THE NON-EQUILIBRIUM PAIR DISTRIBUTION FUNCTION AT LOW DENSITIES

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Since Professor Zernike[1]) in 1927 introduced the first and most important example – the distribution function of distances of pairs of molecules – in his study of X-ray diffraction in liquids, joint distribution functions of the properties of several molecules have become more and more important in statistical physics. Indeed in the work of Yvon[2]), Kirkwood[3]), Born and Green[4]) and Bogoliubov[5]) they have become an object of investigation on a par with the partition function itself. Not the least advantage of such distribution functions is that, unlike the partition function, they have a meaning for time-dependent as well as for equilibrium phenomena. In the present paper we will give a mathematical expression for and discuss some of the qualitative properties of the joint distribution function of the positions and momenta of pair of molecules in a non-equilibrium, but spatially uniform situation occurring in a fairly dilute, imperfect gas.

The most complete statistical description of a system of a large number of identical molecules is the distribution function

$$f^N(p_1 x_1, \ldots p_N x_N) \tag{1}$$

in the phase space of all molecules. Here $p_1 x_1$, $p_2 x_2 \ldots$ are the position and momentum of the first, second and so on molecules. N is the total number of molecules. In what follows it will be convenient to replace $p_1 x_1$, $p_2 x_2 \ldots$ by the integers 1, 2, ... and so write the complete phase space distribution function as $f^N(1, \ldots N)$. Since the molecules are supposed identical f^N is symmetric in the variables $1 \ldots N$. Although complete, this function has the disadvantage that it changes when the number of particles in the system changes even when local properties of the system remain the same. We are led therefore to introduce joint distribution functions of groups of small number n of molecules by the formula

$$f_n(1 \ldots n) = (N!/(N-n)!) \int f^N (1 \ldots n) \, \mathrm{d}(n+1) \ldots \mathrm{d}(N). \tag{2}$$

Most properties of physical interest, and in particular the X-ray scattering intensity, can be determined as soon as the first few members of the sequence of joint distribution functions are known. The normalization constant is

so chosen that the functions f_n do not change for large numbers of particles and volumes of the system so long as the properties of the system in neighborhood of the points $x_1 \ldots x_n$ do not change. Like f^N, the f_n are symmetric functions of their arguments. In the case of spatial uniformity which we consider here the functions f_n depend only on the relative distances of the molecules.

Since they are all derived from the same function f^N, the f_n are not arbitrary, but must satisfy certain mutual conditions. In the limit of an infinite (in volume and number of particles) spatially uniform system it is sufficient to require that the distribution functions f_n satisfy a set of limit conditions:

$$f_{n+m}(1 \ldots n+m) \rightarrow f_n(1 \ldots n) f_m(n+1 \ldots n+m) \qquad (3)$$

if the groups of molecules $(1 \ldots n)$ and $(n+1 \ldots n+m)$ are sufficiently far apart. The conditions 3), which have been called the product property, express a kind of statistical independence of distant parts of the system.

In the equilibrium state of a large system with sufficiently short range intermolecular forces the joint distribution functions have definite values depending on the temperature and density and indeed have the form

$$f_n^0(1 \ldots n) = \frac{c^n}{(2\pi m kT)^{3n/2}} \exp(-\frac{1}{2mkT}(p_1^2 + \ldots p_n^2) \times w_n(x_1 \ldots x_n)) \qquad (4)$$

where c is the concentration or the number of molecules per unit volume, m the mass, T the temperature and the w_n functions of the positions only of the n molecules (and T and c) which are symmetric, spatially uniform, and have the product property. In a non-equilibrium spatially uniform situation the joint distribution functions may be any system of functions satisfying the above conditions and the only question which can be discussed in general is the time-development of some given initial situation. In gases at sufficiently low densities, however, there is a non-equilibrium regime, whose existence was first recognized by Bogoliubov [5] in 1946, in which in a certain sense, only f_1 is freely disposable while all other joint distribution functions are functionals of f_1. In a previous paper [6] the author has used methods which are the time-dependent analogue of the methods of the equilibrium theory of imperfect gases to discuss the development and nature of this regime f_1. The arguments were rather complicated and had the disadvantage that the functional relationship was given only implicitly. In the present paper we will derive and exhibit the first two terms of a series for f_2 in which the existence and explicit form of a functional relationship on f_1 is immediately apparent. We will also be able to show how the Bogoliubov regime develops from an arbitrary initial situation and to discuss qualifications which must be made in the statement of the functional relationship due to traces of the initial situation which remain even after the Bogoliubov regime is set up. We will also show how the formula which we derive reduces to one derived by de Boer and Montroll for the equilibrium case.

In reference (1) it was found convenient to introduce in the non-equilibrium theory of imperfect gases a set of functions, the so-called Ursell-Mayer functions

$$g_1(1), g_2(1, 2), g_3(1, 2, 3) \text{ etc.}$$

which have been widely used in the equilibrium theory of dilute gases. This set of functions contains the same information as the set of joint distribution functions but unlike the f_n's are mutually independent in the limit of an infinite system with statistical independence of distant parts. For such a system, instead of the product property, the g_n's have the property

$$g_{n+m}(1 \ldots n + m) \to 0 \tag{5}$$

if the group of molecules $1 \ldots n$ are separated widely from the group $n + 1, n + m$. The first three of these functions are given in terms of f_1, f_2 and f_3 by the formulas

$$g_1(1) = f_1(1) \tag{6}$$

$$g_2(1, 2) = f_2(1, 2) - f_1(1)f_1(2) \tag{7}$$

$$g_3(1, 2, 3) = f_3(1, 2, 3) - f_1(1) f_2(2, 3) - f_1(2) f_2(3, 1) - \\ - f_1(3) f_2(1, 2) + 2f_1(1) f_1(2) f_1(3). \tag{8}$$

These formulas can be explicitly inverted so that for instance f_2 can be determined as soon as we know g_2 and $g_1 = f_1$.

$$f_2(1, 2) = g_2(1, 2) + g_1(1) g_1(2). \tag{9}$$

We will give an expression for the pair Ursell-Mayer function from which the pair distribution function can be immediately determined. For the general direct and inverse relation and for other properties of the f's and the g's, the reader is referred to reference (1) and to papers cited there.

In a spatially uniform non-equilibrium situation the f's and g's depend on time in a way, which for arbitrary densities must be very complicated. At low densities, however, an important simplification takes place by which the g's can be expressed in a power series in the concentration in which the earlier, and most significant, terms can be expressed through the dynamics of isolated groups of small numbers of molecules. The first two terms of the series for g_1 and g_2 are:

$$g_1(1) = c\xi_1(1) + c^2 \int (\xi_2(1_{12-t}, 2_{12-t}) - \xi_1(1) \xi_1(2)) \, d(2), \tag{10}$$

$$g_2(1, 2) = c^2(\xi_2(1_{12-t}, 2_{12-t}) - \xi_1(1)\xi_1(2)) + \\ + c^3 \int (\xi_3(1_{123-t}, 2_{123-t}, 3_{123-t}) - \xi_1(3) \xi_2(1_{12-t}, 2_{12-t}) \tag{11}$$
$$- \xi_1(1) \xi_2(2_{23-t}, 3_{23-t}) - \xi_1(2) \xi_2(3_{31-t}, 1_{31-t}) + 2\xi_1(1)\xi_1(2)\xi_1(3)) \, d(3).$$

Here $\xi_1(1), \xi_2(1, 2) \xi_3(1, 2, 3)$ etc. are a sequence of functions which satisfy the general conditions for a sequence of distribution functions, i.e. symmetry, spatial uniformity and the product condition. They are otherwise arbitrary

and represent the arbitrariness of the initial state. Indeed at low densities $c\xi_1(1)$, $c^2\xi_2(1, 2)$, $c^3\xi_3(1, 2, 3)$ are good approximations to the arbitrary initial values of $f_1(1)$, $f_2(1, 2)$, $f_3(1, 2, 3)$ respectively. The time dependence of $g_1(1)$, $g_2(1, 2)$ is determined through the fact that the arguments of the ξ's are time dependent. The symbols 1_{12-t}, 2_{12-t} represent the positions and momenta of particles 1 and 2 at time $-t$ considered as functions of their positions and momenta at time zero supposing that 1 and 2 are the only particles present. Similarly 1_{123-t} 2_{123-t} 3_{123-t} represent the positions and momenta of particles 1, 2 and 3 at $-t$ considered as functions of their positions at zero.

The qualitative properties of the function $\psi_2(1, 2, t)$ which appears as the integrand in the second term on the right in equation (11) has been discussed at length in reference (1). We give a short resumé of these properties referring to figure 1 which has been reproduced from that paper. The function $\xi_2(1, 2)$, which represents approximately pair correlations which exist in the initial state, is assumed to break up into a product $\xi_1(1)$ $\xi_1(2)$ when molecules 1 and 2 are separated by a distance greater than r_c. Figure 1 is supposed to represent $\psi_2(1, 2, t)$ for a time which is large compared to r_c/v where v is a representative relative velocity. Now because of spatial uniformity ψ_2 will depend only on p_1, p_2 and $x_2 - x_1$. Fig. 1 is a representation of the relative
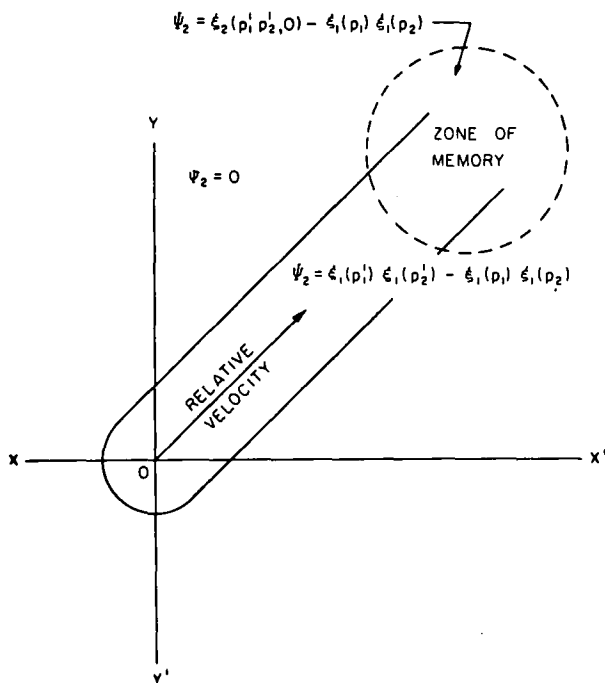

Fig. 1. The function ψ_2 as a function of the relative configuration $x_2 - x_1$ for fixed momenta p_1, p_2.

configuration space of the vector $x_2 - x_1$ for fixed p_1 and p_2. The vector proceeding from the origin is supposed to represent the direction of the relative velocity which is fixed since p_1 and p_2 are fixed. Throughout most of the relative configuration space ψ_2 is zero because the two molecules have suffered no collision in the interval $-t$ to 0, while their relative distance at $-t$ is greater than r_c. The momenta corresponding to 1_{12-t} 2_{12-t} are not different from the initial momenta while the corresponding positions are such that ξ_2 may be replaced by a product $\xi_1(1) \xi_1(2)$. Only in the quasi-cylindrical region surrounding the vector in the direction of the relative velocity and in the region marked zone of memory is ψ_2 different from zero. In the quasi-cylindrical region the two particles have indeed suffered a collision between zero and $-t$. The momenta corresponding to 1_{12-t}, 2_{12-t} are equal to the asymptotic momenta before collision p_1', p_2' which are independent of time. The positions corresponding to 1_{12-t} 2_{12-t} are at a relative distance greater than r_c so that ξ_2 may still be replaced by a product. Throughout this quasi-cylindrical region we have

$$\psi_2(1, 2, t) = \xi_1(p_1') \xi_1(p_2') - \xi_1(p_1) \xi_1(p_2). \tag{12}$$

The region is quasi-cylindrical because except when the particles are initially close together p_1' and p_2' depend only on the component of x_2-x_1 perpendicular to the relative velocity, the so-called collision parameter. The zone of memory represents those initial relative configurations for which the relative distance at $-t$ is less than r_c. Only for configurations in the zone of memory do we need to know the value of $\xi_2(1, 2)$ in regions where correlations exist. As t increases molecules 1 and 2 must be farther and farther apart initially for their distance at $-t$ to be less than r_c. The zone of memory therefore moves outward with the relative velocity. Since as t increases there will be more and more initial configurations for which a collision has taken place between 0 and $-t$, the quasi-cylindrical region grows in length with the relative velocity. Except for the motion of the zone of memory and for the growth of the quasi-cylindrical region, ψ_2 is constant in time.

At this moment we have demonstrated, in the lowest order in c, the existence of the Bogoliubov regime for times t long compared to r_c/v since in the neighbourhood of the origin in relative configuration space ψ_2, which is the lowest order approximation to g_2, depends only on ξ_1, which is the lowest order approximation to f_1. We have seen how the Bogoliubov regime develops by the motion of the zone of memory away from the origin and we know that we must qualify the functional relationship by noting that it does not apply at distances corresponding to the zone of memory and beyond. In this lowest order of c, f_1 and consequently f_2, in the region where the functional relationship is valid, is constant in time. We would like to demonstrate the existence of a Bogoliubov regime in the next order in c where f_1 depends on time.

In order to do this we turn our attention to the qualitative properties of the function $\psi_3(1, 2, 3, t)$ which is the integrand in the second term on the right in equation (11). Figure 2 is supposed to represent the function ψ_3 in the configuration space x_3 for some fixed momentum p_3 and for fixed p_1x_1, p_2x_2 corresponding to a point in the cylindrical portion of figure 1. Our considerations are valid *a fortiori* for all other states of 1 and 2 except those in the zone of memory and beyond. The points 1 and 2 represent the fixed positions x_1 and x_2 of molecules 1 and 2 while the lines 11', 22' represent
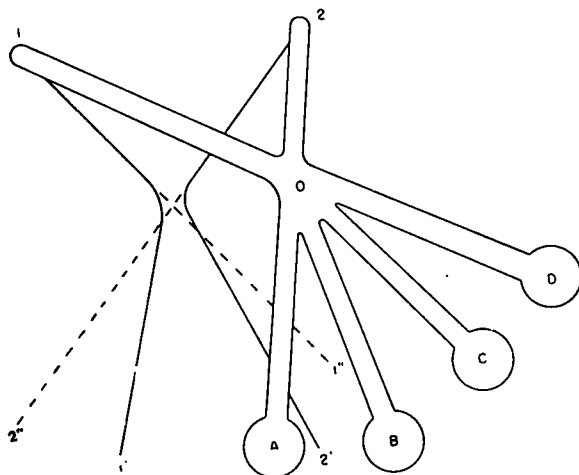

Fig. 2. The function ψ_3 as a function of the position x_3 of molecules for fixed p_1x_1, p_2x_2 and p_3.

the trajectories of these two particles, from $-t$ to 0. According to our assumption about the initial configuration a collision has taken place at some time $-\tau$ with $t - r \gg r_c/v$. The lines 11'', 12'' represent the paths by which molecules 1 and 2 would have arrived at x_1, x_2 had no collision taken place at $-\tau$. The complicated region containing the points 1, 2, O, A, B, C and D are supposed to represent positions of molecule 3 for which ψ_3 is different from zero. We have shown in reference [1] that these points are the initial configurations of the three molecules for which certain collision events have taken place. For instance in the region 1 O molecule 1 has suffered a collision with molecule 3 after its collision with molecule 2. Similarly, the region 2 O. In the region surrounding O a genuine triple collision among the three molecules has occured at $-\tau$. In all these regions, as a consequence of our assumptions about the initial configurations of 1 and 2 the relevant positions at $-t$ are sufficiently separated so that every one of the ξ's occuring in ψ_3 can be replaced by a product of ξ_1's for appropriate arguments. Moreover since ξ_1 is a constant in time ψ_3 is independent of time in these regions.

We turn our attention now to the regions ϴA, OB, OC, OD. These are regions where molecule 3 collides with one of the molecules 1 or 2 before $-\tau$ either in such a way that the collision with the other at $-\tau$ brings both molecules 1 and 2 to the points x_1 and x_2 at time 0 or in such a way the collision with the other prevents both molecules from reaching the points x_1 and x_2 at time 0. The first of these two alternatives has been called in reference (1) an actual binary collision and the second, an hypothetical binary collision. Since the collision with 3 may take place at any time between $-\tau$ and $-t$ the length of these regions increases with time. Moreover at the end of each of these regions, at the points A, B, C. D, molecules 3 and 1 or 2 are close together at $-t$. The neighborhoods of these four points are *zones of memory* where we need ξ_2 as well as ξ_1 to express ψ_3. Everywhere else in the figure ξ_1 is sufficient. It has been shown in reference (1) that in the region OB including the zone of memory A, (but not including the region of triple collisions O) which corresponds to an actual successive binary collision of 3 with 1 then 2 with 1, $\psi_3(1, 2, t)$ reduces to

$$\psi_3(1, 2, 3, t) = \xi_1(2_{12}) \, \psi_2(1_{12}, 3, t) \tag{13}$$

where 1_{12}, 2_{12}, without a time subscript mean the positions and momenta in the indefinite past of particles 1 and 2 respectively projected forward to time zero along straight line trajectories. The corresponding momenta are what we have called p_1', p_2' while the corresponding positions x'_1, x_2' are different from but not far from x_1, x_2. Similarly in the region OC (including C, but excluding O) in which actual successive binary collisions of the type 3 with 2 then 1 with 2 take place we have

$$\psi_3(1, 2, 3, t) = \xi_1(1_{12}) \, \psi_2(2_{12}, 3. \, t). \tag{14}$$

Finally we have in the regions OA, OD,

$$\psi_3(1, 2, 3, t) = - \, \xi_1(1) \, \psi_2(2, 3, t) \tag{15}$$

and

$$\psi_3(1, 2, 3, t) = - \, \xi_1(2) \, \psi_2(1, 3, t) \text{ respectively.} \tag{16}$$

As we have asserted above, and as the explicit formulas (13)–(16) show, under our assumed initial conditions, there are always regions, namely the regions A, B, C, D for which ψ_3 depends not only on ξ_1 but on ξ_2 as well. These regions will contribute to the integral of ψ_3 over the configuration space of molecule 3 no matter how large the time. Therefore the second term on the right in equation (13), unlike the first term is not a functional of ξ_1 only. We recall, however, that our object is not to prove that g_2 is a functional of ξ_1 only, but rather that it is a functional of g_1. To achieve this we note that under our assumed initial conditions the first term on the right is a functional of ξ_1 only. We may therefore use equation (10) to express

this term as a functional of g_1 plus some correction terms of the same order in c as the second term on the right in equation (11). We have

$$\xi_1(1) = 1/c \, g_1(1) - c \int \psi_2 \, (1, 2, t) \, d(2), \quad c^2 \psi_2(1, 2, t) = c^2(\xi_1(1_{12})\xi_1(2_{12}) - \xi_1(1)\xi_1(2))$$
$$= g_1(1_{12})g_1(2_{12}) - g_1(1)g_1(2) - c^2 g_1(1_{12}) \int \psi_2(2_{12}, 3) \, d(3) - c^2 g_1(2_{12}) \int \psi_2(1_{12}, 3) d(3)$$
$$+ c^2 g_1(1) \int \psi_2(2, 3) \, d(3) + c^2 g_1(2) \int \psi_2(1, 3) \, d(3) + O(c^4)$$
$$= g_1(1_{12}) \, g_1(2_{12}) - g_1(1) \, g_1(2) \tag{17}$$
$$- c^3 \int (\xi_1(1_{12}) \, \psi_2(2_{12}, 3) + \xi_1(2_{12}) \, \psi_2(1_{12}, 3) - \xi_1(1) \, \psi_2(2, 3) - \xi_1(2) \, \psi_2(2, 3)) \, d(3).$$

In the last line we have neglected the difference between $c\xi_1$ and g_1 in the correction term as well as other terms of order c^4 and have made use of the fact that 1_{12}, 2_{12} are independent of 3 to collect all terms under a single integral sign. We note the appearance in the correction terms of precisely the same four expressions (equations (13)–(16)) which we have met before as the asymptotic form of ψ_3 in the regions OA, OB, OC, OD. Indeed since in general only one of the four expressions is different from zero for any given configuration of molecule 3, the integrand in the correction term is precisely equal to ψ_3 in these regions but with the opposite sign. We have, combining equations (11) and (18)

$$g_2(1, 2, t) = g_1(1_{12}) \, g_1(2_{12}) - g_1(1) \, g_1(2) +$$
$$+ c^3 \int (\psi_3(1, 2, 3, t) - \xi_1 \, (1_{12}) \, \psi_2 \, (2_{12}, 3, t) - \xi_1(2_{12}) \, \psi_2(1_{12}, 3, t) + \tag{19}$$
$$+ \xi_1(1) \, \psi_2(1, 3, t) + \xi_1(2) \, \psi_2(2, 3, t)) \, d(3).$$

We know from the previous remark that the integral term in equation (19) has no contributions from the regions OA, OB, OC, OD and therefore does not depend on ξ_2 but only on ξ_1. Moreover since the time dependence of the several terms in the integrand is located in these regions the integral itself is explicitly independent of time. Finally we may express the integral terms as a functional of g_1 by again neglecting the difference between g_1 and $c\xi_1$.

The integral term can be expressed in terms of g_1 only by writing out the integrand explicitly in terms of ξ_1, ξ_2 and ξ_3, replacing everywhere ξ_2 and ξ_3 by a product of ξ_1's for appropriate arguments and finally replacing $c\xi_1$ by g_1. The result is

$$g_2(1, 2, t) = g_1(1_{12}, t) \, g_1(2_{12}, t) - g_1(1, t) \, g_1(2, t)$$
$$+ \int (g_1(1_{123}, t) \, g_1(2_{123}, t) \, g_1(3_{123}, t) - g_1(1_{12}, t) \times$$
$$\times g_1(2_{2_{12}3}, t) \, g_1(3_{2_{12}3}, t) - g_1(2_{12}, t) \, g_1(1_{1_{12}3}, t) \times$$
$$\times g_1(3_{1_{12}3}, t) + g_1(3) \, g_1(1_{12}, t) \, g_1(2_{12}, t)) \, d(3). \tag{20}$$

What we have achieved up to this point is an expression for g_2 correct to the third order in c which is valid for all points 1 and 2 except those in the zone of memory. We have shown that the lowest approximation to g_2 as a functional of g_1 retains its form even when the more accurate time- dependent expression for g_1, equation (10), is used. The extra terms introduced thereby are just those required to transform the higher corrections into a functional

of g_1. What is required to prove Bogoliubov's functional relationship in general is to show that when the higher approximations to g_1 are introduced both terms on the right retain their form and that the corrections introduced thereby just transform the higher corrections to g_2 into functionals of g_1. The new functionals of g_1 must of course retain their form in the same process.

We conclude the paper with a discussion of the qualitative properties of g_2 in the region of large relative distance where for instance memory of initial correlations remain. Before we do this however, we show how equation (20) reduces to the first two terms of the well-known equilibrium expansion for the pair function. In order to demonstrate the reduction of equation (20) to the equilibrium formula we insert its equilibrium value for g_1

$$g_1(1) = f_1^\circ(1) = c(2\pi mkT)^{-3/2} \exp(-p_1^2/2mkT)$$

We have

$$g_1(1_{12}) \, g_1(2_{12}) = c^2(2\pi mkT)^{-3} \exp(-(p_1'^2 + p_2'^2)/2mkT)$$

where $p'_1 \, p_2'$ as before are the momenta in the indefinite past of 1 and 2 considered as functions of their present positions and momenta. We note that $(p_1'^2 + p_2'^2)/2m$ is the energy of the two particles in the indefinite past and must therefore be equal to the present energy $(p_1^2 + p_2^2)/2m + V(x_1 - x_2)$ where V is intermolecular potential. Thus

$$g_1(1_{12}) \, g_1(2_{12}) - g_1(1) \, g_1(2) =$$
$$= c^2(2\pi mkT)^{-3} \exp(-(p_1^2 + p_2^2)/2mkT) \exp(-V(x_1 - x_2)/kT - 1) \quad (21)$$

We turn now to the second term in equation (20). We have immediately, by a similar analysis

$$g_1(1_{123}) \, g_1(2_{123}) \, g_1(3_{123}) = c^3(2\pi mkT)^{-9/2} \exp(-(p_1^2 + p_2^2 + p_3^2)/2mkT) \times$$
$$\times \exp(-(V(x_1 - x_2) + V(x_2 - x_3) + V(x_3 - x_1))/2mkT); \quad (22)$$

next:

$$g_1(1_{12}) \, g_1(2_{2_{12}3}) \, g_1(3_{2_{12}3}) = c^3(2\pi mkT)^{-9/2} \exp(-(p_1'^2 + p_2''^2 + p_3''^2)/2mkT)$$

where p_2'' and p_3'' are the momenta in the indefinite past of particles 2 and 3 considered as functions of the present positions and momenta 2_{12} and 3. As before
$(p_2''^2 + p_3''^2)/2m = (2'^2 + 3^2)/2m + V(x_2' - x_3)$ where x_2' is the position corresponding to 2_{12}. Applying the same transformation again we have
$(p_1^2 + p_2''^2 + p_3''^2)/2m = (p_1^2 + p_2^2 + p_3^2)/2m + V(x_1 - x_2) + V(x_2' - x_3)$.
Thus

$$g_1(1_{12}) \, g_1(2_{2_{12}3}) \, g(3_{2_{12}3}) = c^3(2\pi mkT)^{-9/2} \exp(-(p_1^2 + p_2^2 + p_3^2)/2mkT) \times$$
$$\times \exp(-(V(x_1 - x_2) + V(x_2' - x_3))/kT) \quad (23)$$

and similarly

$$g_1(2_{12}) \, g_1(1_{1_{12}3}) \, g_1(3_{1_{12}3}) = c^3(2\pi mkT)^{-9/2} \exp(-(p_1^2 + p_2^2 + p_3^2)/2mkT) \times$$
$$\times \exp[-(V(x_1 - x_2) + V(x_1' - x_3))/kT] \quad (24)$$

Substituting equations (21–24) into equation (20) and integrating over p_3 in the second term we have

$$g_2(1,2) = c^2(2mkT)^{-3} \exp(-(p_1{}^2 + p_2{}^2)/2mkT) . \exp(-(V(x_1-x_2))/kT - 1) +$$
$$+ c(2mkT)^{-3/2} \exp(-V(x_1-x_2)/kT) \int [\exp(-(V(x_1-x_3)+V(x_2-x_3))/kT) -$$
$$- \exp(-V(x_1' - x_3)/kT) - \exp(-V(x_2' - x_3)/kT) + 1] \, dx_3. \qquad (25)$$

We can transform this formula into the one derived by Yvon[2]), De Boer[7]) and Montroll[8]) by noting that x_1' and x_2' are independent of x_3. Thus

$$[\exp(-V(x_1' - x_3)/kT) - \exp(-V(x_1 - x_3)/kT] \, dx_3 =$$
$$= [\exp(-V(x_2' - x_3)/kT) - \exp(-V(x_2 - x_3)/kT)] \, dx_3 = 0.$$

Finally we have

$$f_2{}^0(1,2) = g_2(1,2) + g_1(1)\, g_1(2) = c^2(2\pi mkT)^{-3} \times$$
$$\exp(-((p_1{}^2+p_2{}^2)/2m + V(x_1-x_2))/kT) \times (1 + c \int [\exp(-V(x_1-x_3)/kT) - 1] \times$$
$$\times [\exp(-V(x_2 - x_3)/kT) - 1] \, dx_3). \qquad (26)$$

We make now some qualitative remarks about the function g_2 out of equilibrium in so far as they are indicated by our analysis. We note first of all that, whereas in equilibrium g_2 has a correlation range, r_c of the order of the range of the intermolecular potential, out of equilibrium the correlation range of g_2 is much larger and seems indeed to grow in magnitude with the time. Indeed figure 1 shows that the first approximation to g_2 has correlations which are essentially constant and dependent only on g_1 up to a distance equal to relative velocity times time, at which distance the traces of the initial correlations are located. At greater distances the correlations are zero. The second term in equation (20) also has correlations dependent only on g_1 which extend to the distance relative velocity times time. This distance corresponds, as we have remarked before to the zone of memory, i.e. to collisions between molecules 1 and 2 at $-t$. For this relative distance and only for this relative distance it is possible for molecule 3 to have an initial position for which a triple collision among the three molecules occurs at $-t$. Thus the second term gives a contribution in the zone of memory which depends on ξ_3. We may expect then, in general, that in the quasi-cylindrical region surrounding the relative velocity vector, g_2 has correlations depending only on g_1 while at the distance relative velocity times time, there is a zone of memory of all the initial data. It is not however in general true that the correlations are constant along lines parallel to the relative velocity, i.e. along trajectories of particles 1 and 2 as the case for the first term in equation (20). We note that the longer the time τ to the collision of molecules 1 and 2, the longer the parts 10, 20 of figure 2. Thus the second term of equation (20) changes as the time of collision changes i.e. as the distance from the origin in figure 1 changes. It is not possible from the first two terms in the series for g_2 to determine this function in the neighborhood of the relative velocity vector at large distances from the origin for the

convergence of the series expansion for g_2 must necessarily become worse and worse as the distance increases. We may conjecture, however, that at a distance from the origin along the relative velocity vector measured by the time τ, $g_2(1, 2, t)$ is essentially given by

$$\bar{g}(1_{12}, t - \tau)\, \bar{g}(2_{12}, t - \tau) - \bar{g}(1, t - \tau)\, \bar{g}(2, t - \tau) \tag{27}$$

where

$$\bar{g}(p, t - \tau) \text{ is } \Theta(p, \tau)\, g(p, t - \tau)$$

and Θ represents the fraction of a beam of molecules of momentum p which have not been removed from the beam due collisions with other molecules during time τ. If this conjecture is correct, the correlations along the relative velocity vector do not extend indefinitely but have a range given by the mean free path. In addition to correlations in the neighborhood of the relative velocity vector there are also correlations due to collision events in which molecules 1 and 2 are connected indirectly by collisions with other molecules. These should diminish with the relative distance $x_1 - x_2$ for geometrical reasons.

We may sum up these remarks by saying that in contrast to the equilibrium pair distribution function the non-equilibrium pair distribution function has correlations which extend beyond the range of intermolecular force. These correlations are, for fixed p_1 and p_2, concentrated in the neighborhood of the ray in the direction of the relative velocity vector and diminish to zero at distances large compared to a mean free path. Nevertheless at distances along this ray equal to the relative velocity times the time from the initial instant there are always traces of the correlations which existed at time zero.

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