How Isolated Are Molecules in a Molecular Beam?

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General expressions are developed for the number of collisions per second a molecule makes with other molecules in an effusive molecular beam, a supersonic molecule beam, and a supersonic jet. When characterized by the same density and the same local temperature parameter, we find that the collision frequencies in an effusive beam, supersonic beam, supersonic jet, and a bulb are approximately in the ratio 1:(3/2):3:3. Collision rates appropriate to practical applications are discussed.

I. Introduction

Molecular beams have many special properties that make them well suited for studies of collisional phenomena[1] and molecular structure,[2] e.g., directionality, flux, and internal state distribution. One such attribute that is commonly invoked is absence of collisions in the beam, i.e., the "ideal" beam is imagined to be a stream of molecules moving in parallel paths without undergoing collisions. To the degree that this characteristic is a valid description, it allows the preparation of oriented and/or state-selected reagents for scattering processes[3–9] and the investigation of radiationless processes in isolated large molecules.[10–12] However, real beams only approximate this behavior. Because of the spread in velocities, faster molecules move through the stream of slower ones in the course of the beam expansion. Thus true isolation is only approached in the limit of low density or for monoenergetic beams.

The first to calculate the collision rate in a molecular beam appears to be Troitskii[13] who in 1961 reported that the mean free path of molecules at any point in an effusive molecular beam is almost exactly three times greater than the path length in a bulk gas of the same density. In this article we employ a similar formulation of this problem to extract collision rates for both effusive and supersonic nozzle beams. For completeness we also consider the case of a freely expanding nozzle jet.

We begin in section II by developing a general expression for the number of collisions per second one molecule makes in a beam. This expression is evaluated for the cases of idealized effusive and supersonic nozzle beams in sections III and V, respectively. In section IV we consider the case of a freely expanding jet which is treated simply as an expansion-cooled bulk gas. These calculations are somewhat involved. We take the opportunity to detail our procedure in the hope that it will spare others the necessity of repeating this effort. Finally, we conclude by examining the collision frequency in several cases of practical interest. Graphs are presented of the collision frequency as a function of distance from a nozzle jet orifice which should aid in the design of experiments.

II. Frequency of Collisions in a Molecular Beam

We wish to calculate the number of collisions per second a molecule undergoes in a molecular beam. We consider the case where all beam species are the same; the generalization to more than one component in the beam is straightforward. We assume that we can ignore the small transverse velocities within the beam; then the molecules travel in parallel straight lines. We also suppose that the molecules may be regarded as spheres of collision radius r. In addition, we neglect the effects of secondary collisions.

Let all molecules in the beam have a normalized velocity distribution $f(v)$. Then the probability of finding molecule 1 with a velocity between v_1 and $v_1 + dv_1$ is given by $f(v_1)$ dv_1. Let the density of molecules in the beam be n molecules per unit volume. Consider those molecules with a velocity in the range v_2 to $v_2 + dv_2$. The probability of finding such molecules per unit volume is $n f(v_2) dv_2$. The instantaneous speed of approach of molecule 1 with velocity v_1 and molecule 2 with velocity v_2 is $|v_1 - v_2| \cos \theta$, where θ is the angle between the line of centers and the velocity. Here θ ranges from 0 at infinite separation to a maximum possible value of $\pi/2$ at contact. Then the number of beam molecules whose centers pass in unit time within a distance $2r$ of the center of molecule 1, and hence collide with 1, is the number of beam molecules contained in a cylinder of base $(2r)^2 d\Omega = (2r)^2 \sin \theta d\theta d\phi$ and height $|v_1 - v_2| \cos \theta$. Hence the number of collisions in unit volume per unit time of molecule 1 with velocity v_1 with all other molecules is obtained by integrating over the solid angle element $d\Omega$ and over all velocities v_2:

$$z(v_1) = n(2r)^2 \int_0^{2\pi} \int_0^{\pi/2} \int_0^{\infty} |v_1 -$$

$$v_2| \cos \theta f(v_2) dv_2 \sin \theta d\theta d\phi = n\sigma \int_0^{\infty} |v_1 - v_2| f(v_2) dv_2 \quad (1)$$

where $\pi(2r)^2$ has been replaced by σ, the *velocity-independent* hard-sphere collision cross section.

(1) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, 1964.
(2) N. F. Ramsey, "Molecular Beams", Clarendon Press, Oxford, 1956.
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(10) R. Naaman, D. M. Lubman, and R. N. Zare, *Chem. Phys.*, **32**, 17 (1978); *J. Chem. Phys.*, **71**, 4192 (1980).
(11) A. Amirav, U. Even, and J. Jortner, *Chem. Phys. Lett.*, **67**, 9 (1979).
(12) J. B. Hopkins, D. E. Powers, and R. E. Smalley, *J. Chem. Phys.*, **72**, 5039, 5049 (1980); **73**, 683 (1980).
(13) V. S. Troitskii, *Zh. Eksp. Teor. Fiz.*, **14**, 389 (1961) [*Sov. Phys. JETP* (Engl. Transl.), **14**, 281 (1962)].

The total collision rate for a single molecule is then obtained by averaging $z(v_1)$ over the normalized velocity distribution, $f(v_1)$, of molecule 1:

$$z = n\sigma \int_0^\infty f(v_1) \left[\int_0^\infty |v_1 - v_2| f(v_2) \, dv_2 \right] dv_1 =$$
$$n\sigma \int_0^\infty f(v_1) \left[\int_0^{v_1} (v_1 - v_2) f(v_2) \, dv_2 + \int_{v_1}^\infty (v_2 - v_1) f(v_2) \, dv_2 \right] dv_1 \quad (2)$$

Here the inner integral from 0 to v_1 represents those collisions in which molecule 2 is caught by molecule 1 while the inner integral from v_1 to ∞ represents those collisions in which molecule 2 catches molecule 1. Hence we can rewrite eq 2 as the sum of two double integrals

$$z = n\sigma(I_1 + I_2) \quad (3)$$

where

$$I_1 = \int_0^\infty v_1 f(v_1) \, dv_1 \left[\int_0^{v_1} f(v_2) \, dv_2 - \int_{v_1}^\infty f(v_2) \, dv_2 \right] \quad (4)$$

$$I_2 = -\int_0^\infty f(v_1) \, dv_1 \left[\int_0^{v_1} v_2 f(v_2) \, dv_2 - \int_{v_1}^\infty v_2 f(v_2) \, dv_2 \right] \quad (5)$$

Equations 3–5 form the basis for all subsequent calculations.

III. Collision Frequency in an Effusive Beam

In the beam source the three-dimensional velocities obey the Maxwell–Boltzmann distribution

$$P(v) = N v^2 \exp(-\beta v^2) \quad (6)$$

where

$$\beta = m/(2kT) \quad (7)$$

expresses the dependence on molecular mass m and absolute temperature T and

$$N = (16\beta^3/\pi)^{1/2} \quad (8)$$

is the normalization factor. In an effusive beam the probability of a molecule emerging from the source with velocity v is proportional to v because faster molecules have a greater escape rate than slower ones. Hence the flux becomes $I(v) = vP(v)$. However, for the calculation of the number of collisions in a beam, we require the normalized density,[2] $f(v) = I(v)/v$, i.e.

$$f(v) = N v^2 \exp(-\beta v^2) \quad (9)$$

where eq 9 is appropriate to a collimated effusive beam downstream from the source.

Thus eq 4 and 5 take the form

$$I_1 = N^2 \int_0^\infty v_1^3 \exp(-\beta v_1^2) \, dv_1 \left[\int_0^{v_1} v_2^2 \exp(-\beta v_2^2) \, dv_2 - \int_{v_1}^\infty v_2^2 \exp(-\beta v_2^2) \, dv_2 \right] \quad (10)$$

$$I_2 = -N^2 \int_0^\infty v_1^2 \exp(-\beta v_1^2) \, dv_1 \left[\int_0^{v_1} v_2^3 \exp(-\beta v_2^2) \, dv_2 - \int_{v_1}^\infty v_2^3 \exp(-\beta v_2^2) \, dv_2 \right] \quad (11)$$

The four inner integrals are evaluated by using integration by parts, i.e., $u \, dv = d(uv) - v \, du$, where we make the substitutions $u = v_2^2/2\beta$ and $v = -\exp(-\beta v_2^2)$. The result

TABLE I: Explicit Forms[a] of the Inner Integrals in Eq 10 and 11

integral	solution
$\int_0^{v_1} v_2^2 \exp(-\beta v_2^2) \, dv_2$	$\frac{1}{2}\beta^{-3/2}[-v_1\beta^{1/2} \exp(-\beta v_1^2) + \frac{1}{2}\pi^{1/2} \mathrm{erf}\,(\beta^{1/2}v_1)]$
$-\int_{v_1}^\infty v_2^2 \exp(-\beta v_2^2) \, dv_2$	$\frac{1}{2}\beta^{-3/2}\{-v_1\beta^{1/2} \exp(-\beta v_1^2) + \frac{1}{2}\pi^{1/2}[\mathrm{erf}\,(\beta^{1/2}v_1) - 1]\}$
$\int_0^{v_1} v_2^3 \exp(-\beta v_2^2) \, dv_2$	$-\frac{1}{2}\beta^{-2}[(v_1^2\beta + 1) \exp(-\beta v_1^2) - 1]$
$-\int_{v_1}^\infty v_2^3 \exp(-\beta v_2^2) \, dv_2$	$-\frac{1}{2}\beta^{-2}(v_1^2\beta + 1) \exp(-\beta v_1^2)$

^{a} $\mathrm{erf}\,(x) \equiv 2\pi^{-1/2} \int_0^x \exp(-t^2) \, dt.$

of each integration is collected in Table I, allowing us to rewrite eq 10 and 11 as

$$I_1 = N^2 \left[-\int_0^\infty (v_1^4/\beta) \exp(-2\beta v_1^2) \, dv_1 - \frac{1}{4}\pi^{1/2} \int_0^\infty (v_1^3/\beta^{3/2}) \exp(-\beta v_1^2) \, dv_1 + \frac{1}{2}\pi^{1/2} \int_0^\infty (v_1^3/\beta^{3/2}) \mathrm{erf}(\beta^{1/2}v_1) \exp(-\beta v_1^2) \, dv_1 \right] \quad (12)$$

$$I_2 = N^2 \left[\int_0^\infty (v_1^4/\beta) \exp(-2\beta v_1^2) \, dv_1 + \int_0^\infty (v_1^2/\beta^2) \times \exp(-2\beta v_1^2) dv_1 - \frac{1}{2} \int_0^\infty (v_1^2/\beta^2) \exp(-\beta v_1^2) \, dv_1 \right] \quad (13)$$

Each of these definite integrals can be evaluated by using the expression[14]

$$\int_0^\infty x^n \exp(-ax^2) \, dx = \frac{\Gamma[(n+1)/2]}{2a^{(n+1)/2}} \quad (14)$$

or in the case of the integral containing the error function by using integration by parts. In the latter case we make the substitutions $u = v_1^2 \, \mathrm{erf}(\beta^{1/2}v_1)$ and $dv = v_1 \exp(-\beta v_1^2)$ and use the identity[14]

$$\int_0^\infty x \, \mathrm{erf}(ax) \exp(-bx^2) \, dx = \frac{b}{2a(a + b^2)^{1/2}} \quad (15)$$

In this manner we find that

$$I_1 = \frac{1}{(\pi\beta)^{1/2}} \left(\frac{-3(2)^{1/2} - 8 + 10(2)^{1/2}}{4} \right) \quad (16)$$

$$I_2 = \frac{1}{(\pi\beta)^{1/2}} \left(\frac{7(2)^{1/2} - 8}{4} \right) \quad (17)$$

from which it is seen that $I_1 = I_2$, i.e.

$$I_1 + I_2 = \frac{1}{(\pi\beta)^{1/2}} \left(\frac{7(2)^{1/2} - 8}{2} \right) \quad (18)$$

Since $\bar{v} = 2/(\pi\beta)^{1/2}$ is the mean velocity of molecules in the source we find from eq 3 that the collision frequency of a molecule in an effusive beam is

$$z_{EB} = n\sigma\bar{v} \left(\frac{7(2)^{1/2} - 8}{4} \right) \quad (19)$$

which agrees with the expression previously obtained by Troitskii.[13]

(14) I. S. Gradshtiyn and I. M. Ryzhik, "Tables of Integrals Series and Products", Academic Press, New York, 1965.

In a bulb of molecules with the same density n and collision cross section σ the collision frequency per molecule is given by[1]

$$z_{\text{bulb}} = n\sigma\bar{v}(2)^{1/2} \qquad (20)$$

Hence

$$\frac{z_{\text{EB}}}{z_{\text{bulb}}} = \frac{7 - 4(2)^{1/2}}{4} \simeq 0.336 \qquad (21)$$

i.e., the collision frequency of molecules in an effusive beam is about one-third as great as that in a gas of the same density. It is heuristically pleasing to imagine that a factor of three enters merely as a consequence of the reduction of dimensionality. However, while the collision rate in a three-dimensional system scales roughly with the average speed, that in a beam is highly sensitive to the form of the velocity distribution and in particular to its width. For example, a monoenergetic velocity distribution would produce no collisions in the case of a (one-dimensional) beam, while the three-dimensional rate would be finite. We note that a factor of 1/3 is exactly found if the velocity distribution had the form of an isosceles triangle so that eq 21 is not unexpected.

IV. Collisions in a Free Jet

When relatively high collision rates can be tolerated, the high densities and simplicity of design offered by a free jet may make it the source of choice.[11,12] In such an arrangement, gas leaves a stagnation reservoir through a small orifice or nozzle and undergoes isentropic wall-free expansion.[15]

As the expansion proceeds, both the temperature and density of the gas decrease with increasing distance. Thus the collision rate must fall rapidly with increasing distance from the jet source. This rate eventually reaches a point where no further cooling occurs and there is a transition from continuum (isentropic) to molecular (nonisentropic) expansion. At this point the axial velocity distribution and Mach number (ratio of the stream velocity to the local speed of sound) become effectively "frozen", i.e., unchanging with distance. As an example, the limiting or terminal Mach number for argon is calculated to be given by[15,16]

$$\mathcal{M}_{\text{T}} = 133(P_0 D)^{0.4} \qquad (22)$$

where P_0 is the reservoir chamber pressure in units of atmospheres and D is the nozzle diameter in centimeters. Equation 22 approximates other well-behaved monoatomic gases (but not helium[17]). For diatomic gases, the calculation of the terminal Mach number is similar, but requires a knowledge of the so-called collisional effectiveness constant.[18] Unfortunately this simple picture is complicated by the presence of shock waves in the expanding jet.[15] An axially symmetric isentropic core is surrounded concentrically by a shock boundary, but of particular importance is the shock front formed perpendicular to the flow direction known as the Mach disk. This originates as jet molecules collide with background gas. Such collisions will
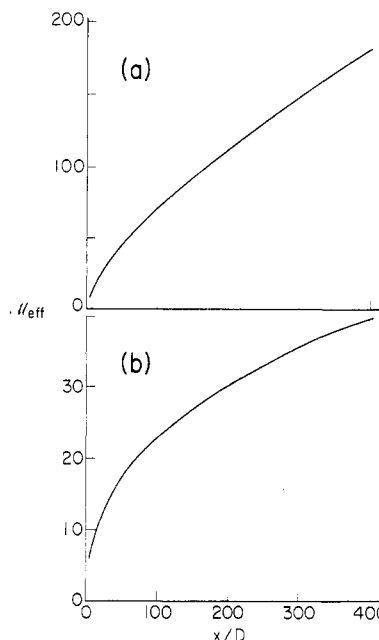

Figure 1. The effective Mach number as a function of the dimensionless distance parameter, x/D, measured in nozzle diameters D for (a) a monoatomic gas and (b) a diatomic gas.

serve to reheat the cooled jet, thereby increasing the collision rate. The distance of this disk, x_{M}, from a nozzle of diameter D varies roughly as[19]

$$x_{\text{M}}/D = 0.67[P_0/P]^{1/2} \qquad (23)$$

where P is the pressure in the expansion chamber. Here we restrict discussion to the isentropic core of a jet, upstream from this front.

We picture the gas in this region as having a Maxwellian velocity distribution at some reduced temperature superimposed on a bulk or stream velocity. In computing the collision rate, this stream velocity is of no consequence. Thus we can treat an idealized freely expanding isentropic jet as a bulk gas, employing eq 20. The temperature, T_{p}, at a given point in such a jet is related to the reservoir temperature T_0 by[15,20]

$$T_{\text{p}} = T_0[1 + \tfrac{1}{2}(\gamma - 1)\mathcal{M}_{\text{eff}}{}^2]^{-1} \qquad (24)$$

where γ is the heat capacity ratio $C_{\text{p}}/C_{\text{v}}$, and $\mathcal{M}_{\text{eff}}$ is the local Mach number. The collision rate can then be written as

$$z_{\text{jet}} = (2)^{1/2} n\sigma\bar{v}_0[1 + \tfrac{1}{2}(\gamma - 1)\mathcal{M}_{\text{eff}}{}^2]^{-1/2} \qquad (25)$$

where $\bar{v}_0$ is the mean velocity in the reservoir.

The density, n, at this point can be expressed in terms of the reservoir density, n_0, as[21]

$$n = n_0[1 + \tfrac{1}{2}(\gamma - 1)\mathcal{M}_{\text{eff}}{}^2]^{-1/(\gamma-1)} \qquad (26)$$

Thus we obtain

$$z_{\text{jet}} = (2)^{1/2} n_0 \sigma\bar{v}_0[1 + \tfrac{1}{2}(\gamma - 1)\mathcal{M}_{\text{eff}}{}^2]^{-(1/2)[(\gamma+1)/(\gamma-1)]} \qquad (27)$$

As discussed above, $\mathcal{M}_{\text{eff}}$ increases with distance along the isentropic expansion. Specifically, Ashkenas and Sherman[19] have given an accurate fitting formula for the var-

(15) J. B. Anderson, R. P. Andres, and J. B. Fenn, *Adv. Chem. Phys.*, 10, 275 (1966); J. B. Anderson in "Molecular Beams and Low Density Gas Dynamics", P. P. Wegener, Ed., Marcel Dekker, New York, 1974.

(16) R. A. Oman, A. Bogan, C. H. Weiser, and C. H. Li, Grumman Research Department Report RE-166, Grumman Aircraft Engineering Co., 1963.

(17) J. P. Toennies and K. Winkelmann, *J. Chem. Phys.*, 66, 3965 (1977).

(18) G. M. McClelland, K. L. Saenger, J. J. Valentini, and D. R. Herschbach, *J. Phys. Chem.*, 83, 947 (1979).

(19) H. Ashkenas and F. S. Sherman in "Rarefied Gas Dynamics", 4th Symposium, Vol. II, J. H. de Leeuw, Ed., Academic Press, New York, 1966, pp 86-7.

(20) A. Kantrowitz and J. Grey, *Rev. Sci. Instrum.*, 22, 328 (1951).

(21) R. E. Smalley, L. Wharton, and D. H. Levy, *Acc. Chem. Res.*, 10, 139 (1977).

TABLE II: Collision Frequency in an Isentropic Jet

	monoatomic		diatomic	
x/D	$\mathcal{M}$ eff	$z_{jet}/(n\sigma\bar{v}_0) \times 10^2$	$\mathcal{M}$ eff	$z_{jet}/(n\sigma\bar{v}_0) \times 10^2$
10	15.1	16.1	8.69	35.24
20	24.2	10.1	11.8	26.43
40	38.6	6.32	15.7	19.94
80	61.4	3.97	20.9	15.04
100	71.0	3.44	22.9	13.74
150	93.6	2.61	27.0	11.67
200	114.0	2.15	30.3	10.41
300	149.0	1.64	35.7	8.839

iation of $\mathcal{M}_{eff}$ with distance, x, from the nozzle exit plane. For a monoatomic gas (Figure 1a)

$$\mathcal{M}_{eff} = 3.26(x/D - 0.075)^{0.67} - 0.61(x/D - 0.075)^{-0.67} \tag{28}$$

and for a diatomic gas (Figure 1b)

$$\mathcal{M}_{eff} = 3.65(x/D - 0.4)^{0.4} - 0.82(x/D - 0.4)^{-0.4} \tag{29}$$

Combining eq 25 with eq 28 or 29 we can compute values of $z_{jet}/(n\sigma\bar{v}_0)$ as a function of x/D. Table II lists the values obtained for monoatomic and diatomic gases for several values of x/D. Note that in accordance with the results of section II and eq 25 the ratio of collision rates for a jet and an effusive beam at the same density will simply be given by

$$z_{jet}/z_{EB} = \frac{1}{0.336}(T_p/T_0)^{-1/2} = $$
$$2.98[1 + \frac{1}{2}(\gamma - 1)\mathcal{M}_{eff}^2]^{-1/2} \tag{30}$$

V. Collision Frequency in a Supersonic Nozzle Beam

Such beams are generated when the Maxwellian gas inside an effusive source is replaced by a supersonic jet of gas already moving in the beam direction.[15,20] This is accomplished by placing a conically shaped aperture or skimmer so as to axially sample the isentropic core discussed in the previous section. So long as there are conditions of continuum expansion, the relationships developed in the previous section for a free jet will hold. However, once conditions of free molecular flow are reached, "overtaking" collisions of the sort discussed in sections II and III will dominate and application of eq 1–5 is required.

For a collimated nozzle beam the idealized velocity density function can be written as[16]

$$f(v) = N_S(v^2/\alpha_S^3) \exp[-(v - v_S)^2/\alpha_S^2] \quad v > 0 \tag{31a}$$
$$f(v) = 0 \quad v < 0 \tag{31b}$$

where

$$v_S = \mathcal{M}(\gamma kT_S/m)^{1/2} \tag{32}$$

is the supersonic flow velocity of the beam of Mach number $\mathcal{M}$

$$\alpha_S = (2kT_S/m)^{1/2} \tag{33}$$

and N_S is the normalization constant. Here T_S denotes the local temperature which will be given by eq 24 with $\mathcal{M} = \mathcal{M}_{eff}$. Thus v_S and α_S depend only on the values of m, T, γ, and $\mathcal{M}$, where the latter is determined from the expansion characteristics.[15]

The normalization factor N_S is found from the expression

$$N_S \int_0^\infty (v^2/\alpha_S^3) \exp[-(v - v_S)^2/\alpha_S^2] \, dv = 1 \tag{34}$$

We make the change of variables

$$z = \mu - \mu_S \tag{35}$$

where

$$\mu = v/\alpha_S \tag{36}$$
$$\mu_S = v_S/\alpha_S \tag{37}$$

Then eq 34 may be rewritten as

$$N_S^{-1} = \mu_S^2 \int_{-\mu_S}^\infty \exp(-z^2) \, dz + 2\mu_S \int_{-\mu_S}^\infty z \exp(-z^2) \, dz + \int_{-\mu_S}^\infty z^2 \exp(-z^2) \, dz \tag{38}$$

Using the definition of the error function[22] and with the help of integration by parts we find

$$N_S^{-1} = \frac{1}{2}\{\pi^{1/2}(\frac{1}{2} + \mu_S^2)[1 + \text{erf}(\mu_S)] + \mu_S \exp(-\mu_S^2)\} \tag{39}$$

Note that N_S^{-1} is purely a function of $\mu_S = \mathcal{M}(\gamma/2)^{1/2}$. For large Mach numbers

$$N_S^{-1} \underset{\mu_S \to \infty}{\to} \pi^{1/2}\mu_S^2 \tag{40}$$

This expression is a good approximation for $\mu_S \geq 4$. We also examine N_S^{-1} in the limit of small μ_S. From eq 39 we find that

$$N_S^{-1} \underset{\mu_S \to 0}{\to} \frac{1}{4}\pi^{1/2} \tag{41}$$

since as $v_S \to 0$, $T_S \to T$, $\mathcal{M} \to 0$, and $\alpha_S \to \beta^{-1/2}$. Indeed, when $v_S = 0$, the expression for $f(v)$ given in eq 31 becomes the same as the effusive beam distribution given in eq 9.

Proceeding in the same manner as in the last section,[23] eq 4 and 5 become

$$I_1 = N_S^2 \int_0^\infty (v_1/\alpha_S)^3 \exp[-(v_1 - v_S)^2/\alpha_S^2] \, dv_1 \bigg\{ \int_0^{v_1} (v_2^2/\alpha_S^3) \exp[-(v_2 - v_S)^2/\alpha_S^2] \, dv_2 - \int_{v_1}^\infty (v_2^2/\alpha_S^3) \exp[-(v_2 - v_S)^2/\alpha_S^2] \, dv_2 \bigg\} \tag{42}$$

$$I_2 = -N_S^2 \int_0^\infty (v_1^2/\alpha_S^3) \exp[-(v_1 - v_S)^2/\alpha_S^2] \, dv_1 \bigg\{ \int_0^{v_1} (v_2/\alpha_S)^3 \exp[-(v_2 - v_S)^2/\alpha_S^2] \, dv_2 - \int_{v_1}^\infty (v_2/\alpha_S)^3 \exp[-(v_2 - v_S)^2/\alpha_S^2] \, dv_2 \bigg\} \tag{43}$$

Once again we make the change of variables indicated in eq 35–37 and integrate by parts to evaluate the inner integrals. The results are collected in Table III.

Then eq 42 and 43 reduce to

$$I_1 = $$
$$\alpha_S N_S^2 \int_{-\mu_S}^\infty (z + \mu_S)^3 \exp(-z^2)\{\frac{1}{4}\pi^{1/2}(1 + 2\mu_S^2)[2 \text{ erf }(z) - \text{erf }(\mu_S) - 1] - (z + 2\mu_S) \exp(-z^2) + \frac{1}{2}\mu_S \exp(-\mu_S^2)\} \, dz \tag{44}$$

$$I_2 = \alpha_S N_S^2 \int_{-\mu_S}^\infty (z + \mu_S)^2 \exp(-z^2)\{\frac{1}{4}\pi^{1/2}\mu_S(3 + 2\mu_S^2) \times [1 - 2 \text{ erf }(z) + \text{erf }(\mu_S)] + (z^2 + 3\mu_S z + 3\mu_S^2 + 1) \exp(-z^2) - \frac{1}{2}(1 + \mu_S^2) \exp(-\mu_S^2)\} \, dz \tag{45}$$

(22) F. Scheid, "Numerical Analysis", McGraw-Hill, New York, 1968, p 141.

(23) One might expect this calculation to be facilitated by transformation to a reference frame moving with the stream velocity v_S. However, molecules in this frame range in velocity from $-v_S$ to ∞ and the resulting integrals were not found to be simplified.

TABLE III: Explicit Forms[a] of the Inner Integrals in Eq 42 and 43

integral	solution
$\int_0^{v_1} (v_2{}^2/\alpha_s{}^3) \exp[-(v_2 - v_S)^2/\alpha_S{}^2]\, dv_2$	${}^1/_4\pi^{1/2}(1 + 2\mu_S{}^2)[\mathrm{erf}\,(z) - \mathrm{erf}(\mu_S)] - ({}^1/_2 z + \mu_S)\exp(-z^2) + {}^1/_2\mu_S \exp(-\mu_S{}^2)$
$-\int_{v_1}^{\infty} (v_2{}^2/\alpha_S{}^3) \exp[-(v_2 - v_S)^2/\alpha_S{}^2]\, dv_2$	${}^1/_4\pi^{1/2}(1 + 2\mu_S{}^2)[\mathrm{erf}\,(z) - 1] - ({}^1/_2 z + \mu_S)\exp(-z^2)$
$\int_0^{v_1} (v_2/\alpha_S)^3 \exp[-(v_2 - v_S)^2/\alpha_S{}^2]\, dv_2$	${}^1/_2\alpha_S\{{}^1/_2\pi^{1/2}\mu_S(3 + 2\mu_S{}^2)[\mathrm{erf}\,(z) - \mathrm{erf}\,(\mu_S)] - (z^2 + 3\mu_S z + 3\mu_S{}^2 + 1)\exp(-z^2) + (1 + \mu_S{}^2)\exp(-\mu_S{}^2)\}$
$-\int_{v_1}^{\infty} (v_2/\alpha_S)^3 \exp[-(v_2 - v_S)^2/\alpha_S{}^2]\, dv_2$	${}^1/_2\alpha_S\{{}^1/_2\pi^{1/2}\mu_S(3 + 2\mu_S{}^2)[\mathrm{erf}\,(z) - 1] - (z^2 + 3\mu_S z + 3\mu_S{}^2 + 1)\exp(-z^2)$

[a] Here $z = (v_1 - v_S)/\alpha_S$ and $\mu_S = v_S/\alpha_S$.

TABLE IV: Collision Frequencies in a Supersonic Argon Beam

$\mu_S{}^a$	$10^{-3}\alpha_S$, cm/s	$10^{-3}[(z_{SB}/(n\sigma)]$, cm/s	T_S, K	$z_{SB}/z_{EB}(298\ \mathrm{K})$	$z_{SB}/z_{EB}(T_S)$
5	10.6	8.31	27.00	0.44	1.46
10	5.49	4.37	7.25	0.23	1.47
20	2.77	2.21	1.85	0.12	1.52
30	1.85	1.48	0.823	0.078	1.48
40	1.39	1.11	0.464	0.059	1.50
50	1.11	0.888	0.297	0.047	1.49
100	0.556	0.444	0.0743	0.023	1.47

[a] $\mu_S = \mathcal{M}(\gamma/2)^{1/2} = 0.914\mathcal{M}$.

TABLE V: Collision Frequencies in a Supersonic Nitrogen Beam

$\mu_S{}^a$	$10^{-3}\alpha_S$, cm/s	$10^{-3}[z_{SB}/(n\sigma)]$, cm/s	T_S, K	$z_{SB}/z_{EB}(298\ \mathrm{K})$	$z_{SB}/z_{EB}(T_S)$
5	14.70	11.6	36.6	0.52	1.47
10	7.74	6.15	10.1	0.27	1.48
20	3.92	3.13	2.58	0.14	1.49
30	2.62	2.09	1.15	0.093	1.49
40	1.97	1.57	0.650	0.070	1.49
50	1.57	1.26	0.417	0.056	1.49
100	0.787	0.629	0.104	0.028	1.49

[a] $\mu_S = \mathcal{M}(\gamma/2)^{1/2} = 0.837\mathcal{M}$.

It is seen that these integrals depend on the values of μ_S and α_S.

As a check on eq 44 and 45 we examine the case where $\mu_S = 0$. Then, as expected, eq 44 and 45 reduce to eq 12 and 13 when $N_S{}^2$ is replaced by $16/\pi$, α_S by $\beta^{-1/2}$, and N^2 by $16\beta/\pi$. Equations 44 and 45 are not totally integrable in closed form. Consequently, we evaluate them numerically for large Mach number. When $\mu_S \geq 4$, terms involving z that differ much from $z = 0$ hardly contribute because of the $\exp(-z^2)$ factor in the integrand. Hence, little error is introduced by extending the lower limit of integration in eq 44 and 45 from $-\mu_S$ to $-\infty$. Then we may apply Gauss-Hermite quadrature[22] in which

$$\int_{-\infty}^{\infty} f(x)\exp(-x^2)\,dx = \sum_{i=1}^{n} A_i\, f(x_i) \qquad (46)$$

where the arguments x_i are the roots of the nth Hermite polynomial, $H_n(x)$, and the coefficients A_i are given by $2^{n+1}n!\pi^{1/2}/[dH_n(x)/dx]^2$.

With the values of x_i and A_i tabulated[22] for $n = 8$, the expression for the collision frequency in a supersonic nozzle beam has been evaluated for several values of μ_S and α_S appropriate to beams of argon and nitrogen. These are listed in Tables IV and V, respectively. Also shown are the values of T_S and the ratios of z_{SB} to both $z_{EB}(298\ \mathrm{K})$ and $z_{EB}(T_S)$. For effusive beams of argon ($m = 40$, $\gamma = 1.67$) and nitrogen ($m = 28$, $\gamma = 1.40$), $z_{EB} = 1.89$ and $2.25 \times 10^4 n\sigma$ cm/s. Notice that in both cases $z_{SB}/z_{EB}(T_S)$ remains essentially constant at about 1.49 ± 0.02. We believe this to be a quite general result, i.e., in a collimated nozzle beam the collision rate is close to $3/2$ times that in an

effusive beam *at the same local "temperature" and density.* By local temperature we mean the source temperature for an effusive beam and the temperature appropriate to the Mach number for a supersonic beam (see eq 24). Of course, a beam does not have a temperature in the thermodynamic sense because it is not in equilibrium. Thus we write

$$z_{SB} \simeq 3z_{EB}/2 \simeq z_{\mathrm{bulb}}/2 \simeq 0.7n\sigma\bar{v}_{SB} \qquad (47)$$

where n is the local beam density and $\bar{v}_{SB} = [8kT_S/(\pi m)]^{1/2}$.

V. Discussion

Molecules can never be regarded as completely isolated in a beam because of the finite spread in velocity, causing some molecules to overtake others. However, the important question is whether the beam species are isolated on the time scale of a given experiment. This period may vary from nanoseconds for studies of the decay of excited electronic states to milliseconds for studies of aligned species. In each case the relevant quantity is the collision rate, which depends not only on the velocity spread but also on the beam density and the destruction cross section appropriate to the process under study.

To answer the question of how isolated are molecules in a beam, we have developed general expressions for the collision frequency in effusive and supersonic nozzle beams and in free jets. We find for the *same density and "temperature"* that

$$z_{EB}:z_{SB}:z_{\mathrm{jet}}:z_{\mathrm{bulb}} \simeq 1:(3/2):3:3 \qquad (48)$$

TABLE VI: Approximate Location (x/D) where the Mach Number Approaches Its Terminal Value^a for Argon as a Function of Nozzle Diameter (D) and Reservoir Pressure (P_0)

D, cm	$P_0 = 0.1$ atm	$P_0 = 0.5$ atm	$P_0 = 1.0$ atm	$P_0 = 2.0$ atm	$P_0 = 5.0$ atm	$P_0 = 10.0$ atm	$P_0 = 20.0$ atm
0.025	7.09	18.5	28.0	42.4	73.2	111	168
0.050	10.7	28.0	42.4	64.1	111	168	253
0.075	13.7	35.7	54.0	81.7	141	213	323
0.10	16.2	42.4	64.1	97.0	168	253	383
0.15	20.7	54.0	81.7	124	213	323	488
0.20	24.5	64.1	97.0	147	253	383	580

^{a} Obtained by equating eq 22 and 28.

Thus the directionality of these sources serves to reduce the collision rate by no more than a factor of about three compared to a simple bulb of gas. However, the *cooling* effect of isentropic expansion can lower markedly this rate for a given density.

Let us now examine the actual collision rates appropriate to these sources, beginning with an effusive beam. In an effusive source it is necessary that the mean free path exceed that of the orifice. For example, for a 1-mm diameter aperture, the density of argon in the source should be less than $\sim10^{15}$ cm^{-3} (~0.03 torr).[24] For a source density n_0, the axial beam density, n, at a distance r from an aperture of area A is given by[25]

$$n = n_0 A / \pi r^2 \qquad (49)$$

Hence at a distance of 1 cm from the source $n = 2.5 \times 10^{12}$ cm^{-3} (8×10^{-5} torr) and the collision rate from eq 19 is calculated for a 1-Å^2 cross section to be about 5 collisions/s, which is negligible for most purposes. Thus, what is significant is not the ratio z_{EB}/z_{bulb} but that the density in an effusive beam is so small because the density in the source is restricted by the mean free path requirement and the density in the beam falls off as the square of the distance from the source. Even with a collision cross section of 10^3 Å^2, molecules can be effectively isolated on a 0.1-ms time scale in an effusive beam.

Nozzle beams may have a density 100–1000 times that of an effusive beam,[15,25] causing a corresponding increase in the collision rate. However, the temperature characterizing a nozzle beam may be much lower than that for an effusive beam, counterbalancing the effect of density, but only as the square root of the temperature. Consequently, in many practical instances the collision frequency in a supersonic beam will exceed that in a typical effusive beam. This conclusion becomes all the more accentuated when the velocity dependence of the cross section is taken into account. Because most scattering cross sections vary as some inverse power of the initial relative velocity, this consideration has the effect of increasing the collision frequency in a supersonic beam. Moreover, for hard spheres the time of collision is infinitesimally short. For realistic potentials, this is not the case and molecules in a supersonic beam spend more time interacting with one another, again because of the smaller spread in relative velocities. However, the distinction between these cases may be academic since in practice both may provide isolation on the time scale of interest.

In a hydrodynamic source the mean free path is much less than the nozzle diameter, and the Mach number $\mathcal{M}$ provides a measure of the local temperature. The latter can be estimated from Figure 1 prior to free flow where the Mach number asymptotically approaches a terminal
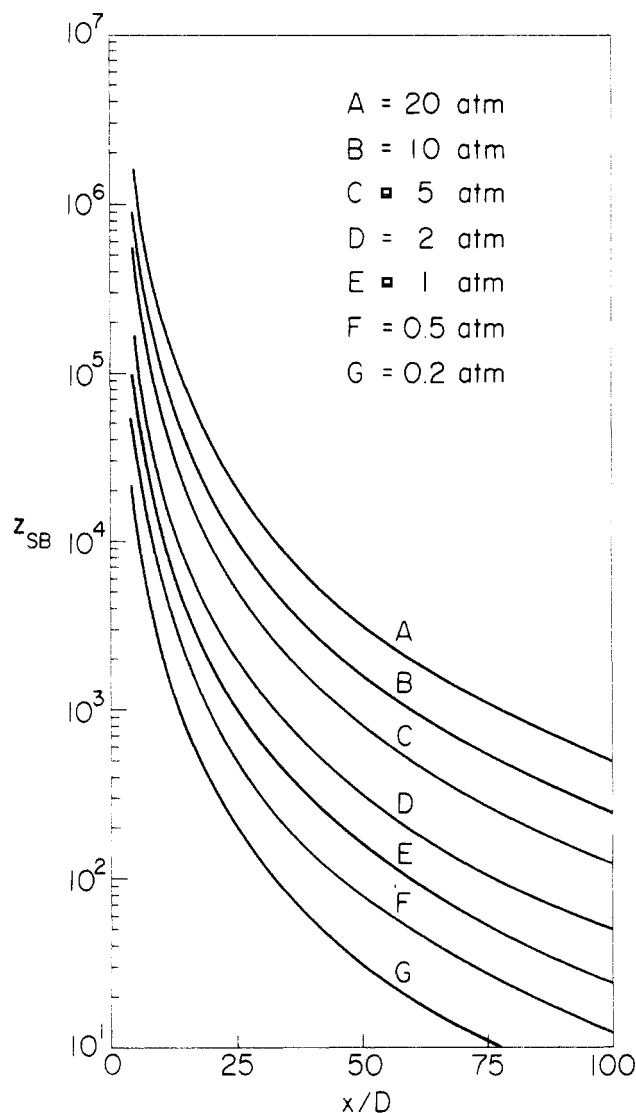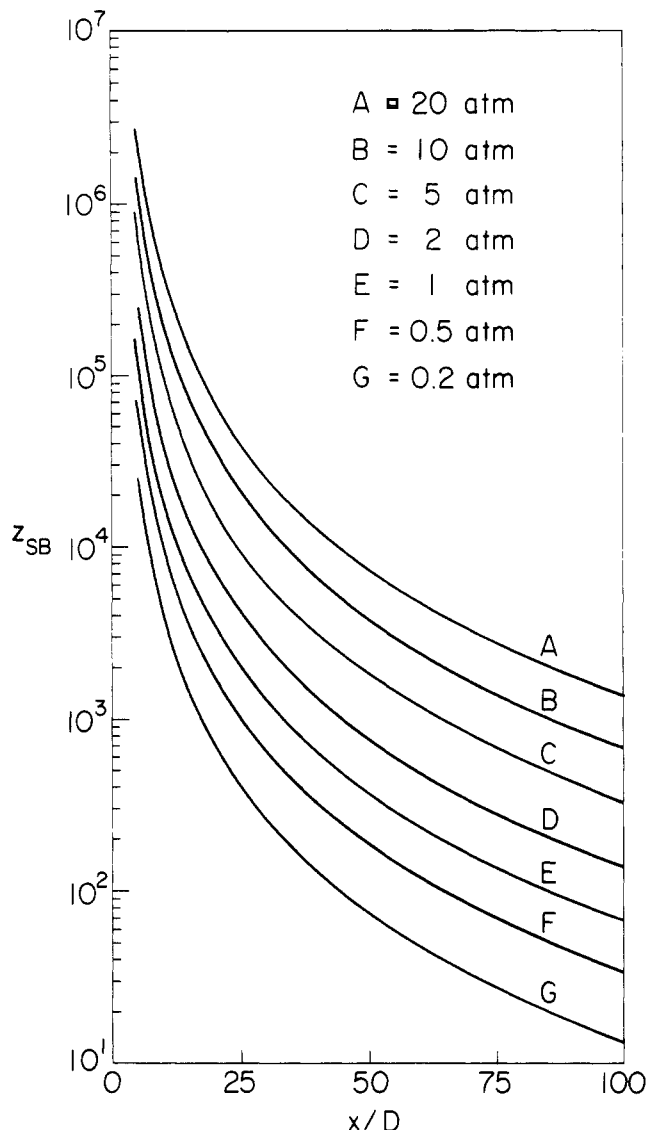
(24) S. Dushman, "Scientific Foundations of Vacuum Technique", Lafferty, Ed., Wiley, London, 1962.
(25) M. A. D. Fluendy and K. P. Lawley, "Chemical Applications of Molecular Beam Scattering", Chapman and Hall, London, 1973.

Figure 2. Logarithm of the collision frequency (s^{-1}) vs. the dimensionless distance parameter, x/D, measured in nozzle diameters D for the monoatomic gas, argon, at different reservoir pressures as indicated. The values of z_{jet} are calculated numerically by assuming continuum flow and a hard-sphere collision cross section of 1 Å^2.

value given approximately by eq 22 for monoatomic gases. Typical terminal Mach numbers range from 10 to 100. For example, a Mach number greater than 5 can be achieved for argon with only about 5 torr behind a nozzle diameter of 0.05 cm, whereas at 1-atm pressure the terminal Mach number is about 40.

Figures 2 and 3 present a family of curves describing the collision rate as a function of distance in nozzle diameters for argon and nitrogen, respectively, at different reservoir pressures. These are based on the expression for the collision rate in a supersonic jet (see eq 27) and the variation of the effective Mach number with distance (see eq

Figure 3. Logarithm of the collision frequency (s^{-1}) vs. the dimensionless distance parameter, x/D, measured in nozzle diameters D for the diatomic gas, N_2, at different reservoir pressures as indicated. The values of z_{jet} are calculated numerically by assuming continuum flow and a hard-sphere collision cross section of 1 $Å^2$.

28 and 29). These calculations apply to continuum flow on the axis of the isentropic core. The values of z_{jet} are given for 1 $Å^2$; *they must be scaled to the destruction cross section appropriate to the process of interest*. Nevertheless, it is seen from Figures 2 and 3 that it is necessary

to be about 50 nozzle diameters from the source to be isolated on a 0.1-ms time scale for a 1-$Å^2$ cross section. Figures 2 and 3 assume that the Mach number continues to increase with distance. However, as the terminal Mach number is approached (see Table VI) the actual collision rate in the jet falls as the square of the distance.

By introducing a skimmer into the jet stream, a supersonic nozzle beam results. Ideally, the skimmer should be placed so as to act as an effusive source, i.e., such that the mean free path in the jet at the skimmer is larger than the skimmer aperture. In practice, the position of the skimmer is a compromise between the source–skimmer interference found at short distances and the Mach disk degradation encountered at large distances.[25]

Once the skimmer is in place the collision rate in the resulting supersonic nozzle beam at a distance r from the skimmer can be estimated from a knowledge of how the beam density scales with distance.[26] We obtain

$$z_{SB}/z_S = (A_S/\pi r^2)(\tfrac{1}{2}\gamma\mathcal{M}_S^2 + \tfrac{3}{2})/\epsilon \qquad (50)$$

where z_S is the collision rate in the jet at the skimmer, $\mathcal{M}_S$ is the Mach number at the skimmer, A_S is the area of the skimmer, and ϵ ranges from 1 at the skimmer to 2 when the transverse velocity components vanish. Actually, eq 50 is strictly valid for $\mathcal{M}_S$ greater than 3. It approaches the form of eq 49 when $\mathcal{M}_S \to 0$. Here ϵ expresses the change from z_{jet} to z_{SB}. Thus, Figures 2 and 3 show that by operating at a sufficient distance downstream from the source the molecules in the jet are nearly collision-free.

In summary, expressions have been derived for the collision rate in an effusive beam (eq 19), a free jet (eq 25 and 27), and a supersonic beam (eq 47 and 50). We find that molecules in a collimated molecular beam can be considered isolated in most practical cases (time scale of experiment less than 0.1 ms; collision cross section less than 100 $Å^2$), but that the use of free jets requires care for distances close to the source. To estimate the collision rate in such cases, a family of curves have been presented for free jets of argon and nitrogen, Figures 2 and 3, respectively. It is hoped that the information contained in this paper will aid in the design of experiments requiring "collision-free" environments.

(26) See eq 5 of J. B. Anderson and J. B. Fenn, *J. Phys. Fluids*, 8, 780 (1963).