \qquad (31)$$

By imposing the Kac limit, $\phi_{12}^{tail} = \lim_{\gamma\to 0} \gamma^3 V(\gamma r)$, which can be effected equivalently by setting $\sigma = 0$ in the mean-field-term integral, the result is obtained

$$\left(\frac{\partial}{\partial t} + \vec{v}_1 \cdot \nabla_1\right) f_1(x_1,t) = \frac{\partial}{\partial \vec{v}_1} f_1(x_1,t) \cdot \int d\vec{r}_2 \nabla_1 V(r_{12}) n_1(\vec{r}_2,t) + C_E(f_1,f_1) \; . \qquad (32)$$

In form this equation has the appearance of an Enskog-Vlasov equation and differs in detail from the equations in ref. [17] only by the specific form of g_2 which appears in C_E.

V.2. H-Theorems

Each of the three theories, (26), (28), (31) is accompanied by the same entropy functional, namely, from (11) and (24)

$$S_1^{den} = k\ln e^{1+\gamma} - k \int dx\, f_1(x,t) \ln \cdot f_1(x,t) + k \int d\vec{r}\, n_1(\vec{r},t) \ln a_1(\vec{r},t) \qquad (33)$$

where

$$a_1(\vec{r},t) = e^{\lambda(x,t)} f_1(x,t) \qquad (34)$$

is a functional of f_1. This form was obtained by Resibois.[4a] Similarly, each has an H-theorem which will be demonstrated explictly. From (33) we have

$$\frac{\partial}{\partial t} S_1^{den} = k e^{-1-\gamma} \frac{\partial}{\partial t} e^{1+\gamma} - k \int dx \frac{\partial f_1}{\partial t} (\ln f_1 + 1) + k \int d\vec{r} \left(\frac{\partial}{\partial t} n_1\right) \ln a_1 + k \int d\vec{r}\, n_1 \frac{\partial}{\partial t} \ln a_1 . \qquad (35)$$

In all three theories (26), (28), and (31) the relation holds

$$\frac{\partial}{\partial t} n_1(\vec{r},t) = -\nabla \cdot \int dv\, \vec{v} f_1(\vec{r},\vec{v},t) \qquad (36)$$

whereas from (24) and (33) there follow

$$\frac{\partial}{\partial t} e^{1+\gamma} = N \int d^N x \Theta \prod_{i=2}^{N} e^{-\lambda(x_i,t)} \frac{\partial}{\partial t} e^{-\lambda(x_1,t)} \qquad (37)$$

and

$$\frac{\partial}{\partial t} \ln a(r,t) = -e^{-1-\gamma} \frac{\partial}{\partial t} e^{1+\gamma} + \int d^{N-1} x \Theta \frac{\partial}{\partial t} \prod_{i=2}^{N} e^{-\lambda(x_i,t)} \times \left[\int d^{N-1} x \Theta \prod_{i=2}^{N} e^{-\lambda(x_i,t)}\right]^{-1} \qquad (38)$$

so that $k e^{-1-\gamma} \frac{\partial}{\partial t} e^{1+\gamma} + k \int d\vec{r}\, n_1(\vec{r},t) \frac{\partial}{\partial t} \ln a(\vec{r},t) = 0.$

The equations (26), (28), and (31) are abbreviated

$$\frac{\partial f_1}{\partial t} + \vec{v}_1 \cdot \nabla_1 f_1 = Mf_1 + C(f_1,f_1) \qquad (39)$$

where M = 0 for (26), (28), and yields the mean field term in (31). The $C(f_1,f_1)$ is the collision integral.

The third term of (35) becomes, using (36) and rearranging

$$k \int d\vec{r} \int d\vec{v}[-\vec{v}\cdot\nabla(f_1 \ell n a) + f_1 \vec{v}\cdot\nabla \ell n a] \ . \qquad (40)$$

The first term can be transformed to a surface integral which vanishes by boundary condition assumptions. Now $a(\vec{r},t)$ depends on $\vec{r}$ only through Θ,

$$\nabla_1 \ell n a(\vec{r}_1,t) = \frac{(N-1)\int d\vec{r}_2 \hat{r}_{12}\delta(r_{12}-\sigma)\int d^{N-2}r\Theta \prod_{i=2}^{N}\rho_i}{\int d^{N-1}r\Theta\prod_{i=2}^{N}\rho_i}$$

where $\rho_i = \int d\vec{v}_i \, e^{-\lambda_i}$ and $\hat{r}_{12} = \frac{\vec{r}_1 - \vec{r}_2}{|\vec{r}_1 - \vec{r}_2|}$. This simplifies to

$$\nabla_1 \ell n a(\vec{r}_1,t) = \int d\vec{r}_2 \hat{r}_{12}\delta(r_{12}-\sigma)n_1(\vec{r}_2,t)g_2(\vec{r}_1,\vec{r}_2|n) \qquad (41)$$

where $g_2(\vec{r}_1,\vec{r}_2|n)$ is the same g_2 in (25). Hence the last term of (40) becomes

$$k \int dx_1 f_1(x_1,t)\vec{v}_1 \cdot \int d\vec{r}_2 \hat{r}_{12}\delta(r_{12}-\sigma)n_1(\vec{r}_2,t)g_2(\vec{r}_1,\vec{r}_2|n) \ . \qquad (42)$$

Recently, Grmela and Garcia-Colin[3] gave a prescription for constructing a term like (42) for the SET.

Substitute (39) into the second term of (35). The $k \int dx \, \vec{v}\cdot\nabla f_1(\ell n f_1 + 1) = k \int dx \, \vec{v}\cdot\nabla(f_1 \ell n f_1)$ which vanishes via boundary condition assumptions. Also $-k \int dx \, Mf_1(\ell n f_1 + 1) = 0$. Thus it remains to evaluate $-k \int dx \, C(f_1,f_1)\ell n f_1$, since $\int dx \, C(f_1,f_1) = 0$ because there is no mass transfer at collision. The approach we take, different than that of Resibois[4] and first described in an earlier report,[28] is particularly enlightening in relation to discussion of irreversible thermodynamics. We break the hard-sphere collision term [RHS of (26)] into two pieces, denoted

$$C_E^{\pm} = \frac{1}{2}\sigma^2 \int d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}[\theta(\hat{\sigma}\cdot\vec{g}) \pm \theta(-\hat{\sigma}\cdot\vec{g})] \times$$
$$[g_2(\vec{r}_1,\vec{r}_1+\sigma\hat{\sigma}|n)f_1(\vec{r}_1,\vec{v}_1',t)f_1(\vec{r}_1+\sigma\hat{\sigma},\vec{v}_2',t)$$
$$- g_2(\vec{r}_1,\vec{r}_1-\sigma\hat{\sigma}|n)f_1(\vec{r}_1,\vec{v}_1,t)f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t)] \ . \qquad (43)$$

Similar forms for the standard Enskog collision term have been termed "reversible" and "irreversible" by Gross and Wisnivesky.[29]

Then $\partial S_C^{\pm}/\partial t \equiv -k \int dx_1 C_E^{\pm} \ell n f_1$ is transformed to

$$\frac{\partial S_C^{\pm}}{\partial t} = +\frac{1}{2}k\sigma^2 \int dx_1 d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}[\theta(\hat{\sigma}\cdot\vec{g}) \pm \theta(-\hat{\sigma}\cdot\vec{g})]$$
$$g_2(\vec{r}_1,\vec{r}_1-\sigma\hat{\sigma}|n)f_1(\vec{r}_1,\vec{v}_1,t)f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t)$$
$$\times \ell n \frac{f_1(\vec{r}_1,\vec{v}_1,t)}{f_1(\vec{r}_1,\vec{v}_1',t)} \qquad (44)$$

by the changes of variable: $(\vec{v}_1,\vec{v}_2) \to (\vec{v}_1',\vec{v}_2')$ such that $d\vec{v}_1'd\vec{v}_2' = d\vec{v}_1 d\vec{v}_2$ and $\hat{\sigma}\cdot\vec{g} = -\hat{\sigma}\cdot\vec{g}'$, $\hat{\sigma} \to -\hat{\sigma}$ and drop primes. Switch $\vec{v}_1 \leftrightarrow \vec{v}_2$, $\hat{\sigma} \to -\hat{\sigma}$ and change $\vec{r}_1$ variable to obtain the alternate form

$$\frac{\partial S_C^{\pm}}{\partial t} = \frac{1}{2} k\sigma^2 \int dx_1 d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}[\theta(\hat{\sigma}\cdot\vec{g}) \pm \theta(-\hat{\sigma}\cdot\vec{g})]$$
$$g_2(\vec{r}_1,\vec{r}_1-\sigma\hat{\sigma}|n) f_1(\vec{r}_1,\vec{v}_1,t) f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t)$$
$$\times \ln \frac{f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t)}{f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2',t)}$$

which is averaged with (44) to yield

$$\frac{\partial S_C^{\pm}}{\partial t} = \frac{1}{4} k\sigma^2 \int dx_1 d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}[\theta(\hat{\sigma}\cdot\vec{g}) \pm \theta(-\hat{\sigma}\cdot\vec{g})]$$
$$g_2(\vec{r}_1,\vec{r}_1-\sigma\hat{\sigma}|n) f_1(\vec{r}_1,\vec{v}_1,t) f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t)$$
$$\times \ln \frac{f_1(x_1,t) f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t)}{f_1(\vec{r}_1,\vec{v}_1',t) f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2',t)} \quad . \tag{45}$$

We want to point out that only velocity independence of g_2 has been used to this point. Thus these manipulations are valid also for the SET, and it is worth noting that by setting $g_2 = 1$ and imposing smoothness on f_1 -- $f_1(\vec{r}-\sigma\hat{\sigma},\vec{v},t) = f_1(\vec{r},\vec{v},t)$ -- we find that $\partial/\partial t\ S_C^+ = 0$ and $\partial/\partial t\ S_C^-$ becomes precisely of the form of the entropy production function given by Boltzmann theory.

Now apply $x \ln \frac{x}{y} \geq x - y$ to the integrand, where $x = f_1(x_1,t) \times f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t)$ and $y = f_1(\vec{r}_1,\vec{v}_1',t) f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2',t)$, to obtain

$$\frac{\partial S_C^{\pm}}{\partial t} \geq \frac{1}{4} k\sigma^2 \int dx_1 d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}[\theta(\hat{\sigma}\cdot\vec{g}) \pm \theta(-\hat{\sigma}\cdot\vec{g})]$$
$$g_2(\vec{r}_1,\vec{r}_1-\sigma\hat{\sigma}|n)\, [f_1(x_1,t) f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t)$$
$$- f_1(\vec{r}_1,\vec{v}_1',t) f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2',t)] \quad . \tag{46}$$

Transforming away primes as before yields

$$\frac{\partial S_C^{\pm}}{\partial t} \geq \frac{1}{4} k\sigma^2 \int dx_1 d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}[\theta(\hat{\sigma}\cdot\vec{g}) \pm \theta(-\hat{\sigma}\cdot\vec{g})]$$
$$[g_2(\vec{r}_1,\vec{r}_1-\sigma\hat{\sigma}|n) f_1(x_1,t) f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t)$$
$$- g_2(\vec{r}_1,\vec{r}_1+\sigma\hat{\sigma}|n) f_1(x_1,t) f_1(\vec{r}_1+\sigma\hat{\sigma},\vec{v}_2,t)]$$

which after rearranging becomes

$$\frac{\partial S_C^{\pm}}{\partial t} \geq \frac{1}{4} k\sigma^2 \int dx_1 d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\theta(\hat{\sigma}\cdot\vec{g})$$
$$\Big\{g_2(\vec{r}_1,\vec{r}_1-\sigma\hat{\sigma}|n) f_1(x_1,t) f_1(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t)\,[1 \pm 1]$$
$$- g_2(\vec{r}_1,\vec{r}_1+\sigma\hat{\sigma}|n) f_1(x_1,t) f_1(\vec{r}_1+\sigma\hat{\sigma},\vec{v}_2,t)\,[1 \pm 1]\Big\} \quad . \tag{47}$$

So $\frac{\partial S_C^-}{\partial t} \geq 0$, which demonstrates that the "irreversible" part of C_E, C_E^-, has irreversible character similar to the Boltzmann collision integral. Rewriting $\frac{\partial S_C^+}{\partial t}$ as

$$\frac{\partial S_C^+}{\partial t} \geq \frac{1}{2} k\sigma^2 \int dx_1 dx_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\theta(\hat{\sigma}\cdot\vec{g})$$
$$g_2(\vec{r}_1,\vec{r}_2|n) f_1(x_1,t) f_1(x_2,t)$$
$$\times\ [\delta(\vec{r}_2 - \vec{r}_1+\sigma\hat{\sigma}) - \delta(\vec{r}_2 - \vec{r}_1-\sigma\hat{\sigma})]$$

or

$$\frac{\partial S_C^+}{\partial t} \geq \frac{1}{2} k\sigma^2 \int dx_1 dx_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\delta(\vec{r}_2 - \vec{r}_1 + \sigma\hat{\sigma}) g_2(\vec{r}_1,\vec{r}_2|n) f_1(x_1,t) f_1(x_2,t)$$

$$= \frac{1}{2} k \int dx_1 dx_2\ \hat{r}_{12}\cdot\vec{g}\ g_2(\vec{r}_1,\vec{r}_2|n) f_1(x_1,t) f_1(x_2,t)\delta(r_{12}-\sigma)$$

$$= \frac{1}{2} k \int dx_1 dx_2 (\hat{r}_{12}\cdot\vec{v}_2 + \hat{r}_{21}\cdot\vec{v}_1) g_2(\vec{r}_1,\vec{r}_2|n) f_1(x_1,t) f_1(x_2,t)\delta(r_{12}-\sigma)$$

$$= k \int dx_1 dx_2\ \hat{r}_{21}\cdot\vec{v}_1\ g_2(\vec{r}_1,\vec{r}_2|n) f_1(x_1,t) f_1(x_2,t)\delta(r_{12}-\sigma)\ . \qquad (48)$$

No use was made of the functional dependence of g_2 on n to arrive at (48) so that a result of similar form holds for the SET as well. Though the sign of (48) is indeterminate, this quantity is the negative of (42). Thus we have shown for (26) and (31) that $\frac{\partial}{\partial t} S_1^{den} \geq 0$, with equality holding when

$$f_1^0(x_1,t) f_1^0(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2,t) = f_1^0(\vec{r}_1,\vec{v}_1',t) f_1^0(\vec{r}_1-\sigma\hat{\sigma},\vec{v}_2',t) \qquad (49)$$

for all $\vec{r}_1$, $\vec{v}_1$, $\vec{v}_2$ and $\hat{\sigma}\cdot\vec{g} \geq 0$. Resibois has shown[4b] that (49) holds also for $\hat{\sigma}\cdot\vec{g} \leq 0$. This condition (49) is not sufficient to make $C_E = 0$ but it does make $C_E^- = 0$, as can be seen from (43) by changing $\hat{\sigma}$ to $-\hat{\sigma}$ in the terms governed by $\theta(-\hat{\sigma}\cdot\vec{g})$. Taking Resibois' approach[4b] we find that the Fourier transform of $\ell n f_1^0(\vec{r},\vec{v},t)$ has the form

$$\Phi(\vec{k},\vec{v},t) = F[\ell n f_1^0(\vec{r},\vec{v},t)] = \alpha(\vec{k},\vec{t}) + \phi(\vec{k},\vec{v},t)\delta_{\vec{k},0} \qquad (50)$$

whereby we find f_1^0 has the form

$$f_1^0(\vec{r},\vec{v},t) = R(\vec{r},t)V(\vec{v},t)\ . \qquad (51)$$

Using (51) we can determine the summational invariants of C_E^-.

Consider

$$I = \int d\vec{v}_1\ \psi(\vec{v}_1)C_E^- \qquad (52)$$

where $\psi(\vec{v}_1)$ is any function, vector or scalar, of $\vec{v}_1$. Using (43) and performing the usual transformations obtain

$$I = \frac{1}{2}\sigma^2 \int d\vec{v}_1 d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\theta(\hat{\sigma}\cdot\vec{g})[\psi(\vec{v}_1') - \psi(\vec{v}_1)] \times \int d\vec{r}_2\ f_1(x_1,t)f_1(x_2,t)g_2(\vec{r}_1,\vec{r}_2|n) \times [\delta(\vec{r}_2-\vec{r}_1+\sigma\hat{\sigma}) + \delta(\vec{r}_2-\vec{r}_1-\sigma\hat{\sigma})]\ . \qquad (53a)$$

Switching $\vec{v}_1 \leftrightarrow \vec{v}_2$ and $\hat{\sigma} \rightarrow -\hat{\sigma}$ yields

$$I = \frac{1}{2}\sigma^2 \int d\vec{v}_1 d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\theta(\hat{\sigma}\cdot\vec{g})[\psi(\vec{v}_2') - \psi(\vec{v}_2)] \int d\vec{r}_2\ f_1(\vec{r}_1,\vec{v}_2,t)f_1(\vec{r}_2,\vec{v}_1,t)g_2(\vec{r}_1,\vec{r}_2|n) \times [\delta(\vec{r}_2-\vec{r}_1+\sigma\hat{\sigma}) + \delta(\vec{r}_2-\vec{r}_1-\sigma\hat{\sigma})]\ . \qquad (53b)$$

Use (51) and add (53,a,b) to obtain

$$I^0 = \frac{1}{4}\sigma^2 \int d\vec{v}_1 d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\theta(\hat{\sigma}\cdot\vec{g})[\psi(\vec{v}_1') + \psi(\vec{v}_2') - \psi(\vec{v}_1) - \psi(\vec{v}_2)] \int d\vec{r}_2\ f_1^0(x_1,t)f_1^0(x_2,t)g_2(\vec{r}_1,\vec{r}_2|n) \times [\delta(\vec{r}_2-\vec{r}_1+\sigma\hat{\sigma}) + \delta(\vec{r}_2-\vec{r}_1-\sigma\hat{\sigma})]\ . \qquad (54)$$

Clearly I^0 vanishes for $\psi = 1, \vec{v}, v^2$. Thus $\ell n f_1^0$ is a linear combination of these only, of the general form $\ell n f_1^0 = a(\vec{r},t) + \vec{b}(t)\vec{v} + c(t)v^2$. That is, f_1^0 has a gaussian form. The usual definitions of density, $n = \int d\vec{v}\, f_1$, of average velocity, $\vec{u} = \int d\vec{v}\, \vec{v} f_1$, and of temperature, $\frac{3}{2} nkT = \int d\vec{v}\, \frac{1}{2}(\vec{v}-\vec{u})^2 f_1$, fix a, $\vec{b}$, c and render the specific forms $R = n =$ constant, $V = (2\pi kT)^{-3/2}\, e^{-v^2/2kT}$ at equilibrium. Note that C_E^- alone cannot determine R. For this, C_E^+ comes into play.[30] Also, there is no inconsistency here between the vanishing of $\frac{\partial}{\partial t} S_1^{den}$ and the nonvanishing of C_E^+. Equation (49) merely characterizes the most general condition under which $\frac{\partial}{\partial t} S_1^{den} = 0$. This does not mean that f_1^0 is achieved and then relaxation proceeds around that form. A similar conclusion was reached by Grad[31] in regard to the Boltzmann theory where the analog of our f_1^0 is the local Maxwellian. Put another way, $\frac{\partial}{\partial t} S_1^{den} = 0$ is a necessary but not sufficient condition for equilibrium. As a last note, (51) precludes the precise local Maxwellian form which is used as a zeroth approximation to f_1 in the asymptotic expansion employed in the Chapman-Enskog development.[8]

To complete the picture for (28), we analyze the remainder term by term, denoted C_2, C_3, C_4, respectively. By manipulation similar to that for $-k \int dx_1\, C_E\, \ell n f_1$ above, we obtain

$$- k \int dx_1 C_4 \ell n f_1 = + \frac{1}{2} kR^2\sigma^2 \int dx_1 \int d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\,\theta(\hat{\sigma}\cdot\vec{g})$$
$$\theta(\sqrt{4\varepsilon} - \hat{\sigma}\cdot\vec{g})\, g_2(\vec{r}_1, \vec{r}_1 + R\sigma^-\hat{\sigma}|n)\, f_1(x_1,t)\, f_1(\vec{r}_1 + R\sigma\hat{\sigma}, \vec{v}_2, t)$$
$$\times \ell n \frac{f_1(x_1,t)\, f_1(\vec{r}_1 + R\sigma\hat{\sigma}, \vec{v}_2, t)}{f_1(\vec{r}_1, \vec{v}_1', t)\, f_1(\vec{r}_1 + R\sigma\hat{\sigma}, \vec{v}_2', t)} \,. \qquad (55)$$

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Also

$$- k \int dx_1 C_2 \ell n f_1 = - kR^2\sigma^2 \int dx_1 \int d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\,\theta(\hat{\sigma}\cdot\vec{g})$$
$$\times \ell n f_1(x_1,t) \Big\{ g_2(\vec{r}_1, \vec{r}_1 + R\sigma^-\hat{\sigma}|n)\, f_1(\vec{r}_1, \vec{v}_1'', t)$$
$$\times f_1(\vec{r}_1 + R\sigma\hat{\sigma}, \vec{v}_2'', t) - g_2(\vec{r}_1, r_1 - R\sigma^+\hat{\sigma}|n)$$
$$\times f_1(x_1,t)\, f_1(\vec{r}_1 - R\sigma\hat{\sigma}, \vec{v}_2, t) \Big\}$$

transforms to

$$- k \int dx_1 C_2 \ell n f_1 = - kR^2\sigma^2 \int dx_1 d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}$$
$$\times \Big\{ \theta(\hat{\sigma}\cdot\vec{g} - \sqrt{4\varepsilon})\, g_2(\vec{r}_1, \vec{r}_1 + R\sigma^-\hat{\sigma}|n)\, f_1(\vec{r}_1 + R\sigma\hat{\sigma}, \vec{v}_2, t)$$
$$\times \ell n f_1(\vec{r}_1, \vec{v}_1''', t) - \theta(\hat{\sigma}\cdot\vec{g})\, g_2(\vec{r}_1, \vec{r}_1 - R\sigma^+\hat{\sigma}|n)$$
$$\times f_1(x_1,t)\, f_1(\vec{r}_1 - R\sigma\hat{\sigma}, \vec{v}_2, t)\, \ell n f_1(x_1,t) \Big\} \qquad (56)$$

under the change of variables in the first term $(\vec{v}_1, \vec{v}_2) \rightarrow (\vec{v}_1'', \vec{v}_2'')$ such that $\hat{\sigma}\cdot\vec{g}'' d\vec{v}_1'' d\vec{v}_2'' = \hat{\sigma}\cdot\vec{g}\, d\vec{v}_1 d\vec{v}_2$ and by use of (29). Similarly, $- k \int dx_1 C_3 \ell n f_1$ transforms to

$$- k \int dx_1 C_3 \ell n f_1 = - kR^2\sigma^2 \int dx_1 d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}$$
$$\times \Big\{ \theta(\hat{\sigma}\cdot\vec{g})\, g_2(\vec{r}_1, \vec{r}_1 - R\sigma^+\hat{\sigma}|n)\, f_1(x_1,t)$$
$$\times f_1(\vec{r}_1 - R\sigma\hat{\sigma}, \vec{v}_2, t)\, \ell n f_1(\vec{r}_1, \vec{v}_1'', t)$$
$$- \theta(\hat{\sigma}\cdot\vec{g} - \sqrt{4\varepsilon})\, g_2(\vec{r}_1, \vec{r}_1 + R\sigma^-\hat{\sigma}|n)\, f_1(x_1,t)$$
$$\times f_1(\vec{r}_1 + R\sigma\hat{\sigma}, \vec{v}_2, t)\, \ell n f_1(x_1,t) \Big\} \,. \qquad (57)$$

Add (56) and (57), exchange $\vec{v}_1 \leftrightarrow \vec{v}_2$, change $\hat{\sigma} \to -\hat{\sigma}$ and rearrange to get

$$
\begin{aligned}
-k\int dx_1(C_2+C_3)\ell n f_1 &= \frac{1}{2}kR^2\sigma^2\int dx_1 d\vec{v}_2\int d\hat{\sigma}\,\hat{\sigma}\cdot\vec{g} \\
&\times\Big\{\theta(\hat{\sigma}\cdot\vec{g})\,g_2(\vec{r}_1,\vec{r}_1-R\sigma^+\hat{\sigma}|n)\,f_1(x_1,t)\,f_1(\vec{r}_1-R\sigma\hat{\sigma},\vec{v}_2,t) \\
&\times \ell n\,\frac{f_1(\vec{r}_1-R\sigma\hat{\sigma},\vec{v}_2,t)\,f_1(x_1,t)}{f_1(\vec{r}_1-R\sigma\hat{\sigma},\vec{v}_2'',t)\,f_1(\vec{r}_1,\vec{v}_1'',t)} \\
&-\theta(\hat{\sigma}\cdot\vec{g}-\sqrt{4\varepsilon})\,g_2(\vec{r}_1,\vec{r}_1+R\sigma^-\hat{\sigma}|n)\,f_1(x_1,t)\,f_1(\vec{r}_1+R\sigma\hat{\sigma},\vec{v}_2,t) \\
&\times \ell n\,\frac{f_1(x_1,t)\,f_1(\vec{r}_1+R\sigma\hat{\sigma},\vec{v}_2,t)}{f_1(\vec{r}_1,\vec{v}_1''',t)\,f_1(\vec{r}_1+R\sigma\hat{\sigma},\vec{v}_2''',t)}\Big\}\,. \qquad (58)
\end{aligned}
$$

Apply $x\ell n\frac{x}{y} \geq x-y$ to the integrands of the sum of (55) and (58) to get

$$
\begin{aligned}
-k\int dx_1(C_2+C_3+C_4)\ell n f_1 &\geq \frac{1}{2}kR^2\sigma^2\int dx_1 d\vec{v}_2\int d\hat{\sigma}\,\hat{\sigma}\cdot\vec{g} \\
&\times\Big\{\theta(\hat{\sigma}\cdot\vec{g})\,\theta(\sqrt{4\varepsilon}-\hat{\sigma}\cdot\vec{g})\,g_2(\vec{r}_1,\vec{r}_1+R\sigma^-\hat{\sigma}|n) \\
&\times[f_1(x_1,t)\,f_1(\vec{r}_1+R\sigma\hat{\sigma},\vec{v}_2,t) - f_1(\vec{r}_1,\vec{v}_1',t)\,f_1(\vec{r}_1+R\sigma\hat{\sigma},\vec{v}_2',t)] \\
&+\theta(\hat{\sigma}\cdot\vec{g})\,g_2(\vec{r}_1,\vec{r}_1-R\sigma^+\hat{\sigma}|n)\,[f_1(x_1,t)\,f_1(\vec{r}_1-R\sigma\hat{\sigma},\vec{v}_2,t) \\
&- f_1(\vec{r}_1,\vec{v}_1'',t)\,f_1(\vec{r}_1-R\sigma\hat{\sigma},\vec{v}_2'',t)] \\
&+\theta(\hat{\sigma}\cdot\vec{g}-\sqrt{4\varepsilon})\,g_2(\vec{r}_1,\vec{r}_1+R\sigma^-\hat{\sigma}|n)\,[f_1(x_1,t)\,f_1(\vec{r}_1+R\sigma\hat{\sigma},\vec{v}_2,t) \\
&- f_1(\vec{r}_1,\vec{v}_1''',t)\,f_1(\vec{r}_1+R\sigma\hat{\sigma},\vec{v}_2''',t)]\Big\}\,. \qquad (59)
\end{aligned}
$$

Transform primed velocities as before to obtain

$$
\begin{aligned}
-k\int dx_1(C_2+C_3+C_4)\ell n f_1 &\geq \frac{1}{2}kR^2\sigma^2\int dx_1 d\vec{v}_2\int d\hat{\sigma}\,\hat{\sigma}\cdot\vec{g} \\
&\times\Big\{\theta(\hat{\sigma}\cdot\vec{g})\,\theta(\sqrt{4\varepsilon}-\hat{\sigma}\cdot\vec{g})\,[g_2(\vec{r}_1,\vec{r}_1+R\sigma^-\hat{\sigma}|n)\,f_1(x_1,t) \\
&\times f_1(\vec{r}_1+R\sigma\hat{\sigma},\vec{v}_2,t) - g_2(\vec{r}_1,\vec{r}_1-R\sigma^+\hat{\sigma}|n) \\
&\times f_1(x_1,t)\,f_1(\vec{r}_1-R\sigma\hat{\sigma},\vec{v}_2,t) \\
&+[\theta(\hat{\sigma}\cdot\vec{g})-\theta(\hat{\sigma}\cdot\vec{g}-\sqrt{4\varepsilon})]\,g_2(\vec{r}_1,\vec{r}_1-R\sigma^+\hat{\sigma}|n) \\
&\times f_1(x_1,t)\,f_1(\vec{r}_1-R\sigma\hat{\sigma},\vec{v}_2,t) \\
&+[\theta(\hat{\sigma}\cdot\vec{g}-\sqrt{4\varepsilon})-\theta(\hat{\sigma}\cdot\vec{g})]\,g_2(\vec{r}_1,\vec{r}_1+R\sigma^-\hat{\sigma}|n) \\
&\times f_1(x_1,t)\,f_1(\vec{r}_1+R\sigma\hat{\sigma},\vec{v}_2,t)\Big\} \\
&= \frac{1}{2}kR^2\sigma^2\int dx_1 d\vec{v}_2\int d\hat{\sigma}\,\hat{\sigma}\cdot\vec{g}\,\theta(\hat{\sigma}\cdot\vec{g})\,\theta(\sqrt{4\varepsilon}-\hat{\sigma}\cdot\vec{g}) \\
&\times f_1(x_1,t)\,f_1(\vec{r}_1-R\sigma\hat{\sigma},\vec{v}_2,t) \\
&\times[g_2(\vec{r}_1,\vec{r}_1-R\sigma^+\hat{\sigma}|n) - g_2(\vec{r}_1,\vec{r}_1-R\sigma^-\hat{\sigma}|n)]\,. \qquad (60)
\end{aligned}
$$

Because g_2 from (25) is continuous at $\vec{r}_2-\vec{r}_1 = R\sigma\hat{\sigma}$, the RHS of (60) vanishes identically. Note that only at this point have we used the form of g_2 from (25) except for lack of velocity dependence. In particular, had we used the DRS Ansatz for g_2, (60) would be indeterminate since the bracket becomes $g_2(\vec{r}_1,\vec{r}_1-R\sigma^+\hat{\sigma};n)[1-e^{\beta\varepsilon}]$. With the vanishing of the RHS of (60) we have established that $\frac{\partial S_1^{den}}{\partial t} \geq 0$ for (28).

VI. TWO-PARTICLE HARD-SPHERE KINETIC THEORY

The attractiveness of the one-particle dense fluid kinetic theories is their mathematical tractability, particularly for eliciting transport coefficient formulae. However, it is clear that the dense fluid state cannot be characterized in general by just the one-particle distribution function since the dominant contributions to the fluxes of momentum and energy are described in terms of the two-particle distribution function. Herein we discuss a new two-particle hard-sphere kinetic theory.

Two-particle hard-sphere dynamics can also be developed from (2) for s = 2, wherein

$$
\begin{aligned}
&F_2(x_1,x_2,t+\tau) - T_{-\tau}^{(2)}F_2(x_1,x_2,t) \\
&\quad = n \int dx_3 \left\{T_{-\tau}^{(3)}F_3(x^3,t) - T_{-\tau}^{(2)}F_3(x^3,t)\right\} \\
&\quad\quad + n^2 \int dx_3dx_4 \left\{\frac{1}{2}\, T_{-\tau}^{(4)}F_4(x^4,t) - T_{-\tau}^{(3)}F_4(x^4,t) \right. \\
&\quad\quad\quad \left. + \frac{1}{2}\, T_{-\tau}^{(2)}F_4(x^4,t)\right\} + \ldots \, . \qquad (61)
\end{aligned}
$$

Change x_1, x_2 as above (4) to obtain for the LHS of (61)

$$T_{+\tau}^{(1)}F_2(x_1,x_2,t+\tau) - T_{-\tau}^{(2)}T_{\tau}^{(1)}F_2(x_1,x_2,t) \qquad (62a)$$

and similarly for the first term on the RHS of (61)

$$n \int dx_3 \left\{T_{-\tau}^{(3)}T_{\tau}^{(1)}F_3(x_1,x_2,x_3,t) - T_{-\tau}^{(2)}T_{\tau}^{(1)}F_3(x_1,x_2,x_3,t)\right\} . \qquad (62b)$$

Nonvanishing contributions to the integrand occur for those configurations of particle 3 which lead to collision with 1 or 2 within time τ. Similarly the four-body-term integrand does not vanish only if particles 3 and 4 can collide with 1 and 2 within time τ. Hence this term and higher ones vanish in the limit $\tau \to 0^+$. Because collisions between 1 and 2 do not contribute to (62b) it may be rewritten

$$n \int dx_3\left\{T_{-\tau}^{(3)}T_{\tau}^{(1)}F_3(x_1,x_2,x_3,t) - F_3(x_1,x_2,x_3,t)\right\} . \qquad (62b')$$

Again, since interaction between 1 and 3 or 2 and 3 only is admissible in the limit $\tau \to 0^+$, (62b') reduces to a form similar to the RHS of (23). Hence we obtain the exact two-particle equation:

$$
\begin{aligned}
&n\sigma^2 \int d\vec{v}_3 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}_{13}\theta(\hat{\sigma}\cdot\vec{g}_{13})\Big\{F_3(\vec{r}_1,\vec{v}_1',\vec{r}_2,\vec{v}_2',\vec{r}_1+\hat{\sigma}\sigma,\vec{v}_3',t) \\
&\quad - F_3(\vec{r}_1,\vec{v}_1,\vec{r}_2,\vec{v}_2,\vec{r}_1-\sigma\hat{\sigma},\vec{v}_3,t)\Big\} \\
&+ n\sigma^2 \int d\vec{v}_3 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}_{23}\theta(\hat{\sigma}\cdot\vec{g}_{23})\Big\{F_3(\vec{r}_1,\vec{v}_1',\vec{r}_2,\vec{v}_2',\vec{r}_2+\sigma\hat{\sigma},\vec{v}_3',t) \\
&\quad - F_3(\vec{r}_1,\vec{v}_1,\vec{r}_2,\vec{v}_2,\vec{r}_2-\sigma\hat{\sigma},\vec{v}_3,t)\Big\} \\
&= \frac{\partial}{\partial t} F_2(\vec{r}_1,\vec{v}_1,\vec{r}_2,\vec{v}_2,t) + \sum_{i=1}^{2} \vec{v}_i\cdot\nabla_i F_2 - \sum_{i=1}^{2} \frac{\partial\phi}{\partial\vec{r}_i}\cdot\frac{\partial}{\partial\vec{v}_i} F_2 \, . \qquad (63)
\end{aligned}
$$

In (63) we note that if $|\vec{r}_1 - \vec{r}_2| < 2\sigma$ then particle 3 cannot occupy all positions denoted by $\hat{\sigma}$ on the precollisional hemisphere, but only those outside the cone whose angle θ_c is given by $\theta_c = \cos^{-1}\frac{|\vec{r}_1 - \vec{r}_2|}{2\sigma}$. This excluded volume is manifest implicitly in F_3.

For closure we return to (14), set $E_N = \Theta$ and obtain

$$W_N = \Theta\, e^{-1-\gamma} \prod_{i\neq j} e^{-\lambda(x_i,x_j,t)} \; . \tag{64}$$

This W_N has the identical form of a canonical equilibrium N-particle distribution function for a potential that is the sum of one body and two body terms, with a hard-sphere two-body core but otherwise arbitrary form. Thus we have[32]

$$f_3(x^3,t) = \frac{f_2(x_1,x_2,t)f_2(x_1,x_3,t)f_2(x_2,x_3,t)}{f_1(x_1,t)f_1(x_2,t)f_1(x_3,t)}\, Y_3(x_1,x_2,x_3,t) \tag{65}$$

where Y_3 is the same functional of f_2 and f_1 as its equilibrium counterpart: Y_3 has a formally exact cluster expansion of the form

$$Y_3(x^3,t) = 1 + \int dx_4\; f_1(x_4,t)h_2(x_1,x_4,t) \times h_2(x_2,x_4,t)h_2(x_3,x_4,t) + \dots \; , \tag{66}$$

where $h_2(x_1,x_2,t) = \dfrac{f_2(x_1,x_2,t)}{f_1(x_1,t)f_1(x_2,t)} - 1$. We note that, though the equilibrium $h_2^{eq}(\vec{r}_1,\vec{r}_2)$ must go to zero in order to insure thermodynamic stability as $|\vec{r}_1 - \vec{r}_2| \to \infty$, the nonequilibrium function does not a priori have a similar spatial cluster property and the expansion (66) may not converge. Clearly it manifests the possibility of long range velocity correlations. We also note that (65) by itself may be regarded as a means of defining Y_3, as Livingston and Curtiss[10] point out. The closure principle provides an explicit form for this function, whereas the latter authors set $Y_3 = 1$, which is the Kirkwood Superposition Approximation (KSA). It is worth noting that the form

(65) is not peculiar to the hard-sphere potential, but is consistent with any form of two-body potential.

Combining (8) and (63) (in generic function language) with (65) we obtain the two-particle kinetic equation

$$\begin{aligned}
&\left(\frac{\partial}{\partial t} + \sum_{i=1}^{2} \vec{v}_i\cdot\nabla_i - \sum_{i=1}^{2} \frac{\partial\phi}{\partial\vec{r}_i}\cdot\frac{\partial}{\partial\vec{v}_i}\right) f_2(x_1,x_2,t) \\
&= \sigma^2 \int d\vec{v}_3 \int d\hat{\theta}\,\hat{\theta}\cdot\vec{g}_{31}\,\theta(\hat{\theta}\cdot\vec{g}_{31}) \times \\
&\quad \Big\{ f_1(\vec{r}_1,\vec{v}_1',t)f_1(x_2,t)f_1(\vec{r}_1+\sigma\hat{\theta},\vec{v}_3',t)g_2(\vec{r}_1,\vec{v}_1',x_2,t) \\
&\qquad \times g_2(\vec{r}_1,\vec{v}_1',\vec{r}_1+\sigma\hat{\theta},\vec{v}_3',t)g_2(x_2,\vec{r}_1+\sigma\hat{\theta},\vec{v}_3',t) \\
&\qquad \times Y_3(\vec{r}_1,\vec{v}_1',x_2,\vec{r}_1+\sigma\hat{\theta},\vec{v}_3',t) \\
&\qquad - f_1(x_1,t)f_1(x_2,t)f_1(\vec{r}_1-\sigma\hat{\theta},\vec{v}_3,t)g_2(x_1,x_2,t) \\
&\qquad\quad \times g_2(x_1,\vec{r}_1-\sigma\hat{\theta},\vec{v}_3,t)g_2(x_2,\vec{r}_1-\sigma\hat{\theta},\vec{v}_3,t) \\
&\qquad\quad \times Y_3(x_1,x_2,\vec{r}_1-\sigma\hat{\theta},\vec{v}_3,t)\Big\} \\
&+ \sigma^2 \int d\vec{v}_3 \int d\hat{\theta}\,\hat{\theta}\cdot\vec{g}_{32}\,\theta(\hat{\theta}\cdot\vec{g}_{32}) \times \\
&\quad \Big\{ f_1(x_1,t)f_1(\vec{r}_2,\vec{v}_2',t)f_1(\vec{r}_2+\sigma\hat{\theta},\vec{v}_3',t)g_2(x_1,\vec{r}_2,\vec{v}_2',t) \\
&\qquad\quad \times g_2(x_1,\vec{r}_2+\sigma\hat{\theta},\vec{v}_3',t)g_2(\vec{r}_2,\vec{v}_2',\vec{r}_2+\sigma\hat{\theta},\vec{v}_3',t) \\
&\qquad\quad \times Y_3(x_1,\vec{r}_2,\vec{v}_2',\vec{r}_2+\sigma\hat{\theta},\vec{v}_3',t) \\
&\qquad - f_1(x_1,t)f_1(x_2,t)f_1(\vec{r}_2-\sigma\hat{\theta},\vec{v}_3,t)g_2(x_1,x_2,t) \\
&\qquad\quad \times g_2(x_1,\vec{r}_2-\sigma\hat{\theta},\vec{v}_3,t)g_2(x_2,\vec{r}_2-\sigma\hat{\theta},\vec{v}_3,t) \\
&\qquad\quad \times Y_3(x_1,x_2,\vec{r}_2-\sigma\hat{\theta},\vec{v}_3,t)\Big\} \; .
\end{aligned} \tag{67}$$

From (11) and (64) we obtain the two-particle entropy

$$S_2^{den} = k\ell n e^{1+\gamma} - \frac{1}{2} k \int dx_1 dx_2 \; f_2(x_1,x_2,t)\ell n f_2(x_1,x_2,t)$$

$$+ \frac{1}{2} k \int dx_1 dx_2 \; f_2(x_1,x_2,t)\ell n a(x_1,x_2,t) \qquad (68)$$

where $a_2(x_1,x_2,t) = e^{2\lambda(x_1,x_2,t)} f_2(x_1,x_2,t)$. We write the kinetic equation (67) in the abbreviated form

$$\left(\frac{\partial}{\partial t} + \sum_{i=1}^{2} \vec{v}_i \cdot \nabla_i - \sum_{i=1}^{2} \frac{\partial \phi}{\partial \vec{r}_i} \cdot \frac{\partial}{\partial \vec{v}_i}\right) f_2(x_1,x_2,t)$$

$$= C_{13}^{+} + C_{13}^{-} + C_{23}^{+} + C_{23}^{-} \qquad (69)$$

where for example

$$C_{13}^{\pm} = \frac{1}{2}\sigma^2 \int d\vec{v}_3 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}_{31}[\theta(\hat{\sigma}\cdot\vec{g}_{31}) \pm \theta(-\hat{\sigma}\cdot\vec{g}_{31})]$$

$$\left\{f_3(\vec{r}_1,\vec{v}_1',x_2,\vec{r}_1+\sigma\hat{\sigma},\vec{v}_3',t) - f_3(x_1,x_2,\vec{r}_1-\sigma\hat{\sigma},\vec{v}_3,t)\right\} . \qquad (70)$$

For convenience we choose to use f_3 instead of carrying all the factors shown in (67). Take the LHS of (69) to be at equilibrium, at which $f_2(x_1,x_2,t) = f_1^{eq}(v_1)f_1^{eq}(v_2)g_2(|\vec{r}_2 - \vec{r}_1|)$. Impose $\int d\vec{v}_1 \int d\vec{v}_2 \; \vec{v}_2$ on this LHS to get

$$\text{equil LHS} = n^2(kT\nabla_2 g_2 + g_2\nabla_2\phi) . \qquad (71)$$

For the RHS we find

$$\int d\vec{v}_1 \; (C_{13}^{+} + C_{13}^{-}) = 0 \qquad (72a)$$

and by the usual transformations

$$\int d\vec{v}_1 \int d\vec{v}_2 \; \vec{v}_2 C_{23}^{\pm} = \frac{1}{2}\sigma^2 \int d\vec{v}_1 \int d\vec{v}_2 \int d\vec{v}_3$$

$$\int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}_{32}(\vec{v}_2' - \vec{v}_2)[\theta(\hat{\sigma}\cdot\vec{g}_{32}) \pm \theta(-\hat{\sigma}\cdot\vec{g}_{32})]$$

$$f_3(x_1,x_2,\vec{r}_2-\sigma\hat{\sigma},\vec{v}_3,t) .$$

Interchange $\vec{v}_2 \leftrightarrow \vec{v}_3$, impose the equilibrium form $f_3(x_1,x_2,x_3) = f_1^{eq}(v_1)f_1^{eq}(v_2)f_1^{eq}(v_3)g_3(\vec{r}_1,\vec{r}_2,\vec{r}_3)$ to obtain

$$\int d\vec{v}_1 \int d\vec{v}_2 \; \vec{v}_2 C_{23}^{-} = 0 \qquad (72b)$$

$$\int d\vec{v}_1 \int d\vec{v}_2 \; \vec{v}_2 C_{23}^{+} = \sigma^2 n^3 \int d\hat{\sigma}\hat{\sigma} g_3(\vec{r}_1,\vec{r}_2,\vec{r}_2-\sigma\hat{\sigma}) . \qquad (72c)$$

Combine (71) and (72) to get

$$kT\nabla_2 g_2(|\vec{r}_2 - \vec{r}_1|) + g_2\nabla_2\phi$$

$$= n\sigma^2 \int d\hat{\sigma}\hat{\sigma} g_3(\vec{r}_1,\vec{r}_2,\vec{r}_2-\sigma\hat{\sigma}) \qquad (73)$$

which is the two-particle member of the YBG hierarchy[19] for the hard-sphere potential, but in (73) we know already the form of g_3 from (65) and (66):

$$g_3(\vec{r}_1,\vec{r}_2,\vec{r}_2-\sigma\hat{\sigma}) = g_2(|\vec{r}_2 - \vec{r}_1|)g_2(\sigma)g_2(|\vec{r}_2-\sigma\hat{\sigma}-\vec{r}_1|)$$

$$\times Y_3(\vec{r}_1,\vec{r}_2,\vec{r}_2-\sigma\hat{\sigma}) .$$

This result shows the importance of the reversible part of the collision operator in two-particle kinetic theory for defining the form of equilibrium integro-differential equations. Wisnivesky[30] had investigated a similar role in one-particle kinetic theory.

VII. CONNECTIONS WITH IRREVERSIBLE THERMODYNAMICS

From the Boltzmann equation (20) and the entropy functional (21) it is straightforward[33] to obtain the equation for the entropy density s, such that $S_1^{dil} = \int d\vec{r}\, s(\vec{r},t)$,

$$\frac{\partial}{\partial t} s(\vec{r},t) + \nabla \cdot [s\vec{u}(\vec{r},t) + \vec{J}_s(\vec{r},t)] = \sigma(\vec{r},t) \qquad (74)$$

where $\vec{u}$ is the local average velocity, $\vec{J}_s = -k \int d\vec{v}\, (\vec{v}-\vec{u}) f_1 \ell n f_1$ is the entropy flux and the entropy production density $\sigma(\vec{r},t)$ is given by

$$\sigma(\vec{r},t) = -k \int d\vec{v}\, \ell n f_1 C_B(f_1,f_1) \geq 0 \qquad (75)$$

where C_B is the Boltzmann collision integral. Clearly

$$\frac{\partial}{\partial t} S_1^{dil} = \int d\vec{r}\, \sigma(\vec{r},t) \qquad (76)$$

since the flux term of (74) vanishes when integrated, by boundary condition assumptions. Generalization of these formulae to mixtures is straightforward.[33] By applying the Chapman-Enskog development[8] to the mixture version of (20) an expansion of f_{1_i} to linear order in gradients of $n_i, \vec{u}, T$ is obtained whereby an explicit expression for $T\sigma$, $T\sigma = \sum_j J_j X_j$, is obtained from the mixture version of (75). From $T\sigma$ can be identified forces, X_j, (gradients) and conjugate fluxes, J_j, and demonstration made of the Onsager reciprocal relations for the kinetic coefficients L_{ij} in the linear relations $J_i = \sum_j L_{ij} X_j$. This embodies the sole kinetic theoretic support for the phenomenological theory of linear irreversible processes.

We note that the Boltzmann theory is readily amenable to a purely local formulation since the Boltzmann collision term is purely local. In the dense fluid, collisions are not spatially localized and so the transport, which is dominated by collisional transfer, embodies non-local effects. So too the production of entropy is not localized and indeed the H-theorems demonstrated earlier are global results. It is an open question to what degree the program outlined above can be carried through for the dense fluid. A fundamental difficulty, in general, is defining a consistent local entropy density. In our discussion here, attention is limited to the pure hard-sphere theory for which some partial results have been described elsewhere.[3,4,9] A number of new features arise when the attractive tail is included and so discussion of this more general case will be made in a separate article.[34]

Utilizing results in the development between Eqs. (35) and (48) we obtain

$$\frac{\partial}{\partial t} S_1^{den} = \frac{\partial}{\partial t}\int d\vec{r}\; s(\vec{r},t)$$
$$= \int d\vec{r}\,(\sigma_c + \sigma_0) + k\int d\vec{r}\;\nabla\cdot\int d\vec{v}\;\vec{v}f_1(\vec{r},\vec{v},t)$$
$$\times\, \ell n[f_1(\vec{r},\vec{v},t)/a(\vec{r},t)] - \frac{k}{N}\,\ell n e^{1+\gamma}\int d\vec{r}\,\nabla\cdot n\vec{u} \qquad (77)$$

where

$$s(\vec{r},t) = \frac{k}{N}n(\vec{r},t)\ell n e^{1+\gamma} - k\int d\vec{v}\; f_1(\vec{r},\vec{v},t)\ell n[f_1/a] \qquad (77a)$$

reduces to the dilute-gas form when low density is imposed,

$$\sigma_c(\vec{r},t) = -k\int d\vec{v}\;\ell n f_1(\vec{r},\vec{v},t)C_E(f_1,f_1) \qquad (77b)$$

and

$$\sigma_0(\vec{r}_1,t) = k\int d\vec{v}\; f_1\vec{v}\cdot\int d\vec{r}_2\;\hat{r}_{12}\delta(r_{12}-\sigma)n_1(\vec{r}_2,t)g_2(\vec{r}_1,\vec{r}_2|n). \qquad (77c)$$

Now the last term on the RHS of (77) can be written

$$-\int d\vec{r}\;\nabla\cdot(s\vec{u} + \vec{J}_s) \qquad (77d)$$

where

$$\vec{J}_s(\vec{r},t) = -k\int d\vec{v}\;(\vec{v}-\vec{u})f_1(\vec{r},\vec{v},t)\ell n[f_1/a]. \qquad (77e)$$

Using the definition of $\vec{u}$, (77e) reduces to the dilute gas form below (74).

From (77) and (77d) we can extract the local equation

$$\frac{\partial}{\partial t}s(\vec{r},t) + \nabla\cdot(s\vec{u} + \vec{J}_s) = \sigma_c^- + \sigma_c^+ + \sigma_0 \qquad (78)$$

where the decomposition

$$\sigma_c^{\pm} = -k\int d\vec{v}[\ell n f_1(\vec{r},\vec{v},t)]C_E^{\pm}(f_1,f_1) \qquad (79)$$

has been employed. Clearly we have

$$\frac{\partial}{\partial t}S_c^{\pm} = \int d\vec{r}\;\sigma_c^{\pm}$$

and the H-theorem proved earlier showed that

$$\int d\vec{r}\;\sigma_c^- \geq 0$$

and

$$\int d\vec{r}\;(\sigma_c^+ + \sigma_0) \geq 0\;.$$

Using (45) it is straightforward to show that

$$\sigma_c^-(\vec{r},t) \geq 0 \tag{80}$$

holds at each point, however we also obtain

$$\sigma_c^+ + \sigma_0 \geq \frac{1}{2} k \int d\vec{r}_2\, \hat{r}_{12} \cdot [\vec{u}(\vec{r}_2,t) + \vec{u}(\vec{r}_1,t)] \times n_1(\vec{r}_1,t) n_1(\vec{r}_2,t) g_2(\vec{r}_1,\vec{r}_2|n)\delta(\vec{r}_{12} - \sigma) \;. \tag{81}$$

Though the RHS is indeterminate in sign, we note that $\int d\vec{r}_1$ RHS = 0. The quantity $\sigma_c^+ + \sigma_0$ therefore appears to manifest a combination of entropy production and entropy flux. Explicit demonstration of this feature is readily achieved for linear perturbations from equilibrium for which [superscript (1) denotes linear regime]

$$f_1^{(1)} = f_1^{(0)}[1 + \Phi] \tag{82}$$

where $f_1^{(0)}$ is a local Maxwellian and Φ is linear in gradients of $\vec{u}$,T as described by the Chapman-Enskog development[8]. We find

$$g_2(\vec{r}_1,\vec{r}_2|n) \simeq g_2(r_{12};n(\vec{r}_1,t)) + \frac{1}{2}\vec{r}_{21} \cdot \nabla_1 n \frac{d}{dn} g_2(r_{12};n(\vec{r}_1,t))$$

when the full g_2 given by (25) is expanded in n about $\vec{r}_1$ and so

$$\sigma_0^{(1)}(\vec{r}_1,t) = -\frac{2}{3}\pi\sigma^3 k\vec{u}\cdot\nabla_1[n^2 g_2(\sigma)] \;, \tag{83}$$

equality holding through second order in gradients. Similarly, starting from the representation for σ_c^+ given by (45) we find

$$\sigma_c^{(1)+}(\vec{r}_1,t) = -\frac{2\pi}{3} g_2(\sigma)\sigma^3 kn^2 \nabla_1 \cdot \vec{u} + \frac{2}{3}\pi\sigma^3 kn^2 g_2(\sigma) \times \left\{ b_0 \overset{\circ}{\overline{\nabla\vec{u}}} : \overset{\circ}{\overline{\nabla\vec{u}}} - \frac{5}{2}\frac{k}{m} a_1 \frac{(\nabla T)^2}{T} \right\} \tag{84}$$

where $\overset{\circ}{\overline{\nabla\vec{u}}} = \frac{1}{2}[\nabla\vec{u} + (\nabla\vec{u})^T] - \frac{1}{3}\nabla\cdot\vec{u}\,\overleftrightarrow{I}$ and $\overleftrightarrow{I}$ is the unit dyadic.

To achieve (84), the expansion of Φ in Sonine polynomials[8]

$$\Phi = -(\vec{v}-\vec{u}) \cdot \frac{\nabla T}{T} \sum_{r=1}^{\infty} a_r S_{3/2}^{(r)}\left[\frac{m}{2kT}(\vec{v}-\vec{u})^2\right] - \frac{m}{2kT}(\vec{v}-\vec{u})^0(\vec{v}-\vec{u}) : \nabla\vec{u} \sum_{r=0}^{\infty} b_r S_{5/2}^{(r)}$$

has been used. We note that $b_0 > 0$ and $a_1 < 0$ so that by combining (83), (84) we find

$$\sigma_c^{(1)+} + \sigma_0^{(1)} = -\nabla \cdot \vec{j}^{(1)}(\vec{r},t) + \sigma'$$

where $\vec{j}^{(1)} = +\frac{2\pi}{3}\sigma^3 kn^2 g_2(\sigma)\vec{u}$, and $\sigma' \geq 0$ follows from (84). Now σ' is not a complete entropy-production density in the sense of irreversible thermodynamics[33] since it does not manifest the leading orders of collisional transport of energy and momentum and in particular omits bulk viscosity altogether; on the other hand, we show below that $\sigma_c^{(1)-}$ can be regarded as such. This means that the local entropy equation in the linear regime does not take the same form in the RET as that found in Boltzmann theory, (74). For RET we find in the linear regime

$$\frac{\partial}{\partial t} s^{(1)}(\vec{r},t) + \nabla\cdot[s^{(1)}\vec{u} + \vec{J}_s^{(1)} + \vec{j}^{(1)}] = \sigma_c^{(1)-} + \sigma' \tag{85}$$

The terms $\vec{j}^{(1)}$ and σ' have no analog in the Boltzmann theory, but do vanish in the low density limit. Furthermore, in the linear form of (74), the $\vec{J}_s^{(1)} = \frac{1}{T}\vec{J}_T$,[35] where $\vec{J}_T$ is the dilute-gas heat flux. A similar result cannot be identified within (85), though therein $\vec{J}_s^{(1)}$ is so related to the streaming part of the heat flux. The collisional part of the heat flux cannot be so accounted by either $\vec{j}^{(1)}$ or σ'.

To fully demonstrate the features of the $\sigma_c^{(1)-}$ necessitates working with a mixture of L species for which the formal results for kinetic equations, entropy functional and H-theorem go through in an obvious way. In this case, σ_c^- takes the form

$$\sigma_c^- = \frac{1}{4} k \sum_{i,j=1}^{L} \sigma_{ij}^2 \int d\vec{v}_1 d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}[\theta(\hat{\sigma}\cdot\vec{g}) - \theta(-\hat{\sigma}\cdot\vec{g})]$$
$$\times g_{ij}(\vec{r}_1,\vec{r}_1-\sigma_{ij}\hat{\sigma}|\{n\}) f_i(\vec{r}_1,\vec{v}_1,t) f_j(\vec{r}_1-\sigma_{ij}\hat{\sigma},\vec{v}_2,t)$$
$$\times \ell n \frac{f_i(\vec{r}_1,\vec{v}_1,t) f_j(\vec{r}_1-\sigma_{ij}\hat{\sigma},\vec{v}_2,t)}{f_i(\vec{r}_1,\vec{v}_1',t) f_j(\vec{r}_1-\sigma_{ij}\hat{\sigma},\vec{v}_2',t)} . \quad (86)$$

To achieve (86) requires symmetry $g_{ij}(\vec{r}_1,\vec{r}_2) = g_{ji}(\vec{r}_2,\vec{r}_1)$ which is exhibited by the RET and also the standard Enskog theory g_{ij}'s. For linear perturbations from equilibrium, wherein $f_i^{(1)} = f_i^{(0)}[1 + \Phi_i]$ and Φ_i is linear in gradients of n_i, $\vec{u}$, T, Eq. (86) takes the form:

$$\sigma_c^{(1)-} = k \sum_{i,j=1}^{L} \sigma_{ij}^2 Y_{ij} \int d\vec{v}_1 d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\theta(\hat{\sigma}\cdot\vec{g})$$
$$\times f_i^{(0)}(\vec{r}_1,\vec{v}_1,t) f_j^{(0)}(\vec{r}_1,\vec{v}_2,t)\Phi_i(\vec{r}_1,\vec{v}_1,t)$$
$$\times [\Phi_i(\vec{r}_1,\vec{v}_1,t) + \Phi_j(\vec{r}_1,\vec{v}_2,t) - \Phi_i(\vec{r}_1,\vec{v}_1',t) - \Phi_j(\vec{r}_1,\vec{v}_2',t)]$$
$$+ \frac{k}{2} \sum_{i,j=1}^{L} \sigma_{ij}^4 Y_{ij} \int d\vec{v}_1 d\vec{v}_2 \int d\hat{\sigma}\hat{\sigma}\cdot\vec{g}\theta(\hat{\sigma}\cdot\vec{g})$$
$$\times f_i^{(0)}(\vec{r}_1,\vec{v}_1,t) f_j^{(0)}(\vec{r}_1,\vec{v}_2,t)\hat{\sigma}\cdot\nabla\ell n f_j^{(0)}(\vec{r}_1,\vec{v}_2,t)\hat{\sigma}\cdot\nabla$$
$$\times \ell n \frac{f_j^{(0)}(\vec{r}_1,\vec{v}_2,t)}{f_j^{(0)}(\vec{r}_1,\vec{v}_2',t)} \quad (86')$$

where Y_{ij} is the contact value of the equilibrium g_{ij} and expansion is made of all functions about $\vec{r}_1$ to linear order in gradients. The conventional expansion[8]

$$\Phi_i = -\vec{A}_i \cdot \nabla\ell nT - \overleftrightarrow{B}_i : \nabla\vec{u} + H_i\nabla\cdot\vec{u} - \sum_{\ell=1}^{L} \vec{D}_{i\ell}\cdot\vec{d}_\ell \quad (87)$$

is made. The second term of $\sigma_c^{(1)-}$ can be evaluated explicitly since

$$f_i^{(0)}(\vec{r},\vec{v},t) = n_i(\vec{r},t) \left[\frac{m_i}{2\pi kT(\vec{r},t)}\right]^{3/2}$$
$$\times \exp\left\{-\frac{m_i}{2kT(\vec{r},t)}[\vec{v} - \vec{u}(\vec{r},t)]^2\right\}$$

and the first abbreviated by using the bracket notation of Chapman and Cowling:[8]

$$\sigma_c^{(1)-} = kn^2\{\Phi,\Phi\} + \frac{4}{3}\sum_{i,j=1}^{L} \sigma_{ij}^4 Y_{ij} n_i n_j \frac{\sqrt{2\pi\mu_{ij}k^3T}}{m_{ij}} \left(\frac{\nabla T}{T}\right)^2$$
$$+ \frac{8}{15}\sum_{i,j=1}^{L} \sigma_{ij}^4 Y_{ij} n_i n_j \frac{\sqrt{2\pi\mu_{ij}kT}}{T} \overset{\circ}{\overline{\overline{\nabla\vec{u}}}} : \nabla\vec{u}$$
$$+ \frac{4}{9}\sum_{i,j=1}^{L} \sigma_{ij}^4 Y_{ij} n_i n_j \frac{\sqrt{2\pi\mu_{ij}kT}}{T} (\nabla\cdot\vec{u})^2 . \quad (88)$$

Here $m_{ij} = m_i + m_j$ and μ_{ij} is the reduced mass. The last three terms are related respectively to the collisional contributions to heat flux, off-diagonal momentum flux (shear viscosity), and diagonal momentum flux (bulk viscosity). Using the linearized integral equation which is satisfied by Φ[26] it is straightforward to show that the mass flux can be expressed as

$$-\frac{n}{n_i m_i}\vec{J}_{mi} = n^2\nabla\ell nT \cdot \{\vec{A},\vec{D}_i\} + n^2\sum_{\ell=1}^{L} \vec{d}_\ell \cdot \{\vec{D}_\ell,\vec{D}_i\}, \quad (89)$$

the heat flux including collisional contribution is

$$\vec{J}_T = -kTn^2\{\vec{A},\vec{A}\} \cdot \nabla\ell nT - kTn^2\sum_{\ell=1}^{L} \vec{d}_\ell \cdot \{\vec{D}_\ell,\vec{A}\}$$
$$- \frac{4}{3}\sum_{i,j=1}^{L} \sigma_{ij}^4 Y_{ij} n_i n_j \frac{\sqrt{2\pi\mu_{ij}k^3T}}{m_{ij}} \nabla T , \quad (90)$$

and the momentum flux, including collision contributions, is

$$\overleftrightarrow{P} = -\frac{4}{9}\sum_{i,j=1}^{L}\sigma_{ij}^4 Y_{ij}n_i n_j\sqrt{2\pi\mu_{ij}kT}\,\nabla\cdot\vec{u}\,\overleftrightarrow{I}$$
$$-\frac{8}{15}\sum_{i,j=1}^{L}\sigma_{ij}^4 Y_{ij}n_i n_j\sqrt{2\pi\mu_{ij}kT}\,\overset{\circ}{\overline{\nabla\vec{u}}}$$
$$-kTn^2\nabla\vec{u}:\{\overleftrightarrow{B},\overleftrightarrow{B}\} - kTn^2\{H,H\}\overleftrightarrow{I}\nabla\cdot\vec{u}\,. \qquad (91)$$

Collecting (88) - (91) we find

$$\sigma_c^{(1)-} = -\frac{1}{T}\vec{J}_T\cdot\nabla\ell nT - k\sum_{i=1}^{L}\frac{n}{n_i m_i}\vec{J}_{m_i}\cdot\vec{d}_i - \frac{\overleftrightarrow{P}}{T}:\nabla\vec{u}\,. \quad (92)$$

This is precisely the form to be gotten by using the Boltzmann equation. Though $\sum_i \vec{d}_i = 0$ and $\sum_i \vec{J}_{m_i} = 0$, it is clear that not both conjugate mass fluxes and forces, represented in the combination $kT\sum\frac{n}{n_i m_i}\vec{J}_{m_i}\cdot\vec{d}_i$, are linearly dependent. Choosing the forces[36] to be $-\vec{d}_i$, we eliminate $\vec{d}_L = -\sum_{i=1}^{L-1}\vec{d}_i$ and obtain

$$T\sigma_c^{(1)-} = -\vec{J}_T\cdot\nabla\ell nT - \overleftrightarrow{P}:\nabla\vec{u}$$
$$-kT\sum_{i=1}^{L-1}\left(\frac{n}{n_i m_i}\vec{J}_{m_i} - \frac{n}{n_L m_L}\vec{J}_{m_L}\right)\cdot\vec{d}_i\,. \quad (93)$$

Let the independent forces be $-\nabla\ell nT$, $-\nabla\vec{u}$, $-\vec{d}_i$, $i = 1\ldots L-1$, then the conjugate fluxes are obtained

$$\vec{J}_T = \vec{J}_T = -n^2kT\{\vec{A},\vec{A}\}\cdot\nabla\ell nT - \frac{4}{3}\sum_{i,j=1}^{L}\sigma_{ij}^4 Y_{ij}n_i n_j\frac{\sqrt{2\pi\mu_{ij}k^3T}}{m_{ij}}\nabla T$$
$$-n^2kT\sum_{\ell=1}^{L-1}\vec{d}_\ell\cdot\{\vec{D}_\ell - \vec{D}_L,\vec{A}\}\,, \quad (94)$$

$$\vec{J}_{m_i} = kT\left(\frac{n}{n_i m_i}\vec{J}_{m_i} - \frac{n}{n_L m_L}\vec{J}_{m_L}\right) = -n^2kT\Bigg[\nabla\ell nT\cdot\{\vec{A},\vec{D}_i - \vec{D}_L\}$$
$$+\sum_{\ell=1}^{L-1}\vec{d}_\ell\cdot\{\vec{D}_L - \vec{D}_\ell,\vec{D}_L - \vec{D}_i\}\Bigg], \quad (95)$$

and $\overleftrightarrow{J}_P = \overleftrightarrow{P}$ as given by (91). We note the following with regard to (94), (95):

1. The coefficients of $\vec{d}_j$ in (94) and of $\nabla\ell nT$ in (95) for $i = j$ are equal because $\{\vec{A},\vec{D}\} = \{\vec{D},\vec{A}\}$, therefore these kinetic coefficients exhibit Onsager reciprocity.[33]

2. The coefficients of $\vec{d}_j$ in (95) for $i = k$ and of $\vec{d}_k$ for $i = j$ are equal and also exhibit Onsager reciprocity.

3. The analyses and results from Eq. (85) through (95) hold for the revised Enskog theory, which is characterized by the mixture analog of (25) and (26). By virtue of the developments made in ref. [3], these also hold in form for the standard Enskog theory, wherein $g_{ij}(\vec{r}_1,\vec{r}_2)$ has the form proper to uniform equilibrium but with densities evaluated at $(\vec{r}_1 + \vec{r}_2)/2$. Thus an entropy production density of the form (93) permits identification of forces and conjugate fluxes in the SET framework and the relevant kinetic coefficients exhibit Onsager reciprocity as described in items 1 and 2. In the context of (93), (94) and (95), the only difference between RET and SET lies in the form of $\vec{d}_i$. For the former we have showed[26]

$$d_i^{RET} = \frac{n_i}{n} \left\{ \frac{1}{kT} (\nabla\mu_i)_T - \frac{m_i}{\rho kT} \nabla P + \frac{\nabla T}{T} \left[1 + \frac{4\pi}{3} \sum_{j=1}^{L} \sigma_{ij}^3 Y_{ij} n_j \frac{m_i}{m_{ij}} \right] \right\}$$

where μ_i is the chemical potential per particle

To obtain $\vec{d}_i^{SET}$, replace $\frac{1}{kT} (\nabla\mu_i)_T$ by $\nabla \ell n n_i + \frac{4\pi}{3} \sum_{j=1}^{L} \sigma_{ij}^3 Y_{ij} \nabla n_j + \frac{2\pi}{3} \sum_{j=1}^{L} \sigma_{ij}^3 n_j \nabla Y_{ij}$ which differs from it (unless all diameters are equal) in second and higher order in density.[9] We note with van Beijeren and Ernst[9] that $\vec{d}_i^{RET}$ conforms to the form expected on the basis of phenomenological treatments[33] whereas $\vec{d}_i^{SET}$ does not. This feature manifests itself, for example, in description of the diffusion coefficient in the critical region of a phase separation point.[37]

4. Because $\sigma_c^{(1)-SET} \neq \sigma_c^{(1)-RET}$, it is not possible to construct an invariant linear transformation[33] from the RET to SET description. Thus it is not possible to use reciprocity of the RET kinetic coefficients as a basis within transformation theory to investigate the presence of reciprocity in the SET, as attempted in [9]. We leave open the question of whether an invariant linear transformation can be applied to the SET to effect internal rearrangement of forces to agree with those of the RET. If such is possible, it is almost certain that the conjugate fluxes will no more each be identifiable with a single conventional transport flux, as depicted in (94) and (95). Furthermore, the maintenance of reciprocity must be checked, since not every transformation will

preserve reciprocity.[38] In any case, the $\sigma_c^{(1)-SET}$ would not exhibit the explicit form given by phenomenological irreversible thermodynamics, whereas the $\sigma_c^{(1)-RET}$ does.

5. The RET entropy equation (85) does not conform to the result (74), so that clearly even the RET, which must be regarded as the superior theory, is at odds with certain phenomenological results. Such phenomenological results that are of a form not satisfied by the RET, however, may themselves bear an oversimplified structure -- adequate for rare gases but not for dense fluids -- rather than bear clear evidence of RET deficiencies. In particular, the terms σ' and $\vec{j}^{(1)}$ appearing in (85) vanish in the low density limit. The disparity between the SET and phenomenology, on the other hand, appears to be of a more fundamental sort.

6. That both the RET and SET should exhibit reciprocity is not surprising since the main ingredient of the phenomenon, microscopic reversibility,[39] is built into both theories at the outset in the scattering cross section in the collision integrals.

7. Because of the reciprocity condition, $T\sigma_c^{(1)-}$ achieves a minimum for steady-state conditions.[40]

VIII. DISCUSSION

The closure principle we have employed yields more information than is used to obtain a closed kinetic equation. For example, in (23) only g_2 for two particles in "precollision" contact is needed. The result (25) is obtained, however, for completely arbitrary $\vec{r}_1$ and $\vec{r}_2$. This might suggest that the method overcharacterizes the ensemble. However, it is the entropy functionals that reflect the full character of the ensembles. Note these developments could have been carried out as well in the framework of the grand ensemble. We emphasize that the H-theorems we have demonstrated are global and not local properties of the theories. In this light, the Boltzmann theory is seen as a degenerate case which readily permits a local interpretation as well.

Closely related to the problem of closure is the problem of chaos propagation. Expression of closure does not have a unique form (cf. 17, 25, 65) but in all cases neglect of some higher-order correlations is a common characteristic. The viability of a closed kinetic equation hinges upon the propagation of this form, i.e., of continued irrelevance of correlations at this higher order to the description at hand. It is not at all clear that this requires destruction of these higher-order correlations, a possibility advocated by Mayer,[13] for example. Thus, in a physical sense, closure of a description may be a practical matter and chaos propagation a manifestation of the irrelevance of other degrees of freedom to the description.

Mathematically there remains the problem of what constitutes a proper framework to model these phenomena. The dilute gas case has received the greatest attention.[23,41] These analyses show the possibility of persistence in time of $g_2 = 1$ [cf. 17], almost everywhere. More generally, that (25) cannot be maintained indefinitely (and that the theory is thus not an exact one for hard spheres) is clear. Discrepancies in form and in numerical values of the transport coefficients derived from the theory compared to results of more exact approaches are evidence of this.

Clearly, one could generate a hierarchy of kinetic theories with our approach by successively setting $s = 2, 3, 4, \ldots$. One would expect a stage to be reached beyond which the added dynamics and statistics becomes irrelevant to the questions one normally asks of a kinetic theory. The two-particle kinetic theory we have introduced offers the ingredients which appear to be minimal for a closed theory, at least as evidenced by the Boltzmann theory. These are an entropy functional, a kinetic equation which yields correct equilibrium forms, and containment of fluxes within the level of description. The kinetic equation (67) appears to be Markovian due to the appearance of one time instant. However, the three-particle correlation function appearing in the theory depends in a non-local way on the two-particle spatial and velocity distribution and through velocity correlations "memory effects" may be built in. This two-particle theory appears to be unique in terms of the structure of the three-particle correlation function, Y_3 (66), which does not obviously show the cluster property assumed by Green.[42] Such an assumption is not obviously necessary in order for our formalism and the approximation that we propose to be meaningful.

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REFERENCES

1. L. Boltzmann, Lectures on Gas Theory (University of California Press, Berkeley, 1964).
2. D. Enskog, K. Sven. Vetenskapsaka. Handl 63 (4) (1922).
3. M. Grmela and L. S. Garcia-Colin, Phys. Rev. A 22, 1295 (1980).
4. P. Resibois, a) Phys. Rev. Lett. 40, 1409 (1978), and b) J. Stat. Phys. 19, 593 (1978).
5. G. E. Uhlenbeck and G. W. Ford, Lectures in Statistical Mechanics (American Mathematical Society, Providence, 1963).
6. N. N. Bogoliubov in Studies in Statistical Mechanics, Vol. 1, J. de Boer and G. E. Uhlenbeck, eds. (North Holland Pub. Co., Amsterdam, (1962).
7. See, for example, a) E. G. D. Cohen in Statistical Mechanics at the Turn of the Decade, E. G. D. Cohen, ed. (Marcel Dekker, New York, 1971) and references therein; b) M. S. Green and R. A. Piccirelli, Phys. Rev. 132, 1388 (1963) and also ref. [42]; c) Y. L. Klimontovich, Sov. Phys. - JETP 33, 732 (1971) and 36, 78 (1973).
8. See S. Chapman and T. G. Cowling, The Mathematical Theory of Non-Uniform Gases (Cambridge U. Press, 1970).
9. H. van Beijeren and M. H. Ernst, Physica 68, 437 (1973); 70, 225 (1973).
10. P. M. Livingston and C. F. Curtiss, Phys. Fl. 4, 816 (1961).
11. J. G. Kirkwood, J. Chem. Phys. 3, 300 (1935).

12. See, for example, M. Born and H. S. Green, A General Kinetic Theory of Liquids (Cambridge U. Press, 1949); A. Isihara, Statistical Physics (Academic Press, New York, 1971).

13. J. E. Mayer, J. Chem. Phys. 33, 1484 (1960).

14. A. D. McLachlan and R. A. Harris, J. Chem. Phys. 34, 1451 (1961).

15. G. V. Ramanathan, J. M. Dawson, and M. D. Kruskal, J. Math. Phys. 11, 339 (1970).

16. R. M. Lewis, J. Math. Phys. 8, 1448 (1967).

17. L. de Sobrino, Can. J. Phys. 45, 363 (1967); M. Grmela, J. Math. Phys. 15, 35 (1974).

18. J. Karkheck and G. Stell, Kinetic Mean-Field Theories, J. Chem. Phys., to appear.

19. See, for example, T. L. Hill, Statistical Mechanics (McGraw-Hill, New York, 1956).

20. R. M. Lewis, J. Math. Phys. 2, 222 (1961).

21. J. H. Irving and J. G. Kirkwood, J. Chem. Phys. 18, 817 (1950).

22. E. T. Jaynes in Statistical Physics, Brandeis Summer Institute 1962, Vol. 3 (W. A. Benjamin, Inc., New York, 1963).

23. H. Grad, Handbuch der Physik, Bd. 12, 205 (1958).

24. G. E. Uhlenbeck and G. W. Ford, In Studies in Statistical Mechanics, Vol. 1, J. de Boer and G. E. Uhlenbeck, eds. (North Holland Pub. Co., Amsterdam, 1962).

25. L. Barajas, L. S. García-Colín, and E. Piña, J. Stat. Phys. 7, 161 (1973).

26. J. Karkheck, Dissertation (Physics), SUNY at Stony Brook, (1978).

27. H. T. Davis, S. A. Rice and J. V. Sengers, J. Chem. Phys. 35, 2210 (1961).

28. J. Karkheck and G. Stell, Kinetic Equations and Irreversibility I. Dynamical and Statistical Foundations, SUNY CEAS Report #334, December, 1979.

29. E. P. Gross and D. Wisnivesky, Phys. Fl. 11, 1387 (1968).

30. D. Wisnivesky, Phys. Fl. 12, 724 (1969).

31. H. Grad, J. Soc. Ind. Appl. Math. 13, 259 (1965).

32. G. Stell, Physica 29, 517 (1963).

33. S. R. de Groot and P. Mazur, Nonequilibrium Thermodynamics (North Holland Pub. Co., Amsterdam, 1962).

34. J. Karkheck, E. Martina and G. Stell, Kinetic Variational Theory for Mixtures: Kac-Tail Limit, SUNY CEAS Report #362, April 1981.

35. E. G. D. Cohen, in Transport Phenomena in Fluids, H. J. M. Hanley editor, (Marcel Dekker, New York, 1969).

36. Alternately, $\vec{J}_{m_L}$ could be eliminated without altering the essence of the results to follow. It is important to note that microscopic theory, such as that described here or Onsager's theory of reciprocity, does not undertake to decide what forms are "correct"; that is the domain of phenomenology. See K. G. Denbigh, The Thermodynamics of the Steady State Methuen, London (1965) pp. 29-30 for a discussion of this point in relation to Onsager's theory (ref. 39).

37. J. Karkheck and G. Stell, J. Chem. Phys. 71, 3620 (1979).

38. B. D. Coleman and C. Truesdell, J. Chem. Phys. 33, 28 (1960).

39. L. Onsager, Phys. Rev. 37, 405; 38, 2265 (1931).

40. H. J. M. Hanley, in Transport Phenomena in Fluids, H. J. M. Hanley editor, (Marcel Dekker, New York, 1969).

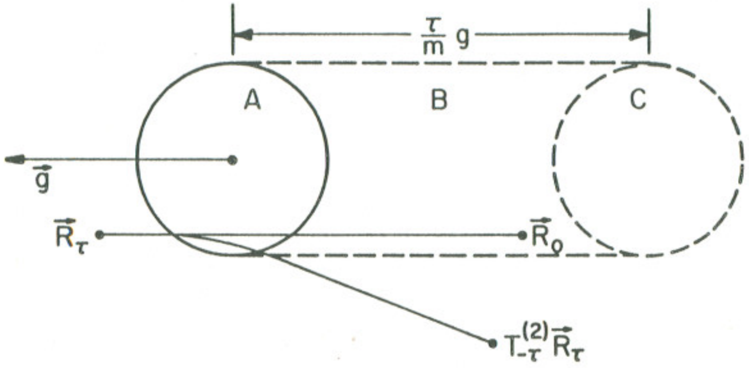
41. O. E. Lanford, in Lecture Notes in Physics 38, J. Moser, ed. (Springer, Berlin, 1975).

42. M. S. Green, J. Chem. Phys. 25, 836 (1956).

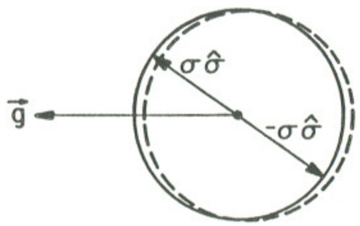
FIGURE CAPTIONS

Figure 1a. Precollision configurations for the Boltzmann equation.

Figure 1b. Geometry of precollision configurations in the hard-sphere limit.



$\frac{\tau}{m}$ g
A
B
C
$\vec{g}$
$\vec{R}_\tau$
$\vec{R}_0$
$T_{-\tau}^{(2)}\vec{R}_\tau$



$\vec{g}$
$\sigma\hat{\sigma}$
$-\sigma\hat{\sigma}$