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On the free molecule quenching of a gas jet by another gas at rest

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THE COLLISION rate of jet molecules with reservoir molecules is considered as a function of the jet velocity and the temperature of the gases. Both the total number of collisions and the collisions with relative velocities bounded by some threshold velocity are found. Further the computation of the relative kinetic energy flux is discussed. The results obtained are a generalization of those known previously. Their applicability to the problem of nucleation of freely expanding vapour is briefly discussed.

Prędkość zderzeń cząsteczek strumienia z cząsteczkami zbiornika rozważono jako funkcję prędkości strumienia i temperatury gazów. Wyznaczono zarówno całkowitą liczbę zderzeń jak i liczbę zderzeń z prędkościami względnymi ograniczonymi przez pewne wartości progowe. Omówiono także strumienie energii kinetycznej. Otrzymane wyniki są uogólnieniem wyników znanych już wcześniej. Przedyskutowano możliwość ich zastosowania do zagadnienia zarodkowania swobodnie rozszerzającej się pary.

Скорость соударения частиц потока с частицами объема рассматривается как функция скорости потока и температуры газов. Определяется как общее число соударений, так и число соударений с относительными скоростями, ограниченными определенными пороговыми значениями. Обсуждаются потоки кинетической энергии. Полученные результаты являются обобщением ранее известных результатов. Рассматривается возможность их применения к задачам образования свободно расширяющегося пара.

PROFESSOR WŁADYSŁAW FISZDON has made many important contributions to our understanding of the dynamics of low density gases and, in particular, to some aspects of the condensation theory. On the seventieth birthday of that excellent friend, the following notes may provide a rarefied aura to our warmest congratulations and best wishes for many further years of creative activity and scholarly leadership.

In a number of situations including the nucleation of a vapor in a freely expanding jet and certain crossed beam experiments, the problem arises of describing the very low density interaction of a jet of one gas (1) with a quiescent different gas (2). In particular, it is necessary to find the collision rate of jet molecules with reservoir molecules as a function of the jet velocity and the temperatures of the gases.

In principle, this involves the analysis of the collision rate per unit volume:

$$(1) \qquad d\mathring{N} = n_1, n_2 \sigma \sqrt{(u_1+W-u_2)^2+(v_1-v_2)^2+(w_1-w_2)^2}\; e\,\frac{-m(u_1^2+v_1^2+w_1^2)}{T_1}$$
$$\times e\,\frac{-M(u_2^2+v_2^2+w_2^2)}{2kT_2}\left(\frac{m}{2\pi kT_1}\right)^{3/2}\left(\frac{M}{2\pi kT_2}\right)^{3/2} du_1dv_1dw_1du_2dv_2dw_2,$$

where n_1, n_2 are the number densitites of the two gases, σ is the collision cross-section (assumed constant for simplicity), W is the jet velocity directed along the x-axis, $u_{1,2}$, $v_{1,2}$, $w_{1,2}$, are the thermal velocities of the two gases, m, M are the molecular masses of the two gases, T_1, T_2 are their temperatures.

We now define the parameter $\alpha = \dfrac{MT_1}{mT_2}$ and normalize all velocities with respect to the thermal velocity of gas (1) so that Eq. (1) becomes

$$(2)\quad d\mathring{N} = n_1 n_2 \sigma \sqrt{\frac{2kT_1}{m}}\, \frac{\alpha^{3/2}}{\pi^3}\, e^{-(q_1^2+\alpha q_2^2)} \sqrt{(u_1+W-u_2)^2+(v_1-v_2)^2+(w_1-w_2)^2}\, d\mathbf{q}_1 d\mathbf{q}_2,$$

where q_i is the length of the (nondimensional) velocity vector, $d\mathbf{q}_i$ is a volume element in the appropriate velocity space.

If we introduce the "modified center of mass" coordinates $\mathbf{Q} = (U, V, W)$; $\mathbf{q} = (u, v, w)$

$$(3)\qquad U, V, W = \frac{u_1, v_1, w_1+\alpha u_2, v_2, w_2}{1+\alpha}, \qquad \bar{u}, \bar{v}, \bar{w} = u_1, v_1, w_1-u_2, v_2, w_2,$$

so that

$$(4)\quad u_1, v_1, w_1 = \frac{U, V, W(1+\alpha)+\alpha\bar{u}, \bar{v}, \bar{w}}{1+\alpha}, \qquad u_2, v_2, w_2 = \frac{U, V, W(1+\alpha)-\bar{u}, \bar{v}, \bar{w}}{1+\alpha},$$

we find that

$$(5)\qquad q_1^2+\alpha q_2^2 = (1+\alpha)Q^2 + \frac{\alpha}{1+\alpha}\bar{q}^2$$

and that

$$(6)\qquad J\begin{pmatrix} q_1, q_2 \\ Q \;\; \bar{q} \end{pmatrix} = 1.$$

These results are a slight generalization of the well-known calculation procedure outlined, for example by JEANS [1].

Substitution of Eqs. (4) and (5) into Eq. (2) yields

$$(7)\qquad d\mathring{N} = n_1 n_2 \sigma \sqrt{\frac{2kT_1}{m}}\, \frac{\alpha^{3/2}}{\pi^3}\, e^{-\left[(1+\alpha)Q^2+\frac{\alpha}{1+\alpha}\bar{q}^2\right]} \sqrt{(\bar{u}+W)^2+\bar{v}^2+\bar{w}^2}\, d\mathbf{Q}\, d\mathbf{q}.$$

The integration over Q is carried out at once

$$(8)\qquad \begin{aligned} d\mathbf{Q} &= 4\pi Q^2 dQ, \\ d\mathring{N} &= n_1 n_2 \sigma \sqrt{\frac{2kT}{m}}\, \frac{\alpha^{3/2}}{1+\alpha}\, \frac{1}{\pi^{3/2}}\, e^{-\frac{\alpha}{1+\alpha}(u^2+v^2+w^2)}\, du\,dv\,dw \end{aligned}$$

or in terms of the "modified reduced mass"

$$(9)\qquad \begin{aligned} \mu &= \frac{\alpha m}{1+\alpha} = \frac{MT_1 m}{MT_1+mT_2}, \qquad q^2 = \frac{\alpha}{1+\alpha}\bar{q}^2 = \frac{q_{\mathrm{phys}}^2 Mm}{mT_2+MT_1}, \\ d\mathring{N} &= n_1 n_2 \sigma \sqrt{\frac{(mT_2+MT_1)k}{\pi^3 mM}}\, e^{-q^2} \sqrt{(u+W)^2+v^2+w^2}\, du\,dv\,dw. \end{aligned}$$

If there is rotational symmetry about the x-axis, then with

$$\begin{aligned} du\,dv\,dw &= 2q^2 \sin\theta\, dq\, d\theta, \\ \sqrt{(u+W)^2+v^2+w^2} &= \sqrt{q^2+W^2+2qW\cos\theta} = V(\theta), \end{aligned} \tag{10}$$

we obtain

$$d\mathring{N} = 2n_1 n_2 \sigma \sqrt{\frac{2k(mT_2+MT_2)}{\pi m M}}\, e^{-q^2} \sqrt{q^2+W^2+2qW\cos\theta}\, q^2 \sin\theta\, d\theta\, dq \tag{11}$$

again a generalization of a classical result. One further step may be taken in a straightforward way: integration over θ.

$$d\mathring{N} = 2n_1 n_2 \sigma \sqrt{\frac{2k(mT_2+MT_1)}{mM}}\, e^{-q^2} \frac{dqd}{3W} [V^3(\theta_2) - V^3(\theta_1)], \tag{12}$$

where $V(\theta)$ is the value of the relative velocity at the limiting angles θ_1, θ_2. The quantity $V(\theta)$ is always nonnegative. The values assigned to $V(\theta)$ depend on the physical questions asked of the system.

The simplest problem to be approached is that of finding the total number of collisions: in that case, the range of q is $[0 < q < \infty]$ and all values of θ are permissible $[0 < \theta < \pi]$.

In that case

$$\begin{aligned} \mathring{N} &= 2n_1 n_2 \sigma \sqrt{\frac{2k(mT_2+MT_1}{\pi m M}} \left\{ \int_0^W e^{-q^2} \frac{q\,dq}{3W} [(W+q)^3 - (W-q)^3] \right\} \\ &\quad + \int_W^\infty e^{-q^2} \frac{q\,dq}{3W} [(q+W)^3 - (q-W)^3] \\ &= n_1 n_2 \sigma \sqrt{\frac{k(mT_2+MT_1)}{2mM}} \left[\frac{1+2W^2}{2} \operatorname{erf} W + \frac{2}{\sqrt{\pi}} e^{-W^2} \right]. \end{aligned} \tag{13}$$

We note in passing that Eq. (13) has the correct limits for large and small values of W

$$\begin{aligned} \lim_{W\to\infty} \mathring{N}(W) &= n_1 n_2 \sigma W \sqrt{\frac{2k(mT_2+MT_1)}{mM}} = n_1 n_2 \sigma W_{\text{phys}}, \\ \lim_{W\to 0} \mathring{N}(W) &= 2n_1 n_2 \sigma \sqrt{\frac{2k(mT_2+MT_1)}{\pi m M}}. \end{aligned} \tag{14}$$

In many problems (e.g. capture of slow monomers by clusters in free expansion, excitation of internal degrees of freedom by energetic collisions etc...) we also need to know how many collisions occur with relative velocities either higher or lower than some specified threshold velocity b (normalized, as W is) with respect to the "modified reduced mass" and the jet temperature

$$b = b_{\text{phys}} \sqrt{\frac{2k(mT_2+MT_1)}{mM}}. \tag{15}$$

The range of q is now $0 < q < b$, but the range of θ calls for an examination of the hodograph of the flow (Fig. 1 a, b, c).

We distinguish three cases there:

a) $0 < W < \frac{b}{2}$,

b) $\frac{b}{2} < W < b$,

c) $b < W < \infty$.

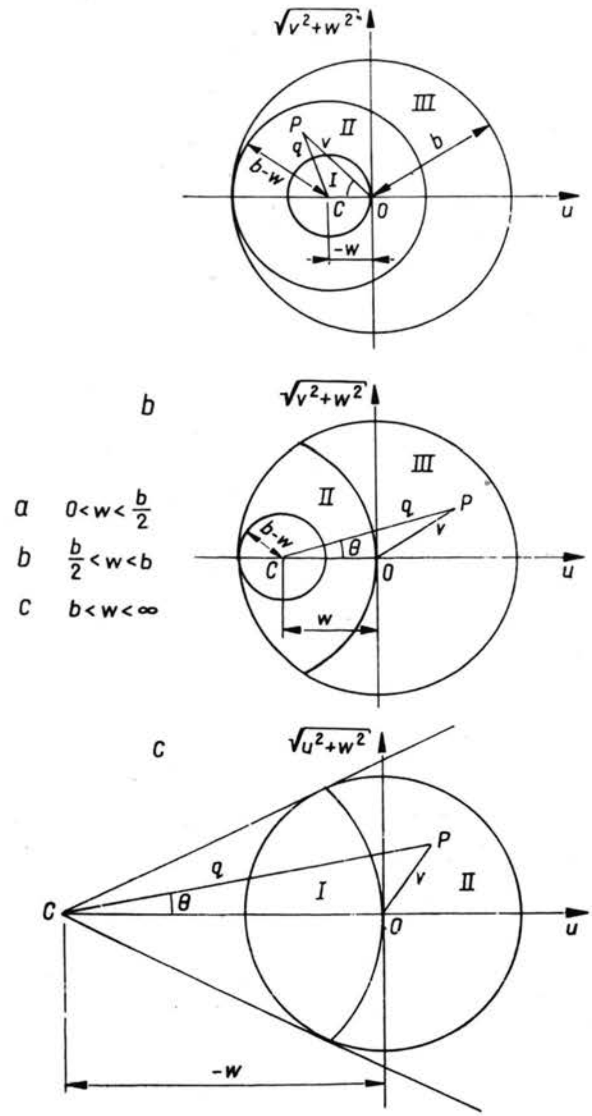

FIG. 1. Integration regions in the hodograph plane for $\mathring{N}(W, b)$, $\mathring{E}(W, b)$.

In all cases the integral must be carried out over the entire circle of radius b, but the way the circle is cut into sub-areas is different in the three cases.

In case a) we have two complete inner circles of radius W and $b-W$ and center located at $(-W)$; for those circles $[0 < \theta < \pi]$; they are distinct because the sign of $[W-q]$ changes at W. We then have a circular section of center $(-W)$ which extends in angular variable from $\theta = 0$ to the interesction with the circle of radius b. At that point, $V = b$.

Thus

$$(16) \qquad \mathring{N}_a = \frac{2n_1 n_2 \sigma}{3W} \sqrt{\frac{2k(mT_2+MT_1)}{\pi mM}} \Bigg\{ \int_0^W e^{-q^2} q[(W+q)^3-(W-q)^3]dq + \int_W^{b-W} e^{-q^2} q[(q+W)^3-(q-W)^3]dq + \int_{b-W}^{b+W} e^{-q^2} q[b^3-(q-W)^3]dq \Bigg\}.$$

A similar argument shows that in case b) there is a full inner circle of radius $(W-b)$ and two circular sections distinct because the sign of $(W-q)$ changes at $q = W$. The integral in b) is, therefore,

$$(16') \qquad \mathring{N}_b = \frac{2n_1 n_2 \sigma}{3W} \sqrt{\frac{2k(mT_2+MT_1)}{\pi mM}} \Bigg\{ \int_0^{b-W} e^{-q^2} q[(W+q)^3-(W-q)^3]dq + \int_{b-W}^{W} e^{-q^2} q[b^3-(W-q)^3]dq \int_W^{b+W} e^{-q^2} q[b^3-(q-W)^3]dq \Bigg\}.$$

Finally, in case c) the center $(-W)$ of the circular sections is outside the region of integration which is divided into two subsections

$$(16'') \qquad \mathring{N}_c = \frac{2n_1 n_2 \sigma}{3W} \sqrt{\frac{2k(mT_2+MT_1)}{\pi mM}} \Bigg\{ \int_{W-b}^{W} e^{-q^2} q[b^3-(W-q)^3]dq + \int_W^{W+b} e^{-q^2} q(b^3-(q-W)^3]dq \Bigg\}.$$

All of these integrals can be carried out in closed form and it turns out that the result in all three cases is the same:

$$(17) \qquad \mathring{N}(W, b) = n_1 n_2 \sigma \sqrt{\frac{k(mT_2+MT_1)}{2mM}} \Bigg\{ \frac{W^2+1/2}{W} [2\mathrm{erf}W + \mathrm{erf}(b-W) - \mathrm{erf}(b+W)] - \frac{1}{W\sqrt{\pi}} [(b+W)e^{-(b-W)^2} - 2We^{-W^2} + (b-W)e^{-(b+W)^2}] \Bigg\}.$$

This is the desired result; its limits lead back to a number of classical results; thus

$$(18) \qquad \lim_{W\to 0} \mathring{N}(W, b) = 2n_1 n_2 \sigma \sqrt{\frac{2k(mT_2+MT_1)}{\pi mM}} [1-(1+b_2)e^{-b^2}].$$

On the other hand,

$$(18') \qquad \lim_{b\to 0} \mathring{N}(W, b) = n_1 n_2 \sigma \sqrt{\frac{2k(mT_2+MT_1)}{\pi m M}}\, b^4 e^{-W^2}\left[1+\left(\frac{4}{9}w^2-\frac{2}{3}\right)b^2+\ldots\right].$$

This result tells us that the number of collisions of relative velocity b where $b \ll 1$ is proportional to $n_1 e^{-W^2}$, the number of jet molecules whose thermal velocity cancels the bulk velocity of the jet, so that they have the opportunity of meeting the requirement ($b \ll 1$). It is also proportional to b^4 and, therefore, very small, because not only are there few molecule pairs which meet this criterion, but their low relative velocity also reduces the rate of collisions. It is easy to verify that as $b \to 0$, the result (18) becomes identical with Eq. (18′).

The main dynamic property one is likely to need in the discussion of free expansion flows of real gases and vapors is the relative kinetic energy, or intensity of collisions, since that is what determines whether a structural change is likely to occur as a result. We therefore next compute the relative kinetic energy flux per unit time. As one can show rather simply in a manner analogous to the derivation of Eq. (12), it is defined by the integral

$$(19) \qquad \mathring{E} = 2n_1 n_2 \sigma \sqrt{\frac{2k(mT_2+MT_1)}{\pi m M}} \cdot \frac{kT_1}{5W}\frac{1+\alpha}{\alpha}\int q e^{-q^2}\left(V^5(\theta_2)-V^5(\theta_1)\right)dq,$$

where the limits of integration are defined as before. After considerable labor, we obtain the result

$$(20) \qquad \mathring{E} = n_1 n_2 \sigma \sqrt{\frac{k^3(mT_2+MT_1)^3}{2mM_3}} \cdot \left\{\frac{W^4+3W^2+3/4}{W}[2\operatorname{erf}W-\operatorname{erf}(W+b)\right.$$

$$-\operatorname{erf}(W-b)]-\frac{1}{W\sqrt{\pi}}[(W+b)(W^2+b^2)e^{-(W-b)^2}-2W^3e^{-W^2}+(W-b)(W^2+b^2)e^{-(W+b)^2}]$$

$$\left.-\frac{5}{4\sqrt{\pi}}[e^{-(W-b)^2}-2e^{-W2}+e^{-(W+b)^2}]-\frac{3b}{4W\sqrt{\pi}}(e^{-(b-W)^2}-e^{-(b+W)^2})\right\}.$$

This is an expression with the same general structure as Eq. (13) for the mass or number flux, although it is more complex. Some limiting behavior features are again of interest.

If all collisions are permitted ($b \to \infty$), the kinetic energy flux is

$$(21) \qquad \mathring{E} = \frac{n_1 n_2 \sigma}{\sqrt{m/2}}\left[\frac{k(mT_2+MT_1)}{M}\right]^{3/2}\left[\frac{(W^4+3W^2+3/4)\operatorname{erf}W}{W}+\frac{2}{\sqrt{\pi}}\left(\frac{W^2}{2}+\frac{5}{4}\right)e^{-W^2}\right]$$

and the average kinetic energy transmitted is

$$(21') \qquad \langle K\varepsilon\rangle = \frac{\mathring{E}}{\mathring{N}} = \frac{k(mT_2+MT_1)}{M}\,\frac{(W^4+3W^2+3/4)\operatorname{erf}W+\frac{W}{\sqrt{\pi}}(W^2+5/2)e^{-W^2}}{(W^2+1/2)\operatorname{erf}W+\frac{W}{\sqrt{\pi}}e^{-W^2}}.$$

In particular,

$$(2.1'') \qquad \begin{aligned} &\lim_{W\to 0}\langle K\varepsilon\rangle = \frac{2k(mT_2+MT_1)}{M},\\ &\lim_{W\to\infty}\langle K\varepsilon\rangle = \frac{k(mT_2+MT_1)}{M}W_2 = \frac{mW^2{}_{\mathrm{phys}}}{2}\end{aligned}$$

both of which are classical results.

When W becomes negligible, we find

$$\mathring{E} = \frac{n_1 n_2 \sigma}{\sqrt{m/2}} \left[\frac{k(mT_2+MT_1)}{M} \right]^{3/4} \left[1 - \left(1+b^2+\frac{b^4}{2} \right) e^{-b^2} \right] \tag{22}$$

the average relative kinetic energy of all impacts of velocity less than b is

$$\langle K\varepsilon \rangle = \frac{\mathring{E}}{\mathring{N}} = 2\,\frac{k(mT_2+MT_1)}{M}\,\frac{1-\left(1+b^2+\frac{b^4}{2}\right)e^{-b^2}}{1-(1+b^2)e^{-b^2}} \tag{22'}$$

$$= \frac{2k(MT_2+MT_1)}{M}\, 1 - \frac{b^4 e^{-b^2}}{2[1-(1+b^2)e^{-b^2}]}$$

and as $b \to 0$

$$\frac{\mathring{E}}{\mathring{N}} = \frac{1}{3} b^2\, \frac{k(mT_2+MT_1)}{M} = \frac{1}{6} m b^2_{\text{phys}}. \tag{22''}$$

It can be shown by direct Taylor expansion of Eq. (20) that Eq. (22)″ is valid for all values of W.

The results of Eqs. (13) and (20) thus give us the information we set out to obtain (unfortunately they are quite complicated); we show that they can be computed fairly simply by means of the auxiliary function

$$f(W,b) = \frac{\sqrt{\pi}}{2}\,[2\,\text{erf}W - \text{erf}(W-b) - \text{erf}(W+b)] \tag{23}$$

whose values are readily available in standard tables. In particular, we find

$$\begin{aligned}
\frac{\partial f}{\partial w} &= 2e^{-W^2}[1-e^{-b^2}\cosh 2bW] = 2e^{-W^2} - e^{-(W-b)^2} - e^{-(W+b)^2},\\
\frac{\partial f}{\partial b} &= 2e^{-(W^2+b^2)}\sinh 2bW = e^{-(W-b)^2} - e^{-(W+b)^2},\\
\frac{\partial^2 f}{\partial W^2} &= 4e^{-W^2}[W(1-e^{-b^2}\cosh 2bW) + be^{-b^2}\sinh 2bW],\\
\frac{\partial^2 f}{\partial b^2} &= 4e^{-(W^2+b^2)}[W\cosh 2bW - b\sinh 2bW] = 2[(W-b)e^{-(W-b)^2} - (W+b)e^{-(W+b)^2}].
\end{aligned} \tag{24}$$

All the terms which appear in Eqs. (13) and (20) can be expressed by the use of Eqs. (23) and (24) in terms of $f(W,b)$ and of its derivatives, which are tabulated. Thus

$$\mathring{N} = \frac{n_1 n_2 \sigma}{2W} \sqrt{\frac{k(mT_2+MT_1)}{2mM}} \left\{ (2W^2+1)f + W\frac{\partial f}{\partial W} - b\frac{\partial f}{\partial b} \right\}. \tag{25}$$

Similarly, after some manipulation

$$\mathring{E} = \frac{n_1 n_2 \sigma}{W\sqrt{m/2}} \left[\frac{k(mT_2+MT_1)}{M} \right]^{3/2} \left\{ (W^4+3W^2+3/4)f + 5/2\left(\frac{\partial f}{\partial W} - b\frac{\partial f}{\partial b} \right) + \left(W^3\frac{\partial f}{\partial W} - b^3\frac{\partial f}{\partial b} \right) - b(W^2+b^2)\frac{\partial f}{\partial b} + b\left(\frac{\partial f}{\partial b} - \frac{\partial^2 f}{2\partial b^2} \right) \right\}. \tag{26}$$

We see that the numerical evaluation of $\mathring{N}$, $\mathring{E}$ involves no more than linear combinations of tabulated error functions and their derivatives.

To illustrate these results, Fig. 2 shows the four functions $f, \frac{\partial f}{\partial b}, \frac{\partial f}{\partial W}, \frac{\partial^2 f}{\partial b^2}$, as functions of b for a given value of W ($W = 1$). Then Figs. 3 and 4 show the number flux $\mathring{N}$ and the mean relative kinetic energy $\mathring{E}/\mathring{N}$ as functions of b for $W = 0, 1, \infty$. [$\mathring{E}/\mathring{N} \to \to \frac{k(mT_2+MT_1)}{M} W^2$ for all b with nonuniform behavior at $b = 0$].

An application of these calculations can be made to the problem of nucleation in a freely expanding vapor jet. The formation of the smallest nuclei (up to some 5 mono-

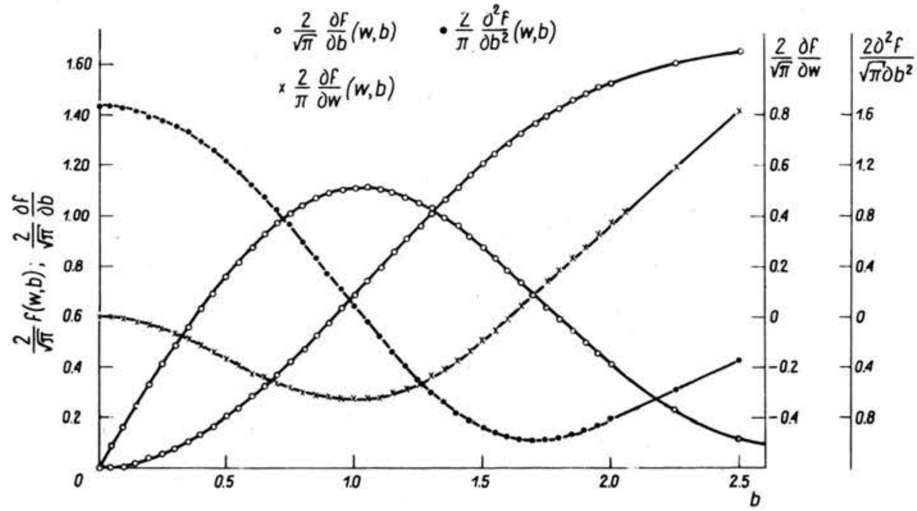

FIG. 2. Plot of $\frac{2}{\sqrt{\pi}} f(w, b)$ for $W = 1.00$.

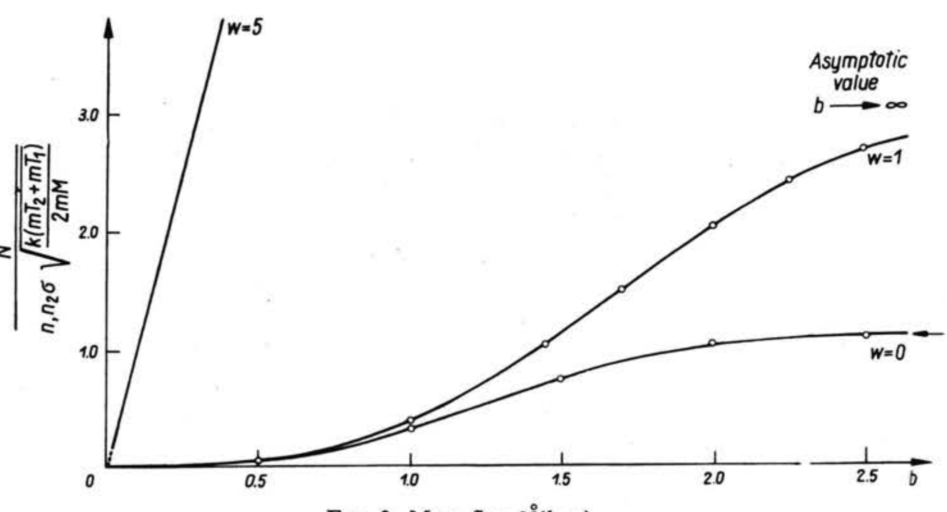

FIG. 3. Mass flux $\mathring{N}(b, w)$.

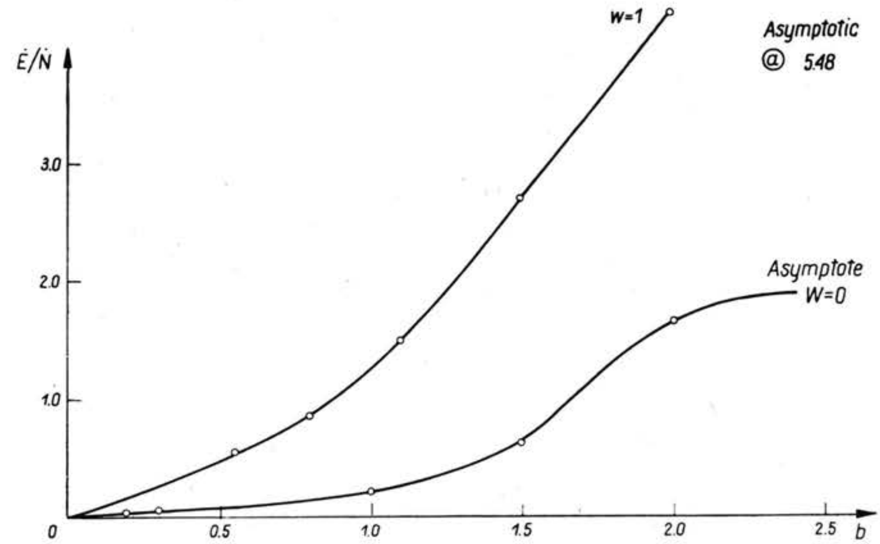

FIG. 4. Mean relative kinetic energy per molecule $\overset{3}{E}/\mathring{N}(b, w)$.

mers) occurs by triple collisions in the early stages of the expansion when the vapor is still in the continuum regime. Since nucleation is exothermic, the heat of formation is carried off by the uncaptured monomer and eventually, by thermal collisions, that heat is distributed to the monomer gas; the monomer gas therefore has higher enthalpy than the cluster gas; at high Mach Numbers where the intermediate-sized clusters are formed, the additional enthalpy appears largely as bulk velocity; to an observer travelling with the cluster gas, therefore, the monomer gas appears as a jet whose velocity is related to the amount of heat released by the formation (upstream) of the dimers, trimers, etc... at the initiation of nucleation.

Various models of cluster growth may be entertained: either by capture of slow monomers (capture coefficient a function of relative velocity with a sharp cutoff at a critical velocity which increases with cluster size) or by a combination of capture and re-emission with capture predominating until the decrease in the number of available monomers and the increase of internal energy of the cluster cause a change of process.

References

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