On the Snider Equation

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We study the physical content of the Snider quantum transport equation and the origin of a puzzling feature of this equation, which implies contradictory values for the one-particle density operator. We discuss in detail why the two values are in fact not very different provided that the studied particles have sufficiently large wave packets and only a small interaction probability, a condition which puts a limit on the validity of the Snider equation. In order to improve its range of application, we propose a reinterpretation of the equation as a "mixed" equation relating the real one-particle distribution function (on the left-hand side of the equation) to the "free" distribution (on the right-hand side), which we have introduced in a recent contribution. In its original form, the Snider equation is valid only when used to generate Boltzmann-type equations where collisions are treated as point processes in space and time (no range, no duration); in this approximation, virial corrections are not included, so that the real and free distributions coincide. If the equation is used beyond this approximation to generate nonlocal and density corrections, we conclude that the results are not necessarily correct.

1. INTRODUCTION

In the study of transport properties of dilute gases with internal quantum numbers (e.g., spin), a well-known starting point is the so-called Waldmann–Snider quantum transport theory.[1,2] Actually, a closer inspection shows that the theories of these two authors are substantially different, even if they both lead to the same results in the limiting case where the duration and range of collisions are ignored: one then simply recovers the Boltzmann equation (or Wang Chang–Uhlenbeck equation[3] if the par-

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ticles have internal variables but only diagonal internal density matrices) with merely the inclusion of quantum instead of classical cross sections inside the collision integral.

Waldmann's approach to the problem is to consider in each cell of the one-molecule phase space a large number of wave packets, each with internal variables described by a density operator, and to study the effect of collisions between the wave packets on the physical observables; from this, he infers a transport equation in which the scattering amplitude for a binary collision appears as a coefficient. In other words, he uses the approach of the atomic or molecular physicist: the effect of each collision is studied as in a beam-to-beam collision experiment, and the results of this study are put almost by hand in the right-hand side of a kinetic equation. This physically intuitive point of view is also that taken more recently[4] for the study of the effects of particle indistinguishability and spin on the transport properties of quantum gases, including spin waves.

Snider, on the other hand, develops more elaborate considerations involving the use of unitary Möller operators Ω, propagators G, and Wigner transforms. His formalism allows one to recover Waldmann's results, and therefore the Boltzmann equation, in the limiting case where the distribution function varies slowly on a microscopic scale; moreover, it can also be pushed beyond these lowest order terms to provide "nonlocal" interaction terms, as we recall in the next paragraph. The basic starting point is an operatorial equation, which we call here the "Snider equation," which is

$$i\hbar \frac{\partial}{\partial t} \rho_I(1) - [H_I(1), \rho_I(1)]$$

$$= \text{Tr}_2\{[V_{II}(1, 2), \Omega \rho_I(1) \times \rho_I(2) \Omega^\dagger]\} \tag{1}$$

where ρ_I is the one-body density operator, H_I is the one-body Hamiltonian (including kinetic energy and, for particles with internal variables, the corresponding Hamiltonian), $V_{II}(1, 2)$ is the two-body interaction Hamiltonian, and Ω is the operator that transforms the base of plane waves into incoming stationary scattering states (Möller operator, which is unitary when the attractive part of the potential is not sufficient to sustain bound states, as we assume throughout this article); Tr_2 denotes the operation of partial trace with respect to all (internal and external) variables of the collision partner, and the brackets a commutator.

When a Wigner transform of the two sides of Eq. (1) is taken,[2,5] the time evolution of the distribution function (more precisely, of the distribution operator if molecules or atoms have several internal states) is obtained; on the left-hand side, one gets the usual drift term plus the evolu-

tion of internal variables (Larmor precession, for example); on the right-hand side, all the effects of the interactions are contained in the Wigner transform of a product of several operators. It is well known[8–10] that the Wigner transform of a product of two operators is not simply the product of the individual Wigner transforms; the Groenewold formula[11] shows that, in addition, it contains an infinite series of terms with higher and higher order space and momentum derivatives. Actually, what appears in (1) is the product of more than two operators, but the principle of the calculation is the same; it gives, in the same way, first a product with no derivative ("local" term, similar to the Boltzmann integral), then corrections with first-order derivatives with respect to position ("molecular field" terms), etc. Equation (68) of the original article[2] gives the local term, and the general structure of the first-order terms can be found in the work of Thomas and Snider[5]; more details can be found in Appendix A to the present article. See also refs. 12–15 for gradient expansions in different contexts.

This clearly shows the generic character of an operatorial equation such as (1), which may be used as a source of various quantum corrections to the Boltzmann equation, and is therefore worth detailed examination. In the present article, we discuss in some detail the physical assumptions behind this equation, and we make the connection with recent work in the same domain.[16] We begin, in Section 2, with the statement of three difficulties or questions which appear in the interpretation of Eq. (1). In Section 3, we discuss these difficulties in more detail, starting from the results of a short intermediate exact calculation valid for a system of two particles; we show that the major assumption behind the Snider equation is that the particles under study have a small interaction probability (large wave packets), which implies that the gas is sufficiently dilute for some density corrections to be neglected. Then, in Section 4, we propose a reinterpretation of the equation which allows one to extend the range of validity of the equation (inclusion of second virial density corrections) and solves all questions of Section 2, we believe, in a satisfactory way. Finally, in Section 5, we examine the consequences of the reinterpretation on the domain of validity of the kinetic equation.

The aim of this article is not to give a rigorous derivation of the Snider equation and its generalization to higher densities. It is rather to discuss the general physical ideas involved, in particular the quality of the approximate value of the two-body density operator which appears in the right-hand side of (1); we shall put the emphasis on the way in which it reconstructs the two-body correlations from an uncorrelated product simply with the help of Möller operators. We refer the reader to ref. 17 for a general discussion of density expansions in transport equations for dilute

gases, as well as to ref. 16 for more details on a formalism where one can obtain in a kinetic equation density corrections which are compatible with second virial corrections at equilibrium.

2. THREE DIFFICULTIES

2.1. A Contradiction

The first equation of the BBGYK hierarchy can be written

$$i\hbar \frac{\partial}{\partial t} \rho_I(1) - [H_I(1), \rho_I(1)]$$

$$= \mathrm{Tr}_2\{[V_{II}(1, 2), \rho_{II}(1, 2)]\} \tag{2}$$

To obtain (1) from (2), the authors of refs. 2 and 5 introduce the following "reasonable choice" for ρ_{II}:

$$\Omega \rho_I(1) \times \rho_I(2) \, \Omega^\dagger \tag{3}$$

The major purpose of the present article is to discuss the quality of this choice in more detail, since its physical content is not apparent at first sight. For a preliminary discussion, it is convenient to introduce the operator

$$\tilde{\rho}(1, 2) = \Omega \bar{\rho}(1) \times \bar{\rho}(2) \, \Omega^\dagger \tag{3'}$$

Now, if one identifies $\tilde{\rho}(1, 2)$ with $\rho_{II}(1, 2)$, the following equation automatically follows:

$$(N-1) \rho_I(1) = \mathrm{Tr}_2\{\rho_{II}(1, 2)\} = \mathrm{Tr}_2\{\Omega \bar{\rho}(1) \times \bar{\rho}(2) \, \Omega^\dagger\} \tag{4}$$

(where N is the number of particles; we choose the normalization of reduced density operators for which this number does not appear in the equations of the hierarchy, but in the relations of partial traces). Thus, the one-particle density operator is not equal to $\bar{\rho}(1)$, because of the effect of the Ω operators in the right-hand side of (4) (except, of course, in the trivial case where the particles do not interact, so that the Ω operators are simply equal to one; in the general case, we discuss their effect in more detail in Section 3). In other words, in (3'), either $\bar{\rho}$ is the one-particle density operator, or $\tilde{\rho}$ is the two-particle density operator, but the two cannot be simultaneously true. Taking (3) for the two-body density operator is, in this sense, self-contradictory.

2.2. One- and Two-Body Hamiltonians

The second question we wish to discuss is actually not independent of the first, but here we put more emphasis on the unsymmetrical treatment of one-body and two-body Hamiltonians in (1). The first BBGYK equation written in (2) is strictly equivalent to

$$(N-1)\,i\hbar\,\frac{\partial}{\partial t}\,\rho_{\mathrm{I}} = \mathrm{Tr}_2\{[H_{\mathrm{I}}(1) + (N-1)\,V_{\mathrm{II}}(1,2), \rho_{\mathrm{II}}(1,2)]\} \qquad (5)$$

It looks natural, if one approximates the two-body density operator by (3), to treat the Hamiltonians H_{I} and V_{II} on the same footing and to insert directly (3) into (5); the result is

$$(N-1)\,i\hbar\,\frac{\partial}{\partial t}\,\rho_{\mathrm{I}} = \mathrm{Tr}_2\{[H_{\mathrm{I}}(1) + (N-1)\,V_{\mathrm{II}}(1,2), \Omega\rho_{\mathrm{I}}(1) \times \rho_{\mathrm{I}}(2)\,\Omega^\dagger]\} \quad (1')$$

From a purely logical point of view, this procedure seems to be as well founded as that which leads to (1), and one could expect (1') to be equivalent to (1), but in fact they are different. The difference occurs only in the "drift term" [the term in $H_{\mathrm{I}}(1)$] of the equations, and can be seen more easily if a Wigner transform is taken: for spinless particles, the drift term of (1) then merely becomes the usual term of the Boltzmann equation, while that of (1') has a more complicated structure which depends in general on the properties of the Möller operator Ω. We do not give this calculation explicitly here (it is actually very similar to that given in the Appendix, the only change being a replacement of the element of the T matrix by the same element of the Ω matrix, multiplied by the square of the wave vector of particle 1). We just note that the Snider approximation treats one- and two-body Hamiltonians in a different way for reasons which are not obvious at first sight (see also footnote 3 in Section 3.3).

2.3. Virial Corrections

We consider again a homogeneous system of spinless particles and now focus on the values of the one-particle Wigner transform $f_{\mathrm{I}}(\mathbf{p})$ at equilibrium. Because the evolution of f_{I} is exactly that predicted by the Boltzmann equation in this particular case, it relaxes toward a Gaussian function of $\mathbf{p}$ in a time of the order of the time between collisions. This is indeed the well-known correct result for the equilibrium of a classical ideal gas, but does not contain the second virial corrections to the distribution, which, quantum mechanically, changes the $\mathbf{p}$ dependence in general (there are corrections due to both interactions and pure statistics). Therefore, if

the Snider equation does not include these corrections in its local terms, one may also question the physical significance of its nonlocal corrections.

The problem of virial corrections to the pressure is in fact discussed in Section 4.1 of ref. 5; from a Gaussian distribution function f_1 the authors find a virial correction which resembles, but does not reproduce exactly, the quantum Beth–Uhlenbeck formula. Later, Snider and Rainwater redid this calculation[19] and showed that, if one adds virial corrections into f_1, two new terms arise in the calculation, a first which cancels the result of ref. 5, and a second which introduces exactly the Beth–Uhlenbeck virial correction. By this method, the exact equilibrium result is recovered. In our opinion, this procedure is nevertheless somewhat self-contradictory: the expression of the pressure tensor is obtained from a study of the conservation laws in the frame of a nonlocal kinetic equation, but the distribution function which is chosen at equilibrium is not a stationary solution of the same kinetic equation.

3. DISCUSSION

In order to obtain a better physical understanding of the preceding difficulties, we begin with the study of a simple case: the evolution of a two-particle system, which can be calculated exactly. This will help clarify the approximations behind (1).

3.1. An Exact Calculation (Two-Body Collision)

Let us consider a simple problem: two atoms (or molecules) are coming toward each other; because they originate from different beams, they are initially uncorrelated. During collision, correlations are of course introduced by the interactions, and the two-body density operator $\rho_{\rm II}$ is no longer a product of two one-body density operators. Nevertheless, if one uses the inverse unitary Möller transformation, which, by definition, transforms the full two-body Hamiltonian into the sum of the two kinetic energies only (it "switches off" the interaction V_{12}), one goes to the "interaction point of view" where each particle becomes free, so that an initial factorization is always perfectly conserved; therefore, if one defines

$$\bar{\rho}_{\rm free}(1, 2) = \Omega^\dagger \rho_{\rm II}(1, 2)\, \Omega \tag{6}$$

one can write

$$\bar{\rho}_{\rm free} = \bar{\rho}_1(1) \times \bar{\rho}_2(2) \tag{7}$$

(initially, the factorization is due to the fact the unitary transformation has no effect before the two wave packets overlap). Although we have not

written explicitly the time dependence of the $\bar{\rho}$'s in the above equations, they are valid at any time t. The operators $\bar{\rho}_{1,2}$ are nothing but the density operators at time t of two free, noninteracting particles which started in the past from the same density operators as the two real atoms. Conversely, one has

$$\rho_{\mathrm{II}} = \Omega\bar{\rho}_{\mathrm{free}}\Omega^{\dagger} = \Omega\bar{\rho}_1(1) \times \bar{\rho}_2(2)\,\Omega^{\dagger} \tag{8}$$

which allows one to express the two-body density operator in terms of the individual operators $\bar{\rho}$ introduced in (6). We can therefore substitute this result into the first BBGKY equation [in either form (2) or (5)] and obtain a result which looks similar to the Snider equation:

$$i\hbar\frac{\partial}{\partial t}\rho_{\mathrm{I}}(1) - [H_{\mathrm{I}}(1),\,\rho_{\mathrm{I}}(1)]$$

$$= \mathrm{Tr}_2\{[V_{12},\,\Omega\bar{\rho}(1) \times \bar{\rho}(2)\,\Omega^{\dagger}]\} \tag{9}$$

(we assume that the initial density operators of the two atoms are the same, so that we no longer have to distinguish between $\bar{\rho}_1$ and $\bar{\rho}_2$, and write $\bar{\rho}$ their common value).

Actually, Eqs. (1) and (9) would be identical if the two density operators ρ_{I} and $\bar{\rho}$ were equal. Nevertheless, this is not the case in general: both operators are obtained from the same initial conditions, but while the former includes the effects of the interations, the latter corresponds to completely noninteracting particles. The discussion of the validity of the Snider equation is closely related to the evaluation of the consequences of substituting ρ_{I} for $\bar{\rho}$ in (8).

3.2. An Approximation

Still considering a two-particle system, we now discuss the quality of the approximation where $\bar{\rho}$ is replaced by ρ_{I}. To evaluate mathematically the difference between these two operators, one can insert the relation

$$\Omega = 1 + GV_{\mathrm{II}}\Omega = 1 + GT \tag{10}$$

inside

$$\rho_{\mathrm{I}}(1) = \mathrm{Tr}_2\{\rho_{\mathrm{II}}(1, 2)\} = \mathrm{Tr}_2\{\Omega\bar{\rho}(1) \times \bar{\rho}(2)\,\Omega^{\dagger}\} \tag{11}$$

(where G is the free-particle propagator and T the transition matrix of ordinary collision theory) and one obtains

$$\rho_{\mathrm{I}}(1) - \bar{\rho}(1) = \mathrm{Tr}_2\{GT\bar{\rho}(1) \times \bar{\rho}(2) + \mathrm{h.c.}\}$$

$$+ \mathrm{Tr}_2\{GT\bar{\rho}(1) \times \bar{\rho}(2)\,T^{\dagger}G^{\dagger}\} \tag{12}$$

where h.c. stands for Hermitian conjugate. Then one can, for example, expand T in powers of the interaction potential to obtain the right-hand side of (12) to all orders in $V_{\mathrm{II}}(1, 2)$. Of course, long before collision, when the wave packets are not yet overlapping, the action of the Möller operator reduces to unity (the incoming stationary scattering states are precisely built for this purpose) and (12) is equal to zero; but this is not a very interesting case because, before collision, the right-hand side of (9) vanishes anyway. In general, during (or after) collision, the two operators $\bar{\rho}$ and ρ_{I} are distinct.

For a more detailed discussion, it is useful to apply a Wigner transformation to relations (8) and (11); this introduces the transform of ρ_{II}, which depends on the positions and momenta of the two particles, or equivalently of the relative position and momentum:

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \tag{13}$$

and

$$\mathbf{p} = (\mathbf{p}_1 - \mathbf{p}_2)/2 \tag{14}$$

as well as of the position $\mathbf{R}$ and momentum $\mathbf{P}$ of the center of mass. The mathematical form of the result can be found in Appendix B, but here we limit ourselves to a general discussion without technical details. The partial trace over the variables of particle 2 which appears in (11) corresponds, in terms of the Wigner transform, to an integration over $\mathbf{r}_2$ and $\mathbf{p}_2$ in all space, or equivalently over $\mathbf{r}$ and $\mathbf{p}$ (with a factor 8 of no importance to the present discussion). The one-particle density operator ρ_{I} can therefore be obtained as the sum of the contributions of three different regions in the phase space:

(i)   The "entering region": When r is large enough (compared to the range of the potential and the de Broglie wavelength) and when the scalar product $\mathbf{p} \cdot \mathbf{r}$ is negative, one is considering a region of the phase space which corresponds to particles coming toward each other (incoming part of the wave packet); they have not yet interacted, and the effect of the Ω operators in (8) can be ignored. For these regions, the Wigner transform of ρ_{II} coincides with the product of the Wigner transforms of $\bar{\rho}_1$ and $\bar{\rho}_2$, and the corresponding contribution to ρ_{I} in the partial trace (11) is simply proportional to $\bar{\rho}_1$.

(ii)   The "interaction region": For small values of the interatomic distance r, the particles are in the middle of a collision and the role of the Ω operators in (8) is now essential: they introduce the short-range correlations which are created by the potential. The Wigner transform of ρ_{II} is therefore significantly different from the product of the Wigner transforms

of the $\bar{\rho}$'s; for example, if the interaction potential includes a hard core, the former vanishes at short relative distances, but not the latter.

(iii)   The "outgoing region": Here r is large, but the scalar product $\mathbf{p} \cdot \mathbf{r}$ is now positive. For this region, the effect of the Ω operators in (8) is to go from free particles, which propagate in straight lines, to interacting particles, which scatter each other. In general, this process can completely change the direction of $\mathbf{p}$ (and that of $\mathbf{p}_1$) as well as the location of a particle after collision. Now, if the wave packets of the particles are not too wide (not much wider than the square root of the collision cross section) and go through the same region of space, they are totally scattered by their mutual interaction; then, because the outgoing region of phase space can only be reached after a scattering process, for this region of phase space ρ_I receives in the partial trace of (11) a contribution which is completely different from $\bar{\rho}$. Nevertheless, in the opposite case, that is, when the initial wave packets are much broader than the scattering cross section, there is a large probability that the particles will "miss" the potential and not be scattered at all, so that the contribution to ρ_I remains proportional to $\bar{\rho}$ in a large fraction of the "outgoing region." There is of course still a part of this region where the effect of the potential is important: the "wake" of the particles, where the potential generates scattered waves and, at the same time, creates by destructive interference a "shadow" in the incident wave corresponding to particles disappearing from the initial velocity; it is clear that this region gives in general very different contributions to the two operators. But, if the wave packets are sufficiently large, most of the outgoing region remains insensitive to the potential and contributes in the same way to ρ and $\bar{\rho}$.

We are now in a position to predict when the substitution of ρ_I for $\bar{\rho}$ is a good approximation: this is the case as long as the total probability that the particles are being scattered, or have been scattered in the past, remains small. This happens, for instance, if the regions of the phase space where the Wigner transform of the density operator ρ_{II} is not zero are mostly regions where $\mathbf{r} \cdot \mathbf{p}$ is negative, extending only slightly over regions of positive values of this scalar product; in other words, in situations where only the "heads" of the wave packets have already scattered each other. But, more generally, it is also true in every situation where the wave packets are wide enough (compared to the square root of the cross section) so that most of them are not scattered and remain insensitive to the effects of the potential. Then, Eq. (3) can be used as a good approximation to ρ_{II}; this is correct even at a short relative distance between the particles, in regions where the potential is strong, because the effect of the Ω operators in (3) is precisely to add to ρ_{II} the appropriate short-range correlations which do not exist in the product of the one-particle operators.

But one must keep in mind that, for small wave packets which are in the middle of a collision and efficiently scattering each other, or after this type of collision has occurred, (3) is a bad approximation to the short-distance properties of ρ_{II} and should not be used; in a sense (3) takes into account the effects of the potential twice, because they already strongly affect ρ_{I} and are added again by the Ω operators. To give a comparison, a similar error would be to replace ρ_{free} by ρ_{II} itself in (8), where the unitary transformation Ω would then introduce again the correlations already contained in ρ_{II}. Using (3) is acceptable only for large wave packets because then the product $\rho_{\mathrm{I}}(1) \times \rho_{\mathrm{I}}(2)$ resembles locally much more ρ_{free} than ρ_{II} itself.

3.3. Relation to the Snider Equation

We now apply the preceding discussion to the derivation of a kinetic equation for the study of a gas containing a large number of particles in a nonequilibrium situation. The gas is supposed to be sufficiently dilute to justify a study in terms of two-body collisions only; three- or higher-particle interactions are therefore ignored. A dilute gas is of course different from a two-particle system; for example, for times long compared to the average time between collision τ_{ic}, practically all atoms have undergone multiple collisions, while this never happens for an isolated system of two particles only. But, for times short compared to τ_{ic}, nothing takes place in the gas but almost isolated binary collisions occurring at various points of space, so that the discussion of the preceding section is indeed a useful guide for the validity of the kinetic equation at short time scales.

Our main purpose in this section is to discuss the validity of the Snider equation in a qualitative way and to show that it is based on a low-density approximation from which second virial corrections are excluded. The arguments we give here rely rather on plausibility than on a rigorous proof (e.g., the discussion below on the size of wave packets). See Chapter 7 of ref. 17 or Eqs. (12)–(23) of ref. 18 for a derivation of the Snider equation given explicitly in terms of a density expansion of the BBGKY equations; for a detailed discussion leading to a precise estimation of the density corrections to the Snider equation (at least up to second virial type corrections), we refer the reader to the formalism developed in ref. 16.

Mathematically, if one inserts (12) into the commutator in the right-hand side of (9), one can have an idea of the kinds of terms ignored in the Snider equation. Because the right-hand side of (12) is already a density correction to the one-body operator, proportional to the square of the one-particle density, its insertion into the commutator containing V_{12} of (9) will give a term cubic in density (this can also be seen by using the density

expansions of ref. 17 and, incidentally, provides a satisfactory answer to the question asked in Section 2.2). Therefore, we expect that the neglected terms are higher-order corrections to the ordinary Boltzmann collision term.

The crucial point for the validity of this equation is not so much the accuracy of the choice made in (3) for $\rho_{\mathrm{II}}(1, 2)$ in itself, but the consequences of this choice on the value of the commutator with $V_{\mathrm{II}}(1, 2)$ which appears in (1). Since the interatomic potential has a finite (microscopic) range, what really matters are the properties of this density operator when the particles are at short relative distance.[3] Now, the unitary transformation associated with Ω can totally modify the direction of $\mathbf{r}$, but not much its length r (the relative distance between the particles), the maximum change being of the order of a few times the potential range or the de Broglie wavelength. Consequently, the short-distance properties of (3) depend mostly on the properties of the Wigner transforms of $\rho_{\mathrm{I}}(1)$ and $\rho_{\mathrm{I}}(2)$ at the same point of space, or in a small microscopic domain centered around the point of collision. The quality of approximation (3) is good, therefore, if locally the Wigner transform of the product $\rho_{\mathrm{I}}(1) \times \rho_{\mathrm{I}}(2)$ is a reasonable approximation to $\bar{\rho}_{\mathrm{free}}$ defined in (6), or equivalently if ρ_{I} is a good approximation to $\bar{\rho}$.

We can thus directly use the conclusions of Section 3.2 to set the limits of validity of an approximation of this type: it is good provided that the atoms in the system can be described by wave packets which are large compared to the potential range. For a many-particle system, one expects that the maximum size of the wave packets which remains compatible with a treatment of two-body interactions only is of the order of the average distance between the particles; otherwise, more than two wave packets would always overlap at every point of space. Therefore, if the gas is very dilute, the particles can indeed be described by large wave packets, and it is reasonable to assume that the local properties of the Wigner transform of the one-particle density operator reflect mostly the part of the wave packets which is uninfluenced by the interactions: any collision partner has

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[3] This remark is sometimes invoked as a solution of the difficulty mentioned in Section 2.2: the Snider approximation (3) for ρ_{II} might be appropriate at short relative distances only. In other words, it could be good for particles in the middle of a collision, but not necessarily between collisions. It would therefore give the evolution due to the two-body Hamiltonian almost correctly, but not for that due to the one-body Hamiltonian. Actually, the discussion of this section (in particular the paragraph before last) shows that this is not true: (3) is not a better (or worse) approximation to ρ_{II} at short distances than at long distances. Mathematically, this arises from the fact that (3), as well as the exact expression (8), both contain a product of operators which cannot have sharp variations when the relative distance between the particles varies over a microscopic length.

a large probability to be at a large distance, at a point of space where it cannot influence (or have influenced) the test particle. The simple decorrelation operation, where ρ_{II} is replaced by the product of its partial traces, therefore reconstructs a good approximation to ρ_{free}; that is, it is almost equivalent to the unitary transformation Ω. This is why applying Ω to the product, as in (3), is almost exactly what is needed to reconstruct the correct two-body correlations which play a crucial role during collisions. We obtain in this way the essence of the physical justification of Eq. (1).

Even if it is not directly relevant to the validity of the equation, it is instructive to discuss the precision with which (3) reproduces the two-body correlations in a dilute gas at large distances. In the "entering region," when the particles are far apart, we have seen in the preceding section that the Möller operators have no effect at all, so that ρ_{II} is predicted to be an uncorrelated product of two ρ_I operators, a well-known correct result. In the "outgoing region," the Ω operators introduce correct correlations only inside the "wake" of the particles, which is physically satisfactory, but this happens without any limit on the distance between the particles. Consequently, they fail to reproduce the progressive attenuation of these correlations when the distance becomes comparable to the mean free path in the gas, under the effect of interactions with other collision partners. Because this is an effect of multiple collisions, it is not surprising that a simple formula such as (3) is totally unable to mimic it; we have already emphasized that, because the potential range is supposed much shorter than the mean free path, this difference does not affect the right-hand side of (1).

We conclude that, for a dilute gas, the Snider procedure[2] is indeed well adapted. It is actually a very elegant way to close the infinite BBGKY hierarchy in terms of ρ_I alone; the basic idea is to replace the unitary transformation (6), which allows one to introduce a factorization, by a simple decorrelation operation. Nevertheless, one should keep in mind the limits of this method, which are clearly related to the limits of using Eq. (1) for the study of a two-particle collision: one must assume a negligibly small probability that the two particles have undergone a collision. Terms of the order of either the range of the potential or the de Broglie wavelength divided by the total length of the wave packets are neglected.[4] In other

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[4] More precisely, the error introduced by the Snider approximation to ρ_{free} is of the order of (some power of) the ratio between a microscopic length and the size of the wave packets; on the other hand, we have seen above that the approach based on the study of two-body interactions can only be valid if the size of the wave packets is not larger than the average distance between the particles. Consequently, the error is at least of the order of (some power of) the ratio between the potential range or the de Broglie wavelength and the average distance between particles, namely a virial correction.

words, one does not keep corrections[5] which are of the order of the probability that a test atom at a given time is engaged in a collision, namely second virial corrections. In the next section, we briefly discuss a method which allows one to obtain the first corrections with the help of the "free Wigner transform."

4. A PROPOSED REINTERPRETATION

Two points of view on the Snider equation are possible. The first is to consider the equation as a quantum version of the Boltzmann equation, including internal states for the particles, which is valid only to lowest order in density (no second virial corrections) and which provides correctly only local terms in the quantum collision integral. Seen in this way, the Snider equation becomes equivalent to the Waldmann equation, and all difficulties of Section 2 either have been solved in the preceding discussion or simply disappear. If one uses systematic density expansions of kinetic equations as in ref. 17, one is led rather naturally to this point of view, and the content of the present article appears mostly as a physical discussion of the lowest density orders. This is of course a perfectly acceptable viewpoint, but automatically casts doubts on the consistency of calculations based on the Snider equation such as those of ref. 19. The second point of view is to try to extend the validity of the equation to second virial corrections and nonlocal terms, and we take this attitude in all the rest of this article.

We retain two main ideas from the preceding discussion. First, in general, there is in a sense more useful information contained in $\bar{\rho}$ than ρ_I for initially uncorrelated particles: from the former one can reconstruct ρ_{II} by (8) and therefore the short-range correlations between particles which play a crucial role during the interaction; the operator ρ_I can be obtained from $\bar{\rho}$, but, in general, the reverse is not true. Since the two operators depend on the same number of parameters (they act in the same state space), $\bar{\rho}$ seems to be a better mathematical object than ρ_I to write a kinetic equation that is compatible with an improved treatment of correlations. The second is that, in the particular case where the particles have wide wave packets, the two operators coincide within corrections which are of the order of second virial corrections, and can therefore be taken equal if one is not interested in such corrections.

These two remarks bring us very close to the formalism of the "free

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[5] See also the discussion given in the paragraph just before Eq. (23) of ref. 2, where mention is made of neglected density corrections. Note also that the operator denoted $\rho^{(1)}$ in the calculation leading to this equation is the one-particle density operator just *before* collision (not during or after collision), that is, an operator very close to the entering part of the free Wigner transform used in ref. 16.

Wigner transform" developed in ref. 16, where care is taken to take into account the differences between the two operators. Roughly speaking, in this formalism, the kinetic equation is indeed written in terms of $\bar{\rho}$ (the "incoming free part") instead of ρ_I, and the correction introduced by the differences are evaluated afterward. Actually, the distribution function appearing in the kinetic equation is not exactly the Wigner transform of $\bar{\rho}$ only, because this operator describes fictitious particles which evolve very differently from the real particles after collision; the free Wigner transform is a mathematical compromise which is equal to ρ_I (and to $\bar{\rho}$) before collision, to $\bar{\rho}$ during collision, and to ρ_I again after, which is a way to switch off the interactions during collision but to retain their long-term effects. As a consequence, the free Wigner transform is a more subtle object than $\bar{\rho}$, so that the corresponding kinetic equation of ref. 16 is not simply obtained from (9), which is limited to a system of two particles.

We therefore propose to reinterpret Eq. (1), or more precisely its Wigner transform, as a mixed equation where in the right-hand side $\rho_I(1) \times \rho_I(2)$ should be replaced by the free Wigner transform (which indeed factorizes), while on the left-hand side no change is made and the usual distribution remains. Because the difference between the distributions associated with the free or the real Wigner transform is second order in density, the error introduced by confusing them is only relevant if one is interested in second-order density corrections, but can be ignored otherwise (for more details on the relation between the two distributions and on how one can carry out precise calculations based on the free distribution, see ref. 16). We come again to the same conclusion, but this time in a more precise frame where the density corrections can be obtained quantitatively: the Snider equation (1) is indeed valid, but only to lowest order in density; it should therefore not be used to obtain second virial corrections.

5. CONCLUSION

If one accepts the above reinterpretation, all the difficulties discussed in Section 2 disappear, even if density corrections to the Snider equation are taken into account. The contradiction of Section 2.1 is no longer present: if one puts the free Wigner transform in the interaction term, the equation of evolution is equivalent to (9), which is strictly exact in a two-body collision. The second virial corrections mentioned in Section 2.3 are automatically correct, since for the free Wigner transform (which characterizes the distribution of the particles only when they are far from all other particles), one has at equilibrium[16]

$$\bar{\rho} = Z^{-1} \exp(-\hat{\mathbf{p}}^2/2m) \qquad (15)$$

(with usual notation), from which the virial corrections to ρ_{I} and ρ_{II} can be obtained.[16] On this matter, we feel that the method of ref. 19 uses the Snider equation beyond its domain of validity. The origin of the unphysical model introduced in Section 2.2 is also clear: if the error made by replacing $\bar\rho$ by ρ_{I} is a first-order-in-density (relative) error, the substitution introduces only higher-order errors when made in the collision term; on the other hand, if the same procedure is applied to the drift term, which is itself only a first-order-in-density term, then an error comparable to the collision term is introduced, so that the theory is no longer valid.

Our conclusion is therefore that Eq. (1) can be used as long as one is only interested in lowest order density effects, as one does when using the Boltzmann equation. It is doubtful that the "nonlocal" terms obtained beyond the lowest order gradient terms (corrections to Boltzmann terms for particles without internal states) are physically meaningful in general, precisely because they are already virial corrections: such terms are naturally considered as "molecular field" terms which change the dispersion relation of the particles (or quasiparticles in the language of the Landau kinetic equation), and act as perturbations to the "drift" term; in other words, they are put on the left-hand side of the equation, where they introduce density corrections to the drift term, and virial corrections to transport coefficients (transport by binary collisions). Because the equation is valid only if the differences between the real and the free distribution are neglected, keeping these terms could lead to corrections which are beyond the accuracy of the calculations.

APPENDIX A. WIGNER TRANSFORM OF THE SNIDER COLLISION INTEGRAL

The Snider collision integral which appears in (1) is

$$I_{\mathrm{S}} = \mathrm{Tr}_2\{(i\hbar)^{-1}\,[V_{\mathrm{II}}(1, 2),\,\Omega\rho_{\mathrm{I}}(1)\times\rho_{\mathrm{I}}(2)\,\Omega^\dagger]\} \tag{A1}$$

Thomas and Snider give an expression of the Wigner transform of this integral and discuss its "localization"; see Eq. (12) and Section 3 of ref. 5. Here we wish to develop this calculation in a little more detail; our aim is in particular to distinguish between the "molecular field" terms which appear in the gradient expansion, and the "retardation" terms, as well as between forward and lateral scattering terms. The Wigner transform F_{W} of the function in curly brackets in (A1) is easily obtained from the general Wigner transform formula, which gives

$$F_{\mathrm{W}}(\mathbf{R}, \mathbf{r}, \mathbf{P}, \mathbf{p}) = (2\pi\hbar)^{-6}\,(i\hbar)^{-1}\int d^3K \int d^3\kappa\, e^{i\mathbf{K}\cdot\mathbf{R}}e^{i\kappa\cdot\mathbf{r}}$$
$$\times \langle \mathbf{K}_+, \mathbf{k}_+|\, V\Omega\rho_{\mathrm{I}}(1)\times\rho_{\mathrm{I}}(2)\,\Omega^\dagger\,|\mathbf{K}_-, \mathbf{k}_-\rangle + \text{c.c.} \tag{A2}$$

where

$$K_{\pm} = \frac{P}{\hbar} \pm \frac{K}{2}, \qquad k_{\pm} = \frac{p}{\hbar} \pm \frac{\kappa}{2} \tag{A3}$$

and c.c. means complex conjugate [we have simplified the notation $V_{II}(1, 2)$ to V]. Since $V\Omega = T$, the right-hand side of (A2) is equal to

$$(2\pi\hbar)^{-6} (i\hbar)^{-1} \int d^3K \int d^3\kappa \int d^3k_1 \int d^3k_2 \, e^{iK \cdot R} e^{i\kappa \cdot r} T(k_+, k_1)$$

$$\times \langle k_2 | \Psi_{k_-}^{(+)} \rangle \langle K_+, k_1 | \rho_I(1) \times \rho_I(2) | K_-, k_2 \rangle + \text{c.c.} \tag{A4}$$

with

$$T(k_+, k_1) = \langle k_+ | T | k_1 \rangle$$
$$\langle k | \Psi_k^{(+)} \rangle = \langle k | \Omega | k' \rangle \tag{A5}$$

Now, using the inverse Wigner transform formula, we can introduce into (A4) the Wigner transform $f(r, p)$ of ρ_I (to avoid unecessary complications, we consider here particles without internal structure, so that the Wigner transform is simply a function of r and p):

$$f(r_1, p_1) = \text{W.T.}\{\rho_I(1)\} \tag{A6}$$

and replace the matrix element of the product of ρ's by

$$\hbar^6 \int d^3R' \int d^3r' \, e^{-iK \cdot R'} e^{i(k_1 - k_2) \cdot r'}$$

$$\times f\left(R' + \frac{r'}{2}, \frac{P + \hbar(k_1 + k_2)}{2}\right) \times f\left(R' - \frac{r'}{2}, \frac{P - \hbar(k_1 + k_2)}{2}\right) \tag{A7}$$

When inserting this result into (A4), a delta function appears:

$$\int d^3K \, e^{iK \cdot (R - R')} = (2\pi)^3 \, \delta(R - R') \tag{A8}$$

and one finally obtains the following expression for the Wigner transform $I_S^W(r_1, p_1)$ of the Snider collision integral (A1):

$$I_S^W(r_1, p_1) = (i\hbar)^{-1} (2\pi)^{-3} \int d^3q \int d^3r \int d^3\kappa \int d^3k_1' \int d^3k_2' \int d^3r'$$

$$\times e^{i\kappa \cdot r} e^{i(k_2' - k_1') \cdot r'} T(k_+, k_1') \langle k_- | \Psi_{k_2'}^{(+)} \rangle *$$

$$\times f\left(r_1 - \frac{r - r'}{2}, \, p_1 - \frac{q}{2} + \frac{\hbar}{2}(k_1' + k_2')\right)$$

$$\times f\left(r_1 - \frac{r + r'}{2}, \, p_1 - \frac{q}{2} - \frac{\hbar}{2}(k_1' + k_2')\right) + \text{c.c.} \tag{A9}$$

with

$$\mathbf{q} = \mathbf{p}_1 - \mathbf{p}_2 = 2\mathbf{p} = 2\hbar\mathbf{k}; \qquad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \qquad (A10)$$

$$\mathbf{k}_\pm = (\mathbf{p} \pm \hbar\mathbf{\kappa})/2\hbar \qquad (A11)$$

and

$$\langle \mathbf{k} \mid \Psi_{\mathbf{k}'}^{(+)} \rangle = \delta(\mathbf{k} - \mathbf{k}') + \frac{1}{\hbar(\omega_k - \omega_{k'}) + i\varepsilon} \, T(\mathbf{k}, \mathbf{k}') \qquad (A12)$$

The right-hand side of (A9) contains a term quadratic in the T matrix, which is the contribution of lateral scattering to the collision integral, and a term linear in T, which corresponds to forward scattering.

As in ref. 5, we now assume that the one-particle distribution function varies slowly in space over microscopic distances and expand the product of f's in (A9) according to

$$f(\mathbf{r}_1, \mathbf{p}_1') f(\mathbf{r}_1, \mathbf{p}_2') - \frac{\mathbf{r}}{2} \cdot \nabla_{\mathbf{r}_1} [f(\mathbf{r}_1, \mathbf{p}_1') f(\mathbf{r}_1, \mathbf{p}_2')]$$

$$+ \frac{\mathbf{r}'}{2} \cdot [f(\mathbf{r}_1, \mathbf{p}_1') \nabla_{\mathbf{r}_1} f(\mathbf{r}_1, \mathbf{p}_2') - f(\mathbf{r}_1, \mathbf{p}_2') \nabla_{\mathbf{r}_1} f(\mathbf{r}_1, \mathbf{p}_1')] + \dots \qquad (A13)$$

with the notation

$$\mathbf{p}_{1,2}' = \mathbf{p}_1 - \frac{\mathbf{q}}{2} \pm \frac{\hbar}{2}(\mathbf{k}_1 + \mathbf{k}_2) \qquad (A14)$$

The first term in (A13) corresponds to the "local" term, the two which follow to first order (in gradients) nonlocal terms.

A1. Local Term

To zeroth order in gradients, the following two integrals occur:

$$\int d^3r \, e^{i\mathbf{\kappa} \cdot \mathbf{r}} = (2\pi)^3 \, \delta(\mathbf{\kappa}) \qquad (A15)$$

and

$$\int d^3r' \, e^{i(\mathbf{k}_2' - \mathbf{k}_1') \cdot \mathbf{r}'} = (2\pi)^3 \, \delta(\mathbf{k}_1' - \mathbf{k}_2') \qquad (A16)$$

The forward scattering term then becomes

$$(i\hbar)^{-1} \int d^3q \, [T_k(1) - T_k^*(1)] \, f(\mathbf{r}_1, \mathbf{p}_1) f(\mathbf{r}_1, \mathbf{p}_1 - \mathbf{q})$$

$$= -\int d^3q \, \frac{q}{m} \, \sigma_T(k) \, f(\mathbf{r}_1, \mathbf{p}_1) f(\mathbf{r}_1, \mathbf{p} - \mathbf{q}) \qquad (A17)$$

where σ_T is the total cross section, defined as usual as a function of the T matrix. In the lateral scattering term, the following function appears under the integral:

$$|T(\mathbf{k}, \mathbf{k}')|^2 \left\{ \frac{1}{\hbar(\omega_k - \omega_{k'}) - i\varepsilon'} - \text{c.c.} \right\} = \frac{2i\pi}{\hbar} \delta(\omega_k - \omega_{k'}) |T(\mathbf{k}, \mathbf{k}')|^2 \quad (A18)$$

so that one gets

$$\int d^3q \int d^2\hat{k}' \, \sigma_k(\mathbf{k}, \mathbf{k}') f\left(\mathbf{r}_1, \mathbf{p}_1 - \frac{\mathbf{q}}{2} + \hbar k\mathbf{k}'\right) f\left(\mathbf{r}_1, \mathbf{p}_1 - \frac{\mathbf{q}}{2} - \hbar k\mathbf{k}'\right) \quad (A19)$$

with the classical notation $\sigma_k(\mathbf{k}, \mathbf{k}')$ for the collision cross section corresponding to a change of the relative momentum from $\hbar k\mathbf{k}$ to $\hbar k\mathbf{k}'$.

Therefore, the local term is nothing but the Boltzmann collision integral for particles without internal levels.

A2. First-Order Terms

A2.1. r Gradients. For the term linear in $\mathbf{r}$, the delta function of (A15) is replaced by the gradient of a delta function, implying that one has to take the derivative with respect to $\boldsymbol{\kappa}$ of the function under the integral. This introduces a contribution proportional to

$$\int d^3q \int d^3k' \, \nabla_{\mathbf{k}} [T(\mathbf{k}, \mathbf{k}')\langle \mathbf{k} | \Psi_{\mathbf{k}'}^{(+)} \rangle + \text{c.c.}]$$

$$\cdot \nabla_{\mathbf{r}_1}\left[f\left(\mathbf{r}_1, \mathbf{p}_1 - \frac{\mathbf{q}}{2} + \hbar\mathbf{k}'\right) f\left(\mathbf{r}_1, \mathbf{p}_1 - \frac{\mathbf{q}}{2} - \hbar\mathbf{k}'\right)\right] \quad (A20)$$

The corresponding terms are "retardation" terms, which contain a single $\mathbf{r}$ derivative of the distribution function; they contain "off-shell" values of the T matrix. Inserting (A12) shows that these retardation effects occur for both forward and lateral scattering. Actually, the off-shell terms in lateral scattering turn out to have convergence problems,[20] but this is not the object of the discussion here.

A2.2. r′ Gradients. These gradients have a more complicated structure, which is natural, since the relative position, more than the center-of-mass position, is the relevant variable modified by the collision. The right-hand side of (A16) is now replaced by the derivative of a delta function of the difference $(\mathbf{k}_2 - \mathbf{k}_1)$, which introduces two kinds of terms:

(i) Taking the derivative of the T's produces more retardation terms, which add to the terms obtained in Section A2.1; we do not write them explicitly, but they are easy to calculate.

(ii) Taking the derivative of the distribution functions themselves introduces new kinds of terms, which are similar to "molecular field" terms. We only sketch here the structure of the forward scattering term:

$$\int d^3q[\cdot]\ [\nabla_{\mathbf{p}_1}\cdot\nabla_{\mathbf{r}_1}-\nabla_{\mathbf{p}_1}\cdot\nabla_{\mathbf{r}_2}-\nabla_{\mathbf{p}_2}\cdot\nabla_{\mathbf{r}_1}+\nabla_{\mathbf{p}_2}\cdot\nabla_{\mathbf{r}_2}]\,f(\cdot)\,f(\cdot)\quad (A21)$$

Strictly speaking, only the first of the four cross-derivatives is really a molecular field term, but the three others are direct generalizations. For the lateral scattering terms, a formula similar to (A21) is obtained, but as in (A19), the integral is a five-dimensional integral. All these terms contain only "on-shell" T-matrix elements.

APPENDIX B. WIGNER TRANSFORM OF RELATIONS (8) AND (11)

Relations (8) and (11) are central in the arguments developed in this article, where we have limited ourselves to qualitative discussions. Here we give the precise expressions of their Wigner transforms. With notation similar to that of Section 1, we obtain the following expression for the Wigner transform of (8):

$$f_{\mathrm{II}}^{\mathrm{W}}(\mathbf{R},\mathbf{r},\mathbf{P},\mathbf{p})=(2\pi)^{-3}\int d^3\kappa\int d^3k_1\int d^3k_2\int d^3r'$$

$$\times e^{i\boldsymbol{\kappa}\cdot\mathbf{r}}e^{i(\mathbf{k}_2-\mathbf{k}_1)\cdot\mathbf{r}'}\langle\mathbf{k}_+\mid\Psi_{\mathbf{k}_1}^{(+)}\rangle\langle\Psi_{\mathbf{k}_2}^{(+)}\mid\mathbf{k}_-\rangle^*$$

$$\times\bar{f}\left(\mathbf{R}+\frac{\mathbf{r}'}{2},\frac{\mathbf{P}+\hbar(\mathbf{k}_1+\mathbf{k}_2)}{2}\right)\bar{f}\left(\mathbf{R}-\frac{\mathbf{r}'}{2},\frac{\mathbf{P}-\hbar(\mathbf{k}_1+\mathbf{k}_2)}{2}\right)$$

$$\text{(B1)}$$

where $f_{\mathrm{II}}^{\mathrm{W}}$ is the Wigner transform of the two-body density matrix, and $\bar{f}$ that of $\bar{\rho}$. Equation (B1) gives the effect of the unitary transformation on the Wigner transform. To obtain the Wigner transform f_{I} of ρ_{I} from this equation, one has to make the following substitutions:

$$\mathbf{R}\Rightarrow\mathbf{r}_1-\mathbf{r}/2\qquad\qquad(B2)$$

$$\mathbf{P}\Rightarrow2\mathbf{p}_1-\mathbf{q}\qquad\qquad(B3)$$

in (B1) and integrate it over d^3r and d^3q in all space, which gives the Wigner transform of (11):

$$f_I(\mathbf{r}_1, \mathbf{p}_1) = (2\pi)^{-3} \int d^3r \int d^3q \int d^3\kappa \int d^3k_1 \int d^3k_2 \int d^3r'$$

$$\times e^{i\kappa \cdot \mathbf{r}} e^{i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}'} \langle \mathbf{k}_+ | \Psi_{k_1}^{(+)} \rangle \langle \Psi_{k_2}^{(+)} | \mathbf{k}_- \rangle^*$$

$$\times \bar{f} \left(\mathbf{r}_1 + \frac{\mathbf{r}' - \mathbf{r}}{2}, \mathbf{p}_1 - \frac{\mathbf{q}}{2} + \hbar \frac{\mathbf{k}_1 + \mathbf{k}_2}{2} \right)$$

$$\times \bar{f} \left(\mathbf{r}_1 - \frac{\mathbf{r}' + \mathbf{r}}{2}, \mathbf{p}_1 - \frac{\mathbf{q}}{2} - \hbar \frac{\mathbf{k}_1 + \mathbf{k}_2}{2} \right) \qquad (B4)$$

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