

# Conversion Between Kinetic Energy and Potential Energy in the Classical Nonlocal Boltzmann Equation

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An important property of the classical Boltzmann equation is that kinetic energy is conserved. This is closely connected to the fact that the Boltzmann equation describes the nonequilibrium properties of an "ideal" gas. Generalizations of the Boltzmann equation to higher density involve, among other things, allowing the colliding particles to be at different positions. This spatial nonlocality is known to contribute to the density corrections of gas transport properties. For soft potentials such a spatial separation of the particles also leads to a conversion between kinetic and potential energy. In evaluating these effects the classical dynamics of the whole collision trajectory must be taken into account, involving also the time for the collision process. The resulting time nonlocality has usually been reinterpreted in terms of a spatial nonlocality. However, for a homogeneous system this is not possible and only the time nonlocality remains, this then being responsible for the conversion between kinetic and potential energy. This paper aims to clarify these properties of the nonlocal corrections to the classical mechanical Boltzmann collision term. Comments on the corresponding problem for the quantum Boltzmann equation are also made.

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**KEY WORDS:** Boltzmann equation; energy conservation.

## 1. INTRODUCTION

Previous work by the author<sup>(1,2)</sup> on the quantum Boltzmann equation has included a description of how binary collisions can convert kinetic energy to potential energy. The present work examines the classical analog of these quantum results. In the Wigner function description of the quantum case it was clear<sup>(1)</sup> that energy conversion is associated with the spatial nonlocality of the collision, namely that the two colliding particles are spatially separated. This is in contrast to the *standard* classical Boltzmann

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collision term in which the (binary) collisions are treated as occurring, as far as their distribution functions are concerned, at one point in space and time. For the Boltzmann equation with such localized collisions, the complete separation between the effects of collisions and the flow of the gas as a whole is responsible for simplifying the description of the nonequilibrium behavior to that of an *ideal* gas. That is, if collisions are treated as localized events, then the flow and collisional effects are strictly additive, with the collisions formally giving no direct contribution to any of the hydrodynamic fluxes and, conversely, the flow processes having no direct influence on the outcome of a collision.

Enskog<sup>(3)</sup> was the first to elaborate on the role of collision nonlocality in gas kinetic theory. However, he dealt only with hard spheres, for which there is no mean potential energy, so the question of a lack of kinetic energy conservation does not arise. Bogoliubov<sup>(4)</sup> and Green<sup>(5)</sup> independently generalized the Boltzmann equation so as to include density corrections to gas kinetic properties associated with the spatial extent of the colliding pair. As presumably their objective was to formulate a theory of dense gas transport properties, they expressed these effects in terms of spatial gradient corrections to the local Boltzmann collision term. Neither author mentions the possibility of conversion of kinetic energy to potential energy. Since such effects should also occur in homogeneous systems, it is not clear from their treatments how such energy conversion could occur via binary collisions in a homogeneous system. The present paper addresses this difficulty.

The hydrodynamic equations of change for a system having arbitrary density were first discussed by Irving and Kirkwood<sup>(6)</sup> as a consequence of the classical Liouville equation. For the change of energy density, this requires, in particular, the need for considering both potential and kinetic energy densities and gives a general expression for the energy flux in terms of the distribution functions for the system. A particularly useful organization of these results has been given by Kreuzer<sup>(7)</sup> which is summarized in Section 2. Of special interest for the present work, emphasis is placed on the rate of conversion between potential and kinetic energy densities. At moderate densities, the evolution of a gaseous system is determined by the free motion of the particles and with increasing density, the successive inclusion of binary, ternary, and higher ordered collisions. The Boltzmann equation includes at most binary collisions, which are in general nonlocal spatially and timewise. It is well known<sup>(8-11)</sup> that such nonlocalities contribute to the density corrections of gas transport coefficients. Other contributions<sup>(12)</sup> to the first-order density corrections are associated with ternary collisions and the possible presence of bound states.<sup>(13)</sup> These same mechanisms can also contribute to the conversion between kinetic and potential energies. The present paper does not address the general problem,

but rather is aimed at understanding how binary collisions contribute to this energy conversion.

Klimontovich<sup>(14)</sup> has described the conversion between kinetic and potential energy as an aspect of the density corrections to the classical Boltzmann equation. His method involves a particular ansatz for the three-particle distribution function. While Klimontovich refers to his method as a binary collision approximation, the presence of a three-particle distribution function can lead to the impression that three-particle effects are at the root of such an energy conversion. This is particularly true since energy conversion is discussed in his treatment only in the context of the role of the three-particle distribution function. A recent article<sup>(15)</sup> attempts to clarify Klimontovich's method, which is similar in philosophy to a quantum method by Boercker and Dufty,<sup>(16)</sup> by elaborating what is probably the physical meaning of the ansatz for the three-particle distribution function that they use for deriving the Boltzmann equation. Specifically this article<sup>(15)</sup> shows in an explicit manner how the structure that is assumed for the three-particle distribution function is related to binary collisions. In contrast, the present paper shows how kinetic-potential energy conversion can arise explicitly in the binary collisions of classical particles, with no role being required for the three-particle distribution function.

Section 2 discusses energy conservation from the point of view of the BBGKY hierarchy,<sup>(4, 17-19)</sup> presenting formal equations for the kinetic energy production and the various contributions to the energy flux. The present treatment is restricted to assuming that the  $N$ -body potential is pairwise additive. This restriction has the simplifying consequence that kinetic and potential energies are described completely by the single and pair distribution functions. Binary collision dynamics and the Boltzmann equation are introduced in Section 3 using Green's<sup>(5)</sup> notation, which is elaborated in Appendix A. The Boltzmann equation is specialized to treating only homogeneous systems, to discuss the conversion between kinetic and potential energy for a homogeneous gas via binary collision dynamics. Section 4 deals with the general inhomogeneous case. The homogeneous and inhomogeneous cases each have their own novelty; in the former there is no possibility of spatial nonlocality, so the classic corrections derived by Green<sup>(5)</sup> have to be reexamined (see Section 5) so that both effects can be included as corrections to the Boltzmann equation. Section 6 comments on Bogoliubov's closure of the BBGKY hierarchy and demonstrates that his form for the nonlocal Boltzmann equation is in general inconsistent with energy conservation. It is also noted that the quantum closure that has been introduced<sup>(21)</sup> for deriving the quantum Boltzmann equation has the same form as does Bogoliubov's classical closure. Thus energy conversion for the (nonlocal) quantum Boltzmann equation is subject to the same

constraints as in the classical approach of Bogoliubov. Specifically, neither Boltzmann equation describes energy conversion for homogeneous systems. Boercker and Dufty<sup>(16)</sup> introduced a "binary collision approximation" for quantum systems, essentially similar to that introduced by Klimontovich,<sup>(14)</sup> which they emphasize<sup>(24)</sup> conserves total energy. The classical analog of their result is given in Section 6, while the form for the pair distribution function deduced from the binary collision approximation is presented in Appendix B. Also in Appendix B, it is argued that a first-order in space and time nonlocality approximation to this pair distribution function is identical to that introduced in Section 5 to get a unified description of energy conversion for both homogeneous and inhomogeneous cases. The paper ends with a discussion, Section 7, which includes a summary of three consistent schemes for energy conservation.

## 2. EXACT KINETIC ENERGY-POTENTIAL ENERGY CONVERSION

The classical dynamics of an  $N$ -particle system is determined exactly by the Liouville equation

$$\frac{\partial f^{(N)}}{\partial t} = - \sum_{i=1}^N \frac{\mathbf{p}_i}{m} \cdot \frac{\partial f^{(N)}}{\partial \mathbf{r}_i} + \sum_{i \neq j}^N \frac{\partial V_{ij}}{\partial \mathbf{r}_i} \cdot \frac{\partial f^{(N)}}{\partial \mathbf{p}_i} \quad (1)$$

Here  $\mathbf{r}_i$ ,  $\mathbf{p}_i$  are the position and momentum of particle  $i$ , respectively, and the particles are assumed to interact via a pairwise additive potential  $V_{ij}$ . The function  $f^{(N)}$  is the  $N$ -particle phase space distribution function  $f^{(N)}(\mathbf{r}_1, \dots, \mathbf{p}_N; t)$  normalized,  $\int \dots \int f^{(N)} d\mathbf{r}_1 \dots d\mathbf{p}_N = 1$ , at each time  $t$  to 1. It is an immediate consequence of integrating by parts that the mean total energy

$$U \equiv \int \dots \int H^{(N)} f^{(N)} d\mathbf{r}_1 \dots d\mathbf{p}_N$$

defined in terms of the total Hamiltonian

$$H^{(N)} \equiv \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i < j}^N V_{ij}$$

is constant. Inherently, both for the normalization and the evaluation of the total energy, there is an assumed convergence condition, namely that  $f^{(N)}$  vanishes sufficiently rapidly at large distances, for one reason or another. Of particular interest are those systems having a large number of particles in a large, but finite volume. It is further assumed in this work

that  $f^{(N)}$  is symmetric to the interchange of any pair of particles, i.e., that Boltzmann statistics is obeyed. Also assumed for simplicity is that the particles are structureless and that the interparticle potential is repulsive so that it is incapable of supporting bound states.

Integration over subsets of particles defines reduced distribution functions

$$f_{1\dots k}^{(k)} \equiv N(N-1)\dots(N-k+1) \int \dots \int f^{(N)} d\mathbf{r}_{k+1} \dots d\mathbf{p}_N \quad (2)$$

satisfying the BBGKY hierarchy,<sup>(4, 17-19)</sup> whose first two members are

$$\frac{\partial}{\partial t} f_1^{(1)} = -\frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} f_1^{(1)} + \iint \frac{\partial V_{12}}{\partial \mathbf{r}_1} \cdot \frac{\partial}{\partial \mathbf{p}_1} f_{12}^{(2)} d\mathbf{p}_2 d\mathbf{r}_2 \quad (3)$$

and

$$\begin{aligned} \frac{\partial}{\partial t} f_{12}^{(2)} = & -\frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} f_{12}^{(2)} - \frac{\mathbf{p}_2}{m} \cdot \frac{\partial}{\partial \mathbf{r}_2} f_{12}^{(2)} + \frac{\partial V_{12}}{\partial \mathbf{r}_1} \cdot \left( \frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2} \right) f_{12}^{(2)} \\ & + \iint \left( \frac{\partial V_{13}}{\partial \mathbf{r}_1} \cdot \frac{\partial}{\partial \mathbf{p}_1} + \frac{\partial V_{23}}{\partial \mathbf{r}_2} \cdot \frac{\partial}{\partial \mathbf{p}_2} \right) f_{123}^{(3)} d\mathbf{p}_3 d\mathbf{r}_3 \end{aligned} \quad (4)$$

The  $k$ -particle phase-space distribution functions  $f_{1\dots k}^{(k)}$  are functions of the position  $\mathbf{r}_i$  and momenta  $\mathbf{p}_i$  ( $i = 1, \dots, k$ ) of the  $k$  particles with normalization such that its momentum integral (over all  $k$  momenta) reduces, for  $k \ll N$ , to  $\prod_{i=1}^k n(\mathbf{r}_i, t)$ , associated with the gas density  $n(\mathbf{r}, t)$  at position  $\mathbf{r}$  and time  $t$ , when the  $k$  particles are all far apart.

For the particular case of a homogeneous system,  $f^{(1)}$  is independent of position, while  $f^{(2)}$  depends on the positions  $\mathbf{r}_1$  and  $\mathbf{r}_2$  only through the relative distance  $\mathbf{r}_{12} \equiv \mathbf{r}_1 - \mathbf{r}_2$ . The rate of change of the kinetic energy density  $nu_K \equiv \int (\mathbf{p}_1^2/2m) f^{(1)} d\mathbf{p}_1$  for a homogeneous system is thus

$$\begin{aligned} \frac{\partial nu_K}{\partial t} = & \iiint \frac{\mathbf{p}_1^2}{2m} \frac{\partial V_{12}}{\partial \mathbf{r}_1} \cdot \frac{\partial}{\partial \mathbf{p}_1} f_{12}^{(2)} d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 \\ = & \iiint \frac{\mathbf{p}_1}{m} \cdot \frac{\partial V_{12}}{\partial \mathbf{r}_2} f_{12}^{(2)} d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 \\ = & - \iiint V_{12} \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_2} f_{12}^{(2)} d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 \end{aligned}$$

$$\begin{aligned}
&= \frac{1}{2} \iiint V_{12} \left( \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} + \frac{\mathbf{p}_2}{m} \cdot \frac{\partial}{\partial \mathbf{r}_2} \right) f_{12}^{(2)} d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 \\
&= \frac{1}{2} \iiint V_{12} \left( -\frac{\partial}{\partial t} f_{12}^{(2)} + \iint \cdots d\mathbf{r}_3 d\mathbf{p}_3 \right) d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 \\
&= -\frac{\partial nu_V}{\partial t} \tag{5}
\end{aligned}$$

which is minus the rate of change of the potential energy density.

$$nu_V \equiv \frac{1}{2} \iiint V_{12} f_{12}^{(2)} d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{r}_2$$

It is noted that the three-particle term vanishes when integrated over the momenta  $\mathbf{p}_1$  and  $\mathbf{p}_2$ , while the production of kinetic energy density is given by the expression

$$\begin{aligned}
\sigma_K &= \frac{1}{2} \iiint V_{12} \left( \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} + \frac{\mathbf{p}_2}{m} \cdot \frac{\partial}{\partial \mathbf{r}_2} \right) f_{12}^{(2)} d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 \\
&= \frac{1}{2} \iiint \frac{\mathbf{p}_{12}}{\mu} \cdot \left( -\frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \right) f_{12}^{(2)} d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 \tag{6}
\end{aligned}$$

Here the relative momentum  $\mathbf{p}_{12} \equiv (\mu/m)(\mathbf{p}_1 - \mathbf{p}_2)$  and reduced mass  $\mu$  enter since the potential is independent of the center-of-mass position  $\mathbf{R}_{12} \equiv (1/2)(\mathbf{r}_1 + \mathbf{r}_2)$ . The kinetic energy production is recognized as due to the product of the intermolecular force and the relative velocity, essentially as minus the rate of change of potential energy along the pair particle trajectory.

In the general case when the gas is inhomogeneous there are flux contributions to the rate of change of the kinetic energy density. In addition, the detailed treatment of the pair interaction term is complicated by the need to distinguish whether a quantity should be centered at the position of a single particle or at the center of mass of the pair. The results of this classic calculations (see, for example, the treatment by Kreuzer<sup>(7)</sup>) are summarized here.

There are a number of auxiliary quantities that first need defining for inhomogeneous systems. The gas properties are to be calculated at position  $\mathbf{r}$  and time  $t$ ; for example, the local gas (number) density is  $n(\mathbf{r}, t)$ . Other quantities are:

- (i) The stream velocity (mass average velocity)

$$\mathbf{v}(\mathbf{r}, t) \equiv \frac{1}{nm} \int \mathbf{p}_1 f_1^{(1)}(\mathbf{r}, \mathbf{p}_1; t) d\mathbf{p} \tag{7}$$

(ii) The mean kinetic energy per particle

$$u_K(\mathbf{r}, t) \equiv \frac{1}{n} \int \frac{(\mathbf{p}_1 - m\mathbf{v})^2}{2m} f_1^{(1)}(\mathbf{r}, \mathbf{p}_1; t) d\mathbf{p}_1 \tag{8}$$

(iii) The kinetic heat flux

$$\mathbf{q}_K(\mathbf{r}, t) \equiv \frac{1}{n} \int \left( \frac{\mathbf{p}_1}{m} - \mathbf{v} \right) \frac{(\mathbf{p}_1 - m\mathbf{v})^2}{2m} f_1^{(1)}(\mathbf{r}, \mathbf{p}_1; t) d\mathbf{p}_1 \tag{9}$$

(iv) The kinetic pressure tensor

$$\mathbf{P}_K(\mathbf{r}, t) \equiv \int \left( \frac{\mathbf{p}_1}{m} - \mathbf{v} \right) (\mathbf{p}_1 - m\mathbf{v}) f_1^{(1)}(\mathbf{r}, \mathbf{p}_1; t) d\mathbf{p}_1 \tag{10}$$

These are all defined relative to the stream velocity. With these definitions the kinetic energy equation of change is obtained from the first BBGKY equation (3); explicitly, we have

$$\begin{aligned} \frac{\partial nu_K}{\partial t} + \nabla \cdot (nu_K \mathbf{v} + \mathbf{q}_K) + \mathbf{P}_K : \nabla \mathbf{v} \\ = - \iiint \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \cdot \frac{\mathbf{p}_1 - m\mathbf{v}}{m} f_{12}^{(2)}(\mathbf{r}, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t) d\mathbf{r}_2 d\mathbf{p}_2 d\mathbf{p}_1 \\ = - \nabla \cdot \mathbf{q}_{\text{coll}} - \mathbf{P}'_V : \nabla \mathbf{v} + \sigma_K \end{aligned} \tag{11}$$

The potential interaction term is written out for reference so it can be compared with equations that will be discussed later. Its reduction into identifiable physical quantities involves symmetrization between the two interacting particles, with the exact pair particle property definitions being as follows:

(v) The collisional contribution to the kinetic heat flux, given by

$$\begin{aligned} \mathbf{q}_{\text{coll}} \equiv - \frac{1}{8} \iiint \mathbf{r}_{12} \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \cdot \frac{\mathbf{p}_1 + \mathbf{p}_2 - 2m\mathbf{v}}{m} \\ \times \int_{-1}^1 \delta \left[ \mathbf{r} - \mathbf{R}_{12} - \frac{\lambda}{2} \mathbf{r}_{12} \right] f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t) d\lambda d\mathbf{r}_1 d\mathbf{p}_2 d\mathbf{r}_2 d\mathbf{p}_2 \end{aligned} \tag{12}$$

(vi) (The transpose ' of) the collisional transfer pressure tensor

$$\mathbf{P}_V \equiv -\frac{1}{4} \iiint \mathbf{r}_{12} \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \times \int_{-1}^1 \delta \left[ \mathbf{r} - \mathbf{R}_{12} - \frac{\lambda}{2} \mathbf{r}_{12} \right] f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t) d\lambda d\mathbf{r}_1 d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 \quad (13)$$

(vii) The production of kinetic energy

$$\sigma_K \equiv -\frac{1}{2} \iiint \frac{\mathbf{p}_{12}}{m} \cdot \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \times \delta(\mathbf{r} - \mathbf{r}_1) f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t) d\mathbf{r}_1 d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 \quad (14)$$

Since the kinetic energy is not conserved, it is appropriate to examine:

(viii) The potential energy density

$$nu_V \equiv \frac{1}{2} \iiint V_{12} \delta(\mathbf{r} - \mathbf{r}_1) f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t) d\mathbf{r}_1 d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 \quad (15)$$

localized here so that half the potential energy is at the position of each of the particles. The equation of change of the potential energy density is then

$$\frac{\partial nu_V}{\partial t} = -\nabla \cdot (nu_V \mathbf{v} + \mathbf{q}_V) - \sigma_K \quad (16)$$

with

(ix) The potential energy heat flux

$$\mathbf{q}_V \equiv \frac{1}{2} \iiint \left( \frac{\mathbf{p}_1}{m} - \mathbf{v} \right) \times V_{12} \delta(\mathbf{r} - \mathbf{r}_1) f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t) d\mathbf{r}_1 d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 \quad (17)$$

These exact equations demonstrate the form for the conversion between kinetic and potential energies to give energy conservation.

### 3. BOLTZMANN EQUATION DESCRIPTION OF KINETIC ENERGY-POTENTIAL ENERGY CONVERSION IN A CLASSICAL HOMOGENEOUS GAS

Kinetic energy conservation (or lack of) is now discussed for a homogeneous system, but from the point of view of the classical Boltzmann



equation. The approach followed here draws on Green's classic work.<sup>(5)</sup> In classical mechanics, an isolated binary collision implies via Liouville's theorem for the isolated pair that the phase space pair distribution function satisfies

$$f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t) = f^{(2)}(\mathbf{r}_{10}, \mathbf{p}_{10}, \mathbf{r}_{20}, \mathbf{p}_{20}; t_0) \quad (18)$$

Here the positions and momenta at time  $t_0$  are determined by Hamilton's equations from their values at time  $t$ . If  $t_0$  to be a time prior to a collision [in practice set as the time when the particle separation is equal to the (assumed finite) range of the potential  $r_0$ ], the Stosszahlansatz for the Boltzmann equation assumes that at the precollision time the pair distribution function factors into a product of singlets. For the present discussion, the gas is spatially homogeneous, so that there is no position dependence of the singlets and the pair distribution function can be written, taking into account only isolated binary collisions and the Stosszahlansatz,

$$f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t) = f^{(1)}(\mathbf{p}_{10}; t_0) f^{(1)}(\mathbf{p}_{20}; t_0) \quad (19)$$

The standard Boltzmann collision term is obtained by ignoring the difference in times  $t_0$  and  $t$  in the product of singlet distribution functions. This can be rationalized on the basis that the distribution functions vary slowly with time, while  $t - t_0$  is a short time, namely of the order of the mean time of duration of a collision. With this approximation the first BBGKY equation (3) for a spatially homogeneous system can be written

$$\frac{\partial}{\partial t} f^{(1)}(\mathbf{p}_1; t) = \iint \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \cdot \frac{\partial}{\partial \mathbf{p}_{12}} f^{(1)}(\mathbf{p}_{10}; t) f^{(1)}(\mathbf{p}_{20}; t) d\mathbf{p}_2 d\mathbf{r}_2 \quad (20)$$

Here the two replacements (i) of  $\partial V_{12}/\partial \mathbf{r}_1$  by  $\partial V_{12}/\partial \mathbf{r}_{12}$ , since the potential depends only on the relative coordinate, and (ii) of  $\partial/\partial \mathbf{p}_1$  by  $\partial/\partial \mathbf{p}_{12} = \partial/\partial \mathbf{p}_1 - \partial/\partial \mathbf{p}_2$ , valid since  $\mathbf{p}_2$  is integrated over and the resulting surface integral vanishes because the distribution functions vanish for large momenta, emphasize that the quantities in the integrand are really associated with relative (collisional) motion. Green<sup>(5)</sup> recognizes, as does Klimontovich,<sup>(14)</sup> that the only dependence on relative position and momentum in the product of singlet distribution functions is through  $\mathbf{p}_{10}$  and  $\mathbf{p}_{20}$  and that these are collisional invariants. Any collisional invariant satisfies Eq. (A.1) [see Appendix A], so that

$$\frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \cdot \frac{\partial}{\partial \mathbf{p}_{12}} f^{(1)}(\mathbf{p}_{10}; t) f^{(1)}(\mathbf{p}_{20}; t) = \frac{\mathbf{p}_{12}}{\mu} \cdot \frac{\partial}{\partial \mathbf{r}_{12}} f^{(1)}(\mathbf{p}_{10}; t) f^{(1)}(\mathbf{p}_{20}; t) \quad (21)$$

Integration over the relative position  $\mathbf{r}_{12}$  gives for this term a surface integral whose evaluation leads to the standard Boltzmann equation for a homogeneous gas

$$\frac{\partial}{\partial t} f^{(1)}(\mathbf{p}_1; t) = \iiint [f^{(1)}(\mathbf{p}_{10}; t) f^{(1)}(\mathbf{p}_{20}; t) - f^{(1)}(\mathbf{p}_1; t) f^{(1)}(\mathbf{p}_2; t)] \left| \frac{\mathbf{p}_{12}}{\mu} \right| b \, db \, d\epsilon \, d\mathbf{p}_2 \quad (22)$$

The impact parameter  $b$  and angle  $\epsilon$  describing the orientation of the plane of the collision are defined, for example, in ref. 20. As is well known, this collision term conserves kinetic energy. Since this term is obtained by dropping the time difference  $t - t_0$ , this reflects how the classic Boltzmann equation depends on collision instantaneity (time locality) for kinetic energy conservation and so implies the gas is ideal.

Retention of  $t_0$  as the time for the evaluation of the singlets in Eq. (20) reflects the finite time duration of the collisions. It is this effect which gives rise to conversion of kinetic and potential energies. Specifically the density of kinetic energy production is, for a homogeneous gas, equal to the rate of change of kinetic energy density. This is calculated from the first BBGKY equation according to [derived using the first line of Eq. (5) together with Eq. (19)]

$$\sigma_K = \iiint \frac{\mathbf{p}_1^2}{2m} \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \cdot \frac{\partial}{\partial \mathbf{p}_{12}} f^{(1)}(\mathbf{p}_{10}; t_0) f^{(1)}(\mathbf{p}_{20}; t_0) \, d\mathbf{r}_2 \, d\mathbf{p}_2 \, d\mathbf{p}_1 \quad (23)$$

It is to be stressed that this vanishes if  $t_0$  is replaced by  $t$ , since then the integral becomes equivalent to the kinetic energy production of the standard Boltzmann equation (22), which vanishes. Thus the nonvanishing of Eq. (23) is necessarily associated with the appearance of  $t_0$  in the distribution functions. For a homogeneous system the integral over the position of particle 2 is equivalent to integrating over the relative position  $\mathbf{r}_{12}$  and the individual particle momentum integrals can be replaced by center-of-mass  $\mathbf{P}_{12}$  and relative  $\mathbf{p}_{12}$  momentum integrals. By particle symmetry of the integral, the kinetic energy of particle 1 can be replaced by

$$\frac{\mathbf{p}_1^2}{2m} \rightarrow \frac{1}{2} \left[ \frac{\mathbf{P}_{12}^2}{2\mu} + \frac{\mathbf{p}_{12}^2}{4m} \right] \quad (24)$$

Now integration by parts, both with respect to  $\mathbf{r}_{12}$  and  $\mathbf{p}_{12}$  gives

$$\sigma_K = \frac{1}{2} \iiint V_{12} \frac{\mathbf{p}_{12}}{\mu} \cdot \frac{\partial}{\partial \mathbf{r}_{12}} f^{(1)}(\mathbf{p}_{10}; t_0) f^{(1)}(\mathbf{p}_{20}; t_0) \, d\mathbf{r}_{12} \, d\mathbf{p}_{12} \, d\mathbf{P}_{12} \quad (25)$$

The surface integrals vanish, for  $\mathbf{r}_{12}$  because of the potential factor  $V_{12}$  and for  $\mathbf{p}_{12}$  because of the assumption that the distribution functions vanish sufficiently rapidly at large momenta. The singlet distribution functions in these expressions depend on  $\mathbf{r}_{12}$  only through the initial relative momentum  $\mathbf{p}_0$  and the time  $t_0$ . Only  $t_0$  is not a collisional invariant. For any dependence via a collisional invariant, Eq. (A.1) of Appendix A implies that the spatial derivative  $(\mathbf{p}_{12}/\mu) \cdot \partial/\partial \mathbf{r}_{12}$  can be replaced by the corresponding relative momentum derivative  $(\partial V_{12}/\partial \mathbf{r}_{12}) \cdot \partial/\partial \mathbf{p}_{12}$ . The consequent integration by parts with respect to the relative momentum results in a surface integral in momentum space which vanishes because the distribution functions must vanish for large momenta. Thus the derivative with respect to  $\mathbf{r}_{12}$  in the expression for the kinetic energy production can be limited to being taken with all collision invariants constant, denoted by  $|_r$ . Since the "non-collision-invariant" dependence of the distribution functions is only through  $t_0$ , Eq. (A.5) can be used to evaluate the derivative with the consequent result

$$\begin{aligned} \sigma_K &= \frac{1}{2} \iiint V_{12} \frac{\mathbf{p}_{12}}{\mu} \cdot \frac{\partial t_0}{\partial \mathbf{r}_{12}} \Big|_r \frac{\partial}{\partial t_0} f^{(1)}(\mathbf{p}_{10}; t_0) f^{(1)}(\mathbf{p}_{20}; t_0) d\mathbf{r}_{12} d\mathbf{p}_{12} d\mathbf{P}_{12} \\ &= -\frac{1}{2} \iiint V_{12} \frac{\partial}{\partial t_0} f^{(1)}(\mathbf{p}_{10}; t_0) f^{(1)}(\mathbf{p}_{20}; t_0) d\mathbf{r}_{12} d\mathbf{P}_{12} d\mathbf{p}_{12} \\ &= -\frac{\partial nu_V}{\partial t} \end{aligned} \quad (26)$$

The kinetic energy production is thus minus the rate of change of the potential energy density

$$\begin{aligned} nu_V &\equiv \frac{1}{2} \iiint V_{12} f_{12}^{(2)} d\mathbf{r}_{12} d\mathbf{P}_{12} d\mathbf{p}_{12} \\ &= \frac{1}{2} \iiint V_{12} f^{(1)}(\mathbf{p}_{10}; t_0) f^{(1)}(\mathbf{p}_{20}; t_0) d\mathbf{r}_{12} d\mathbf{P}_{12} d\mathbf{p}_{12} \end{aligned} \quad (27)$$

For the evaluation of the potential energy density the Stosszahlansatz has again been used to relate  $f^{(2)}$  to the product of singlets before the collision begins. In Eq. (26) the derivative with respect to  $t_0$  has been replaced by the corresponding derivative with respect to  $t$ , which can then be taken outside the position and momentum integrals. As stated earlier, the method of approach used here was motivated by Green's treatment<sup>(5)</sup> of the corrections to the Boltzmann equation, although the details of the treatment are different. But it does demonstrate that only binary collision

dynamics is needed for the description (at low density) of the conversion between kinetic and potential energy.

There are some hidden complexities in the interpretation of this work, associated with the density dependence of the various quantities. This discussion has emphasized that the energy conversion is a binary collision process and thus involves only pairs of particles. It is natural to equate this with being an expansion to second order in the density, but this is not true. First,  $f^{(1)}$  itself is a nonlinear function of the density, in particular if there is any time dependence (necessarily due to collisions in a homogeneous system, which implies that all relaxation rates are density dependent), and second, related to that,  $\partial f^{(1)}/\partial t$  is proportional to  $n^2$ , so  $\partial n u_\nu/\partial t$  is at least of order  $n^3$ . Thus the classification according to the maximum number of particles taking part in some molecular event is unique, but the power of the density is not.

Klimontovich<sup>(14)</sup> writes the pair distribution function in terms of an earlier time, much as in Eq. (19), but with an extra term arising from his assumption about the form for the three-particle distribution function. Essentially he carries out an integration by parts which allows the two terms to be combined, the result then being expanded in terms of a time interval to arrive at the same result as above. One interpretation of the present work is to deduce that the introduction of the three-particle term in Klimontovich's work is unnecessary. But what should be recognized is that there is a difference in philosophy of approach and that the three-particle factorization that Klimontovich introduced is the result of the previous binary collisions, at least that is this author's understanding<sup>(15)</sup> of Klimontovich's method. Thus no direct comparison of the details of the calculation should be made. It is of course this author's opinion that the present treatment is simpler, but hopefully, the present discussion at least helps to clarify how the conversion between kinetic and potential energy occurs during binary collision processes.

#### 4. CLASSICAL INHOMOGENEOUS GAS

For an inhomogeneous gas there are, in contrast to the homogeneous gas, various flux contributions to the equations of change (see Section 2). As well, any quantity depending on a pair of interacting particles is affected by the position dependence of the distribution function that enters into the calculation of the macroscopic quantity. Specifically the spatial nonlocality of binary collisions contributes to the conversion between kinetic and potential energy. Here this is discussed within the Boltzmann equation description of gas kinetic theory.

Within the philosophy of the Boltzmann equation the pair distribution function of a colliding pair is determined in terms of the singlet, Eq. (19), according to the dynamics of isolated binary collisions and the assumption that the pair distribution function factors *before* a collision. Green<sup>(5)</sup> expands the position and time dependence of the product of singlets to give corrections to the time and space local product, namely

$$\begin{aligned}
 f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t) &= f^{(1)}(\mathbf{r}_{10}, \mathbf{p}_{10}; t_0) f^{(1)}(\mathbf{r}_{20}, \mathbf{p}_{20}; t_0) \\
 &= f^{(1)}(\mathbf{r}_1, \mathbf{p}_{10}; t) f^{(1)}(\mathbf{r}_1, \mathbf{p}_{20}; t) + \mathcal{A}_1 + \mathcal{A}_2 \quad (28)
 \end{aligned}$$

with

$$\begin{aligned}
 \mathcal{A}_1 &\equiv f^{(1)}(\mathbf{r}_{10}, \mathbf{p}_{10}; t_0) f^{(1)}(\mathbf{r}_{20}, \mathbf{p}_{20}; t_0) - f^{(1)}(\mathbf{R}_{12}, \mathbf{p}_{10}; t) f^{(1)}(\mathbf{R}_{12}, \mathbf{p}_{20}; t) \\
 &\simeq (t_0 - t) \frac{\partial}{\partial t} f_{10} f_{20} + f_{20}(\mathbf{r}_{10} - \mathbf{R}_{12}) \cdot \nabla f_{10} + f_{10}(\mathbf{r}_{20} - \mathbf{R}_{12}) \cdot \nabla f_{20} \quad (29)
 \end{aligned}$$

and

$$\begin{aligned}
 \mathcal{A}_2 &\equiv f^{(1)}(\mathbf{R}_{12}, \mathbf{p}_{10}; t) f^{(1)}(\mathbf{R}_{12}, \mathbf{p}_{20}; t) - f^{(1)}(\mathbf{r}_1, \mathbf{p}_{10}; t) f^{(1)}(\mathbf{r}_1, \mathbf{p}_{20}; t) \\
 &\simeq \frac{1}{2}(\mathbf{r}_2 - \mathbf{r}_1) \cdot \nabla f_{10} f_{20} \quad (30)
 \end{aligned}$$

For ease of writing, the abbreviated notations

$$f_{j0} \equiv f^{(1)}(\mathbf{r}_1, \mathbf{p}_{j0}; t) \quad (31)$$

for  $j=1$  and  $2$  and  $\partial/\partial \mathbf{r}_1 = \nabla$  have been introduced. That all distribution functions are evaluated at  $\mathbf{r}_1$  is appropriate since in using the Boltzmann equation, all gas properties are evaluated at the position of particle 1, namely by setting  $\mathbf{r}_1 = \mathbf{r}$ . Clearly the first term of Eq. (28) gives the Boltzmann equation, as stressed in the previous section. The correction from locality,  $\mathcal{A}_2$ , is solely associated with how the distribution functions differ according to whether they are evaluated at their position of center of mass  $\mathbf{R}_{12}$  or at the position of particle 1.  $\mathcal{A}_1$  relates to the relative motion that the particles undergo during the collision. By expanding to keep only those terms that are first order in  $t_0 - t$ ,  $\mathbf{r}_{10} - \mathbf{R}_{12}$ , and  $\mathbf{r}_{20} - \mathbf{R}_{12}$ , and using the first BBGKY equation, Green<sup>(5)</sup> relates the time derivative of the singlet distribution function to the position gradient so that  $\mathcal{A}_1$  is simplified to

$$\mathcal{A}_1^G \equiv \frac{1}{2}[\mathbf{r}_0 + \mathbf{g}_0(t - t_0)] \cdot [f_{10} \nabla f_{20} - f_{20} \nabla f_{10}] \quad (32)$$

where  $\mathbf{r}_0$  and  $\mathbf{g}_0$  are the relative position and velocity before the collision, namely at time  $t_0$  where the relative separation of the particles  $r_0$  is equal

to the range of the potential. Other than for the implicit dependence of  $f_{j0}$  on  $t$  and  $\mathbf{r}_1$  and the explicit dependence on the time interval  $t-t_0$ ,  $\Delta_1^G$  depends only on collisional invariants.

Green's<sup>(5)</sup> method thus allows the Boltzmann collision integral to be written as a sum of three parts,  $J_0 + J_1 + J_2$ , with  $J_0$  the standard collision integral [see Eq. (22)] with the singlet distribution functions evaluated at  $\mathbf{r}_1$ , while the inhomogeneity corrections  $J_1$  and  $J_2$  arise respectively from  $\Delta_1^G$  and  $\Delta_2$ . As discussed in Section 6, Bogoliubov's closure gives a spatially nonlocal collision term which is identical to this. The correction due to evaluating the distribution functions at the center of mass rather than at the position of particle 1 is

$$\begin{aligned} J_2 &= \iint \frac{\partial V_{12}}{\partial \mathbf{r}_{21}} \cdot \frac{\partial \Delta_2}{\partial \mathbf{p}_{21}} d\mathbf{r}_2 d\mathbf{p}_2 \\ &= \frac{1}{2} \nabla \cdot \iint \mathbf{r}_{21} \frac{\partial V_{12}}{\partial \mathbf{r}_{21}} \cdot \frac{\partial}{\partial \mathbf{p}_{21}} f_{10} f_{20} d\mathbf{r}_2 d\mathbf{p}_2 \end{aligned} \quad (33)$$

while the relative motion contribution is

$$\begin{aligned} J_1 &= \iint \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \cdot \frac{\partial \Delta_1^G}{\partial \mathbf{p}_{12}} d\mathbf{r}_2 d\mathbf{p}_2 \\ &= \frac{1}{2} \iint \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \cdot \frac{\partial}{\partial \mathbf{p}_{12}} \{ [\mathbf{r}_0 + \mathbf{g}_0(t-t_0)] \cdot [f_{10} \nabla f_{20} - f_{20} \nabla f_{10}] \} d\mathbf{r}_2 d\mathbf{p}_2 \end{aligned} \quad (34)$$

The Boltzmann equation with these nonlocal corrections was discussed by Green<sup>(5)</sup> for calculating the density corrections for the transport coefficients. This program was formally carried out by Snider and Curtiss<sup>(8)</sup> and has been incorporated into a practical method<sup>(12)</sup> of approximating the first-order density corrections for the viscosity and thermal conductivity of simple gases.

The equation of change for the kinetic energy density deduced from the Boltzmann equation with nonlocal corrections is calculated according to

$$\begin{aligned} \frac{\partial n u_K}{\partial t} + \nabla \cdot (n u_K \mathbf{v} + \mathbf{q}_K) + \mathbf{P}_K : \nabla \mathbf{v} \\ = \int \frac{(\mathbf{p}_1 - m \mathbf{v})^2}{2m} (J_0 + J_1 + J_2) d\mathbf{p}_1 \end{aligned} \quad (35)$$

The integral involving  $J_0$  has no contribution. Evaluation of the contribution involving  $J_2$  proceeds as follows:

$$\begin{aligned}
 & \int \frac{(\mathbf{p}_1 - m\mathbf{v})^2}{2m} J_2 d\mathbf{p}_1 \\
 &= \frac{1}{4m} \iiint (\mathbf{p}_1 - m\mathbf{v})^2 \nabla \cdot \mathbf{r}_{21} \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \cdot \frac{\partial f_{10} f_{20}}{\partial \mathbf{p}_{21}} d\mathbf{r}_2 d\mathbf{p}_2 d\mathbf{p}_1 \\
 &= \frac{1}{4m} \iiint (\mathbf{P}_{12} - 2m\mathbf{v}) \cdot \mathbf{p}_{12} \nabla \cdot \mathbf{r}_{21} \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \cdot \frac{\partial f_{10} f_{20}}{\partial \mathbf{p}_{21}} d\mathbf{r}_2 d\mathbf{p}_2 d\mathbf{p}_1 \\
 &= \frac{1}{4m} \iiint (\mathbf{P}_{12} - 2m\mathbf{v}) \cdot \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \mathbf{r}_{21} \cdot \nabla f_{10} f_{20} d\mathbf{r}_2 d\mathbf{p}_2 d\mathbf{p}_1 \\
 &= -\nabla \cdot \mathbf{q}_{\text{coll}}^{\text{Boltz}} - [\mathbf{P}_V^{\text{Boltz}}]' : \nabla \mathbf{v}
 \end{aligned} \tag{36}$$

In this series of steps, the second equality arises from particle symmetry, the third equality by integrating by parts with respect to  $\mathbf{p}_{12}$  retaining the center-of-mass momentum  $\mathbf{P}_{12}$  constant, and finally recognizing the Boltzmann equation equivalent to the collisional heat flux

$$\mathbf{q}_{\text{coll}}^{\text{Boltz}} \equiv -\frac{1}{4} \iiint \mathbf{r}_{12} \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \cdot (\mathbf{P}_{12} - 2m\mathbf{v}) f_{10} f_{20} d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 \tag{37}$$

and the collisional transfer pressure tensor

$$\mathbf{P}_V^{\text{Boltz}} \equiv -\frac{1}{2} \iiint \mathbf{r}_{12} \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} f_{10} f_{20} d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 \tag{38}$$

These expressions differ from the exact expressions, Eqs. (12) and (13), in that each is localized at the position of particle 1 and the pair distribution function is determined by the Stosszahlansatz. Within a linear-in-gradients approximation these results are thus consistent with a binary collision approximation to the corresponding exact expressions.

The evaluation of the contribution from  $J_1$  to the kinetic energy equation of change is considered next. Since  $\Delta_1^G$  is symmetric to particle exchange, it is appropriate to start by symmetrizing the kinetic energy with respect to the two particles. This is followed by two integrations by parts, first with respect to  $\mathbf{p}_{12}$  and then with respect to  $\mathbf{r}_{12}$ . This sequence of steps gives

$$\begin{aligned}
 & \int \frac{(\mathbf{p}_1 - m\mathbf{v})^2}{2m} J_1 d\mathbf{p}_1 \\
 &= \iiint \frac{(\mathbf{p}_1 - m\mathbf{v})^2}{2m} \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \cdot \frac{\partial \Delta_1^G}{\partial \mathbf{p}_{12}} d\mathbf{r}_2 d\mathbf{p}_2 d\mathbf{p}_1
 \end{aligned}$$

$$\begin{aligned}
&= \iiint \left[ \frac{\mathbf{P}_{12} - 2m\mathbf{v}}{8m} + \frac{\mathbf{p}_{12}^2}{2m} \right] \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \cdot \frac{\partial \Delta_1^G}{\partial \mathbf{p}_{12}} d\mathbf{r}_2 d\mathbf{p}_2 d\mathbf{p}_1 \\
&= \iiint V_{12} \frac{\mathbf{p}_{12}}{m} \cdot \frac{\partial \Delta_1^G}{\partial \mathbf{r}_{12}} d\mathbf{r}_2 d\mathbf{p}_2 d\mathbf{p}_1 \tag{39}
\end{aligned}$$

In this form it is appropriate to proceed as in the treatment of Eq. (25) in Section 3. For the evaluation of the  $\mathbf{r}_{12}$  derivative, any dependence of  $\Delta_1^G$  on a collisional invariant vanishes on the basis that  $\mathbf{p}_{12} \cdot \partial/\partial \mathbf{r}_{12}$  can be replaced by a  $\mathbf{p}_{12}$  derivative [see Eq. (A.1)] and a subsequent integration by parts with respect to  $\mathbf{p}_{12}$  then gives a surface integral that vanishes for large momenta. Since Green's<sup>(5)</sup> approximation for  $\Delta_1^G$  depends on non-collisional invariants only through  $t_0$ ,  $t$  and  $\mathbf{r}_1$ , whose only relative position derivative is determined by Eq. (A.5), the  $J_1$  contribution to the equation of change for the energy density becomes

$$\sigma_K^{\text{inhomog}} = \frac{1}{4} \iiint V_{12} \mathbf{g}_0 \cdot [f_{10} \nabla f_{20} - f_{20} \nabla f_{10}] d\mathbf{r}_2 d\mathbf{p}_2 d\mathbf{p}_1 \tag{40}$$

Clearly this is not the divergence of some quantity, so is a contribution to the production of kinetic energy and has been labeled as such. Moreover, it is linear in position gradients and thus will vanish for a homogeneous system, hence the "inhomog" label. The exact expression for the production of kinetic energy is given by Eq. (14). That involves the exact pair distribution function, so it can be seen that the exact expression for the kinetic energy production reduces to the above if the ansatz (28) together with Eqs. (30) and (32) is used as an approximation for the pair distribution function. Since the exact equations of change for the kinetic and potential energies are consistent with the overall conservation of energy and the expression for the kinetic energy production deduced from the Boltzmann equation is consistent with an appropriate approximation for the pair distribution function being introduced into the exact expression for the kinetic energy production, it follows that the Boltzmann equation expressions are consistent with total energy conservation and the conversion between kinetic and potential energy densities.

## 5. UNIFIED CLASSICAL TREATMENT

Section 3 has described how the nonlocal (in time) Boltzmann collision term gives rise to the conversion between kinetic and potential energy for a homogeneous gas, while Section 4 describes this energy conversion for an inhomogeneous gas. It is noticed, however, that the expression for the



kinetic energy production derived for an inhomogeneous gas vanishes when the gas becomes homogeneous. This is inconsistent with the results of Section 3, to which the Section 4 expressions should reduce when the system becomes homogeneous. The object is now to understand how a unified treatment for both cases can be formulated.

Both cases arise from nonlocal aspects of the Boltzmann collision term, so Eqs. (28)–(30) constitute a common starting point. The approximate evaluation of the time derivative in Eq. (29) as discussed in deriving Eq. (32) is where the missing homogeneous term is lost. Essentially the time derivative of  $f_{10}f_{20}$  must be generalized to include the change due to collisions, that is,

$$\frac{\partial}{\partial t} f_{10}f_{20} = -f_{20}\mathbf{p}_{10} \cdot \nabla f_{10} - f_{10}\mathbf{p}_{20} \cdot \nabla f_{20} + f_{20} \left. \frac{\partial f_{10}}{\partial t} \right|_{\text{coll}} + f_{10} \left. \frac{\partial f_{20}}{\partial t} \right|_{\text{coll}} \quad (41)$$

This arises naturally from the first BBGKY equation (3) written in a form to emphasize the collisional rate of change

$$\frac{\partial f_1^{(1)}}{\partial t} = -\frac{\mathbf{p}_1}{m} \cdot \frac{\partial f_1^{(1)}}{\mathbf{r}_1} + \left. \frac{\partial f_1^{(1)}}{\partial t} \right|_{\text{coll}} \quad (42)$$

or more directly from the collision term of the standard Boltzmann equation (22). Introducing this into Eq. (29) for  $\Delta_1$  gives

$$\Delta_1 \simeq \Delta_1^{\text{homog}} + \Delta_1^G \quad (43)$$

with the inhomogeneous contribution given by Green's<sup>(5)</sup> form  $\Delta_1^G$  while the homogeneous contribution is

$$\Delta_1^{\text{homog}} = (t_0 - t) \left( \left. \frac{\partial f_{10}}{\partial t} \right|_{\text{coll}} f_{20} + f_{10} \left. \frac{\partial f_{20}}{\partial t} \right|_{\text{coll}} \right) \quad (44)$$

It should be clear, but is to be emphasized, that the collisional rate of change, for example, for  $f_{10}$ , is to describe how  $f_{10}$  changes with time due to binary collisions with other molecules in the gas, particle 2 not being responsible for this change, so that this is NOT to be considered as a three-particle collision between particles 1, 2, and some other particle. Essentially  $f^{(1)}$  changes with time because collisions occur, and this effect must be taken into account as one of the consequences of a finite time of duration for a collision. Use of this combination for  $\Delta_1$  when evaluating the  $J_1$  contribution to the equation of change for the kinetic energy implies that the kinetic energy production is the sum

$$\sigma_K = \sigma_K^{\text{homog}} + \sigma_K^{\text{inhomog}} \quad (45)$$

of the homogeneous contribution [compare Eq. (26)]

$$\sigma_K^{\text{homog}} = -\frac{1}{2} \iiint V_{12} \left( \frac{\partial f_{10}}{\partial t} \Big|_{\text{coll}} f_{20} + f_{10} \frac{\partial f_{20}}{\partial t} \Big|_{\text{coll}} \right) d\mathbf{r}_{12} d\mathbf{P}_{12} d\mathbf{p}_{12} \quad (46)$$

and the inhomogeneous contribution, Eq. (40), derivable from Green's approximation.

## 6. ON CLOSURES OF THE BBGKY HIERARCHY

Bogoliubov's<sup>(4)</sup> functional assumption states that the time dependence of all distribution functions is governed through their functional dependence on the singlet distribution function. This functional assumption is stressed in most discussions (see, for example, refs. 9–11) of the generalization of the Boltzmann equation to higher density. But also needed is an initial condition so as to complete the closure of the BBGKY hierarchy. Bogoliubov<sup>(4)</sup> argues that the reduced distribution functions should factorize in the infinite past. For the Boltzmann equation, it is the factorization of the pair distribution that is relevant. To make use of this initial factorization, Bogoliubov introduces a comparison of time evolutions between isolated pair and free motions so that

$$f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t) = \mathfrak{S}_{12}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2) f^{(1)}(\mathbf{r}_1, \mathbf{p}_1; t) f^{(1)}(\mathbf{r}_2, \mathbf{p}_2; t) \quad (47)$$

Here

$$\mathfrak{S}_{12}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2) = \lim_{t \rightarrow -\infty} e^{\mathcal{L}_{12}t} e^{-\mathcal{K}_{12}t} \quad (48)$$

contrast the motion of the interacting pair of particles with their free evolution from the infinite past. These evolutions are described by the pair Liouville operator

$$\mathcal{L}_{12} \equiv \mathcal{K}_{12} - \Theta_{12} \quad (49)$$

given in terms of the pair free motion

$$\mathcal{K}_{12} \equiv \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} + \frac{\mathbf{p}_2}{m} \cdot \frac{\partial}{\partial \mathbf{r}_2} \quad (50)$$

and interaction

$$\Theta_{12} \equiv \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} \cdot \left( \frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2} \right) \quad (51)$$

Liouville operators. Substitution of Eq. (47) into the first BBGKY equation (3) provides a closure of the BBGKY hierarchy at the one-particle level.

$\mathfrak{S}_{12}$  is a phase space transformation, with the result being equivalently expressed as

$$f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t) = f^{(1)}(\mathbf{r}'_1, \mathbf{p}_{10}; t) f^{(1)}(\mathbf{r}'_2, \mathbf{p}_{20}; t) \tag{52}$$

where the momenta  $\mathbf{p}_{10}$  and  $\mathbf{p}_{20}$  are the same as introduced by Green (see Section 4), namely the momenta of the particles just before they begin to collide. The primed positions  $\mathbf{r}'_1$  and  $\mathbf{r}'_2$  are obtained from  $\mathbf{r}_1$  and  $\mathbf{r}_2$  by going back via a binary collision trajectory to a time before the particles started to collide and then forward an equivalent time via free motion. Thus they have the same center-of-mass position, but their relative position is given by

$$\mathbf{r}' \equiv \mathbf{r}'_2 - \mathbf{r}'_1 = \lim_{t_0 \rightarrow -\infty} \mathbf{r}_0 + \mathbf{g}_0(t - t_0) \tag{53}$$

In this way, an expansion of the position dependence of the product, Eq. (52), to first order in gradients is exactly as in Green's treatment of the inhomogeneous gas, specifically

$$f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t) \approx f_{10} f_{20} + \mathcal{A}_1^G + \mathcal{A}_2 \tag{54}$$

Because of the inherent limit in Eq. (48), there is no remaining time parameter  $t_0$  and thus no way to indicate the time of duration of the collision. Hence it is not possible to describe the conversion between kinetic and potential energy in a homogeneous gas using the closure (47). Moreover, it appears to be inconsistent with total energy conservation, as is now displayed.

With the use of Eq. (47), the Boltzmann equation is conveniently written

$$\begin{aligned} \frac{\partial}{\partial t} f_1^{(1)} &\equiv -\mathcal{K}_1 f_1^{(1)} + \left. \frac{\partial f_1^{(1)}}{\partial t} \right|_{\text{coll}} \\ &= -\mathcal{K}_1 f_1^{(1)} + \iint \Theta_{12} \mathfrak{S}_{12} f_1^{(1)}(t) f_2^{(1)}(t) d\mathbf{r}_2 d\mathbf{p}_2 \end{aligned} \tag{55}$$

The rate of change of the total kinetic energy

$$U_K \equiv \iint \frac{\mathbf{p}_1^2}{2m} f_1^{(1)} d\mathbf{r}_1 d\mathbf{p}_1$$

is given according to this Boltzmann equation by

$$\begin{aligned}
 \frac{\partial U_K}{\partial t} &= \iint \frac{\mathbf{p}_1^2}{2m} \frac{\partial f_1^{(1)}(t)}{\partial t} d\mathbf{r}_1 d\mathbf{p}_1 \\
 &= \int \cdots \int \frac{\mathbf{p}_1^2}{2m} \Theta_{12} \mathfrak{S}_{12} f_1^{(1)} f_2^{(1)} d\mathbf{r}_1 \cdots d\mathbf{p}_2 \\
 &= \int \cdots \int V_{12} \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} \mathfrak{S}_{12} f_1^{(1)} f_2^{(1)} d\mathbf{r}_1 \cdots d\mathbf{p}_2 \\
 &= \frac{1}{2} \int \cdots \int V_{12} \mathcal{L}_{12} \mathfrak{S}_{12} f_1^{(1)} f_2^{(1)} d\mathbf{r}_1 \cdots d\mathbf{p}_2 \\
 &= \frac{1}{2} \int \cdots \int V_{12} \mathfrak{S}_{12} \mathcal{K}_{12} f_1^{(1)} f_2^{(1)} d\mathbf{r}_1 \cdots d\mathbf{p}_2 \\
 &= -\frac{1}{2} \frac{\partial}{\partial t} \int \cdots \int V_{12} \mathfrak{S}_{12} f_1^{(1)} f_2^{(1)} d\mathbf{r}_1 \cdots d\mathbf{p}_2 + \frac{1}{2} \int \cdots \int V_{12} \mathfrak{S}_{12} \\
 &\quad \times \left\{ \left. \frac{\partial f_1^{(1)}(t)}{\partial t} \right|_{\text{coll}} f_2^{(1)}(t) + f_1^{(1)}(t) \left. \frac{\partial f_2^{(1)}(t)}{\partial t} \right|_{\text{coll}} \right\} d\mathbf{r}_1 \cdots d\mathbf{p}_2 \quad (56)
 \end{aligned}$$

In deriving this set of equalities, the second equality involves integrating by parts with respect to each of  $\mathbf{r}_1$ ,  $\mathbf{p}_1$ , and  $\mathbf{p}_2$ . The third equality symmetrizes between the two particles and recognizes that the interaction term  $\Theta_{12}$  can be introduced since on integration it contributes nothing. The fourth equality uses the classical analog

$$\mathcal{L}_{12} \mathfrak{S}_{12} = \mathfrak{S}_{12} \mathcal{K}_{12} \quad (57)$$

of the quantum scattering theory intertwining relation. Finally the first BBGKY equation is used for each particle to eliminate  $\mathcal{K}_{12} f_1^{(1)} f_2^{(1)}$  in terms of time derivatives.

Thus Eq. (56) is an exact consequence of the first BBGKY equation and the closure (47). On identifying the first term in the last expression of Eq. (56) as (minus) the rate of change of the potential energy, it is noted that Eq. (56) implies that the total energy  $U_K + U_V$  is not constant and thus inconsistent with energy conservation. This must be the consequence of the closure (47) determining  $f_{12}^{(2)}$  in terms of  $f_1^{(1)}$  and  $f_2^{(1)}$ . There appear to be two ways to recover energy conservation. One way is to drop the collisional time rates of change in the first BBGKY equation when used in evaluating  $\mathcal{K}_{12} f_1^{(1)} f_2^{(1)}$  in Eq. (56). This could be argued as reasonable since  $\mathfrak{S}_{12}$  is obtained by contrasting interacting and free motion for the pair of particles. Essentially this treats the colliding pair as if they are completely

isolated from all the other particles in the gas, so the possibility of collisions with other particles should not be taken into account. For this method of obtaining consistency, energy conversion between kinetic and potential energy occurs only via spatial inhomogeneity; in particular no energy conversion occurs for homogeneous systems. This can be explicitly seen from the factor  $\mathcal{K}_{12} f_1^{(1)} f_2^{(1)}$  in the fifth equality in Eq. (56), which vanishes unless  $f^{(1)}$  is position dependent, equivalently, unless the gas is inhomogeneous. An alternate way of recovering energy conservation is to consider the gas as essentially homogeneous over the range of the collision. Then  $\mathcal{K}_{12} f_1^{(1)} f_2^{(1)}$  is zero. In this case there is no energy conversion and kinetic energy is conserved. This is exactly the classic treatment of Boltzmann! A collision essentially occurs at one point in space and time as far as the macroscopic properties of the gas are concerned.

It is concluded that the retention of an explicit dependence on the time of duration of a collision as in Green's<sup>(5)</sup> treatment has the advantage of being capable of describing in a consistent manner the binary collision conversion between kinetic and potential energies, in both homogeneous and inhomogeneous systems (see Secion 4). An alternate approach of obtaining consistency is to use Klimontovich's<sup>(14)</sup> binary collision approximation for closing the BBGKY hierarchy. This is described later in this section. But first some comment is made on the quantum analog of the above equations.

For the "derivation" of the quantum Boltzmann equation from the first BBGKY equation, the pair density operator  $\rho_{12}^{(2)}$  entering into the collision term is expressed in terms of the singlet  $\rho^{(1)}$  according to<sup>(21-23)</sup>

$$\rho_{12}^{(2)}(t) = \Omega_{12} \rho_1^{(1)}(t) \rho_2^{(1)}(t) \quad (58)$$

on the basis of the Stosszahlansatz. Here  $\Omega_{12}$  is the Møller superoperator, having a structure exactly parallel to Eq. (48). It should be remarked that inherently this expression involves a spatial nonlocality. Thus has been explicitly used<sup>(1)</sup> to account for angular momentum transfer between spin and translational degrees of freedom, and the same discussion includes a description of the conversion between kinetic to potential energies via binary collisions in the quantum Boltzmann equation. What should also be noted is that any constraints on nonlocality in Bogoliubov's form for the classical Boltzmann collision term are also applicable to the standard quantum Boltzmann equation since the latter is based on Eq. (58). In fact, the previous work<sup>(1, 2)</sup> on energy conversion by the quantum Boltzmann equation provided motivation for examining the classical case. But it was not recognized that energy conversion in a homogeneous gas was inadequately described in that work. Inherently the Møller superoperator  $\Omega$  has no time dependence, so the collision duration time does not enter the formalism. This apparently is the reason for not being able to describe energy

conversion via binary collisions in homogeneous gases. It may be possible to adapt Green's<sup>(5)</sup> treatment to the quantum case and consider a finite-ranged potential with a finite collision duration time, but to the author's knowledge this has not been explored. Alternately, Boercker and Dufty<sup>(16)</sup> introduced a "binary collision approximation" for closing the quantum BBGKY hierarchy which appears to be analogous to Klimontovich's<sup>(14)</sup> classical method, but without the mean-field terms that Klimontovich introduces to account for long-ranged (in particular, Coulombic) forces. A recent paper by Dufty and Boercker<sup>(24)</sup> emphasizes that their binary collision approximation conserves total energy. Here it is verified that the classical analog of their binary collision approximation does conserve total energy. This approximation also provides a means of expressing the pair distribution function in terms of the singlets in a way that is consistent with total energy conservation; see Appendix B for the detailed form.

Klimontovich<sup>(14)</sup> expresses his "binary collision approximation" in terms of correlation functions instead of the corresponding distribution functions. Here the classical analog of the quantum theory of Boercker and Dufty<sup>(16)</sup> is followed. Phrased in classical mechanics, their binary collision approximation assumes that the term responsible for interaction with a third particle in the second BBGKY equation

$$\frac{\partial f_{12}^{(2)}}{\partial t} = -\mathcal{L}_{12}f_{12}^{(2)} + \iint (\Theta_{13} + \Theta_{23}) f_{123}^{(3)} d\mathbf{r}_3 d\mathbf{p}_3 \quad (59)$$

can be approximated according to

$$\begin{aligned} \iint (\Theta_{13} + \Theta_{23}) f_{123}^{(3)} d\mathbf{r}_3 d\mathbf{p}_3 &\simeq \iint (\Theta_{13} f_{13}^{(2)} f_2^{(1)} + \Theta_{23} f_{23}^{(2)} f_1^{(1)}) d\mathbf{r}_3 d\mathbf{p}_3 \\ &= \left\{ f_2^{(1)} \frac{\partial f_1^{(1)}}{\partial t} \Big|_{\text{coll}} + f_1^{(1)} \frac{\partial f_2^{(1)}}{\partial t} \Big|_{\text{coll}} \right\} \\ &= \left( \frac{\partial}{\partial t} + i\mathcal{K}_{12} \right) f_1^{(1)} f_2^{(1)} \end{aligned} \quad (60)$$

Here the collisional rate of change of a singlet has been denoted by

$$\frac{\partial f_1^{(1)}}{\partial t} \Big|_{\text{coll}} \equiv \iint \Theta_{13} f_{13}^{(2)} d\mathbf{r}_3 d\mathbf{p}_3 = \frac{\partial f_1^{(1)}}{\partial t} + \mathcal{K}_1 f_1^{(1)} \quad (61)$$

which, according to the first BBGKY equation [last equality in Eq. (61)], can be reexpressed in terms of the time and free motion properties of the singlet, leading to the last form for Eq. (60). In a previous paper<sup>(15)</sup> it has

been rationalized that this method of implementing a “binary collision approximation” is to reflect the consequences of the previous collisions that particles 1 and 2 have just undergone before they start to collide with each other. But the net result is that the second BBGKY equation is replaced by

$$\left(\frac{\partial}{\partial t} + \mathcal{L}_{12}\right) f_{12}^{(2)}(t) = \left(\frac{\partial}{\partial t} + \mathcal{K}_{12}\right) f_1^{(1)}(t) f_2^{(1)}(t) \quad (62)$$

which together with the first BBGKY equation (61) gives a pair of closed equations for  $f^{(1)}$  and  $f^{(2)}$ . The rate of change of potential energy is then predicted, according to Eq. (62), to be

$$\begin{aligned} \frac{\partial U_V}{\partial t} &= \frac{1}{2} \int \dots \int V_{12} \frac{\partial f_{12}^{(2)}}{\partial t} d\mathbf{r}_1 \dots d\mathbf{p}_2 \\ &= \frac{1}{2} \int \dots \int V_{12} \left[ -\mathcal{L}_{12} f_{12}^{(2)} \right. \\ &\quad \left. + \iint (\Theta_{13} f_{13}^{(2)} f_2^{(1)} + \Theta_{23} f_{23}^{(2)} f_1^{(1)}) d\mathbf{r}_3 d\mathbf{p}_3 \right] d\mathbf{r}_1 \dots d\mathbf{p}_2 \\ &= -\frac{1}{2} \int \dots \int V_{12} \mathcal{K}_{12} f_{12}^{(2)} d\mathbf{r}_1 \dots d\mathbf{p}_2 \\ &= \frac{1}{2} \int \dots \int \frac{\mathbf{p}_1 - \mathbf{p}_2}{m} \cdot \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} f_{12}^{(2)} d\mathbf{r}_1 \dots d\mathbf{p}_2 \\ &= \int \dots \int \frac{\mathbf{p}_1}{m} \cdot \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} f_{12}^{(2)} d\mathbf{r}_1 \dots d\mathbf{p}_2 \\ &= \int \dots \int \left( \frac{\partial}{\partial \mathbf{p}_1} \frac{\mathbf{p}_1^2}{2m} \right) \cdot \frac{\partial V_{12}}{\partial \mathbf{r}_{12}} f_{12}^{(2)} d\mathbf{r}_1 \dots d\mathbf{p}_2 \\ &= - \int \dots \int \frac{\mathbf{p}_1^2}{2m} \Theta_{12} f_{12}^{(2)} d\mathbf{r}_1 \dots d\mathbf{p}_2 \\ &= - \iint \frac{\mathbf{p}_1^2}{2m} \left( \frac{\partial f_1^{(1)}}{\partial t} + \mathcal{K}_1 f_1^{(1)} \right) d\mathbf{r}_1 d\mathbf{p}_1 \\ &= - \frac{\partial U_K}{\partial t} \end{aligned} \quad (63)$$

Use has been made of various integrations by parts as well as Eqs. (60) and (61). This completes the proof that the “binary collision approximation” closure of the BBGKY equation as expressed by Eq. (62) is consistent with

total (kinetic plus potential) energy conservation with binary collisions providing the mechanism for the conversion between kinetic and potential energy. Equation (62) provides a relation between  $f^{(2)}$  and  $f^{(1)}$  which can be solved to express  $f^{(2)}$  in terms of  $f^{(1)}$ . Such a result is interesting since it shows at least one way in which Eq. (47) can be modified in order to make it consistent with energy conservation. This calculation is presented in Appendix B.

## 7. DISCUSSION

There appear to be two different philosophies for “deriving” the Boltzmann equation from the BBGKY hierarchy. To emphasize the differences, these are discussed in turn:

(a) Following Boltzmann’s original arguments that a pair of particles entering into a collision are statistically independent, Green<sup>(5)</sup> starts with the first BBGKY equation and then explicitly uses *isolated* binary collision dynamics to relate the pair distribution function in terms of the singlets just before the collision begins, Eq. (28). The author’s quantum Boltzmann equation was “derived”<sup>(21)</sup> with the same philosophy, namely that a specific form for the pair density operator is introduced which is valid while the pair of particles are colliding. That form for the pair distribution function (or quantumly, for the pair density operator) is appropriate only while the particles are colliding and not generally valid if the particles are not in the process of colliding. Specifically, neither does the integration over the coordinates of particle 2 give the singlet [as required by their definitions, Eq. (2)], nor does it satisfy the second BBGKY equation, nor for that matter the pair Liouville equation without further restrictions. A resolution of the normalization problem has been discussed<sup>(2)</sup> while introducing a density-corrected quantum Boltzmann equation. Since the evaluation of the mean potential energy density requires the general form for the pair distribution function, it is perfectly valid to use the second BBGKY equation to get the formal rate of change of potential energy, and then after the expression for the potential energy production is identified as involving collision processes, the form for the pair distribution function, Eq. (28), can be used in the evaluation of the potential energy production. In this way, energy conservation is obtained. In summary, the consistent treatment of energy conservation really arises from the exact equations of change for the kinetic and potential energy as given in Section 2, and only if the detailed evaluation of the conversion rate is desired, is Eq. (28) needed. Three different levels of treating energy conversion in a consistent manner can be recognized; these involve treating the position and time dependence of the



singlets in Eq. (28) in the following ways: (i) Local collision approximation; by this is meant that only the first term in Eq. (28) is retained. This gives the (original) local Boltzmann equation and no conversion between kinetic and potential energy. (ii) Spatial nonlocality; any time nonlocality is interpreted in terms of spatial nonlocality (see Section 4). This is the approach used by Green<sup>(5)</sup> and by the author<sup>(8)</sup> for density corrections to the transport coefficients. Energy conversion has also been discussed<sup>(1,2)</sup> for quantum systems within this same approach. (iii) Full time and spatial nonlocality. This allows energy conversion both in homogeneous and inhomogeneous gases; see Section 5. This approach has not been presented before, to the author's knowledge.

(b) According to Bogoliubov's functional assumption,<sup>(4)</sup> the pair distribution function is a functional of the singlet distribution function and all time dependence of the former is determined through this functional. If such a philosophy is taken literally, this implies that the combination of the first BBGKY equation and the functional equation constitute a complete closure of the BBGKY hierarchy, equivalently that none of the higher members of the hierarchy are to be considered. It is this philosophy which is behind labelling Section 6 as being devoted to closures of the BBGKY hierarchy. Two specific closures limited to treating binary collisions are discussed in that section. Equation (47) is the first closure discussed. It is shown there [see Eq. (56)] that this closure is generally inconsistent with energy conservation. If the further constraint is made that the collision is local, the kinetic energy is conserved and the original Boltzmann equation obtained. Discussions of the general equations of change (see in particular ref. 10) often refer to Bogoliubov's functional assumption and the closure, Eq. (47). But in carrying out such calculations they appear to follow the same procedure as discussed in the previous paragraph, namely they use both the first BBGKY equation to describe the rate of change of kinetic energy and the second BBGKY equation for the potential energy. In this way they appear to violate the concept that the functional assumption is to determine the pair distribution function and replace the second BBGKY equation. Consistency in energy conversion effectively corresponds to approach (ii) in the previous paragraph since Eq. (47) is equivalent to describing all nonlocal aspects of the collision process in terms of spatial inhomogeneities. In contrast, a consistent closure of the BBGKY hierarchy is the "binary collision approximation" of Klimontovich<sup>(14)</sup> and Boercker and Dufty.<sup>(16)</sup> A strict use of the first BBGKY equation and Eq. (62) is consistent with total energy conservation; Correctly this pair of equations is more general than the Boltzmann equation. A solution of Eq. (62) for the pair distribution function in terms of the singlet is given in Appendix B, which inserted into the first BBGKY equation formally gives a closed

equation for the singlet. But the result involves the complete past history of the singlet, so it constitutes a generalization of the Boltzmann equation. Appendix B also shows how the form for the pair distribution function discussed in Section 5 is produced as an approximation to the form deduced from the binary collision approximation.

Some comment was already made in Section 3 about the density dependence of the various quantities that enter into the "derivation" of the Boltzmann equation. It is common to think of the singlet distribution function as being first order in the density, and collision processes as being second order. This association is correct at equilibrium for an ideal gas, but as soon as  $f^{(1)}$  changes with time, due to a combination of streaming and collisional processes, there is an extra density dependence of  $f^{(1)}$  that is associated with this evolution. As a consequence, the behavior of the low-density gas is not adequately described by expanding all quantities as power series in the density. The governing kinetic equation, the Boltzmann equation, is similarly affected. Since  $f^{(1)}$  is in general a very complicated function of the density (often of exponential decay form), it might be more useful to think of the Boltzmann equation as the result of expanding the Liouville equation in powers of the singlet distribution function rather than of the density.

Even after deciding to restrict the description of a low-density gas to retaining only binary collisions with a molecular chaos assumption determining the state of the particles before they enter into collision, there is still the question of assigning a macroscopic position and time to a particular collision process. Boltzmann's original assumption was that the collision is local, equivalently that it occurs macroscopically at one position and time. Essentially there is then a complete separation of time and distance scales between macroscopic (fluid) properties and microscopic (collisional) processes. This is certainly a consistent scheme and nicely describes the properties of a (relaxing) ideal gas. But if one starts to ask for density corrections to relaxation rates or transport coefficients, the nonlocality of the collision process is important. It has been well known that Bogoliubov's<sup>(4)</sup> and Green's<sup>(5)</sup> method of accounting for collision nonlocality leads to corrections to the transport properties (see in particular ref. 8-12 and the literature cited therein). But the conversion between kinetic and potential energy via a classical Boltzmann equation has been seldom discussed, the major reference known to the author being that of Klimontovich.<sup>(14)</sup> According to Bogoliubov<sup>(4)</sup> and Green,<sup>(5)</sup> the collision nonlocality is always reduced to a position nonlocality and so depends on the inhomogeneity of the gas. Such position nonlocalities are irrelevant in a homogeneous system, but the conversion between kinetic and potential energy still can occur. This has been described in detail in Sections 3 and 5. Thus it is

seen that the time nonlocality is not completely reducible to a position nonlocality, so in general both effects need to be taken into account. It does appear that a truncation of the nonlocality to include only the inhomogeneous terms gives a consistent scheme, but has something been lost? Such a truncation is also quite appealing since it has the appearance of being an expansion of the kinetic equation to retain only terms second order in density. But as emphasized above, this is illusory since the density appears in all of the time dependence of the (singlet) distribution function. Retaining both inhomogeneous and homogeneous nonlocality corrections to the Boltzmann equation appears to be consistent with the inclusion of all binary collision processes, but seems to be of higher order in the density since the homogeneous term involves the effect of a binary collision rate for one particle while the other particle is a spectator. Care must be exercised in interpreting this formula. The present work emphasizes that these (spectator) collisional rates of change reflect how the distribution function changes with time because of the accumulation of binary collision processes rather than that all three (or more) particles are simultaneously colliding.

Finally one should comment on the fact that an experimental measurement can select the density range in which the measurement is carried out, but cannot select that only binary collision processes are of importance. It is well known that there are other effects besides the nonlocality of the binary collisions that contribute to density corrections to, for example, transport processes. The best present theory,<sup>(12)</sup> in that it gives the best agreement with measured transport virials, takes into account in an approximate manner the presence of bound states and three-particle collisions as well as the binary collision nonlocality. This paper has examined only one related aspect of this whole question, namely how kinetic and potential energies are interconverted via binary collisions, with possible ramifications as to how the nonlocality of the binary collisions should be treated. There is, on the other hand, a need for a concerted theory including all effects (collision nonlocality, bound states, and triple collisions), which would have the advantage of clarifying if and how these different effects influence each other.

## APPENDIX A. ASPECTS OF BINARY COLLISION DYNAMICS

In an isolated binary collision, any function  $F$  of the positions and momenta of the pair of particles satisfies the pair Liouville equation [Eq. (4) without the three-particle terms]. Those functions  $I$  that are also time independent are collisional invariants in that they have the same value at every point of a collision trajectory. Since all center-of-mass motion is

trivially a collision invariant, it is sufficient to emphasize only the constraints associated with relative motion. Specifically, then, a collisional invariant  $I$  must satisfy

$$\frac{\partial V}{\partial \mathbf{r}} \cdot \frac{\partial I}{\partial \mathbf{p}} = \frac{\mathbf{p}}{\mu} \cdot \frac{\partial I}{\partial \mathbf{r}} \quad (\text{A.1})$$

in terms of its dependence on the relative position  $\mathbf{r}$  and momentum  $\mathbf{p}$ .

Given a particular relative position  $\mathbf{r}$  and momentum  $\mathbf{p}$ , these determine a collision trajectory as well as where the particles are at along the trajectory. The trajectory is determined by five independent collision invariants. This leaves one variable to describe the progress along the trajectory. Clearly the energy

$$E = \frac{\mathbf{p}^2}{2\mu} + V(\mathbf{r}) \quad (\text{A.2})$$

and the three-dimensional angular momentum

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \quad (\text{A.3})$$

serve as four if the independent collision invariants. The direction of  $\mathbf{L}$  is perpendicular to the plane of the collision trajectory, and so defines this plane. Outside the range  $r_0$  of the potential (assumed for simplicity of presentation to be finite) the initial momentum  $\mathbf{p}_0$  must lie in the plane of the collision and have its magnitude determined by the energy,  $p_0 = (2\mu E)^{1/2}$ . Its orientation within the plane of the collision provides a fifth independent collision invariant. The radial distance  $r$  is taken in this work as the variable parametrizing where the particles are along the collision trajectory. This parametrization is unique provided it is also specified whether the particles are on an incoming,  $\mathbf{r} \cdot \mathbf{p} < 0$ , or outgoing  $\mathbf{r} \cdot \mathbf{p} > 0$ , part of the trajectory.

Clearly any collisional invariant can be rewritten as a function of the five independent collisional invariants  $E$ ,  $\mathbf{L}$  and the orientation of  $\mathbf{p}_0$  within the plane of the collision. In particular, the initial relative momentum  $\mathbf{p}_0$  as well as the individual initial momenta  $\mathbf{p}_{10}$  and  $\mathbf{p}_{20}$  are combinations of the five independent collisional invariants. So is the impact parameter  $b = L/p_0$ . Another collision invariant is the distance of closest approach  $\xi_0$ , which is the largest root of  $E = V(\xi_0) + L^2/2\mu\xi_0^2$ . The time  $t_0$  at which a collision begins is identified here as the time when the particles are a distance  $r_0$  apart and on the incoming part of the trajectory. Standard integration of

Newton's equations give  $t_0$  in terms of the time  $t$  at which the particles were at  $\mathbf{r}$ ,  $\mathbf{p}$  according to

$$\begin{aligned}
 t - t_0 &= -\left(\frac{\mu}{2}\right)^{1/2} \int_{r_0}^r \frac{d\xi}{[E - V(\xi) - L^2/(2\mu\xi^2)]^{1/2}}, & \mathbf{r} \cdot \mathbf{p} \leq 0 \\
 &= -\left(\frac{\mu}{2}\right)^{1/2} \int_{r_0}^{\xi_0} \frac{d\xi}{[E - V(\xi) - L^2/(2\mu\xi^2)]^{1/2}} \\
 &\quad + \left(\frac{\mu}{2}\right)^{1/2} \int_{\xi_0}^r \frac{d\xi}{[E - V(\xi) - L^2/(2\mu\xi^2)]^{1/2}}, & \mathbf{r} \cdot \mathbf{p} > 0 \quad (\text{A.4})
 \end{aligned}$$

$E$ ,  $L$ , and  $\xi_0$  are all collision invariants. Thus  $t - t_0$  is a function of collisional invariants as well as a function of the position  $r$  which parametrizes where along the collision trajectory the particles are to be considered at phase point  $\mathbf{r}$ ,  $\mathbf{p}$ . It follows that at constant  $E$  and  $L$

$$\left[ \frac{\partial(t - t_0)}{\partial \mathbf{r}} \right]_{E, L} = \frac{\mu \mathbf{r}}{\mathbf{p} \cdot \mathbf{r}} \quad (\text{A.5})$$

This is used in the evaluation of Eq. (26).

### APPENDIX B. THE PAIR DISTRIBUTION FUNCTION ACCORDING TO THE BINARY COLLISION APPROXIMATION

The binary collision approximation as introduced by Boecker and Dufty<sup>(16)</sup> for quantum systems and by Klimontovich<sup>(14)</sup> for classical systems including mean-field forces implies, for classical systems and dropping the mean-field effects, Eq. (62) as a relation between the singlet  $f^{(1)}$  and pair  $f^{(2)}$  distribution functions. This appendix solves this equation in order to express the pair distribution function in terms of the singlet. The result is found to involve the memory of the complete time history of the singlet. Its importance is that Eq. (62) provides one way of closing the BBGKY hierarchy in a manner consistent with the binary collision conversion between kinetic and potential energies.

An immediate integration of Eq. (62) between times  $t'$  to  $t$  gives

$$\begin{aligned}
 f_{12}^{(1)}(t) &= f_1^{(1)}(t) f_2^{(1)}(t) + e^{-\mathcal{Q}_{12}(t-t')} [f_{12}^{(2)}(t') - f_1^{(1)}(t') f_2^{(1)}(t')] \\
 &\quad + \int_{t'}^t e^{-\mathcal{Q}_{12}(t-t'')} \Theta_{12} f_1^{(1)}(t'') f_2^{(1)}(t'') dt'' \quad (\text{B.1})
 \end{aligned}$$

According to this expression, the value of  $f^{(2)}$  at time  $t$  depends on the whole time history of  $f^{(1)}$  and some initial condition at  $t'$ . An appropriate

initial condition is to take  $t' \rightarrow -\infty$  and assume that the pair density operator factors into a product of singlets in the infinite past. This follows the original treatment of Boercker and Dufty.<sup>(16)</sup> As discussed in ref. 15, this time can be considered as the time at which the gaseous system was initially set up for observation. But independent of interpretation, this determines a unique pair distribution function in terms of the singlet

$$f_{12}^{(2)}(t) = f_1^{(1)}(t) f_2^{(1)}(t) + \int_{-\infty}^t e^{-\mathcal{L}_{12}(t-t'')} \Theta_{12} f_1^{(1)}(t'') f_2^{(1)}(t'') dt'' \quad (\text{B.2})$$

To connect and compare this result with Bogoliubov's form,<sup>(4)</sup> Eq. (47), for the pair distribution function used to obtain the Boltzmann equation, the integrated form of the first BBGKY equation

$$f_1^{(1)}(t'') = e^{-\mathcal{K}_1(t''-t)} f_1^{(1)}(t) + \int_t^{t''} e^{-\mathcal{K}_1(t''-s)} \left. \frac{\partial f_1^{(1)}(s)}{\partial s} \right|_{\text{coll}} ds \quad (\text{B.3})$$

can be used to give the time dependence of the singlets in the  $t''$  integral. Here the collisional rate of change of the singlet is given by Eq. (61), in particular it is determined by the properties of  $f_1^{(1)}(s)$ . Substituting this into Eq. (B.2) for both singlets leads to a complicated expression involving three separate types of terms, being of zeroth, first, and second order in the collisional rate of change of the singlets. In each case it is possible to analytically integrate over  $t''$ . After recognizing the limit of the product of interacting and free evolution operators as  $\mathfrak{S}_{12}$  and reorganizing the remaining integrals, the result can be written

$$\begin{aligned} f_{12}^{(2)}(t) = & \mathfrak{S}_{12} f_1^{(1)}(t) f_2^{(2)}(t) \\ & + \int_{-\infty}^t ds \left[ e^{-\mathcal{L}_{12}(t-s)} e^{\mathcal{K}_{12}(t-s)} - \mathfrak{S}_{12} \right] \left\{ e^{-\mathcal{K}_2(t-s)} f_1^{(1)}(t) \left. \frac{\partial f_2^{(1)}(s)}{\partial s} \right|_{\text{coll}} \right. \\ & \left. + e^{-\mathcal{K}_1(t-s)} f_2^{(1)}(t) \left. \frac{\partial f_1^{(1)}(s)}{\partial s} \right|_{\text{coll}} \right\} \\ & - \int_{-\infty}^t ds \int_{-\infty}^s ds' \left[ e^{-\mathcal{L}_{12}(t-s')} e^{\mathcal{K}_{12}(t-s')} - \mathfrak{S}_{12} \right] \\ & \times \left\{ e^{-\mathcal{K}_1(t-s)} e^{-\mathcal{K}_2(t-s')} \left. \frac{\partial f_1^{(1)}(s)}{\partial s} \right|_{\text{coll}} \left. \frac{\partial f_2^{(1)}(s')}{\partial s'} \right|_{\text{coll}} \right. \\ & \left. + e^{-\mathcal{K}_1(t-s')} e^{-\mathcal{K}_2(t-s)} \left. \frac{\partial f_1^{(1)}(s')}{\partial s'} \right|_{\text{coll}} \left. \frac{\partial f_2^{(1)}(s)}{\partial s} \right|_{\text{coll}} \right\} \quad (\text{B.4}) \end{aligned}$$

This shows that the pair distribution function deduced from the binary collision approximation gives the Bogoliubov closure plus corrections

associated with the collisional rate of change of the singlets. As it must, this equation for the pair distribution function satisfies Eq. (62), so that it is consistent with total energy conservation, including both inhomogeneous and homogeneous contributions for the conversion between kinetic and potential energy. Possibly there are simpler ways of writing this result and possibly there are alternate, simpler forms for the pair distribution function that are consistent with total energy conservation.

Equation (B.4) gives the pair distribution functions as having the Bogoliubov closure, Eq. (47), plus corrections associated with the collisional rate of change of the singlet. Recognizing that the leading term includes the spatial gradient corrections to the purely local expression for the pair distribution function in terms of singlet distribution functions, a comparison with the general expansion, Eq. (28), of the pair distribution function for a finite-ranged potential using in particular Eqs. (43) and (44) suggest questioning whether there is a connection between these two forms. This is indeed the case, as is now demonstrated. On the basis that the collisional rate of change is slow,

$$e^{-\mathcal{X}_1(t''-s)} \left. \frac{\partial f_1^{(1)}(s)}{\partial s} \right|_{\text{coll}}$$

can be approximated by

$$e^{-\mathcal{X}_1(t''-t)} \left. \frac{\partial f_1^{(1)}(t)}{\partial t} \right|_{\text{coll}}$$

and an expansion of the integral in Eq. (B.3) gives

$$f_1^{(1)}(t'') \approx e^{-\mathcal{X}_1(t''-t)} \left\{ f_1^{(1)}(t) + (t''-t) \left. \frac{\partial f_1^{(1)}(t)}{\partial t} \right|_{\text{coll}} \right\} \quad (\text{B.5})$$

Substitution of this into Eq. (B.2), truncation to keep at most linear terms in the collisional rate of change, recognizing that the lower limit of the  $t''$  integral can be set at the (finite) collision starting time  $t_0$  for the finite-ranged potential, and integration by parts leads to

$$\begin{aligned} f_{12}^{(2)}(t) &= f_1^{(1)}(t) f_2^{(1)}(t) + \int_{t_0}^t e^{-\mathcal{L}_{12}(t-t'')} \Theta_{12} e^{-\mathcal{X}_{12}(t''-t)} \\ &\quad \times \left\{ f_1^{(1)}(t) f_2^{(1)}(t) - (t-t'') \left. \frac{\partial f_1^{(1)} f_2^{(1)}}{\partial t} \right|_{\text{coll}} \right\} dt'' \\ &= \mathfrak{G}_{12} \left\{ f_1^{(1)}(t) f_2^{(1)}(t) - (t-t_0) \left. \frac{\partial f_1^{(1)} f_2^{(1)}}{\partial t} \right|_{\text{coll}} \right\} \\ &\quad + \int_{t_0}^t e^{-\mathcal{L}_{12}(t-t'')} e^{-\mathcal{X}_{12}(t''-t)} dt'' \left. \frac{\partial f_1^{(1)} f_2^{(1)}}{\partial t} \right|_{\text{coll}} \end{aligned} \quad (\text{B.6})$$

In evaluating this result it has been recognized that for a finite-ranged potential the limit in Eq. (48) is unnecessary; it is only necessary to go back to the time  $t_0$  at the start of the collision from the present time  $t$ . Thus the appropriate phase transformation is related to the (negative) time interval  $t_0 - t$ , so that

$$\mathfrak{S}_{12} = e^{\mathcal{L}_{12}(t_0 - t)} e^{-\mathcal{K}_{12}(t_0 - t)}$$

Since the integral in the last term involves oscillating exponentials, a reasonable approximation is to assume that the integral vanishes. Since  $\mathfrak{S}_{12}$  replaces the two-particle momenta by their binary collision initial values, Eq. (B.6) contains the same first-order corrections to nonlocality as does Eq. (28) provided the homogeneous correction term as discussed in Section 5 is included in the latter. In conclusion, the binary collision approximation gives the same first-order corrections to the local Boltzmann equation as does Green's method as long as the latter includes as a contribution the collisional rate of change of the singlet.

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## REFERENCES

1. M. W. Thomas and R. F. Snider, *J. Stat. Phys.* **2**:61 (1970).
2. R. F. Snider, *J. Stat. Phys.* **61**:443 (1990).
3. D. Enskog, *Kgl. Svenska Vetenskapskad. Handl.* **63**(4) (1922).
4. N. Bogoliubov, *J. Phys. U.S.S.R.* **10**:265 (1946); Problems of a dynamical theory in statistical physics, in *Studies in Statistical Physics*, Vol. I, Part A, J. de Boer and G. E. Uhlenbeck, eds. (North-Holland, Amsterdam, 1962).
5. H. S. Green, *The Molecular Theory of Fluids* (Dover, New York, 1969).
6. J. H. Irving and J. G. Kirkwood, *J. Chem. Phys.* **18**:817 (1950).
7. H. J. Kreuzer, *Nonequilibrium Thermodynamics and Its Statistical Foundations* (Oxford University Press, Oxford, 1981).
8. R. F. Snider and C. F. Curtiss, *Phys. Fluids* **1**:122 (1958); **3**:903 (1960).
9. S. T. Choh, Dissertation, University of Michigan, Ann Arbor, Michigan (1958) (University Microfilms No. mic. 58-7696, Ann Arbor, Michigan).
10. J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972).
11. J. R. Dorfman and H. van Beijeren, *The kinetic theory of gases*, in *Statistical Mechanics*, Part B, B. J. Berne, ed. (Plenum Press, New York, 1977).
12. J. C. Rainwater, *J. Chem Phys.* **81**:495 (1984); D. G. Friend and J. C. Rainwater, *Chem. Phys. Lett.* **107**:590 (1984); J. C. Rainwater and D. G. Friend, *Phys. Rev.* **36**:4062 (1987).
13. D. E. Stogryn and J. O. Hirschfelder, *J. Chem. Phys.* **31**:1545 (1959); **33**:942 (1960).



14. Yu. L. Klimontovich, *Kinetic Theory of Nonideal Gases and Nonideal Plasmas* (Pergamon Press, Oxford, 1982).
15. R. F. Snider, F. Laloë, and W. J. Mullin, *Physica A*, in press.
16. D. B. Boercker and J. W. Dufty, *Ann. Phys.* **119**:43 (1979).
17. M. Born and H. S. Green, *Proc. Soc. Lond. A* **188**:10 (1946).
18. J. G. Kirkwood, *J. Chem. Phys.* **14**:180 (1946).
19. J. Yvon, *La Théorie Statistique des Fluides et l'Équation d'État* (Hermann, Paris, 1935).
20. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
21. R. F. Snider, *J. Chem. Phys.* **32**:1051 (1960).
22. R. F. Snider and B. C. Sanctuary, *J. Chem. Phys.* **55**:1555 (1971).
23. J. Yvon, *J. Phys. Radium* **21**:569 (1960).
24. J. W. Dufty and D. B. Boercker, *J. Stat. Phys.* **57**:827 (1989).