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Kinetic Theory beyond the Stosszahlansatz

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Abstract: In a recent paper (Chliamovitch, et al., 2015), we suggested using the principle of maximum entropy to generalize Boltzmann's Stosszahlansatz to higher-order distribution functions. This conceptual shift of focus allowed us to derive an analog of the Boltzmann equation for the two-particle distribution function. While we only briefly mentioned there the possibility of a hydrodynamical treatment, we complete here a crucial step towards this program. We discuss bilocal collisional invariants, from which we deduce the two-particle stationary distribution. This allows for the existence of equilibrium states in which the momenta of particles are correlated, as well as for the existence of a fourth conserved quantity besides mass, momentum and kinetic energy.

Keywords: kinetic theory; non-equilibrium statistical mechanics; maximum entropy principle

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1. Introduction

From the very beginnings and at the very heart of the kinetic theory of gases lies a restrictive technical assumption (known as Stosszahlansatz or assumption of molecular chaos) about the state of particles entering a binary collision, namely that the momenta of such colliding particles are statistically independent. Of course this assumption did not prevent kinetic theory from achieving remarkable successes in diversified areas of statistical mechanics, fluid dynamics and others, and even from a purely conceptual standpoint, the controversies raised by the time irreversibility resulting from the Stosszahlansatz have been settled to a large extent, so that the molecular chaos can no longer be considered a central issue of theoretical physics [1].

Still, however, although exact results have been obtained regarding its range of validity [2,3], from a purist's perspective, the Stosszahlansatz is little more than an ad hoc assumption. Unfortunately, the way it could be complemented or generalized is anything but obvious, so it might seem that the ansatz is here to stay. Nonetheless, our point in this paper, first raised in [4], is to suggest that such a generalization can be achieved at the cost of a conceptual shift as to the actual meaning of the Stosszahlansatz itself. At first glance, the scope of this assumption seems unambiguous, for the factorization hypothesis should be no more than the mathematical translation of a physical (though statistical) property of the system.

Readers familiar with the maximum entropy approach to statistical inference [5–8] will remember, however, that a factorized joint distribution is the maximum entropy estimate based on the knowledge of univariate marginal distributions. In other words, the factorization of the two-particle function describing the particles entering a collision can be envisaged as a heuristic hypothesis rather than a purely physical statement.

So far, this may appear to be a rhetoric move, since from a mathematical standpoint the move is harmless; however, from a conceptual perspective, it makes quite a difference, for while the factorization hypothesis is hard to amend on physical grounds, on the other side, the maximum entropy factorization lends itself nicely to generalization. This maximum entropy ansatz on the three-particle distribution then allows closing the BBGKY hierarchy at the second order and deriving a kinetic equation describing the evolution of the two-particle distribution.

Once the kinetic equation is set up, it becomes possible to follow the usual steps leading to the equilibrium distribution and macroscopic balance equations. There is however on the road a subtlety related to the definition of collisional invariants appropriate to the bilocal events under consideration here, and it happens that, besides conservation of (bilocal) mass, momentum and kinetic energy, it is necessary to consider a fourth invariant that eventually accounts for the momentum correlation of particles.

The aim of this paper is to discuss these conceptual points in detail. In Sections 2 and 3, we derive the BBGKY equation at the second order. In Section 4, we introduce the maximum entropy ansatz for the three-particle distribution and the resulting closure of the hierarchy. Bilocal collisional invariants are discussed in Section 5, equilibrium distributions in Section 6, and balance equations in Section 7. We conclude with some remarks of a more philosophical flavour, emphasizing among others that what appears to be intuitive when working in the one-particle description does not necessarily hold any longer in the two-particle description.

2. Liouville Equation and BBGKY Hierarchy

Let us consider N particles of mass m, whose coordinates in phase space are their positions $\mathbf{x}_i$ and momenta $\mathbf{p}_i$. It will be convenient to define a condensed notation $\xi_i = (\mathbf{x}_i, \mathbf{p}_i)$. We let $f_N(\xi_1, ..., \xi_N, t)$ denote the joint distribution function characterizing the system; f_N obeys Liouville's equation [9]

$$\frac{df_N}{dt} = \frac{\partial f_N}{\partial t} + \sum_{i=1}^{N} \frac{\mathbf{p}_i}{m} \frac{\partial f_N}{\partial \mathbf{x}_i} + \sum_{i=1}^{N} \mathbf{F}_i \frac{\partial f_N}{\partial \mathbf{p}_i} = 0 \tag{1}$$

where $\mathbf{F}_i$ denotes the force exerted on particle i. We shall restrict ourselves to the case without an external force and where particles interact pairwise through some radial potential $V(|\mathbf{x}_i - \mathbf{x}_j|) = V_{ij}$, so that $\mathbf{F}_i = -\sum_{j\neq i} \frac{\partial V_{ij}}{\partial \mathbf{x}_i}$. Considering that f_N itself is normalized to $N!$, we can introduce the reduced s-particle distribution $f_s(\xi_1, ..., \xi_s, t) = \frac{N!}{(N-s)!} \int d\xi_{s+1}, ..., d\xi_N f_N(\xi_1, ..., \xi_N, t)$.

Liouville's equation is a direct consequence of Newtonian dynamics, and as such is reversible. In particular, it should be recalled [10–12] that, in contradistinction with the entropy of the one-particle distribution, the entropy of the N-particle density, namely

$$H(f_N) = -\int d\xi_1 ... d\xi_N f_N(\xi_1, ..., \xi_N) \ln f_N(\xi_1, ..., \xi_N) \tag{2}$$

is conserved by Equation (1). The emergence of irreversibility in the reduced one-particle description has been discussed more than extensively (for an interesting elementary presentation, see [13]), but it is clear nowadays that it results unavoidably from integrating out degrees of freedom that are irrelevant to the description [14].

By integrating Liouville's equation $(N - s)$ times, one obtains a dynamical equation for f_s, which, however, lets intervene $f_{(s+1)}$; we actually obtain a hierarchy of implicit kinetic equations, the so-called BBGKY hierarchy (from the non-chronological list of its co-discoverers' names: Bogoliubov, Born, Green, Kirkwood, Yvon). The typical term of the hierarchy for f_s is

$$\frac{\partial f_s}{\partial t} + \sum_{i=1}^{s} \frac{\mathbf{p}_i}{m} \frac{\partial f_s}{\partial \mathbf{x}_i} - \sum_{i=1}^{s} \sum_{j\neq i}^{s} \frac{\partial V_{ij}}{\partial \mathbf{x}_i} \frac{\partial f_s}{\partial \mathbf{p}_i} - \int d\xi_{s+1} \sum_{i=1}^{s} \frac{\partial V_{i,s+1}}{\partial \mathbf{x}_i} \frac{\partial f_{s+1}}{\partial \mathbf{p}_i} = 0 \tag{3}$$

Certainly, each equation can be deduced from its higher-order precursor by integration, at the cost of an information loss. The first two members, BBGKY1 and BBGKY2, in which we are primarily interested here, read

$$\frac{\partial f_1}{\partial t} + \frac{\mathbf{p}_1}{m}\frac{\partial f_1}{\partial \mathbf{x}_1} = \int d\xi_2 \frac{\partial V_{12}}{\partial \mathbf{x}_1}\frac{\partial f_2}{\partial \mathbf{p}_1} \tag{4}$$

and

$$\frac{\partial f_2}{\partial t} + \frac{\mathbf{p}_1}{m}\frac{\partial f_2}{\partial \mathbf{x}_1} + \frac{\mathbf{p}_2}{m}\frac{\partial f_2}{\partial \mathbf{x}_2} - \frac{\partial V_{12}}{\partial \mathbf{x}_1}\left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2}\right) f_2 = \int d\xi_3 \left(\frac{\partial V_{13}}{\partial \mathbf{x}_1}\frac{\partial f_3}{\partial \mathbf{p}_1} + \frac{\partial V_{23}}{\partial \mathbf{x}_2}\frac{\partial f_3}{\partial \mathbf{p}_2}\right) \tag{5}$$

where we have put for convenience, $f_1 = f_1(\mathbf{p}_1, \mathbf{x}_1, t)$, $f_2 = f_2(\mathbf{p}_1, \mathbf{x}_1, \mathbf{p}_2, \mathbf{x}_2, t)$ and $f_3 = f_3(\mathbf{p}_1, \mathbf{x}_1, \mathbf{p}_2, \mathbf{x}_2, \mathbf{p}_3, \mathbf{x}_3, t)$. Our purpose is to investigate the second of these equations by truncating it in order to obtain a single self-standing equation for f_2.

3. From BBGKY2 to the Kinetic Equation

We now proceed to write down the kinetic equation for f_2. Throughout, we shall retain the usual assumptions of kinetic theory [9,12,15], leading us to neglect triple collisions: the streaming term for the two-particle distribution characterizing particles 1 and 2 will thus be altered by: (1) binary collisions between particle 1 and another particle, 2 being a spectator; and (2) binary collisions between particle 2 and another particle, 1 being a spectator. Sticking tightly to the assumptions made in the one-particle theory is important in order to guarantee that any new prediction arising in the present two-particle description can be ascribed to the statistical description considered and not to the introduction of new physical assumptions.

The binary interaction is defined as the occurrence of two particles meeting in a ball B of radius R. Defining ternary interactions is more subtle since, inasmuch as the interaction potential is the same whatever the order of the interaction, it seems artificial to introduce a specific cutoff. We shall therefore define the range of triple collisions as the lenticular overlap of balls $B_R^{(1)}$ and $B_R^{(2)}$ characterizing the domain of interaction with particles 1 and 2, respectively. Neglecting triple collisions thus amounts us to assume that $|\mathbf{x}_1 - \mathbf{x}_2| > 2R$.

We first compute the contribution of collisions of particle 1 with particle 3, particle 2 being left aside. Let us recall that the collision term is given by

$$\left(\frac{\partial f_2}{\partial t}\right)_{coll} = \int d\xi_3 \left(\frac{\partial V_{13}}{\partial \mathbf{x}_1}\frac{\partial f_3}{\partial \mathbf{p}_1} + \frac{\partial V_{23}}{\partial \mathbf{x}_2}\frac{\partial f_3}{\partial \mathbf{p}_2}\right) \tag{6}$$

In the usual derivation of the Boltzmann equation from the BBGKY hierarchy, the right-hand side of BBGKY1 is transformed using BBGKY2. Similarly, we can transform $(\partial_t f_2)_{coll}$ using BBGKY3, which reads

$$\begin{aligned}\frac{\partial f_3}{\partial t} + \frac{\mathbf{p}_1}{m}\frac{\partial f_3}{\partial \mathbf{x}_1} + \frac{\mathbf{p}_2}{m}\frac{\partial f_3}{\partial \mathbf{x}_2} + \frac{\mathbf{p}_3}{m}\frac{\partial f_3}{\partial \mathbf{x}_3} - \frac{\partial V_{12}}{\partial \mathbf{x}_1}\left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2}\right) f_3 \\ - \frac{\partial V_{13}}{\partial \mathbf{x}_1}\left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_3}\right) f_3 - \frac{\partial V_{23}}{\partial \mathbf{x}_2}\left(\frac{\partial}{\partial \mathbf{p}_2} - \frac{\partial}{\partial \mathbf{p}_3}\right) f_3 = \left(\frac{\partial f_3}{\partial t}\right)_{coll}\end{aligned} \tag{7}$$

(we do not make explicit the collision term $(\partial_t f_3)_{coll}$, as we shall cancel it soon anyway). Under usual dimensional assumptions, we can write $\partial_t f_3 \approx 0$ and $(\partial_t f_3)_{coll} \approx 0$, so that, substituting in the collision term, $(\partial_t f_2)_{coll}$ is rewritten as

$$\begin{aligned}\left(\frac{\partial f_2}{\partial t}\right)_{coll} &= \int d\xi_3 \left(\frac{\mathbf{p}_1}{m}\frac{\partial f_3}{\partial \mathbf{x}_1} + \frac{\mathbf{p}_2}{m}\frac{\partial f_3}{\partial \mathbf{x}_2} + \frac{\mathbf{p}_3}{m}\frac{\partial f_3}{\partial \mathbf{x}_3} - \frac{\partial V_{12}}{\partial \mathbf{x}_1}\left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2}\right) f_3 + \left(\frac{\partial V_{13}}{\partial \mathbf{x}_1} + \frac{\partial V_{23}}{\partial \mathbf{x}_2}\right)\frac{\partial f_3}{\partial \mathbf{p}_3}\right) \\ &= \int d\xi_3 \left(\frac{\mathbf{p}_1}{m}\frac{\partial f_3}{\partial \mathbf{x}_1} + \frac{\mathbf{p}_3}{m}\frac{\partial f_3}{\partial \mathbf{x}_3}\right)\end{aligned} \tag{8}$$

(the last term vanishes due to the boundary condition $f_3(|\mathbf{p}_3| \to \infty) = 0$, the penultimate because particles 1 and 2 are supposed far apart from each other (i.e., they do not interact directly) and the second because f_3 depends weakly on $\mathbf{x}_2$). More precisely,

$$\left(\frac{\partial f_2}{\partial t}\right)_{coll} = \int_{\mathbf{x}_3 \in B_R^{(1)}} d\mathbf{x}_3 d\mathbf{p}_3 \left(\frac{\mathbf{p}_1}{m}\frac{\partial f_3}{\partial \mathbf{x}_1} + \frac{\mathbf{p}_3}{m}\frac{\partial f_3}{\partial \mathbf{x}_3}\right) \tag{9}$$

The following is standard [9]. We introduce the relative coordinate $\mathbf{r}_{13} = \mathbf{x}_3 - \mathbf{x}_1$ and use Gauss's theorem in order to rewrite $(\partial_t f_2)_{coll}$ as a surface integral, so that

$$\begin{aligned}\left(\frac{\partial f_2}{\partial t}\right)_{coll} &= \int_{\mathbf{r}_{13} \in B_R} d\mathbf{r}_{13} d\mathbf{p}_3 \frac{\mathbf{p}_3 - \mathbf{p}_1}{m}\frac{\partial f_3}{\partial \mathbf{r}_{13}} \\ &= \int_{S_R} d\mathbf{p}_3 d\Sigma \cdot \frac{\mathbf{p}_3 - \mathbf{p}_1}{m} f_3 \\ &= \int_{S_R^- \cup S_R^+} d\mathbf{p}_3 d\Sigma \cdot \frac{\mathbf{p}_3 - \mathbf{p}_1}{m} f_3\end{aligned} \tag{10}$$

where $d\Sigma$ denotes the surface element of the sphere S_R such that $|\mathbf{r}_{13}| = R$. The southern hemisphere is interpreted as the contribution of oncoming collisions, since $(\mathbf{p}_3 - \mathbf{p}_1) \cdot d\Sigma < 0$, while the northern hemisphere is the contribution of ending collisions, since $(\mathbf{p}_3 - \mathbf{p}_1) \cdot d\Sigma > 0$.

Orienting the polar axis along $\mathbf{p}_3 - \mathbf{p}_1$, we have $d\Sigma \cdot (\mathbf{p}_3 - \mathbf{p}_1) = |\mathbf{p}_3 - \mathbf{p}_1| R^2 \sin\theta \cos\theta d\theta d\phi$. This can be re-expressed in terms of the surface element of the azimuthal plane, such that $\theta = \pi/2$. Letting r denote the radial component on the plane, we have $r = R\sin\theta$, whence $dr = \pm R\cos\theta d\theta$ (depending on θ being lesser or larger than $\pi/2$) and $d\Sigma \cdot (\mathbf{p}_3 - \mathbf{p}_1) = \pm|\mathbf{p}_3 - \mathbf{p}_1| d\omega$. The collision term can thus be rewritten as (approximating $\mathbf{x}_3 \approx \mathbf{x}_1$, as $|\mathbf{x}_3 - \mathbf{x}_1| \ll |\mathbf{x}_2 - \mathbf{x}_1|$):

$$\begin{aligned}\left(\frac{\partial f_2}{\partial t}\right)_{coll} &= \int_{after} d\mathbf{p}_3 d\omega \frac{|\mathbf{p}_3 - \mathbf{p}_1|}{m} f_3(\mathbf{x}_1, \mathbf{p}_1, \mathbf{x}_2, \mathbf{p}_2, \mathbf{x}_1, \mathbf{p}_3, t) \\ &\quad - \int_{before} d\mathbf{p}_3 d\omega \frac{|\mathbf{p}_3 - \mathbf{p}_1|}{m} f_3(\mathbf{x}_1, \mathbf{p}_1, \mathbf{x}_2, \mathbf{p}_2, \mathbf{x}_1, \mathbf{p}_3, t)\end{aligned} \tag{11}$$

4. The Ansatz for BBGKY2

The procedure leading from the BBGKY1 equation to a consistent kinetic equation for f_1 is standard: the Stosszahlansatz asserts that, before colliding, two particles are uncorrelated, i.e., f_2 factorizes as $f_2(\xi_1, \xi_2) = f_1(\xi_1) f_1(\xi_2)$. This allows us to express the collision integral in terms of f_1, so that BBGKY1 becomes a closed equation for f_1. Because this factorization hypothesis may be supported from a physical standpoint, it is tempting to also use this ansatz in the collision term for BBGKY2. However, this raises an issue: if BBGKY2 can be cast into an equation relating a streaming term expressed in terms of f_2 to a collision term expressed in terms of f_1, then this equation is clearly not consistent by itself, and has to be supplemented, so as to obtain a system of coupled equations.

Our point is that this issue vanishes if the molecular chaos is reconsidered as a heuristic ansatz instead of a physically-grounded assumption. This ansatz should then be formulated as follows: because the exact codependence of particles entering the collision range is unknown, one must make a reasonable guess on it, and the maximum entropy distribution steps out at this point because the maximum entropy guess for f_2, compatible with the univariate distribution appearing in the streaming term, is the factorized one.

The maximization problem is most usually formulated for constraints over averages rather than marginals, but the latter can be recovered from the former after some δ-functions gymnastics. For constraints over averages, we are looking for a distribution $p(r)$ such that $H(r) = -\int dr p(r) \ln p(r)$ is maximal, while the constraint $\int dr f_k(r) p(r) = \mu_k$ is enforced (k takes its value in $\{1, ..., K\}$ where K is the total number of constraints imposed to the distribution). Using Lagrange's multipliers, the problem reduces to solving

$$
\begin{aligned}
0 &= \frac{\partial}{\partial p(r)}\left(-\int dsp(s)\ln p(s) + \lambda_0\left(\int dsp(s) - 1\right) + \sum_{k=1}^{K}\lambda_k\left(\int dsf_k(s)p(s) - \mu_k\right)\right) \\
&= -\int ds\delta_{r,s}\ln p(s) - \int ds\delta_{r,s} + \lambda_0\int ds\delta_{r,s} + \sum_{k=1}^{K}\lambda_k\int dsf_k(s)\delta_{r,s} \\
&= -\ln p(r) - 1 + \lambda_0 + \sum_{k=1}^{K}\lambda_k f_k(r) \qquad (12)
\end{aligned}
$$

Denoting the partition function by $Z = \int dr\exp\left(\sum_{k=1}^{K}\lambda_k f_k(r)\right)$, the sought-after distribution may therefore be written as

$$p(r) = \frac{1}{Z}\exp\left(\sum_{k=1}^{K}\lambda_k f_k(r)\right) \qquad (13)$$

The standard result for averages, Equation (13), may be generalized to the case of constrained marginals [7]. Taking for illustration, the case of three variables (i.e., $r = (w, y, z)$) and assuming the bivariate marginal $p_{12}(a, b)$ is fixed, let us set $f(r) = \delta_{w,a}\delta_{y,b}$. Then,

$$
\begin{aligned}
\int drf(r)p(r) &= \int dwdy\delta_{w,a}\delta_{y,b}\int dzp(r) \\
&= \int dwdy\delta_{w,a}\delta_{y,b}p_{12}(w, y) \\
&= p_{12}(a, b) \qquad (14)
\end{aligned}
$$

Applying Equation (13) to all possible values of the arguments then yields

$$
\begin{aligned}
p(r) &= \frac{1}{Z}\exp\left(\int dadb\lambda(a, b)f(r)\right) \\
&= \frac{1}{Z}\exp\left(\int dadb\lambda(a, b)\delta_{w,a}\delta_{y,b}\right) \\
&= \frac{1}{Z}\exp\left(\lambda(w, y)\right) \qquad (15)
\end{aligned}
$$

where λ now denotes a well-chosen multiplying function. The extension to any number of marginals is straightforward; for instance, if, besides p_{12}, the marginals p_{13} and p_{23} are fixed, we obtain

$$p(r) = \frac{1}{Z}\exp\left(\lambda_{12}(w, y) + \lambda_{13}(w, z) + \lambda_{23}(y, z)\right) \qquad (16)$$

We leave it to the reader to show that, as mentioned above, the maximum entropy distribution compatible with univariate marginals is the factorized distribution.

Coming back to our reduced distribution functions, it is now obvious that the maximum entropy guess for f_3, compatible with the f_2 appearing in the left-hand side, is more involved than a direct factorization. Indeed, defining $\Lambda = \exp\lambda$, it follows from Equation (16) that, given bivariate marginals, the maximum entropy estimate for $f_3(\xi_1, \xi_2, \xi_3)$ takes the form (note the condensed notation $\xi_i = (\mathbf{x}_i, \mathbf{p}_i)$ introduced above)

$$f_3^{ME}(\xi_1, \xi_2, \xi_3) = \Lambda_1(\xi_1, \xi_2)\Lambda_2(\xi_1, \xi_3)\Lambda_3(\xi_2, \xi_3) \qquad (17)$$

for some functions Λ_1, Λ_2 and Λ_3 that have to be found so as to match the marginals on the first and second, first and last, and second and last variables. This result is, generally speaking, of limited practical range, but fortunately, particle distribution functions have the crucial peculiarity of being symmetric under exchange of the particles. This implies that these marginals are the same for each pair, and accordingly all three Λ's are actually the same. One is therefore allowed to write that

$$f_3^{ME}(\xi_1, \xi_2, \xi_3) = G(\xi_1, \xi_2)G(\xi_1, \xi_3)G(\xi_2, \xi_3) \tag{18}$$

for a function G that is nevertheless still unknown, except for the fact that it has to satisfy the marginal constraint:

$$G(\xi_1, \xi_2) \int d\xi_3 G(\xi_1, \xi_3)G(\xi_2, \xi_3) = f_2(\xi_1, \xi_2) \tag{19}$$

It results from the previous consideration that, before the collision, the maximum entropy estimation of the three-particle distribution function can be written as

$$f_3(\mathbf{x}_1, \mathbf{p}_1, \mathbf{x}_2, \mathbf{p}_2, \mathbf{x}_1, \mathbf{p}_3, t) = G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_2} G^{\mathbf{x}_1,\mathbf{x}_1}_{\mathbf{p}_1,\mathbf{p}_3} G^{\mathbf{x}_2,\mathbf{x}_1}_{\mathbf{p}_2,\mathbf{p}_3} \tag{20}$$

where, for the sake of readability, we have used the shortcut $G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_2} = G(\mathbf{x}_1, \mathbf{p}_1; \mathbf{x}_2, \mathbf{p}_2; t)$. The ansatz may be extended after the collision using the fact that, by the Liouville equation, $f_3(\mathbf{x}_1, \mathbf{p}_1, \mathbf{x}_2, \mathbf{p}_2, \mathbf{x}_1, \mathbf{p}_3, t) = f_3(\mathbf{x}_1^{-\tau}, \mathbf{p}'_1, \mathbf{x}_2^{-\tau}, \mathbf{p}'_2, \mathbf{x}_1^{-\tau}, \mathbf{p}'_3, t-\tau)$, where τ is the retardation such that, at $t-\tau$, the particles are entering the collision range with momenta $\mathbf{p}'_1$ and $\mathbf{p}'_3$. Because $\mathbf{x}_i^{-\tau} \approx \mathbf{x}_i$ and $t \approx t - \tau$, and because $\mathbf{p}'_1$ and $\mathbf{p}'_3$ are pre-collisional momenta, the ansatz may also be introduced in the first integral with the arguments $\mathbf{p}'_1$ and $\mathbf{p}'_3$. We are therefore eventually led to the following Boltzmann-like form for the second-order BBGKY equation (note that $\mathbf{p}'_2 = \mathbf{p}_2$ in the first integral as particle 2 does not take part in the event, and similarly $\mathbf{p}'_1 = \mathbf{p}_1$ in the second integral):

$$\begin{aligned}\frac{\partial f_2}{\partial t} + \frac{\mathbf{p}_1}{m}\frac{\partial f_2}{\partial \mathbf{x}_1} + \frac{\mathbf{p}_2}{m}\frac{\partial f_2}{\partial \mathbf{x}_2} &= \int d\mathbf{p}_3 d\omega \frac{|\mathbf{p}_3 - \mathbf{p}_1|}{m}\left(G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}'_1,\mathbf{p}_2} G^{\mathbf{x}_1,\mathbf{x}_1}_{\mathbf{p}'_1,\mathbf{p}'_3} G^{\mathbf{x}_2,\mathbf{x}_1}_{\mathbf{p}_2,\mathbf{p}'_3} - G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_2} G^{\mathbf{x}_1,\mathbf{x}_1}_{\mathbf{p}_1,\mathbf{p}_3} G^{\mathbf{x}_2,\mathbf{x}_1}_{\mathbf{p}_2,\mathbf{p}_3}\right) \\ &+ \int d\mathbf{p}_4 d\omega \frac{|\mathbf{p}_4 - \mathbf{p}_2|}{m}\left(G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}'_2} G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}'_4} G^{\mathbf{x}_2,\mathbf{x}_2}_{\mathbf{p}'_2,\mathbf{p}'_4} - G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_2} G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_4} G^{\mathbf{x}_2,\mathbf{x}_2}_{\mathbf{p}_2,\mathbf{p}_4}\right)\end{aligned} \tag{21}$$

The first term corresponds to the contribution of collisions undergone by particle 1 (detailed above), while the second accounts for the contribution of collisions undergone by particle 2.

Equation (21) is coherent for f_2, as G can, in principle, be solved in terms of f_2. This implicit form of the collision term bears a close ressemblance with that appearing in the standard Boltzmann equation. This resemblance might however turn deceptive, as G is likely to be a complicated functional of f_2, but it happens that in spite of this mathematical complication we can push the analysis further.

5. Collisional Invariants

Our immediate purpose is to deduce the equilibrium distribution resulting from Equation (21). To this end, we need to define collisional invariants that are appropriate to the scheme developed here. The form assumed by the collision term in Equation (21) makes it necessary (see Section 7) to introduce bilocal invariants χ that are quantities conserved in a bilocal collision of particle pairs (1,2) and (3,4), which occur in $\mathbf{x}_1$ and $\mathbf{x}_2$ for the (1,3) and (2,4) collisions, respectively. A collisional invariant has to be defined in this case such that (in this context, spatial arguments are not relevant and can be dropped out).

$$\chi(\mathbf{p}'_1, \mathbf{p}'_2) + \chi(\mathbf{p}'_3, \mathbf{p}'_4) = \chi(\mathbf{p}_1, \mathbf{p}_2) + \chi(\mathbf{p}_3, \mathbf{p}_4) \tag{22}$$

However, although collisions of external particles with both particle 1 and particle 2 have to be taken into consideration, these events do not, with overwhelming probability, occur simultaneously, and either particle 1 or particle 2 will not undergo a collision and will thus be left unaltered. In other words, the description of the events is expressed in bilocal terms, but the events that alter the particle pair (1,2) still consist of local collisions. In such spurious bilocal collisions, we argue that Equation (22) should therefore instead read

$$\chi(\mathbf{p}'_1, \mathbf{p}'_2) + \chi(\mathbf{p}'_3, \mathbf{p}'_2) = \chi(\mathbf{p}_1, \mathbf{p}_2) + \chi(\mathbf{p}_3, \mathbf{p}_2) \tag{23}$$

or

$$\chi(\mathbf{p}_1', \mathbf{p}_2') + \chi(\mathbf{p}_1', \mathbf{p}_4') = \chi(\mathbf{p}_1, \mathbf{p}_2) + \chi(\mathbf{p}_1, \mathbf{p}_4) \tag{24}$$

for the first and second term on the rhs of Equation (21), respectively. This interpretation amounts to introducing a free fictitious extra particle so as to treat these two simple collisions as pair–pair collisions. For instance, in Equation (28), the role of particle 4 is taken on by a particle that mimics particle 2 (which does not take part in the local collision involving particles 1 and 3) exactly. The crucial point is that the extra particles so introduced are free; hence, the operation is harmless as far as the collision term is concerned.

Taking in consideration the above, we are now in a position to discuss invariants themselves. Beside mass invariance, obvious invariants are $\chi(\mathbf{p}_1, \mathbf{p}_2) = (\mathbf{p}_1 + \mathbf{p}_2)$ describing the conservation of momentum, hence

$$(\mathbf{p}_1' + \mathbf{p}_2') + (\mathbf{p}_3' + \mathbf{p}_4') = (\mathbf{p}_1 + \mathbf{p}_2) + (\mathbf{p}_3 + \mathbf{p}_4) \tag{25}$$

and $\chi(\mathbf{p}_1, \mathbf{p}_2) = (\mathbf{p}_1^2 + \mathbf{p}_2^2)$ describing the conservation of kinetic energy, hence

$$(\mathbf{p}_1'^2 + \mathbf{p}_2'^2) + (\mathbf{p}_3'^2 + \mathbf{p}_4'^2) = (\mathbf{p}_1^2 + \mathbf{p}_2^2) + (\mathbf{p}_3^2 + \mathbf{p}_4^2) \tag{26}$$

We assert that, in our case, these invariants should be complemented by $\chi(\mathbf{p}_1, \mathbf{p}_2) = (\mathbf{p}_1 \cdot \mathbf{p}_2)$, whose conservation equation reads

$$(\mathbf{p}_1' \cdot \mathbf{p}_2') + (\mathbf{p}_3' \cdot \mathbf{p}_4') = (\mathbf{p}_1 \cdot \mathbf{p}_2) + (\mathbf{p}_3 \cdot \mathbf{p}_4) \tag{27}$$

The rationale for introducing this exotic invariant is not obvious at first, but at the light of the discussion above, Equation (27), should actually be understood as

$$(\mathbf{p}_1' \cdot \mathbf{p}_2') + (\mathbf{p}_3' \cdot \mathbf{p}_2') = (\mathbf{p}_1 \cdot \mathbf{p}_2) + (\mathbf{p}_3 \cdot \mathbf{p}_2) \tag{28}$$

or

$$(\mathbf{p}_1' \cdot \mathbf{p}_2') + (\mathbf{p}_1' \cdot \mathbf{p}_4') = (\mathbf{p}_1 \cdot \mathbf{p}_2) + (\mathbf{p}_1 \cdot \mathbf{p}_4) \tag{29}$$

for the first and second terms of the rhs of Equation (21), respectively. Because $\mathbf{p}_2' = \mathbf{p}_2$ in the former and $\mathbf{p}_1' = \mathbf{p}_1$ in the latter, we finally obtain

$$\mathbf{p}_2 \cdot (\mathbf{p}_1' + \mathbf{p}_3') = \mathbf{p}_2 \cdot (\mathbf{p}_1 + \mathbf{p}_3)$$

and

$$\mathbf{p}_1 \cdot (\mathbf{p}_2' + \mathbf{p}_4') = \mathbf{p}_1 \cdot (\mathbf{p}_2 + \mathbf{p}_4)$$

whose validity is obvious. As we shall see below, this exotic collisional invariant is necessary to enforce momentum correlation between particles at equilibrium.

6. Equilibrium State

To proceed towards the two-particle distribution at equilibrium, let us first note that $G^{\mathbf{x}_1,\mathbf{x}_1}_{\mathbf{p}_1',\mathbf{p}_3'} = G^{\mathbf{x}_1,\mathbf{x}_1}_{\mathbf{p}_1,\mathbf{p}_3}$ and $G^{\mathbf{x}_2,\mathbf{x}_2}_{\mathbf{p}_2',\mathbf{p}_4'} = G^{\mathbf{x}_2,\mathbf{x}_2}_{\mathbf{p}_2,\mathbf{p}_4}$. This property is certainly true of f_2 itself by Liouville's theorem, so we can reasonably suppose it passes to G; this can also be verified directly from Equation (31), as, for a binary collision, we have that $\mathbf{p}_1' \cdot \mathbf{p}_3' = \mathbf{p}_1 \cdot \mathbf{p}_3$ (this relation follows from expressing post-collisional velocities in terms of the apsidal vector characterizing the event [11]). This property is helpful, as it allows us to proceed even though we do not have at hand a $\mathcal{H}$ theorem for f_2, which seems to raise substantial mathematical issues.

Then, the condition for the collision integrals to vanish is

$$\begin{cases} G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}'_1,\mathbf{p}_2} G^{\mathbf{x}_2,\mathbf{x}_1}_{\mathbf{p}_2,\mathbf{p}'_3} = G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_2} G^{\mathbf{x}_2,\mathbf{x}_1}_{\mathbf{p}_2,\mathbf{p}_3} \\ \\ G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}'_2} G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}'_4} = G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_2} G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_4} \end{cases} \tag{30}$$

Taking the logarithm of both sides, we recognize in $\ln G^{eq}$ a collisional invariant as defined by Equations (28) and (29), so that this quantity is necessarily a linear combination of the invariants introduced above, that is,

$$G^{eq}(\mathbf{p}_1;\mathbf{p}_2) = e^{A+\mathbf{B}\cdot(\mathbf{p}_1+\mathbf{p}_2)+C(\mathbf{p}_1^2+\mathbf{p}_2^2)+D\mathbf{p}_1\cdot\mathbf{p}_2} \tag{31}$$

This form is actually not the most general, since the coefficients could possibly depend on the space variables. While letting A, $\mathbf{B}$ and C depend on $\mathbf{x}_1, \mathbf{x}_2$ might seem an unnecessary subtlety, this dependence would be relevant for the coefficient in front of $\mathbf{p}_1 \cdot \mathbf{p}_2$, allowing for correlations depending on the inter-particle distance. This, however, introduces additional complications when connecting coefficients to observable quantities. Because both cases are equivalent for illustrating the points of interest here, we shall focus on the case of constant coefficients, although for practical applications it will be necessary to deal with the general case $D = D(\mathbf{x}_1, \mathbf{x}_2)$.

From this expression for G^{eq}, we can now deduce the expression for the three-particle distribution f_3^{eq} that makes the collision term vanish. Substituting $\mathbf{p}_3 \to \mathbf{k}$ in order to single out the integration variable, we obtain

$$\begin{aligned} f_3^{eq}(\mathbf{p}_1,\mathbf{p}_2,\mathbf{k}) &= G^{eq}(\mathbf{p}_1,\mathbf{p}_2)G^{eq}(\mathbf{p}_1,\mathbf{k})G^{eq}(\mathbf{p}_2,\mathbf{k}) \\ &= e^{3A+2\mathbf{B}(\mathbf{p}_1+\mathbf{p}_2+\mathbf{k})+2C(\mathbf{p}_1^2+\mathbf{p}_2^2+\mathbf{k}^2)+D(\mathbf{p}_1\mathbf{p}_2+\mathbf{p}_2\mathbf{k}+\mathbf{p}_1\mathbf{k})} \end{aligned} \tag{32}$$

It remains to integrate on $\mathbf{k}$ in order to obtain f_2^{eq} as

$$\begin{aligned} f_2^{eq}(\mathbf{p}_1,\mathbf{p}_2) &= e^{3A+\mathbf{B}(\mathbf{p}_1+\mathbf{p}_2)+2C(\mathbf{p}_1^2+\mathbf{p}_2^2)+D\mathbf{p}_1\mathbf{p}_2} \int d\mathbf{k} e^{(2\mathbf{B}+D\mathbf{p}_1+D\mathbf{p}_2)\mathbf{k}+2C\mathbf{k}^2} \\ &= \left(-\frac{\pi}{2C}\right)^{3/2} e^{3A-\frac{\mathbf{B}^2}{2C}} e^{\left(2-\frac{D}{2C}\right)\mathbf{B}(\mathbf{p}_1+\mathbf{p}_2)+\left(2C-\frac{D^2}{8C}\right)(\mathbf{p}_1^2+\mathbf{p}_2^2)+\left(D-\frac{D^2}{4C}\right)\mathbf{p}_1\mathbf{p}_2} \end{aligned} \tag{33}$$

The coefficients have now to be determined so as to match observational constraints on the average momentum, average kinetic energy ϵ, and momentum correlation φ. Because the average momentum is proportional to $\mathbf{B}$, we can restrict ourselves, for simplicity, to the case of a gas without global translational motion and set $\mathbf{B} = 0$, so that

$$f_2^{eq}(\mathbf{p}_1,\mathbf{p}_2) = \left(-\frac{\pi}{2C}\right)^{3/2} e^{3A} e^{\left(2C-\frac{D^2}{8C}\right)(\mathbf{p}_1^2+\mathbf{p}_2^2)+\left(D-\frac{D^2}{4C}\right)\mathbf{p}_1\mathbf{p}_2} \tag{34}$$

Regarding the average energy (keeping in mind that f_2 is normalized, by convention, to $N(N-1) \approx N^2$), we should have

$$\epsilon = \frac{\int d\mathbf{p}_1 d\mathbf{p}_2 \left(\frac{\mathbf{p}_i^2}{2m}\right) f_2^{eq}}{\int d\mathbf{p}_1 d\mathbf{p}_2 f_2^{eq}} = \frac{V^2}{2mN^2}\langle \mathbf{p}_i^2 \rangle \tag{35}$$

Regarding the correlation coefficient of momenta, it follows from our assumption of a gas without global translational motion that

$$\varphi = \frac{\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle - \langle \mathbf{p}_1 \rangle \cdot \langle \mathbf{p}_2 \rangle}{\sqrt{\langle \mathbf{p}_1^2 \rangle - \langle \mathbf{p}_1 \rangle^2}\sqrt{\langle \mathbf{p}_2^2 \rangle - \langle \mathbf{p}_2 \rangle^2}} = \frac{\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle}{\langle \mathbf{p}^2 \rangle} \tag{36}$$

where

$$\langle O \rangle = \int d\mathbf{p}_1 d\mathbf{p}_2 O f_2^{eq} \tag{37}$$

Performing integrations on $\mathbf{p}_1, \mathbf{p}_2$ therefore allows relating φ to C and D as

$$\varphi = \frac{D^2 - 4CD}{16C^2 - D^2} \tag{38}$$

so that $D = -4C\varphi/(1+\varphi)$. Using the expression for ϵ, the coefficient C can then be related to φ as

$$C = \frac{3(\varphi+1)}{8m\epsilon(2\varphi+1)(\varphi-1)} \tag{39}$$

Normalizing, we finally arrive at the conclusion that

$$f_2^{eq}(\mathbf{p}_1;\mathbf{p}_2) = \left(\tfrac{N}{V}\right)^2 \left(\tfrac{3}{4\pi m\epsilon}\right)^3 (1-\varphi^2)^{-3/2} \exp\left(-\tfrac{3}{4m\epsilon(1-\varphi^2)}\left(\mathbf{p}_1^2+\mathbf{p}_2^2\right) + \tfrac{3\varphi}{2m\epsilon(1-\varphi^2)}\mathbf{p}_1\cdot\mathbf{p}_2\right) \tag{40}$$

It therefore appears that equilibrium distributions, such as Equation (40), can, at least in principle (the existence of correlations eventually being an experimental issue), be found for which particles stay correlated with each other over time. This correlation is nonetheless hidden as long as one-particle distributions only are examined, since by integrating on $\mathbf{p}_2$ we recover Maxwell's usual distribution of velocities:

$$f_1^{eq}(\mathbf{p}_1) = \frac{N}{V}\left(\frac{3}{4\pi m\epsilon}\right)^{3/2} \exp\left(-\frac{3}{4m\epsilon}\mathbf{p}_1^2\right) \tag{41}$$

7. Balance Equations

Allowing for momentum correlation between particles has a two-fold consequence as to the macroscopic description of the fluid. First, it makes it necessary to take account of this correlation in the usual balance equations for mass, momentum and energy; second, these have to be complemented by a fourth balance equation corresponding to the collisional invariant of Equation (27).

The macroscopic conservation equations are derived from Equation (21) by multiplying both sides by $\chi(\mathbf{p}_1, \mathbf{p}_2)$ and integrating on momenta, so as to obtain

$$\begin{aligned}
&\int d\mathbf{p}_1 d\mathbf{p}_2 \chi(\mathbf{p}_1,\mathbf{p}_2)\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m}\frac{\partial}{\partial \mathbf{x}_1} + \frac{\mathbf{p}_2}{m}\frac{\partial}{\partial \mathbf{x}_2}\right) f_2(\mathbf{x}_1,\mathbf{p}_1;\mathbf{x}_2,\mathbf{p}_2;t) \\
&= \int d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{p}_3 d\omega \chi(\mathbf{p}_1,\mathbf{p}_2)\frac{|\mathbf{p}_3-\mathbf{p}_1|}{m}\left(G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1',\mathbf{p}_2} G^{\mathbf{x}_1,\mathbf{x}_1}_{\mathbf{p}_1',\mathbf{p}_3'} G^{\mathbf{x}_2,\mathbf{x}_1}_{\mathbf{p}_2,\mathbf{p}_3'} - G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_2} G^{\mathbf{x}_1,\mathbf{x}_1}_{\mathbf{p}_1,\mathbf{p}_3} G^{\mathbf{x}_2,\mathbf{x}_1}_{\mathbf{p}_2,\mathbf{p}_3}\right) \\
&\quad + \int d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{p}_4 d\omega \chi(\mathbf{p}_1,\mathbf{p}_2)\frac{|\mathbf{p}_4-\mathbf{p}_2|}{m}\left(G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_2'} G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_4'} G^{\mathbf{x}_2,\mathbf{x}_2}_{\mathbf{p}_2',\mathbf{p}_4'} - G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_2} G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_4} G^{\mathbf{x}_2,\mathbf{x}_2}_{\mathbf{p}_2,\mathbf{p}_4}\right)
\end{aligned} \tag{42}$$

We now have to go through the usual sequence of relabeling and permutations [9,15]. We first substitute $\mathbf{p}_1 \leftrightarrow \mathbf{p}_3$ in the first integral of the collision term and $\mathbf{p}_2 \leftrightarrow \mathbf{p}_4$ in the second (which is allowed as both are dummy variables) so as to have two equivalent forms of the collision term, of which we take the average. In this averaged collision term, we now relabel $\mathbf{p}_1 \leftrightarrow \mathbf{p}_1'$, $\mathbf{p}_2 \leftrightarrow \mathbf{p}_2'$, $\mathbf{p}_3 \leftrightarrow \mathbf{p}_3'$ and $\mathbf{p}_4 \leftrightarrow \mathbf{p}_4'$. Using the fact that $d\mathbf{p}_1' d\mathbf{p}_2' d\mathbf{p}_3' = d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{p}_3$ and $d\mathbf{p}_1' d\mathbf{p}_2' d\mathbf{p}_4' = d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{p}_4$, and that $|\mathbf{p}_3' - \mathbf{p}_1'| = |\mathbf{p}_3 - \mathbf{p}_1|$ and $|\mathbf{p}_4' - \mathbf{p}_2'| = |\mathbf{p}_4 - \mathbf{p}_2|$, both terms can be averaged again and we finally obtain the collision term as

$$\frac{1}{4}\int d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{p}_3 d\omega\,[\chi(\mathbf{p}_1,\mathbf{p}_2)+\chi(\mathbf{p}_3,\mathbf{p}_2)-\chi(\mathbf{p}_1',\mathbf{p}_2')-\chi(\mathbf{p}_3',\mathbf{p}_2')]\,\frac{|\mathbf{p}_3-\mathbf{p}_1|}{m}$$
$$\cdot\,(G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1',\mathbf{p}_2}G^{\mathbf{x}_1,\mathbf{x}_1}_{\mathbf{p}_1',\mathbf{p}_3'}G^{\mathbf{x}_2,\mathbf{x}_1}_{\mathbf{p}_2,\mathbf{p}_3'}-G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_2}G^{\mathbf{x}_1,\mathbf{x}_1}_{\mathbf{p}_1,\mathbf{p}_3}G^{\mathbf{x}_2,\mathbf{x}_1}_{\mathbf{p}_2,\mathbf{p}_3})$$
$$+\frac{1}{4}\int d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{p}_4 d\omega\,[\chi(\mathbf{p}_1,\mathbf{p}_2)+\chi(\mathbf{p}_1,\mathbf{p}_4)-\chi(\mathbf{p}_1',\mathbf{p}_2')-\chi(\mathbf{p}_1',\mathbf{p}_4')]\,\frac{|\mathbf{p}_4-\mathbf{p}_2|}{m}$$
$$\cdot\,(G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_2'}G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_4'}G^{\mathbf{x}_2,\mathbf{x}_2}_{\mathbf{p}_2',\mathbf{p}_4'}-G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_2}G^{\mathbf{x}_1,\mathbf{x}_2}_{\mathbf{p}_1,\mathbf{p}_4}G^{\mathbf{x}_2,\mathbf{x}_2}_{\mathbf{p}_2,\mathbf{p}_4}) \tag{43}$$

which vanishes by the definition of collisional invariants from Equations (28) and (29).

Therefore, Equation (42) reduces to

$$\int d\mathbf{p}_{1,2}\chi(\mathbf{p}_1,\mathbf{p}_2)\left(\frac{\partial}{\partial t}+\frac{\mathbf{p}_1}{m}\frac{\partial}{\partial \mathbf{x}_1}+\frac{\mathbf{p}_2}{m}\frac{\partial}{\partial \mathbf{x}_2}\right)f_2=0 \tag{44}$$

From this generic balance equation, we can deduce particular expressions for the invariants considered above. For $\chi=1$, Equation (44) becomes

$$\frac{\partial}{\partial t}\int d\mathbf{p}_{1,2}f_2+\frac{1}{m}\frac{\partial}{\partial \mathbf{x}_1}\int d\mathbf{p}_{1,2}\mathbf{p}_1 f_2+\frac{1}{m}\frac{\partial}{\partial \mathbf{x}_2}\int d\mathbf{p}_{1,2}\mathbf{p}_2 f_2=0 \tag{45}$$

For $\chi=p_1^j+p_2^j$ it becomes

$$\frac{\partial}{\partial t}\int d\mathbf{p}_{1,2}(p_1^j+p_2^j)f_2+\frac{1}{m}\frac{\partial}{\partial \mathbf{x}_1}\int d\mathbf{p}_{1,2}(p_1^j+p_2^j)\mathbf{p}_1 f_2+\frac{1}{m}\frac{\partial}{\partial \mathbf{x}_2}\int d\mathbf{p}_{1,2}(p_1^j+p_2^j)\mathbf{p}_2 f_2=0 \tag{46}$$

For $\chi=\mathbf{p}_1^2+\mathbf{p}_2^2$ we have

$$\frac{\partial}{\partial t}\int d\mathbf{p}_{1,2}(\mathbf{p}_1^2+\mathbf{p}_2^2)f_2+\frac{1}{m}\frac{\partial}{\partial \mathbf{x}_1}\int d\mathbf{p}_{1,2}(\mathbf{p}_1^2+\mathbf{p}_2^2)\mathbf{p}_1 f_2+\frac{1}{m}\frac{\partial}{\partial \mathbf{x}_2}\int d\mathbf{p}_{1,2}(\mathbf{p}_1^2+\mathbf{p}_2^2)\mathbf{p}_2 f_2=0 \tag{47}$$

and $\chi=\mathbf{p}_1\cdot\mathbf{p}_2$ yields

$$\frac{\partial}{\partial t}\int d\mathbf{p}_{1,2}(\mathbf{p}_1\cdot\mathbf{p}_2)f_2+\frac{1}{m}\frac{\partial}{\partial \mathbf{x}_1}\int d\mathbf{p}_{1,2}(\mathbf{p}_1\cdot\mathbf{p}_2)\mathbf{p}_1 f_2+\frac{1}{m}\frac{\partial}{\partial \mathbf{x}_2}\int d\mathbf{p}_{1,2}(\mathbf{p}_1\cdot\mathbf{p}_2)\mathbf{p}_2 f_2=0 \tag{48}$$

When re-expressed in terms of macroscopic quantities, Equation (45) takes the form of two independent copies of the usual local conservation equation for mass density (which is expected, as only momenta are correlated), while Equations (46) and (47) each represent two coupled copies of the corresponding local equations. Integrating out Equations (45)–(47), one would recover the corresponding local conservation equations. Equation (48) alone contains the physics brought in by switching from the one-particle to the two-particle description.

8. Remarks

It appears from our analysis that applying the criterion of maximum entropy as a heuristic tool to infer the three-particle distribution based on a requirement of compatibility with two-particle marginals allows us to set up a self-standing equation for the dynamics of pairs of particles, with the consequences that equilibrium states potentially exhibit correlation, and that a conservation equation exists besides the conservation of mass, momentum and energy. Two remarks are in order here:

1. Because the criterion of maximum entropy relies on a subjective ingredient (namely the physicist's uncertainty about the exact three-particle distribution), the reader might feel uncomfortable using this approach here. In fact, it often comes as a surprise to physicists foreign to the maximum entropy community that the maximum entropy approach to statistical mechanics, relying on a subjective ingredient, allows re-deriving the supposedly exact and objective Maxwellian distribution [5]. It should be pointed out that there exists an objective rationale supporting

the principle of maximum entropy, namely that the distribution having the largest entropy is also the most probable (but is not necessarily overwhelmingly probable) in the absence of an a priori, as discussed at length in [16,17]. Postulating the maximum entropy estimate of f_3 therefore amounts to replacing the actual f_3 by the most probable distribution compatible with f_2. In this respect, the maximum entropy approach is not subjective, properly phrased. Moreover, our result (Equation (40)) makes it particularly clear that Maxwell's distribution is but the result of our relative lack of interest in dealing with more than one particle at a time, and provides only a first-order approximation. In this respect, it is not particularly objective.

2. The equilibrium two-particle distribution might be expected to follow the standard canonical distribution, in which case the correlating term in Equation (40) would appear to come into contradiction with standard results of statistical mechanics; however this is not the case for two reasons. If the canonical distribution is supposed to apply to the system as a whole, it should be recalled that the canonical ensemble is concerned with systems immersed in a heat bath; hence, it would be a pointless assumption to regard the isolated N-particle system as canonically distributed. More importantly, it must be underlined that the conservation of the N-particle entropy comes in contradiction with the microcanonical postulate, i.e., the assumption that systems are distributed equiprobably on the shell of constant energy. Because this postulated equiprobable distribution f_N^* is the (only) distribution maximizing $H(f_N)$, then a kinetic description is essentially pointless, as then $f_N(t) = f_N^*$. On the other side, if the canonical distribution is justified using the combinatorial argument of the most probable distribution, it should be recalled that the derivation relies on the assumption that individual particles can be distributed independently over the μ-space. This is no longer the case when dealing with pairs of particles, since assigning a pair (a,b) to a point of the (bilocal) μ-space puts constraints on all pairs that involve either particle a or b (in other words, pairs do not obey Boltzmann's statistics).

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