One suggestion which is obvious from this consideration is to attempt a measurement of the shear-wave deformation by taking the difference between the experimental and predicted residual attenuation at large ql values.

CONCLUSION

This article reports and interprets experiments which were conducted to determine the temperature dependence of shear-wave attenuation in superconducting aluminum. Some of the main results are:

(1) In contrast to the longitudinal-wave attenuation, the experiments showed a strong frequency dependence of the reduced attenuation (α_s/α_n) as a function of temperature.

(2) The temperature variation of (α_s/α_n) could be separated into two parts:

(a) a very sharp decrease with temperature very close to the transition temperature and

(b) a residual attenuation having a temperature dependence similar to that for longitudinal waves.

(3) A theoretical formulation was made which used approximations expected to be valid near the transition temperature. This theory employed a self-consistent treatment of the electron-impurity collisions and qualitatively reproduced the features of the experimental data.

(4) It was found that the specific details of the data could be predicted by this theory when the function $2f(\epsilon)$ was used for the normal electron density.

(5) In particular the residual attenuation was shown to be $g[2f(\epsilon)]$, and the width of the region of rapid-falling attenuation was shown to be determined by $\omega\tau$.

ACKNOWLEDGMENTS

We should like to express particular thanks to Dr. M. S. Said for his assistance in performing the experiments and to M. T. Thomas for programing the numerical calculations.

PHYSICAL REVIEW VOLUME 136, NUMBER 4A 16 NOVEMBER 1964

Surface Integral Form for Three-Body Collision in the Boltzmann Equation

M. S. Green

National Bureau of Standards, Washington, D. C.

(Received 29 June 1964)

A new form is given for the triple-collision term in the generalized Boltzmann equation which is more similar to the well-known binary-collision expression than those given heretofore. The form involved is a surface integral over a five-collision parameter space which is the generalization of the two-dimensional collision parameter space for binary collisions. For "soft" repulsive interactions, the expression involves both the asymptotic properties of three-body collisions before and after the collision, and the dynamics of binary collisions during the collision process. For hard spheres, the expression involves only the asymptotic properties of ternary and binary collisions.

I. INTRODUCTION

In recent years, several authors[1–17] have written on the structure of the asymptotic three-body collision term in a modified Boltzmann equation appropriate to dense gases. At the present time, it appears that all methods of derivation lead to the same result, albeit in different mathematical forms.[3,9,17] In a form derived by the author,[3] this operator may be written

$$I_3=\int \theta_{12}[S(123)-S(12)S(23)-S(12)S(13)+S(12)] \times f(1)f(2)f(3)d(2)d(3)\,, \quad \text{(I)}$$

where 1, 2, etc., are abbreviations for the momentum and configuration $\mathbf{p}_1$, $\mathbf{x}_1$; $\mathbf{p}_2$, $\mathbf{x}_2$ of particles 1, 2, etc., $S(123)$, $S(12)$ are the substitution operators which have been defined for instance in Ref. 10, and will be

[1] N. N. Bogolyubov, "Problems of a Dynamical Theory in Statistical Physics," translation by E. K. Gora from *Studies in Statistical Mechanics*, edited by J. deBoer and G. E. Uhlenbeck (North-Holland Publishing Company, Amsterdam, 1962), Vol. I.
[2] M. S. Green, J. Chem. Phys. **25**, 836 (1956).
[3] M. S. Green, unpublished letter to G. E. Uhlenbeck.
[4] M. S. Green, Physica **24**, 393 (1958).
[5] S. T. Choh and G. E. Uhlenbeck, thesis, University of Michigan, 1958 (unpublished).
[6] R. M. Lewis, J. Math. Phys. **2**, 222 (1961).
[7] S. Rice, J. Kirkwood, and R. Harris, Physica **27**, 717 (1961).
[8] E. G. D. Cohen, Physica **28**, 1025, 1045, 1060 (1962).
[9] E. G. D. Cohen, *Fundamental Problems in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1960).
[10] M. S. Green and R. A. Piccirelli, Phys. Rev. **132**, 1388 (1963).
[11] P. Resibois, J. Math. Phys. **4**, 166 (1963).
[12] E. G. D. Cohen, J. Math. Phys. **4**, 183 (1963).
[13] S. Ono and T. Shizume, J. Phys. Soc. Japan **18**, 29 (1963).
[14] R. Zwanzig, Phys. Rev. **129**, 486 (1963).
[15] J. Weinstock, Phys. Rev. **132**, 470 (1963).
[16] G. Sandri, Ann. Phys. (N.Y.) **24**, 332, 380 (1963).
[17] P. Resibois (private communication).

defined explicitly in Eq. (3) below,

$$\theta_{12}=\mathbf{F}_{12}\cdot(\nabla_{p_1}-\nabla_{p_2}). \quad (1)$$

$\mathbf{F}_{12}$ is the force exerted by particle 2 on particle 1.

Although expression (I) has a very symmetric and compact form, it is disparate in several important respects from the corresponding well-known expression for the two-body collisions in the spatially uniform case.

$$I_2=\int[f(\mathbf{p}_1')f(\mathbf{p}_2')-f(\mathbf{p}_1)f(\mathbf{p}_2)] \times(|\mathbf{p}_1-\mathbf{p}_2|/m)d\mathbf{b}d\mathbf{p}_2, \quad \text{(II)}$$

where $\mathbf{p}_1'\mathbf{p}_2'$ are the momenta of particles 1 and 2 before the collision, considered as functions of the momenta $\mathbf{p}_1\mathbf{p}_2$ and collision-parameter vector $\mathbf{b}$ after the collision. Expression (II) also can be written more compactly in terms of S operators as

$$I_2=\int[S(12)-1]f(1)f(2)(|\mathbf{p}_1-\mathbf{p}_2|/m)d\mathbf{b}d\mathbf{p}_2. \quad \text{(II}')$$

Perhaps the most obvious disparity between (I) and (II′) is the absence of the operator θ_{12} in (II′). A second disparity is the fact that in (II′) the collision parameter $\mathbf{b}$ runs over a plane perpendicular to the relative final velocity $\mathbf{p}_1-\mathbf{p}_2$, and not over the full configuration space of particle 2, while in expression (I) the integration is over the complete configuration space of particles 1 and 2. The most significant disparity from a practical point of view, however, is that, while expressions (II) and (II′) involve dynamics of two-body collisions only through the asymptotic relationship between momenta before and after the collision, expression (I) involves the dynamics of three- (and two-) body collisions while the collision is in progress.

The purpose of this paper is to exhibit the three-body collision term in a form which in many, but not all ways, is analogous to expressions (II) or (II′) for the binary-collision term. More particularly, we will exhibit the three-body term as a configuration integral over a five-dimensional collision space, analogous to the two-dimensional collision space for binary collisions in which the only aspect of three-body dynamics involved is the asymptotic relation between the momenta of the particles before any collision event has begun, and the momenta of the particles after all collision events are completed. The operator θ_{ij}, however, is not completely eliminated. But it appears only in conjunction with two-body substitution operators $S(i,j)$. In the last part of the paper we make this form more explicit for the hard-sphere model.

There are two means by which the transformation is effected. The first means is a commutation relation satisfied by the $S(1\cdots n)$ operators. Let us write the Liouville operator in the form

$$\mathfrak{L}_n(1\cdots n)=\sum_{i=1}^{n}\mathfrak{L}_1(i)-\sum_{i<j}\theta_{ij} =\mathfrak{L}_n^0(1\cdots n)-\sum_{i<j}\theta_{ij}, \quad (2)$$

where $\mathfrak{L}_1(i)=(\mathbf{p}_i/m)\cdot\nabla_{x_i}$. Then

$$S(1\cdots n)=\lim_{t\to\infty}\exp(-t\mathfrak{L}_n)\exp(t\mathfrak{L}_n^0). \quad (3)$$

If we write this as

$$S(1\cdots n)=\lim_{t\to\infty}\exp[-(t+\tau)\mathfrak{L}_n]\exp[(t+\tau)\mathfrak{L}_n^0], \quad (4)$$

the result is of course independent of τ. Differentiating with respect to τ we have

$$0=\lim_{t\to\infty}-\mathfrak{L}_n\exp[-(t+\tau)\mathfrak{L}_n]\exp[(t+\tau)\mathfrak{L}_n^0] +\exp[-(t+\tau)\mathfrak{L}_n]\exp[(t+\tau)\mathfrak{L}_n^0]\mathfrak{L}_n^0, \quad (5)$$

or

$$0=\mathfrak{L}_nS_n-S_n\mathfrak{L}_n^0. \quad (6)$$

Using Eq. (1), we may also write[18]

$$\mathfrak{L}_n^0S_n-S_n\mathfrak{L}_n^0=\sum_{i<j}\theta_{ij}S_n. \quad (7)$$

If we operate with the right-hand side of Eq. (6) on a function $\phi_n(\mathbf{p}_1\cdots\mathbf{p}_n)$ of momentum only, we obtain

$$\mathfrak{L}_nS_n=\sum_{i<j}\theta_{ij}S_n, \quad (8)$$

which is an expression of the well-known fact that $S_n\mathfrak{L}_n(\mathbf{p}_1\cdots\mathbf{p}_n)$ is an integral of motion for n-particle dynamics. Equation (6) or (7) can be considered to be the modification and generalization of this statement to arbitrary functions.

The second means is the symmetrization of the integrand in (I) with respect to the indices of all three particles. We may write

$$I_3=\frac{1}{2}\int[\theta_{12}\tau_2(12,3)+\theta_{13}\tau_2(13,2)+\theta_{23}\tau_2(23,1)] \times f(1)f(2)f(3)d(2)d(3), \quad (9)$$

where

$$\tau_2(12,3)=S(123)-S(12)S(13) -S(12)S(23)+S(23). \quad (10)$$

The contribution of the second term in parentheses to the integral is equal to that of the first term, since 2 and 3 are dummy indices, while the contribution of the third term is zero. Expanding Eq. (9), we obtain

[18] I am indebted to Robert Piccirelli for this formula.

the expression (I′) for the triple-collision contribution

$$I_3=\frac{1}{2}\int(\theta_{12}+\theta_{13}+\theta_{23})S(123)-\theta_{12}S(12)[S(13)+S(23)]-\theta_{13}S(13)[S(23)+S(13)]-\theta_{23}S(23)[S(12)+S(13)]+\theta_{12}S(12)+\theta_{13}S(13)+\theta_{23}S(23)f(1)f(2)f(3)d(2)d(3). \quad (\mathrm{I}')$$

II. TRANSFORMATION OF THE BINARY OPERATOR

We propose to transform the six-dimensional volume integral in Eq. (I) to a five-dimensional surface integral using Eq. (7). Before we do this, let us consider the well-known transformation which takes the form (II″) for the binary-collision integral (the form which arises first in the Bogolyubov theory) into the form (II′) or (II). The form (I″) is

$$I_2=\int\theta_{12}S(12)f(1)f(2)d(2), \quad (\mathrm{II}'')$$

First of all, it should be emphasized that I_2 has a nonlocal significance; it depends on a variety of spatial points. I_2 can only be transformed into the form (II′) or (II) for spatially independent f's. The nonlocal part, the so-called collisional transfer term, is included in (II″) but not in (II′) or (II). This is also true of the transformation of I_3 to a surface integral form; the transformation can only be effected for spatially uniform f_1.

For fixed $\mathbf{p}_2$ and, of course, $\mathbf{p}_1$ and $\mathbf{x}_1$, the configuration integration in (II″) can be considered to be carried out with respect to the relative configuration $\mathbf{R}_{21}=\mathbf{x}_2-\mathbf{x}_1$. We may use the commutation relation, Eq. (7), to replace $\theta_{12}S(12)f_1(1)f_1(2)$ in (II″) by

$$[\mathcal{L}_2{}^0S(12)-S(12)\mathcal{L}_2{}^0]f_1(1)f_1(2).$$

Because we are dealing with the spatially uniform case, we have

$$I_2=\int\frac{|\mathbf{p}_2-\mathbf{p}_1|}{m}\cdot\nabla_R[S(12)-1]f(1)f(2)d\mathbf{p}_2d\mathbf{R}_{12}, \quad (11)$$

since for this case we may replace Eq. (7) by Eq. (8), $S(12)f_1(1)f_1(2)$ depends only on $\mathbf{R}_{12}$ and $\mathcal{L}_2{}^0=[(\mathbf{p}_2-\mathbf{p}_1)/m]\cdot\nabla_R$. Now since θ_{12} contains the intermolecular force as a factor, we may suppose the configuration integration in Eq. (12) to be over the interior of a closed surface of large diameter compared to the range R_0 of intermolecular forces. As has been pointed out elsewhere,[1] the function $[S(12)-1]f_1(1)f_1(2)$ is different from zero on this surface only in a region of diameter R_0 surrounding the point of intersection with the surface of the ray from the origin in the direction of the relative velocity vector. It is possible to transform Eq. (11) by Gauss's theorem. It is simpler, however, to proceed by breaking up R_{12} into a component $[(\mathbf{p}_2-\mathbf{p}_1)/m]\tau$ parallel to the relative velocity vector and a component $\mathbf{b}$ perpendicular to this vector. Then

$$\mathcal{L}_0\equiv\partial/\partial\tau.$$

$$I_2=\int\frac{\partial}{\partial\tau}[S(21)-1]f(1)f(2)\frac{|\mathbf{p}_2-\mathbf{p}_1|}{m}d\tau d\mathbf{b}d\mathbf{p}_2. \quad (12)$$

Integrating first with respect to τ for fixed $\mathbf{b}$, we obtain

$$I_2=\int[S(12)-1]f(1)f(2)\frac{|\mathbf{p}_2-\mathbf{p}_1|}{m}d\mathbf{b}d\mathbf{p}_2, \quad (13)$$

in which the integrand is evaluated on the portion of the boundary surface in the neighborhood of the positive ray. For such points, of course, $S(12)f(1)f(2)=f(\mathbf{p}_1')f(\mathbf{p}_2')$, where $\mathbf{p}_1'\mathbf{p}_2'$ are the initial momenta considered as functions of the final momenta and collision parameter.

III. TRIPLE-COLLISION INTEGRAL

We turn now to the transformation of the expression (I′) for the triple-collision contribution for spatially uniform f. For fixed $\mathbf{p}_2\mathbf{p}_3$ and, of course, $\mathbf{p}_1\mathbf{x}_1$, we may consider the configuration integration in (I′) to be confined to a large region V with surface S surrounding the origin in the six-dimensional relative-configuration space $\mathbf{x}_2-\mathbf{x}_1$, $\mathbf{x}_3-\mathbf{x}_1$, and we may attempt by means of the commutation relation to transform (I′) into a surface integral over S. For the first term in the integrand, we may immediately apply Eq. (7) or, since f is supposed to be spatially uniform, Eq. (8), for $n=3$. In the remaining terms, which contain factors of the form $\theta_{ij}S(ij)$, it is convenient to modify Eq. (7) for $n=2$. We have, for instance,

$$\mathcal{L}_3{}^0S(12)-S(12)\mathcal{L}_3{}^0=\theta_{12}S(12), \quad (14)$$

since $\mathcal{L}_1{}^0(3)$ commutes with $S(12)$. Applying Eq. (8) for $n=3$ and Eq. (14), we obtain

$$I_3=\frac{1}{2}\int\Big[\mathcal{L}_3{}^0\{S(123)-S(12)[S(13)+S(23)]-S(13)[S(12)+S(23)]-S(23)[S(12)+S(13)]+S(12)+S(23)+S(13)\}-\{S(12)\mathcal{L}_3{}^0[S(13)+S(23)]+S(13)\mathcal{L}_3{}^0[S(12)+S(23)]+S(23)\mathcal{L}_3{}^0[S(13)+S(12)]\}\Big]f(1)f(2)f(3)d(2)d(3). \quad (15)$$

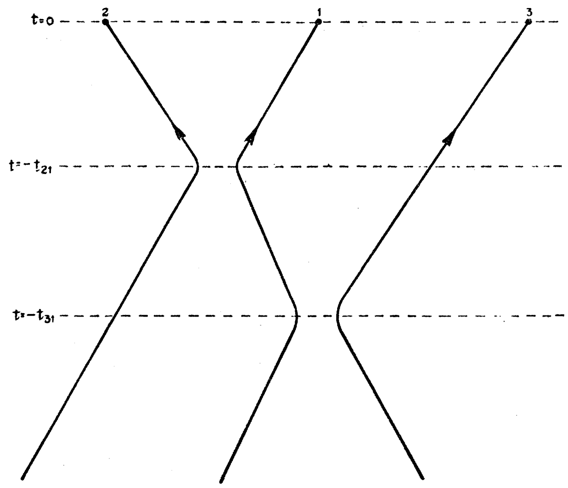

FIG. 1. Actual successive binary collision.

The first group of terms in Eq. (15), in which the operator $\mathcal{L}_3^0$ appears to the left, can be transformed immediately to a surface integral. We may proceed as we did in the transformation of the binary-collision term and break up the six-dimensional configuration integral in relative-configuration space $(\mathbf{x}_2-\mathbf{x}_1, \mathbf{x}_3-\mathbf{x}_1)$ into an integral along lines parallel to the six-dimensional relative velocity vector and an integral over the five remaining spatial coordinates. Now the volume element in the relative-configuration space can be represented as

$$dt_{12}(|\mathbf{p}_2-\mathbf{p}_1|/m)d\mathbf{b}_{12}\cdot dt_{31}(|\mathbf{p}_3-\mathbf{p}_1|/m)d\mathbf{b}_{31}$$

where t_{21}, $\mathbf{b}_{21}$ are the time[19] and collision parameter, respectively, of the 21 collision and similarly t_{31}, $\mathbf{b}_{31}$. The volume element $dt_{21}dt_{31}$, moreover, may be written $dtd\tau$, where $t=t_{21}$ and $\tau=t_{31}-t_{21}$. Variation in t with fixed τ, $\mathbf{b}_{21}$, and $\mathbf{b}_{31}$ (and $\mathbf{p}_1$, $\mathbf{p}_2$, and $\mathbf{p}_3$) corresponds to the motion of the representative point in configuration space along a line parallel to the six-dimensional relative velocity vector $(\mathbf{p}_2-\mathbf{p}_1, \mathbf{p}_3-\mathbf{p}_1)$. We may therefore represent the five-dimensional surface element as[20] $(|\mathbf{p}_2-\mathbf{p}_1|/m)(|\mathbf{p}_3-\mathbf{p}_1|/m)d\tau d\mathbf{b}_{21}d\mathbf{b}_{31}$.

The boundary S may be divided into two parts S_1 and S_2 such that for a point on S_1 the representative point moving with the relative velocity vector will leave V, and for a point on S_2 the representative point will enter V. It is clear that the boundary surfaces S_1 and S_2 may be chosen so that lines parallel to the relative velocity vector will intersect S_1 once for $t=t_1(\mathbf{b}_{31},\mathbf{b}_{21},\tau)$, and will intersect S_2 once for $t=t_2(\mathbf{b}_{31},\mathbf{b}_{21},\tau)$; and that on S_1 all three particles are receding from each other, and on S_2 all three particles are approaching each other.

[19] To be specific, we may define the time of a collision to be the time when the two particles, moving along the asymptotic straight line paths would have been closest.

[20] This, of course, is not the only possible representation of the surface element. We may, for instance, construct two others based on the pairs 23, 21 and 31, 32.

We may immediately carry out the integration for the first group of terms with respect to t by evaluating the integrand for $t_1(\mathbf{b}_{31},\mathbf{b}_{21},\tau)$ and for $t_2(\mathbf{b}_{31},\mathbf{b}_{21},\tau)$. We have for their contribution

$$\int \{S(123)-S(12)[S(13)+S(23)] -S(13)[S(12)+S(23)]-S(23)[S(12)+S(13)] +S(12)+S(23)+S(13)+2\} \times f(1)f(2)f(3)(|\mathbf{p}_3-\mathbf{p}_1|/m)(|\mathbf{p}_2-\mathbf{p}_1|/m) \times d\tau d\mathbf{b}_{31}d\mathbf{b}_{21}. \quad (16)$$

On S_2, all S operators and products of S operators become unity, and the $+2$ in Eq. (17) represents their net contribution. The remaining terms represent the contribution from S_1.

The second group of terms in Eq. (15) cannot, of course, be represented as a difference of contributions from S_2 and S_1. We may, nevertheless, carry out first the integration with respect to t keeping all other variables fixed. The resulting expression will be a function of τ, $\mathbf{b}_{31}$, $\mathbf{b}_{21}$, and may then be combined with the expression [Eq. (16)] in a single integral. We have

$$I_3=\int_s \Big\{ \tau(123)-\int_{t_2}^{t_1} dt \Big[S(12)\mathcal{L}_3^0[S(13)+S(23)] +[S(13)]\mathcal{L}_3^0[S(12)+S(23)] +[S(23)]\mathcal{L}_3^0[S(12)+S(13)] \Big] \Big\} \times f_1(1)f_1(2)f_1(3)\frac{|\mathbf{p}_3-\mathbf{p}_1|}{}\frac{|\mathbf{p}_2-\mathbf{p}_1|}{} \times d\tau d\mathbf{b}_{21}d\mathbf{b}_{31}d\mathbf{p}_2d\mathbf{p}_3, \quad (17)$$

where $\tau(123)$ is the operator in curly brackets in Eq. (16). The integration over dt is for fixed values of τ, $\mathbf{b}_{21}$, $\mathbf{b}_{31}$ (and, of course, $d\mathbf{p}_2d\mathbf{p}_3$), and the limits of integration over τ, $\mathbf{b}_{21}$, $\mathbf{b}_{31}$ indicated by the subscript S on the integral are over values of these variables for which the corresponding line in configuration space intersects S_1 and S_2.

This expression [Eq. (17)] for I_3 is independent on the choice of the region V in configuration space in two ways: the integral with respect to t is limited by t_2 and t_1, and the integration over $\tau\mathbf{b}_{24}\mathbf{b}_{31}$ is limited to the projection of V onto the space of these variables. Since we know, however, that the original expression (I) for I_3 is independent of the choice of V, the dependence of Eq. (17) on V must be only apparent. If we could be assured that the integrand in the t integral is different from zero only for small t, and that the integrand of the remaining integrations is different from zero only for small values of τ, $|\mathbf{b}_{31}|$, and $|\mathbf{b}_{21}|$, we then could remove the limits of integration and the apparent dependence on V. Neither statement is true for the individual parts, but both are true for the total integrand. In order to see this, it is convenient to make several rearrangements in the integrand in Eq. (17). First we re-express the integrand in terms of U operators (Ursell operators) defined below. If we replace $S(12)$, $S(13)$, etc., everywhere in the time integral in Eq. (17) by $U(12)=S(12)-1$, $U(13)=S(13)-1$, etc., the change in the time integral thereby produced can be compensated by adding $2S(12)+2S(23)+2S(13)-6$ to $\tau(123)$. It is then easy to see that Eq. (17) can be written

$$I_3=\frac{1}{2}\int_{s1}\left\{U(123)-\sum_{\alpha\neq\beta}\left[U(\alpha)U(\beta)-\int_{t_2}^{t_1}dtU(\alpha)\mathcal{L}_3{}^0U(\beta)\right]\right\}\times f(1)f(2)f(3)\frac{|\mathbf{p}_2-\mathbf{p}_1|}{m}\frac{|\mathbf{p}_3-\mathbf{p}_1|}{m}\times d\tau d\mathbf{b}_{21}d\mathbf{b}_{31}d\mathbf{p}_2d\mathbf{p}_3, \quad (18)$$

where

$$U(123)=S(123)-S(12)-S(13)-S(23)+2 \quad (19)$$

and α, β represent any one of the three pairs 12, 13, 23.

Secondly, we note that since $\mathcal{L}_3{}^0$ is simply d/dt, we can integrate the time integrals by parts. We have

$$\int_{t_2}^{t_1}dtU(\alpha)\frac{d}{dt}U(\beta)=U(\alpha)U(\beta)\Big|_{t_2}^{t_1}-\int_{t_2}^{t_1}dt\left[\frac{d}{dt}U(\alpha)\right]U(\beta). \quad (20)$$

Since $U(\alpha)U(\beta)$ is zero at t_2, the first term in Eq. (20) is simply $U(\alpha)U(\beta)$ evaluated on S_1, which cancels the product $U(\alpha)U(\beta)$ already appearing in Eq. (18). We have finally

$$I_3=\frac{1}{2}\int_{s}\left\{U(123)-\sum_{\alpha\neq\beta}\int_{t_2}^{t_1}dt\left[\frac{d}{dt}U(\alpha)\right]U(\beta)\right\}\times f(1)f(2)f(3)\frac{|\mathbf{p}_2-\mathbf{p}_1|}{m}\frac{|\mathbf{p}_3-\mathbf{p}_1|}{m}\times d\tau dl_{31}dl_{21}d\mathbf{p}_2d\mathbf{p}_3. \quad (21)$$

As has been pointed out elsewhere, $U(123)$ is different from zero for large values of τ, $\mathbf{b}_{31}$, $\mathbf{b}_{21}$ for two types of collision events, which have been called real and hypothetical successive binary collisions.[10] For a real successive binary collision (Fig. 1), particles 12 are aimed so that they collide if their present paths are carried backward in time to $-t_{21}$. Particle 3 is aimed to collide with the continuation of *the actual path* of particle 1 at some time $-t_{31}'$ earlier than $-t_{21}$; for a hypothetical binary collision (Fig. 2), particles 12 are aimed to collide at $-t_{21}$, but particle 3 is aimed to collide with the continuation of the motion of particle 1 *along a hypothetical straight line path* at some time $-t_{31}$ earlier than $-t_{21}$. For the events of Fig. 1 and Fig. 2, $U(123)$ reduces to the product $U(12)U(13)$. In general, for any real or hypothetical successive binary collision, $U(123)$ reduces to $U(\alpha)U(\beta)$, where the α collision is the latter and the β the earlier event. As long as the three momenta and the collision parameter of the α and β collisions are fixed, the time between collisions can be varied at will without changing the value of $U(123)$. Thus, the first term in the integrand in Eq. (21) yields contributions for large values of τ, $|\mathbf{b}_{31}|$, $|\mathbf{b}_{21}|$.

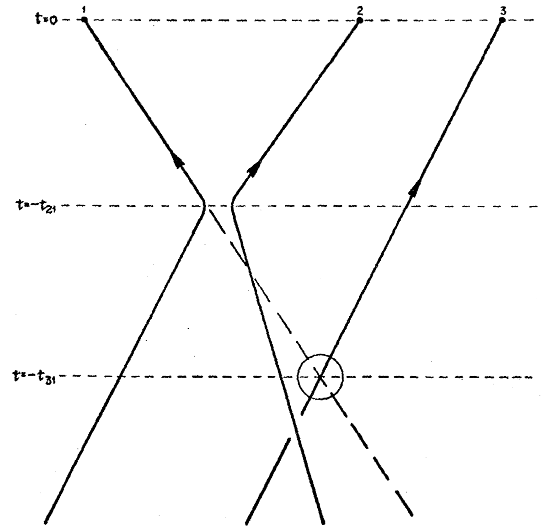

FIG. 2. Hypothetical successive binary collision.

We turn now to the evaluation of the time integral terms in Eq. (21). Now $(d/dt)U(\alpha)$ is different from zero only when the particles of the pair α are close together. Otherwise $U(\alpha)$ is either zero or independent of t. Thus, in order for a term of the second group in Eq. (21) to be different from zero, τ, $\mathbf{b}_{21}$, $\mathbf{b}_{23}$ must have such values that the pair α are aimed to collide when their paths are projected backwards in time. Let us suppose this takes place for values of t in an interval $(\tau_0-\delta, \tau_0+\delta)$. If the pair β is also aimed to collide at a time in this interval, both operators in the time integral depend on t and no reduction is possible. If, however, this is not the case, $U(\beta)$ is constant during the interval $(\tau_0-\delta, \tau_0+\delta)$, and we may write

$$\int_{t_2}^{t_1}dt\left[\frac{d}{dt}U(\alpha)\right]U(\beta)=\int_{\tau_0-\delta}^{\tau_0+\delta}dt\left[\frac{d}{dt}U(\alpha)\right]U(\beta)=U(\alpha)\Big|_{\tau_0-\delta}^{\tau_0+\delta}U(\beta)=U(\alpha)_tU(\beta)_{t_0}, \quad (22)$$

where in the last expression $U(\alpha)$ is evaluated at $\tau_0+\delta$ [$U(\alpha)$ evaluated at $\tau_0-\delta$ is zero], or what is the same thing, at t_1. $U(\beta)$ of course is evaluated in the neighborhood of τ_0. For $U(\beta)|_{\tau_0}$ to be different from zero, the pair β must be aimed so as to collide at some time earlier than τ_0 either actually or hypothetically. If this is the case, its value for τ_0 is equal to its value for t_1. The value of the time integral [Eq. (22)] is zero except for genuine triple collisions and successive binary collisions in which α is the later, β the earlier collision. For such a successive binary collision, the time integral is equal to $U(\alpha)U(\beta)$ evaluated on the surface S_1. Note that the product $U(\alpha)U(\beta)$ is different from zero for other events than successive binary collisions, but the time integral vanishes for these.

We see that the second group of terms in Eq. (21) yields contributions for precisely the same difficult events (successive binary collisions) as the first term. The values of the first term and the second group of terms for these events are equal, and their net is zero. We have proved therefore that contributions from successive binary collisions are not really present in the integrand of Eq. (21) [or Eq. (17)]. The net contribution from the time integrals comes only for genuine triple collisions (i.e., for small values of τ, $|\mathbf{b}_{31}|$, $|\mathbf{b}_{21}|$), for a small range of t in the neighborhood of the time of the genuine triple collision. Thus, we may extend the limits of integration of Eq. (21) to $-\infty$, ∞ for t, and for $U(123)$ evaluated for an arbitrary distant and indefinitely extended outgoing surface of configuration space. We have, finally

$$I_3=\frac{1}{2}\int\left\{U(123)-\sum_{\alpha\neq\beta}\int_{-\infty}^{\infty}dt\left[\frac{d}{dt}U(\alpha)\right]U(\beta)\right\}\times\frac{|\mathbf{p}_2-\mathbf{p}_1|}{m}\frac{|\mathbf{p}_3-\mathbf{p}_1|}{m}d\tau d\mathbf{b}_{31}d\mathbf{b}_{21}d\mathbf{p}_2d\mathbf{p}_3. \quad (23)$$

IV. THE HARD-SPHERE CASE

In the previous section, we have shown how the three-body collision contribution to a modified Boltzmann equation for dense gases can be transformed to a surface integral form [Eq. (23)] which is analogous to the well-known expression (II) for the binary collision integral. The main significance of this form is that the dynamics of three-body collisions enters into the expression only through the asymptotic relationships among the parameters of the approaching and receding particles. The dynamics of binary collisions, however, enters into Eq. (23) in a more complex way than in expression (II) because the evaluation of the integral terms in Eq. (23) involves the details of the binary collision while the two particles are close together, whereas expression (II) involves only asymptotic relationships between approaching and receding particles.

In the case of the hard-sphere model, all collision events are complexes of binary collisions of infinitesimal duration, so that it should be possible to express Eq. (23) completely in terms of the parameters of approaching and receding pairs of particles. We shall not carry out the reduction of $U(123)$ to pairwise collisions. We shall, however, show how, for the hard-sphere model, the time integral in Eq. (23) can be carried out. In fact, we have already pointed out that, except for cases in which an α collision and β collision overlap in time, the integral expression, Eq. (22), is different from zero only for successive binary events in which the α collision is prior to the β collision, and for such events it has the value $U(\alpha)U(\beta)$. Since two binary collisions between hard spheres cannot overlap in time, the later expression is valid whenever the time integral is different from zero. Thus we may write

$$I_3=\frac{1}{2}\int[U(123)-\sum_{\alpha>\beta}U(\alpha)U(\beta)]\times\frac{|\mathbf{p}_2-\mathbf{p}_1|}{m}\frac{|\mathbf{p}_3-\mathbf{p}_1|}{m}d\tau,d\mathbf{b}_{31}d\mathbf{b}_{21}d\mathbf{p}_2d\mathbf{p}_3, \quad (24)$$

where the symbol $\alpha>\beta$ means that for any set of collision parameters the sum is taken only over those terms (usually one or none) for which the (real) α collision is prior to the (real or hypothetical) β collision.

ACKNOWLEDGMENTS

I would like to thank the Organization of American States for a grant which made possible a visiting lectureship at the Instituto Politécnico Nacional de México (I.P.N.) during which part of the research reported here was carried out. I would like also to thank Ing. José Antonio Padilla-Segura, Director of the I.P.N., and Dr. Arturo Rosenblueth, Director of the Centro de Investigación y de Estudios Avanzados del I.P.N., for the hospitality of their institutions; and my colleagues, Dr. Leopoldo S. García-Colin and Dr. Fernando Chaos, of the Centro, and Dr. Robert Piccirelli and Dr. Jan Sengers of the National Bureau of Standards, for illuminating conversations.