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Abstract

A closure at the third order moment is presented for the problem of the decay of reactants which obey a second order equation and whose initial description is given stochastically. The closure satisfies prescribed realizability conditions for all possible initial assignments of the mean, the mean square fluctuations and the skewness of the concentration field.

1 Introduction

In a recent paper[1] several kinds of closure approximations that have been employed in turbulence studies were applied to the simple but still non-linear system of stochastically distributed second order reactants. Such a system has many features which make it attractive as a testing ground for complex closure schemes. There are no geometric complications, exact stochastic solutions exist and most important of all there is no conserved quantity which can play the role of keeping the magnitude of the error due to a closure in bounds in the way that inviscid conservation of energy can in the turbulence problem. It is also likely that an understanding of this ideal stochastic situation is necessary before the more complicated real situations of non-linear chemical reactions in the presence of turbulent mixing can be fruitfully studied. In fact it appears that for large enough reaction rates the statistics of stochastically distributed second order reactants describes quite well the behavior of a turbulently convected second order reaction over a significant portion of its decay[2]

However, there has been one unfortunate feature of the non-convected stochastic system which has seriously detracted from its usefulness as a vehicle for the study of closures. Namely, when the relative intensity of the initial fluctuations are too high none of the existing closures behave satisfactorily. This difficulty was avoided in the original study[1] by taking low enough initial relative intensities that over the moderate time range studied all the closures were well behaved. The consequences of this strategy were twofold. The distinction between closures became less pronounced and the 'exact' solution to which they were compared, and which was assigned an initially normal distribution of concentration, was in fact not exact since the distribution was truncated at the origin at every instant. If this had not been done the 'exact' solution would ultimately have produced unbounded moments. Although these criticisms do not affect the limited conclusions of the prior work they do indicate a need for a closure which is not limited by the range of initial relative intensity with which it can cope in a physically sensible way. It is also clearly a difficulty which must be removed before there can be any general progress in describing the statistics of the behavior of reactions other than first order for media in turbulent motion.

In order to obtain a closure which is satisfactorily in a global sense, that is one which will be physically acceptable for any possible specification of initial conditions, we have borrowed from the viewpoints of Kraichnan[3] and Orszag[4], in particular by assigning a central role to certain realizability conditions. The system with which we deal is less complicated, mathematically and physically than those on which these authors have published and it may in fact be interpreted in part as a study of the extent to which the satisfying of important realizability conditions determines the accuracy of a closure. As Orszag[4] has pointed out a distribution function is not determined by the specification of a few lowest order moments and it is clearly untenable to expect that a specific statistical description will be accurate for all possible distribution functions that display the same initial values of the three lowest moments. We will at an appropriate point remember the origin of this problem in turbulent mixing and be guided partly by a principle similar to that of maximal randomness to which Kraichnan first made explicit appeal.

2 The Statistical Problem

The system is described by the equation

$$\frac{d\Gamma}{dt} = -\Gamma^2 \tag{2.1}$$

where Γ is the concentration which will be a random variable with the following bounds $0 \leq \Gamma \leq \infty$ and t is the time which has been normalized by a constant reaction rate.

The problem is made stochastic by assigning initial conditions in a statistical manner[1]. For example if $P[\Gamma(0)]$ is a prescribed initial probability density for the concentration field then the exact solution for any order moment exists in the following form[1]

$$\overline{\Gamma^n} = \int_0^\infty \left(\frac{x}{1 + xt}\right)^n P(x)\, dx \tag{2.2}$$

There are some asymptotic properties of (2.2) which will play a role in determining the form of the moment closure we will suggest:

$$\lim_{t\to\infty} \overline{\Gamma}(t) = t^{-1} \tag{2.3}$$

$$\lim_{t\to\infty} \overline{\gamma^2}(t) = C_1 t^{-4} \qquad C_1 \geq 0 \tag{2.4}$$

$$\lim_{t\to\infty} \overline{\gamma^3}(t) = -C_2 t^{-6} \qquad C_2 \geq 0 \tag{2.5}$$

These follow simply from an asymptotic expansion of (2.2) and the presumption that $\int_0^\infty x^{-n} P(x)\, dx$ exist, n = 1,2,3.

Since we expect to have available only the first few moments of the initial concentration distribution a moment formulation is pertinent. In fact our closure scheme will involve only the mean square and skewness of the concentration field which are related by the following moment equations, and others, in an infinite unclosed hierarchy

$$\frac{d\bar{\Gamma}}{dt} = -\bar{\Gamma}^2 - \overline{\gamma^2} \tag{2.6}$$

$$\frac{d\overline{\gamma^2}}{dt} = -4\bar{\Gamma}\,\overline{\gamma^2} - 2\overline{\gamma^3} \tag{2.7}$$

$$\frac{d\overline{\gamma^3}}{dt} = -6\bar{\Gamma}\,\overline{\gamma^3} - 3\left(\overline{\gamma^4} - \overline{\gamma^2}^2\right) \tag{2.8}$$

The overbar denotes an ensemble average and the decomposition $\Gamma(t) = \bar{\Gamma}(t) + \gamma(t)$ has been employed.

We will suppose that $\bar{\Gamma}(0)$, $\overline{\gamma^2}(0)$ and $\overline{\gamma^3}(0)$ are prescribed and ask that $\overline{\gamma^3}$ be replaced by specified functions of $\bar{\Gamma}$ and $\overline{\gamma^2}$ whose forms do not depend on the initial data but are such that (2.6) and (2.7) yield physically acceptable descriptions of the first three moments. Since $\overline{\gamma^4}(0)$ is not prescribed we cannot employ (2.8) even to the extent of evaluating $\frac{d\overline{\gamma^3}}{dt}(0)$.

The realizability conditions which we impose and which specify a certain degree of physical reasonableness to the solution are

$$0 \leq \bar{\Gamma}(t) < \infty \tag{2.9}$$

$$0 \leq \overline{\gamma^2}(t) < \infty \tag{2.10}$$

$$\overline{\gamma^3}(t) > \left(\frac{\overline{\gamma^2}^2(t)}{\bar{\Gamma}(t)} - \overline{\gamma^2}(t)\,\bar{\Gamma}(t)\right) \tag{2.11}$$

The relationship (2.11) arises from a restriction[5] on the skewness of any probability density which is zero for values of the random variable that are less than or equal to zero, and there exists a hierarchy of such relationships as the order of the moments become higher. For example one can derive that for such a random variable as Γ

$$\left(\bar{\Gamma}^{2}+\overline{\gamma^{2}}\right)\overline{\gamma^{4}} > r^{2}\,\overline{\gamma^{2}}^{\,3}+3\bar{\Gamma}^{2}\,\overline{\gamma^{2}}^{\,2}+2\bar{\Gamma}\,\overline{\gamma^{2}}^{\,5/2}-r^{4}\,\overline{\gamma^{2}}^{\,3}-2r\bar{\Gamma}^{3}\,\overline{\gamma^{2}}^{\,3/2} \tag{2.12}$$

where r is the skewness, $\dfrac{\overline{\gamma^{3}}}{\overline{\gamma^{2}}^{\,3/2}}$.

It is our purpose in the next section to propose a closure which satisfies the realizability conditions (2.9) (2.10) and (2.11) for all values of $\bar{\Gamma}(0)$, $\overline{\gamma^{2}}(0)$ and $\overline{\gamma^{3}}(0)$ which themselves do not violate (2.9) (2.10) and (2.11). We also will require that the asymptotic behaviors (2.3) (2.4) and (2.5) are satisfied and that the closure be a simple functional form which is not specified variously for different initial data. Evidently with the adoption of such restrictions, spectacular precision for all possible initial statistics cannot be expected. However, the global nature of the closure is our primary concern and it is this property which should be valuable for studies of turbulent mixing. It will be evident from the following how the closure might be improved for specific values of initial data.

3 A Proposed Closure

The inequality (2.11) suggests a closure form of the kind

$$\overline{\gamma^3}(t) = C\left(\frac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma}\right)$$

where C is determined by the values $\overline{\Gamma}(0)$, $\overline{\gamma^2}(0)$ and $\overline{\gamma^3}(0)$. However, it is easy to show that such a closure can violate (2.5), the asymptotic condition on $\overline{\gamma^3}(t)$, so following Orszag[6] we investigate instead combinations of simple, dimensionally correct, simultaneous functions.

One such collection of functions could be as follows

$$\overline{\gamma^3}(t) = \sum_{n=-\infty}^{n=+\infty} A_n\,\overline{\gamma^2}^{\,\frac{n+3}{2}}\,\overline{\Gamma}^{\,-n} \tag{3.1}$$

and it is (3.1) which we shall pursue, realizing that there is no reason other than simplicity to reject non-integer powers of the mean. We do note that only integer powers of the mean occur in the realizability conditions and the governing equations while the existence of a possible dependence of $\overline{\gamma^3}$ on $\overline{\gamma^2}^{\,3/2}$ for example is indicated by the asymptotic statements (2.4) and (2.5).

These same asymptotic results and (2.3) are sufficient to eliminate from (3.1) all terms in which $n < -1$. This fact and the inequality (2.11) suggests a rewriting of (3.1) in the form

$$\overline{\gamma^3}(t) = \alpha\frac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}}\left[-1 + Y_2^{-1}(0) + \alpha^{-1}A_0 Y_2^{-1/2}(0) + \alpha^{-1}A_2 Y_2^{1/2}(0) + \cdots\right] - A_0\overline{\gamma^2}^{\,3/2} - A_2\overline{\gamma^2}^{\,5/2}\,\overline{\Gamma}^{\,-2} \tag{3.2}$$

where $Y_2(0) = \overline{\gamma^2}(0)\,\overline{\Gamma}(0)^{-2}$, α is obtained unequivocably from the initial values $\overline{\Gamma}(0)$, $\overline{\gamma^2}(0)$, $\overline{\gamma^3}(0)$ and A_0, A_2, A_3, etc. are arbitrary constants.

The closure (3.2) when combined with the inequality (2.11) yields the following information about α

$$\text{If } Y_2(0) > 1 \;,\; \alpha < -1 \tag{3.3}$$

$$\text{If } Y_2(0) < 1 \;,\; \alpha > -1 \tag{3.4}$$

The situation $Y_2(0) = 1$ is very special since the form of the closure in this case would force $\mathfrak{f}^3(0) \equiv 0$. whereas, from (2.11), the only restriction should be $\mathfrak{f}^3(0) > 0$. If $Y_2(0)$ is not identically unity this difficulty does not arise. For the remainder of the paper we will assume that $Y_2(0) \neq 1$ but can be made as close to unity as we please.

When (3.2) is incorporated into (2.7) and we define $\Gamma(t) = Y_1(t)$ (2.6) and (2.7) transform into

$$\frac{dY_1}{dt} = -\left[1 + Y_2\right] Y_1^2 \tag{3.6}$$

$$\frac{dY_2}{dt} = -2Y_1\left\{Y_2 - Y_2^2\left[(\alpha+1) - \alpha Y_2^{-1}(0) - A_0 Y_2^{-1/2}(0) - A_2 Y_2^{1/2}(0) \cdots\right] - A_0 Y_2^{3/2} - A_2 Y_2^{5/2} \cdots\right\} \tag{3.7}$$

One immediate consequence of the form of (3.6) and (3.7) and the fact that $Y_1(0) \geq 0$, $Y_2(0) \geq 0$ is that if $Y_1(t_1) = 0$ for some $t = t_1$, then so is $\frac{d^n Y_1(t_1)}{dt^n}$ for all n. Similarly if $Y_2(t_2) = 0$ so is $\frac{d^n Y_2(t_2)}{dt^n}$ for all n. Thus $Y_1(t) \geq 0$ and $Y_2(t) \geq 0$.

The formal solution of (3.6) and a simpler version of (3.7) are possible. Define

$$T = \int_0^t \left[1 + Y_2(t')\right]dt' \, ; \quad \tau = \int_0^t 2Y_1(t')\,dt'$$

then $$\frac{dY_1}{dT} = -Y_1^2 \, , \quad Y_1(T) = Y_1(0)\left[1 + Y_1(0)T\right]^{-1} \tag{3.8}$$

and $$\frac{dY_2}{d\tau} = -Y_2 + Y_2^2\left[(\alpha+1) - \alpha Y_2(0)^{-1} - A_0 Y_2(0)^{-1/2} - A_2 Y_2(0)^{1/2} - \cdots\right] + A_0 Y_2^{3/2} + A_2 Y_2^{5/2} + \cdots \tag{3.9}$$

Furthermore, $T \geq 0, \tau \geq 0$ and from (3.8) the realizability condition (2.9) is satisfied.

These are limitations on the values that A_0, A_2---,A_n, can assume and still have (3.2) be a closure which satisfies (2.11), for all possible values of $\overline{\Gamma}(0)$, $\overline{\gamma^2}(0)$ and $\overline{\gamma^3}(0)$. One way to determine these is the following: It is convenient to rewrite (3.1) in the form

$$\overline{\gamma^3}(t) = \alpha\left[-\frac{\overline{\gamma^2}^2}{\overline{\Gamma}} + \frac{Y_2(t)}{Y_2(0)}\overline{\gamma^2}\,\overline{\Gamma}\right] + A_0\overline{\gamma^2}^{3/2}\left[\left(\frac{Y_2(t)}{Y_2(0)}\right)^{1/2} - 1\right] + A_2\frac{\overline{\gamma^2}^{5/2}}{\overline{\Gamma}^2}\left[\left(\frac{Y_2(0)}{Y_2(t)}\right)^{1/2} - 1\right] + \cdots + A_n\frac{\overline{\gamma^2}^{\frac{2n+1}{2}}}{\overline{\Gamma}^2}\left[\left(\frac{Y_2(0)}{Y_2(t)}\right)^{\frac{2n-3}{2}} - 1\right] + \cdots \tag{3.10}$$

Also, from (3.9), we have

$$\frac{dY_2(0)}{d\tau} = -(\alpha+1)\,Y_2(0) + (\alpha+1)\,Y_2^2(0)$$

which with (3.3) and (3.4) yields $\frac{dY_2(0)}{d\tau} < 0$. For arbitrary assignments of α it is clear that the inequality (2.11) can only hold for small times in all circumstances if $A_0 \leq 0$ $A_2 \geq 0$ ...,A_n ≥ 0. But from (3.10) if the closure is satisfactory the asymptotic behavior of $\overline{\gamma^3}(t)$ will be $\overline{\gamma^3}(t) = -A_0\overline{\gamma^2}^{3/2}$.

Now from (2.5) $A_o \geq 0$ and the only globally satisfactory choice of A_o is $A_o \equiv 0$.

We will show in the next section that the closure (3.1) with $A_o = 0$, $A_n \geq 0$, $n \geq 2$ is indeed satisfactory in the sense that all the realizability conditions, initial conditions and asymptotic conditions are satisfied for all permissable values of $\overline{\Gamma(0)}$, $\overline{\Gamma^2(0)}$ and $\overline{\Gamma^3(0)}$ and we will argue that the most universally satisfactory choice of constants is $A_2 = A_3 = --- = A_n = 0$.

4 Properties of the Closure

In the previous section we proposed the closure

$$\overline{\gamma^3}(t) = \alpha\frac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}}\left[-1 + Y_2^{-1}(0) + \alpha^{-1} A_2 Y_2^{1/2}(0) + \cdots\right] - \sum_{n=2}^{\infty} A_n \overline{\gamma^2}^{\frac{2n+1}{2}}\, \overline{\Gamma}^{-2n+2}, \quad A_n \geq 0 \qquad (4.1)$$

where α is obtained from $\overline{\Gamma}(0)$, $\overline{\gamma^2}(0)$ and $\overline{\gamma^3}(0)$.

Such a closure automatically satisfies the initial conditions and in order to show that the realizability conditions (2.9) (2.10) and (2.11) and the asymptotic behaviors (2.3) (2.4) and (2.5) are also obtained it is valuable to consider first the closure (4.1) with $A_n = 0$ for all n.

Defining
$$\mathring{\overline{\gamma^3}}(t) = \alpha\frac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}}\left[-1 + Y_2^{-1}(0)\right] \qquad (4.2)$$

and denoting the solutions of (3.8) and (3.9) for such a closure by $\mathring{Y}_1(t)$ and $\mathring{Y}_2(t)$ we have

$$\frac{d\mathring{Y}_1}{dT} = -\mathring{Y}_1^{\,2} \qquad (4.3)$$

$$\frac{d\mathring{Y}_2}{d\tau} = -\mathring{Y}_2(t) + \mathring{Y}_2^{\,2}(t)\left[(\alpha+1) - \alpha\,\mathring{Y}_2^{-1}(0)\right] \qquad (4.4)$$

for which the formal solutions exist and are

$$\mathring{Y}_1(T) = Y_1(0)\left[1 + Y_1(0)\,T\right]^{-1} \qquad (4.5)$$

$$\frac{\mathring{Y}_2(\tau)}{\mathring{Y}_2(\tau) - \left[(\alpha+1) - \alpha Y_2^{-1}(0)\right]} = \frac{Y_2(0)}{Y_2(0) - \left[(\alpha+1) - \alpha Y_2^{-1}(0)\right]}\, e^{-\tau} \qquad (4.6)$$

Now from (3.3) and (3.4) one has $Y_2(0) < \left[(\alpha+1) - \alpha Y_2^{-1}(0)\right]^{-1}$ which when combined with the earlier result $T \geq 0$, $\tau \geq 0$ shows that $\mathring{Y}_1(t), \mathring{Y}_2(t)$ are monotonically decreasing functions and consequently

$$\lim_{t\to\infty} \overset{o}{Y}_1(t) = t^{-1}$$

$$\lim_{t\to\infty} \overset{o}{Y}_2(t) = O(t^{-2}) \quad \text{or} \quad \lim_{t\to\infty} \overset{o}{\overline{\gamma^2}}(t) = O(t^{-4})$$

These results, and those obtained in section 3 which were $\overline{\Gamma} \geq 0$, $\overline{\gamma^2} \geq 0$ indicate that (2.3) (2.4) (2.9) and (2.10) are satisfied. Also from (4.2) and the above asymptotic results it is clear that (2.5) is also satisfied. In fact $C_2 \equiv 0$.

It remains to show for the closure (4.2) that the inequality (2.11) is satisfied. That is, given (4.2) we need to demonstrate that $\overset{o}{\overline{\gamma^3}}(t) > \frac{\overline{\gamma^2}^2}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma}$ for all t and to do so it is convenient to consider three distinct situations

Case I

Suppose $\overline{\gamma^3}(0) < 0$ then $Y_2(0) < 1$ and $0 > \alpha > -1$

or $$\overset{o}{\overline{\gamma^3}}(t) = -|\alpha| \frac{\overline{\gamma^2}^2}{\overline{\Gamma}} \left(-1 + Y_2^{-1}(0)\right), \quad 0 < |\alpha| < 1.$$

Since $Y_2(t) \leq Y_2(0) < 1$

$$\overset{o}{\overline{\gamma^3}} = |\alpha| \left[\frac{\overline{\gamma^2}^2}{\overline{\Gamma}} - \frac{Y_2(t)}{Y_2(0)} \overline{\gamma^2}\,\overline{\Gamma} \right] > |\alpha| \left[\frac{\overline{\gamma^2}^2}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma} \right]$$

and also
$$\frac{\overline{\gamma^2}^2}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma} = \overline{\Gamma}^3 \overset{o}{Y}_2(t) \left[\overset{o}{Y}_2(t) - 1 \right] < 0$$

Hence
$$\overset{o}{\overline{\gamma^3}}(t) > |\alpha| \left[\frac{\overline{\gamma^2}^2}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma} \right] > \frac{\overline{\gamma^2}^2}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma}$$

Case II

Suppose $\overline{\gamma^3}(0) > 0$ and $Y_2(0) < 1$

then $$\overset{o}{\overline{\gamma^3}}(t) = \alpha \frac{\overline{\gamma^2}^2}{\overline{\Gamma}} \left[-1 + Y_2^{-1}(0) \right] \qquad 0 < \alpha < \infty$$

or $\qquad \overline{\overset{o}{\gamma^3}}(t) = \alpha\, \overline{\gamma^2}\,\overline{\Gamma}\, Y_2(t)\left[Y_2^{-1}(0) - 1\right] > 0$

But $\qquad \dfrac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma} = \overline{\Gamma}^{3}\, \overset{o}{Y}_2(t)\left[\overset{o}{Y}_2(t) - 1\right] < 0$

and therefore $\qquad \overline{\overset{o}{\gamma^3}} > \dfrac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma}$

Case III $\quad$ Suppose $\quad \overline{\gamma^3}(0) > 0,\ Y_2(0) > 1$.

then $\quad \overline{\overset{o}{\gamma^3}}(t) = \alpha\, \dfrac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}}\left[-1 + Y_2^{-1}(0)\right], \quad -1 > \alpha > -\infty$

Since $\quad \dfrac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}}\left[-1 + Y_2^{-1}(0)\right] < 0 \qquad$ the following inequalities hold:

$$\overline{\overset{o}{\gamma^3}}(\alpha) = |\alpha|\left[\frac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}} - \frac{\overset{o}{Y}_2(t)}{Y_2(0)}\,\overline{\gamma^2}\,\overline{\Gamma}\right] > |\alpha|\left[\frac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma}\right] > \frac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma}.$$

Thus the closure (4.2) satisfies all the specified realizability and asymptotic conditions for every possible set of initial data $\overline{\Gamma}(0)$, $\overline{\gamma^2}(0)$ and $\overline{\gamma^3}(0)$.

To show that the more general closure (4.1) also satisfies the same specified conditions we note from (3.10), with $A_o \equiv 0$, that since $A_n \geq 0$ for all n and $\dfrac{dY_2(0)}{d\tau} < 0$ then $\overline{\gamma^3} > \overline{\overset{o}{\gamma^3}}$ for the same values of $\overline{\gamma^2}$ and $\overline{\Gamma}$. From (2.6) and (2.7) it is further evident that $\overline{\gamma^2}(t) < \overline{\overset{o}{\gamma^2}}(t), \overline{\Gamma}(t) > \overline{\overset{o}{\Gamma}}(t)$. In particular $Y_2(t) < \overset{o}{Y}_2(t)$. From (2.6) since $Y_1 \geq 0, Y_2 \geq 0$ then $Y_1 \leq Y_1(0)$ and the following bounds remain valid;

$$0 \leq \overline{\Gamma}(t) \leq \overline{\Gamma}(0)$$

$$0 \leq \overline{\gamma^2}(t) \leq \overline{\gamma^2}(0)$$

Furthermore, since $Y_2(t) < \overset{o}{Y}_2(t)$ the asymptotic result $Y_2(t) = O(t^{-2})$ remains in effect. From (2.6) $\overset{o}{Y}_1(t) < Y_1(t) < \overset{1}{Y}_1(t)$ where $\overset{1}{Y}_1(t) = Y_1(0)\left[1 + Y_1(0)\,t\right]^{-1}$

But $\lim\limits_{t\to\infty} \overset{1}{Y}_1(t) = \lim\limits_{t\to\infty} \overset{o}{Y}_1(t) = t^{-1} = \lim\limits_{t\to\infty} Y_1(t)$.

Since $\overline{\gamma^2}(t)$ and $\overline{\Gamma}(t)$ have the same asymptotic behaviors as $\overline{\overset{o}{\gamma^2}}(t)$

and $\overset{\circ}{\overline{\Gamma}}(t)$ then, from (4.1) $\overline{\gamma^3}(t)$, $\overset{\circ}{\overline{\gamma^3}}(t)$ also display similar asymptotic rates of decay.

It remains to demonstrate that the inequality (2.11) is preserved by the closure (4.1). The proof follows closely the arguments already advanced for the closure (4.2) and we reproduce just one of the three cases.

<u>Case I</u> Suppose $\overline{\gamma^3}(0) < 0$ then $Y_2(0) < 1$ and $0 > \alpha > -1$ and

$$\overline{\gamma^3}(t) = |\alpha|\left[\frac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}} - \frac{Y_2(t)}{Y_2(0)}\overline{\gamma^2}\,\overline{\Gamma}\right] + \sum_{n=2}^{\infty} A_n \frac{\overline{\gamma^2}^{\,\frac{2n+1}{2}}}{\overline{\Gamma}^{\,2n-2}}\left[\left(\frac{Y_2(0)}{Y_2(t)}\right)^{\frac{2n-3}{2}} - 1\right].$$

Since $A_n \geq 0$ $\quad \overline{\gamma^3}(t) > |\alpha|\left[\frac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma}\right] > \frac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma}$.

Since the general closure (4.1) satisfies all the required conditions it is pertinent to ask whether there is any one choice of the non-negative constants A_n which might be most useful over the whole range of possible initial data and more importantly whether there is any statistical principle on which to base a plausible choice. As was mentioned in section 3 we appeal to a kind of maximal randomness[3,4] condition the only basis for which can be the intuitive hope that if a reaction is carried by a fluid in turbulent motion at a high enough Reynolds number then the statistics of the concentration field will be as chaotic as possible consistent with the kinetic equations. Since the ultimate utility of the closure discussed here will be in its role when turbulence is the agent that induces the randomness the principle seems to be pertinent. In our case we will require that the constants A_n be so chosen as to minimize $|\overline{\gamma^3}(t)|$.

The consequences of this requirement are clear for the situation in which $\overline{\gamma^3}(0) \geq 0$, the choices $A_2 = A_3 = \cdots = A_n = 0$ minimize $|\overline{\gamma^3}(t)|$. It should also be mentioned that on the basis of this principle alone A_1

would again be chosen to be zero. From (2.11) if $\overline{\Gamma}(0) < \overline{\gamma^2}(0)$ then $\overline{\gamma^3}(0) > 0$ so that the condition under which the principle can be applied corresponds to the situation which could not be handled by previous closures. It is therefore a region of particular interest.

The principle of mimimum $|\overline{\gamma^3}(t)|$ has no sensible application for situations in which $\overline{\gamma^3}(0) < 0$. It is easy to show that its adoption and the use of a subsidiary one, $\overline{\gamma^3}(t) \leq 0$ for all t which is inspired by (2.5), lead to closures of the kind

$$\overline{\gamma^3}(t) = -\alpha\, Y_2(0)^{-\frac{n-1}{2}} \left(1 - Y_2^{-1}(0)\right) \frac{\overline{\gamma^2}^{\,\frac{n+3}{2}}}{\overline{\Gamma}^{\,n}}$$

These can clearly be made to approach zero as rapidly as one pleases by taking n sufficiently large. Since $\overline{\gamma^3}(0)$ can only be negative if $\overline{\gamma^2}(0) < \overline{\Gamma}(0)^2$ this is not only the region of less interest but it can also be argued that it is the situation in which the higher powers of $Y_2(t)$ may be less and less significant to the skewness. In the interest of proposing a specific globally satisfactory closure it is suggested that one which may be acceptably accurate at all levels of initial intensity is (4.2). If one is specifically interested in reactions with low initial relative intensity it would be possible for example to add the first few terms which involve say A_2, A_3, etc. and choose their value by matching moments as accurately as possible with the exact initial behavior of the moments of an appropriate truncated distribution. It is probable that without a correction of this kind the closure behaves most poorly under the circumstance in which $\overline{\gamma^3}(0) = 0$ or, in the terms of the closure, $\alpha = 0$ and $\overline{\gamma^3}(t) \equiv 0$. In this case the higher powers in $\overline{\gamma^2}$ and $\overline{\Gamma}$ are being ignored as compared to zero which is clearly unfortunate. A measure of the accuracy of the suggested closure in this instance can be obtained from the previous paper[1] since it coincides with the zero third moment approximation. In interpreting the results presented there it should be remembered that if initial relative intensity much greater than 40% had been used all of the other closures (and the 'exact' solution) would become unbounded.

5 Conclusion

The method that has been detailed in the previous sections has yielded a satisfactory closure at the third moment and there is every possibility that by adopting further realizability conditions like (2.12) and by knowing the asymptotic behavior of each order moment similar successful closures can be obtained at higher orders. The problem is of course more complex then for two reasons. The number of simultaneous equations increase and the realizability inequalities become more and more awkward. There seems to be no alternative to this strategy of building in physically acceptable behavior by using realizability conditions of the kind discussed here and the necessity for doing this seems to become more urgent as the level in order of the moment at which the closure is made increases. For example, if the plausible closure

$$\overline{\gamma^4} = 3\,\overline{\gamma^2}^{\,2} + 2\,\overline{\gamma^3}^{\,2}\cdot\overline{\gamma^2}^{\,-1}$$

is adopted on the basis that is dimensionally correct, always positive and gives the proper initial behavior of $\overline{\gamma^2}(t)$ out to the sixth order in time one can prove that for initial intensities $Y_2(0)^{1/2} > \frac{\pi}{20}$ the moments become unbounded. This is much lower initial intensity than that with which the direct interaction closure at the third moment was unable to cope.

The method of deducing a globally satisfactory closure which we have discussed in this paper should be directly applicable to non-linear reactions of other than second order. Since concentrations are by nature non-negative quantities the realizability conditions employed here will be relevant to any problem involving a statistical description of reactions. It is only in the cases of first order reactions where the mean concentration and the fluctuations in concentration do not interact that this special nature of concentration as a random variable can be ignored except of course that even then the specification of initial moments must be proper.

When reactants are turbulently mixed, closures of the kind presented here can be usefully applied to moments that consist only of the concentration variables. Velocity field moments and those with mixed velocity and concentration variables will require the input of a closure suitable to them, such as results for example from the Lagrangian History Direct Interaction Hypothesis[7].

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Footnotes

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