

The H -theorem in the Boltzmann approximation for molecular association and dissociation processes

R. L. Stratonovich

M. V. Lomonosov State University, Moscow

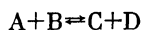
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In the Boltzmann (and consequently nonquantum) approximation we prove in the case of spatial homogeneity an H -theorem for chemical reactions of the form $A + B \rightleftharpoons C$ and $A + B + C \rightleftharpoons D$ taking place in gases. We assume the molecules to have internal degrees of freedom. After we have chosen the bound state region we analyze in detail the various contributions from the molecular associations and dissociations to the time derivative of the entropy density.

1. INTRODUCTION

It is well known that Boltzmann introduced an equation, named after him, and proved the H -theorem assuming that there were no chemical reactions in the gas (see, e.g., Refs. 1–3). The same assumption is the basis of the more detailed theory of processes in gases with a moderate density developed by Bogolyubov, Green, and Cohen.^{4–6} It is natural to pose the problem of generalizing those theories to the case of chemical transformations. Simplest is the generalization of Boltzmann's theory to the case of bimolecular reactions of the form



(see Refs. 7–9 in this connection). In Ref. 9 the H -theorem was also proved (under some assumptions which restricted the generality) for the case when the number of molecules in a single interaction process is not conserved, but the number of molecules up to the interaction and after it is two or more, as, for instance, in the reaction $A + B \rightleftharpoons C + D + G$. We consider here the special case of an associative reaction leading to a single molecule and a spontaneous dissociation of the form



In the usual approximation for physical chemistry one can describe reaction (1.1a) by the equations

$$\dot{n}_1 = \dot{n}_2 = -k_+ n_1 n_2 + k_- n_3, \quad \dot{n}_3 = -k_- n_3 + k_+ n_1 n_2. \quad (1.2)$$

Here n_1 , n_2 , and n_3 are, respectively, the number of A, B, and C molecules per unit volume and k_+ and k_- are kinetic constants. Our problem will be to prove the H -theorem for this case in the Boltzmann approximation.

Note that the theory proposed below cannot be applied to the dissociation or association of a hydrogen atom, i.e., to the $p + e \rightleftharpoons H$ process. The fact is that it is well known that for the association of p and e one needs a third body since otherwise one cannot satisfy the momentum and energy conservation laws at the same time. This process should therefore be written in the form $p + e + M \rightleftharpoons H + M$, where M is the third body, i.e., this process differs from (1.1a). The H -theorem for this case was proved in Ref. 10 by an interesting method, namely, without introducing independent distribution functions for all three particles, H, p, e (M was the same as one of these particles).

According to Eq. (1.2), in the case (1.1a) we must have an exponential spontaneous decay:

$$\dot{n}_3 = -k_- n_3, \quad n_3(t) = n_3(0) \exp(-k_- t). \quad (1.3)$$

This is possible only if at least one of the molecules A or B is complex. It is then possible to simultaneously satisfy the momentum and energy conservation laws for association and dissociation.

The analysis of the case (1.1b) is, in principle, carried out by the same method as in the case (1.1a). It is true that here one must overcome additional technical difficulties connected with the multidimensionality of the combined space, the coordinates of which are the combined arguments of the distribution functions.

We note that the theory proposed here requires a quantum generalization, especially with respect to the internal degrees of freedom of complex molecules. The justification for presenting a classical discussion is that the present paper is the first on this topic and also that in the classical approximation the features of the method applied stand out clearly.

2. INTERNAL AND EXTERNAL DYNAMIC VARIABLES

Let k_i be the number of particles which make up the molecule E_i ($E_1 = A$, $E_2 = B$, $E_3 = C$). It is clear that for (1.1a) we have $k_3 = k_1 + k_2$ where (in agreement with the complexity of the A and B molecules mentioned above) we have $k_3 \geq 3$. Moreover, let the k_i particles of the molecule E_i have the coordinates and momenta $\mathbf{q}_1^{(i)}, \mathbf{p}_1^{(i)}, \dots, \mathbf{q}_{k_i}^{(i)}, \mathbf{p}_{k_i}^{(i)}$. It is convenient to transform the dynamic variables. We introduce new coordinates

$$\mathbf{r}_i = \sum_{\alpha=1}^{k_i} \mu_{\alpha}^{(i)} \mathbf{q}_{\alpha}^{(i)}, \quad \mathbf{q}_{i\sigma}' = \mathbf{q}_{\sigma}^{(i)} - \mathbf{q}_1^{(i)}, \quad \sigma=2, \dots, k_i, \quad (2.1)$$

where we have $\mu_{\alpha}^{(i)} = m_{\alpha}^{(i)} / M_i$, $M_i = m_1^{(i)} + \dots + m_{k_i}^{(i)}$, $m_{\alpha}^{(i)}$ is the mass of the α th particle of the i th molecule, and \mathbf{r}_i is the center of mass radius vector of the E_i molecule. The coordinate transformation (2.1) induces a momentum transformation and the simultaneous transformation of the coordinates and the momenta is a contact or canonical transformation. Using the definition of the momenta one can prove easily that for a linear coordinate transformation $\mathbf{q}' = L\mathbf{q}$ the momenta are transformed by means of the inverse and transposed matrix: $\mathbf{p}' = (L^{-1})^T \mathbf{p}$. The momentum transformation must thus be the following:

$$P_i = \sum_{\alpha=1}^{k_i} p_{\alpha}^{(i)}, \quad p_{i\sigma} = p_{\sigma}^{(i)} - \mu_{\sigma} \sum_{\alpha=1}^{k_i} p_{\alpha}^{(i)}, \quad \sigma=2, \dots, k_i. \quad (2.2)$$

Both the transformation (2.1) and (2.2) have a unit Jacobian. To simplify the notation it is convenient to denote the set of internal variables $q'_{i2}, p'_{i2}, \dots, q'_{ik_i}, p'_{ik_i}$ by ξ_i . The distribution function of the E_i molecule will then be $f_i(r_i, P_i, \xi_i)$.

We must note that all Eqs. (2.1) and (2.2) for all $i = 1, 2, 3$ can be used both when the molecules A and B are far from one another and when they are combined into C. Clearly the following relation holds:

$$r_3 = \frac{M_1}{M_3} r_1 + \frac{M_2}{M_3} r_2, \quad P_3 = P_1 + P_2. \quad (2.3)$$

We also introduce the notation

$$r_2' = r_{21} = r_2 - r_1, \quad P_2' = P_2 - \frac{M_2}{M_3} (P_1 + P_2). \quad (2.4)$$

The transformations (2.3) and (2.4) are the same as (2.1) and (2.2) if we take instead of $k_i, q^{(i)}, p^{(i)}, q_2^{(i)}, p_2^{(i)}$, respectively, $2, r_1, P_1, r_2, P_2$. From the properties of the transformations (2.1) and (2.2) mentioned earlier one concludes easily that the variables $q'_{i2}, \dots, q'_{ik_i}$ can be expressed in terms of $r_2', q'_{i2}, \dots, q'_{ik_i}, q'_{22}, q'_{2k_2}$ through a linear transformation with a Jacobian equal to unity. The same also holds for the variables $p'_{i2}, \dots, p'_{ik_i}$ and $P_2', p'_{i2}, \dots, p'_{ik_i}, p'_{22}, \dots, p'_{2k_2}$, while the combined transformation is canonical. As the internal variables of the C molecule we can thus take together with ξ_3 the variables $\xi_3' = (r_2', P_2', \xi_1, \xi_2)$.

In the following we shall assume that the condition of spatial homogeneity, $\partial f_i / \partial r_i = 0, i = 1, 2, 3$, is satisfied. The distributions can then be written as $f_1(P_1, \xi_1) \equiv f_1(1), f_2(P_2, \xi_2) \equiv f_2(2), f_3(P_3, \xi_3) \equiv f_3(3)$.

3. BOUND STATE AND EXPONENTIAL SPONTANEOUS DECAY

In our case it is important that the decay of a C molecule be spontaneous, i.e., caused by the nonquantum dynamic evolution of the particles making up the C molecule when they are combined. To check that such a decay can proceed following the exponential law (1.3) it is useful to consider the following auxiliary model of a bound state. Let there be a rectangular well with ideally elastic walls in which some particles move. In the wall of the well there is a small hole through which particles cannot pass out which are inside and which have a rather large radius, but a special particle P_0 can move in and out. We shall assume a state to be bound if P_0 is inside the well and unbound in the opposite case. We can finally simplify this system by assuming the well to be two-dimensional, the particles inside the well to be fixed "columns," and the moving particle to be a point mass in the plane. Even in this simple variant the motion of the P_0 particle in the well is self-randomizing, i.e., there occurs dynamic chaos (mixing).

We assume that there is a statistical ensemble of identical wells with "columns," each of which corresponds to a P_0 particle being inside or outside the well. Thanks to the self-randomization for any velocity distribution of P_0 particles moving into the well (it is only important that it not be a delta function) there will rapidly be established inside the

well a quasistationary distribution of the form $f(r, p, t) \approx c(t) w_0(r, p)$, where $w_0(r, p)$, which is a time-independent probability density, is normalized to unity. Thus, due to the fact that the hole is small the shape of w_0 of the distribution f is kept constant and the time-dependent coefficient c decreases exponentially thanks to the fact that the form is constant, i.e., we have the exponential decay (1.3), produced solely by dynamic processes.

The self-randomization of the dynamic process in the model described here, for which the C molecule must be sufficiently complex, is similar to the cause of the exponential spontaneous decay of the molecule in the model. Moreover, it is necessary that the time for self-randomization be much shorter than the decay time constant. Furthermore, it is necessary that the probability density $w_0(r_{21}, P_2', \xi_1, \xi_2)$ be concentrated far from the boundary of the bound state region and on it take relatively small values. Here $w_0(r_{21}, P_2', \xi_1, \xi_2)$, which is established as a result of the self-randomization, is the probability density occurring in the following expression for the quasistationary distribution function:

$$f_3 \approx \text{const} \cdot \exp(-k_- t) w_3(P_3) w_0(r_{21}, P_2', \xi_1, \xi_2). \quad (3.1)$$

We note that apart from P_3 , in (3.1) we should relate the other integrals of motion, namely the angular momentum M_3 of the C molecule to the arguments of the probability density w_3 . Correspondingly we should retain among the arguments of the density w_0 only the other variables. This, however, would complicate the notation.

The density w_0 is concentrated in the region $r_{21} \sim r_{\text{int}}$, where r_{int} is the interaction radius, and it decreases rapidly with increasing r_{21} . It takes very small values (as compared with the maximum ones) for $r_{21} \gg r_{\text{int}}$. This fact must be taken into account when we define the bound state region R , i.e., when we define which states must be considered to be a C molecule. Finally, the choice of the boundaries of this region is connected with some arbitrariness but the freedom of choice is unimportant for the theory. For instance, we can define this region by the condition

$$r_{21} \leq r_0, \quad P_2', \xi_1, \xi_2 - \text{arbitrary}, \quad (3.2)$$

where r_0 is a quantity determined by the inequalities

$$r_{\text{int}} \ll r_0 \ll v^{1/3}. \quad (3.3)$$

Here $v = V/N_3$ is the average volume pertaining to one C molecule. A choice of the value of r_0 satisfying (3.3) is possible since we have the inequality $r_{\text{int}} \ll v^{1/3}$. We bear in mind that the basis of the Boltzmann approximation is the condition

$$r_{\text{int}} \ll v^{1/3} \ll \lambda, \quad (3.4)$$

where λ is the mean free path. We assume that the inequalities (3.4) are satisfied for all molecular shapes and forms of the interaction. As an actual possible value we can take $r_0 = r_{\text{int}}^{1/2} v^{1/6}$. It is more convenient for us to choose the means of determining the bound-state region in a somewhat more complicated way than (3.2), i.e., we take instead of a sphere the cylinder

$$|nr_{21}| \leq r_0, \quad |\sigma_{21}| \leq r_0 \quad (3.5)$$

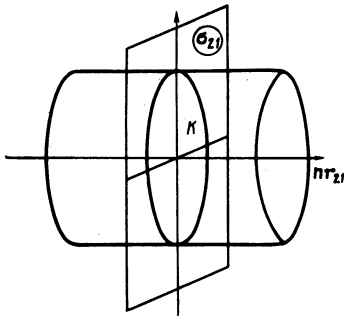


FIG. 1.

(see Fig. 1), where $\mathbf{n} = \mathbf{v}_{21}/v_{21}$ is a unit vector directed along the vector $\mathbf{v}_{21} = \mathbf{P}_2/M_2 - \mathbf{P}_1/M_1 = (M_1^{-1} + M_2^{-1})\mathbf{P}_2'$ and $\boldsymbol{\sigma}_{21} = \mathbf{r}_{21} - \mathbf{n}(\mathbf{n} \cdot \mathbf{r}_{21})$ is the component of the vector \mathbf{r}_{21} transverse to \mathbf{n} . Apart from $\boldsymbol{\sigma}_{21}$ we shall consider the two-component vector \mathbf{s}_{21} corresponding to it. If \mathbf{m}_1 and \mathbf{m}_2 are unit vectors perpendicular to \mathbf{n} and to one another, we can define \mathbf{s}_{21} as $(\mathbf{m}_1 \cdot \mathbf{r}_{21}, \mathbf{m}_2 \cdot \mathbf{r}_{21})$, i.e., $\boldsymbol{\sigma}_{21} = (\mathbf{s}_{21})_1 \cdot \mathbf{m}_1 + (\mathbf{s}_{21})_2 \cdot \mathbf{m}_2$.

For different acceptable choices of the bound state region R and also of r_0 values the differences δn_3 in the number of particles per unit volume

$$n_3 = \int_R f_3(\mathbf{P}_3, \xi_3') d\mathbf{P}_3 d\xi_3'$$

are relatively small, viz., $|\delta n_3| \ll n_3$, by virtue of the condition (3.3). Among the number n_3 of C molecules apart from long-lived molecules we count some number of short-lived formations. The number of short-lived formations is much smaller than the number of long-lived molecules, just because their lifetime is short.

4. DERIVATIVE OF THE ENTROPY DENSITY

We turn to a consideration of the entropy and its time derivative. To begin with we assume that there are structureless particles of one kind. The total entropy of N particles in some large volume V is given by the formula proposed by Gibbs,

$$S = -k \int w(\mathbf{r}_1, \mathbf{p}_1, \dots, \mathbf{r}_N, \mathbf{p}_N) \ln w d\mathbf{r}_1 d\mathbf{p}_1 \dots d\mathbf{r}_N d\mathbf{p}_N, \quad (4.1)$$

in which the combined probability density of all coordinates and momenta appears. When there is a small parameter $\varepsilon = r_{\text{int}}^3/v$ we can write the entropy (4.1) in the form of an expansion in that parameter:

$$S = S^{(1)} + \varepsilon S^{(2)} + \varepsilon^2 S^{(3)} + \dots, \quad (4.2)$$

where the first term in the expansion has the form (see Ref. 11, and also Ref. 3, p. 26)

$$S^{(1)} = -k \int [\ln f_1(\mathbf{r}, \mathbf{p}) - 1] f_1(\mathbf{r}, \mathbf{p}) d\mathbf{r} d\mathbf{p}. \quad (4.3)$$

In the spatially homogeneous case we have

$$S^{(1)}/V = -k \int [\ln f_1(\mathbf{p}) - 1] f_1(\mathbf{p}) d\mathbf{p}. \quad (4.4)$$

In (4.2) in the Boltzmann approximation we can neglect the terms in the expansion of higher order in comparison with (4.4). Boltzmann himself considered the functional

$$H = \int d\mathbf{p} f_1(\mathbf{p}) \ln f_1(\mathbf{p}),$$

connected with the entropy density $\tilde{S}/V = -kH$, which differs from (4.4). When there are no chemical reactions the number of molecules $V \int f_i d\mathbf{p}$ of each kind remains unchanged, i.e., the difference $S^{(1)} - \tilde{S}$ is constant and it then makes no difference whether we take Eq. (4.4) or the quantity $-kH$ as the definition of the entropy in the proof of the irreversibility of the process. When we admit chemical transformations of the molecules the difference between these expressions becomes important and we must use Eq. (4.4) and not the functional H .

Expression (4.4) can be generalized in an obvious way to the case of different molecules and the presence of internal degrees of freedom, i.e., we have

$$s_i = \frac{S_i}{V} = -k \int [\ln f_i(\mathbf{P}_i, \xi_i) - 1] f_i(\mathbf{P}_i, \xi_i) d\mathbf{P}_i d\xi_i, \quad (4.5)$$

for each of three kinds of molecules, A, B, and C ($i = 1, 2, \text{ or } 3$). As we have noted, we can take ξ_3' instead of ξ_3 for s_3 . The total entropy density s is equal to the sum $s_1 + s_2 + s_3$ and therefore

$$\dot{s} = \dot{s}_1 + \dot{s}_2 + \dot{s}_3, \quad (4.6)$$

Apart from the molecular association and dissociation (1.1a) there are at the same time molecular collisions which do not lead to transformations, namely, collisions of A with A, A with C, B with B, B with C, and C with C. We can split the increase in entropy into parts caused by the different processes

$$\dot{s} = \dot{s}_{as} + \dot{s}_{dis} + \dot{s}_{AA} + \dot{s}_{AC} + \dot{s}_{BB} + \dot{s}_{BC} + \dot{s}_{CC}.$$

According to the usual Boltzmann H -theorem we have

$$\dot{s}_{AA} \geq 0, \dot{s}_{AC} \geq 0, \dot{s}_{BB} \geq 0, \dot{s}_{BC} \geq 0, \dot{s}_{CC} \geq 0.$$

The required inequality $\dot{s} \geq 0$ will thus be proved if we can prove the inequality $\dot{s}_{as} + \dot{s}_{dis} \geq 0$. We can thus forget the other collisions mentioned above and concentrate our attention on \dot{s}_{as} and \dot{s}_{dis} . By virtue of (4.6) we then have

$$\dot{s}_{as} = (\dot{s}_1)_{as} + (\dot{s}_2)_{as} + (\dot{s}_3)_{as}, \quad \dot{s}_{dis} = (\dot{s}_1)_{dis} + (\dot{s}_2)_{dis} + (\dot{s}_3)_{dis}.$$

5. EVALUATION OF CONTRIBUTIONS DUE TO ASSOCIATION AND DISSOCIATION

The part of the derivatives of f_1 (1) and f_2 (2) which corresponds to association, i.e., the disappearance of A and B molecules, is given by the term in the Boltzmann collision integral with the minus sign, namely

$$\begin{aligned} f_1(1)_{as} &= - \int_K f_1(1) f_2(2) v_{21} d\mathbf{s}_{21} d2, \\ f_2(2)_{as} &= - \int_K f_1(1) f_2(2) v_{21} d\mathbf{s}_{21} d1. \end{aligned} \quad (5.1)$$

Here K is that part of the plane perpendicular to \mathbf{v}_{21} which corresponds to the formation of bound states. Taking into consideration the bound-state region (3.5) and also the fact that we have $|\boldsymbol{\sigma}_{21}| = |\mathbf{s}_{21}|$ we see easily that K is a circle for $s_{21} \ll r_0$. Using (5.1) and (4.5) we find

$$(\dot{s}_1)_{as} + (\dot{s}_2)_{as} = k \int d1 d2 \int_K d\mathbf{s}_{21} v_{21} \ln(f_1 f_2) f_1 f_2. \quad (5.2)$$

Turning to \dot{s}_3 we have by virtue of (4.5)

$$\dot{s}_3 = \int \frac{\partial s(f_3)}{\partial f_3} f_3(\mathbf{3}) d\mathbf{3}, \quad (5.3)$$

where $s(f) = -k(\ln f - 1)f$. When we neglect the collisions of the C molecules with A, B, and C, the distribution function f satisfies the Liouville equation

$$f_3(\mathbf{P}_3, \xi_3') = L_3 f_3 = -\xi_3' \nabla_{in} f_3, \quad (5.4)$$

where L_3 is the Liouville operator of the internal variables of an isolated C molecule and ∇_{in} denotes the gradient with respect to the internal variables ξ_3' . The Liouville theorem is then valid:

$$\nabla_{in} \xi_3' = 0. \quad (5.5)$$

Because of (5.3)–(5.5) we have

$$(\dot{s}_3)_{aa} + (\dot{s}_3)_{dis} = - \int \xi_3' \frac{\partial s}{\partial f_3} \nabla_{in} f_3 d\mathbf{3} = - \int \nabla_{in} [\xi_3' s(f_3)] d\mathbf{3},$$

or, using Stokes' theorem,

$$(\dot{s}_3)_{aa} + (\dot{s}_3)_{dis} = - \int_{\Gamma} (\xi_3')_{\nu} s(f_3) d\Gamma, \quad (5.6)$$

where Γ is the surface of the bound state region R , and $(\xi_3')_{\nu}$ is the component of the vector ξ_3' along the external normal to Γ . Using also the form (3.5) of the region R indicated earlier we change (5.6) to the form

$$\begin{aligned} (\dot{s}_3)_{aa} + (\dot{s}_3)_{dis} &= k \int d\mathbf{P}_3 d\mathbf{P}_2' d\xi_1 d\xi_2 \\ &\times \int_{\kappa} d\mathbf{s}_{21} v_{21} \{ [(\ln f_3 - 1) f_3]_{n\mathbf{r}_{21}=r_0} - [(\ln f_3 - 1) f_3]_{n\mathbf{r}_{21}=-r_0} \}. \end{aligned} \quad (5.7)$$

We bear in mind that for $\mathbf{v}_{21} \cdot \mathbf{r}_{21} / v_{21} = -r_0$, i.e., at the entrance to the bound state region, the molecules do not yet interact with one another, since we have $r_0 \gg R_{int}$. Hence we have $[f_3]_{n\mathbf{r}_{21}=-r_0} \equiv f_3(\mathbf{P}_3, \boldsymbol{\sigma}_{21} - r_0 \mathbf{n}, \mathbf{P}_2', \xi_1, \xi_2) = f_1(\mathbf{P}_1, \xi_1) f_2(\mathbf{P}_2, \xi_2)$, where we have $\boldsymbol{\sigma}_{21} = (\mathbf{s}_{21})_1 m_1 + (\mathbf{s}_{21})_2 m_2$; $\mathbf{P}_3, \mathbf{P}_2'$ and $\mathbf{P}_1, \mathbf{P}_2$ are connected with one another through the transformation $\mathbf{P}_3 = \mathbf{P}_1 + \mathbf{P}_2, \mathbf{P}_2' = (-M_2 \mathbf{P}_1 + M_1 \mathbf{P}_2) / M_3$ [see (2.3) and (2.4)] with a unit Jacobian. Hence $d\mathbf{P}_3 d\mathbf{P}_2' = d\mathbf{P}_1 d\mathbf{P}_2$ and $d\mathbf{P}_3 d\mathbf{P}_2' d\xi_1 d\xi_2 = d\mathbf{1} d\mathbf{2}$. Moreover, for $\mathbf{n} \cdot \mathbf{r}_1 = r_0$, i.e., at the exit from the bound-state region the arguments of the function f_3 in turn can be expressed in terms of the variables 1 and 2, i.e., we can write $f_3' = f_3(G(1, 2, \mathbf{s}_{21}))$, where $f_3(G(1, 2, \mathbf{s}_{21})) = f_3(\mathbf{P}_1 + \mathbf{P}_2, \boldsymbol{\sigma}_{21} + r_0 \mathbf{n}, (M_1 \mathbf{P}_2 - M_2 \mathbf{P}_1) / M_3, \xi_1, \xi_2)$. Thanks to the previous result (5.7) can be written in the form

$$\begin{aligned} (\dot{s}_3)_{aa} + (\dot{s}_3)_{dis} &= k \int d\mathbf{1} d\mathbf{2} \int_{\kappa} d\mathbf{s}_{21} v_{21} [(\ln f_3' - 1) f_3' \\ &\quad - (\ln f_1 f_2 - 1) f_1 f_2]. \end{aligned} \quad (5.8)$$

After the decay of a C molecule the variables of the A molecule are in general correlated with the variables of the B molecule so that we cannot use the factorization $f_3' = f_1' f_2'$.

One sees easily that the expression

$$d\Gamma_{-}(\xi_3')_{\nu} f_3 = d\mathbf{P}_3 d\mathbf{P}_2' d\xi_1 d\xi_2 d\mathbf{s}_{21} v_{21} [f_3]_{n\mathbf{r}_{21}=r_0}$$

determines the number of C molecules per unit volume with dynamical variables within the volume element $d\mathbf{P}_3 d\mathbf{P}_2' d\xi_1 d\xi_2$ leaving the bound state region through the surface element $d\mathbf{s}_{21}$ per unit time. Formally speaking, the C molecule then instantaneously decays into an A molecule characterized by the variables $\mathbf{P}_1 = (M_1/M_3)\mathbf{P}_3 - \mathbf{P}_2'$ and ξ_1 and a B molecule characterized by the variables $\mathbf{P}_2 = (M_2/M_3)\mathbf{P}_3 + \mathbf{P}_2'$ and ξ_2 . The variables ξ_1 and ξ_2 remain in this case unchanged. One understands easily that for the first molecule the dissociative part of the time derivative of f_1 is equal to

$$\begin{aligned} f_1(1)_{dis} &= \int d\mathbf{P}_3 d\mathbf{P}_2' d\theta_2 \int_{\kappa} d\mathbf{s}_{21} v_{21} \delta\left(\mathbf{P}_1 - \frac{M_1}{M_3} \mathbf{P}_3 + \mathbf{P}_2'\right) \\ &\quad \times [f_3(\mathbf{P}_3, \xi_3')]_{n\mathbf{r}_{21}=r_0}, \end{aligned}$$

or

$$\begin{aligned} f_1(1)_{dis} &= \int d\mathbf{P}_2 d\mathbf{P}_3 d\mathbf{P}_2' d\xi_2 \int_{\kappa} d\mathbf{s}_{21} v_{21} \delta\left(\mathbf{P}_1 - \frac{M_1}{M_3} \mathbf{P}_3 + \mathbf{P}_2'\right) \\ &\quad \times \delta\left(\mathbf{P}_2 - \frac{M_2}{M_3} \mathbf{P}_3 - \mathbf{P}_2'\right) [f_3]_{n\mathbf{r}_{21}=r_0}. \end{aligned}$$

When integrating over \mathbf{P}_3 and \mathbf{P}_2' we replace the function $f_3(\mathbf{P}_3, \xi_3')$ by $f_3(G(1, 2, \mathbf{s}_{21})) \equiv f_3'$ and we then get

$$f_1(1)_{dis} = \int d\mathbf{2} \int_{\kappa} d\mathbf{s}_{21} v_{21} f_3'. \quad (5.9)$$

A similar formula also holds for $f_2(2)_{dis}$. The complete equation for f_1 is the following:

$$f_1 = L_1 f_1 + f_1(1)_{aa} + f_1(1)_{dis} + I_{AA} + I_{AC}, \quad (5.10)$$

where I_{AA} and I_{AC} are Boltzmann collision integrals of no interest to us, and L_1 is the Liouville operator for an isolated A molecule. Dropping I_{AA} and I_{AC} and using (4.5) and also the stability of the molecule, we get

$$(\dot{s}_1)_{aa} + (\dot{s}_1)_{dis} = -k \int d\mathbf{1} \ln f_1 [f_1(1)_{aa} + f_1(2)_{dis}],$$

where we must substitute (5.1) and (5.9). Similarly we find a relation for f_2 and \dot{s}_2 . Apart from (5.2) we find thus the dissociative contributions

$$(\dot{s}_1)_{dis} + (\dot{s}_2)_{dis} = -k \int d\mathbf{1} d\mathbf{2} \int d\mathbf{s}_{21} v_{21} \ln(f_1 f_2) f_3'. \quad (5.11)$$

Summing (5.2), (5.7), and (5.11) we finally obtain

$$\dot{s}_{aa} + \dot{s}_{dis} = k \int d\mathbf{1} d\mathbf{2} \int_{\kappa} d\mathbf{s}_{21} v_{21} [(\ln f_3' - 1) f_3' + f_1 f_2 - \ln(f_1 f_2) f_3']. \quad (5.12)$$

Taking f_3' from inside the bracket we can write the integrand in the form

$$f_3' [f_1 f_2 / f_3' - 1 - \ln(f_1 f_2 / f_3')].$$

This expression is nonnegative because the function $y - 1 - \ln y$ is nonnegative. This proves the inequality $\dot{s}_{aa} + \dot{s}_{dis} \geq 0$ and hence also $\dot{s} \geq 0$.

6. THREE-PARTICLE COLLISIONS AND THE BOUND-STATE REGION

We now turn to considering the (1.1b) reactions. It is necessary in this case to give details of the three-particle collision in which A, B, and C molecules combine into D. In the classical approximation the dynamics of the three particles is described by the combined Hamiltonian

$$H_{123} = H_1(\mathbf{r}_1, \mathbf{p}_1) + H_2(\mathbf{r}_2, \mathbf{p}_2) + H_3(\mathbf{r}_3, \mathbf{p}_3) + V(\mathbf{r}_{21}, \mathbf{r}_{31}), \quad (6.1)$$

where $\mathbf{r}_{i1} = \mathbf{r}_i - \mathbf{r}_1$, H_i is the Hamiltonian of an isolated A molecule, and so on. To begin with we assume the molecules to be structureless.

In order to describe in detail the three-particle collision integral which corresponds to removal of the A, B, and C molecules, it is useful to compare it with a collision of two particles moving in six-dimensional configuration space. Thus, a particle characterized by position and momentum 6-vectors $\rho_1 = (\mathbf{r}_1, \mathbf{r}'_1)$, $\pi_1 = (\mathbf{p}_1, \mathbf{p}'_1)$ collides with a particle characterized by the position and momentum vectors $\rho_0 = (\mathbf{r}_2, \mathbf{r}_3)$, $\pi_0 = (\mathbf{p}_2, \mathbf{p}_3)$ and we assume that the additional conditions $\mathbf{r}'_1 = \mathbf{r}_1$, $\mathbf{p}'_1 = \mathbf{p}_1$ are satisfied. Let the dynamics of these particles be characterized by the Hamiltonian

$$\begin{aligned} H(\rho_1, \pi_1, \rho_0, \pi_0) = & H_1(\mathbf{r}_1, \mathbf{p}_1) + H_1(\mathbf{r}'_1, \mathbf{p}'_1) \\ & + H_2(\mathbf{r}_2, \mathbf{p}_2) + H_3(\mathbf{r}_3, \mathbf{p}_3) \\ & + V_0(\mathbf{r}_2 - \mathbf{r}_1, \mathbf{r}_3 - \mathbf{r}_1) + V_0(\mathbf{r}_2 - \mathbf{r}'_1, \mathbf{r}_3 - \mathbf{r}'_1), \end{aligned} \quad (6.2)$$

where V_0 is some potential while H_1 , H_2 , and H_3 are the same as in (6.1). Writing down the Hamiltonian equations corresponding to (6.2) we check easily that when the conditions $\mathbf{r}'_1 = \mathbf{r}_1$, $\mathbf{p}'_1 = \mathbf{p}_1$ are satisfied initially they will remain satisfied in what follows. Using these conditions and also the statistical independence of the B and C molecules it is natural to take the following particle distribution function in six-dimensional space:

$$\begin{aligned} F_1(\rho_1, \pi_1) = & f_1(\mathbf{r}_1, \mathbf{p}_1) \delta(\mathbf{r}'_1 - \mathbf{r}_1) \delta(\mathbf{p}'_1 - \mathbf{p}_1), \\ F_0(\rho_0, \pi_0) = & f_2(\mathbf{r}_2, \mathbf{p}_2) f_3(\mathbf{r}_3, \mathbf{p}_3). \end{aligned} \quad (6.3)$$

The collision integral of two particles in the six-dimensional case can be written by analogy with the usual collision integral:

$$\begin{aligned} \dot{F}_1 = & \mathcal{L}_1 F_1 + \int [F_1(\rho_1, \pi_1') F_0(\rho_1, \pi_0') \\ & - F_1(\rho_1, \pi_1) F_0(\rho_1, \pi_0)] g d\mathbf{S} d\pi_0. \end{aligned} \quad (6.4)$$

Here $g = (v_{21}^2 + v_{31}^2)^{1/2}$ is the magnitude of the relative velocity vector $\mathbf{g} = (\mathbf{v}_{21}, \mathbf{v}_{31})$, and \mathbf{S} is a five-dimensional vector indicating the position of the point [with radius vector $\rho_{01} - \mathbf{n}(\mathbf{n} \cdot \rho_{01})$, where $\rho_{01} = (\mathbf{r}_{21}, \mathbf{r}_{31})$, $\mathbf{n} = \mathbf{g}/g$] on the hypersurface perpendicular to \mathbf{g} . Substituting (6.3) into (6.4) and integrating over \mathbf{r}'_1 and \mathbf{p}'_1 we find

$$\begin{aligned} \dot{f}_1(\mathbf{r}_1, \mathbf{p}_1) = & \mathcal{L}_1 f_1 + \int [f_1(\mathbf{r}_1, \mathbf{p}_1'') f_2(\mathbf{r}_1, \mathbf{p}_2'') f_3(\mathbf{r}_1, \mathbf{p}_3'') \\ & - f_1(\mathbf{r}_1, \mathbf{p}_1) f_2(\mathbf{r}_1, \mathbf{p}_2) f_3(\mathbf{r}_1, \mathbf{p}_3)] g d\mathbf{S} dp_2 dp_3. \end{aligned}$$

It is clear that the same equation must also hold for the Hamiltonian (6.1) and the ternary collision. Therefore, the part of the derivative \dot{f}_1 which is caused by the removal of an A molecule through association can be written in the form

$$\dot{f}_1(1)_{as} = - \int_{\tau} f_1(1) f_2(2) f_3(3) g d\mathbf{S} d2 d3 \quad (6.5)$$

and similarly for \dot{f}_2 and \dot{f}_3 . Here τ is the region of five-dimensional space including those points \mathbf{S} for which association occurs. We changed in (6.5) to considering molecules which have internal degrees of freedom.

We need a more detailed identification of the vector \mathbf{S} and the region τ . Let $\mathbf{n}, \mathbf{v}_1, \dots, \mathbf{v}_5$ be an orthonormalized set for the six-dimensional space of the vectors ρ_{01} . We then have

$$\rho_{01} - \mathbf{n}(\mathbf{n} \cdot \rho_{01}) = \sum_{l=1}^5 \mathbf{v}_l (\mathbf{v}_l \cdot \rho_{01}),$$

where the vector \mathbf{S} has the components $(\mathbf{v}_1 \cdot \rho_{01}), \dots, (\mathbf{v}_5 \cdot \rho_{01})$. If we introduce orthogonal three-dimensional unit vectors \mathbf{m}_1 and \mathbf{m}_2 , perpendicular to \mathbf{v}_{21} and orthogonal unit vectors \mathbf{m}'_1 and \mathbf{m}'_2 perpendicular to \mathbf{v}_{31} , four of this set of vectors can be defined as

$$\mathbf{v}_1 = (\mathbf{m}_1, 0), \quad \mathbf{v}_2 = (\mathbf{m}_2, 0), \quad \mathbf{v}_3 = (0, \mathbf{m}'_1), \quad \mathbf{v}_4 = (0, \mathbf{m}'_2). \quad (6.6)$$

One easily checks that they are orthogonal to one another and to the vector $\mathbf{n} = \mathbf{g}/g$. The fifth vector \mathbf{v}_5 is sought in the form of a linear combination of the vectors $(\mathbf{v}_{21}, 0)$ and $(0, \mathbf{v}_{31})$. Using the orthogonality condition $\mathbf{v}_5 \cdot \mathbf{n} = 0$ one finds easily

$$\mathbf{v}_5 = (v_{31} \mathbf{n}_1, -v_{21} \mathbf{n}_2) / g, \quad (6.7)$$

where $\mathbf{n}_1 = \mathbf{v}_{21}/v_{21}$, $\mathbf{n}_2 = \mathbf{v}_{31}/v_{31}$. Knowing the vectors (6.6) and (6.7) one easily identifies the differential

$$d\mathbf{S} = \prod_{l=1}^5 d(\mathbf{v}_l \cdot \rho_{01}). \quad (6.8)$$

which occurs in (6.5). Using $\rho_{01} = (\mathbf{r}_{21}, \mathbf{r}_{31})$ we find by means of (6.6)

$$d(\mathbf{v}_1 \cdot \rho_{01}) d(\mathbf{v}_2 \cdot \rho_{01}) = d\mathbf{s}_{21}, \quad d(\mathbf{v}_3 \cdot \rho_{01}) d(\mathbf{v}_4 \cdot \rho_{01}) = d\mathbf{s}_{31}.$$

Here $\mathbf{s}_{21} = (\mathbf{m}_1 \cdot \mathbf{r}_{21}, \mathbf{m}_2 \cdot \mathbf{r}_{21})$ is the two-dimensional vector used in preceding sections, and $\mathbf{s}_{31} = (\mathbf{m}'_1 \cdot \mathbf{r}_{31}, \mathbf{m}'_2 \cdot \mathbf{r}_{31})$ is a two-dimensional vector which indicates a point in the plane perpendicular to \mathbf{v}_{31} in \mathbf{r}_{31} space. Moreover, using (6.7) we can introduce the parameter

$$l = \mathbf{v}_5 \cdot \rho_{01} = g^{-1} v_{21} v_{31} (\mathbf{n}_1 \cdot \mathbf{r}_{21} / v_{21} - \mathbf{n}_2 \cdot \mathbf{r}_{31} / v_{31}), \quad (6.9)$$

so that (6.8) takes the form $d\mathbf{S} = d\mathbf{s}_{21} d\mathbf{s}_{31} dl$. The expression $\mathbf{n}_1 \cdot \mathbf{r}_{21} / v_{21} = t_1(\mathbf{r}_{21})$ has the meaning of the time required to move with a velocity $\dot{\mathbf{r}}_{21} = \mathbf{v}_{21}$ from the point \mathbf{r}_{21} to the point of closest approach of the A and B molecules, if their interaction would not destroy the uniformity of the motion. Similarly, $\mathbf{n}_2 \cdot \mathbf{r}_{31} / v_{31} = t_2(\mathbf{r}_{31})$ is the time for uniform motion from the point \mathbf{r}_{31} to the point of closest approach of the B and C molecules, if there were no interactions. The parameter (6.9) is proportional to the time difference $t_1 - t_2$. One checks easily that the difference $t_1[\mathbf{r}_{21}(t)] - t_2[\mathbf{r}_{31}(t)]$, like \mathbf{s}_{21} and \mathbf{s}_{31} , is a constant of the motion, i.e., is independent of t when the A, B, and C molecules are not yet interacting.

Using $\mathbf{S} = (\mathbf{s}_{21}, \mathbf{s}_{31}, l)$, we define the bound state region. Allowing a certain amount of arbitrariness we shall assume that A, B, and C combine into D, if

$$|\mathbf{n}\rho_{01}| = g^{-1} |\mathbf{v}_{21}\mathbf{r}_{21} + \mathbf{v}_{31}\mathbf{r}_{31}| \leq r_0, \quad (6.10)$$

$$s_{21} \leq r_0, \quad s_{31} \leq r_0, \quad |l| \leq r_0$$

and do not combine in the opposite case. Here r_0 is the quantity introduced earlier, defined by the inequalities (3.3). We must then take for the five-dimensional region τ in (6.5) the region defined by the conditions $s_{21} < r_0$, $s_{31} < r_0$, $|l| < r_0$ where we can write the first two inequalities in the form $\mathbf{s}_{21} \in K$ and $\mathbf{s}_{31} \in K$. Thus, (6.5) takes the form

$$f_1(1)_{as} = - \int d^2 d^3 \int_K d\mathbf{s}_{21} \int_K d\mathbf{s}_{31} \int_{-r_0}^{r_0} dl (v_{21}^2 + v_{31}^2)^{1/2} f_1(1) f_2(2) f_3(3). \quad (6.11)$$

Moreover,

$$f_2(2)_{as} = - \int d^1 d^3 \int_K d\mathbf{s}_{21} \int_K d\mathbf{s}_{31} \int_{-r_0}^{r_0} dl (v_{21}^2 + v_{31}^2)^{1/2} f_1(1) f_2(2) f_3(3) \quad (6.12)$$

and similarly for $f_3(3)_{as}$ since the expression

$$d^1 d^2 d^3 f_1(1) f_2(2) f_3(3) \int_K d\mathbf{s}_{21} \int_K d\mathbf{s}_{31} \int_{-r_0}^{r_0} dl (v_{21}^2 + v_{31}^2)^{1/2}$$

is equal to the number of processes (per unit time and per unit volume) where the three molecules A, B, and C with dynamic variables which lie, respectively, in the ranges d^1 , d^2 , and d^3 disappear simultaneously. By virtue of (6.11), (6.12), and (4.5) we get

$$(\dot{s}_1)_{as} + (\dot{s}_2)_{as} + (\dot{s}_3)_{as} = k \int d^1 d^2 d^3 \times \int_K d\mathbf{s}_{21} \int_K d\mathbf{s}_{31} \int_{-r_0}^{r_0} dl g \ln(f_1 f_2 f_3) f_1 f_2 f_3. \quad (6.13)$$

7. OTHER CONTRIBUTIONS TO THE DERIVATIVE OF THE ENTROPY DENSITY

Other contributions to $\dot{s}_{as} + \dot{s}_{dis}$ can be found by the same method as was used for the $A + B = C$ reaction. We can apply Eqs. (2.1) and (2.2) also to D molecules, if we set $i = 4$. In that case

$$\mathbf{r}_4 = \sum_{i=1}^3 \frac{M_i}{M_4} \mathbf{r}_i, \quad \mathbf{P}_4 = \sum_{i=1}^3 \mathbf{P}_i, \quad \mathbf{r}'_2 = \mathbf{r}_{21}, \quad \mathbf{r}'_3 = \mathbf{r}_{31}, \quad (7.1)$$

$$\mathbf{P}'_2 = \mathbf{P}_2 - \frac{M_2}{M_4} \sum_{i=1}^3 \mathbf{P}_i, \quad \mathbf{P}'_3 = \mathbf{P}_3 - \frac{M_3}{M_4} \sum_{i=1}^3 \mathbf{P}_i,$$

where the transition from $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{P}_1, \mathbf{P}_2, \mathbf{P}_3$ to $\mathbf{r}_4, \mathbf{r}'_2, \mathbf{r}'_3, \mathbf{P}_4, \mathbf{P}'_2, \mathbf{P}'_3$ is a contact transformation. For the internal variables of the D molecule we can choose not only the variables $\xi_4 = (\mathbf{q}_{4\sigma}, \mathbf{p}_{4\sigma}, \sigma = 2, \dots, k_4)$, but also $\xi'_4 = (\mathbf{r}_{21}, \mathbf{r}_{31}, \mathbf{P}'_2, \mathbf{P}'_3, \xi_1, \xi_2, \xi_3)$ and we have $f_4(\mathbf{P}_4, \xi'_4) \equiv f_4(4)$.

By analogy with (5.6) the formula

$$(\dot{s}_1)_{as} + (\dot{s}_4)_{dis} = k \int_{\Gamma'} (\dot{\xi}'_4) \cdot (\ln f_4 - 1) f_4 d\Gamma', \quad (7.2)$$

holds where Γ' is the hypersurface in the space of the ξ'_4 variables which encloses the bound state region (6.10) where instead of s_{21} and s_{31} we must take the magnitude of the vectors $\boldsymbol{\sigma}_{21} = \mathbf{r}_{21} - \mathbf{n}_1(\mathbf{n}_1 \cdot \mathbf{r}_{21})$ and $\boldsymbol{\sigma}_{31} = \mathbf{r}_{31} - \mathbf{n}_2(\mathbf{n}_2 \cdot \mathbf{r}_{31})$, and $(\dots)_\nu$ denotes the component along the external normal. Only those sections where the hypersurface Γ' is orthogonal to the vector ξ'_4 are important (in other places it is parallel to this vector) in the integral (7.2). These sections are the entrance region where

$$(\mathbf{v}_{21}\mathbf{r}_{21} + \mathbf{v}_{31}\mathbf{r}_{31})/g = -r_0, \quad \sigma_{21} \leq r_0, \quad \sigma_{31} \leq r_0, \quad |l| \leq r_0, \quad \mathbf{P}'_2, \dots, \xi_3 - \text{arbitrary},$$

where the external normal is directed in the opposite direction to ξ'_4 , and the exit region where

$$(\mathbf{v}_{21}\mathbf{r}_{21} + \mathbf{v}_{31}\mathbf{r}_{31})/g = r_0, \quad \sigma_{21} \leq r_0, \quad \sigma_{31} \leq r_0, \quad |l| \leq r_0, \quad \mathbf{P}'_2, \dots, \xi_3 - \text{arbitrary},$$

where the external normal is directed in the same direction. Using this we can transform (7.2) to the form

$$(\dot{s}_1)_{as} + (\dot{s}_4)_{dis} = k \int d\mathbf{P}_4 d\mathbf{P}'_2 d\mathbf{P}'_3 d\xi_1 d\xi_2 d\xi_3 \times \int_K d\mathbf{s}_{21} \int_K d\mathbf{s}_{31} \int_{-r_0}^{r_0} dl g \{ [(\ln f_4 - 1) f_4]_{\rho_{01}=1} - [(\ln f_4 - 1) f_4]_{\rho_{01}=-1} \}.$$

Changing the integration variables and using the fact that in the entrance region, i.e., before the molecules interact, we have $f_4 = f_1 f_2 f_3$, we find from this

$$(\dot{s}_1)_{as} + (\dot{s}_4)_{dis} = k \int d^1 d^2 d^3 \int_K d\mathbf{s}_{21} \int_K d\mathbf{s}_{31} \times \int_{-r_0}^{r_0} dl g \{ (\ln f'_4 - 1) f'_4 - [(\ln(f_1 f_2 f_3) - 1) f_1 f_2 f_3] \}, \quad (7.3)$$

where $f'_4 = f_4 [G(1, 2, 3, \mathbf{s}_{21}, \mathbf{s}_{31}, l)]$. The latter means that the arguments $\mathbf{P}_4, \mathbf{P}'_2$ and \mathbf{P}'_3 of the function f_4 are expressed in terms of $\mathbf{P}_1, \mathbf{P}_2$, and \mathbf{P}_3 [see (7.1)] and \mathbf{r}_{21} and \mathbf{r}_{31} are expressed in terms of $\mathbf{s}_{21}, \mathbf{s}_{31}$ and l :

$$(\mathbf{r}_{21}, \mathbf{r}_{31}) = \rho_{01} = (\mathbf{s}_{21})_1 \mathbf{v}_1 + (\mathbf{s}_{21})_2 \mathbf{v}_2 + (\mathbf{s}_{31})_1 \mathbf{v}_3 + (\mathbf{s}_{31})_2 \mathbf{v}_4 + l \mathbf{v}_5 + r_0 \mathbf{n},$$

i.e.,

$$\mathbf{r}_{21} = (\mathbf{s}_{21})_1 \mathbf{m}_1 + (\mathbf{s}_{21})_2 \mathbf{m}_2 + g^{-1} (v_{21} r_0 + v_{31} l) \mathbf{n}_1, \quad \mathbf{r}_{31} = (\mathbf{s}_{31})_1 \mathbf{m}'_1 + (\mathbf{s}_{31})_2 \mathbf{m}'_2 + g^{-1} (v_{31} r_0 - v_{22} l) \mathbf{n}_2.$$

We still must consider $(\dot{s}_1)_{dis} + (\dot{s}_2)_{dis} + (\dot{s}_3)_{dis}$. By analogy with (5.9) we have

$$f_1(1)_{dis} = \int d2 d3 \int_K ds_{21} \int_K ds_{31} \int_{-r_0}^{r_0} dl g f_1'$$

and similarly for $f_2(2)_{dis}$ and $f_3(3)_{dis}$. Hence, using (4.5) we get

$$(\dot{s}_1)_{dis} + (\dot{s}_2)_{dis} + (\dot{s}_3)_{dis} = k \int d1 d2 d3 \times \int_K ds_{21} \int_K ds_{31} \int_{-r_0}^{r_0} dl g \ln(f_1 f_2 f_3) f_1'. \quad (7.4)$$

We now add (6.13), (7.3), and (7.4). This gives

$$\dot{s}_{as} + \dot{s}_{dis} = k \int d1 d2 d3 \int_K ds_{21} \int_K ds_{31} \int_{-r_0}^{r_0} dl g f_1 F\left(\frac{f_1 f_2 f_3}{f_1'}\right),$$

where the function $F(y)$ equals $y - 1 - \ln y$. As it is nonnegative we have $\dot{s}_{as} + \dot{s}_{dis} \geq 0$, and hence $\dot{s} \geq 0$.

8. CONCLUDING REMARKS

1. In the foregoing we defined the bound-state region so that among the C molecules we had not only long-lived, but also short-lived formations. One can modify the theory so that short-lived states are eliminated. We explain how this can be done. We introduce a time τ_0 which is much shorter than the time $1/k_-$ for the decay of a molecule and much longer than the mean free time of the interaction sphere, i.e., the time r_{int}/u_{21} , where $u_{21} = \langle v_{21} \rangle$ is the average relative velocity. We assume that a C molecule is formed if the lifetime τ of the (A, B) formation is longer than τ_0 and that no molecule is formed, if $\tau < \tau_0$. Analysis of the dynamic interaction enables us to distinguish on the s_{21} plane the region K' , which depends on P_1, ξ_1 and P_2, ξ_2 such that C is formed when $s_{21} \in K'$. The remaining part of the plane can be denoted by K'' and on it impact vectors s_{21} occur for which

there is no C formation. Instead of using (3.5) we must then define the bound state region by the formulae $|\mathbf{n} \cdot \mathbf{r}_{21}| < r_0$, $s_{21} \in K'$. Corresponding to this in Eqs. (5.1) and (5.2) and in a number of others we must replace the circle K by K' . For such a modified theory on the right-hand side of Eq. (5.10) we must write for the collision integral

$$I_{AB} = \int d2 \int_{K''} ds_{21} v_{21} (f_1' f_2' - f_1 f_2).$$

Similar changes must be introduced in the discussion of the three-particle collisions, i.e., in the two preceding sections.

2. We can consider molecular association and dissociation not only in the Boltzmann model, but also in more accurate approximations, generalizing the theory of Bogolyubov and others to the case of chemical reactions. It is well known that the basis of such a theory is the Bogolyubov-Born-Green-Kirkwood-Yvon chain of exact equations. These equations can be generalized to the case where chemical reactions occur. However, that material goes beyond the framework of the present paper.

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