

ON STATISTICAL MODELS AND PRIOR DISTRIBUTIONS IN THE THEORY OF CHEMICAL REACTIONS

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Statistical models which yield rate expressions involving the asymptotic channel states are classified according to three main characteristics: (i) The ensemble in which framework the basic statistical assumption is formulated. This assumption states that the initial and final states of the collision are, partly or completely, independent. (ii) The "measure in phase" associated with the product state distribution. (iii) The extent to which dynamical considerations are incorporated into the model. In this connection the discussion will be confined to the effects of angular momentum restrictions. The diversity in statistical models is demonstrated by comparing the product vibrational and rotational distributions obtained from several models for atom-diatom exchange reactions. Numerical results are presented for two exoergic reactions which involve different mass combinations. Particular attention is paid to a comparison between the objectives, assumptions and the final expressions for product state distributions corresponding to the so called phase space theory on the one hand and the prior (zero surprisal) limit of the information theoretic approach to molecular dynamics on the other.

1. Introduction

Many theories of molecular [1–4] and nuclear [5, 6] collisions employ (various) statistical assumptions to describe collision processes and to predict their outcomes. In molecular physics the main success of these theories is in the area of large molecules where many degrees of freedom are involved so that detailed dynamical calculations are impractical while statistical approximations seem reasonable (see, however, e.g. refs. [7,8]). Since detailed calculations are difficult to perform, partly due to the lack of accurate potential energy surfaces, even for small systems, such as atom-diatom molecule, various statistical models were formulated in order to account for at least some aspects of the collision [9–41]. For example, the symmetric product angular distributions observed in certain bimolecular reactions can be interpreted as the result of intermediate complex formation followed by "statistical" breakdown probabilities [3,4,9–11,19, 27]. The statistical models are less successful in predicting, for instance, the product vibrational and rotational energy distributions in exoergic chemical reactions; especially in those ending with population

inversion. In such cases one may use the statistical models as standards against which actual results can be compared [18] or as bases for the development of more elaborate models. In the information theoretic approach to molecular collision dynamics [42–72] such standards can serve as the prior distributions (rate constants, cross sections) used in surprisal and entropy analyses of experimental data. When supplemented by appropriate dynamical constraints the prior distributions play a major role in the predictive scheme (synthesis) based on the maximum entropy principle.

The central assumption of the statistical models is that past and future with respect to the collision event are partly or completely independent; subject to symmetry and conservation requirements. The symmetry requirements refer in particular to microscopic reversibility while the conservation rules concern the total (center of mass) energy E , total angular momentum K and the normalization of probabilities. Approximate dynamical information, e.g. on the range of allowed angular momenta, is usually incorporated into the models in order to increase their dynamical character. The concepts of intermediate, "long lived"

(see, e.g. refs. [1–4, 7–11]) or “strongly coupled” [14–19], collision complexes play important roles in various statistical theories. They serve to account for “quasi-equilibrium” (“energy randomization”) [1–4, 7, 28, 33, 34] or “strong coupling” [4, 11, 14–19] postulates on the basis of which the neglect of correlation between reactants and products can be justified. In the traditional formulations of transition state theory a quasi-equilibrium is assumed to exist between the reactants and the systems crossing the activated complex hypersurface (see e.g. refs. [4, 7, 37]). Recent work [36, 37] (utilizing variational principles to locate the transition hypersurface, see e.g. refs. [12, 38–41]) indicates that transition state theory is appropriate to a “direct”, as opposed to “complex”, reaction mechanism, whereas the well known [14–27] phase space theory of Light, Pechukas [14–19] and Nikitin [29, 21] (LPN) is only applicable to reactions proceeding via the formation of long lived complexes. This interpretation of the phase space theory is somewhat different from the one suggested in some of its original formulations [14–19] where a strongly coupled complex defined by the region of strong interaction in configuration space rather than by its lifetime was assumed to be formed.

To conclude this background survey it should be mentioned that the LPN theory, to which considerable attention will be given in the following, can be derived as a limiting case of other statistical-dynamical approaches. For example, it can be viewed as transition state theory for “loose complexes” [37, 41]. Also, and this is of greater interest in the present context, with the aid of a random phase type approximation the phase space model can be derived through formal assumptions on the structure of the scattering matrix [4, 11, 19, 22]; similar to those made in the statistical theory of rotational excitation [13].

The main concern of this paper is the statistical, rather than the dynamical, aspects of statistical-dynamical approaches to small collision systems. We shall only consider models that lead to rate expressions (e.g., cross sections or product state distributions) involving the asymptotic reactant and product states, or equivalently the phase space regions corresponding to the asymptotic channels. Thus, many (interesting) questions regarding, for example, the behaviour and structure of the colliding system at intermediate separations, are beyond the perspectives of the present

discussion. Yet, even within the limited scope of “asymptotic channel statistical approaches” there is room for diverse, actually an infinity of, different models.

The general purpose of this paper is to characterize the various aspects of diversity in a systematic fashion. Particular attention will be paid to a comparison between two familiar rate expressions. Namely, the cross sections and related quantities obtained in the phase space theory of Light, Pechukas and Nikitin [14–28] and the prior distributions appearing in the information theoretic approach developed by Levine, Bernstein and others [42–72]. Unlike the phase space theory the prior distributions do not contain any dynamical information and therefore do not attempt to predict experimental results. In fact, they are meant to represent the dynamically “least biased” (or “most random”) distributions [42–50]. As such they can either be used as standards for entropy-surprisal analyses or else as starting points in the predictive scheme (synthesis) which constitutes another direction of the information theoretic method. Although the LPN and the prior distributions involve different statistical ensembles (E, K versus E) and different measures in phase space (“uniform” versus “flux”), one can also observe certain similarities. We shall elaborate upon these differences and similarities within the general classification framework of statistical models presented in the following sections. Among the special models considered, we have included an extended version of the prior distribution which explicitly includes the conservation of angular momentum (i.e., appropriate to the E, K ensemble). As specific examples illustrating the consequences of different statistical assumptions, we have chosen the $\text{Cl} + \text{HI} \rightarrow \text{HCl} + \text{I}$ and the $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$ reactions.

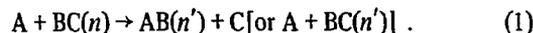
Two more remarks should precede the discussion. First, some points related to the objectives of this paper have already been dealt with in the literature [11, 27, 43, 45, 49–55] (to a greater or lesser extent). In our opinion, however, no clear distinctions have been provided. Hence the motivation for this paper. Second, for reasons to be clarified throughout the paper, the presentation of the various models and the analyses of their physical significance will not be accompanied by judgements or evaluations.

The paper is organized as follows: The basic definitions and the general structure of statistical models

are presented in the next section. Different choices of statistical ensembles, measures in phase space and dynamical constraints are considered in sections 3, 4 and 5, respectively and tested for two specific examples in section 6. Section 7 provides some remarks on the derivation based on the assumption of complex formation and the beginning of the derivation based on formal assumptions on the S -matrix. Section 8 is devoted to a discussion. In appendix A we list the elementary state representations and density of state expressions relevant to sections 2–8. Appendix B supplements section 7 in providing the details of the formal derivation.

2. The statistical assumptions

Many different statistical approximations are consistent with the basic framework of no correlation between reactants and products subject to symmetry and conservation rules. Diversity is possible, and exists, in four main respects: (1) the “ensemble”, Γ , within the framework of which the assumptions are made, (2) the “measure in phase space (or, Hilbert space)”, $m(n; \Gamma)$, associated with the product state, n , (3) the extent to which dynamical considerations and information on the potential energy surface are incorporated into the model, (4) the absolute total value, $Q(\Gamma)$, of various rate variables (rate constants, cross sections, yields). We shall elaborate on these points, mainly on the first three, using as a specific example the atom–diatom collision



Here n and n' denote the, completely (i.e. $n = v, J, m_J$) or partially (e.g. $n = v$) specified, internal state of the reactant and product diatoms. Whenever necessary we shall use a channel symbol, α , to denote the chemical composition, $\alpha = A + BC$ or $AB + C$. We assume that the total collision energy does not suffice for the formation of reaction products other than an atom and a diatomic molecule (e.g. ionization or dissociation products) and that the reaction is electronically adiabatic.

Our attention will be focused on two ensembles: $\Gamma_1 = E, K$ and $\Gamma_2 = E$. By $\Gamma_2 = E$ we refer to a “microcanonical” ensemble of collisions – all with the same total energy E (in the c.m. system). $\Gamma_1 = E, K$ is a

more specific ensemble, $\Gamma_1 \subset \Gamma_2$, representative of collisions with well defined total energy E and total angular momentum K . (Averaged, not summed, over the $2K + 1$ equivalent values of M_K .) The “canonical” ensemble $\Gamma_3 = T$, ($\Gamma_2 \subset \Gamma_3$), which is a Boltzmann superposition of microcanonical ensembles will briefly be mentioned in section 8. To ensure consistency with microscopic reversibility the statistical assumptions will be made on quantities which are symmetric with respect to interchanging ωn and $\alpha' n'$. These are, for example, the averaged (elementary) state-to-(elementary)-state transition rates $\bar{\omega}(\omega n, \alpha' n'; \Gamma)$, the yield function $Y(\omega n, \alpha' n'; \Gamma)$ [4,42,73] or the S and the T matrices. Elementary states are defined in appendix A. In the $\Gamma = E$ ensemble $\bar{\omega}$ and Y are uniquely related to each other as well as to the detailed rate constants $k(n \rightarrow n'; E)$ and cross sections $\sigma(n \rightarrow n'; E)$, through eq. (2) below [4,42,49,73,74]. We now extend these relationships in order to define $k(n \rightarrow n'; \Gamma)$ and $\sigma(n \rightarrow n'; \Gamma)$ for $\Gamma = E, K$ (for $\Gamma = T$ see refs. [73,74,54]). The implications of this generalization are considered below. We thus write

$$\begin{aligned} h^{-1} Y(n, n'; \Gamma) &= \rho(n; \Gamma) \rho(n'; \Gamma) \bar{\omega}(n, n'; \Gamma) = \rho(n; \Gamma) k(n \rightarrow n'; \Gamma) \\ &= u_n \rho(n; \Gamma) \sigma(n \rightarrow n'; \Gamma) = u_{n'} \rho(n'; \Gamma) \sigma(n' \rightarrow n; \Gamma) \\ &= \rho(n'; \Gamma) k(n' \rightarrow n; \Gamma) = \rho(n; \Gamma) \rho(n'; \Gamma) \bar{\omega}(n', n, \Gamma) \\ &= h^{-1} Y(n'; n; \Gamma), \end{aligned} \quad (2)$$

where the channel symbols were omitted for the sake of brevity. In eq. (2) which is also the statement of microscopic reversibility $\rho(n; \Gamma)$ is the density of states, including the degeneracy of n , of the reactants in the Γ ensemble (appendix A). u_n or in full notation $u_{\alpha, n}$ is the relative initial velocity

$$u_{\alpha, n} = (2\epsilon_\alpha / \mu_\alpha)^{1/2} = [2(E - E_{\alpha, n}) / \mu_\alpha]^{1/2},$$

where ϵ_α is the relative translational energy, μ_α is the reduced mass of the colliding species and $E_{\alpha, n} = E_\alpha + E_n(\alpha)$ is the internal energy. E_α is the ground state energy in channel α measured on a common energy scale for all channels. (The channel symbols will be omitted until we arrive at sections 5 and 6.) Note that the equalities involving σ are valid only when $u_n, u_{n'}$ are well defined, that is when $n = v, J$ or $n = v, J, m_J$ but not when $n = v$.

From the definitions of $\bar{\omega}(n, n'; \Gamma)$ and $\rho(n; \Gamma)$ it follows that

$$\bar{\omega}(n, n'; E) = \sum_K (2K+1) \frac{\rho(n; E, K) \rho(n'; E, K)}{\rho(n; E) \rho(n'; E)} \times \bar{\omega}(n, n'; E, K), \quad (3)$$

where $\rho(n; E, K)/\rho(n; E)$ is the fraction, in $\Gamma = E$, of all reactant states with total angular momentum K , and arbitrary M_K . (Explicit expressions for $\bar{\omega}$ are given in appendix B.) Similarly

$$Y(n, n'; E) = \sum_K (2K+1) Y(n, n'; E, K). \quad (4)$$

Now, according to (2), (3) and (4)

$$\sigma(n \rightarrow n'; E) = \sum_K (2K+1) \frac{\rho(n; E, K)}{\rho(n; E)} \sigma(n \rightarrow n'; E, K), \quad (5)$$

and similarly for the rate constants. We note that (5) differs from the conventional resolution of the cross section into angular momentum components [4, 11]

$$\sigma(n \rightarrow n'; E) = \sum_K (2K+1) \sigma^K(n \rightarrow n'; E). \quad (6)$$

The difference between (5) and (6) is entirely formal and corresponds (see section 7 and appendix B) to using different representations of the S -matrix. However, to avoid confusion we shall base the discussion on the yield function which besides being symmetric is uniquely resolved, according to (4).

The basic statistical assumption, namely, that the product state distribution $P(n'; \Gamma)$ is independent of the reactant state n can be expressed in one of the following alternative forms

$$\tilde{Y}(n, n'; \Gamma) = Y(n; \Gamma) Y(n'; \Gamma) / Y(\Gamma) \quad (7)$$

$$= Y(n; \Gamma) P(n'; \Gamma) = P(n; \Gamma) Y(n'; \Gamma) \quad (8)$$

$$= Y(\Gamma) P(n; \Gamma) P(n'; \Gamma), \quad (9)$$

where

$$P(n; \Gamma) = Y(n; \Gamma) / Y(\Gamma), \quad (10)$$

and

$$Y(\Gamma) = \sum_{n, n'} Y(n, n'; \Gamma) = \sum_n Y(n; \Gamma) = \sum_{n'} Y(n'; \Gamma). \quad (11)$$

The quantities appearing in (7)–(11) have the following significance. \tilde{Y} denotes the statistical approximation of the yield function. $Y(n; \Gamma)$ represents both the rate of formation of the state n and the rate of its disappearance. It is related to the cross section and the rate constant via

$$Y(n; E) = u_n \rho(n; E) \sigma(n \rightarrow ; E) = \rho(n; E) k(n \rightarrow ; E), \quad (12)$$

where $\sigma(n \rightarrow ; E)$ and $k(n \rightarrow ; E)$ are the total cross section and rate constant for reactants in n . $P(n; \Gamma)$ and $P(n'; \Gamma)$, both defined by (10), represent the overall collision probability of state n and the product state distribution respectively. They are related to each other and to the "reaction matrix" [54, 55] $P(n, n'; \Gamma) = Y(n, n'; \Gamma) / Y(\Gamma)$ through

$$\sum_{n, n'} P(n, n'; \Gamma) = \sum_n P(n; \Gamma) = \sum_{n'} P(n'; \Gamma) = 1. \quad (13)$$

Thus, the statistical approximation (7) is equivalent to the statement that the reaction from initial state n and the formation of product state n' are disjoint events,

$$P(n, n'; \Gamma) = \tilde{P}(n, n'; \Gamma) = P(n; \Gamma) P(n'; \Gamma). \quad (14)$$

If a collision complex is assumed to be formed then $P(n; \Gamma)$ and $P(n'; \Gamma)$ can be interpreted as the probabilities for complex formation (from n) and decomposition (into n'). Finally, recall that we have used an abbreviated notation, omitting the channel notation α . The full notation obtains by replacing n by α , n and n' by α' , n' everywhere in (7)–(14).

3. The statistical ensemble

One of the immediate consequences of (7)–(9) or (14) is that independent (simultaneous) statistical assumptions in different ensembles may lead to inconsistencies. Consider our two basic ensembles $\Gamma_1 = E, K$ and $\Gamma_2 = E$ and suppose the statistical assumption (7) is made in Γ_1 . Thus

$$\begin{aligned} \tilde{Y}(n, n'; E) &= \sum_K (2K+1) \tilde{Y}(n, n'; E, K) \\ &= \sum_K (2K+1) \frac{Y(n; E, K) Y(n'; E, K)}{Y(E, K)}, \end{aligned} \quad (15)$$

where (using general notation) $\tilde{Y}(n, n'; \Gamma_2)$ is the resulting expression for the yield function in Γ_2 when the statistical assumption (7) is applied to the yield function in the partial ensemble Γ_1 . From (15) we see that in general (except under a certain condition, see below) $\tilde{Y}(n, n'; \Gamma_2) \neq \tilde{Y}(n, n'; \Gamma_2)$ where the latter quantity represents the yield function when the statistical assumption (7) is applied directly to $Y(n, n'; \Gamma_2)$. Thus when stating, for example, that a chemical reaction "behaves non-statistically" it is necessary to specify the ensemble in which framework this behavior is displayed. Numerical examples to illustrate the different results obtained from "similar" statistical assumptions in different ensembles are given in section 5. The term "similar" refers to using the same type of a measure in phase space, section 4, and the same type of dynamical restrictions, section 5. These two factors determine the explicit form of $Y(n; \Gamma)$ and consequently of $\tilde{Y}(n, n'; \Gamma)$.

In order that both $Y(n, n'; E, K)$ and $Y(n, n'; E)$, or more generally $Y(n, n'; \Gamma_1)$ and $Y(n, n'; \Gamma_2)$ where $\Gamma_1 \subset \Gamma_2$, will fulfil the basic statistical requirement, (7), it is necessary that $\tilde{Y}(n, n'; E) = \tilde{Y}(n, n'; E)$ or explicitly, cf. (15)

$$\frac{Y(n; E) Y(n'; E)}{Y(E)} =$$

$$\sum_K (2K + 1) \frac{Y(n; E, K) Y(n'; E, K)}{Y(E, K)}. \quad (16)$$

Using the general relationships [cf. (4) and (11)],

$$Y(n; E) = \sum_K (2K + 1) Y(n; E, K), \quad (17)$$

$$Y(E) = \sum_K (2K + 1) Y(E, K), \quad (18)$$

we find that the condition for the existence of (16) is that for every n' (or n) and K

$$P(n'; E, K) = \frac{Y(n'; E, K)}{Y(E, K)} = \frac{Y(n'; E)}{Y(E)} = P(n'; E). \quad (19)$$

The significance of (19) is that the product state distribution in $\Gamma_1 = E, K$ is independent of K . On the other hand, if $P(n'; E, K)$ depends on K the micro-canonical yield is not strictly statistical, in the sense that (7) is not fulfilled for $\Gamma = E$. Therefore we say that the conservation of angular momentum K intro-

duces correlation, or "relevance" [47–50], into $Y(n, n'; E)$. If K were not a conserved quantity then we would have to write $Y(nK, n'K'; E)$ instead of $Y(n, n'; E, K)$ etc., and replace every sum over K by a double sum on K and K' . In this, hypothetical, case (16) would trivially be satisfied. It will be shown below that if (19) is fulfilled then the measures in phase space in $\Gamma_1 = E, K$ and $\Gamma_2 = E$ can not be of the same type.

4. The measure in phase space

So far we have not specified the form of $Y(n; \Gamma)$ which, via (7), determines the explicit expressions of $\tilde{Y}(n, n'; \Gamma)$ and related functions such as the product state distribution $P(n'; \Gamma)$. Being an essential component of the statistical model $Y(n; \Gamma)$ is usually chosen as some "physically reasonable" function of n in the phase space region available to the various collision products (including the reactant channel). Yet, since the term "physically reasonable" is not uniquely defined the choice of this function, also known as the "measure in phase space" [15–18], may differ from one statistical model to another. We define the measure in phase space, $m(n; \Gamma)$, in the general form

$$Y(n; \Gamma) = Q(\Gamma) m(n; \Gamma). \quad (20)$$

The, meanwhile unspecified, proportionality factor $Q(\Gamma)$ determines the absolute value of the yield (rate constants, cross sections); It does not appear in normalized quantities such as $P(n'; \Gamma)$. The fourth respect of diversity in statistical models mentioned in section 2 concerns the specification of $Q(\Gamma)$, see below. We define

$$M(\Gamma) = \sum_n m(n; \Gamma), \quad (21)$$

so that, cf. (11), $Y(\Gamma) = Q(\Gamma) M(\Gamma)$. For (7) and (10) we obtain, respectively

$$\tilde{Y}(n, n'; \Gamma) = Q(\Gamma) m(n; \Gamma) m(n'; \Gamma) / M(\Gamma), \quad (22)$$

$$P(n'; \Gamma) = m(n'; \Gamma) / M(\Gamma). \quad (23)$$

The measures used in the information theoretic approach [42–52] and the phase space theory [15–27] are, respectively

$$m_0(n; E) = \rho(n; E) \quad (24)$$

$$m_{f,d}(n; E, K) = u_n \rho_d(n; E, K) = N_d(n; E, K). \quad (25)$$

Here $\rho(n; E)$ is the density of states of the molecular collision system, triatomic in the case of (1), at given E and n . $\rho_d(n; E, K)$ is the modified density in $\Gamma = E, K$ obtained by imposing dynamical restrictions, (section 5) on $\rho(n; E, K)$ – the density of states at given E, K and n , see appendix A. Both $m_0(n; E)$ and $m_{f,d}(n; E, K)$ have a simple physical meaning. Since these two measures involve different statistical ensembles and different extents of dynamical input it will be instructive to first generalize (24) and (25) and only then consider their meaning. To this end we postpone the discussion [formally, by deleting the symbol d from (25)] about the effects of dynamical restrictions on $\rho(n; \Gamma)$ to the next section, and define

$$m_0(n; \Gamma) = \rho(n; \Gamma), \quad (26)$$

$$m_f(n; \Gamma) = u_n \rho(n; \Gamma) = N(n; \Gamma). \quad (27)$$

These two functions will be called, the “uniform” (“volume”, “microcanonical”) and the “flux” measures, respectively. In appendix A it is shown that $\rho(n; \Gamma)$ is proportional to the number of elementary states, or equivalently to the volume in phase space, of a (triatomic) system in internal state n in the Γ ensemble. In other words, using the first measure in a statistical model is equivalent to assuming that all elementary states of the triatomic system are equally (or uniformly) probable [42–52, 73]. Hence, the product state distribution, (10), corresponding to (26)

$$P_0(n'; \Gamma) = m_0(n'; \Gamma)/M(\Gamma) = \rho(n'; \Gamma)/\rho(\Gamma), \quad (28)$$

is proportional to the phase space volume occupied by n ; $\rho(\Gamma) = \sum \rho(n'; \Gamma)$. Setting $\Gamma = E$ in (28) we obtain the microcanonical prior distribution [40]. The physical reasoning for choosing (28) is that in the absence of any information all states of the same energy are equally probable; in analogy to the “a-priori equal probabilities” postulate of statistical mechanics [75] and in accordance with the principles of information theory [76]. The same type of argument and consequently the same type of measure, $m_{o,d}(n; E, K) = \rho_d(n; E, K)$ (i.e. uniform) was assigned to the complex breakdown probability in Light’s original version of phase space theory [14],

(see section 8). Using a different approach Eu and Ross [30] arrived at essentially the same conclusion. Horie and Kasuga [35] used a uniform measure to explain (successfully) their experimental results on electron impact induced dissociation of H_2O . A uniform microcanonical measure appropriate to many particles in a finite volume (the interaction volume) was employed by Fermi in his statistical theory of nuclear reactions [77]. Other authors in this field studied the effects of angular momentum on this measure [78].

The second measure (27), being the product of a density (of states) and a velocity can be regarded as the phase space “flux” of the group of trajectories leading to (or originating in) the internal state n . It has been shown [4,11,22] (see also appendix A), that $\pi \hbar N(v, J; E, K)$ is the number of combinations of orbital l , and rotational, J , angular momenta consistent for a given $J = |J|$ with a total angular momentum K . Thus $N(n; E, K)$ has a simple geometrical meaning. When (27) is restricted to inelastic rotational transition the choice $m_f(J; E, K) = N(J; E, K)$ leads to the statistical theory of Bernstein et al. [13]. It should also be noted that (27) is closely related to transition state and RRKM theories [1–4, 7,12,20,33,38,39]. According to these theories the probability that a reaction will lead to products in the final state n is proportional to the flux of molecules, along the reaction coordinate, in the complex region. This flux is $u^\ddagger \rho^\ddagger(n, E) = N^\ddagger(n; E)$ where u^\ddagger is the velocity and ρ^\ddagger is the total density of complex states. Since there is only one translational degree of freedom and its density of states is proportional to $1/u^\ddagger$, N^\ddagger is the density of internal modes. The analogy to (27) is evident.

To conclude this section we note that $\rho(n; E, K)$ and $\rho(n; E)$ display different n -dependencies. Specifically, if $n = v, J$ then $\rho(n; E, K) \propto u_n^{-1} \propto (E - E_n)^{-1/2}$ whereas $\rho(n; E) \propto u_n \propto (E - E_n)^{1/2}$. Hence, from (20) and (26) it is clear that (16) or (19) are not fulfilled for $m_0(n; E)$ and $m_0(n; E, K)$. Or, in other words, if two uniform or two flux measures (in different ensembles) are said to be of the same “type” then for the fulfilment of (19), $m(n; E)$ and $m(n; E, K)$ which determine $P(n; E)$ and $P(n; E, K)$, respectively, must be of different types; as remarked at the end of the previous section.

5. Dynamical restrictions

The densities of states $\rho(n; \Gamma)$ appearing in (26) and (27) are defined on all phase space regions allowed by the symmetry and conservation rules. Some of these regions, e.g. those corresponding to very high orbital angular momenta (impact parameters), are not likely to affect the outcomes of real collisions. It is therefore expected that every statistical model will be more realistic by excluding such regions from the definition of $m(n; \Gamma)$. However, by setting more and more restrictions on the allowed phase space regions, and moreover by assigning them different weights, the statistical nature of the model is gradually lost and one approaches a dynamical theory. Thus in the information theoretic approach it is suggested to choose $m_0(n; \Gamma)$ as the "dynamically least biased" measure. The dynamical bias is incorporated in the form of constraints into the maximum entropy procedure [44,64–67] which finally yields, say, the product state distribution. On the other hand in LPN theory the dynamical restrictions are built into $m_T(n; E, K)$ [14–27]. In this section we consider the effects of such "built in" restrictions on both the flux and the uniform measures and the corresponding yield functions. The discussion will be limited to angular momentum constraints.

The simplest route to eliminating the contribution of very large orbital angular momenta to $\rho(n; E)$ is to postulate the existence of some maximal, energy independent, impact parameter b_m , so that only $l \leq l_m = kb_m$ contribute to, say, $\rho_T(E)$, cf. (A.11). In this case the "dynamically restricted" translational density and consequently all $\rho_d(n; E)$ differ from the corresponding unrestricted densities by a constant multiplicative factor (see appendix A) and $P(n; E)$ remains unchanged. On the other hand, the restriction $l \leq kb_m$ can modify $\rho(n; E, K)$. Moreover, if the restriction is

$$l \leq kb_m(\epsilon) = (2\mu\epsilon/\hbar^2)^{1/2} b_m(\epsilon), \quad (29)$$

where $b_m(\epsilon)$ is a function of the translational energy both $\rho(n; E, K)$ and $\rho(n; E)$ are modified. To clarify these points let us consider more systematically the effects of angular momentum constraints. The suitable ensemble for their implementation is $\Gamma_1 = E, K$. The discussion will be brief since the constraints are familiar [14–27].

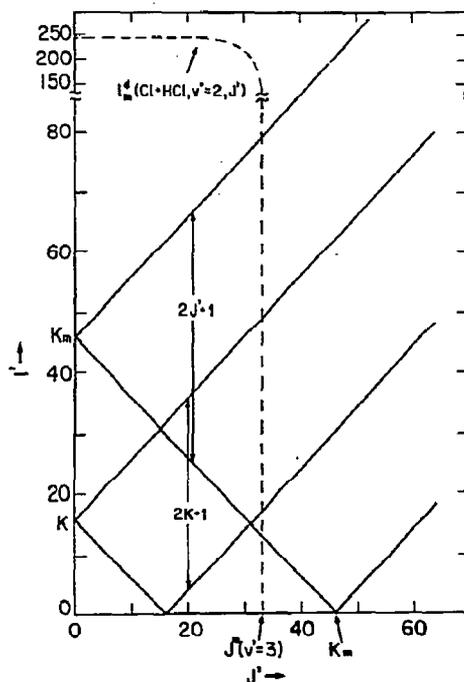


Fig. 1. Geometrical interpretation of angular momentum restrictions. Shown are typical results for the products in the reaction $H + Cl_2 \rightarrow HCl + Cl$. Due to the small reactant mass, K_m is small so that K and J' are, typically, of similar magnitude. Consequently, for many terms in (39), i.e., those with $J' > K$ the effective degeneracy $N(v'J'; E, K)$ [cf. (31) or (36)], is less than the normal (free rotor) degeneracy $2J' + 1$. Dynamical constraints resulting from the existence of a centrifugal barrier, eqs. (33) and (35), are less restrictive than the triangle rule (31).

If all orbital angular momenta consistent with the triangle rule

$$|K - J| \leq l \leq K + J \quad (30)$$

are allowed then the flux measure, (27), is given by, see appendix A and fig. 1,

$$m_T(\alpha, v, J; E, K) = N(\alpha, v, J; E, K)$$

$$= \begin{cases} 2J + 1; & J \leq K \\ 2K + 1; & J \geq K \end{cases} = K + J - |K - J| + 1. \quad (31)$$

The channel symbol, $\alpha = A + BC$ or $AB + C$, is introduced now to emphasize that the measure is different for different channels. The uniform measure corresponding to the same conditions, i.e. eq. (30), is

$$m_0(\alpha, v, J; E, K) = \rho(\alpha, v, J; E, K) \\ = N(\alpha, v, J; E, K)/u_{\alpha v J} \quad (32)$$

The dynamical restrictions in LPN theory are on the upper limit in (30). Specifically, it is assumed that inelastic and reactive collisions (which involve the formation of a "strong coupling complex") can only occur if the colliding species can surmount the centrifugal barrier. If the location of the barrier is at an intermolecular distance smaller than the assumed hard sphere radius, R_0 , then R_0 is taken as the maximal impact parameter, $l \leq kR_0$. For a $-C/R^6$ attractive potential, appropriate for neutral molecules, these restrictions imply the existence of a maximal impact parameter given, in obvious notation, by

$$b_m(\alpha, v, J; E) = \\ \max \{ [27C^{\alpha}/4(E - E_{\alpha, v, J})]^{1/6}; R_0^{\alpha} \} \quad (33)$$

Consequently, the range of allowed orbital angular momenta in channel α is modified from (30) into

$$|K - J| \leq l \leq l_m(\alpha, v, J; E, K) = \\ \min \{ K + J; l_m^d(\alpha, v, J; E) \} \quad (34)$$

where

$$l_m^d(\alpha, v, J; E) = k_{\alpha v J} b_m(\alpha, v, J; E) \\ = [2(E - E_{\alpha v J})\mu_{\alpha}]^{1/2} b_m(\alpha, v, J; E) \quad (35)$$

The number of partial waves l allowed by (34) is the dynamically restricted flux measure which appears in (25)

$$m_{f,d}(\alpha, v, J; E, K) = N_d(\alpha, v, J; E, K) \\ = l_m(\alpha, v, J; E, K) - |K - J| + 1 \quad (36)$$

Of course, $m_{f,d} \leq m_f$, fig. 1. Note that when $l_m^d(\alpha, v, J; E) > K + J$, that is when the dynamical restrictions are weaker than the conservation rule (30), eq. (34) reduces to (30) and (36) to (31), as expected. Thus (34) and (36) can be considered as general relationships which yield the dynamically unrestricted expressions in the limit of high values of $l_m^d(\alpha, v, J; E, K)$. $N_d(\alpha, v, J; E, K)$ can be viewed as the "effective degeneracy" of the rotational level J . The dynamically restricted uniform measure is given by

$$m_{0,d}(\alpha, v, J; E, K) \equiv \rho_d(\alpha, v, J; E, K) \\ = N_d(\alpha, v, J; E, K)/u_{\alpha v J} \quad (37)$$

The four explicit expressions (31), (32), (36) and (37) enable us to compare the influence of different measures in phase space, e.g. (31) versus (32), and different extents of dynamical input, e.g. (32) versus (37), on rate variables in $\Gamma_1 = E, K$. However, it is more instructive to test these different measures in $\Gamma_2 = E$ since: (a) $Y(\alpha n, \alpha' n'; E, K)$ and related quantities such as $P(\alpha', n'; E, K)$, as distinguished from the corresponding functions in $\Gamma_2 = E, K$, are not observed experimentally. (b) We also want to compare the rate variables resulting from the application of the statistical assumption (7) in different ensembles. To these ends we have to compare $\tilde{Y}(\alpha n, \alpha' n'; E)$ and $\bar{Y}(\alpha n, \alpha' n'; E)$, cf. (15). Using (15) and (20) or (22) we find

$$\tilde{Y}(\alpha n, \alpha' n'; E) = Q(E) m(\alpha, n; E) m(\alpha', n'; E) / M(E) \quad (38)$$

$$\bar{Y}(\alpha n, \alpha' n'; E) = \sum_K (2K + 1) Q(E, K) \\ \times m(\alpha, n; E, K) m(\alpha', n'; E, K) / M(E, K) \quad (39)$$

In order to compare (38) and (39) we consider two measures in $\Gamma_2 = E$ in addition to the four we already have in E, K . The obvious choice is $m_0(\alpha, n; E)$ and $m_f(\alpha, n; E)$, cf. (26) and (27). Their explicit form for $n = v, J$ is (see appendix A),

$$m_0(\alpha, v, J; E) = \rho(\alpha, v, J; E) \\ = A_T^{\alpha} (2J + 1) (E - E_{\alpha, v, J})^{1/2} \quad (40)$$

$$m_f(\alpha, v, J; E) = u_{\alpha v J} \rho(\alpha, v, J; E) \\ = B_T^{\alpha} (2J + 1) (E - E_{\alpha, v, J}) \quad (41)$$

where $B_T = (2/\mu^{\alpha})^{1/2} A_T$. Having specified the measures $m(\alpha n; \Gamma)$ in (38) or (39) the absolute values of \tilde{Y} and \bar{Y} are fixed by $Q(E)$ and $Q(E, K)$. These factors also determine the E -dependency of $Y(\alpha n, \alpha' n'; E)$ the knowledge of which is necessary for calculating, say, rate constants in the canonical ensemble. To determine $Q(E)$ and $Q(E, K)$ one has to rely either on additional assumptions or on additional information, e.g. experimental data. In the LPN [14-21] theory the choice of $m_{f,d}(n; E, K)$ as the measure in phase space is accom-

panied by the assumption $Q(E, K) = 1$ ($K \leq K_m$). Based on dynamical considerations several authors have derived alternative forms for $Q(E, K)$ which, for example, reduce the reaction probability at high velocities [27]. In the information theoretic approach (40) is usually accompanied by $Q(E) = R(E) \times \exp(-E/kT)/q(T)$ where $q(T)$ is the translation partition function of the reactants and $R(E)$ is either equal to $m_0(E)$, cf. (21) [53,62,63] or a constant [65].

In the numerical examples presented in the next section we consider only normalized quantities in $\Gamma_2 = E$ and can therefore disregard different choices of $Q(E)$ (or $Q'(E)$ which appears in (42) below). For $Q(E, K)$ we take, similar to the phase space theory,

$$Q(E, K) = Q'(E)\theta(K_m - K), \quad (42)$$

where $\theta(x)$ is the step function; $\theta(x \geq 0) = 1$, $\theta(x < 0) = 0$. It should be kept in mind however that (42) represents only one possible choice of $Q(E, K)$. By substituting (42) in (39) the sum over K is restricted by the maximal total angular momentum K_m whose choice depends on the dynamical input. If as in (35) dynamical restrictions set an upper bound to the orbital angular momenta the K -summation in (39) is bounded by, cf. (35)

$$K_m = K_m^d(\alpha v, J; E) \quad (43)$$

$$= \min \{ J_m^d(\alpha, v, J; E) + J; J_m^d(\alpha', v', J'; E) + J' \}$$

where α, v, J and α', v', J' refer to the reactant and product channels in (1), respectively. If, say, the minimum in (43) obtains for the reactants then the number of product states or equivalently the volume of product phase space contributing to (39) is limited by dynamical constraints on the entrance channel. Unless very unusual mass combinations or very high product levels are involved i.e. $E_{v', J'} \approx E - E_{\alpha'}$ this is typically the situation in highly exoergic chemical reactions for which $E - E_{\alpha'} \ll E - E_{\alpha'}$, cf. (35).

The upper limit (43) should be used in (39) when the measure in phase space is of the type $m_{0,d}$ or $m_{f,d}$. If the measure is m_0 or m_f then K is essentially unrestricted (except, formally by the radius of the container R ; $K_m = I_m + J \approx I_m = kR$, appendix A). In practice, as long as K_m is sufficiently large, say $K_m \gg J, J'$ or $K_m \gg K_m^d$, the functional dependence of $\tilde{Y}(\alpha, \alpha', E)$, (39), on α, n, α' and n' is not sensitive to the value of K_m . To verify this claim note that

for large K values m_f and m_0 are independent of K , cf. (31) and (32), respectively. Thus, in the limit of very high K_m the terms corresponding to $J, J' \ll K$ have a negligible contribution to (39) so that

$$\tilde{Y}_f(\alpha v, \alpha' v' J'; E) = Q_f''(E)(2J + 1)(2J' + 1) \quad (44)$$

for the flux measure (31), and

$$\tilde{Y}_0(\alpha v, \alpha' v' J'; E)$$

$$= Q_0''(E) \frac{(2J + 1)(2J' + 1)}{(E - E_{\alpha v})^{1/2}(E - E_{\alpha' v' J'})^{1/2}} \quad (45)$$

for the uniform measure (32). The E -dependent factors are given by

$$Q_f''(E) \approx Q_f'(E)K_m^2/N(E), \quad (46)$$

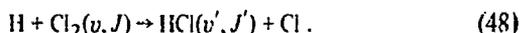
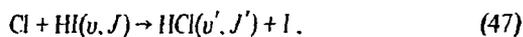
where K_m^2 replaces the sum $\Sigma(2K + 1)$ and $N(E) = \Sigma_{\alpha, v, J}(2J + 1) \propto \Sigma_{\alpha, v}(E - E_{\alpha v})$. The analogous expression for $Q_0''(E)$ is straightforward.

We note that both (44) and (45) fulfil (15), (16) and (19). The physical reason for that is clear; when large K values are allowed the effective degeneracies of both the reactant and the product rotational levels, cf. (31), become the normal degeneracies $2J + 1$ and $2J' + 1$. Consequently the correlation between products and reactants due to the conservation of K is lost as required in (19). However, as remarked at the end of section 3 the flux (44) and uniform (45) measures in $\Gamma_1 = E, K$ do not reduce to the yield expressions resulting from same types of measure in $\Gamma_2 = E$, compare (44) with (40) and (45) with (41).

Based on the six explicit measures $m_0(n; E, K)$, $m_{0,d}(n; E, K)$, $m_f(n; E, K)$, $m_{f,d}(n; E, K)$, $m_0(n; E)$ and $m_f(n; E)$ the next section is devoted to a more detailed and specific discussion of different statistical models.

6. Comparison of different models, examples

In order to demonstrate the variety in statistical theories we employ the six representative models described in the previous sections to calculate the product state distribution in the reactions



The product vib-rotational distributions in these reactions are known from the infrared chemiluminescence experiments of Polanyi and co-workers [79,80]. Since both reactions are highly exoergic, $-\Delta E_0 \gg kT$, the total reaction energy E , measured from the ground internal state of the products, is sharply defined; $E \approx -\Delta E_0 + E_a + \frac{5}{2}kT \gg \delta E$ where E_a is the activation energy and $\delta E \approx kT$ is the width of the reactant energy distribution. This implies that at ordinary temperatures the measured product state distributions are, to a good approximation, proportional to $Y(\tilde{v}, v', J'; E)$ where \tilde{v}, J' is the most populated internal level [81] and E is the average total energy; $E \approx -\Delta E_0 + E_a + \frac{5}{2}kT + E_v + E_j$. In (47), (48) $\tilde{v} = 0, J' = 3$ and $\tilde{v} = 0, J' \approx 20$, respectively, $E_j \approx kT$. Thus besides comparing the various statistical expressions for $Y(n, n'; E)$ we may test them against the experimental results. Another reason for choosing (47), (48) is that because of the different reactant masses in these reactions, H-LH and L-HH, respectively (L = light, H = heavy), angular momentum constraints are expected to display different effects on the product state distributions.

Using full and general notation the product vib-rotational distribution resulting from reactants in v, J and total energy $E = E_\alpha + E_{vJ} + \epsilon = E_{\alpha'} + E_{v'J'} + \epsilon'$ is

$$P(v', J' | \alpha', \alpha, v, J; E) = \frac{Y(\alpha, v, J; \alpha', v', J'; E)}{\sum_{v', J' \in \alpha'} Y(\alpha, v, J; \alpha', v', J'; E)} = \frac{Y(\alpha, v, J; \alpha', v', J'; E)}{Y(\alpha, v, J; \alpha'; E)} \quad (49)$$

where the sum extends over all product states with $E_{v'J'} \leq E - E_{\alpha'}$. We take $E_{v=0} = E_{v'=0} = 0$ and $E_{\alpha'} = 0$ so that $E_{\alpha'} = -\Delta E_0$. Since in all calculations below α and α' correspond to the lhs and rhs of (47) or (48) respectively, and only one $v, J = \tilde{v}, \tilde{J}$ level is considered, we will usually use the shortened notation $P(v', J'; E)$.

The vib-rotational distributions obtained from substituting the six measures (31), (32), (36), (37), (40) and (41) into the appropriate yield function, (38) or (39), and then into (49) are listed in table 1. The vibrational distribution $P(v'; E)$ and the (conditional) rotational distribution within $v', P(J' | v'; E)$ are defined

and normalized according to

$$P(v', J'; E) = P(v'; E) P(J' | v'; E), \quad (50)$$

$$\begin{aligned} \sum_{v', J' \in \alpha'} P(v', J'; E) &= \sum_{v' \in \alpha'} P(v'; E) \\ &= \sum_{J' \in \alpha', v'} P(J' | v'; E) = 1. \end{aligned} \quad (51)$$

At a given total energy E it is more convenient to employ the fractional variables $f_v = E_v/E, f_R = E_R/E = E_j/E$ and $f_T = (E - E_w)/E = \epsilon/E; f_v + f_R + f_T = 1$. In these variables the product state distributions $P(f_x) = P(E_x) dE_x/df_x$ corresponding to the first four models in table 1, i.e. those which do not incorporate dynamical input, are independent of the reactive system and can be expressed in a closed form. (Except for the weak dependence of $P(f_{v'})$ on $B_{v'}$ when the VR rather than the RRHO model is employed.) The variable g_R is defined by [45, 72]

$$g_R = f_R / (1 - f_v). \quad (52)$$

We note that for the "completely non-dynamical" models $P(g_R | f_v) = P(g_R) = (1 - f_v) P(f_R | f_v)$ is independent of f_v . In other words the partitioning of the residual, non-vibrational, energy $(1 - f_v)$ among the translational and the rotational degrees of freedom is independent of v . This trend was observed also in real systems [45, 72, 79]. The average fractional energies presented in table 1 correspond to the classical RRHO model where all degrees of freedom, including the vibration, are treated as continuous variables so that for $x, y = v, R, T$

$$\langle f_x \rangle = \int_0^1 f_x P(f_x) df_x = \int_0^1 \int_0^{1-f_x} f_x P(f_x, f_x) df_x df_y. \quad (53)$$

Noting that for the four non dynamical models in table 1

$$P(f_v) = (\gamma + 1)(1 - f_v)^\gamma, \quad (54)$$

$$P(g_R | f_v) = P(g_R) = \gamma(1 - g_R)^{\gamma-1}, \quad (55)$$

with $\gamma = 2, 3/2, 1$ and $1/2$ respectively, we find

$$\langle f_v \rangle = \langle f_R \rangle = (1 - \langle f_T \rangle) / 2 = 1 / (\gamma + 2). \quad (56)$$

In deriving (56) we have used the fact $P(g_R | f_v) = P(g_R)$ so that

Table 1
Statistical models

Statistical model	$P(J^1 v^1; E)$	$P(E_R^1 / f_{v^1})^a$	$P(v^1; E)$ ^b	$P(f_{v^1})^c$ (RRHO) ^d	$\langle f_{v^1} \rangle$ (RRHO)
yield	eqs.		(VR)		
(1) \tilde{Y}_f	$\alpha(2J^1 + 1)(E - E_{v^1 J^1})$	$2(1 - \delta_{R^1})$	$\alpha B_{v^1}^{-1}(E - E_{v^1})^2$	$3(1 - f_{v^1})^2$	$\frac{1}{4}$
(2) \tilde{Y}_o	$(2J^1 + 1)(E - E_{v^1 J^1})^{1/2}$	$\frac{3}{2}(1 - \delta_{R^1})$	$B_{v^1}^{-1/2}(E - E_{v^1})^{3/2}$	$\frac{5}{2}(1 - f_{v^1})^{3/2}$	$\frac{2}{7}$
(3) \tilde{Y}_f	$(2J^1 + 1)$	1	$B_{v^1}^{-1}(E - E_{v^1})$	$2(1 - f_{v^1})$	$\frac{1}{3}$
(4) \tilde{Y}_o	$(2J^1 + 1)(E - E_{v^1 J^1})^{1/2}$	$\frac{1}{2}(1 - \delta_{R^1})^{-1/2}$	$B_{v^1}^{-1/2}(E - E_{v^1})^{1/2}$	$\frac{3}{2}(1 - f_{v^1})^{1/2}$	$\frac{1}{5}$
(5) $\tilde{Y}_{f,d}$	$\sum_{K=0}^{K_m} \frac{N_d(\alpha, v, J; E, K) N_d(\alpha', v', J'; E, K)}{(2K+1) N_d(E, K)}$		$\sum_{J' \in \alpha' v'} P(v', J'; E)$		variable
(6) $\tilde{Y}_{o,d}$	$\sum_{K=0}^{K_m} \frac{\rho_d(\alpha, v, J; E, K) \rho_d(\alpha', v', J'; E, K)}{(2K+1) \rho_d(E, K)}$		variable		variable

a) Normalized according to $\int P(g_R / f_{v^1}) dg_R = 1$.

b) VR = vibrating rotor level scheme.

c) Normalized according to $\int P(f_{v^1}) df_{v^1} = 1$.

d) RRHO = rigid rotor harmonic oscillator level scheme.

Table 2
Parameters employed in the calculations a)

Reaction, channel	d_α ^b	E_α (kcal/mole)	E (kcal/mole)	C_6 (10^{-60} erg cm ⁶)	μ_α (10^{-24} g)	$R_{\alpha-s}$ (10^{-8} cm)	$I_m^d(\alpha, v, J^1)$ ^c	ω_e (cm ⁻¹)	$\omega_e X_e$ (cm ⁻¹)	B_e (cm ⁻¹)	α_e (cm ⁻¹)
Cl + I(1,0,3)	1	31.3	2.7	160	46.41	3.0	162	2309.5	4.00	6.55	0.18
HCl(v', J') + I	1	0	34.0	190	47.37	3.0	(226)	2989.0	5.25	10.58	0.30
H + Cl ₂ (0,20)	1	45.1	3.2	45	1.66	2.52	26	564.9	0.40	0.244	-
HCl(v', J') + Cl	2	0	48.3	93	30.05	2.19	(220)	2989.0	5.25	10.58	0.30

a) Based on refs. [82-84].

b) The "degeneracy" of the channel.

c) See eq. (35). The values in brackets are representative of the product channel, corresponding to I_m^d of the most populated v', J' level. These are $v', J' = 3, 12$ and 2, 13 for the first and second reactions respectively.

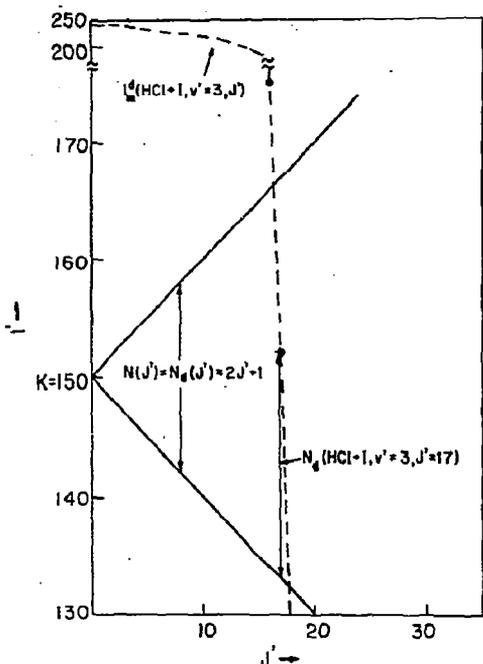


Fig. 2. Angular momentum restrictions on the products of reaction (47) [cf. eqs. (34) and (36) and table 2]. Since for this reaction K is typically much larger than J' the effective degeneracy $N_\alpha(J')$ is practically equal to the normal degeneracy $2J' + 1$, except for the very high J' s (e.g. $J' = 17$ in $v' = 3$). The centrifugal barrier (cf. (33)), is far less important than the triangle rule (31).

$$\begin{aligned} \langle f_R \rangle &= \int_0^1 \int_0^1 f_R P(f_R) df_R = \int_0^1 \int_0^{1-f_R} f_R P(f_v, f_R) df_R df_v \\ &= \int_0^1 \int_0^1 g_R P(g_R) (1 - f_v) P(f_v) dg_R df_v \\ &= \langle g_R \rangle (1 - f_v) = [1/(\gamma + 1)] (\gamma + 1)/(\gamma + 2). \quad (57) \end{aligned}$$

Approximate closed form expressions can be derived also for the "dynamically biased" distributions, models 5 and 6 in table 1. The resulting expressions are however rather involved and a graphical presentation is more instructive, see below. Qualitatively, if the major contribution to the sums comes from high total angular momenta, i.e. from $K > J$, or, equivalently if $K_m \gg J'$, then $\tilde{P}_{0,d}$ is nearly equal to \tilde{P}_0 and $\tilde{P}_{f,d}$ to \tilde{P}_f . Unless $E_{v',J'} \approx E$ the value of K_m for exoergic reactions is fixed by the reactants i.e. $K_m = I_m^d(\alpha, v, J; E) + J$. cf.

(35) and (43).

Consider now the reaction (47). For energies corresponding to thermal reactants $K_m = I_m^d(\text{Cl} + \text{HI}, 0, 3) + 3 = 165$, see table 2, which is substantially larger than the average typical product rotational angular momenta, $J' \approx 15$. The restrictions are expected to be more stringent when $E_{J'}$ approaches $E - E_{v'}$. Toward this limit J' increases, K_m decreases and the relative contribution of $K > J'$ terms also decreases. This means that the dynamical restrictions will mainly reduce the effective degeneracy, or equivalently, the phase space volume of rotational levels near the energy limit $E_{J'} \approx E - E_{v'}$, cf. (36) and (31) and fig. 2.

A different behavior is expected in reaction (48). Here, due to the small reduced mass of the reactants I_m^d and K_m are small. Except for product levels near the energy limit K_m is fixed by the reactants. In our example $K_m = I_m^d(\text{H} + \text{Cl}_2, 0, 20) + 20 = 46$, cf. fig. 1

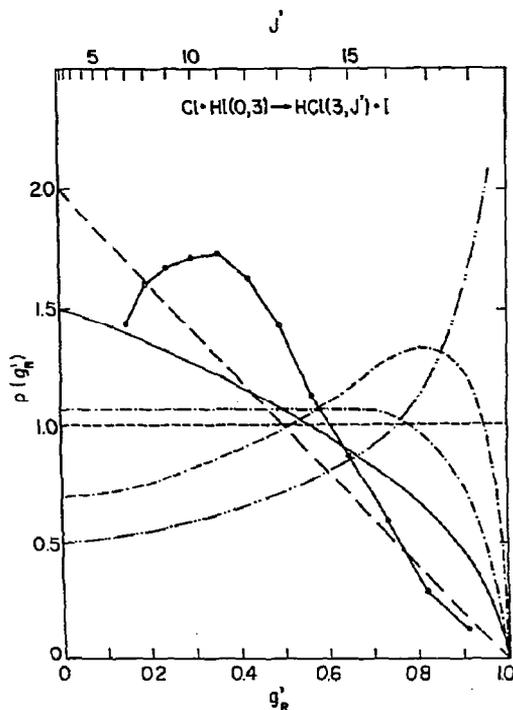


Fig. 3. Product rotational energy distributions for reaction (47), computed using the models listed in table 1 and the data of table 2. Model (1): ----; (2): —; (3): dashed horizontal line; (4): - · - · -; (5): · · · · ·; (6): - - - - -. Dots indicate the experimental results [79].

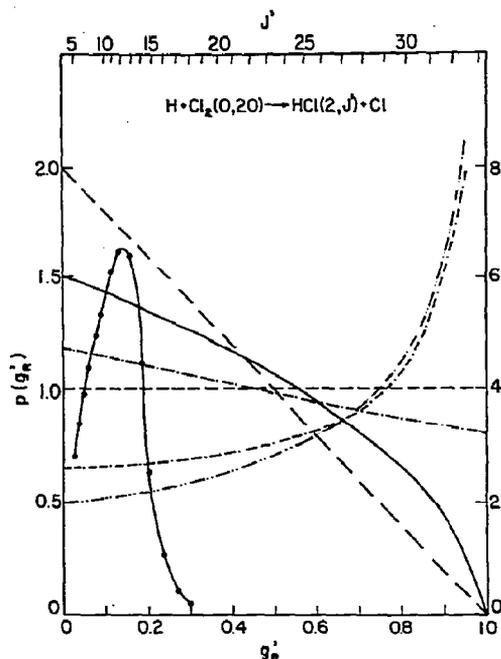


Fig. 4. Product rotational energy distributions for reaction (48). Notation as in fig. 3. Experimental results from ref. [80].

and table 2. Since $J' \approx 0-40$ is of the order of K_m , the effective degeneracy of small J 's will also be reduced.

Representative rotational distributions obtained from calculations based on the six models listed in table 1 are shown in figs. 3 and 4 for reactions (47) and (48), respectively. The experimental distributions are shown for the sake of comparison. The two-fold degeneracy of the product channel in (48), $\alpha' = \text{Cl} + \text{HCl}$, affect the computation of product state distributions only via $M(E, K) = N_d(E, K)$ or $\rho_d(E, K)$ in models 5 and 6. This fact was taken into account by writing, in general and obvious notation, $M(E, K) = d_{\alpha} m(\alpha; E, K) + d_{\alpha'} m(\alpha'; E, K)$, where d_{α} is the degeneracy (or multiplicity) of channel α , see table 2.

Figs. 3 and 4 confirm quantitatively that while in (47) the dynamical restrictions modify only the population of high J 's in (48) they affect, although to a lesser extent, also low J 's. [In the, hypothetical, extreme case of very low K_m the effective degeneracy of J' would be 1 instead of $2J' + 1$, so that $\tilde{P}_{f,d}(g'_R) \propto \tilde{P}_f(g'_R)/(2J' + 1) \propto 1/(g'_R)^{1/2}$. Fig. 4 indicates, as

expected, that this is not the case and high J' are more sensitive to the angular momentum constraints. Similar arguments hold for $\tilde{P}_{0,d}$.] The very steep rise of $\tilde{P}_{0,d}(g'_R) \propto 1/(g'_R)^{1/2}$ at large g'_R values is bounded by the value corresponding to $J'^*(v')$ — the highest J' below the energy limit. Yet, since at a given E it might be that for one or more v' values $E_{J'^*(v')} \approx E - E_{v'}$ the larger contribution of $J'^*(v')$ may affect not only the rotational distribution but also the vibrational one, see below. These "resonance" effects will be smoothed out by averaging over E . It is interesting that a similar rise in the rotational distribution of OH radicals produced by electron impact dissociation of H_2O was predicted and observed experimentally by Horie and Kasuga [30]. To summarize, inspection of figs. 3 and 4 supports our earlier statement that "statistical behavior" is a feature of the model employed and therefore not an unambiguous concept.

At a given total energy E the volume in phase space available to the products decreases with v' . In table 1 we see that the weights assigned to these regions are proportional to $(E - E_{v'})^{\gamma}$ with γ positive and of the

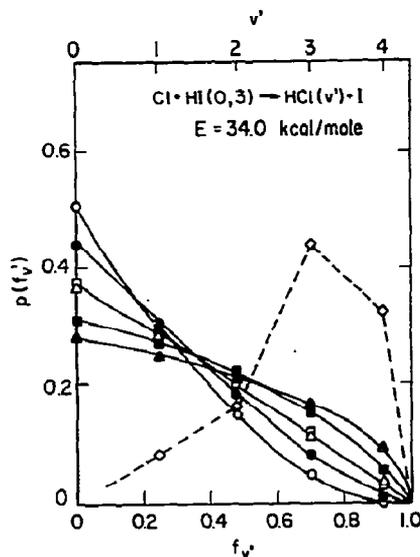


Fig. 5. Product vibrational energy distributions for reaction (47), computed using the models of table 1 and normalized according to $\sum_{v'} P(f_{v'}) = 1$. Model (1): open circles; (2): solid circles; (3): open squares; (4): solid squares; (5): open triangles; (6): solid triangles. The experimental results [79], (diamonds) are markedly different from the statistical models and indicate population inversion.

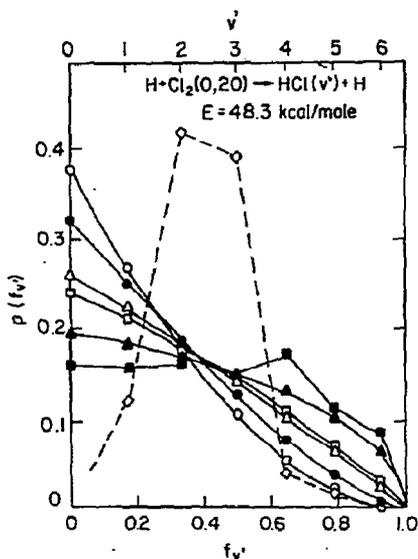


Fig. 6. Product vibrational energy distribution for reaction (48) computed using the models of table 1. Notation as in fig. 5. The experimental results [80] (diamonds), differ substantially from the statistical models.

order of 1. Therefore, the differences between the various statistical vibrational distributions are less pronounced than those in the rotational distributions, as shown in figs. 5 and 6. The irregularity in $\tilde{P}_{0,d}(v'=4)$ in fig. 6 is due to the "resonance" effect mentioned above; it is not seen for $\tilde{P}_{0,v}(v')$ since this distribution was computed in the classical (J' continuous) VR model, i.e. $\tilde{P}_{0,v}(v') \propto (E - E_{v'})^{1/2}/B_{v'}$, table 1.

7. Alternative derivations

It has been shown that several statistical models based on the hypothesis of intermediate complex formation can also be derived by appropriate formal assumptions on the structure of the scattering matrix [4,6,11,13,18,19,22,23]. In this section and in appendix B we show that our formulation and classification of statistical models which involve both formal (e.g. factorability of Y) and pictorial (e.g., flux versus uniform measures, available regions in phase space) considerations is simply related to generalized versions of the "formal" and "complex" derivations.

Consider first the formulation based on the assumption of complex formation. (Or, compound nucleus in nuclear reactions [5,6].) As mentioned in section 2 this assumption accounts for the lack of correlation between products and reactants and helps to define the phase space regions available to the reaction products. Generalizing this approach to any Γ the cross section for the process $\alpha, n \rightarrow \alpha', n'$, eq. (1), is written as

$$\tilde{\sigma}(\alpha, n \rightarrow \alpha', n'; \Gamma) = \sigma(\alpha, n \rightarrow c; \Gamma) P(c \rightarrow \alpha', n'; \Gamma) \quad (58)$$

where the factors on the rhs of (58) represent, respectively, the cross section for complex formation from reactants in α, n and the probability of the complex to yield products with $\alpha' n'$. Summing (58) over $\alpha' n'$ and using the general relation (12) (which by (2) holds for every Γ) we obtain

$$\sigma(\alpha, n \rightarrow ; \Gamma) = \sigma(\alpha, n \rightarrow c; \Gamma)$$

$$= Y(\alpha, n; \Gamma) / u_{\alpha n} \rho(\alpha, n; \Gamma) \quad (59)$$

Similarly, multiplying by $u_{\alpha n} \rho(\alpha, n; \Gamma)$, summing over α, n and using (2), (10) and (11), we find

$$P(c \rightarrow \alpha', n', \Gamma) = P(\alpha', n'; \Gamma)$$

$$= Y(\alpha', n'; \Gamma) / Y(\Gamma) = m(\alpha', n'; \Gamma) / M(\Gamma) \quad (60)$$

Substitution of (59) and (60) into (58) and then using (2) yield the basic statistical hypothesis (7). Thus (58) and (7) are completely equivalent. Any assumption on the form of $\sigma(\alpha, n \rightarrow c; \Gamma)$ or $P(c \rightarrow \alpha', n'; \Gamma)$ can be regarded as an assumption on the form of $Y(\alpha, n; \Gamma)$ or, cf. (20), on the measure in phase space. It has to be remembered however that the two factors on the rhs of (58), both having a simple dynamical meaning, are related by microscopic reversibility and therefore cannot be chosen independently.

From here on the classification of statistical models follows along similar lines to sections 2–6. However, we linger at this point in order to (briefly) elaborate on the dynamical significance of the uniform and flux measures as well as to demonstrate the validity of the somewhat uncommon relation (5).

If the assumption on complex formation (58) is made in $\Gamma_1 = E, K$ then, using (12), (20), (58)–(60) the cross section in $\Gamma_2 = E$ is of the form

$$\tilde{\alpha}(\alpha, n \rightarrow \alpha', n'; E) =$$

$$\sum_K (2K+1) [\rho(\alpha, n; E, K)/\rho(\alpha, n; E)] \times \sigma(\alpha, n \rightarrow c; E, K) P(c \rightarrow \alpha', n'; E, K) \quad (61a)$$

$$= \frac{1}{u_{\alpha, n} \rho(\alpha, n; E)} \sum_K (2K+1) Q(E, K) \times m(\alpha, n; E, K) m(\alpha', n'; E, K) / M(E, K). \quad (61b)$$

The last result could, of course, be directly derived from (2) and (39). Summing in (61) over $\alpha'n'$ and using (42) in (61b) we find

$$\tilde{\alpha}(\alpha, n \rightarrow c; E) = \sum_K (2K+1) [\rho(\alpha, n; E, K)/\rho(\alpha, n; E)] \times \sigma(\alpha, n \rightarrow c; E, K) \quad (62a)$$

$$= Q'(E) [1/u_{\alpha, n} \rho(\alpha, n; E)] \sum_{K=0}^{K_m} (2K+1) m(\alpha, n; E, K). \quad (62b)$$

The cross sections for complex formation corresponding e.g. to the "dynamical" flux and uniform measures are obtained by substituting (36) and (37) into (62b). After some angular momentum algebra and using the exact expressions for $\rho(\alpha, n; E)$ and $\rho(\alpha, n; E, K)$ from appendix A we find

$$\tilde{\sigma}_{f, d}^d(\alpha, v, J \rightarrow c; E) = \frac{\pi \hbar^2 Q'(E)}{\mu_{\alpha} (2J+1) (E - E_{\alpha v J})} \sum_{l=0}^{l_m^d} (2l+1), \quad (63)$$

$$\tilde{\sigma}_{0, d}^d(\alpha, v, J \rightarrow c; E) = \frac{\pi \hbar^2 Q'(E)}{\mu_{\alpha} (2J+1) (E - E_{\alpha v J})} \times \sum_{l=0}^{l_m^d} (2l+1) \rho_R(E - E_{\alpha v J}), \quad (64)$$

with l_m^d given by (35). The equations for $\tilde{\sigma}_f$ and $\tilde{\sigma}_0$ obtain by setting $l_m^d(\alpha, v, J; E) = k_{\alpha v J} b_m$ where b_m is some large and energy independent impact parameter. Eq. (63) is a fundamental relation in the phase space theory [15–27], whose significance is that apart from the degeneracy factor all partial waves contribute equally to the cross section. The classical analogue of

this result is that the probability for complex formation from collisions with impact parameter b is proportional to $2\pi b$ so that $\sigma(\alpha, n \rightarrow c; E) = \pi b_m^2$. On the other hand, (64) implies that the contribution of each partial wave l is proportional to the number of elementary states "conjugated" to it. The classical result for the complex formation cross section is $\sigma(\alpha, v, J \rightarrow c; E) \propto \pi b_m^2 / u_{\alpha v J}$. The interpretation of this inverse velocity dependence of the cross section (strictly so only for a constant b_m) is less obvious than that for the flux measure. However, its meaning becomes quite clear when viewed as the direct result (via microscopic reversibility) of the assumption that the probability of the complex to form products with $\alpha'n'$ is proportional to the phase space volume associated with $\alpha'n'$,

$$P_{0, d}(c \rightarrow \alpha', v', J'; K) =$$

$$\rho_d(\alpha', v', J'; E, K) / \sum \rho_d(\alpha', v', J'; E, K). \quad (65)$$

The proof that (65) and (64) are essentially equivalent is immediate. Also, the extension of (65) to $P_{f, d}$, P_0 and P_f as well as the proof of their equivalence to $\tilde{\sigma}_{f, d}$, $\tilde{\sigma}_0$ and $\tilde{\sigma}_f$, respectively, is straightforward.

The structure and properties of the S and T matrices corresponding to several statistical models were described by several authors [4, 11, 13, 18, 19, 22, 49]. It has been shown that one of the most general parametrizations of the S matrix is [11]

$$\langle |S_{ij}|^2 \rangle = \delta_{ij} (1 - f_i) + f_i f_j / \sum_j f_j, \quad (66)$$

where $0 \leq f_i \leq 1$ and $|d| = |v, J, d|$. The symbol $\langle \rangle$ refers to "statistical averaging". It involves the random phase approximation (RPA) and associates (66) with the additional assumption $\langle \text{Re } S_{ii} \rangle = 0$. The first term on the rhs represents the shadow contribution to the elastic scattering, necessary to ensure the normalization condition $\sum_j |S_{ij}|^2 = 1$. The similarity between (66) and say, (7), is apparent. By extending (66), or more precisely the corresponding equation for the T matrix, to general representation and normalization schemes of the states i , one can account for the general characterization of a statistical model in terms of Γ , m and Q as was done in the previous sections. Since the proof of this statement, although straightforward, involves lengthy and formal derivations, the details and the interpretations are provided in appendix B.

Table 3
Partition of energy among products' degrees of freedom^{a)}

Model	Cl + HI (0,3) → HCl(v', J') + I			H + Cl ₂ (0,20) → HCl(v', J') + Cl		
	$\langle f_{v'} \rangle$	$\langle f_{R'} \rangle$	$\langle f_{T'} \rangle$	$\langle f_{v'} \rangle$	$\langle f_{R'} \rangle$	$\langle f_{T'} \rangle$
(1) \tilde{P}_f	0.18 (0.18)	0.27 (0.27)	0.55 (0.55)	0.21 (0.21)	0.23 (0.23)	0.46 (0.46)
(2) \tilde{P}_0	0.22 (0.22)	0.31 (0.31)	0.47 (0.47)	0.25 (0.25)	0.30 (0.30)	0.45 (0.45)
(3) \tilde{P}_f	0.27 (0.28)	0.36 (0.36)	0.37 (0.36)	0.32 (0.31)	0.32 (0.34)	0.36 (0.35)
(4) \tilde{P}_0	0.32 (0.36)	0.42 (0.38)	0.26 (0.26)	0.43 (0.39)	0.36 (0.37)	0.21 (0.24)
(5) $\tilde{P}_{f,d}$	0.26	0.35	0.38	0.33	0.31	0.36
(6) $\tilde{P}_{0,d}$	0.42	0.40	0.28	0.43	0.34	0.23

^{a)} Calculated using the discrete form of Y , second column in table 1, in the VR model. Values in brackets correspond to (1) $\langle f_{v'} \rangle$ calculated in the continuous VR model, that is J' -continuous, fourth column in table 1, (2) $\langle f_{R'} \rangle / \langle f_{T'} \rangle$ as in the RRHO model; last column in table 1.

8. Discussion

The marked differences between the various statistical models reflected by the rotational state distributions, figs. 3 and 4, are largely masked by the averaging which yield the vibrational distributions, figs. 5 and 6 respectively. For reactions involving more degrees of freedom, the differences in, say, the distribution of energy in one vibrational mode will be even less pronounced. Considering in addition that none of the statistical models (of which table 1 presents only a sample) provides an accurate description of small collision systems, the question whether there is one preferred or unique model is irrelevant. A more reasonable starting point for comparing the different theories is to consider their origins and objectives. In discussing these aspects we shall mainly refer to the phase space theory [15–27] (model 5 in tables 1 and 3) and the microcanonical prior distribution (model 2) employed in the information theory approach [42–72].

Although the final expressions for the product state distributions (cf. tables 1 and 3) obtained by the phase space theory and the prior limit of the information theory approach may be quite similar there is a rather fundamental difference in the way of processing dynamical information by the two methods. In the phase space theory all the available or predicted

dynamical information is built into the final statistical expressions in one stage. On the other hand, the prior distributions intend to represent the dynamically "least biased" ("most ignorant", "random") situation. The dynamical bias is reflected by the so-called surprisal function (see below) which provides a convenient and meaningful measure for the deviation of actual distributions from their prior ("thermodynamic") expectation values.

The choice of the ensemble, the measure, the angular momentum restrictions and the weighting function, Q , in the phase space theory [14–26] (and other statistical dynamical theories [7–13, 27–41]) is guided by dynamical considerations. In fact, the use of the flux measure, (36), and the "opacity function", (42), is a necessary consequence (via microscopic reversibility) of the dynamical assumption that all angular momenta below the cut-off, cf. (35) and (43), contribute equally to the reactive, or inelastic, cross section. Indeed, as mentioned in section 4, the uniform phase space measure was used in one of the original formulations of the phase space theory [14], but has been replaced by the flux measure in order to make it consistent, on microscopic reversibility grounds [15], with the angular momentum restrictions on the complex formation cross section. Of course, if the uniform measure was retained but

the angular momentum requirements were modified, the result would be the (dynamically modified) prior distribution in the E, K ensemble, model 6.

The procedure of restricting the available phase space regions employed in the phase space theory does not suffice to account for extreme, but common, phenomena such as population inversion, cf. figs. 5 and 6. It was suggested [14,73] that in such cases the statistical models may serve as bases for comparison with experimental results. An explicit, quantitative, implementation of this notion is provided by the surprisal-entropy analyses which constitute one, important, element of the information theoretic method. The method is, however, more general and beside analytic means provides also algorithms for predicting (synthesis), say, product state distribution. Since the general approach has been extensively described elsewhere [49,50,72] we shall only emphasize a few points pertinent to the present discussion.

The basic quantities used in surprisal-entropy analyses are the entropy S , or the entropy deficiency ΔS , the surprisal I and the prior distribution P^0 ,

$$\begin{aligned} \Delta S &= S_0 - S = \ln \Omega - \sum_s P(s) \ln P(s) \\ &= - \sum_n P(n) \ln [P(n)/P^0(n)] = \sum P(n) I(n) = \langle I \rangle. \end{aligned} \quad (67)$$

Here, as in statistical mechanics, the s -summation extends over all the accessible elementary states (appendix A) of the system of interest. The n -summation is over groups of states; all the states in a given group are equally probable. Thus, if the system is composed of the atom plus the diatomic products in (1), the total (center of mass) energy is between E and $E + dE$ and $n = v$ then the group v contains all rotational-translational states consistent with this specification. The number of these states is $\rho(n; E) dE$, appendix A. $\Omega = \sum \rho(n; E) dE = \rho(E) dE$ is the total number of accessible states. Hence, according to (67), $P^0(n)$ is simply proportional to the number of states in the group n or equivalently, to the volume in phase space occupied by n . Obviously, for our example $P^0(n)$ is simply the microcanonical prior distribution $\tilde{P}_0(n)$ of table 1 corresponding to the uniform probability $P^0(s) = 1/\Omega$. As in ordinary statistical mechanics this is the distribution which, in the classical RRHO approximation, leads to the equipartition limit [46]; in our example $\langle f_T \rangle : \langle f_R \rangle : \langle f_v \rangle = 3 : 2 : 2$, cf. table 3. This form of the

prior distribution is the dynamically least biased one if the only available information on the system is that all collisions proceed with the same total energy E , $E + dE$. Deviations from the complete microcanonical behaviour correspond to non-zero surprisals $-\ln [P(n)/P^0(n)]$ or non-vanishing entropy deficiency $\Delta S > 0$. If the surprisal happens to be a linear function of some variable, e.g. $f_v = E_v/E$, the maximum entropy principle which is the major theoretical (analytic and predictive) tool of the information theoretic method, implies that $\langle f_v \rangle$ is the only informative dynamical constraint [44]. Surprisal analysis thus helps to identify dynamical constraints. Alternatively, if the dynamical constraints are known, the maximum entropy principle can be employed to predict the actual distribution $P(n)$. In particular, when the dynamical input can be represented in terms of the average value of the observable A , $\langle A \rangle = \sum P(n) A_n = \text{const.}$ (e.g. $n = v, A_v = f_v$), the predicted distribution will be of the canonical form $P(n) = P^0(n) \exp(-\lambda A_n)/Q$. As in ordinary statistical mechanics λ is a lagrangian multiplier which can be interpreted as a generalized (reciprocal) temperature parameter and Q is a normalization constant equivalent to a partition function.

If surprisal analysis is viewed just as a convenient quantitative measure of deviations from a "given statistical behaviour" any statistical-dynamical model $\tilde{P}(n)$ [or $\tilde{P}(n)$] can be used as a prior reference. Considering as specific examples the product vibrational distributions in (47) and (48) this means that one can compute different surprisals corresponding, say, to the different models of tables 1,

$$\tilde{I}(v) = -\ln [P(v)/\tilde{P}(v)] . \quad (68)$$

Figs. 7 and 8 show the results of these surprisal analyses. Due to the apparent similarities between the vibrational distributions of the six statistical models, the surprisals are also similar. They are nearly linear for the Cl + HI reaction indicating that $\langle f_v \rangle$ is the most important constraint and non-linear in the H + Cl₂ reaction indicating that either $\langle f_v \rangle$ is not a relevant (informative) constraint or that there is at least one additional constraint beside $\langle f_v \rangle$ [64b, 66, 67].

Among the various distributions which can serve as a reference for surprisal analysis there is only one which maximizes the entropy S (minimizes ΔS), (67), in the limit of no constraints. For experimental situations where only the total collision energy is known, this is

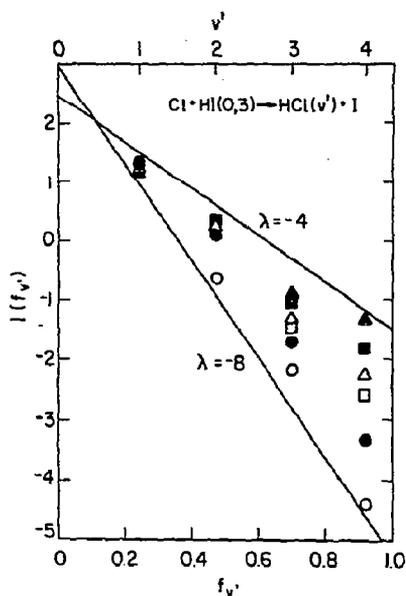


Fig. 7. Surprisal analysis for reaction (47) using as reference prior distributions $P^0(f_{v'})$ the six models of table 1. $I(f_{v'}) = -\ln[P(f_{v'})/P^0(f_{v'})]$ where $P(f_{v'})$ is the experimental [79] distribution. Notation as in fig. 5. The near linearity of the surprisal implies that $(f_{v'})$ is the main informative dynamical constraint.

the uniform-microcanonical distribution employed in most of the applications of the information theory method. Thus, when surprisal analysis is regarded as one component in the general statistical-information theoretic approach, there is a unique prior distribution defined by the a-priori known (asymptotic, boundary) conditions on the system. In statistical mechanics these conditions are known as the external parameters of the ensemble [75]. The choice of the ensemble, in our case $\Gamma_2 = E$ or $\Gamma_1 = E, K$, should be consistent with these conditions. If experiments could be performed with angular momentum selected reagents, then the appropriate prior distribution should be the uniform one in the $\Gamma = E, K$ ensemble. The actual functions in each E, K shell should be computed by maximizing the entropy corresponding to all states consistent with E, K subject to whichever constraints that can be identified. Quantities such as cross sections or rate constants in $\Gamma = E$ can then be calculated by properly superposing [this requires a weighting function $Q(E, K)$] all the possible E, K components. An analo-

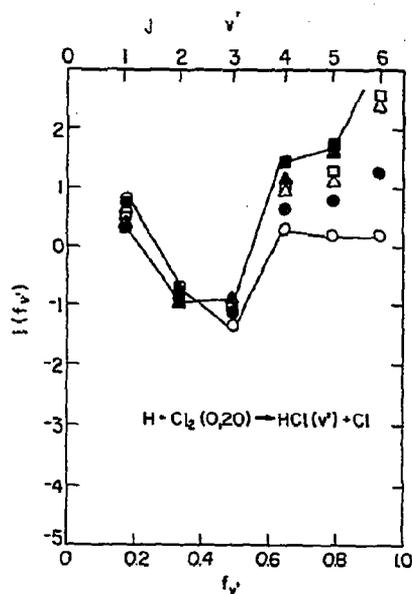


Fig. 8. Surprisal analysis for reaction (48). Notation as in fig. 7. The non-linear behaviour of the surprisal indicates that $(f_{v'})$ is either not the only dynamical constraint, or that $(f_{v'})$ is not the appropriate constraint. Note that explicit consideration of angular momentum restrictions does not significantly alter the surprisal curve.

gous procedure has been employed to calculate quantities in the thermal (canonical) ensembles $\Gamma_3 = T$, i.e. by superposing the contributions from different energy shells $\Gamma_2 = E$ [53,62,63]. If, however, angular momentum components cannot be resolved the information theoretic route to handle angular momentum restrictions is to express them, if possible, in the form of constraints which would modify the microcanonical prior distribution to a canonical-type distribution. This procedure has been recently applied with considerable success [64b,66,67].

Finally, it should be noted that the prior distributions which maximize the entropy are the ones which provide the link between the microscopic (single isolated collisions) and macroscopic (relaxation, thermodynamic functions) characteristics of a disequilibrium molecular system and its approach to equilibrium [68-72].

9. Concluding remarks

An attempt was made to emphasize that statistical behaviour, mainly in small collision systems, can be differently interpreted. Various models can be formulated within the framework of different statistical ensembles using different measures in phase space and incorporating different extents of dynamical information. Some of the more common models were formulated for predictive purposes but can also be used on a comparative basis. The prior distributions of the information theory approach combines these aspects. They can be used as a reference for measuring deviations from microcanonical behaviour or as zero-order expressions to be supplemented and modified by dynamical constraints. The unambiguous prior distribution is the one which maximizes the appropriately defined entropy function of the system. Once the boundary conditions (external parameters) defining the accessible states of the system are known, the entropy or, in the information theoretic language, the information content is also uniquely defined. One may still argue which are the external parameters defining a general collision system. However, this non-trivial, interesting – and still not entirely solved – question is beyond the rather descriptive and didactic scope of the present paper.

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Appendix A: Elementary states and state densities

Elementary states [5] of a free particle (or of a particle in a box or a sphere) are the solutions of the Schrödinger equation normalized on the momentum scale. As distinguished from, say, states normalized on the energy scale, the elementary states have a uniform density in the classical phase space (equal to $1/h^3$ for a structureless particle in a three-dimensional

volume). In this appendix we list the elementary states in the plane wave, spherical wave and total angular momentum representations. This procedure is essential for evaluating the density of states factors $\rho(n; \Gamma)$ appearing in the text. The beginning of the derivation is based on ref. [85].

The plane wave solutions of the Schrödinger equation for a particle in a cubic box of volume V are, in obvious notation,

$$\chi_{\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | \mathbf{k} \rangle = V^{-1/2} \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (\text{A.1})$$

with \mathbf{k} quantized according to $k_x = (2\pi/V^{1/3})n_x$, $n_x = 0, \pm 1, \pm 2 \dots$ etc., corresponding to (translational) energy quantization $\epsilon = \hbar^2 k^2 / 2\mu = (2\pi^2 \hbar^2 / \mu V^{2/3}) \times (n_x^2 + n_y^2 + n_z^2)$. Each n_x, n_y, n_z (or k_x, k_y, k_z , or p_x, p_y, p_z ; $\mathbf{p} = \hbar \mathbf{k}$) combination is an elementary state occupying a volume of h^3 in the classical phase space ($\sum_{n_x, n_y, n_z} \leftrightarrow h^{-3} \int d\mathbf{p} d\mathbf{r} = h^{-3} V \int d\mathbf{p}$). The number of these states per unit translational energy and unit volume, that is, the density of translational states is given by

$$\dot{\rho}_{\text{T}}(\epsilon) = (2^{1/2} \pi^2 \hbar^3)^{-1} \mu^{3/2} \epsilon^{1/2} = A_{\text{T}} \epsilon^{1/2}. \quad (\text{A.2})$$

The quantization of momentum and energy of a particle in a spherical volume, $V = \frac{4}{3}\pi R^3$, obtains from the boundary conditions on the spherical wave solutions

$$\chi_{k,l,m}(r, \theta, \phi) = a_{jl}(kr) Y_l^m(\theta, \phi), \quad (\text{A.3})$$

where a is a (k -dependent, see below) normalization constant. From the boundary condition $j_l(kR) = 0$ we get, for $l \ll kR$,

$$kR = k_n R = n\pi + l\pi/2. \quad (\text{A.4})$$

The translational energy $\epsilon = \hbar^2 k^2 / 2\mu$ is independent of m . Every set n, l, m or equivalently k_n, l, m represents an elementary state in the spherical wave representation. From the normalization condition

$$\langle k_n, l, m | k_n', l', m' \rangle = \delta_{k_n, k_n'} \delta_{l, l'} \delta_{m, m'}, \quad (\text{A.5})$$

it follows that the normalization constant in (A.3) is $a = (2/R)^{1/2} k_n$. The elementary states in the plane wave and the spherical wave representations are related by

$$|k'\rangle = \sum_{k_n, l, m} |k_n, l, m\rangle \langle k_n, l, m | k' \rangle, \quad (\text{A.6})$$

where

$$\langle \hat{k}_n, l, m | \hat{k}' \rangle = \delta_{k_n, k'} (4\pi/V^{1/2}) k^{-1} (\frac{1}{2}R)^{1/2} \\ \times (-i)^l Y_l^m(\hat{k}') \quad (\text{A.7})$$

Hence

$$\langle r | \hat{k}' \rangle = \sum_{l,m} (4\pi/V^{1/2}) k^{-1} (\frac{1}{2}R)^{1/2} \\ \times (-i)^l Y_l^m(\hat{k}') \chi_{klm}(r, \theta, \phi), \quad (\text{A.8})$$

which, using the addition theorem, reduces to the more familiar form

$$\exp(i\hat{k} \cdot r) = \sum_l [4\pi(2l+1)]^{1/2} \\ \times i^l j_l(kr) Y_l^0(\hat{k} \cdot \hat{r}). \quad (\text{A.9})$$

To compute the density of states in the k, l, m representation we first evaluate $\rho_R(\epsilon)$ the density of radial states (per unit length), i.e. those associated with k ,

$$R\rho_R(\epsilon) = (\partial n/\partial \epsilon)_{l,m} = (\partial n/\partial k) (\partial k/\partial \epsilon) \\ = (R/\pi) \mu/\hbar^2 k = (R/\pi\hbar) (\mu/2\epsilon)^{1/2}. \quad (\text{A.10})$$

This is the usual expression for a one-dimensional density of states. It should be noted however that in deriving (A.10) we have used the asymptotic solutions (A.4). If $l \approx kR$ then $\rho_R(\epsilon)$ will depend on l and R . The total, three-dimensional, density of states obtains from (A.10) by summing over l and m .

$$\rho_T(\epsilon)V = R \sum_{l,m} \rho_R(\epsilon) = R\rho_R(\epsilon) \sum_{l=0}^{l_m} (2l+1) \\ = R\rho_R(\epsilon) l_m^2 = V(3\sqrt{2}/\pi^4) \mu^{3/2} \epsilon^{1/2} / \hbar^3, \quad (\text{A.11})$$

where, in order to regain (A.2), we set $l_m = kR$, the highest possible angular momentum of a particle (with $\epsilon = \hbar^2 k^2/2\mu$) in a sphere of radius R . Obviously, in applications to collision problems, l_m is constrained to much lower values than kR as, for example, in eq. (35). Note however that the ϵ dependence of $\rho_T(\epsilon)$ is unchanged if we chose $l_m = kb_m$ where $b_m < R$ is some maximal impact parameter. It should be noticed that the numerical factors in (A.2) and (A.11) are somewhat different ($\rho_{\text{box}}/\rho_{\text{sphere}} \approx 1.5$). The difference is due to: (i) The use of the asymptotic solutions (A.4) (the roots of $j_l(kr)$ are denser when $l \approx kR$). (ii) The different shapes of the volume.

(iii) The neglect of higher order terms in approximating the sum over l in (A.11) by an integral [86].

The normalization of elementary states and the state densities for the atom-diatom (center of mass) system obtain by extending the free (structureless) particle results above. We consider three elementary state representations: (a) $|k_x, k_y, k_z, v, J, m_J\rangle$, (b) $|k, l, m_l, v, J, m_J\rangle$ and (c) $|k, K, M, l, J, v\rangle$. The plane wave, a, and spherical wave, b, representations are related according to (A.7). The former is related to the total angular momentum representation, c, via

$$|k, v, J, m_J\rangle = \sum_{J, M, l} \theta^{1/2} k^{-1} \\ \times D_{K, l, J}^{M m_J}(\hat{k}) |k, K, M, l, J, v\rangle, \quad (\text{A.12})$$

where, $\theta \equiv 8\pi^2 R/V$ and

$$D_{K, l, J}^{m m_J}(\hat{k}) = \sum_{m_l} \langle J m_J m_l | J l K M \rangle Y_l^{m_l}(\hat{k}). \quad (\text{A.13})$$

The appearance of the $1/k$ factor in (A.12) is due to using elementary states i.e. states normalized on the momentum scale. More familiar is the expansion in terms of states normalized on the energy scale for which [4,85]

$$|k, v, J, m_J\rangle = \sum_{J, M, l} D_{K, l, J}^{M m_J}(\hat{k}) |E, K, M, l, J, v\rangle. \quad (\text{A.14})$$

The density of states of an atom-diatom system with a total energy E when the internal state of the diatomic molecule is specified by $n = v, J$ or v, J is given by

$$\rho(n; E) = \sum_{s \in n} g_s \rho_T(E - E_s), \quad (\text{A.15})$$

where $s = v, J, m_J$ and $g_s = 2J + 1$. Hence

$$\rho(v, J; E) = (2J + 1) \rho_T(E - E_{vJ}) \\ = A_T (2J + 1) [E - E_v - B_v J(J + 1)]^{1/2}, \quad (\text{A.16})$$

$$\rho(v; E) = \sum_J \rho(v, J; E) \approx A_v (E - E_v)^{3/2}, \quad (\text{A.17})$$

where in deriving the second equality in (A.17) the sum over J was replaced by an integral; $A_v = (\frac{2}{3} B_v) A_T$ varies very slowly with v ; it is a constant in the rigid rotor approximation, $B_v = B_e$.

If both internal and orbital quantum numbers

specify the state of the triatomic system then $\rho_R(\epsilon)$ and not $\rho_T(\epsilon)$ contributes to the state density. Hence

$$\rho(v, J, l; E) = (2J + 1)(2l + 1)\rho_R(E - E_{vJ}). \quad (\text{A.18})$$

Eq. (A.16) is regained by using (A.11) and summing over l ,

$$\rho(v, J; E) \sum_{l=0}^{l_m} \rho(v, J, l; E) = (2J + 1)\rho_T(E - E_{vJ}), \quad (\text{A.19})$$

where, as in (A.11), $l_m = kR$. Dynamical constraints of the kind of (34) can be imposed to restrict the summation over l .

For a triatomic system with given v, J, E and K the relevant density of state function (averaged, not summed, over the $2K + 1$ equally probable values of M_K , the projection of K) is

$$\begin{aligned} \rho(v, J; E, K) &= \sum_l' \rho(v, J, l; E, K) \\ &= \frac{1}{(2K + 1)} \sum_l' \frac{(2K + 1)}{(2J + 1)(2l + 1)} \rho(v, J, l; E) \\ &= \sum_l' \rho_R(E - E_{vJ}) = [\mu/2\pi^2\hbar^2(E - E_{vJ})]^{1/2} \sum_l' 1 \\ &= (\pi\hbar u_{vJ})^{-1} \bar{N}(v, J; E, K) \equiv u_{vJ}^{-1} N(v, J; E, K). \end{aligned} \quad (\text{A.20})$$

In these equations the primed summation symbols indicate that l is confined to the region allowed by the triangle rule $|K - J| \leq l \leq |K + J|$. Note that in the second equality in (A.20), which can be viewed as the definition of $\rho(v, J, l; E, K)$, the factor $(2K + 1)/(2J + 1)(2l + 1)$ is the fraction of J, l combination consistent with K (but irrespective of M_K). The third and fourth equalities follow from the use of (A.18) and (A.10) respectively. Finally, $u_{vJ} = [2(E - E_{vJ})/\mu]^{1/2}$ is the velocity and $\bar{N}(v, J; E, K)$ is the number of l values consistent with v, J, E and K , fig. 1. Explicitly,

$$\bar{N}(v, J; E, K) = \begin{cases} 2K + 1; & K \leq J \\ 2J + 1; & J \leq K \end{cases} = K + J - |K - J| + 1. \quad (\text{A.21})$$

This quantity can be regarded as the "effective rotational degeneracy" of the diatomic molecule in the triatomic system with total angular momentum K .

As mentioned with respect to (A.18) dynamical constraints can be imposed on the l -summation in (A.20) with a consequent reduction of the effective rotational degeneracy (section 4, fig. 1). The quantity

$$\bar{N}(v; E, K) = \sum_{J=0}^{J^*(v, E)} \bar{N}(v, J; E, K), \quad (\text{A.22})$$

where $E_{J^*(v, E)} \lesssim E - E_v$ is the highest rotational energy below $E - E_v$, is the number of allowed J, l combinations at given v, E, K . [In sections 3 and 4 we absorb the factor $(\pi\hbar)^{-1}$ into $Q(E, K)$ and identity \bar{N} with N , eq. (A.20).] Because of the J dependence of the velocity u_{vJ} in (A.20), $\bar{N}(v; E, K)$ is not simply related to

$$\rho(v; E, K) = \sum_{J=0}^{J^*(v, E)} \rho(v, J; E, K). \quad (\text{A.23})$$

Finally we note that by definition

$$\begin{aligned} \rho(v, J; E) &= \sum_{K, M_K} \rho(v, J; E, K) \\ &= \sum_{K=0}^{K_m} (2K + 1)\rho(v, J; E, K). \end{aligned} \quad (\text{A.24})$$

If as in (A.11) $l_m = kR \gg J$ (J is always bounded via $E_J \leq E - E_v$, $k \propto u_{vJ}$), then the contribution of $K \leq J$ terms to (A.24) is negligible and $K_m \approx l_m$. Substituting (A.20) and (A.21) into (A.24) we obtain, as expected, eqs. (A.16) or (A.19).

Appendix B

In this appendix we derive the statistical models through formal assumptions on the S and T matrices. It will be shown that the classification of models in terms of Γ, m and Q can be related to the quantum mechanical representation and normalization schemes within the framework of which the T matrix is assumed to be a constant. In addition to product energy distribution we will briefly consider also angular distributions.

Using the notation of appendix A we first list the basic definitions and relationships. Absorbing again the channel symbol α into n ($n = \alpha, v, J, m_J$), the state to state transition rate, the differential cross

section and the detailed (including angle variables) yield function are given, respectively, by [4]

$$\omega(n\hat{k}, n'\hat{k}') = (2\pi/\hbar) \langle n\hat{k} | \hat{T} | n'\hat{k}' \rangle^2 \delta(E_{n\hat{k}} - E_{n'\hat{k}'}), \quad (\text{B.1})$$

$$\begin{aligned} d\sigma(n\hat{k} \rightarrow n'\hat{k}'; E) / d\hat{k}' &= (\pi^2/k^2) \rho(n; E) \rho(n'; E) \\ &\times \langle n\hat{k} | T | n'\hat{k}' \rangle^2, \end{aligned} \quad (\text{B.2})$$

$$\begin{aligned} h^{-1} Y(n\hat{k}, n'\hat{k}', E) &= \rho(n\hat{k}; E) (\hbar k/\mu) d\sigma/d\hat{k}' \\ &= \frac{1}{4} \rho(n; E) \rho(n'; E) \langle n\hat{k} | T | n'\hat{k}' \rangle^2, \end{aligned} \quad (\text{B.3})$$

where $\mathbf{k} = k, \hat{\mathbf{k}}; \rho(n\hat{\mathbf{k}}; E) = \rho(n; E)/4\pi$. In (B.2) and (B.3) the T matrix connects momentum (elementary) states on the energy shell, that is $E = E_{n\hat{\mathbf{k}}} = E_{n'\hat{\mathbf{k}'}}$.

The momentum states are related to the energy states, i.e. the states normalized on the energy scale, via

$$\begin{aligned} |E n\hat{\mathbf{k}}\rangle &= [\rho(n\hat{\mathbf{k}}; E)]^{1/2} |n\hat{\mathbf{k}}\rangle \\ &= [\rho(n; E)/4\pi]^{1/2} |n\hat{\mathbf{k}}\rangle. \end{aligned} \quad (\text{B.4})$$

The T matrices on the energy shell in these two representations are related to the S matrix through

$$\begin{aligned} \langle n\hat{\mathbf{k}} | S | n'\hat{\mathbf{k}}' \rangle &= \delta_{nn'} \delta(\hat{\mathbf{k}} - \hat{\mathbf{k}}') \\ &- \frac{1}{2} i [\rho(n; E) \rho(n'; E)]^{1/2} \langle n\hat{\mathbf{k}} | T | n'\hat{\mathbf{k}}' \rangle \end{aligned} \quad (\text{B.5})$$

$$= \delta_{nn'} \delta(\hat{\mathbf{k}} - \hat{\mathbf{k}}') - 2\pi i \langle n\hat{\mathbf{k}} | T(E) | n'\hat{\mathbf{k}}' \rangle, \quad (\text{B.6})$$

where $\langle n\hat{\mathbf{k}} | T(E) | n'\hat{\mathbf{k}}' \rangle = \langle E n\hat{\mathbf{k}} | T | E n'\hat{\mathbf{k}}' \rangle$. Hence,

$$Y(n\hat{\mathbf{k}}, n'\hat{\mathbf{k}}'; E) = (2\pi)^2 \langle n\hat{\mathbf{k}} | T(E) | n'\hat{\mathbf{k}}' \rangle^2 \quad (\text{B.7})$$

$$= \langle n\hat{\mathbf{k}} | S | n'\hat{\mathbf{k}}' \rangle - \delta_{nn'} \delta(\hat{\mathbf{k}} - \hat{\mathbf{k}}')^2, \quad (\text{B.8})$$

where in (B.7) and henceforth the \hbar^{-1} factor will be absorbed into Y . The normalization of S is

$$\int d\hat{\mathbf{k}}' \sum_{n'} \langle n\hat{\mathbf{k}} | S | n'\hat{\mathbf{k}}' \rangle^2 = 1. \quad (\text{B.9})$$

Since the angular dependence of all quantities in (B.1)–(B.9) is through $\hat{\mathbf{k}}' - \hat{\mathbf{k}}$ integration of these equations over $\hat{\mathbf{k}}'$ yields for, say, $\sigma(n \rightarrow n'; E)$ and $Y(n \rightarrow n'; E)$ the same expressions as in (B.1)–(B.9) with the $\hat{\mathbf{k}}, \hat{\mathbf{k}}'$ notation omitted.

We now generalize (B.8) to any specification of the quantum state i and any shell (ensemble) Γ , that is

$$Y(i, j; \Gamma) = |S_{ij} - \delta_{ij}|^2 = (2\pi)^2 |T_{ij}(E)|^2. \quad (\text{B.10})$$

Based on (66) and the assumption $\langle \text{Re} S_{ii} \rangle = 0$ the generalized statistical approximation for (B.10) reads

$$\begin{aligned} \tilde{Y}(i, j; \Gamma) &= \langle Y(i, j; \Gamma) \rangle = \delta_{ij} + \langle |S_{ij}|^2 \rangle \\ &= \delta_{ij} (2 - f_i) + f_i f_j / \sum_i f_i. \end{aligned} \quad (\text{B.11})$$

Henceforth, to simplify the expressions we will consider only $i \rightarrow j \neq i$ transitions. Setting

$$f_i = f(i; \Gamma) = Q(\Gamma) m(i; \Gamma), \quad (\text{B.12})$$

we find (for $i \neq j$)

$$\tilde{Y}(i, j; \Gamma) = Q(\Gamma) m(i; \Gamma) m(j; \Gamma) / M(\Gamma), \quad (\text{B.13})$$

with $M(\Gamma) = \sum m(i; \Gamma)$. Note that to ensure $0 \leq f_i \leq 1$ it is necessary that $1/Q(\Gamma) \geq \max \{m(i; \Gamma)\}$. Eq. (66) supplemented by (B.10)–(B.12) is thus equivalent to (22) or (7).

We first apply (B.10)–(B.13) to $i = n, \hat{\mathbf{k}} = \alpha, \nu, J, m, j\hat{\mathbf{k}}$ and $\Gamma = E$. If, in analogy, to (26) and (27) we choose

$$\begin{aligned} f_0(n\hat{\mathbf{k}}; E) / Q_0(E) &= m_0(n\hat{\mathbf{k}}; E) \\ &= \rho(n\hat{\mathbf{k}}; E) = \rho(n; E) / 4\pi, \end{aligned} \quad (\text{B.14})$$

$$\begin{aligned} f_f(n\hat{\mathbf{k}}; E) / Q_f(E) &= m_f(n\hat{\mathbf{k}}; E) = u_n \rho(n\hat{\mathbf{k}}; E) \\ &= u_n \rho(n; E) / 4\pi \equiv N(n; E) / 4\pi \end{aligned} \quad (\text{B.15})$$

then

$$\tilde{Y}_0(n\hat{\mathbf{k}}, n'\hat{\mathbf{k}}'; E) = [Q_0(E) / (4\pi)^2] \rho(n; E) \rho(n'; E) / \rho(E), \quad (\text{B.16})$$

$$\tilde{Y}_f(n\hat{\mathbf{k}}, n'\hat{\mathbf{k}}'; E) = [Q_f(E) / (4\pi)^2] N(n; E) N(n'; E) / N(E). \quad (\text{B.17})$$

Both (B.16) and (B.17) predict completely uniform (in space) angular distributions. Namely, all final angles $\hat{\mathbf{k}}'$ are equivalent as in the case of hard sphere collisions. Integration over the angles yields our previous expressions for $\tilde{Y}(n, n'; E)$. Comparison of (B.3) and (B.16) indicates that (B.14) is equivalent to the assumption that the T matrix on the $\Gamma_1 = E$ shell expressed in terms of elementary states in the plane wave representation is a constant

$$|\langle nk|T|n'k'\rangle|^2 = c_1 Q_0(E)/\rho(E) \equiv F_0(E), \quad (\text{B.18})$$

or, cf. (B.7)

$$|\langle nk|T(E)|n'k'\rangle|^2 = c_2 [Q_0(E)/\rho(E)] \rho(n; E) \rho(n'; E), \quad (\text{B.19})$$

where $c_1 = 4\pi^2$ and $c_2 = 64\pi^4$.

From (B.1)–(B.3), (B.16) and (B.18) we realize again that the (elementary) state-to-state transition rate corresponding to the uniform measure is independent of the initial and final states and is only a function of $\Gamma = E$. The flux expression, (B.17), results from (B.3) by setting

$$|\langle nk|T|n'k'\rangle|^2 = c_1 [Q_f(E)/N(E)] u_n u_{n'}, \quad (\text{B.20})$$

or, from (B.7) via

$$|\langle nk|T(E)|n'k'\rangle|^2 = c_2 [Q_f(E)/N(E)] N(n; E) N(n'; E). \quad (\text{B.21})$$

To formulate the statistical hypothesis in $\Gamma = E, K$ we transform the S and T matrices from the plane wave $|u_{Jm_jk}\rangle$ representation to the total angular momentum representation $|u_{KM_K lJk}\rangle$. Using (A.14) and the RPA, we find

$$\begin{aligned} Y(n\hat{k}, n'\hat{k}'; E) &= \frac{1}{4} \rho(n; E) \rho(n'; E) \\ &\times \sum_K (2K+1) \sum_{l'l'} |D_{KU}^{MKm_j}(\hat{k})|^2 |D_{K'l'J'}^{MKm_j'}(\hat{k}')|^2 \\ &\times (\theta/kk')^2 |\langle u_{Kl} | T(K) | u_{J'l'} \rangle|^2 \end{aligned} \quad (\text{B.22})$$

$$\begin{aligned} &= \frac{1}{4} \rho(n; E) \rho(n'; E) \\ &\times \sum_K (2K+1) \sum_{l'l'} |D_{KU}^{MKm_j}(\hat{k})|^2 |D_{K'l'J'}^{MKm_j'}(\hat{k}')|^2 \\ &\times |\langle u_{l'} | T(E, K) | u_{J'l'} \rangle|^2 \end{aligned} \quad (\text{B.23})$$

$$\begin{aligned} &= \sum_K (2K+1) \sum_{l'l'} |D_{KU}^{MKm_j}(\hat{k})|^2 |D_{K'l'J'}^{MKm_j'}(\hat{k}')|^2 \\ &\times |\langle u_{l'} | S(K) | u_{J'l'} \rangle - \delta_{uv} \delta_{J'l'} \delta_{n'}|^2, \end{aligned} \quad (\text{B.24})$$

where $n = v, J, m_j$. We have used

$$\begin{aligned} \langle u_{Kl} | T(K) | u_{J'l'} \rangle &= \delta_{KK'} \delta_{M_K M_{K'}} \\ &= \langle u_{Kl} | T(K) | u_{J'l'} \rangle \delta_{KK'} \delta_{M_K M_{K'}} \end{aligned}$$

and

$$\begin{aligned} \langle u_{l'} | T(E, K) | u_{J'l'} \rangle &= \delta_{KK'} \delta_{M_K M_{K'}} \\ &= \langle u_{l'} | T(E, K) | u_{J'l'} \rangle \delta_{KK'} \delta_{M_K M_{K'}} \end{aligned}$$

Applying (B.10)–(B.13) to $i = u_{l'}$ and $\Gamma = E, K$ we find

$$\begin{aligned} \tilde{Y}(n\hat{k}, n'\hat{k}'; E) &= \sum_K (2K+1) Q(E, K) \\ &\times \sum_{l'l'} |D_{KU}^{MKm_j}(\hat{k})|^2 |D_{K'l'J'}^{MKm_j'}(\hat{k}')|^2 \\ &\times m(v, J, l; E, K) m(v', J', l'; E, K) / M(E, K) \end{aligned} \quad (\text{B.25})$$

First we note that irrespective of the choice of $m(u_{l'}; E, K)$ the angular distribution is symmetric around $\theta = \pi/2$. This is usually interpreted as an indication for complex formation [4,9]. Note that this symmetric distribution differs from the completely uniform (in θ, ϕ) distributions (B.16) and (B.17) resulting from application of the statistical assumption in $\Gamma = E$. Integrating over the angles and summing over l and l' in (B.25) we obtain

$$\begin{aligned} \tilde{Y}(n, n'; E) &= \sum_K (2K+1) Q(E, K) \\ &\times m(v, J; E, K) m(v', J'; E, K) / M(E, K), \end{aligned} \quad (\text{B.26})$$

where

$$m(v, J; E, K) = \sum_l m(v, J, l; E, K). \quad (\text{B.27})$$

Restricting the l summation by the triangle rule or by dynamical constraints we obtain respectively the “dynamics free” and “dynamically biased” measures in E, K . Using (A.18) and (A.20) we find that the uniform and flux measures are given, in complete analogy to sections 3–6, by

$$\begin{aligned} f_0(v, J, l; E, K) / Q_0(E, K) &= M_0(v, J, l; E, K) \\ &= \rho(v, J, l; E, K) = \rho_R(E - E_{vJ}), \end{aligned} \quad (\text{B.28})$$

$$\begin{aligned} f_f(v, J, l; E, K) / Q_f(E, K) &= m_f(v, J, l; E, K) \\ &= N(v, J, l; E, K) = u_{vJ} \rho_R(E - E_{vJ}). \end{aligned} \quad (\text{B.29})$$

Note that since $\rho_R \propto 1/u_{vJ}$ (B.29) is a constant. Similarly, cf. (A.20) and (B.27)

$$\begin{aligned} f_0(v, J; E, K) / Q_0(E, K) &= m_0(v, J; E, K) \\ &= \rho(v, J; E, K), \end{aligned} \quad (\text{B.30})$$

$$f_f(v, J; E, K)/Q_f(E, K) = m_f(v, J; E, K) \\ = N(v, J, l; E, K). \quad (\text{B.31})$$

The dynamical measures $f_{0,d}$, $f_{f,d}$ are obtained by restricting the l summations over (B.28) and (B.29) respectively.

To evaluate \tilde{Y}_0 either (B.28) should be substituted into (B.25) or (B.30) into (B.26). Similarly for \tilde{Y}_f we substitute (B.29) into (B.25) or (B.31) into (B.26). The forms of the T matrices in (B.22) and (B.23) leading to \tilde{Y}_0 and \tilde{Y}_f are: (a) for \tilde{Y}_0

$$\langle wkl|T(K)|v'j'k'l'\rangle^2 = \\ = c_1 [Q_0(E, K)|\rho(E, K)] \equiv F_0(E, K), \quad (\text{B.32})$$

which means that the assumption leading to \tilde{Y}_0 is that the T matrix on the $\Gamma_2 = E, K$ shell expressed in terms of elementary states in the total angular momentum representation is a constant. The same assumption expressed in terms of states normalized on the energy scale is

$$\langle wkl|T(E, K)|v'j'k'l'\rangle^2 = c_2 [Q_0(E, K)|\rho(E, K)] \\ \times \rho(v, J, l; E, K)\rho(v', J', l'; E, K); \quad (\text{B.33})$$

(b) for \tilde{Y}_f

$$\langle wkl|T(K)|v'j'k'l'\rangle^2 \\ = c_1 [Q_f(E, K)/N(E, K)] u_{vj}u_{v'j'}, \quad (\text{B.34})$$

or

$$\langle wkl|T(E, K)|v'j'k'l'\rangle^2 = c_2 [Q_f(E, K)/N(E, K)] \\ \times u_{vj}u_{v'j'}\rho(v, J, l; E, K)\rho(v', J', l'; E, K) \\ \equiv F_f(E, K). \quad (\text{B.35})$$

Hence, the assumption leading to \tilde{Y}_f is that the T matrix on $\Gamma_2 = E, K$ expressed in terms of states normalized on the energy scale is constant.

To summarize, every statistical model can be derived by assuming that an appropriate T matrix is a constant. In particular, the uniform models correspond to constant matrices in elementary state representations. From the models considered above \tilde{Y}_f , cf. (B.17) and (B.21), is somewhat exceptional since its appropriate constant T -matrix does not in-

volve one of the familiar representations $|nk\rangle$ or $|Enk\rangle$ but, rather the uncommon representation $u_n^{-1/2}|nk\rangle = [N(n; E)]^{-1/2}|nk\rangle$, cf. (B.21).

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