

CHAPTER 4

Chapter 4 contains

- *an introduction to the problem of modeling nonlinear chemical reactions in turbulent flows, including a general literature survey and classification of existing methods,*
- *an exposition of the fundamentals of the Eulerian Statistical Approach for both direct and indirect chemical closure methods,*
- *a detailed presentation of the "concentration field splitting method," that is the particular indirect closure technique employed in the formulation of the TRPM*

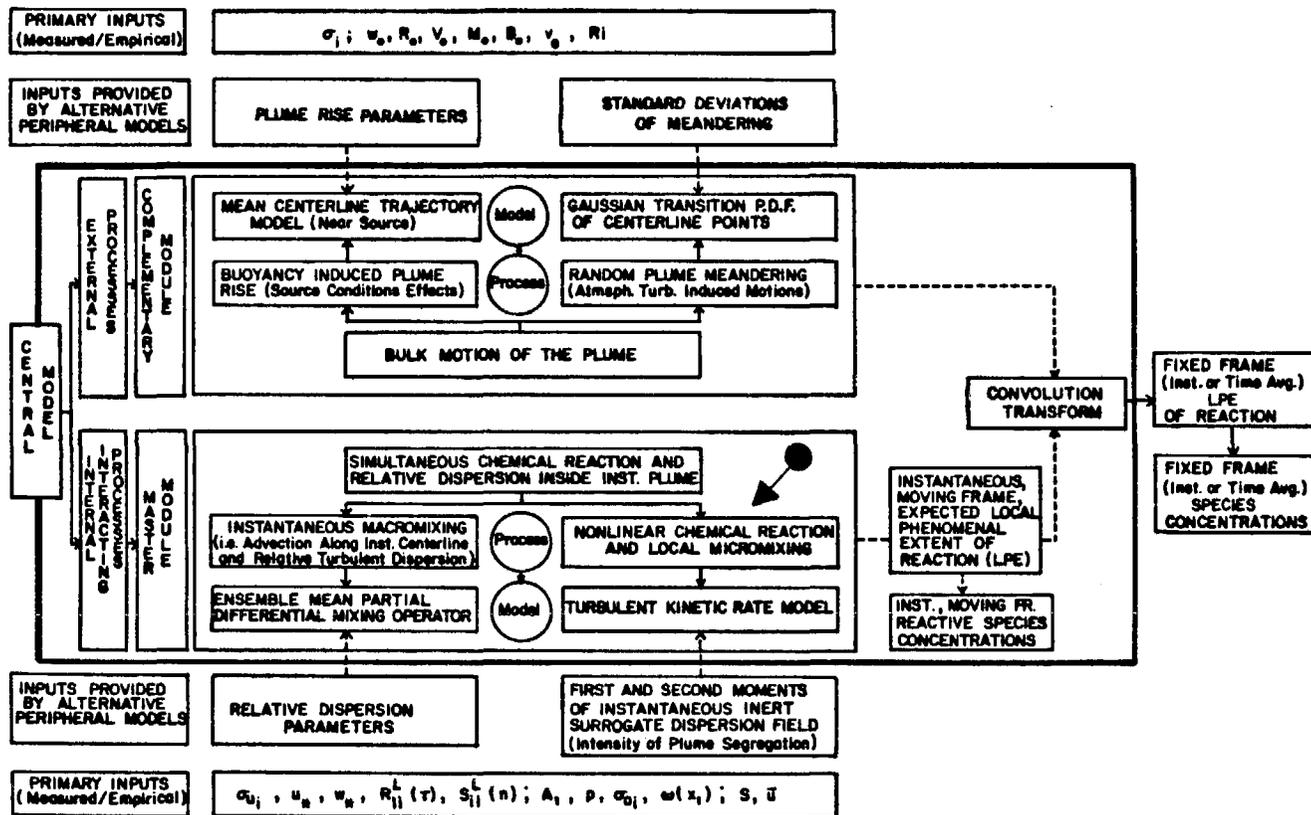


Figure 2-1a

TRPM Components Discussed in Chapter 4

CHAPTER 4

CHEMICAL REACTIONS IN TURBULENT FIELDS

4.1 INTRODUCTION

Many chemical reactions, either single-phase (on which we focus attention here) or multi-phase, of importance in both natural (environmental) and industrial systems, take place in turbulent flow fields. In general both the properties of the flow field in which the reaction occurs and the way the reactants are introduced in it will affect the spatial and temporal evolution of these systems. Further, the state of a particular system will be determined by the nature of the reaction kinetics involved (monomolecular or multimolecular) and by the relative rates of the simultaneously occurring chemical and dispersion processes.

The state of environmental systems (e.g. atmospheres and oceans) is turbulent for almost all common circumstances; on the other hand industrial flow and reaction systems are also deliberately, in most cases, in a turbulent state, in order to utilize the enhanced rates of heat and mass transfer resulting from turbulent motions (commonly called "turbulent mixing").(*) As a consequence, the problem of simultaneous

(*) One should keep in mind that the term (turbulent) mixing is used in somewhat different context by different authors. Thus, for example, in some works turbulent mixing processes are assumed to involve just turbulent diffusion due to small scale turbulent eddies and in others to involve both this turbulent diffusion and "bulk convection" due to eddies of larger scales. It is therefore necessary to always specifically define terms like "mixing" in the analysis of systems where multiscale dispersion processes occur simultaneously.

turbulent mixing and chemical reaction is commonly encountered in a vast variety of different situations. Table 4-1 gives a typical list of cases of engineering interest where this problem has been realized and research is active towards its analysis. Although the selection of subjects in this list is far from being exhaustive, it is at least indicative of the broad range of areas in which significant interaction between turbulence and chemistry appears. The relevant research studies problems arising in fields such as chemical and environmental engineering, combustion and propulsion aerodynamics, laser and plasma chemistry etc. The major interest today appears in the area of combustion research (see, e.g., Libby and Williams, 1980; Chigier, 1981; Williams, 1985, and the proceedings of the Symposia (International) on Turbulent Combustion – the proceedings of the 20th published in 1985) where the problem of interaction between reaction and turbulent mixing seems to assume its most complex levels. (*) Increasing interest has also been arising recently in various other fields, especially in environmental applications. More specifically, Donaldson and Hilst (1972) and Lamb (1973) (see also Lamb and Seinfeld, 1974; Seinfeld, 1977) recognized the importance of incomplete turbulent mixing phenomena in the processes of photochemical smog formation and a number of related works have appeared since then (e.g. Bilger, 1978; Kewley and Post, 1978; Kewley and Bilger, 1979; Kewley, 1980; see also Chapter 1).

Due to both the variety of the problems in which the problem of reactive turbulence is encountered and the wide range of approaches through which this problem is attacked (not to mention the differences, in both method and terminology, that appear in the treatment of equivalent problems in different scientific disciplines), an attempt to get familiar with the essentials of the entire spectrum of modeling tech-

(*) The complexity of the problem in the field of combustion is basically associated with the large heat releases accompanying combustion reactions and the resulting intense variation of temperatures, densities and pressures. This leads to a complicated multidirectional coupling among the processes of heat, momentum and mass transport and the chemistry. On the contrary, in many typical environmental applications the transport processes can be assumed decoupled. The complexity of the mixing-reaction problem in environmental systems is thus associated more with the complexity and the peculiarities of the turbulent environmental flow per se (temporal and spatial variation of turbulence characteristics, many scales, unknown parameters, etc.).

niques in the field would constitute a most difficult task. Basic aspects of such techniques are covered in standard textbooks in chemical engineering (see, e.g., Froment and Bischoff, 1979) and in combustion theory (see, e.g., Williams, 1985). However the interested reader will eventually have to confront a plethora of specialized articles and publications; some comprehensive reviews (usually focusing on a specific topic) and compilations of works dealing with particular applications are available to help in his quest. In particular the collections edited by Murthy (1975), Brodkey (1975) and Libby and Williams (1980), contain a wide range of applications from various fields and some excellent reviews of specific approaches. Among the review papers with a more general perspective, those of Hill (1976), which covers mainly the "fluid mechanical" approach to the mixing-reaction problem (together with some discussion on spectral and "micro-structural" techniques - see the analysis that follows) and of Pratt (1979), which contains a brief summary of modern chemical reactor theory on the basis of population balance approaches, can serve as tutorial introductions to the subject of reactive turbulence. Some more recent developments not contained in the above works can be found in the reviews of Villermaux (1983) and Pope (1985). (*)

It would be beyond the scope of the present work to attempt a detailed exposition of the various modeling methodologies and techniques which have appeared in the vast literature that deals with turbulence and chemistry interactions. However, the importance of these phenomena in atmospheric applications - and in particular in relevance to moderately fast reactions in point source plumes (see Chapter 1) - is a subject that merits further study and development of procedures for proper modeling

(*) Three other comprehensive review articles, (published together), that give an overview of the reactive turbulence field from a "chemical engineering viewpoint" are those of Brodkey (1981), Nauman (1981) and Patterson (1981). One must also note that, even in order to deal exclusively with single-phase reactions (homogeneous at equilibrium systems), it is very useful to realize the analogy of the behavior of these systems with the behavior of reactive dispersions in turbulence (see, e.g., Rietema, 1964; Olson and Stout, 1967; Tavlarides and Stamatoudis, 1981) Structural methods now commonly used to model small scale turbulence effects on reaction originated in the analysis of dispersions (e.g., Curl's "coalescence-redispersion" approach); in fact one should keep in mind that before complete mixing is achieved the reactive mixture is essentially a multiphase system.

in order to improve current atmospheric dispersion and reaction models. This fact, together with the lack of an exposition of the fundamentals of the simultaneous mixing and reaction problems covering specifically the spectrum of methods that can be used in environmental applications, dictates the necessity for a concise and coherent presentation of the subject. So, in this chapter after discussing briefly some basic concepts and terms, we attempt to show the range and interrelationship of the various approaches to the mixing-reaction problem by classifying them according to a general organizational scheme.

Thus we distinguish between

- *Eulerian Statistical* (or *global "fluid mechanical" or "mechanistic"*) approaches, and
- *Structural* approaches (not to be confused with the structural approaches employed in the modeling of turbulence in recent years), that include
 - (a) *Lagrangian trajectory methods*,
 - (b) distributed and lumped *Population Balance methods*, which encompass classical chemical reactor theories (e.g., the residence time distribution approach), and
 - (c) *"micro-structural"* (or *"micro-mechanistic" or "local fluid mechanical"*) modeling techniques, that focus on the description of the local concentration structure in small control volumes ("reacting laminae") at scales below the microscale of turbulence, and then attempt to deduce global properties of the turbulent system by viewing it as a random collection of such control volumes.

Naturally, a specific modeling application may contain elements from more than one of the above approaches.

In this chapter Sections 4.2 and 4.3 are devoted to an exposition of the fundamentals of the reactive turbulence problem. Basic terminology is reviewed and clarified, and important concepts are introduced. Then a comprehensive overview of the different modeling methods available, compactly organized in figures and tables

completes this exposition. The following sections deal with the systematic development of Eulerian models that are appropriate for spatially varying environmental systems. The focus is on methods that can be employed in the modeling of turbulent atmospheric plumes, the criteria being scientific validity and computational simplicity. In particular, pure and mixed conserved scalar closure approximations, including the "concentration field splitting method" that is adopted in this work, are developed to directly usable forms.

Presentation of details not directly related to the framework of atmospheric plume modeling that was described in Chapter 1 will be avoided in this chapter. Instead, references to original works and, more often, to reviews of particular problems or approaches will be given.

In conclusion, the scope of this chapter is to provide both a comprehensive introduction to the relevant literature and at the same time present a concise but structured exposition of the fundamental principles and methods underlying approaches for modeling reactions in turbulent fields.

Table 4-1
Examples of Applications
with Significant Interaction of Turbulence and Chemistry

APPLICATION	EXAMPLE
• <i>Continuous Flow Stirred Tank Reactors</i>	Kattan and Adler (1972)
• <i>Tubular Flow Reactors</i>	Pratt (1979)
• <i>Jet Stirred Reactors</i>	Clegg and Coates (1967)
• <i>Turbulent Jets</i>	Shea (1977)
• <i>Turbojet Plumes</i>	Borghini (1974)
• <i>Turbulent Shear Layers</i>	Broadwell and Breidenthal (1982)
• <i>Pollutant Dispersion from Stacks</i>	Builtjes (1983)
• <i>Photochemical Smog Formation</i>	Kewley and Bilger (1979)
• <i>Biological Flow Reactors and Waste Treatment</i>	Fan et al. (1971)
• <i>Combustors and Combustion Processes</i>	Williams (1985)
• <i>Turbulent Flames</i>	Chigier (1981)
• <i>Weakly Ionized Plasmas</i>	Shkarofsky (1974)
• <i>Hypersonic Ballistic Wakes</i>	Proudian (1969)
• <i>Reacting Gas Coolants for Heat Exchangers</i>	Richardson and Getz (1968)
• <i>Chemical Lasers</i>	Hayday and Chung (1979)

4.2 SIMULTANEOUS TURBULENT MIXING AND REACTION: BASIC CONCEPTS AND TERMINOLOGY

The evolution of a system of reacting species in a turbulent field is determined by the combined action of three processes: turbulent dispersion (or random local advection), molecular diffusion and chemical reaction.

Turbulent dispersion transfers the species through the action of the fluctuating random velocity. It reduces gradients of the mean concentration field and at the same time creates local inhomogeneities at the molecular level which, in a continuum description manifest themselves as random concentration fluctuations. These inhomogeneities are dissipated by the action of molecular diffusion. Chemical reactions take place at the same time and will in general be affected by the spatial distribution of species concentrations at both macroscopic and local (molecular) levels to a degree that depends upon the reaction order and rate as well as on the initial mixing state of the reactants.

Consider, for example, the process of turbulent mixing of two "feeds" – or portions of fluid in general – which at equilibrium (that is after a long enough time period) (*) can be mixed down to the molecular level and constitute a single phase-system; we call this a homogeneous-at-equilibrium system. Each feed is assumed to be perfectly mixed down to the molecular level at the inception of the mixing process; it may contain one or more species that may react with species of the same or of the other feed. Various situations are possible with two fluid feeds, e.g.:

- (a) mixing of finite amounts of two fluids in a process vessel, or in general in a confined space
- (b) mixing of a finite amount of one fluid with an "infinite" amount of another, as in the dispersion of an instant release of material – or "puff" – in the atmosphere,

(*) Such an equilibrium can be reached either in time, e.g., for a batch mixing process taking place in a vessel, or in space as for, e.g., a steady atmospheric plume where complete mixing is obtained only far enough downwind the source.

- (c) mixing of a continuous feed with an "infinite" fluid, as in the dispersion of a continuous plume in the atmosphere,
- (d) mixing of two continuous feeds,
- (e) mixing of a continuous feed with a mass of fluid which retains constant composition via chemical reaction, as in the ideal continuous flow stirred tank reactor, etc.

In cases (a) and (b) the mixing process evolves in time whereas in (c) and (d) it evolves in space. In case (e) the mixing process is in a steady state (possibly non-equilibrium) after an initial start-up phase has passed.

4.2.1 Stream and Age Mixing

The terms *stream mixing* (or *cross-stream mixing* or *reactant mixing* or simply *mixing*) and *age mixing* (or *self mixing* or *backmixing*) have been employed, respectively, to characterize the extreme cases of mixing between two "fresh" separate fluid feeds and of mixing of one or more feeds with fluid that achieved its current identity (different from its initial) through the action of processes (such as mixing and reaction) that take place in the flow system under consideration. Some authors go as far as to stress that stream and self mixing are completely different physical processes (e.g. Brodkey, 1967); in general these processes usually coexist but in certain cases one is dominant. Thus, stream mixing is more important in flows that show a dominant upstream-to-downstream character and are described by parabolic transport equations, whereas age mixing is more important in flows where convective recirculation is dominant; transport in such situations is described adequately by elliptic equations. As far as chemical reactions are concerned, stream mixing is more important in situations of parabolic type transport for the cases of both premixed and unpremixed reactants. In situations of elliptic type transport age mixing is the important process when the reactants are premixed but both stream and age mixing affect critically the evolution of the reaction system when the reactants are unpremixed. These qualitative notions are summarized in Table 4-2. Pratt (1979) presents some simple models

for the quantification of the description of pure as well as combined stream and age mixing processes. Other, more specific or technical terms such as *channeling*, *bypassing*, *dead-space flow* etc. are also used to describe special patterns of mixing, usually in process vessels, but they will not concern us here. (See, e.g., Himmelblau and Bischoff, 1968; Wen and Fan, 1975; Oldshue, 1983, for relevant discussions and details.)

4.2.2 Micromechanics of Mixing:

Relevant Scales

Let us now return to the mechanics of the mixing process of two fluid portions. Whether stream or age mixing is dominant (or are combined), portions of fluid of different chemical composition are first brought in contact – by the action of the turbulent velocity field and – then give origin to regions of fluid (“mixed zones”) of new chemical identity through the processes of molecular diffusion and perhaps chemical reaction. Assume for simplicity that molecular diffusivities of all species as well as kinematic viscosities of the two, initially separate but individually uniformly mixed, feeds are of the same order of magnitude, D and ν respectively. The turbulent energy of the flow field is dissipated at a rate ϵ . Then at scales large compared to the *Kolmogorov micro-length scale* ℓ_K , where

$$\ell_K \equiv \left(\frac{\nu^3}{\epsilon} \right)^{1/4} \quad (4.2 - 1)$$

turbulent velocity fluctuation distort the initial portions of different feeds by breaking, carrying, pulling and squeezing them into convoluted sheets and ribbons of decreasing thickness. The stretching, squeezing and breaking would continue indefinitely in the absence of molecular diffusion effects, that is if the Schmidt number

$$Sc \equiv \frac{\nu}{D}$$

was infinite ($D \rightarrow 0$). In reality molecular diffusion acts from the start of the mixing process and slowly – in comparison to turbulent phenomena – creates regions of fluid

Table 4-2
Dominant Type of Mixing Process
in Relation to the Initial State of Reactants
and the Type of Flow

INITIAL CONDITION OF REACTANTS	GOVERNING PDE FOR THE CONCENTRATION FIELD	DOMINANT TYPE OF MIXING
premixed or un-premixed	parabolic for flows with a dominant upstream-to-downstream character	stream-mixing
premixed	elliptic	age-mixing
un-premixed	elliptic	combined

that are mixed down to the molecular scale at the interphases of portions of different feeds. In fact, if Sc is of order unity or larger, Batchelor (1959) showed that when the patches of fluid approach a thickness of order $O(\ell_B)$, where

$$\ell_B = \left(\frac{\nu D^2}{\epsilon} \right)^{1/4} = \ell_K Sc^{-1/2} \quad (4.2 - 2)$$

is the *Batchelor micro-length scale*, concentration gradients normal to the patch are sufficiently large that the molecular fluxes balance the compression of the patch by the straining motion, and the creation of fluid zones mixed at the molecular level is the dominant physical process. If Sc is much smaller than unity, i.e. $\nu \ll D$, then the relevant microscale is the *Corrsin-Obukhov microscale* ℓ_C defined as

$$\ell_C = \left(\frac{D^3}{\epsilon} \right)^{1/4} = \ell_K Sc^{-3/4} \quad (4.2 - 2a)$$

(This is not to be confused with "Corrsin's dissipation scale" that is defined as the counterpart of Taylor's microscale for scalar diffusion and is discussed in Section 4.4 and in Chapter 5).

For diffusion of gases like CO, NO, NO₂, SO₂, etc., in the atmosphere, Sc is of order 1 and ℓ_K , ℓ_B assume approximately equal values; thus either scale is relevant.

Other microscales, of similar nature, have also been introduced in various models of local diffusion and reaction; among them the "*striation thickness*", first defined by Mohr (1957) as a measure of the thickness of "patches" of completely mixed material, has been very popular in the modeling of "lamellar microstructures" (see Section 4.3.2) in turbulent reacting flows (see, e.g., Ranz, 1979; Ou and Ranz, 1983ab).

Another quantity of interest in detailed descriptions of reaction-diffusion phenomena at the local level of laminar conditions is the rate at which the thickness of perfectly mixed "patches" diminishes with time. A simplified analysis assuming a uniform local (laminar) velocity gradient gives for the thickness $\ell(t)$ of the mixed zone (Middleman, 1977)

$$\ell(t) = \ell(0)(1 + \gamma^2 t^2)^{-1/2}$$

where γ is the constant strain rate of the laminar shear, approximately given by (see, e.g., Bourne, 1982; Baldyga and Bourne, 1984)

$$\gamma \simeq 0.5 \left(\frac{\epsilon}{\nu} \right)^{1/2}$$

4.2.3 Macro-fluids versus Micro-fluids

Macro-mixing versus Micro-mixing

So, before final equilibrium is achieved, any mixture will have some of the characteristics of a two-phase (or multi-phase) system, as for a certain period of time portions of the different feeds will be intermixed by turbulent motion down to a rather fine but still macroscopic level of very small “*fluid elements*” or “*fluid particles*” which preserve their different identity defined by chemical composition. A fluid which can be viewed in this way, i.e. as consisting of elements of different identity, is often called a *macro-fluid* in contrast to a *micro-fluid* (*) in which all different species are mixed down to the molecular level (see, e.g., Levenspiel, 1972). The small “structural elements” of a macro-fluid (which, when it corresponds to a homogeneous-at-equilibrium system is of course always in a transition state) are not always identified in the same way but we will not discuss this subject in detail here. Use of the term “fluid particle” dictates however a few comments. The concept of a fluid particle is widely used in Lagrangian descriptions of turbulent diffusion (see, e.g., Monin and Yaglom, 1971, 1975; Hinze, 1975; Seinfeld, 1975) as well as in population balance methods for modeling both single and multi-phase flow and reaction systems (see, e.g., Himmelblau and Bischoff, 1968). The identity of a fluid particle in such treatments is not necessarily determined by its composition; other properties such as, e.g., its temperature or its “age” (time it has spent in the flow field) are often used instead. Many other terms like “fluid element,” “material point of fluid”, “fluid lump”, “fluid clump”, “continuum element of fluid”, “fluid molecule”, have also been employed in

(*) Sometimes the terms macromixed and micromixed fluid (or reactor) are used instead (see, e.g., Pratt 1979).

the literature; however the context in which these terms are used is not always the same. For some authors a fluid particle (or element) has completely uniform "internal properties" (concentrations, pressure) and is so small (smaller than the appropriate microscale of turbulence) that its structure cannot be affected (e.g. distorted) by the turbulent motions. In this way it corresponds to a "point" of the *fluid continuum*. For others it can have larger dimensions, non-uniform internal structure and can be distorted by the action of the turbulent motions. In this way it corresponds simply to a Lagrangian *material volume* of fluid. Hinze (1975) discriminates between a *fluid particle* (which can only be advected by turbulence) and larger *fluid lumps* (which can be distorted and separated into smaller lumps or fluid particles). According to such a definition the only interaction of a fluid particle with its environment can only be purely molecular in nature (but of course can be approximately modeled as a larger scale random process, i.e. a coalescence and redispersion model of fluid particles can be used to simulate a "spreading" of properties actually due to molecular diffusion). Hinze (1975, §5.1) further distinguishes between *volume particles* and *property or substance particles*. A volume-particle is defined as a small constant volume of fluid following the (random or not) flow, whereas a property-particle is defined in terms of some property of the material constituting it and thus can be viewed as a collection of marked (by their chemical identity or age, etc.) molecules. If molecular effects are negligible the volume and property particle remain identical during any dispersion processes; otherwise the motion of the centroid of the property particle deviates from that of the original volume particle. A point worthy of noting here is that in fact the dispersion of a property due to molecular diffusion is *not* statistically independent of that due to macroscopic random turbulent velocities; see, e.g., Hinze (1975, §5.5).

The way in which fluid particles of different identities are distributed spatially in the flow field determines the *state* or *degree of macromixing* of the system (or "*the system's macrostate*"). Mean continuum properties, (that is first means of stochastic continuum quantities defined over "points" which are of the size of fluid particles), reveal and characterize this macrostate. Thus, if fluid particles from two feeds of

different chemical composition are uniformly distributed over a volume or area of the flow field, the mean concentration of any conserved species of the mixture will also appear to be uniform there. (*) As time passes compositions of individual volume fluid particles may change through the process of molecular diffusion until all such particles are identical and molecular uniformity has been achieved, but mean concentrations of the of the conserved species will remain the same. Thus, the degree of macromixing is determined (locally for a spatially varying system) by the "gross" characteristics of the flow i.e. *first moments* of random variables and characterizes uniformity of mixing at the level of fluid particles. Further, it is *insensitive* to the *degree* or *state* of *micromixing* (or "*system's microstate*") which refers to the finer structure of the flow field, at scales smaller than those of the fluid particles, down to the molecular level. For a given macrostate the instantaneous degree of micromixing of a system may vary from *complete segregation*, in which no observable zones of microscopically mixed fluid have been created and the fluid particles retain unaltered their initial identities (the mixture is a macro-fluid), to *maximum mixedness*, in which molecular diffusion has brought intimate mixing of individual molecules in the entire system (the mixture is a micro-fluid). This however does not necessarily imply that concentrations are also uniform in the mixture. In terms of continuum variables of the flow field, micromixing is revealed by their fluctuations and the variation of their higher order moments and correlations.

The distinction between these two different kinds or levels of mixing in a given system is of crucial importance, as far as the evolution of chemical reactions is concerned, for both premixed and unpremixed reactants. This was recognized in the 1950's by Danckwerts (1953, 1958) who introduced this distinction of mixing con-

(*) Some authors (e.g., Patterson, 1975) use the term macromixing in a different context, that is to describe a mixture is in a state of complete segregation (which in our terminology is one extreme state of micromixing) and the term micromixing to describe the state of maximum mixedness. This use of a term in very different contexts is unfortunately very common in the field and unavoidably causes confusion to anyone not familiar with the terminology of different authors.

cepts in chemical reactor theory (*) with ideas that were soon extended by Zwietering (1958) and Van Krevelen (1958). Danckwerts also introduced quantitative measures for the description of macrostates and microstates which since then have been used in chemical engineering literature almost exclusively to describe premixed reactants systems where age mixing is the dominant process.

Thus the *residence time distribution* (RTD), defined as the time response at the exit of a reactor for an instantaneous concentration pulse of inert tracer acting as input at time $t = 0$ at its entrance, where all properties are considered uniform over the exit and entrance, characterizes the state of macromixing of the reactor as a whole (see, e.g., Himmelblau and Bischoff, 1968; Levenspiel, 1972). Another *equivalent* definition, more closely related to the concept of *age mixing*, views the RTD as the probability density that a fluid particle which enters the reactor at time $t = 0$ will leave at time t .

RTD models defined in this way represent a method of modeling through macroscopic averaging and treat the reaction-flow field as a *lumped system* with a single entrance and a single exit (a "global concept"). Hence they are not appropriate to describe systems where stream mixing is dominant (since stream mixing is a process that basically evolves in space and not in time) and in general distributed systems that do not have a single entrance and exit and the complete distribution of properties in their "interior" is of interest. Although such an approach is not common in the literature one can generalize the classical lumped-system RTD concept to such distributed systems by defining it as a function of both time and *two* sets of spatial coordinates – one for a "source" and one for a "receptor" – again as the response (concentration) at the receptor for an instantaneous release of inert tracer at the source (i.e. a Green's function for the inert mixing – i.e. advection-diffusion – boundary value problem). In general the spatial distribution of mean concentrations (steady or not) in a flow system gives a complete characterization of its macrostate.

(*) Actually Danckwerts wrote of "scales of mixing and segregation" and of "mixing at the molecular level"; the prefixes "micro" and "macro" were introduced by Van Krevelen (1958).

4.2.4 Scale and Intensity of Segregation

According to Danckwerts the degree of micromixing of a system needs *two* parameters for a *local* description. These parameters are usually called the *scale* L_s and the *intensity*, I , of segregation. A variety of other names is also used for the concept of I such as *mixing effectiveness* (Pratt 1979), simply *segregation* (Brodkey 1966, 1967) and *unmixedness* (Hawthorne et al., 1948). Also the term *mixing parameter* is used for $-I$ and the term *contact index* for $(1 - I)$ (see Hill, 1976; Donaldson and Hilst, 1972).

Often the intensity of stream segregation is distinguished from the intensity of age segregation and different symbols such as I_s and I_α respectively are used (see, e.g., Brodkey 1967, 1975, 1981; Pratt, 1979).

The scale of segregation describes the degree to which the dispersing material has been "spread out" by the action of turbulence. In the case of stream mixing it is a measure of some typical average size of unmixed lumps of different feeds. As these lumps are pulled, contorted and break into smaller ones the scale of segregation is reduced. Quantitative definitions of L_s can be constructed in terms of spatial correlations of concentration fluctuations. Thus, if c' is the fluctuation of the instantaneous concentration of an inert species about its ensemble mean value $\langle c \rangle$, Brodkey (1967, 1981), for example, defines for the case of *uniform* $\langle c'^2 \rangle$ the scale L_s by

$$L_s = \int g_c(\mathbf{r}) d\mathbf{r} \quad (4.2 - 3)$$

where

$$g_c(\mathbf{r}) = \frac{\langle c'(\mathbf{x}) c'(\mathbf{x} + \mathbf{r}) \rangle}{\langle c'^2 \rangle}$$

L_s is an average over relatively large distances and thus it is a measure of the "large scale breakup process", "but not of the small scale diffusional process" (Brodkey, 1981). Quantities like g_c and L_s are in general difficult to be calculated and various methods have been proposed for their estimation (see, e.g., Brodkey, 1967; Patterson, 1981, 1983).

The intensity of segregation describes the effect of molecular diffusion on the mixing process. For the case of stream mixing it is basically a measure of the difference in concentration between neighboring lumps of fluid particles of the mixture; for age mixing it is defined as a measure of the difference in age of such lumps. Quantitative definitions of I appear in the literature in a variety of different forms (some of which are appropriate only for stream mixing and others only for age mixing). In the perspective of the present work particularly useful is the definition of I as the local intensity of fluctuations of an inert scalar

$$I = \frac{\langle c'^2 \rangle}{\langle c \rangle^2} \quad (4.2-4)$$

where $\langle c'^2 \rangle$ and $\langle c \rangle$ refer to the same space-time point. The intensity I as defined in (4.2-4) describes the quality of micromixing of an inert species with the background environment, the latter seen as a single component. Such a definition is useful mainly for cases of dominant *stream mixing*.(*) This quantity is a basic parameter of the Turbulent Reactive Plume Model described in Chapter 2 and we devote Chapter 5 to its estimation in the case of steady atmospheric point source plumes.

If stream mixing is complete on a molecular scale (maximum mixedness micromixing), or if only inert tracer is present for all ensemble realizations, then $\langle c'^2 \rangle = I = 0$. For steady state cases time averages are usually used as estimates of theoretical (ensemble) means. According to the definition (4.2-4) I will be equal to unity in the particular case of complete segregation with equal probabilities of tracer existing or not existing at the point and instant of measurement (in other words in cases with local concentration *intermittency* equal to 1/2; see Chapter 5). A major disadvantage of the definition (4.2-4) is the behavior of I for tracer concentrations tending to zero. Thus in the plume case both nominator and denominator of (4.2-4) go to zero as the plume boundaries are approached but the denominator decreases faster with I tending to infinite values.

(*) Pratt (1979) defines the intensity of segregation through (4.2-4) exclusively for stream mixing.

Other definitions of I attempt to express the state of mixing of two particular species A and B and thus use two stochastic concentration fields instead of the one employed in definition (4.2-4), e.g.,

$$I = -\frac{\langle c'_A c'_B \rangle}{\langle c_A \rangle \langle c_B \rangle} = 1 - \frac{\langle c_A c_B \rangle}{\langle c_A \rangle \langle c_B \rangle} \quad (4.2-5)$$

In this case I varies from zero, for a uniformly micromixed solution, to one, when A and B do not coexist anywhere. If non reacting A and B are mixed, and B is defined as *not* - A then $c'_A = -c'_B$, and (4.2-5) gives

$$I = \frac{\langle c'^2_A \rangle}{\langle c_A \rangle \langle c_B \rangle} = \frac{\langle c'^2_B \rangle}{\langle c_A \rangle \langle c_B \rangle} \quad (4.2-6)$$

which is very similar to (4.2-4). A possible advantage of (4.2-6) over (4.2-4) is that the denominator now does not go to zero as fast as in (4.2-4), since $\langle c_A \rangle$ and $\langle c_B \rangle$ cannot both be simultaneously zero, and thus its change is more easily compensated by changes in the nominator. For complete segregation $I = 1$ and

$$\langle c'^2_A \rangle = \langle c'^2_B \rangle = \langle c_A \rangle \langle c_B \rangle$$

Hence, for unpremixed reactants - where their initial variances of fluctuations

$$\langle c'^2_A \rangle_0, \langle c'^2_B \rangle_0,$$

correspond necessarily to complete segregation - we can write

$$I = I_s = \frac{\langle c'^2_A \rangle}{\langle c'^2_A \rangle_0} = \frac{\langle c'^2_B \rangle}{\langle c'^2_B \rangle_0} = -\frac{\langle c'_A c'_B \rangle}{\langle c_A \rangle_0 \langle c_B \rangle_0} \quad (4.2-7)$$

which is another definition of I , holding *only* for stream mixing.

For the definition of intensity of segregation in cases of dominant age mixing concentrations are viewed as functions of the species ages, that is the elapsed time $\alpha = t - t_0$ since the species molecule was introduced in the flow field. So let $c(\alpha)$ be the

instantaneous concentration at a point of tracer molecules that have age α . The mean of this variable at a point and instant can be expressed only as an ensemble average and any estimate would be the average over, say, N realizations of the dispersion phenomenon, in each of which the random variable $c(\alpha)$ takes the value $c_i(\alpha)$, $i = 1, \dots, N$:

$$\langle c_A(\alpha) \rangle = \frac{1}{N} \sum_{i=1}^N c_i(\alpha)$$

(Time averages are meaningless in this case.) The mean age of molecules at the point of measurement will be

$$\alpha_p = \frac{\int_0^{\infty} \alpha \langle c(\alpha) \rangle d\alpha}{\int_0^{\infty} \langle c(\alpha) \rangle d\alpha}$$

Then, the intensity of age segregation at a point is defined (see, e.g., Pratt, 1979) as the ensemble average of variances of the $c_i(\alpha)$'s about $\langle c(\alpha) \rangle$ at that point:

$$I_\alpha = \frac{\frac{1}{N} \sum_{i=1}^N \int_{\alpha^-}^{\alpha^+} [c_i(\alpha) - \langle c(\alpha) \rangle]^2 d\alpha}{\left[\int_0^{\infty} \langle c(\alpha) \rangle d\alpha \right]^2} \quad (4.2-8)$$

The limits of the integral in the summation of (4.2-8) are the lower and upper values of α for which $\langle c(\alpha) \rangle$ is non-zero.

Danckwerts (1958) defined a measure of age segregation for the reactor as a whole, i.e. the ratio of the variance of point ages to the variance of molecule ages throughout the reaction field

$$J = \frac{\text{var}\alpha_p}{\text{var}\alpha} \quad (4.2-9)$$

where

$$\text{var}\alpha = \overline{(\alpha - \langle \alpha \rangle)^2} \quad (4.2-10)$$

is the variance of the ages of all the molecules in the system ($\langle \alpha \rangle$ is the mean age of all molecules which are at some particular instant in the system), and

$$\text{var}\alpha_p = \overline{(\alpha_p - \langle \alpha \rangle)^2} \quad (4.2-11)$$

is the variance of mean ages at a point. In (4.2-10) averaging is meant over all molecules of the system whereas in (4.2-11) is meant over all continuum points of the system.

J is a global measure of the degree of molecular homogeneity in a system whereas I (for both stream and age mixing) is a local measure. J and I_α are measures only of atom ages and do not consider the chemical identify of atoms; thus they have no utility as measures of stream mixing effectiveness.

Another point that needs to be stressed here is that I (or I_α) as well as L_s are *expected* local properties of the field; obviously in an actual random realization of the field the mixing at a "point" will always correspond either to complete segregation or to maximum mixedness.

4.2.5 Mixing in Atmospheric Plumes

In the *dispersion of an atmospheric plume* it is typically assumed that axial diffusion is negligible and that recirculative convection phenomena do not take place. In such a case, where advection by the mean wind field and lateral dispersion are the only significant physical processes, the mixing of effluents with the background air down to the molecular scale is accompanied by a decrease of I (for stream segregation) from 1 to 0 in the downwind direction but I_α and J will always be equal to 1. They will be reduced from this value only if diffusion mixes effluent molecules of different ages; however as long as there are advection effects they will assume non-zero values.

4.2.6 Interaction of Mixing and Chemical Reaction

The effect of the mixing state on the evolution of reactions taking place in the flow field has already been stressed in the introduction of this chapter as well as in Chapter 1. Monomolecular reactions (that is with intrinsic linear kinetics) are affected only by the macrostate and their temporal and spatial evolution depends only on the mean concentration field of the reacting species. Thus, for lumped systems, the RTD alone is adequate to describe the macroscopically averaged evolution of linearly reactive

networks.

(a) The Effect of Rate Order

Reactions of order different from unity are in general affected by both the macro- and micro- state of the system as well as by the initial state of the reactants (pre-mixed or unpremixed) and the nature of the dominant mixing process (stream or age mixing). It must also be clarified here that controlling macro- and micro- states of evolving flow and reaction systems must always be identified for a stage of their evolution that is relevant to the reactions of interest. Thus, if a reaction is very slow and occurs in a flow system that evolves quickly towards equilibrium with respect to the mixing processes, it will not be practically affected by the early mixing states – since they correspond to times for which conversions are very close to zero. Hence, when slow reactions take place in a homogeneous-at-equilibrium flow system it is usually assumed that the latter has achieved its maximum mixedness microstate before the chemical processes have advanced significantly. On the other hand instantaneous or fast reactions are affected to a varying degree by the early mixing states of the system since the intrinsic kinetics of the reactions, under conditions of equilibrium mixing, would have produced non-negligible conversions at short times corresponding to these states. The comparison of the different rates at which the chemical and mixing processes evolve in a particular system and the subsequent characterization of a reaction as slow or fast should be done on the basis of appropriate characteristic time scales for the various processes. Such scales as well as nondimensional characteristic groups were used in Chapter 1 and will be further discussed in section 4.4.1 of this chapter.

(b) The Effects of Initial Conditions

The different effects of *molecular dispersion* processes on reaction evolution and their dependence on the *initial condition* of the reactants should also be mentioned here. Thus, in the case of *unpremixed* reactants, molecular diffusion is necessary to bring the reactants together at the molecular level so that reaction occurs. In this way it enhances the effective kinetic rate, for reactions of order greater than unity,

by homogenizing the mixture. The action of the same phenomenon, i.e. molecular diffusion, has opposite effects on the case of *premixed* reactants. Its action homogenizes the reactive mixture with inert dilutant (in the case of stream mixing) or with older, converted, mixture (in the case of age mixing). As a result it lowers the levels of concentration that determine the local kinetic rates and consequently the effective rate of reactions of order greater than unity decreases too.

Similarly, *random flow field* (turbulent dispersion) effects also depend on the initial state of the reactants. Although the action of both molecular and turbulent diffusion typically results in "spreading" of material this is done at different levels, that is at the molecular and the fluid particle level respectively. At the local fine scale level they are actually *antagonizing* processes. Indeed, turbulence creates local random concentration gradients and fluctuations which are dissipated by the action of the molecular diffusion. The correlations of fluctuating concentrations will be positive for premixed and negative for unpremixed species and therefore opposite effects on the observed ("phenomenal") rates are to be expected for these two cases.

In Table 4-3 we have summarized the different effects of molecular and turbulent dispersion phenomena on single-phase reactions of order greater than unity for both premixed and unpremixed reactants. (For reactions of order less than unity the various effects mentioned are generally reversed).

Table 4-3

Effect of Mixing on Reaction:
 Dependence on Initial State of Reactants
 (for Reaction Order Greater than Unity)

<i>DISPERSION PHENOMENON</i>	<i>SINGLE/PREMIXED SPECIES</i>	<i>UN-PREMIXED SPECIES</i>
<i>Molecular Diffusion</i>	Depresses the overall rate; it homogenizes the reactive mixture with the diluent	Enhances the overall rate by dissipating concentration fluctuations; its rates are more critical than for premixed species since it is necessary to bring the reactants together
<i>Turbulence (and stochastic initial conditions)</i>	Creates positive correlations of concentration fluctuations and enhances the overall rate because at non-diluted spots reaction takes place at faster rates	Creates negative correlations of concentration fluctuations and depresses the overall rate

4.3 METHODOLOGIES FOR THE DESCRIPTION OF TURBULENT REACTIVE SYSTEMS

As it was stated in Section 4.1, modeling methods for turbulent reacting systems can be classified as

- (a) *Eulerian Statistical* (or Global Fluid Mechanical or Mechanistic), and
- (b) *Structural*, including Lagrangian Trajectory Schemes, Population Balance Methods and/or Models of Local Laminar Micro-structures.

Elements of both approaches can be present in a particular model formulation at different organizational levels (Figure 4-1).

The choice and application of a particular method depends mainly on the *dimensionality* of the model that is assumed to describe satisfactorily the system under study. (e.g., lumped in space or in time etc.).

4.3.1 Fundamental Concepts of the (Global) Eulerian Statistical Approach

The Global Eulerian Approach is presented in relative detail in Sections 4.4 to 4.6, with emphasis on formulations and results that are simple and directly applicable to situations of interest in the present study. This systematic presentation also contains a survey of methods that have appeared in the literature. In the present sub-section we introduce this approach through a brief overview which, in combination with the brief survey of Structural Approaches of the next sub-section, reveal the range, complexity and diversity as well as the relationships of methods that have been used to attack the problem of reactions in turbulent fields.

Global Eulerian Statistical Approaches are based on the Eulerian local and instantaneous species transport equations, which incorporate reaction terms, perhaps in combination with the respective equations for momentum and energy transport (Section 4.4.1). These equations are assumed to describe globally (everywhere) the

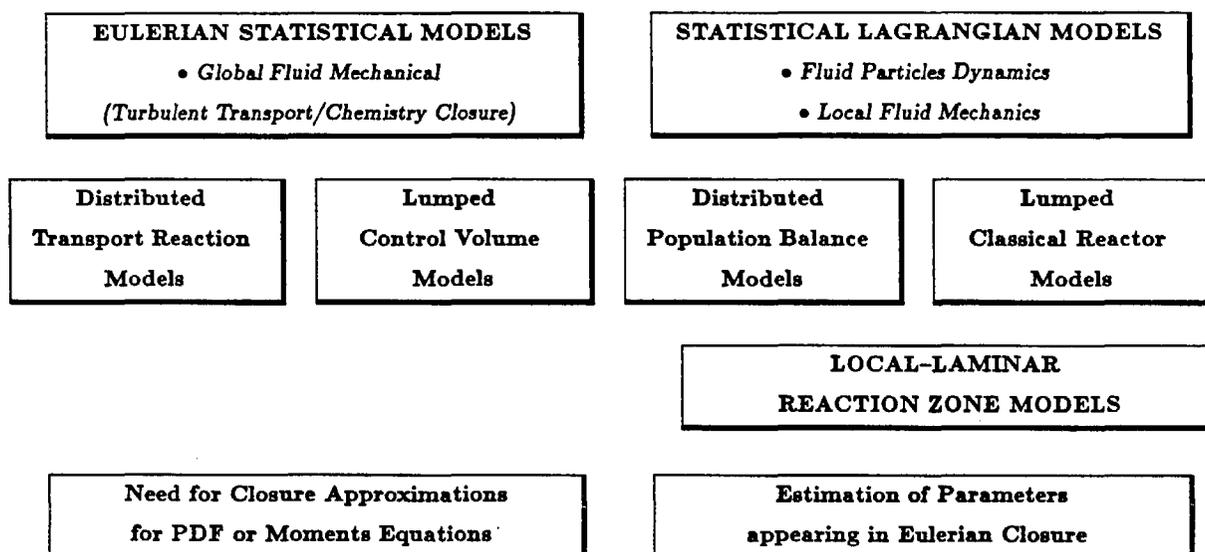


Figure 4-1
Modeling Approaches
for Chemical Reactions in Turbulent Fields

turbulent flow and reaction field, always at an instantaneous pointwise basis, and therefore, with the appropriate initial and boundary conditions constitute the starting point for model development. The stochastic nature of the flow field imposes the necessity for a statistical formulation that will provide information for the probabilistic characteristics of the unknown concentration (and perhaps temperature etc.) fields. The common procedure for constructing such a formulation is to derive, through ensemble averaging of the stochastic transport equations, equations for the first (or subsequently the higher order) moments of the unknown random quantities. As is well known, such an equation for the n -th moment will necessarily contain as new unknowns the correlations of fluctuations of stochastic variables of total order greater than n . Nonlinear chemical kinetic rates are responsible for the appearance of more such unknowns. Formulation of evolution equations for these new terms leads progressively to an infinite hierarchy which excludes the possibility of exact solutions (Closure Problem). An approximation scheme must be introduced at some level to account for the correlations of fluctuations. Such a scheme is called an *n -th order closure* if it is incorporated as a correlation approximation in the governing equations for the n -th moments. We shall further call "*chemical closure schemes*" the approximations of the correlations that arise because of nonlinear chemical rates to distinguish from "*transport closure schemes*" which account for the interaction of the random velocity and transferred quantity fields. Once estimates of moments (either joint or of a single random variable) are available, they can also be used as parameters in probability density functions of appropriate (assumed) form, a practice that has been extensively applied. In addition to moments or correlations modeling, a relatively limited range of reactive turbulence studies employing spectral schemes (for the reactive concentrations) has appeared in the literature (Section 4.5.3).

The alternative to deriving equations for the moments is to construct *functional evolution equations* for the entire joint probability density function of the unknown stochastic fields, starting again from the local instantaneous transport equations. The need of closure remains in these formulations too. Further, obtaining solutions for

such equations is a very difficult task. Other, heuristic schemes for the construction of such pdf's assume a certain artificial random picture of the structure of the flow continuum and therefore actually belong in the Structural Approaches that are discussed later.

The main modeling effort has been focused on 2nd order reactions of either premixed or unpremixed species. Various schemes have been formulated starting from the basic Eulerian framework. Their complexity depends mainly on the relative rates of chemical and dispersion processes. Thus, if the reaction rate is *very slow* we have seen that complete micromixing is achieved before the reaction starts, and fluctuation effects are negligible. Also, if the rate is *much faster* than the diffusion (case of "infinite" reaction rate) the effect of turbulence is controlling but the analytical presentation of the problem can still be simplified greatly. Indeed, equilibrium (for reversible reactions), or a limiting stoichiometry (for irreversible reactions) are assumed to be achieved instantaneously and hold pointwise wherever the reactants are micromixed. So, an algebraic steady state relation between random concentrations is available to reduce the complexity of the mathematical description. If the reaction rate cannot be considered infinitely fast, but still is not slow enough for equilibrium to be assumed with respect to mixing processes, the local instantaneous kinetics are also in an evolving state which depends on both macro and micro-mixing conditions. In this case further evolution equations for appropriate reaction progress variables must be derived in the place of the stoichiometric or equilibrium relations.

For both the cases of finite and infinite rate chemistry the tasks of formulating chemical and transport closure schemes have been in general pursued on two different lines:

(a) The most tractable (and presently successful) approaches attempt a *decoupling of mixing and reaction processes* or *indirect closure* (Section 4.6). Thus some conserved quantities ("conserved scalars"), such as stoichiometric invariants of the reactions or inert surrogate concentrations, are introduced to account separately for the transport effects. The probabilistic characteristics of the spatial and temporal

distributions of the conserved quantities (which of course are also random variables) are determined with the use of appropriate Eulerian transport equations, incorporating closure schemes of first or higher order. The respective characteristics of reactive species concentrations are related to them *a posteriori*. This step involves approximations equivalent to chemical closure in an indirect way. The above technique is more natural and effective for infinite rate chemistry but certain extensions have appeared for finite rate cases.

(b) The alternative is to invoke *directly* a chemical closure approximation either using the moments or the joint pdf evolution equations formulations (Section 4.5). The usual approach, employing moment transport equations is to relate correlations resulting from nonlinear chemistry to lower order moments or correlations of the reactive species concentrations. This can be done in principle either at the level of governing equations for the first moments or at a higher level after forming first dynamic equations for the correlation and introducing estimates for the new unknowns.

The general organization of Eulerian methodologies is given schematically in Figure 4-2 which is supplemented by Table 4-4.

4.3.2 Fundamental Concepts of the Structural Approach

Under the general title of Structural Approaches we classify all those methodologies that instead of starting by developing governing equations for the entire distributed flow and reaction field, considering it as a continuum, they focus on small scale entities which are assumed to be "structural units" of the field. The average behavior of these entities then determines locally or globally the evolution of the overall system.

Many different theoretical treatments are based on the concept of structural units. Their variation depends mainly

- (i) on how "complex" they assume this structural unit is, and
- (ii) on whether they attempt a detailed (spatially distributed) description of the flow

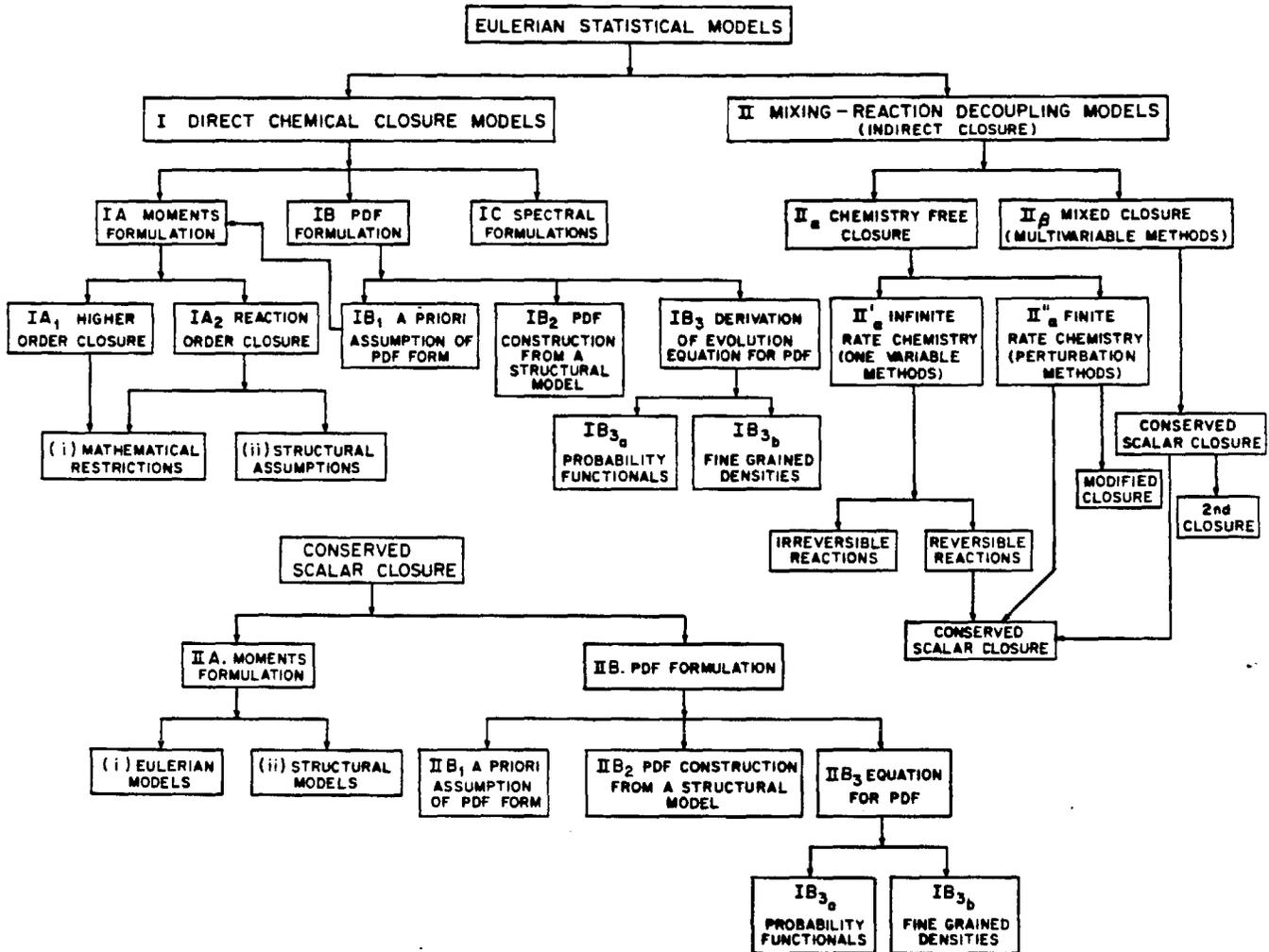


Figure 4-2

Eulerian Statistical Approaches
for the Treatment of Chemistry in Turbulent Fields

Table 4-4
Eulerian Statistical Approaches:
Selected References

TYPE OF MODEL	EXAMPLE
I Direct Chemical Closure	
IA Moments Formulation	
IA ₁ Higher Order Closure	<i>McCarthy (1970)</i>
IA ₂ Reaction Order Closure	<i>Patterson (1981)</i>
IB PDF Formulation	
IB ₁ A priori Assumption of PDF Form	<i>Bilger (1980b)</i>
IB ₂ Structural Model for PDF Construction	<i>Patterson (1973)</i>
IB ₃ Evolution Equation for PDF	
(a) Probability Functionals	<i>Petty and Reed (1972)</i>
(b) Fine Grained Densities	<i>O'Brien (1980)</i>
IC Spectral Formulations	<i>Lundgren (1985)</i>
II Indirect Chemical Closure	
II_α Chemistry Free Closure	
II' _α Infinite Rate Chemistry	<i>Toor (1962)</i>
II'' _α Finite Rate Chemistry	<i>Bilger (1980a)</i>
II _β Mixed Closure	<i>Lamb and Shu (1978)</i>

and reaction system or just develop estimates of macroscopic averages (a lumped picture of the system).

In some cases the structural entity can be viewed as a Lagrangian material volume following the flow which is large enough for the material fluxes through its boundaries (that are in general distorted by flow shear) to be caused not only by molecular diffusion but also by small eddies. In other cases this Lagrangian volume is considered smaller than the smallest eddies of the field and therefore it becomes equivalent to the (volume) fluid particle concept that was discussed in Section 4.2. Here we will use the term fluid particle (either volume or property particle) for the latter case and the term fluid lump or simply material volume for larger volumes. A fluid lump will in general have at any instant a non-uniform, random, internal structure. On the other hand a fluid particle is usually considered to possess completely uniform internal structure.

(a) First Structural Level Models

We shall call approaches that adopt the concept of fluid particles, as described above *1st structural level models*. The widest class of models relevant to arbitrary reaction and flow fields, the *Population Balance Models*, follows this line (see, e.g., Himmelblau and Bischoff, 1968; Froment and Bischoff, 1979, for introductions to the method). A set of properties is used to identify the various fluid particles. In a distributed description the properties include the three spatial coordinates of the particle ("external coordinates") plus properties that characterize the physicochemical state of the particle such as mass, volume, chemical composition, etc. ("internal coordinates"). If continuum properties, such as species concentration, density, pressure, temperature, etc., are to be used, they are taken to assume constant values over the internal continuum of the fluid particle. Distribution functions denoting how a population of fluid particles is distributed (or, more precisely, is expected to be distributed – see, e.g., Ramkrishna and Borwanker, 1973) in an extended coordinate or phase space that incorporates both internal and external coordinates can be defined.

Then evolution equations for these distribution functions in the extended space are constructed. The difficult part here is to devise appropriate models for terms in the equations that will account for mixing and reaction (that is molecular scale processes) among the constituent species of fluid particles. For premixed species each fluid particle behaves initially (that is at states of complete segregation of the reactive mixture and diluent system) as a batch reactor. Thus for very fast reactions the description is very simple. For moderately fast reactions the effects of stream mixing can be incorporated into dilution factors that will in general be proportional to the age of the particle. For unpremixed species however, some artificial mechanism of interaction between fluid particles must be invented.

(a1) *Lumped (1 dimensional) Systems*

Usually the Population Balance Equations are spatially averaged over control volumes with a single entrance and exit, or at least over control surfaces. When the only internal coordinate considered is the *age* of the fluid particles then these macroscopically averaged population distribution functions reduce to the well known *residence time distributions* or other similar concepts of the conventional chemical reactor theory which is based on lumped models formulations and considers mainly conditions of age mixing.

The original formulations of this method considered only extreme micromixing conditions, i.e. either complete segregation (Danckwerts, 1958; Zwietering, 1959), or maximum mixedness (Zwietering 1959), combined with arbitrary macromixing of the lumped system.

Different microstates of a system can also be modeled within the fluid particle framework. Thus one can assume that the fluid particles spend successive intervals of their residence time in the field under conditions of different but definite degree of segregation (e.g. they are completely segregated for an initial period and then they spend the rest of their residence time under conditions of maximum mixedness); these are the *Many-Environments models* (abbreviated as ME models). Two-Environment (see,

e.g., Goto and Matsubara, 1975), Three-Environment, as well as Four-Environment Models have appeared in the literature (see Mehta and Tarbell, 1983, for references). Typically these models are formulated for arbitrary macromixing (RTD) of the lumped system.

Alternatively, the evolution of microstates, which takes place through the action of molecular scale effects, can be approximated by processes of coalescence of fluid particles with initial different composition which form fluid lumps that immediately redisperse into new fluid particles of common composition. These are the *Coalescence and Redispersion models*, often referred to as "c-r" or "c-d" models, that provide an artificial but often useful model of molecular mixing that was originated in the work of Curl (1963) (for examples see, e.g., Kattan and Adler, 1967; Evangelista et al., 1969; Flagan and Appleton, 1974). (The analyses contained in these works are formulated for macromixing corresponding to either cstr or pfr conditions; Kattan and Adler (1972) presented a study for arbitrary macromixing).

Combinations of the ME and "c-r" approaches have also appeared in the literature. (see, e.g., Richie, 1980).

It must be stressed again that the main body of work that utilizes these approaches refers to systems that are at least partially lumped.

(a2) *Multidimensional Models*

Another approach, still at the 1st structural level, in principle appropriate to describe spatially distributed systems, is to develop schemes for the prediction of *random Lagrangian trajectories* of fluid particles. Such an approach would require the estimation of joint particle transition probability density functions. Reaction between unpremixed species will occur if two particles of the different feeds "collide". Of course in a formal Lagrangian description, individual particle trajectories cannot cross each other at a given time instant because of continuity constraints and thus a "collision" is interpreted as the approach of two trajectories at a micro-distance small enough to permit molecular interaction. This methodology is in principle an

extension of the Lagrangian theories for turbulent diffusion to nonlinearly reactive systems; however it seems too complicated to be of practical use in the near future (see also Shu, 1976; Lamb 1976)

(b) Second Structural Level Models

Models that consider as structural entities *fluid lumps* that have a non-uniform internal structure and can also be distorted or broken by the action of turbulence can be named *2nd structural level models*. In such approaches the focus is on the progress of reaction and molecular diffusion phenomena in a control volume small enough so that all fluid motions inside it can be described in a deterministic manner. The major interest in such approaches concerns unpremixed species reactions.

The simplest approaches in this area confine their control volume around the "interface" of two fluid particles or fluid "patches" (or "slabs" or "drops" etc.) of different feeds and try to develop estimates and evolution patterns for the *mixing and reaction zone* that is created at this interface based solely on the relative rates of diffusion and reaction. In this category we can classify models such as Mao and Toor's (1970) "slab diffusion model," Nauman's (1975) "droplet diffusion model," David and Villermaux' (1975) "interaction by exchange with the mean model," Klein et al.'s (1980) "droplet diffusion and erosion model," etc. These approaches in general assume that the macroscopic configuration of the system is simple enough so that conclusions concerning conversions etc. for the entire system can be deduced from the local results.

More complicated models consider effects of turbulent shear on local fluid volume deformation on the evolution of the reaction zone. Some formulations try to model "*lamellar structures*" of many reaction zones separated by unmixed material (see, e.g. Ottino, 1980, 1982; Ou and Ranz 1983ab). A similar approach is examined in a series of papers of both theoretical and experimental content by Bourne and coworkers under the general title "Mixing and Fast Chemical Reaction" (see, e.g., Angst et al., 1984 - see also Baldyga and Bourne, 1984). All these models use Eulerian molecular

diffusion-reaction equations at the local scale where flow is laminar.

4.3.3 Comments on the Interrelationships of the Models

An overall view of the range, diversity, and interrelationships of Eulerian and Structural Approaches is given schematically in Figures 4-1, 4-2 and 4-3. These Figures are supplemented by Tables 4-4 and 4-5 which contain selective lists of references arranged according to the general organizational scheme presented in these figures. It should be clear that a particular model intended for practical application may contain aspects of both methodologies at different levels of its structure. The various levels of description of the mixing processes that are common in chemical reactor theory and their connection are shown schematically in Figure 4-4.

The Eulerian Approach is more straightforward (although it provides less insight on the local evolution of mixing) than the Structural Approaches (which, nevertheless, make extensive use of ad hoc assumptions and have been limited mainly to turbulent fields of very simple average macroscopic configuration). Thus the Eulerian methodology seems more appropriate for describing complex, spatially varying, systems that occur in environmental applications. For such studies the role of the structural approach can be supportive by providing estimation of certain parameters arising from closure approximations.

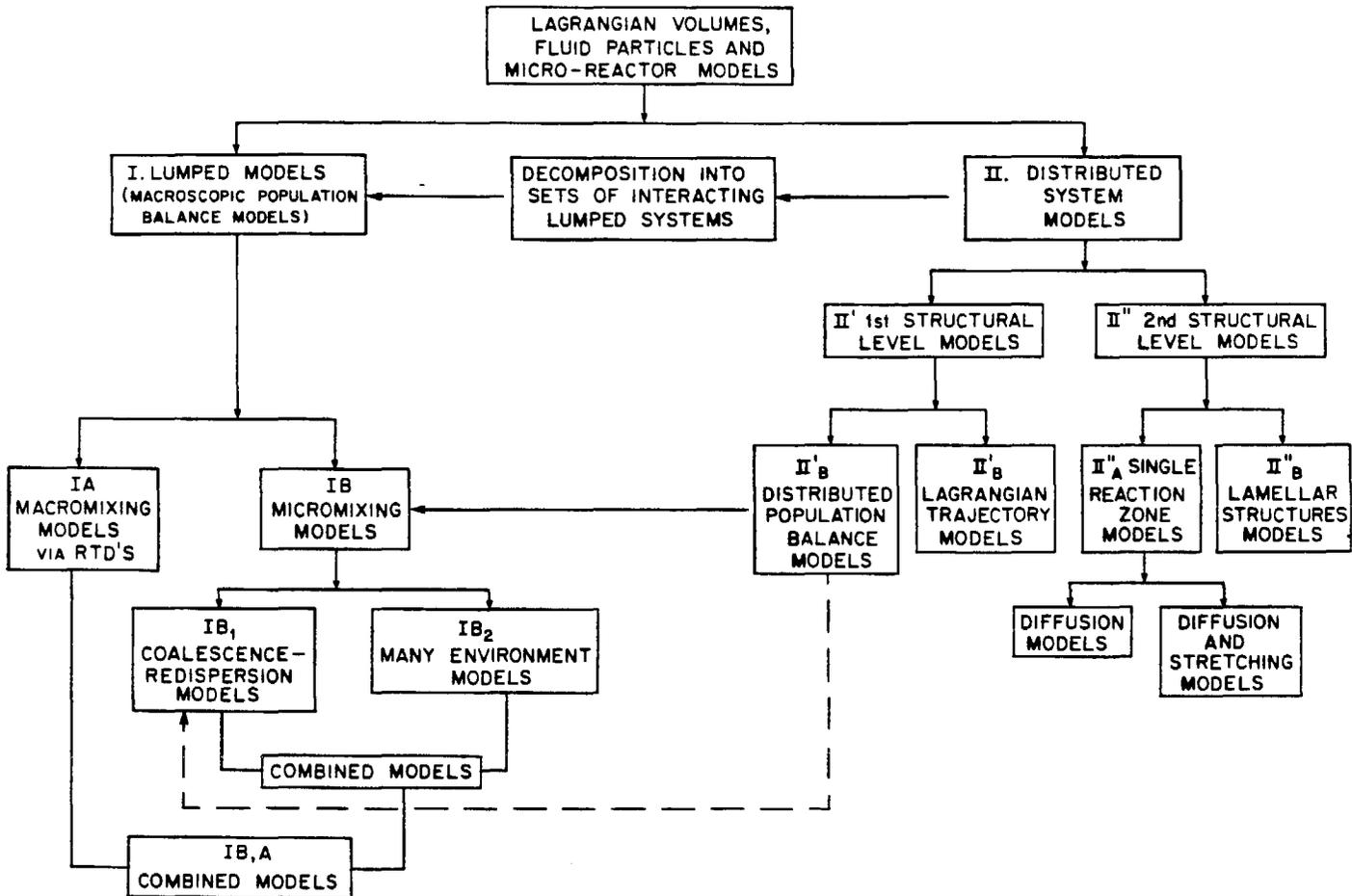


Figure 4-3
 Lagrangian Statistical Approaches
 for the Treatment of Chemistry in Turbulent Fields

Table 4-5
Lagrangian Statistical Approaches:
Selected References

TYPE OF MODEL	EXAMPLE
I Lumped Models	
IA Macromixing via RTD's	<i>Naumann (1981)</i>
IB Micromixing Models	
IB₁ Coalescence-Redispersion	<i>Kattan and Adler (1967)</i>
IB₂ Many Environments	<i>Mechta and Tarbell (1983)</i>
IB_{1,2} Combined M-E/C-R Models	<i>Richie (1980)</i>
IAB Combined Macro- and Micro-Mixing	<i>Kattan and Adler (1972)</i>
II Distributed Systems	
II' 1st Structural Level	
II'_A Distributed Population Balances	<i>Himmelblau and Bischoff (1968)</i>
II'_B Lagrangian Trajectories	<i>Lamb (1976)</i>
II'' 2nd Structural Level	
II''_A Single Reaction Zone	<i>Bourne (1982)</i>
II''_B Lamellar Structures	<i>Ou and Ranz (1983ab)</i>

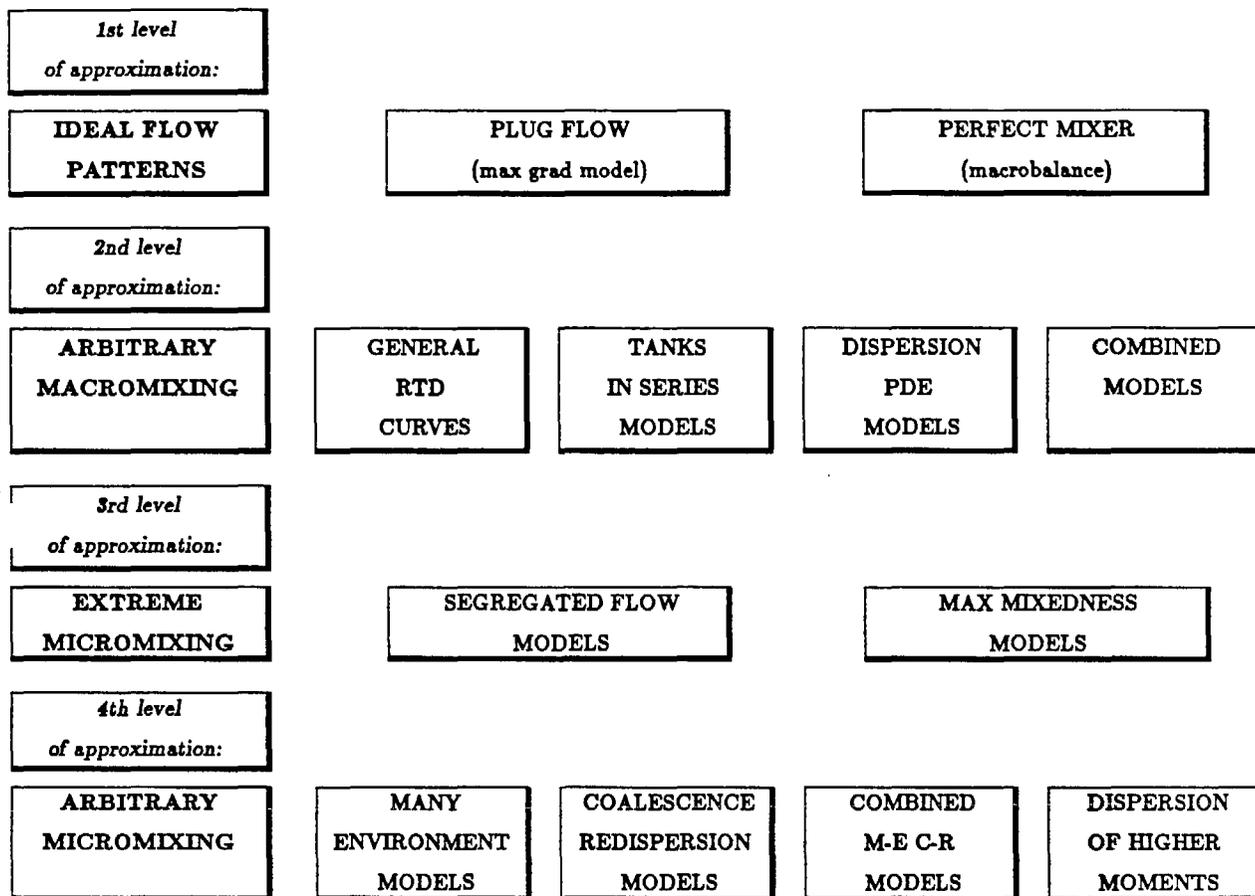


Figure 4-4
Levels of Description of Mixing
in Reactive Systems

4.4 THE EULERIAN STATISTICAL APPROACH: MODEL DEVELOPMENT

4.4.1 General Considerations

The starting point of the Eulerian Statistical or Global Fluid Mechanical Approach to turbulent reacting flows is the continuity equation for each of the species of the reacting and diffusing mixture. This equation is assumed to hold instantaneously and pointwise in the field. A general form for it is (see, e.g., Bird et al., 1960; Slattery, 1972) in the case of a binary mixture

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{u}) = -\nabla \cdot \mathbf{j}_A + \tilde{r}_A \quad (4.4-1)$$

where \mathbf{u} is the instantaneous mass average velocity of the mixture, ρ_A is the mass density (or mass concentration) of the species A , \mathbf{j}_A is the rate of molecular diffusion of A (diffusive flux) with respect to \mathbf{u} , and \tilde{r}_A is the rate of production (or dissipation) of A by chemical reaction per unit volume expressed in terms of the mass densities of A and of the species that participate in reaction with it. Equation (4.4-1) can of course be written for the instantaneous value of molar concentration c_A ; however, in this case the molar average velocity must be used instead of the mass average velocity and such an approach is not very convenient for systems of variable density (Hill, 1976). The way it is stated in (4.4-1) species transport describes equally well both compressible and incompressible flows. With the use of the mass fraction Y_A and assuming that Fick's law for a binary mixture is valid

$$\mathbf{j}_A = -\rho D_A \nabla Y_A$$

where Y_A is the mass fraction of A , ρ is the mixture density and D_A is the molecular diffusion coefficient of the species A with respect to the mixture (usually a strong function of concentration), and if

- (a) either $Y_A \ll 1$, or
 (b) the mass density ρ is uniform and constant in time

then we can write (4.4-1) as

$$\frac{\partial c_A}{\partial t} + \mathbf{u} \cdot \nabla c_A - \nabla \cdot (D_A \nabla c_A) = r_A \quad (4.4-2)$$

where the reaction rate r_A is expressed in terms of the molar concentration of the reacting species. When D_A can be assumed constant (4.4-2) becomes

$$\frac{\partial c_A}{\partial t} + \mathbf{u} \cdot \nabla c_A - D_A \nabla^2 c_A = r_A \quad (4.4-2a)$$

This form of species transport equation is strictly applicable to isothermal, constant-pressure, binary mixtures of uncharged substances. For multicomponent mixtures \mathbf{j}_A will depend upon the gradients of chemical potential of all species in the mixture as well as on the temperature gradients.

For atmospheric applications one can usually assume that the overall mass density of the air and pollutant mixture is uniform and constant and that this mixture is sufficiently dilute with respect to the relative species so that (4.4-2) is valid. Further the heat of reaction and reaction induced density changes in these situations are small enough so that the velocity $\mathbf{u}(\mathbf{x}, t)$ and the temperature $T(\mathbf{x}, t)$ fields can be considered independent of the reaction, the latter field being practically uniform for not very large spatial scales. Under such conditions the species transport equation is uncoupled from the simultaneous momentum and energy transport dynamics and is adequately approximated by (4.4-2), always on a stochastic instantaneous-pointwise basis (see, e.g., Seinfeld, 1975, Section 6.1.1). One can then proceed to develop equations for the moments of concentration by ensemble averaging this equation (traditional approach) or follow statistical-mechanical approaches (see Sections 4.5.2, 4.5.3) to formulate functional equations for the probability density functions of concentrations.

In a rather simplifying approach – which is more directly related to the perspective of environmental systems analysis and the present work — one can assume that

the interaction between the random concentration and temperature fields takes place only through the dependence of the chemical reaction rate term on the temperature and the system is insensitive to other temperature and flow field interactions which can be considered negligible. Such an approach can also be extended to treat effects of fluctuations of solar radiation on the evolution of photochemical reactions. The key modeling assumption is that all effects of gradients and turbulent fluctuations of the temperature or the radiation field can be incorporated completely in spatially varying and fluctuating chemical kinetic coefficients. Kewley (1978) employed such a technique for a simplified study of the effect of temperature fluctuation on the value of the photostationary state parameter in the ozone-nitrogen oxides photolytic cycle in the atmosphere (see Chapter 3 and Appendix A3.3). His conclusion, specifically for the $\text{NO}_x - \text{O}_3$ system, was that, when the action of temperature variations is felt only through the dependence of the kinetic coefficients on them, their effect can be neglected, at least at a first approximation.

Thus, here we focus attention mainly on equation (4.4-2) for stochastic transport and reaction with reaction terms depending practically only on concentrations of the species. A set of equations of this type, with one corresponding to each reactive species, together with the appropriate initial and boundary conditions, and given the appropriate statistical characteristics of the independently varying velocity field $\mathbf{u}(\mathbf{x}, t)$, is assumed to describe completely the evolution of the system of concentrations. The reaction term appearing in (4.4-2), $r_A(\mathbf{x}, t)$, will be a *local* function of the reactive species concentration where the latter are assumed instantaneous, random point variables. The kinetic rate forms that have been most extensively studied up to now are

$$r_A = -kc_A^n \quad (4.4 - 3)$$

for a single-species reaction with $n = 1$ (linear kinetics) or $n = 2$, and

$$r_A = -kc_Ac_B \quad (4.4 - 4)$$

for 2nd order reactions between two species A and B :



Extension to reversible reactions with the reverse reaction also obeying one of the above laws are straightforward and on the same lines as the irreversible reactions. (*)

The stochastic nature of equation (3.4-2) and therefore of the dependent variable c is due to the stochastic nature of the turbulent velocity field. Another possible source for randomness in c may be due to the presence of statistical initial conditions; however, we will not be concerned with this possibility here (see, however, Section 3.5.1 for some relevant references).

The stochastic nature of the governing Eulerian transport equations for dispersion with reaction leads to the same fundamental problems of analytical description as inert dispersion. Thus a complete description of the random concentration fields is possible only through the knowledge of the probability density functions of concentrations at each point in space and time. The standard alternative to seeking these pdf's is a description through equations for moments of the stochastic fields. Such a procedure starts typically by introducing Reynolds type decomposition of the random variables, that is $\mathbf{u} = \langle \mathbf{u} \rangle + \mathbf{u}'$, $c = \langle c \rangle + c'$, in the equations and of course leads to a moments closure problem, typical and unavoidable in turbulence theory. (Eulerian formulations for evolution equations of the entire pdf have analogous closure problems). A major difference between describing inert and reactive species

(*) One must keep in mind that relations like (4.4-3) and (4.4-4) do not necessarily reveal the kinetic mechanism of the chemistry at the molecular level (see, e.g., Laidler, 1965; Emmanuel and Knorre, 1973). They are phenomenological approximations of molecular processes at the continuum level - exactly as the common transport equations of mass, momentum and energy - and must always be interpreted in this way. Certain approximations may have been incorporated in such laws; thus, for example a bimolecular reaction is often approximated by a linear (or pseudo-linear) kinetic law by use of the assumption that the concentration of one of the reacting species is so large that is not practically affected by the evolution of the reaction. However, despite this assumption the effects of turbulent mixing on such a reaction will be similar to those for a higher order (non-linear reaction) since, e.g., from unpremixed reactants dispersion processes are necessary to bring the two species together in order to react although formally the rate seems to depend on one reactant only.

dispersion occurs however in the case of nonlinear chemical kinetic rates as it was discussed earlier in this chapter as well as in Chapter 1. Such a reaction rate produces *self-interaction*, as in the Navier-Stokes equations, which leads to the appearance of higher order correlation terms between the fluctuating parts of concentrations. This makes the closure problem more complicated because of the presence of more and higher order unknowns than in the case of inert dispersion.

Thus, for example, the rate $r_A = -kc_Ac_B$ will induce, after ensemble averaging, a second order correlation appearing in the dynamic equation for the first moment of c_A :

$$\langle r_A \rangle = -k \langle c_A \rangle \langle c_B \rangle - k \langle c'_A c'_B \rangle$$

The magnitude, and hence the importance, of these higher order correlations which describe the local homogeneity, or completeness of mixing, in the reaction field depends in general on the relative intensity of all three phenomena that take place simultaneously, that is the mixing processes (molecular and turbulent diffusion) and the chemical reaction .

In order to estimate the relative importance of these phenomena one can proceed directly from (4.4-2a) by transforming it into dimensionless form (see Hill, 1976)

$$\frac{\partial C}{\partial t_*} + N_T \mathbf{U} \cdot \nabla_* C - N_D \nabla_*^2 C = N_R \quad (4.4 - 5)$$

Here

$$t_* = \frac{t}{\tau}, \quad \nabla_* = L_0 \nabla, \quad C = \frac{c}{c_0}, \quad U = \frac{u}{u_0}$$

where L_0 , τ , u_0 , c_0 , are characteristic length, time, turbulent velocity, and concentration scales. A reaction rate scale r_0 is used to non-dimensionalize the chemistry.

Here N_T , N_D , N_R are dimensionless time ratios

$$N_T = \frac{\tau}{t_T} \quad (4.4 - 6a)$$

$$N_D = \frac{\tau}{t_D} \quad (4.4 - 6b)$$

$$N_R = \frac{\tau}{t_R} \quad (4.4 - 6c)$$

with t_T , t_D , t_R characteristic times scales of the turbulent dispersion, molecular diffusion and chemical reaction processes. τ must be set equal to one of them; then the above time ratios become either equal to unity or to typical dimensionless groups which are in use in reaction and dispersion analyses (Peclet and Damköhler numbers). From the non-dimensionalization procedure the time scales have to be

$$t_T = \frac{L_0}{u_0} \quad (4.4 - 8a)$$

$$t_D = \frac{L_0^2}{D} \quad (4.4 - 8b)$$

$$t_R = \frac{c_0}{|r_0|} \quad (4.4 - 8c)$$

However, special care is needed in interpreting the significance of this direct approach, mainly as far as the choice of an appropriate L_0 is concerned. This is due to the fact that molecular and turbulent dispersion processes do not actually "compete" regarding how fast they will reduce gradients of concentration over the same *macroscopic* distance, say L_0 . From that perspective one would expect that $t_D \gg t_T$ in general, and of course, as is well known, molecular dispersion is usually neglected in inert scalar turbulent transport studies. The importance of molecular diffusion is in producing micromixed spots where reaction can occur; thus its rate seems to be relevant mainly with respect to distances corresponding to neighboring random concentration differences maxima that occur in volumes locally macromixed but incompletely micromixed. (*)

Considering these facts some researchers (see, e.g., Brodkey, 1975) assume that it is more reasonable to define t_T in terms of some macroscopic turbulent length scale L_0 which is characteristic of the spatial persistence of mean gradients, and t_D in terms of another length scale ℓ_0 typical of the spatial scales at which the effect of

(*) For the problems of interest in this study it is the comparison between this particular rate and the reaction rate that is most important. In the closure "solution" adopted by the TRPM the effects of molecular diffusion are actually incorporated in the phenomenal conversion rate term of the governing equation and not in the transport term.

molecular processes is felt directly (see, e.g., Bourne, 1982). Thus

$$t_T = \frac{L_0}{u_0} \quad (4.4 - 7'a)$$

$$t_D = \frac{\ell_0^2}{D} \quad (4.4 - 7'b)$$

$$t_R = \frac{c_0}{|r_0|} \quad (4.4 - 7'c)$$

Thus a global description, as provided by (4.4-5) is essentially abandoned and the analysis proceeds separately at two different scale levels, the local scale being viewed in the spirit of the second level structural models of Section 4.3.2. However, even in this approach, it is still in general difficult to decide which is the most appropriate choice for the characteristic scales. A first problem is the selection of a proper turbulent macro-length scale, especially in cases like the atmospheric plume where turbulence of different scales interacts in different ways with the other processes. (See also Builtjes, 1983; Libby and Williams, 1980 - Section 1.16; Bilger, 1980, for relevant discussions). A second problem is what the most appropriate scale ℓ_0 should be. Typically one of the microscales discussed in Section 4.2.2 (depending on the value of Sc) is assumed to be a good choice. If we set, e.g., $\ell_0 = \ell_K$, the Kolmogorov length microscale given by (4.2-1), we obtain $t_D = t_K$ where $t_K = (\nu/\epsilon)^{1/2}$ is the Kolmogoroff time scale.

The three characteristic time scales introduced here are measures of the time needed for

- (i) achieving *mean* uniformity by turbulent mixing (t_T),
- (ii) achieving detailed local uniformity (i.e. complete micromixing) by molecular diffusion, thus being a characteristic time for the decay of fluctuations of a scalar field (t_D), and
- (iii) of reaching chemical equilibrium or some limiting stoichiometry (t_R).

The magnitude of the ratios of these time scales, given by the dimensionless groups N_T , N_D , N_R after a choice of τ has been made, characterizes the relative rates of the processes corresponding to the nominator and denominator of the group. Traditionally, the ratios of turbulent and molecular dispersion to chemical rates are

named first and second type Damköhler groups respectively and denoted as Da_I , Da_{II} .

When there are *no* gradients in the mean concentration field then the single dimensionless ratio N_R defined for $\tau = t_D$ – in which case it is a second type Damköhler group Da_{II} , (*) also called *mixing modulus* by some authors (e.g., Bourne, 1982) – is sufficient to determine the relative importance of the terms $\langle c_A \rangle \langle c_B \rangle$ and $\langle c'_A c'_B \rangle$ in the kinetic rate term (when we consider the reaction $A + B \rightarrow \text{Products}$) and the degree at which the evolution of the reactive system is determined by the intrinsic kinetics or the rate of molecular diffusion. This was discussed in Chapter 1 where, for small to moderate intensities of segregation, and for species that have molecular diffusion coefficients of approximately the same magnitude D , it was shown how

$$N_R = Da_{II} = \frac{t_D}{t_R} = \frac{k[\langle c_A^* \rangle + \langle c_B^* \rangle] \ell_d^2}{2D}$$

can be suggested as a local estimate of the second Damköhler group when appropriate values of the concentration scales $\langle c_A^* \rangle$ and $\langle c_B^* \rangle$ are used.

Finally, if we want to characterize a chemical reaction as slow or fast in an arbitrary turbulent concentration field we must take into account the relative magnitude of both the first and second Damköhler groups. If for example we assume that $t_T > t_D$, then $Da_I > Da_{II}$ and the various regimes of chemical rates can be identified as follows:

- (a) $Da_{II} \ll 1$: (infinitely) fast chemistry, mixing limited conversions,
- (b) $Da_{II} < 1 < Da_I$: moderately fast chemistry, interaction of turbulence and chemical reaction,
- (c) $Da_I \ll 1$: slow chemistry, no effects of turbulence on reaction rate.

4.4.3 Chemical Closure

As it has been already mentioned, Chemical Closure can be obtained by either “direct” or “indirect” (i.e. mixing–reaction decoupling) methods; the different routes

(*) It is very interesting to note that the Damköhler group is analogous to the Thiele modulus in heterogeneous catalysis and to the Hatta number that appears in modeling absorption with simultaneous reaction.

followed by these approaches as well as their interrelationships were also briefly presented there. In the following sections we consider a more detailed development of these methods, following basically the moments formulation and providing information and references for the pdf formulation. The focus is on the methods that seem more promising for applications from the viewpoint of justification, generality and computational simplicity. The presentation here is confined mainly to practically isothermal-constant density conditions, relevant to those of typical atmospheric systems. For discussions of the problems related to non-isothermal cases see, e.g., Libby and Williams (1980), Williams (1985).

4.5 DIRECT CHEMICAL CLOSURE

4.5.1 Moments Formulation

Direct closure methods that employ moments approximations attempt to express correlations of the type appearing in the last term of the r.h.s. of (1.3-8) in terms of more tractable (i.e. more easily estimated) variables.

As introductory attempts towards a better understanding of the problem there have been several studies of the most simple nonlinear rate case, i.e. that of a single species-2nd order reaction evolving in a monodimensional system (e.g. a macroscopically mixed volume or a pfr). The governing (stochastic) equation will be

$$\frac{dc_A}{dt} = -kc_A^2 \quad (4.5 - 1)$$

The initial conditions may also be assumed stochastic.

O'Brien (1966) compared expressions for $\langle c_A(t) \rangle$ and $\langle c_A'^2 \rangle$ obtained by averaging the exact solutions of this equation for Gaussian initial conditions with the predictions for these quantities computed using the third moment discard, quasinormal, and direct interaction (DIA) approximations. (*) None of the approximations behaved satisfactorily when the relative amplitude of initial fluctuations was large. Later O'Brien (1968) recognized that since c_A is a nonnegative random variable, its moments must satisfy Liapounov's inequality (Uspensky, 1937):

$$\langle c_A^b \rangle^{a-c} \leq \langle c_A^c \rangle^{a-b} \langle c_A^a \rangle^{b-c}, \quad a > b > c \geq 0 \quad (4.5 - 2)$$

where a, b, c are constants. As an illustration, the third central moment of c_A must satisfy

$$\langle c_A'^3 \rangle \geq \langle c_A \rangle \langle c_A'^2 \rangle \left(\frac{\langle c_A'^2 \rangle}{\langle c_A \rangle^2} - 1 \right)$$

(*) See, e.g., Leslie (1973) for details on the quasinormality assumption and the DIA.

It is obvious that if one adopts, say, the third moment discard approximation, $\langle c_A'^2 \rangle / \langle c_A \rangle^2$ must be ≤ 1 at all times. To avoid unrealistic restrictions on the initial fluctuations, O'Brien (1968) proposed a so-called "inequality preserving closure approximation" (IPCA) so that Liapunov's inequality is always satisfied. O'Brien again compared the predictions of his IPCA with the exact solutions of (4.5-1) and found satisfactory agreement. O'Brien and Eng (1970) generalized the closure for reaction order one to three, and O'Brien and Lin (1972) used a different IPCA for two-species reaction with spatial dependence. Lee (1973) presented a "generalized direct interaction approximation". All of these approximations appeared to behave satisfactorily when tested against (4.5-1). However, since each of these closure schemes was developed and tested mainly on a simple system, namely (4.5-1), there is no assurance that they will hold when applied to the full continuity equations.

There are relatively few direct closure schemes that have been applied to either single- or multi-species reactions using the full continuity equations for reactive scalars (i.e. (4.4-2)). A "brute force" approach was that of McCarthy (1970). By discarding fifth order cumulants, he developed a hierarchy of (seventy eight) differential equations for single-point concentration moments and microscales.

Later Lin and O'Brien (1972) presented a closure theory which incorporates Lin's (1971) third order IPCA for the reaction terms and Lee's (1966) modification of the quasnormal approximation for the convective terms. Computations of the decay of moments and spectra of A were carried out for various conditions. The decay of $\langle c_A \rangle$ and $\langle c_A'^2 \rangle$ was found to depend primarily on the second Damköhler number (see Section 4.4).

Hilst et al. (1973) combined a third order IPCA (different from that of Lin, 1971) for the reaction term $c_A' c_B'$ with an "invariant model" (Donaldson and Rosenbaum, 1969) for the convection term. Hilst et al. then applied the model to the reaction of O_3 and NO emanating from four cross-wind freeway line sources and solved the resulting 12 coupled differential equations numerically. Borghi (1974, 1979) has also investigated the probability of higher order direct closure; he addressed non-isothermal

problems with all the consequent complications.

Donaldson and Varma (1976) discussed second-order techniques for both transport and chemical closure and applied them to idealized dispersion-reaction problems (among which there was the case of point source dispersion-2nd order reactions with the background). They further discussed issues related to more realistic situations.

Due to their mathematical complexity and the lack of experimental support, none of the closure schemes mentioned above appears to be useful at this time in applications to chemical and environmental engineering (in particular atmospheric pollution) problems.

Some steps towards a more simple approach have been proposed by Patterson (1981, 1983) whose closure suggestion is based on a "quasi-equilibrium" hypothesis (*) that assumes irreversible chemistry so fast that segregation is complete everywhere, all the time ($I = 1$), but the mixing rate still affects chemical conversions (obviously through dilution of the reactants concentrations in their segregated volumes caused by the diffusion of product and/or inert material). Consider the reaction $A + B \rightarrow P$ of unpremixed A and B , which is so fast that A and B remain totally segregated from one another. Hence (from Section 4.2.4),

$$\langle c_A'^2 \rangle = \langle c_B'^2 \rangle = \langle c_A \rangle \langle c_B \rangle$$

The rate of decrease of $\langle c_A \rangle \langle c_B \rangle$ due to reaction may be expressed as follows:

$$-\left(\frac{\partial (\langle c_A \rangle \langle c_B \rangle)}{\partial t}\right)_r = -(\langle c_A \rangle \langle c_B \rangle) \left(\frac{\partial \langle c_A \rangle}{\partial t}\right)_r \quad (4.5 - 3)$$

because

$$\left(\frac{\partial \langle c_A \rangle}{\partial t}\right)_r = \left(\frac{\partial \langle c_B \rangle}{\partial t}\right)_r \quad (4.5 - 4)$$

when they are due only to chemistry.

(*) Unfortunately Patterson's assumptions are not always stated explicitly; he just proposes the formulation we discuss here for "infinite rate irreversible kinetics." However in such a case mixing and reaction are naturally uncoupled and the closure problem is trivial (see Section 4.6).

We also have

$$-\left(\frac{\partial \langle c_A \rangle \langle c_B \rangle}{\partial t}\right)_r = \left(\frac{\partial \langle c_A'^2 \rangle}{\partial t}\right)_r \quad (4.5 - 5)$$

Patterson (1981, 1983) now sets

$$\left(\frac{\partial \langle c_A'^2 \rangle}{\partial t}\right)_r = \left(\frac{\partial \langle c_A'^2 \rangle}{\partial t}\right)_m \quad (4.5 - 6)$$

This means that the rate of dissipation of fluctuations of the reactive species due to chemical processes alone is exactly the rate of dissipation caused by molecular diffusion effects. This assumption expresses the fact that all reactive material coming to a state of complete micromixing through molecular diffusion is immediately consumed by chemical reaction. Hence, now in the place of the chemical rates expressions one can put

$$\begin{aligned} r_A = r_B &= \left(\frac{\partial \langle c_A \rangle}{\partial t}\right)_r = \left(\frac{\partial \langle c_B \rangle}{\partial t}\right)_r = \\ &= \frac{1}{\langle c_A \rangle + \langle c_B \rangle} \left(\frac{\partial \langle c_A'^2 \rangle}{\partial t}\right)_m \end{aligned} \quad (4.5 - 7)$$

The dissipation term can subsequently be modeled as in the case of inert scalars; this subject is examined in detail in Chapter 5. In particular, Patterson (1981) uses Corrsin's (1964a) relations (see Chapter 5) for isotropic turbulent mixers, adopting a scalar segregation length scale equal to that of the turbulence macroscale. This last assumption is not justified in the cases of localized sources since the concentration field cannot be assumed locally isotropic. This is a major limitation in Patterson's modeling schemes. Nevertheless, in spite of the various deficiencies of the complete approach, we believe that the approximation just described is useful in showing how one can introduce significant simplifications into a turbulent kinetic model, at least for rather extreme conditions like those of "quasi-equilibrium". Approximations at a similar level, usually for very simple (1-dimensional) systems like the multijet plug flow reactor etc., have been proposed by various investigators; see, e.g., Brodkey

(1975) and Murthy (1975) for relevant references. One such approximation results from Patterson's (1973) simple "interdiffusion model" (essentially a simple microstructural model; see also Section 4.5.2 and Figure 4-5) which gives

$$\langle c'_A c'_B \rangle = - \langle c'^2_A \rangle \frac{(1 - \gamma)}{\beta(1 + \gamma)} \quad (4.5 - 8)$$

where

$$\beta = \frac{\langle c_A \rangle_0}{\langle c_B \rangle_0}$$

and

$$\gamma = \frac{\beta \langle c_A \rangle \langle c_B \rangle - \langle c'^2_A \rangle}{\beta \langle c_A \rangle \langle c_B \rangle + \langle c'^2_A \rangle}$$

(A relation for $\langle c'^2_A c'_B \rangle$ can also be obtained but Patterson (1981) suggests setting these correlations equal to zero.)

It must be emphasized that extensions of the above equations to more complicated, 3-dimensional situations, localized sources e.t.c., common in environmental problems, would be questionable.

4.5.2 PDF Formulation

Probability density schemes use the joint probability density function, or a related quantity (like a moments generating functional) of reactive species concentrations, and possibly of other random variables such as velocities, to describe the reacting system. One-point or multi-point densities (or related functions) may be the object of study depending on the complexity of the case modeled and on the desired level of approximation. All statistical characteristics like first and higher order moments and correlations of all kinds are then derived directly from the pdf.

A "degenerate" type of pdf formulation is that in which the pdf form is chosen *a priori* on the basis of relevant experimental information (or just by guessing). Then the parameters of the pdf have to be estimated (this being an auxiliary "closure step"). After that, any other statistic of the random field is evaluated from

the pdf. Hence, since the parameters of the pdf (usually two or more) are directly related to moments, this scheme actually reduces to moment closure (of appropriate order) plus the primary closure assumption involved in the selection of the pdf, which subsequently will determine higher order moments. Pdf's that are marginally (and jointly) Gaussian have been usually assumed in the past; see, e.g., Lockwood and Naguib (1975). However such an assumption might be highly unrealistic, especially for arbitrary types of mixing or localized injection of material (see, e.g., Hill, 1976).

Another type of pdf formulation is based on simple structural models that assume special, simple, random or pseudo-random structures of the concentration fields. This results in discrete ("spiked") pdf's for the reactive concentrations. For example Patterson's (1973) "interdiffusion model" assuming idealized concentration distributions of unpremixed species (Figure 4-5), produces a probability distribution that is nonzero only for three values of the concentration (i.e. for zero, for the unpremixed stream value and for a value corresponding to completely mixed feeds). Donaldson's (1975) "most typical eddy" model similarly postulated a joint pdf consisting of delta functions at fixed locations in the composition space. The strengths of these delta functions are parameters that require appropriate estimation. Much more elaborate models have also been constructed on the basis of structural (Lagrangian) assumptions. Kuznetsov and Frost (1973) assumed that both the turbulence and the scalar fields obey Langevin's equations and proceeded from there to model their statistics. Following a different line, Pope (1981) presented an approach that utilizes Monte Carlo schemes of dispersion. His method conceptually stands between older structural approaches and the Eulerian models to be discussed next.

Pdf models that are really Eulerian in nature proceed from the fundamental transport principles (e.g. equation (4.4-2)) to derive evolution equations not for the moments and correlations of the reactive species concentrations but for their (joint) probability density functions (possibly jointly with properties of the turbulence field). Typically enough, the problem of turbulence will lead again, as in the moments case, to an infinite hierarchy of equations and some kind of closure approximation will have

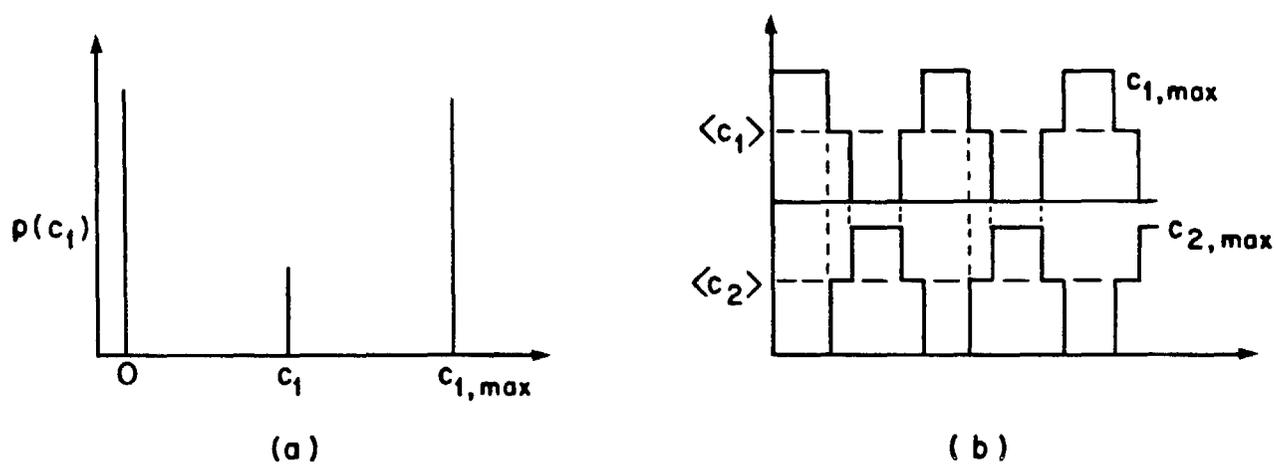


Figure 4-5
Local Concentration Profiles
(and the associated concentration probabilities)
assumed in Patterson's (1981, 1983) "Interdiffusion Model"

to be invoked. The schemes for deriving the pdf evolution equations are provided by modern Statistical Mechanics. In particular two different methods have been used in the study of reactive turbulence.

The first is the *method of probability functionals*. Here, from an equation for the probability density functional (Hopf, 1952), which is linear and closed, one deduces an unclosed n-point pdf evolution equation. Lewis and Kraichnan (1962) first studied the probability functional of the turbulent velocity field; (see also Leslie, 1973; Monin and Yaglom 1975). Petty and Reed (1972), Ievlev (1973), Dopazo and O'Brien (1974) (see also Dopazo and O'Brien, 1975, 1976) studied the analogous equations for reacting species in turbulent flows. However, quoting O'Brien (1980), "there seems little prospect that a broad range of applicable results can be obtained at present by such a direct approach".

The second method was introduced by Lundgren (1967) in modeling turbulent velocity fields. It is sometimes called the "*fine grained probability densities method*" and is simpler and more efficient (although not as general and straightforward) than the previous one. It produces the pdf evolution equations directly from the partial differential equations which define the conservation laws of the system. The hierarchy of equations derived in this way is analogous to the BBGKY hierarchy in the kinetic theory of gases (see, e.g., Reichl, 1981). Hill (1970) used a similar scheme to study chemical reactions in turbulence and, after him, many researchers offered different versions of this approach. Dopazo and O'Brien have published a series of papers exploiting the method. Two of these publications are, at least formally, studies of the turbulent reacting plume problem (Dopazo, 1976; O'Brien et al., 1976 – see also Chapter 1). Relatively recently O'Brien (1980) reviewed the method and the closure approximations proposed by various authors; this review should be consulted for further information on the subject. For another recent comprehensive review (but with a more general perspective) on PDF methods for turbulent reactive flows see Pope (1985).

4.5.3 Spectral Formulations

Some researchers have tried to describe simple cases of reactive transport in turbulence by means of spectral models for the concentration fields. Such models have been developed exclusively for *single species reactions*, usually 1st order, and most computations have been limited to the use of spectral transfer theories for the universal equilibrium range. The second order irreversible reaction $A + A \rightarrow P$ has been studied by Corrsin (1964b) and Dash (1973). They used the "Further Generalized Onsager Model" (Corrsin, 1964b) and the Corrsin-Pao "Unified Spectral Cascade Concept" (Pao, 1964).

Recently Lundgren (1985) constructed a model for the analytical estimation of the form of the concentration spectrum of the product of a fast bimolecular chemical reaction of the $A + B \rightarrow P$ type for wavenumbers greater than the Kolmogorov wavenumber. This analysis considered unpremixed reactants in a stirred tank and assumed a vortical microscale structure for the turbulent fluid motion in the tank. (*)

The Schmidt number was large and the volume of one of the reactants was small. Under these conditions Lundgren found that the spectra first decrease like k^{-1} (i.e. as for a passive scalar) and then increase linearly with wavenumber, peaking near the Batchelor wave number from which it drops off like k^{-4} for large wavenumbers, to finally decay exponentially.

As far as relevant experimental information is concerned, Kewley et al. (1978) have measured co-spectra of O_3 - NO_2 in photochemical smog.

Nevertheless, spectral methods do not seem at the moment very promising for describing reactions under conditions relevant to environmental flows (although some information from the spectral approaches can be useful in other modeling schemes). For more information and references one may consult the reviews by Hill (1976) and Bilger (1980) and Lundgren's (1985) paper.

* The whole development of this model is based on an advanced microstructural approach of the 2nd level (Section 4.3.2). However, since its major results concern concentration spectra, we mention it here.

4.6 INDIRECT CHEMICAL CLOSURE

4.6.1 Methods of Decoupling Mixing and Chemistry

Among the methods that use Equations (4.4-1) or (4.4-2) as a starting point, the ones that have led up to now to more tractable final working schemes, at least for not very complex physical situations, are based on techniques which decouple and in some way "isolate" the analytical description of the phenomena of mixing and chemical reaction. The underlying concept is rather old and early applications appeared in theories of turbulent combustion (Burke and Schumann, 1928; Hawthorne et al., 1949). The recent interest in the method originated mainly from the work of Toor (1962) and his coworkers who considered infinitely fast reactions of nonpremixed species in tubular flow reactors. A rather recent review of the approach for the case of nonpremixed reactants, containing many details and references, is given by Bilger (1980b); however some of the existing techniques are not discussed and thus certain aspects and capabilities of the method are not revealed.

Consider for simplicity the case of an isothermal reaction system where all the dependent (unknown) variables are members of the random concentration vector $\mathbf{c} = (c_1, c_2, \dots, c_n)$. (In case of non-isothermal systems more unknowns such as the temperature, density etc., must also be included in the treatment.) Then the general idea of the method, expressed in rather crude terms, consists of the two following steps:

- First, introduce a set (vector) of quantities,

$$\mathbf{c}_s = (c_{s_1}, c_{s_2}, \dots, c_{s_n})$$

such that

$$\mathcal{L}^M c_{s_i} = 0 \tag{4.6-1}$$

holds for all i with the appropriate boundary and initial conditions. Here \mathcal{L}^M is the overall mixing operator defined in Chapter 1 [equation (1.3-4)]. The

quantities c_{s_i} are thus conserved scalars. They are random quantities and their evolution is governed by stochastic equations like (4.6-1).

- Second, construct a general relation of the form

$$\Psi(\langle \mathbf{c} \rangle, \langle \mathbf{c}^* \rangle, \mathbf{f}(\mathbf{c}_s)) = 0 \quad (4.6-2)$$

which will connect the expected values of the members of the unknown reactive species concentration vector \mathbf{c} to *deterministic* functions $f_i(\mathbf{c}_s)$ of the random vector of conserved scalars \mathbf{c}_s . The vector function \mathbf{f} will usually be a vector of moments or pdf's of the c_{s_i} 's. A vector of *auxilliary variables* with expected value $\langle \mathbf{c}^* \rangle$ may also have to be introduced in this step and appear in the general relation (4.6-2) depending on the complexity of the particular problem and the details of the formulation. Construction of (4.6-2) will unavoidably (except in the simplest case of irreversible infinite rate reaction) require *closure hypotheses* regarding either higher order moments or pdf's. If such hypotheses involve functions of the conserved scalar only they will be referred to as *pure conserved scalar closure models*. If the approximations involve functions of the conserved scalar and reacting species they will be referred to as *mixed indirect closure models*.

In this way the f_i 's, which in general will be estimated by a procedure that starts from equations (4.6-1), describe analytically the mixing state of the system, with chemistry effects having been "removed" from it. Then relation (4.6-2) supplements the description with the a posteriori consideration of these effects.

Both steps of the modeling procedure pose various questions. The obvious problems in the first step is how many conserved scalars must be introduced and how are they chosen. The answers to these depend on basic characteristics of the system like number and uniformity of feeds etc. The second step raises more difficult questions directly connected to the complexity of the given problem and the level at which it is wished to be modeled.

4.6.2 Number and Forms of the Conserved Scalars

There has been a great variation in the choice of conserved scalars in the literature (see, e.g., Bilger, 1980b, for a review and relevant references). There is also a certain confusion with respect to the merits of various choices. In many circumstances the conserved scalars are all linearly related so that solution for one yields all of the others. The choice is then arbitrary up to a point, depending perhaps on requirements arising from other points of the modeling procedure. Under other circumstances there may be factors that directly favor the choice of one or more relative to the others. Such factors include nonequal molecular diffusivity effects, the number and uniformity of the reactant feeds and the complexity of the chemical mechanism.

A complete analysis of a general situation with an arbitrary number of feeds and reactions is not available, neither it seems to be very useful, so we limit the present discussion mainly to the case of two "feeds", under conditions of dominant stream mixing *which is the situation relevant to the atmospheric plume problem*.

A condition particularly useful for practical purposes, is that of equal (in practice of the same order of magnitude) molecular diffusivities for all the species of the system. In fact these molecular diffusivities are usually and considered negligible in magnitude in comparison to turbulent dispersion and the above condition is satisfied for almost all cases. (*) Then, since the transport properties are characteristic of the flow field and not of the species that are present there, the number of conserved scalars needed to describe the mixing state of the system is minimum. Thus, for two feeds or streams of distinct but *constant initial chemical identity* the state of mixing is uniquely determined by one conserved scalar variable. In general for n feeds $n - 1$ conserved scalar variables will be adequate to determine this state (Bilger, 1980b). This results from the fact that all differentiation of different feeds arises from chemical

(*) Significant differences in molecular diffusivities of importance in practical applications appear when light gases, as for example molecular hydrogen, are present. These species have very high diffusivities relative to other species as, e.g., oxygen, nitrogen, etc. and therefore rather strong differential diffusion source terms will appear in transport equations for linear combinations of concentrations incorporating them.

identity only and not from difference in transport properties. Any more conserved scalars that could be defined will be necessarily linearly dependent with the initial ones under the condition that each feed is initially perfectly mixed. (If a feed is not perfectly mixed then it can further be seen as composed by other, perfectly mixed feeds). Bilger (1980b) states this condition as a requirement for uniformity, that is "spatial and temporal constancy" of each feed, with respect to elemental composition only, whereas, "each feed may be in several streams each of which may have any state of chemical aggregation, e.g. it may be partially reacted or pyrolyzed".

In general, conserved scalars can be chosen either from the stoichiometric invariants of the reaction under consideration or they can be "artificially conserved" quantities like fictitious inert surrogate concentrations of the actual reactive species. When they correspond to a stoichiometric invariant of the system they actually correspond to a conserved quantity; the term conserved scalar in the literature has been used almost exclusively for choices of this type.

In principle any quantity that is conserved during the reaction process can be adopted as a conserved scalar. The "fundamental" conserved scalars are naturally the atomic mass fractions Z_i or the gram-atomic concentrations \hat{c}_i of the different *elements* in the reactive system. If the number of elements is M then, since the total mass in the system is constant, there are in general $M - 1$ independent variables. Solution of the $M - 1$ equations of the type (4.6-1) yields the instantaneous and mean (after ensemble averaging of the equations) elemental composition throughout the field and this may be looked upon as a description of the mixing of the system. Constancy of the composition of the feeds provides further relations between the fundamental conserved scalars when differences in the molecular diffusivities of the species are assumed negligible. Then the required number of equations of the type (4.6-1) is reduced significantly.

In practice other conserved scalars have been used in both chemical engineering and combustion applications and have already appeared in the modeling of photochemical pollution and plume dispersion processes (Bilger, 1978; Kewley, 1978, 1980).

In the case of a one-step reaction such as



where the (molar) formation rates of A, B and P are related through

$$r_A = \frac{r_B}{m} = -\frac{r_P}{n} \quad (4.6 - 4)$$

one can define the so-called *Shvab-Zeldovich coupling functions* (see, e.g., Williams, 1985).

$$\zeta_{AB} = c_A - \frac{c_B}{m} \quad (4.6 - 5a)$$

$$\zeta_{AP} = c_A + \frac{c_P}{n} \quad (4.6 - 5b)$$

$$\zeta_{BP} = c_B + \frac{mc_P}{n} \quad (4.6 - 5c)$$

or

$$\hat{\zeta}_{AB} = m\zeta_{AB} = mc_A - c_B,$$

and so on, which are immediately seen to satisfy (4.6-1). Depending on the particular application *Favre averaged* (see, e.g., Hinze, 1975) concentrations or mass fractions can be used in the definitions (4.6-5) whereas other conserved scalars of the same type can be formed using the sensible specific enthalpies of the feeds in the case of highly exothermal reactions (see, e.g. Bilger, 1980b). Toor (1962, 1975) refers to the same technique, which he applies for conditions of equal molecular diffusivities, as the *Burke-Schumann transformation* of the reactive transport equation (see Burke and Schumann, 1928).

With the assumption of equal molecular diffusivities the balance equation for a conserved scalar becomes free of artificial source terms resulting from differential diffusion effects and is exactly the same for all conserved scalars. In two-feed problems the conserved scalars can be *normalized* in such a way that boundary conditions also become identical (see, e.g., Bilger, 1979a). A normalized conserved scalar which can

alone describe the mixing state of the system is the *mixture fraction* χ which is defined through (see, e.g., Toor, 1975; Bilger, 1979a).

$$\chi = \frac{Z_i - Z_i^{(2)}}{Z_i^{(1)} - Z_i^{(2)}} = \frac{\zeta - \zeta^{(2)}}{\zeta^{(1)} - \zeta^{(2)}} \quad (4.6 - 6)$$

where superscripts (1) and (2) refer to the uniform composition of the two different feeds, Z_i is the mass fraction of any element and ζ is any Shvab-Zeldovich function of the type defined in (4.6-5).

Then, in feed (1) we have

$$\chi = 1 \quad (4.6 - 7a)$$

and in feed (2)

$$\chi = 0 \quad (4.6 - 7b)$$

So, χ can be physically interpreted as the mass (or mass per volume) fraction of the material in the mixture at a given point and time instant which originated in feed (1) with $1 - \chi$ the fraction originating in feed (2). Thus the result of turbulent and molecular diffusion on the composition of the whole mixture at a point is the same as if we took a quantity of mass χ from feed (1) and mix it *thoroughly* with a quantity of mass $1 - \chi$ of feed (2) and *then let reaction occur*. Of course the instantaneous χ is a random quantity like the quantities in terms of which it is defined.

Any conserved scalar c_s is related to χ and its initial values in the two separate feeds denoted by superscripts (1) and (2) through

$$c_s = \chi c_s^{(1)} + (1 - \chi) c_s^{(2)} \quad (4.6 - 8)$$

(Necessary condition for the validity of this relation is the equality of molecular diffusivities of all the reacting species of the system.)

Considering now the case where in feed (1)

$$c_A = c_{A_0}, \quad c_B = 0, \quad \zeta_{AB}^{(1)} = c_{A_0} \quad (4.6 - 9a)$$

and in feed (2)

$$c_A = 0, c_B = c_{B_0}, \zeta_{AB}^{(2)} = -\frac{c_{B_0}}{m} \quad (4.6-9b)$$

we obtain the following expression for χ

$$\chi = \frac{m\zeta_{AB} + c_{B_0}}{mc_{A_0} + c_{B_0}} = \frac{\hat{\zeta}_{AB} + c_{B_0}}{mc_{A_0} + c_{B_0}} \quad (4.6-10)$$

in terms of the "pure stream" concentrations c_{A_0} , c_{B_0} . There will be a special value of χ , χ_s at which the two feed materials coexist at a point in exact stoichiometric proportion. For the one step reaction (4.6-4), with conditions as in (4.6-9) we have

$$\chi_s = \frac{c_{B_0}}{mc_{A_0} + c_{B_0}} \quad (4.6-11)$$

This value of χ corresponds to $\zeta_{AB} = 0$ and has a particular significance. For a one-step irreversible reaction with infinitely fast kinetics $\chi = \chi_s$ corresponds to the random instantaneous location of the surface (of infinitesimal thickness) on which chemical reaction is confined. For reversible multi-step reactions as well as for slower chemistry this location will be an approximate center for the instantaneous reaction zone. It is important to realize that, although all quantities in the r.h.s. of (4.6-11) are deterministic, the position at which $\zeta_{AB} = 0$ and (4.6-10) reduces to (4.6-11) is random at any time instant.

Another point to be mentioned here is that, for the two feeds case, the most important of the quantities describing the degree of micromixing, that is the intensity of segregation, can be defined e.g. through (4.2-4), in terms of any conserved scalar, e.g.

$$I = \frac{\langle \zeta'_{AB}{}^2 \rangle}{\langle \zeta_{AB} \rangle^2} = \frac{\langle \chi'^2 \rangle}{\langle \chi \rangle^2}$$

The use of the concept of inert surrogates for conserved scalars is examined in more detail in section 4.6.3.

Now we proceed in examining the various possible model formulations in terms of conserved scalars for the two cases of infinite and finite rate chemical kinetics, as outlined in Figure 4-2.

4.6.3 Pure Conserved Scalar Closure

(a) The Case of Infinite Rate Chemical Kinetics

As it has already been mentioned, when chemical processes can be assumed much faster than the dispersion processes the problem of reactive turbulence modeling simplifies greatly. Indeed, if we focus on the problem of nonpremixed reactants(*) contained in two feeds of uniform composition and assume that all species have approximately equal molecular diffusivities it is easy to see that in the limit of infinitely fast chemistry all concentrations are instantaneously related to the value of an arbitrarily chosen conserved scalar. Actually in this case the statistics not only of concentrations but of all thermodynamic variables of the system should be obtainable from sufficient knowledge of the statistics of that scalar. This is the situation where *pure conserved scalar closure* is either not needed at all or is directly applicable and most useful.

(a1) Irreversible Reaction

In the case of one-step irreversible reactions (e.g. reaction (4.6-3) in the forward direction only) we will have $c_B = 0$ when $\chi > \chi_s$ and $c_A = 0$ when $\chi < \chi_s$ whereas both c_A and c_B will be zero when $\chi = \chi_s$. Thus the following functional relationships will hold:

$$\zeta_{AB} \leq 0, \chi \leq \chi_s : c_A = 0$$

$$c_B = n\zeta_{AB} = n\tilde{c}(\chi_s - \chi) \quad (4.6 - 12a)$$

$$c_P = m\tilde{c}\chi(1 - \chi_s) \quad (4.6 - 12b)$$

$$\zeta_{AB} \geq 0, \chi \geq \chi_s : c_A = \zeta_{AB} = \tilde{c}(\chi_s - \chi)$$

$$c_B = 0 \quad (4.6 - 13a)$$

$$c_P = m\tilde{c}\chi_s(1 - \chi) \quad (4.6 - 13b)$$

* Of course a case of premixed reactants which react with infinitely fast rate cannot exist.

where

$$\tilde{c} = c_{A_0} + \frac{c_{B_0}}{n} = \frac{c_{A_0}}{\chi_s} \quad (4.6 - 14)$$

So we see how, at a given point in the flow, the value of χ at any particular instant defines the complete composition of the reactive mixture. Hence the problem for the steady state actually reduces to solving

$$\mathcal{L}^M \chi = 0$$

with (known) appropriate boundary conditions. Since all the above relations for c_A , c_B , c_P are linear in χ , there is no difficulty in relating the expected values $\langle c_A \rangle$, $\langle c_B \rangle$, $\langle c_P \rangle$ to $\langle \chi \rangle$ which is obtained from the solution of

$$\langle \mathcal{L}^M \chi \rangle \simeq \mathcal{L}_*^M \langle \chi \rangle = 0 \quad (4.6 - 15)$$

where \mathcal{L}_*^M is an approximation of $\langle \mathcal{L}^M \rangle$ resulting from a closure approximation.

(a2) Reversible Reaction

If the infinitely fast reaction is reversible (with both forward and backward rates being very fast compared to the mixing processes) c_A and c_B will both have nonzero values not only for $\chi = \chi_s$ but for a range of values from χ^- to χ^+ where

$$1 \geq \chi^+ > \chi_s > \chi^- \geq 0$$

The values χ^+ , χ^- define the local boundaries of the *reaction zone*. The reaction zone, for infinitely fast chemistry is exactly that local portion of the space of the entire system which is micromixed (not necessarily uniformly). This will be called the *mixed zone*. The composition of the mixture at any given point of the reaction zone, at any particular instant, will be the same as that if the mixture were isolated and allowed to come to chemical equilibrium. The species concentrations will again be unique functions of the conserved scalar. However, now the existing relations for chemical equilibrium replace limiting stoichiometry equations for the attainment of mathematical closure of the system of unknown concentrations. These equilibrium relations,

in contrast to limiting stoichiometry, will be in general nonlinear and this creates a chemical closure problem as higher order statistical characteristics of the conserved scalar c_s (χ , ζ_{AB} , or whatever else) are needed for the estimation of the expected values of species concentrations. Even for many species and multiple reactions the fast chemistry assumption implies that these will be effectively equilibrated. There will be sufficient equilibrium constants available to enable calculations of species concentrations in terms, e.g., of elemental composition which is directly related to any conserved scalar. Thus a set of relations of the form

$$c_i = c_i^e(c_s) \quad (4.6 - 16)$$

where the superscript e denotes equilibrium and c_s is the random conserved scalar will be available. (In general not only for concentration but also for other thermodynamic variables such as temperature and density). These c_i^e 's are exactly the functions f_i that appear in the general equation (4.6-2). So now the problem is actually how, starting from (4.4-16), to relate the $\langle c_i \rangle$'s to the field $\langle c_s \rangle$, the latter being governed by $\mathcal{L}_*^M \langle c_s \rangle = 0$ with the appropriate boundary conditions. As an example let us consider again the reaction



which obeys the kinetic law

$$R = k_f c_A c_B - k_b c_P \quad (4.6 - 18)$$

When equilibrium is assumed we have $R = 0$ and

$$\frac{c_A c_B}{c_P} = \frac{k_f}{k_b} = K \quad (4.6 - 19)$$

This equation can be combined with two relations of the type (4.6-5) and with (4.6-6) to give c_A , c_B , c_P in terms of K and χ . Indeed, in terms of the mixture fraction we have, for the conditions described in (4.4-23), and if there is no P in the feed streams,

the following relations:

$$c_A - c_B = (c_{A_0} + c_{B_0}) \chi - c_{B_0} \quad (4.6 - 20a)$$

$$c_A + c_P = c_{A_0} \chi \quad (4.6 - 20b)$$

which, together with (4.6-19), provide a closed system for c_A , c_B , c_P . So, for this case we obtain

$$c_A = \frac{K}{2} (-B + \sqrt{D}) \quad (4.6 - 21)$$

with

$$A = \frac{1}{K} \quad (4.6 - 22a)$$

$$B = 1 + c_{B_0} - (c_{A_0} + c_{B_0}) \chi \quad (4.6 - 22b)$$

$$D = B^2 - 4 \frac{c_{A_0}}{K} \chi \quad (4.6 - 22c)$$

The nonlinearity of these instantaneous relations between concentrations and the conserved scalar does not allow a direct connection of expected values of these quantities by ensemble averaging. Thus one has to invoke an appropriate closure scheme either

(a) by introducing the probability density function of the conserved scalar c_s , $p(c_s)$ in which case expected values of the c_i 's will be obtained through

$$\langle c_i \rangle = \int_0^\infty c_i^e(c_s) p(c_s) dc_s \quad (4.6 - 23)$$

(“pdf closure”)

or

(b) by ensemble averaging (4.6-16) (i.e.(4.6-21)) so that after some algebraic manipulations one has

$$\langle c_i \rangle = f(\langle c_s \rangle, \langle c_s^2 \rangle, \dots) \quad (4.6 - 24)$$

This is an equation involving only the first few moments of the conserved scalar. (“moment closure”).

So, the chemical closure problem is reduced to the estimation of moments and/or pdf's of the conserved scalar; thus it has been "transferred" to the closure problem appearing in the governing equations for these quantities.

For the particular system under study, i.e. reaction (4.6-17), the function $c_A^e(c_s)$ is given directly by (4.6-21) with $\chi = c_s$. The function f can also be obtained from (4.6-21) after ensemble averaging of both sides, but this is not a trivial task. For this reason practically all models that have followed the methodology described in this sub-section adopt equation (4.6-23) for their calculations.

Now, when pdf closure is employed, the problem is very similar to that of pdf modeling for reactive species (Section 4.5.2). However there is a definite advantage in dealing with pdf's of conserved scalars because their form and properties are much more predictable for a great variety of flow geometries. Both experimental as well as theoretical information is much more extensive for pdf's of inert scalars than for reactive ones; the same is true for moments also, whose study, e.g., through Eulerian transport equations, is not complicated by chemical interaction terms.

The pdf of the conserved scalar can be studied theoretically exactly on the lines described in Section 4.5.2, i.e., either by formulation of pdf evolution equations (methods of probability functionally and of fine grained densities), or by employing some structural model that describes mixing in terms of processes that are experienced by the fluid particles (see, e.g., Bilger, 1979b; O'Brien, 1980; Pope, 1981; Kollmann and Janicka, 1982). However, the most common approach in applications is the a priori assumption of the probability density form.

In combustion applications (where the method of this sub-section has been applied most extensively in many variations) there has been a variety of choices for the conserved scalar pdf. Modelers have used more commonly "Clipped Gaussian" (or semi-Gaussian: see Chapter 5) pdf's (see, e.g., Bilger, 1980b) and Beta function distributions; other choices that have also appeared in the literature are the sinusoidal and the triangular pdf's (see Murthy, 1975, and Effersberg and Peters, 1983, for relevant references). In air pollution problems, where the method has been applied

by Bilger (1978) and Kewley (1978, 1980), the semi-Gaussian pdf has been the only choice. In particular Kewley (1978) assumed a semi-Gaussian distribution for the plume concentration field; this also incorporates the effect of intermittency too (see Chapter 5). However, since only the "internal" concentration fluctuations, and not the ones caused by meandering, affect chemical reactions in plumes, it seems that such a distribution might not be the most appropriate choice. Actually, as it has been discussed in the previous chapters, it is needed to disengage instantaneous dispersion and meandering effects and to attempt statistical description of each process separately. A lognormal (or some other positively skewed distribution) seems to be a reasonable choice for the instantaneous concentrations when viewed in a frame that follows the random meandering of the centerline. This and related problems are discussed in more detail in Chapter 5 where the moment estimation problem (specifically: second moment estimation for atmospheric plumes) is studied extensively; hence the present section is complemented by Chapter 5.

(b) The Case of Finite Rate Chemical Kinetics

For moderately fast reactions pure conserved scalar closure is not directly possible, i.e. immediately from the equations (4.6-23), (4.6-24). Indeed now there are no algebraic equilibrium equations to relate in a simple fashion reactive species and conserved scalar concentrations. Hence mixed (or "multivariable") closure of the type to be described in the next subsection is more appropriate. However there have been attempts to extent pure conserved scalar closure to finite rate kinetics by viewing the actual solution of the problem as a "departure" (or perturbation) from the equilibrium solution that is obtained for infinite rate kinetics. Thus, perturbations of the conserved scalar are introduced as extra variables (Bilger 1979b, 1980ab). Until now, however, the method has been applied in a very limited number of situations.

4.6.3 Mixed Indirect Closure and the Concentration Field Splitting Technique

Application of the conserved scalar approach to finite rate chemistry requires the introduction of extra variables, besides the conserved scalars. These will be affected by the chemistry. One of the reactive species concentrations can be such a variable but it would be better if one could introduce other parameters easier to treat when closure complications appear. Indeed, closure assumptions now have to accommodate these "auxilliary" variables too. So, the underlying idea of the method is to define them in a way such that their correlations (or perhaps cross-correlations with the conserved scalar) are easily predictable for the given problem.

Bilger (1980) discusses these "Two-Variables" approaches. Another model that has implicitly followed this line is that of Shu (1976), Lamb (1976), and Lamb and Shu (1978). The fundamental idea of this model was chosen in the present Reacting Plume study to assess the effects of turbulent fluctuations on the kinetics because of its generality, its relative simplicity (especially for the plume case), and its significant potential for future improvement.

The formulation (and hence the subsequent application) of the model in the works of Shu and Lamb is limited (because of the restrictive use of spatial averaging over the mixed zone and other similarly defined volumes) to one-dimensional problems (where variation of mean concentrations takes place only in one, spatial or temporal, dimension). Furthermore, some results of their analysis, relevant to local microstructures, are not directly extendable to a global statistical picture of the flow. In Chapter 2 we presented a new, generalized, formulation of this model that holds for pointwise defined instantaneous concentrations in arbitrary, non uniform, fields, and formally deals with the global statistical equations. In the following we further discuss this formulation, presenting the proofs that were omitted in Chapter 2 and commenting on various points of the modeling procedure. The exposition of Chapter 2 is essentially repeated here to facilitate reading of the next paragraphs by avoiding repeated references to definitions and equations in Chapter 2; furthermore, in

this way the present chapter provides a self-contained treatment of chemical closure modeling.

The "Concentration Field Splitting" Method

Let $c_A^I(\mathbf{x}, t)$, $c_B^I(\mathbf{x}, t)$ be the hypothetical concentrations of A and B that would exist at the space-time point (\mathbf{x}, t) if they did not react with each other but, still, were transported in the field by exactly the same molecular and convective mechanisms. (A point to note here is that the present analysis implicitly assumes that differences in the molecular diffusivities of the various species under consideration are negligible.) We can define these new variables as concentrations of fictitious *inert surrogates* A^I , B^I , of A and B . The quantities c_A , c_B , as well as c_A^I , c_B^I at any (\mathbf{x}, t) are random variables. The approach proposed in this work accounts for the possible states of mixing of the two species by viewing each of the above concentration fields not only as random functions of (\mathbf{x}, t) but also as *functionals* of the entire ensembles of realizations of the inert surrogate of their "mixing partners" at (\mathbf{x}, t) . Indeed, the possible micromixing states of, say, A or A^I at any point depend on the probabilistic characteristics of the concentration of B^I at this point. Thus $c_A(\mathbf{x}, t)$ and $c_A^I(\mathbf{x}, t)$ are functionals of the ensemble of all possible values of $c_B^I(\mathbf{x}, t)$. This dependence is expressed formally through the following integral representation of each random realization of, say, $c_A(\mathbf{x}, t)$:

$$c_A(\mathbf{x}, t; [c_B^I(\mathbf{x}, t) = \gamma_B^I]) = \int c_A(\mathbf{x}, t; [c_B^I]) \delta(\gamma_B^I - c_B^I(\mathbf{x}, t)) dc_B^I \quad (4.6 - 25a)$$

$$c_B(\mathbf{x}, t; [c_A^I(\mathbf{x}, t) = \gamma_A^I]) = \int c_B(\mathbf{x}, t; [c_A^I]) \delta(\gamma_A^I - c_A^I(\mathbf{x}, t)) dc_A^I \quad (4.6 - 25b)$$

$$c_A^I(\mathbf{x}, t; [c_B^I(\mathbf{x}, t) = \gamma_B^I]) = \int c_A^I(\mathbf{x}, t; [c_B^I]) \delta(\gamma_B^I - c_B^I(\mathbf{x}, t)) dc_B^I \quad (4.6 - 25c)$$

$$c_B^I(\mathbf{x}, t; [c_A^I(\mathbf{x}, t) = \gamma_A^I]) = \int c_B^I(\mathbf{x}, t; [c_A^I]) \delta(\gamma_A^I - c_A^I(\mathbf{x}, t)) dc_A^I \quad (4.6 - 25d)$$

Then, defining

$$a = c_A(\mathbf{x}, t; [c_B^I = 0]), \quad \alpha = c_A(\mathbf{x}, t; [c_B^I = \gamma_B^I \neq 0]) \quad (4.6 - 26a)$$

$$b = c_B(\mathbf{x}, t; [c_A^I = 0]), \quad \beta = c_B(\mathbf{x}, t; [c_A^I = \gamma_A^I \neq 0]) \quad (4.6 - 26b)$$

$$a^I = c_A^I(\mathbf{x}, t; [c_B^I = 0]), \quad \alpha^I = c_A^I(\mathbf{x}, t; [c_B^I = \gamma_B^I \neq 0]) \quad (4.6 - 26c)$$

$$b^I = c_B^I(\mathbf{x}, t; [c_A^I = 0]), \quad \beta^I = c_B^I(\mathbf{x}, t; [c_A^I = \gamma_A^I \neq 0]) \quad (4.6 - 26d)$$

one has

$$c_A(\mathbf{x}, t) = a(\mathbf{x}, t) + \alpha(\mathbf{x}, t)$$

$$c_A^I(\mathbf{x}, t) = a^I(\mathbf{x}, t) + \alpha^I(\mathbf{x}, t)$$

$$c_B(\mathbf{x}, t) = b(\mathbf{x}, t) + \beta(\mathbf{x}, t)$$

$$c_B^I(\mathbf{x}, t) = b^I(\mathbf{x}, t) + \beta^I(\mathbf{x}, t)$$

One advantage of this representation ("concentration field splitting") lies in the fact that the evolution of a , a^I , α , α^I , etc., or, more precisely, of their statistical moments and correlations, is more easily predictable than of the reactant concentrations themselves. Thus it should be in general easier to make reasonable assumptions (based on physical insight and simplified pictures of the mixing process) involving these statistical quantities. Another advantage of the integral functional formulation, that will be used in the following, is that it allows a particularly useful interpretation of ensemble averages:

- Means and correlations of c_A , c_A^I , a , a^I , α , α^I are the result of integration over the domain of γ_B^I (after the definitions (4.6-25) and (4.6-26) have been introduced).
- Means and correlations of c_B , c_B^I , b , b^I , β , β^I are the result of integration over the domain of γ_A^I (after the definitions (4.6-25) and (4.6-26) have been introduced).
- Cross-correlations of c_A and c_B , a and b , etc., are obtained by simultaneous integration over the domains of both γ_A^I and γ_B^I .

Definitions (4.6-25abcd) and the ensemble averaged form of (1.3-3)

$$\mathcal{L}^M c_S = r_S \quad (1.3 - 3)$$

(where S stands for A , B or P) can be used to deduce relations between correlations of c_A , c_B and a , α , b , β , a^I , α^I , b^I and β^I . Thus, when the forward reaction in (1.3-1)



dominates the backward (a situation which is expected to be valid in the near field of plume dispersion), and therefore

$$\langle c_A^I(\mathbf{x}, t) \rangle \geq \langle c_A(\mathbf{x}, t) \rangle, \quad \langle c_B^I(\mathbf{x}, t) \rangle \geq \langle c_B(\mathbf{x}, t) \rangle$$

$$\langle c_A^I(\mathbf{x}, t) c_B^I(\mathbf{x}, t) \rangle \geq \langle c_A(\mathbf{x}, t) c_B(\mathbf{x}, t) \rangle$$

$$\langle c_A^I(\mathbf{x}, t) c_B(\mathbf{x}, t) \rangle \geq \langle c_A(\mathbf{x}, t) c_B(\mathbf{x}, t) \rangle$$

$$\langle c_A(\mathbf{x}, t) c_B^I(\mathbf{x}, t) \rangle \geq \langle c_A(\mathbf{x}, t) c_B(\mathbf{x}, t) \rangle$$

it can be shown that

$$\langle c_A c_B \rangle = \langle \alpha \beta \rangle, \quad \langle c_A^I c_B^I \rangle = \langle \alpha^I \beta^I \rangle \quad (4.6 - 27)$$

and

$$\langle a(\mathbf{x}, t) \rangle = \langle a^I(\mathbf{x}, t) \rangle, \quad \langle b(\mathbf{x}, t) \rangle = \langle b^I(\mathbf{x}, t) \rangle \quad (4.6 - 28)$$

Indeed (4.6-27) is a direct consequence of the definitions (4.6-26abcd) and the inequalities listed above, from which one can deduce the *independence relations*

$$\langle ab \rangle = \langle a\alpha \rangle = \langle a\beta \rangle = \langle b\alpha \rangle = \langle b\beta \rangle \quad (4.6 - 27a)$$

$$\langle a^I b^I \rangle = \langle a^I \alpha^I \rangle = \langle a^I \beta^I \rangle = \langle b^I \alpha^I \rangle = \langle b^I \beta^I \rangle \quad (4.6 - 27b)$$

Relations (4.6-28) are proved as follows: Consider the equations

$$\mathcal{L}^M (a + \alpha) = c_A c_B$$

$$\mathcal{L}^M (a^I + \alpha^I) = 0$$

Multiplying the first of these equations by a , the second by a^I and then using the definitions (4.4-25) and integrating both equations over the entire domain of γ_B^I , one finds that

$$\begin{aligned}\langle a \mathcal{L}^M a \rangle &= -\langle a \mathcal{L}^M \alpha \rangle \\ \langle a^I \mathcal{L}^M a^I \rangle &= -\langle a^I \mathcal{L}^M \alpha^I \rangle\end{aligned}$$

Now since a and α and a^I and α^I are statistically independent (see relations (4.6-27ab), the same will be true for arbitrary linear transformations of these quantities. Thus the r.h.s. of both the above equations is zero and therefore (realizing also that initial conditions, which can actually be incorporated in the mixing operator anyway, are identical for a and a^I and for α and α^I) one has $\langle a(\mathbf{x}, t) \rangle = \langle a^I(\mathbf{x}, t) \rangle$, and similarly $\langle b(\mathbf{x}, t) \rangle = \langle b^I(\mathbf{x}, t) \rangle$

Now, we introduce the *mixing functions*

$$M_{c_1 c_2} = \frac{\langle c_1 c_2 \rangle}{\langle c_1 \rangle \langle c_2 \rangle}, \quad M_{c_1 c_2}^I = \frac{\langle c_1^I c_2^I \rangle}{\langle c_1^I \rangle \langle c_2^I \rangle} \quad (4.6 - 29)$$

which allow formulation of the expression:

$$\langle c_A c_B \rangle = \frac{\varphi}{\mu_A \mu_B} M_{AB}^I [\langle c_A \rangle - (1 - \mu_A) \langle c_A^I \rangle] [\langle c_B \rangle - (1 - \mu_B) \langle c_A^I \rangle] \quad (4.6 - 30)$$

where φ is the *reaction parameter* and μ_A, μ_B are the *mixing parameters* defined by

$$\varphi = \frac{M_{\alpha\beta}}{M_{\alpha\beta}^I} \quad (4.6 - 31)$$

and

$$\mu_A = \frac{\langle \alpha^I \rangle}{\langle c_A^I \rangle}, \quad \mu_B = \frac{\langle \beta^I \rangle}{\langle c_B^I \rangle} \quad (4.6 - 32)$$

In the special case of macroscopically uniformly mixed fields μ_A and μ_B represent the fractions of the total quantities of the fictitious inert surrogates of A and B that coexist in completely micromixed volumes. For arbitrarily macromixed feeds these fractions can be interpreted as the probabilities for a structural unit of A or B respectively to be in a micromixed state at a given space-time point.

Equation (4.6-30) is an exact relation. It expresses the unknown correlation in terms of mean values of the unknowns and in terms of parameters all of which except one, namely φ , depend only on inert scalar mixing. The problem of course has been transformed in the problem of estimation of these parameters.

A substantial simplification of (4.6-30) can be obtained in the special case where $\langle c_B(\mathbf{x}, 0) \rangle$ is nonzero for all \mathbf{x} . This situation (which of course contains the case of an ideally point source of A in a background containing B) means that $\langle c_B^I(\mathbf{x}, t) \rangle$ is also nonzero for all \mathbf{x} and t and therefore $\langle a^I(\mathbf{x}, t) \rangle \equiv 0$, $\langle \alpha^I(\mathbf{x}, t) \rangle \equiv \langle c_A^I(\mathbf{x}, t) \rangle$, which give $\mu_A = 1$ for all (\mathbf{x}, t) (notice, however, that $\mu_B \neq 1$ in general). As it was discussed in Chapter 2 this result can be utilized for a typical atmospheric plume where the emissions of A (e.g. NO) have near source concentrations that are orders of magnitude higher than those of B (e.g. O₃). The fact $\langle c_A \rangle \gg \langle c_B \rangle$ near source implies that it will make no observable difference to the conversions of A if it were assumed that B is perfectly mixed with the emissions at the source, at a concentration equal to that of the ambient (in agreement with the idealization of the point source). Indeed, in such a case it does not make an appreciable difference to the overall evolution of reaction and the observed conversions of A if A and B are initially premixed or unpremixed. This further means that fine scale segregation of A and B inside the plume is induced mainly by the chemical reaction. This simplifies the analysis considerably, especially if it is assumed that the reaction is not infinitely fast and a local steady state with microscopic coexistence of A and B prevails. It is then possible using intuitive arguments to suggest that

$$\mu_B \simeq \frac{1}{M_{AA}^I}, \text{ and } M_{AB}^I \simeq 1$$

are acceptable *closure assumptions*. It can further be shown, by examining the significance of the participating correlations under the aforementioned conditions, that φ should be of order one. This is corroborated by the analysis of Shu (1976) and Lamb and Shu (1978) the main results of which are summarized in Appendix A4.1.

Hence, to recapitulate, in the case of a point release of A into an initially uniform

field of B , and under the assumption that the concentrations of A , at least near the plume axis, are much greater than the background concentration of B , we can approximate the term $\langle c_A c_B \rangle = \langle c_A \rangle \langle c_B \rangle + \langle c'_A c'_B \rangle$ by

$$\langle c_A c_B \rangle \simeq M_{AA}^I \langle c_A \rangle \langle c_B \rangle + (1 - M_{AA}^I) \langle c_B^I \rangle \langle c_A \rangle \quad (4.6 - 33)$$

where M_{AA}^I is a function characteristic of the state of *inert* species mixing in the plume.

Alternatively, if we consider the fluctuations c_A^I about $\langle c_A^I \rangle$, M_{AA}^I can be written as $M_{AA}^I = 1 + I_A^I$ where

$$I_A^I = \frac{(\sigma_A^I)^2}{\langle c_A^I \rangle^2} \quad \text{where} \quad (\sigma_A^I)^2 = \langle (c_A^I)' ^2 \rangle \quad (4.6 - 34)$$

is the relative intensity of concentration fluctuations of an inert emitted species in a plume (i.e. the intensity of stream segregation).

Introducing I_A^I we can write (4.6-33) as

$$\langle c_A c_B \rangle \simeq \langle c_A \rangle \langle c_B \rangle + I_A^I \langle c_A \rangle (\langle c_B^I \rangle - \langle c_B \rangle) \quad (4.6 - 35)$$

which of course is equivalent to

$$\langle c'_A c'_B \rangle \simeq I_A^I (\langle c_B^I \rangle - \langle c_B \rangle)$$

The overall mean rate of reaction (1.3-1) at a point will therefore be

$$\langle R \rangle \simeq \tilde{R} = k_f \langle c_A \rangle \langle c_B \rangle - k_f I_A^I \langle c_A \rangle (\langle c_B^I \rangle - \langle c_B \rangle) - k_b \langle c_P \rangle \quad (4.6 - 36)$$

Hence, all the effects of turbulence (or incomplete mixing) on the chemical kinetics have been incorporated in the second term of (4.6-36) which involves

- (i) the mean concentrations of the reactive species $\langle c_A \rangle$, $\langle c_B \rangle$ which are the actual unknown variables we want to estimate,
- (ii) the mean concentrations of inert surrogate species $\langle c_A^I \rangle$, $\langle c_B^I \rangle$, and

(iii) the variance of fluctuations of an inert emitted species.

The form of the second term of (4.6-36) suggests that it can be interpreted as representing a *fictitious reverse reaction* that retards the overall kinetic scheme in comparison to perfectly mixed conditions. The kinetic constant $k_f I_A^I$ of this "reaction" will depend on position in the plume because I_A^I shows a strong dependence on axial and radial position. The "reactants" participating in this fictitious step are A and the portion of B at any point that has already undergone chemical reaction (and therefore it is not actually available at that point). Thus the term $\langle c_B^I \rangle - \langle c_B \rangle$ can be viewed as representing "occupied" or "de-activated" B molecules that participate in a backward reaction with A , with a kinetic constant that is determined by the intensity of turbulent fluctuations. The behavior of this term is determined by the relative magnitude of I_A^I , $\langle c_A \rangle$ and $(\langle c_B^I \rangle - \langle c_B \rangle)$.

4.7 CONCLUSIONS

The major conclusions arising from the preceding exposition of the nature of the reactive turbulence problem and of the methods used to study it, in connection to the interest of the present study in environmental systems, and, in particular, atmospheric plumes are:

- (I) While the problem is extremely complex, it is sufficiently important to warrant a quantitative description.
- (II) There is not currently a specific method available that is definitely superior to the others with respect to applicability in distributed parameters environmental systems.

The spectrum of methods dealing with simultaneous mixing and reaction is very wide, ranging from very simple, empirical or heuristic, models that simulate highly idealized systems, to very complex mathematical formulations that either require excessive computational effort to produce results, or, simply, cannot give results in usable form. Somewhere in the middle lie the schemes on which we focused here: Eulerian Statistical Formulations with approximations for transport closure that are as simple as possible to keep the number of required partial differential equations to a minimum.

As far as chemical closure is concerned we believe that indirect methods (Section 4.6) are presently at a better state of development (if there is a demand for simplicity) and seem to be able to utilize more extensive and reliable theoretical and experimental information (regarding behavior of inert scalars in turbulence) than that available for direct methods (regarding the respective behavior of reactive species). So they should be preferred in practical modeling procedures. Mixed closure methods are needed to treat finite rate kinetics; however it is not always clear when the chemistry (especially for reversible reactions) must be characterized not slow but also not "infinite". Future

research should insist on identifying the importance of the differences in predictions between simple and well developed models for infinite rate chemistry and the more complex models formulated for finite rate chemistry.

Specifically for atmospheric plumes, and if the reaction rate is assumed finite, the Concentration Splitting model described in subsection 4.6.3 should be considered an appropriate choice at the present time, in terms of generality and computational simplicity (especially when integrated with the concept of the *local phenomenal extent of reaction* defined in Chapter 2). Its disadvantage is the limited knowledge on the behavior of its parameters. From this perspective other models may be better supported for special conditions. For example, if the chemistry is infinitely fast, there might be more reliable information for a model utilizing equations (4.6-21), (4.6-23). In any case, current research promises substantial improvement of the prediction of scalar behavior in turbulence and in particular in atmospheric boundary layers. Closure schemes should be constructed in such a way as to utilize the most reliable information available regarding this behavior.

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APPENDIX A4.1

**Discussion
of the Chemical Closure Assumptions
in the Concentration Field Splitting Method**

Chemical closure through the Concentration Field Splitting Method reduces to the estimation of the mixing and reaction parameters μ_A , μ_B and φ which are defined as

$$\mu_A = \frac{\langle \alpha^I \rangle}{\langle c_A^I \rangle}, \quad \mu_B = \frac{\langle \beta^I \rangle}{\langle c_B^I \rangle} \quad (A4.1 - 1)$$

and

$$\varphi = \frac{M_{\alpha\beta}}{M_{\alpha\beta}^I} \quad (A4.1 - 2)$$

respectively. In the following we discuss these parameters.

The Mixing Parameters

Estimation of the mixing parameters in the case of a point source of A in a background containing B (or in the more realistic case of a finite-dimensions source of A emitting at concentrations much higher than those of the ambient concentrations of B) is particularly simple. The reason for this simplicity is that the point character of the source and the finite speed at which the dispersion process actually proceeds (despite the parabolic character of the approximate models that are used to describe the latter process) produce a situation in which A is always and everywhere perfectly mixed (locally) with B while B is not perfectly mixed with A . Thus

$$\langle a^I \rangle \equiv 0$$

everywhere, and

$$\langle \alpha^I \rangle = \langle c_A^I \rangle$$

which implies that

$$\mu_A = 1 \quad (A4.1 - 3)$$

everywhere. Furthermore, in typical environmental applications the ambient concentrations of the species (pollutants) under consideration have very small absolute magnitudes. Thus it is reasonable, for all practical situations, to assume that the local values of the concentration of the inert surrogate

B^I are not affected by the presence of A^I and, furthermore, that c_B^I is *almost deterministic*. This leads directly to the relations

$$M_{AB}^I = M_{\alpha\beta}^I = 1 \quad (\text{A4.1-4a})$$

and

$$M_{BB}^I = M_{bb}^I = M_{\beta\beta}^I = 1 \quad (\text{A4.1-4b})$$

On the other hand, straightforward calculations produce the following *general* expression for μ_B :

$$\mu_B = \frac{M_{AB}^I}{m_{AA}^I} \frac{\langle \alpha^I \rangle M_{\alpha\alpha}^I (1 - \mu_A) + \mu_A}{\frac{M_{\alpha\beta}^I}{M_{\alpha\alpha}^I}} \quad (\text{A4.1-5})$$

(A similar expression holds for μ_A).

Introduction of equations (A4.1-3) and (A4.1-4ab) into (A4.1-5) gives

$$\mu_B = \frac{M_{\alpha\alpha}^I}{M_{AA}^I} \quad (\text{A4.1-6})$$

In deriving the final operational turbulent kinetics equations for use with the TRPM (Chapters 2 and 4) it was assumed that

$$\mu_B \simeq \frac{1}{M_{AA}^I} \quad (\text{A4.1-7})$$

that is, equivalently

$$M_{\alpha\alpha}^I \simeq 1 \quad (\text{A4.1-8})$$

which is essentially the *closure approximation for the mixing parameters* (all previous approximations being derived directly from the idealized model of the system under consideration). Intuitively, (A4.1-7) can be justified by realizing that the probability of B^I "molecule" to be surrounded by A^I "molecules" at a given point is inversely proportional to the intensity of segregation of A^I at that point. This approximation is also consistent with the general closure assumption of Lamb and Shu (1978) for unpremixed reactants in a monodimensional (i.e. macroscopically homogeneous) system, which essentially states that

$$\mu_A = \frac{M_{AB}^I}{M_{BB}^I}, \quad \mu_B = \frac{M_{AB}^I}{M_{AA}^I}$$

(The above closure approximation is basically justified on the basis of the asymptotic behavior of an unpremixed system where $\mu_A, \mu_B \rightarrow 1$ as $t \rightarrow \infty$ and $\mu_A = \mu_B = 0$ at $t = 0$).

A more formal evaluation of (A4.1-8) can in principle be performed on the basis of a microstructural model that considers the local dynamics of a typical (laminar) mixing zone at a point (at a scale comparable to Batchelor's microscale ℓ_B —see Chapter 4), whose properties are assumed

representative of the average properties of the entire ensemble of such mixing zones at this point. In this approach the macroscopic variations of the mean concentration field (as well as of the higher concentration moments) should be incorporated in the local model in the form of appropriate initial and boundary conditions. However, although sophisticated microstructural models, that examine in detail the mechanics of fluid mixing at the level of the microscale, have been appearing in recent years (see, e.g., Ou et al., 1985), incorporation of the aforementioned side conditions in these models to produce results relevant to the point source problem does not seem to be an easy task. Nevertheless, some insight can be gained by the simple analysis of Shu (1976, p.33) who considered a simple $B - A - B$ configuration of "three adjacent layers" of unpremixed species (initially uniform), of total thickness $2\ell_B$, and approximated $M_{\alpha\alpha}^I$ at a given time instant by the "spatial" average of $c_A^I c_A^I$ over a single cross-section of thickness $2\ell_B$. In this extremely idealized situation c_A^I is governed by the one-dimensional molecular diffusion equation

$$\frac{\partial c_A^I}{\partial t} = D_A \frac{\partial^2 c_A^I}{\partial x^2}$$

with initial condition

$$c_A^I(x, 0) = \begin{cases} (c_A^I)_0, & \text{if } -\frac{1}{2}\ell_B \leq x \leq \frac{1}{2}\ell_B; \\ 0, & \text{otherwise.} \end{cases}$$

Shu (1976) found $M_{\alpha\alpha}^I$ to increase from a value of 1.0 at $t = 0$ to a maximum value of about 2.0 at $t = 0.1\ell_B^2/D_A$, and then to decay to a final value of 1.0 within a period of about $10^4\ell_B^2/D_A$. These calculations, although stemming from a very simplified picture of the mixing process, corroborate the assumption that $M_{\alpha\alpha}^I$ is in general of order unity (and actually is very close to unity for most of the time).

Finally, before closing the discussion of the mixing parameters, it is interesting to examine their form in a case of very simple mixing conditions, i.e. that corresponding to a tubular chemical reactor in which the reactants are injected through alternate jets clustered over the entire cross-sectional area of one end of the tube. For reactors of this type Toor (1969) predicted, and later confirmed by measurements, that reactants that are fed into the reactor in stoichiometric ratio and that subsequently undergo extremely fast reactions satisfy

$$\langle c_A' c_B' \rangle = \langle c_A' c_B' \rangle$$

(where ensemble averages are approximated by spatial averages over a cross-section of the reactor). This result provides a means of estimating $\mu = \mu_A = \mu_B$ for this reactor: If one makes the pseudo-steady state assumption $\partial \langle c_A \rangle / \partial t \simeq 0$, which is valid for very fast reactions, one finds that

$$\langle c_A \rangle = (1 - \mu) \langle c_A^I \rangle$$

$$\langle c_B \rangle = (1 - \mu) \langle c_B^I \rangle$$

(where the analysis of Chapter 4 has been applied). Utilizing the fact that for very fast reactions $\langle \alpha\beta \rangle \simeq 0$, one finally obtains

$$\mu_A = \mu_B = 1 - \sqrt{1 - M_{AB}^I}$$

The Reaction Parameter

The reaction parameter φ (equation (A4.1-2)) was assumed approximately equal to 1.0 in the point-source plume case. Although this again is essentially a closure approximation it seems sufficiently supported by the analysis of simplified cases.

The complete governing equation for φ can be formulated directly from the transport-reaction balances for the various random fields, for a given reaction system such as $A + B \rightarrow P$, but it is too complicated to allow direct deduction of (even qualitative) conclusions for the behavior of φ . However, some insight can be gained if one considers some idealized situations. Thus, if one assumes a situation where the mean concentration fields are spatially uniform (although this contradicts the point source concept), as it was done by Lamb and Shu (1978), and that (a) $D_A = D_B = D$, (b) the reaction between A and B is irreversible (with rate constant k), then the φ -equation reduces to

$$\begin{aligned} \frac{1}{\varphi} \frac{\partial \varphi}{\partial t} = & -2D (A_* - A_*^I) - k \frac{\langle \alpha\beta (a + \beta) \rangle}{\langle \alpha\beta \rangle} + k\varphi \frac{\langle \alpha^I \beta^I \rangle}{\langle \alpha^I \rangle \langle \beta^I \rangle} + \\ & + \left(\frac{1}{\langle \alpha^I \rangle} - \frac{1}{\langle \alpha \rangle} \right) \frac{\partial \langle \alpha^I \rangle}{\partial t} + \left(\frac{1}{\langle \beta^I \rangle} - \frac{1}{\langle \beta \rangle} \right) \frac{\partial \langle \beta^I \rangle}{\partial t} \end{aligned}$$

with

$$A_* = \frac{\left\langle \frac{\partial \alpha}{\partial x_i} \frac{\partial \beta}{\partial x_i} \right\rangle}{\langle \alpha\beta \rangle}$$

$$A_*^I = \frac{\left\langle \frac{\partial \alpha^I}{\partial x_i} \frac{\partial \beta^I}{\partial x_i} \right\rangle}{\langle \alpha^I \beta^I \rangle}$$

If one further assumes that $\langle \alpha\beta \rangle$ and $\langle \beta \rangle$ are in a pseudo-steady state, which is a reasonable approximation when a high-source/low-ambient concentrations (of A and B respectively) situation exists, one obtains

$$\frac{1}{\varphi} \frac{\partial \varphi}{\partial t} = 2DA_*^I + \left(\frac{1}{\langle \alpha^I \rangle} - \frac{1}{\langle \alpha \rangle} \right) \frac{\partial \langle \alpha^I \rangle}{\partial t} + \left(\frac{1}{\langle \alpha \rangle} + \frac{1}{\langle \beta^I \rangle} \right) \frac{\partial \langle \beta^I \rangle}{\partial t}$$

Initially the reactants A and B are totally segregated with A uniformly distributed in the source emissions and B uniformly distributed in the ambient. However, suppose that B were present in the

source stream of A in the same concentration as in the ambient fluid. In this case we have $\langle c_A^I \rangle = \langle \alpha^I \rangle$ and $\langle \alpha^I \beta^I \rangle = \langle \alpha^I \rangle \langle \beta^I \rangle$ and (during the time when $\langle \alpha^I \rangle \gg \langle \beta^I \rangle$) the above equation simplifies to

$$\frac{\partial \ln \varphi}{\partial t} = \frac{\partial}{\partial t} \ln \left(\frac{\langle \beta^I \rangle}{\langle \alpha^I \beta^I \rangle} \right) = 0$$

with initial condition

$$\varphi(0) = 1.0$$

Hence

$$\varphi(t) = 1.0$$

Considering a typical industrial stack and taking into account the great disparity in the initial levels of (source) NO and (ambient) O₃, whether ozone is actually present in the source stream has virtually no effect on the evolution of NO concentrations in the plume. One concludes, therefore, that $\varphi = 1$ is in general a reasonable approximation as long as $\langle \alpha^I \rangle \gg \langle \beta^I \rangle$ initially, and the reaction is fast, i.e.

$$k \langle \alpha^I \rangle \langle \beta^I \rangle \gg \frac{\partial \langle \beta^I \rangle}{\partial t}$$

Since the same result applies when the reaction is very slow (this can be seen easily by taking the limit $k \rightarrow 0$), Lamb and Shu (1978) assumed that in point source problems in general, $\varphi = 1$.

We will now finish this discussion of the estimation of φ by summarizing the conclusions from a simple one-dimensional microstructural model of the mixing-reaction process, studied by Shu (1976), that is similar to the laminar layers model for the estimation of the mixing parameters that was discussed earlier. This model is directly relevant to the multijet plug flow reactor case, that was also mentioned earlier, where, due to the reactor design, the regions of mixed and unmixed reactants compose a mosaic of small, intermingling patches of fluid which, statistically speaking, have identical concentration probability distributions (at any fixed axial distance from the reactor head), and give rise to time mean reactant concentrations that are uniform over any plane normal to the reactor axis.

Shu (1976) assumed that $D_A = D_B = D$, that the turbulent fluid has kinematic viscosity ν , and that turbulent energy is being dissipated at a rate ϵ . Since at scales large compared to ℓ_B , concentration gradients are too weak to cause significant mixing Shu further assumed that the generation of the (laminar) mixed zone is confined primarily to those portions of the fluid where the reactant sheet thickness is comparable to ℓ_B . Thus he developed expressions for φ based on a one-dimensional model of slugs of reactant fluids of initial widths and separations of the order of ℓ_B immersed in an inert convecting fluid.

Since the expansion of reactant fluid sheets of widths smaller than or comparable to ℓ_B is dominated by molecular diffusion, the governing equations are assumed to be

$$\frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial x^2} - kc_A c_B$$

$$\frac{\partial c_B}{\partial t} = D_B \frac{\partial^2 c_B}{\partial x^2} - kc_A c_B$$

$$\frac{\partial c_A^I}{\partial t} = D_A \frac{\partial^2 c_A^I}{\partial x^2}$$

$$\frac{\partial c_B^I}{\partial t} = D_B \frac{\partial^2 c_B^I}{\partial x^2}$$

with initial and boundary conditions

$$c_A(x, 0) = c_A^I(x, 0) \begin{cases} A_0, & -\frac{3}{2}\ell_B \leq x \leq -\frac{1}{2}\ell_B; \\ 0, & \text{otherwise;} \end{cases}$$

$$c_B(x, 0) = c_B^I(x, 0) \begin{cases} B_0, & -\frac{3}{2}\ell_B \leq x \leq -\frac{1}{2}\ell_B; \\ 0, & \text{otherwise;} \end{cases}$$

$$c_A(x, t) = c_B(x, t) = 0 \quad x \rightarrow \pm\infty$$

Shu (1976) solved these equations numerically for a variety of values of feed ratio $\varrho = B_0/A_0$, diffusivity ratio D_B/D_A , and local (molecular) Damköhler number

$$\kappa = \frac{k\ell_B^2 A_0}{D_A}$$

and from the results estimated φ using spatial (cross-section) averages. Although these estimates were based on reactant and surrogate concentrations averaged over only the two patches of material considered, rather than an entire reactor cross-section as is implicit in the mean values used in the definition of φ , the uniformity mentioned earlier of the concentration probability distributions within the multijet reactor renders the patch and the actual cross-sectional averages equal.

The calculations showed that for the case of stoichiometric feed ($\varrho = 1$) and given κ , φ drops quickly from unity to some minimum value (the higher the κ the lower this value) until $t^* = tD_A/\ell_B^2 \simeq 10^4$. However, when $\varrho \neq 1$ the value of φ returns to unity more quickly, but not, as it turns out, until the reactant in the smaller quantity has been almost completely consumed. Thus, during the period within which most of the chemical reaction occurs, φ has its minimum value φ_{\min} . Lamb and Shu (1978) found from the analysis of the above numerical results that the dependence of φ_{\min} on the variables A_0 , B_0 , D_A , D_B is described by the simple expression

$$\varphi_{\min} = \frac{1}{1 + 0.16\kappa}$$

where

$$\kappa = \frac{kL_B^2 \min[A_0, B_0]}{\max[D_A, D_B]}$$

Shu (1976) also performed numerical calculations for the case of premixed reactants, in a completely analogous manner, considering the case of a single fluid pulse containing uniform concentrations of both A and B . The temporal behavior of φ in this case was found to show two distinct patterns: For the case of $\varrho = 1$, φ stays at unity for all times; but for the cases where $\varrho \neq 1$, φ decays to the same minimum value as its nonpremixed counterpart.

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CHAPTER 5

Chapter 5 contains

- *an introduction to the problem of modeling concentration fluctuations in point source plumes, including a brief literature survey,*
- *an exposition of the fundamental concepts and problems of a meandering frame Eulerian Approach for modeling the instantaneous "internal" plume concentration variance, with extensive discussion of the self similarity concept,*
- *a detailed discussion of the new "Localized Production of Fluctuations Method," that is the first choice for use with the TRPM.*

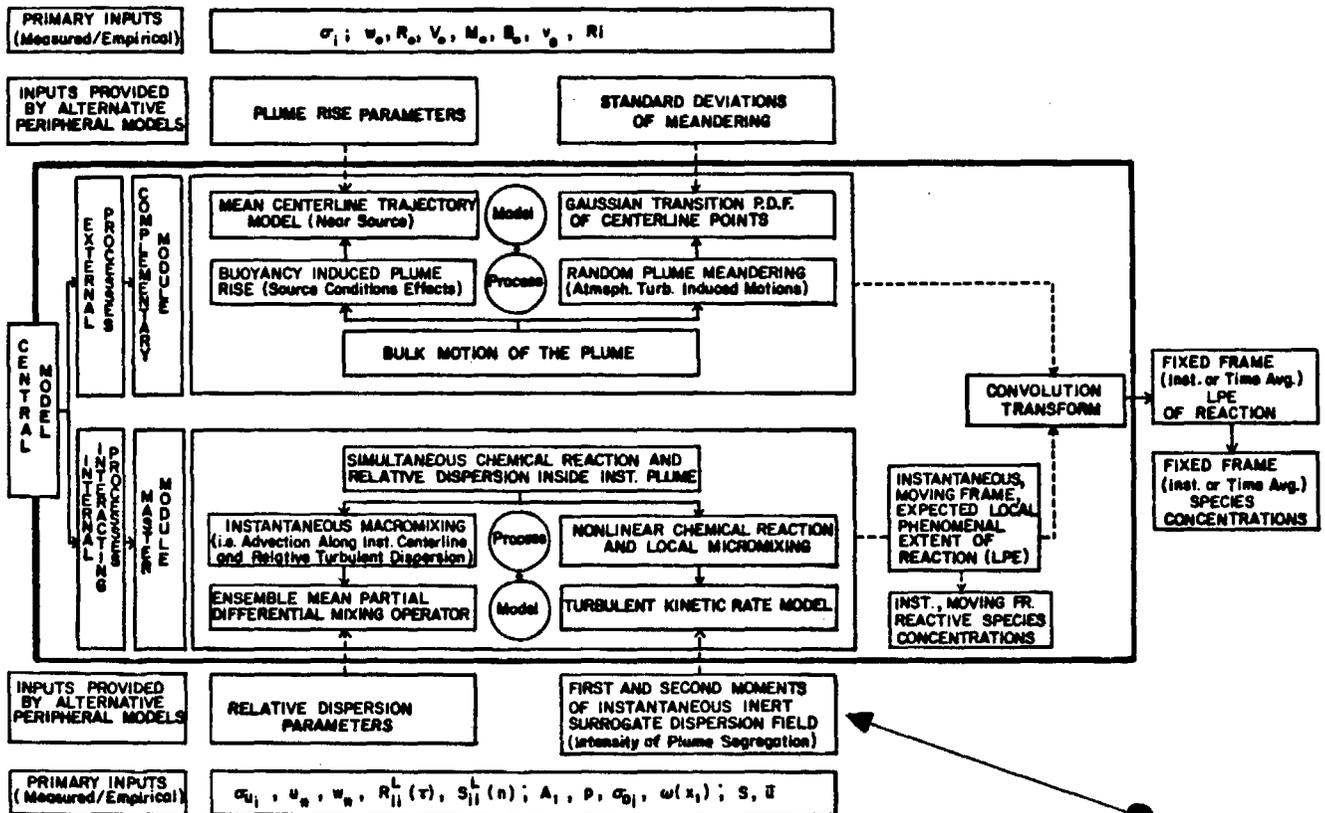


Figure 2-1b

TRPM Components Discussed in Chapter 5

CHAPTER 5

INSTANTANEOUS CONCENTRATION FLUCTUATIONS
IN POINT SOURCE PLUMES

5.1 INTRODUCTION

Prediction of expected concentration fluctuation levels in point-source plumes is a key need that arises in many problems related to turbulent dispersion. Typical examples are:

- (i) *Estimation of quantitative measures for the inherent uncertainty in models of contaminant dispersion in the environment.*

This uncertainty is associated with the stochastic nature of the dispersion phenomenon per se, as opposed to the potentially reducible uncertainty associated with errors and approximations in the model structure and the input data (Fox, 1984; Weil, 1985). Inherent uncertainty has to be taken into account for the proper interpretation of model calculations for the mean field, e.g., in their comparison with available measured values and in connection with the definition and evaluation of air quality standards.

Indeed, consider for example Figure 3-2a, where short-term averages of plume concentrations measured at source height at various distances downwind in a wind tunnel and reported by Bultjes (1981), are plotted versus the non-dimensionalized cross-wind distance y/σ_y . These are compared to calculations from a Gaussian plume model that utilizes parameters directly measured from the plume. At first sight, it

would seem that the model predictions are not very relevant to the actual physical phenomenon. However, this is not true: the model calculations correspond to ensemble averages and not individual realizations of the random concentration field. When averages of the measurements corresponding roughly at the same y/σ_y (actually lying between $0.9y/\sigma_y$ and $1.1y/\sigma_y$) are taken as approximations of the respective ensemble values and compared against the model calculations (Figure 3-2b) the performance of the model should be considered satisfactory. Another, even more illustrating, example of the same nature is given in Figure 5-1 which is based on measurements reported in Csanady (1973).

- (ii) *Modeling situations concerned with the exceedance of some critical value by a rapidly changing concentration, even for very short times.*

Examples of such situations are the accidental release of toxic or flammable gases (Chatwin, 1982), and the creation of smoke screens for defense purposes (Ohmstede et al., 1982). In these cases probabilistic properties of the concentration field are essential in assessing the environmental impact.

- (iii) *Modeling nonlinear processes (usually chemical) within plumes.*

For processes such as reactions with nonlinear kinetics, the effective conversion rates may depend critically on the level and spatial distribution of turbulent concentration fluctuations (i.e., on the quality or completeness of the fine scale mixing locally inside the instantaneous plume boundaries). The local intensity of segregation I_s , involving the variance of fine scale "in plume" fluctuations, can be used to quantify the interaction of mixing and chemistry for second order chemical reactions.

In dealing with such problems it is essential to discern the spatial scales associated with a given portion of the fluctuations spectrum as they may affect the phenomenon under study and its consequences in qualitatively very different ways. Thus turbulent eddies that at a given location are of size comparable to and larger than the local plume dimensions result in its irregular meandering, i.e., a bulk motion (Figure 5-2). Only eddies smaller than these are responsible for the mixing process inside the instantaneous plume boundaries, the state of which is described by the level

of instantaneous "internal" concentration fluctuations and thus associated with the processes of relative or two-particle dispersion. Thus, for example, rates of nonlinear chemical reactions between plume constituents and the ambient are affected solely by the internal fine scale fluctuations. On the other hand, assessing physiological effects from the varying concentration of a pollutant requires taking into account the total variability of the concentration field at the fixed receptor location.

A complete description of the fluctuations problem would require knowledge of the entire probability density of random concentrations, and in the case of interacting concentration fields (e.g. of chemically reacting species) of their joint probability densities. Probability densities at every point in a fixed frame of reference, and the associated statistics, reflect the total randomness of the concentration field which results from absolute diffusion; the respective densities and statistics for every point in a frame of reference whose origin follows the random meandering motion of the center of mass of an instantaneous release, or the instantaneous centerline of a continuous plume, reflect internal randomness due to relative dispersion. To deduce fixed frame probability densities and non-central moments of concentrations from the corresponding moving frame quantities one has to calculate the convolution of the latter with the spatial position probability density of the meandering origin of the moving frame (see Appendix A5.1 and Csanady, 1973, Chapters IV and VII).

Although the problem of calculating probability densities of concentration fields (of both conserved and reactive scalars) has been pursued through a variety of approaches (see, e.g., Hill, 1976; O'Brien, 1980; Pope, 1982, 1985) its complexity does not presently allow for simple, practical models. (see also Chapter 4). A more feasible goal is the prediction of the second moment $\langle c^2 \rangle$, or of the variance σ_c^2 , of the random instantaneous concentration field, which, combined with the knowledge of the mean $\langle c \rangle$, would provide a description adequate for most applications. Theoretical study of the σ_c^2 dynamics originated in the works of Corrsin (1952, 1964) and Batchelor (1959). Major results concerning σ_c^2 behavior in different turbulent flows are summarized in various sources (e.g. Brodkey, 1967; Monin and Yaglom, 1971, 1975; Hinze,

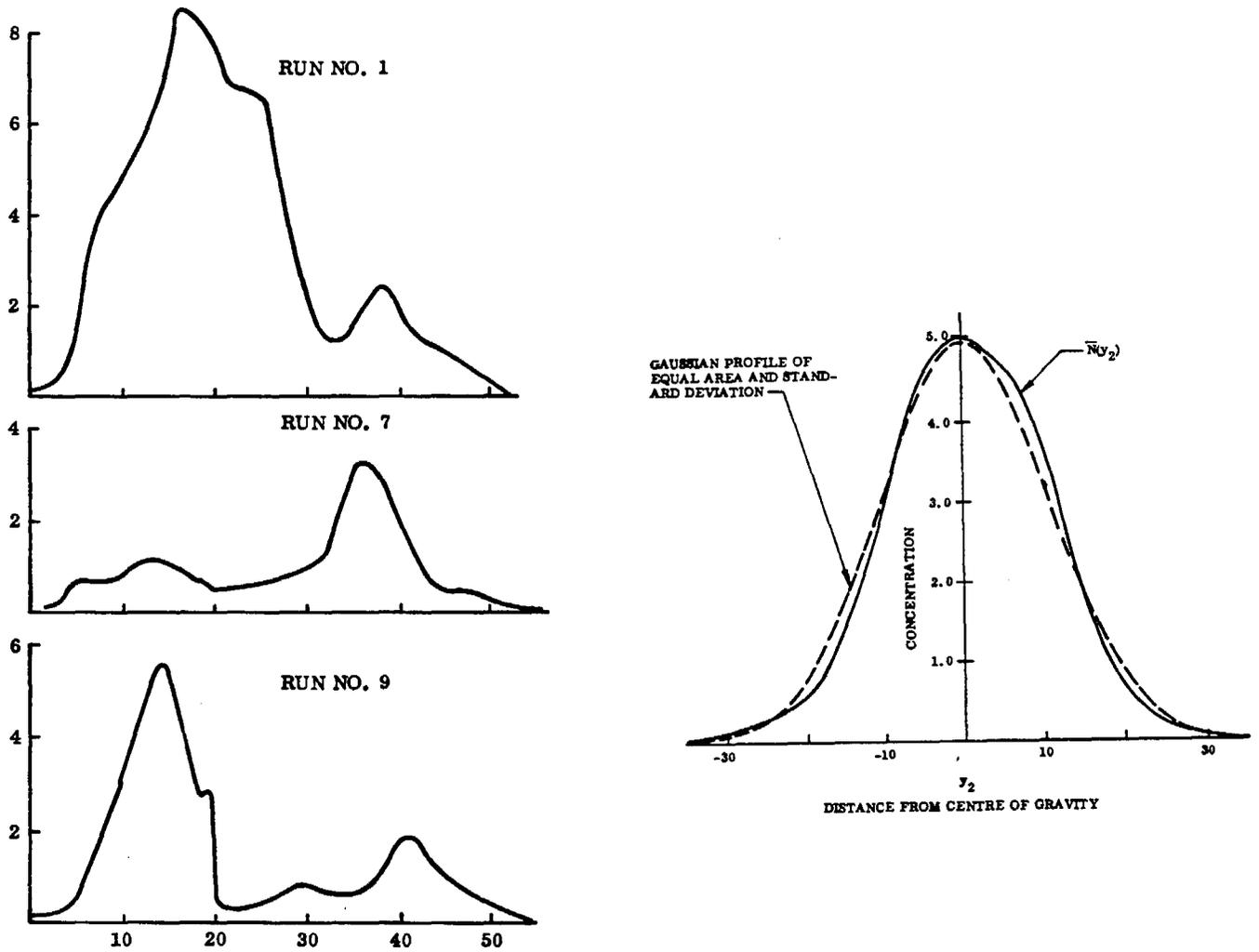


Figure 5-1
Instantaneous and average plume concentration profiles
measured relative to the plume centerline
(Source: Csanady, 1966, 1973)

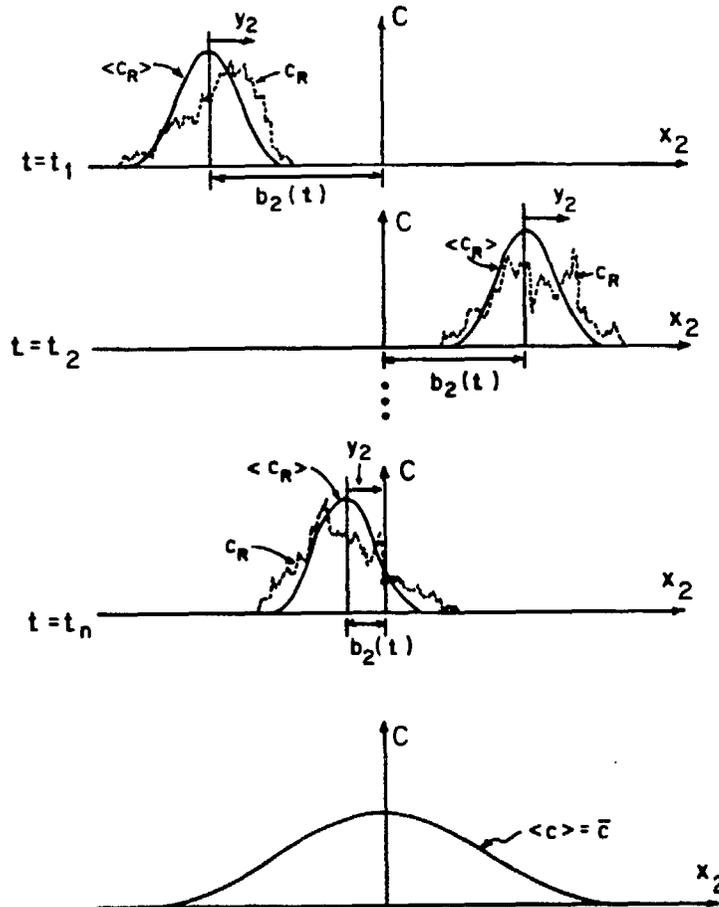


Figure 5-2

Cross-flow profiles of expected instantaneous concentrations in a fixed and in a meandering frame of reference ($\langle c \rangle$ and $\langle c_R \rangle$ respectively) at the same downwind distance x_1 and at various times t_1, t_2, \dots, t_n , for a plume that is assumed to be transferred essentially intact by meandering. "Actual" instantaneous realizations of the concentration field $c \equiv c_R$ are also presented. (Note that $\langle c \rangle$ is the long term time average of the ensemble average $\langle c_R \rangle$ at a fixed position.)

1975; Townsend, 1976; Bradshaw, 1978; Fischer et al., 1979). As far as dispersion in ambient turbulence is concerned, the three major approaches commonly employed in modeling the mean field, i.e. Eulerian and Lagrangian statistical methods (including Langevin models) and dimensional (similarity) analysis have also been used, often combined, to study the variance of concentration fields resulting from *passive releases (*) from strongly localized sources* (Csanady, 1967, 1973; Thomas, 1979; Chatwin and Sullivan, 1979a, 1980; Robins and Fackrell, 1979; Durbin, 1980, 1982; Sawford, 1982, 1983, 1985; Sykes et al., 1984; Hanna, 1984 – see also Weil, 1985). A separate class of models originated with Gifford's (1959) fluctuating plume concept which considers fluctuations produced exclusively by the bulk meandering of the plume ("external" fluctuations), neglecting all randomness inside the instantaneous plume boundaries, and therefore calculates what we will call here the "external" variance. Various applications and extensions of this concept (Scriven, 1965; Diamante et al., 1976; Fackrell and Robins, 1982b) as well as related formulations (Venkatram, 1979; Hanna, 1984) have appeared in the literature. (A new generalization of the traditional fluctuating plume model so that it accounts *explicitly* for both the external and internal fluctuations is presented in Appendix A5.3 of the present chapter). Finally, the empirical models of Wilson et al. (1982ab) provide expressions for σ_c^2 constructed so as to fit wind tunnel data where meandering was recognized as the dominant source of observed fluctuations (Fackrell and Robins, 1982ab).

Available data of short term fluctuation statistics for pure plumes from point sources, that is for dispersion governed *exclusively by the ambient turbulence*, are basically relevant to the total variance observed at a fixed point, and include mainly wind tunnel (Fackrell, 1978, 1980; Fackrell and Robins, 1981, 1982ab; Robins, 1978, 1979; Gad El Hak and Morton, 1979) and atmospheric field (Gosline, 1952; Barry, 1971; Ramsdell and Hinds, 1971; Kimura et al., 1981; Jones, 1983; Sawford et al.,

(*) The term "passive" is used in the sense that this release does not affect the properties of the ambient flow.

1985) measurements. Data on in-plume fluctuations, definitely more scarce, are also available, both from laboratory flows with insignificant meandering (Becker et al., 1966), and field measurements performed relevant to the meandering center of mass of continuous oceanic (Murthy and Csanady, 1971; Sullivan, 1971; Chatwin and Sullivan, 1979b) and atmospheric (Eidsvik, 1980) plumes. Finally, some related information can be found in the substantial fluid-mechanical literature on momentum jets and buoyant plumes (List, 1982; Gebhard et al., 1984).

The brief preceding analysis is complemented by Appendix A5.2 where one can find some further comments and explanations relevant to the works surveyed here.

Some rather general results on plume fluctuations, based mainly on data from pipe flows and from wind tunnels simulating either homogeneous and isotropic turbulence or the neutral atmospheric boundary layer are:

- (i) Production of both internal and external fluctuations is in general significant only close to the source.
- (ii) Meandering is typically the most significant source of fluctuations in the near field whereas internal fluctuations prevail far downwind. Further analysis suggests that the external intensity of fluctuations at the centerline (i.e. the ratio of external variance to the square of the mean concentration) reaches a maximum at some distance downwind and decays towards zero thereafter; the corresponding internal intensity does not decay but seems to tend towards some constant nonzero value.
- (iii) Intermittency effects are very significant in the near field and are typically associated with meandering; relative concentration measurements are very often free of intermittency effects in the "core" of the instantaneous plume.
- (iv) The variance of atmospheric concentrations from ground level sources exhibits profiles that are approximately self-similar in both the horizontal and vertical directions; further, it does not show significant dependence on source size.
- (v) The same variance for elevated sources initially shows dependence on source size that is eventually "forgotten." Horizontal profiles of σ_c^2 are again approximately

self-similar, but vertical profiles show a more complicated behavior: In the immediate vicinity of the source they are self-similar until the effect of the ground is felt. In the far field, however, these profiles become again self-similar, resembling those of a ground level source.

- (vi) A power law concentration probability density resulting from Gifford's fluctuating plume model seems to provide the best fit to experimentally measured densities of fixed frame data in most cases. Log-normal densities offer the best fit to sets of non-intermittent data.

However, in spite of the recent advances in analyzing and understanding the problem of turbulent concentration fluctuations, a simple, rational scheme for routine calculation of the instantaneous *internal* plume concentration variance, for use in conjunction with the Gaussian relative dispersion formulas for the instantaneous mean field does not exist. Such a model can, in fact, be viewed as a counterpart of Gifford's (1959) model for the *external* variance. The development of such a practical scheme is the object of this work. We start from the Eulerian transport equation for σ_c^2 , modeling the processes described by its components in terms of known or measurable quantities, and continuing with an analysis of potential simplifications of the mathematical description through self-similarity assumptions for σ_c^2 . The information that is systematized in this way is subsequently utilized in the formulation of a new model that provides simple, closed form, analytical expressions for σ_c^2 for the case of a continuous passive "point" release of material in a turbulent field of uniform mean velocity.

Before proceeding to the development of models for the concentration variance it is useful to recall the effects of averaging time on this property (compare also with the discussion of Appendix A6.1). When the ensemble under study contains time averages and not instantaneous values, the variance for this ensemble $\sigma_{c,T}^2$ is directly related to the variance of instantaneous concentrations σ_c^2 through (see, e.g., Tennekes

and Lumley, 1972, p. 212)

$$\sigma_{c,T}^2 = \frac{2\sigma_c^2}{T} \int_0^T \left(1 - \frac{\tau}{T}\right) \rho(\tau) d\tau \quad (5.1 - 1a)$$

where T is the averaging time and $\rho(\tau)$ is the temporal auto-correlation coefficient of concentration fluctuations, commonly assumed of exponential form. For large times, i.e. for $T \gg T^*$, where T^* is the integral time scale of the correlation, (5.1-1a) reduces to the approximate relation

$$\sigma_{c,T}^2 = 2\sigma_c^2 \frac{T^*}{T} \quad (5.1 - 1b)$$

(Note that in the special case of exponential correlation of concentration fluctuations (5.1-1b) is valid under the milder restriction $(T/T^*)^2 \gg 1$.)

5.2 THE TRANSPORT EQUATION FOR THE CONCENTRATION VARIANCE

5.2.1 General Considerations

Eulerian models for the estimation of σ_c^2 are based on the fundamental transport equation for c for a fixed frame of reference

$$\frac{\partial c}{\partial t} + u_i \frac{\partial c}{\partial x_i} = D \frac{\partial^2 c}{\partial x_i \partial x_i} \quad (5.2-1)$$

(summation convention implied) where u_i , c are stochastic variables that can be viewed as consisting of a mean and a fluctuating part (Reynolds decomposition), i.e. $u_i = \langle u_i \rangle + u'_i$, $c = \langle c \rangle + c'$. In the following the operation $\langle \cdot \rangle$ denotes always ensemble averaging; for (locally) homogeneous and stationary turbulence this can be replaced by spatial or temporal averaging, under an ergodic hypothesis (see, e.g., Hinze 1975) as far as the velocities are concerned. For strongly localized sources the concentration field cannot be homogeneous and thus only time averages can approximate ensemble means (when, of course, the specific phenomenon under study is in steady state).

The equation for the variance of c as obtained from (5.2-1) is

$$\begin{aligned} & \frac{\partial \langle c'^2 \rangle}{\partial t} + \overbrace{\langle u_i \rangle \frac{\partial \langle c'^2 \rangle}{\partial x_i}}^{(i)} = \\ & = \overbrace{-2 \langle u_i c' \rangle \frac{\partial \langle c \rangle}{\partial x_i}}^{(ii)} + \overbrace{\frac{\partial}{\partial x_i} \left(D \frac{\partial \langle c'^2 \rangle}{\partial x_i} - \langle u'_i c'^2 \rangle \right)}^{(iii)} - \overbrace{2D \frac{\partial \langle c' \partial c' \rangle}{\partial x_i \partial x_i}}^{(iv)} \end{aligned} \quad (5.2-2)$$

This equation expresses the fact that the level of $\sigma_c^2 = \langle c'^2 \rangle$ changes through an imbalance of

- (i) advection,
- (ii) the generation rate of scalar fluctuations by gradients in the mean concentration,

- (iii) the diffusive transfer produced by molecular dispersion and turbulent velocity fluctuations (the former being usually negligible), and
- (iv) the dissipation of fluctuations due to molecular diffusion in the fine scale structure.

The relative importance of the different processes in the σ_c^2 budget depends on the particular type of flow (see e.g. Launder, 1978); bulk meandering and internal fine scale motions will contribute in a qualitatively different manner not only to the observed overall level of fluctuations at a given point but to the relative balance of terms in the governing equation for σ_c^2 as well. Here we confine attention to relative dispersion in turbulence with a uniform mean velocity \bar{u} , and to internal fluctuations in plumes that generate an ensemble of instantaneous realizations which is in a steady state with respect to a frame of reference that follows the randomly meandering centerline translating parallel to itself. (The steady state concept here is, of course, relevant to the mean of the ensemble and not to the actual concentration field.) Equations (5.2-1) and (5.2-2) with $\partial(\cdot)/\partial t = 0$, $\langle u_1 \rangle = \bar{u}$, $\langle u_2 \rangle = \langle u_3 \rangle = 0$ are assumed to hold for this moving frame of reference. In other words, if the moving frame coordinates in the crosswind plane at x_1 are y_2, y_3 where $y_2 = x_2 - b_2$, $y_3 = x_3 - b_3$, b_2, b_3 being the random coordinates of the instantaneous plume centerline in this plane, then (5.2-1) and (5.2-2) are assumed to adequately describe mass transport in the meandering frame (see Chapter 6, for further discussion of this point). In the case where flow conditions are such that the mean plume centerline is not a straight line parallel to the horizontal plane (i.e. $\langle b_k \rangle$, $k = 2, 3$, are not constant for all x_1), then the above equations are still sufficient approximations (for a translating frame meandering about this centerline) for very small values of the derivatives ($\partial \langle b_k \rangle / \partial x_1$), $k = 2, 3$, $l = 1, 2, 3$. The situation considered here is schematically represented in Figure 5-2: The mean concentration in (5.2-1) is $\langle c_R \rangle$ and the fluctuations in (5.2-2) represent deviations of actual realizations c_R from this value. In the present work we limit attention to c_R and $\langle c_R \rangle$; fixed frame properties (such as $\langle c \rangle$ of Figure 5-2) will not be examined. Thus in the following the subscript R for the concentration

will be dropped without any loss of clarity. Another point to note is that in this approach intermittency effects are attributed to bulk motions, in compliance with available experimental evidence; the probability of exactly zero concentrations in the vicinity of the origin of the meandering frame is assumed negligible.

5.2.2 Modeling Individual Terms of The Variance Transport Equation

(a) The Production Term

In the perspective of this study we will consider as adequate a description of $\langle u'_i c' \rangle$ in terms of eddy diffusivities K_{R_i} that will be assumed to be in general functions of the distance from the source, and to correspond to the effects of small scale dispersion processes (the subscript R used to denote the relevance to relative dispersion – or absolute dispersion without significant meandering). In this way (5.2-2) continues to hold locally inside the instantaneous plume. In a sense this is a “Lagrangian” modeling step, since K_{R_i} 's thus defined are not properties of the flow field but functions of the dispersion time for specific emissions. Thus, locally

$$\langle u'_i c' \rangle = -K_{R_i}(x_1) \frac{\partial \langle c \rangle}{\partial y_i} \quad (5.2 - 3)$$

where the point species source is located at $x_1 = 0$. The variation of K_{R_i} with downwind distance from the source will be calculated from

$$K_{R_i}(x_1) = \frac{\langle u_1 \rangle}{2} \frac{d\sigma_{R_i}^2}{dx_1} = \frac{1}{2} \frac{d\sigma_{R_i}^2}{dt} \quad (5.2 - 4)$$

where σ_{R_i} is the standard deviation of relative dispersion in the i direction. Methods for estimating σ_R 's can be found in Hinze (1975, p.406), Monin and Yaglom (1975), and Seinfeld (1983). Thus

$$\Pi_c = -2 \langle u'_i c' \rangle \frac{\partial \langle c \rangle}{\partial y_i} = 2K_{R_i}(x_1) \left(\frac{\partial \langle c \rangle}{\partial y_i} \right)^2 \quad (5.2 - 5)$$

(b) The Diffusive Flux Term

Most approaches for modeling the diffusive flux of σ_c^2 have also adopted a gradient type representation of $\langle u'_i c'^2 \rangle$, usually neglecting all molecular diffusion effects (see Launder, 1978). Various forms of gradient type formulas have been used (Bradshaw and Ferris, 1968; Spalding, 1971; Wyngaard, 1975; Thomas, 1979; Sykes et al., 1984). A simple approach, especially when eddy diffusivities are used in representing $\langle u'_i c' \rangle$, is to assume a gradient transport relationship of the form

$$\langle u'_i c'^2 \rangle - D \frac{\partial \sigma_c^2}{\partial x_i} = -\tilde{K}_i \frac{\partial \sigma_c^2}{\partial x_i} \quad (5.2-6)$$

Assuming that the same dispersive mechanisms account for the spread of both $\langle c \rangle$ and σ_c^2 we set $\tilde{K}_i = K_{R_i}$. Data from geophysical flows provide supportive but certainly not conclusive indication for the validity and the limitations of such a gradient transport scheme (Csanady, 1973; Nettekville and Wilson, 1980). In any case, since higher order closure schemes are beyond the scope of the present analysis, we will adopt the closure assumption of (5.2-6) with $\tilde{K}_i = K_{R_i}$ given by (5.2-4).

(c) The Dissipation Term

Many studies have attempted to model this term by analogy to the dissipation of velocity fluctuations (kinetic energy dissipation) for which there is more extensive experimental information available. The most common procedure is to adopt an expression of the general form

$$\Phi \equiv 2\epsilon_c = 2D \frac{\langle \partial c' \partial c' \rangle}{\partial y_i \partial y_i} = \frac{nD\sigma_c^2}{\ell_d^2} = \frac{\sigma_c^2}{t_d} \quad (5.2-7)$$

where ℓ_d is a "dissipative length scale" (a "hybrid" Corrsin scale) analogous to the Taylor scale for the dissipation of velocity fluctuations, and $nD/\ell_d^2 = 1/t_d$ is the reciprocal of a characteristic *decay time* scale t_d . The choice of the numerical factor n in this relation is a matter of convention (e.g. $n = 4, 6$ and 12 are used in the literature). The time scale t_d is the single most important quantity in the characterization of the mixing process; actually in most approaches all the effects of molecular diffusion on mixing are lumped into this parameter.

For the case of homogeneous, quasi-isotropic, turbulent velocity and concentration fields both theoretical considerations and experimental evidence suggest that (Gibson and Schwarz, 1963; Hinze, 1975; Launder, 1978; Warhaft and Lumley, 1978; Sreenivasan et al., 1980; Durbin, 1982).

$$t_d = kt + k_0 \quad (5.2 - 8)$$

where k lies in the range $1/3$ to $2/3$, $t = x_1/\langle u_1 \rangle$, and k_0 is a constant that can be assumed equal to zero when the production of fluctuations is localized at $t = 0$.

In the case of a continuous plume generated by a concentrated point (or line) source in a field of homogeneous turbulence we may also expect the rate of dissipation of concentration fluctuations to be proportional to fluctuation intensity σ_c^2 , because essentially the same physical factors must govern across-the-spectrum transfer of contributions to σ_c^2 , regardless of the manner in which the fluctuation were generated (Csanady, 1973). However, now the "ages" of the concentrations fluctuations cover a broad range and the decay time-scale may vary in an unknown manner. Thus one should set locally $\Phi = \sigma_c^2/t_d$ with $t_d = t_d(x_1, y_2, y_3)$, i.e. assume that t_d is some function of position that has to be determined.

The approach described by (5.2-7) has appeared in some works relevant to air pollution. Thus Donaldson and Hilst (1972) estimated a typical (constant) value of $t_d \simeq 5\text{min}$ for a (hypothetical) average turbulent mass of atmospheric air. This (constant) value of the decay time scale was used by Kewley (1978) in a reactive plume model. However, in plumes, the factors affecting the intensity of dissipation (and therefore t_d) will change significantly with travel time and the assumption of constant t_d is not an appropriate one. In a more justifiable approach Csanady(1967, 1973) and Thomas (1979) adopted (5.2-8) with the theoretical value $k = 2/3$ (Hinze, 1975, p.301) and $k_0 = 0$. Modified forms of (5.2-8) were also suggested by Fackrell and Robins (1979) and Netterville (1979) and utilized by Wilson et al. (1982ab) in an empirical model for the total level of atmospheric plume fluctuations. However in the latter case the dominant component in the overall observed variance values was

bulk variance (Fackrell and Robins, 1982ab), the dissipation of which mainly reflects the expansion of the instantaneous plume to the size of the time average envelope; the approach of Sykes et al. (1984) is more appropriate for this situation.

For the dissipation of fine scale fluctuations by molecular diffusion in the moving frame of reference we adopt (5.2-8) in the form

$$t_d = \frac{x_1 + x_0}{A_1 \langle u_1 \rangle} = \frac{1}{A_1} (t + t_0) \quad (5.2 - 9)$$

where $A_1 = 1/k$ and x_0 is a "virtual origin correction" which accounts for the initial production dominated region near the source. This equation should be viewed as a reasonable first estimate for $t_d(x_1, y_2, y_3)$ for a relatively "slender" plume. The success of this approximation for a given range of downwind distances will rely heavily on the proper choice of A_1 ; unfortunately, the uncertainty involved in this choice is large, even for relatively ideal flow situations. Some further insight on this problem can be obtained by examining the transport equation for Φ (Launder, 1978). Indeed, for point sources the generation terms involving mean concentration field gradients will play a significant role in the overall Φ balance, especially in the vicinity of the source, thus resulting in higher dissipation rates and lower characteristic dissipation times in comparison with the quasi-isotropic cases to which most of the available information is relevant.

5.2.3 The Effects of Boundaries

The presence of a boundary parallel to the mean flow \bar{u} (e.g. the ground in the case of atmospheric dispersion) affects the balance of σ_c^2 in two ways:

First, if this boundary does not interact chemically or otherwise with the plume species, it imposes a condition of zero transfer of plume material, which, in addition to increasing the mean concentration near the surface, affects the intensity of concentration fluctuations by controlling the production of σ_c^2 . Since $\partial \langle c \rangle / \partial x_1$ is normally small compared to the lateral gradients, a decrease in $\partial \langle c \rangle / \partial y_3$ will reduce the production of fluctuations significantly, especially near the horizontal centerline of the plume where $\partial \langle c \rangle / \partial y_2$ will also be small.

Second, the boundary affects the flow field in such a way that advection and turbulent transfer terms are expected to be small near the surface. In this analysis it will be assumed that the mean velocity is uniform except for a very thin layer near the boundary. However the no-slip boundary condition near the surface results in high local mean shear and intensity of turbulence which rapidly distort and stretch plume filaments, thus increasing the surface area available for molecular diffusion which dissipates concentration fluctuations. Thus, in general the presence of production and dissipation processes accounts for different behavior of $\langle c \rangle$ and σ_c^2 near the surface. Wind tunnel studies suggest that very close to the ground there might be a well mixed layer, where dissipation practically reduces σ_c^2 to zero; however, available data do not extend close enough to the surface to show explicitly this effect (Wilson et al., 1982a).

Hence, $\partial\sigma_c^2/\partial y_3$ is not expected to approach zero gradually at the surface. It is more appropriate to view the latter as an absorbing (possibly not perfectly) boundary with respect to σ_c^2 and thus

$$\sigma_c^2 \rightarrow 0 \quad \text{at } x_3 = y_3 + b_3 = 0 \quad (5.2 - 10)$$

5.2.4 The Effects of Source Size

The assumption of a point source is an extreme idealization that is actually incompatible with the process of relative diffusion, since the latter requires a nonzero initial separation of the diffusing fluid particles (see, e.g., Durbin, 1980). The degree to which concentration fluctuations are influenced by source conditions, such as source size (or initial separation) has been a subject of both theoretical analysis (Chatwin and Sullivan, 1979a; Durbin, 1980, 1982; Sawford, 1983), and experimental study (Fackrell and Robins, 1982a). The available experimental evidence for continuous plumes relates important source effects to meandering processes and shows that they persist for distances where bulk fluctuations are dominant; far downstream the variance tends to "forget" these effects. Theoretical considerations (Durbin, 1980; Sawford, 1983) show that the intensity of internal fine scale fluctuations tends to a

constant value that in general must depend on the initial size of an instantaneous release. However, the available data on relative dispersion of continuous plumes are not adequate to provide reliable quantitative estimates of source size effects. In fact, far enough from the source, data on both the total and the fine scale variance, and for both elevated and ground level sources, show that under constant flow conditions the centerline intensity of fluctuations approaches a constant value that is (almost) independent of source size. In the present work, in order to retain simplicity, source effects will not be accounted for explicitly; the species source is assumed localized at a point and necessary corrections to this idealization are invoked a posteriori when the mathematical manipulations cannot accommodate the point source concept. The effects of the finite size of the actual source will have to be incorporated (either explicitly or implicitly) in a parameter of the model.

5.2.5 The Assumption of Self Similarity

Introducing the approximation of (5.2-9) and the transport closure schemes of (5.2-3), (5.2-6), equation (5.2-2) reduces to the following form for the steady state (in the (x_1, y_2, y_3) frame) point source plume in a mean flow field $\bar{u} = \langle u_1 \rangle$ along the $x_1 \equiv y_1$ direction:

$$\begin{aligned} \overbrace{\bar{u} \frac{\partial \sigma_c^2}{\partial x_1}}^{(i)} = & \overbrace{2K_{R_2}(x_1) \left[\left(\frac{\partial \langle c \rangle}{\partial x_1} \right)^2 + \left(\frac{\partial \langle c \rangle}{\partial y_2} \right)^2 \right] + 2K_{R_3}(x_1) \left(\frac{\partial \langle c \rangle}{\partial y_3} \right)^2}^{(ii)} + \\ & \overbrace{+ K_{R_2}(x_1) \frac{\partial^2 \sigma_c^2}{\partial y_2^2} + K_{R_3}(x_1) \frac{\partial^2 \sigma_c^2}{\partial y_3^2}}^{(iii)} - \overbrace{\frac{\sigma_c^2}{t_d(x_1)}}^{(iv)} \end{aligned} \quad (5.2-11)$$

where terms (i) to (iv) represent the respective terms of (5.2-2).

A rational approach towards the simplification of (5.2-11) is based on the hypothesis of self-similarity for both the instantaneous $\langle c \rangle$ and σ_c^2 fields. As already mentioned, this hypothesis has considerable experimental support (Csanady, 1973; Fackrell and Robins, 1982a); it was first introduced as an approximation in the Eule-

rian modeling of σ_c^2 by Csanady (1967) who studied the construction of self-similarity models for isotropic turbulence and for an unbounded flow.

If (5.2-11) is satisfied by $\langle c \rangle$ and σ_c^2 that obey the self similar relations

$$\langle c \rangle = \langle c_0(x_1) \rangle f(\hat{r}), \quad \sigma_c^2 = \langle c_0(x_1) \rangle^2 g(\hat{r}) \quad (5.2 - 12)$$

where

$$\langle c_0(x_1) \rangle = \frac{S}{2\pi \bar{u} \sigma_{R_2} \sigma_{R_3}}, \quad f(\hat{r}) = \exp\left(-\frac{\hat{r}^2}{2}\right)$$

(S is the source strength) and

$$\hat{r} = \check{r}/\check{s}$$

with

$$\check{r} = \sqrt{y_2^2 \sigma_{R_3}^2 + y_3^2 \sigma_{R_2}^2}, \quad \check{s} = \sigma_{R_2} \sigma_{R_3}$$

(notice that \check{r} , \check{s} have units of $(\text{length})^2$), then it can be shown that two necessary conditions for (5.2-11) to have self-similar solutions are

$$\frac{d\sigma_{R_3}}{d\sigma_{R_2}} = \frac{\sigma_{R_3}}{\sigma_{R_2}} \quad \text{or} \quad \sigma_{R_3} = \kappa \sigma_{R_2} \quad (5.2 - 13)$$

and

$$\frac{\sigma_{R_2} \sigma_{R_3}}{\bar{u} t_d} = \hat{\alpha} \left(\frac{\sigma_{R_2}^3 y_3^2}{\check{r}^2} \frac{d\sigma_{R_3}}{dx_1} + \frac{\sigma_{R_3}^3 y_2^2}{\check{r}^2} \frac{d\sigma_{R_2}}{dx_1} \right) \quad (5.2 - 14)$$

where κ and $\hat{\alpha}$ are constants.

Here we will in general assume that the increase of σ_{R_2} and σ_{R_3} with distance from the source obeys *locally* the same exponential law within a multiplicative factor. (This exponential law will be different in the various phases of relative dispersion.) Regarding atmospheric dispersion, experience shows the above assumption to be usually a reasonable approximation.

Now, for $\sigma_{R_2} = \kappa \sigma_{R_3}$ one has

$$\hat{\alpha} = \frac{\sigma_{R_2}}{\left(\frac{d\sigma_{R_2}}{dx_1}\right) \bar{u} t_d} \frac{1}{\kappa}$$

If σ_{R_2} obeys the power law

$$\sigma_{R_2} = \sigma_{0_2} x_1^p$$

σ_{0_2} being a constant of appropriate dimensions, then

$$\hat{\alpha} = \frac{x_1}{p} \frac{1}{\bar{u} t_d}$$

and, employing (5.2-9),

$$\hat{\alpha} = \frac{A_1}{p} \frac{x_1}{x_1 + x_0}$$

Thus, if A_1 and p are constants over a finite range of x_1 , the necessary condition for self-similar solutions of (5.2-11) becomes $x_0 = 0$, in which case $\hat{\alpha} = A_1/p$. Hence, the theoretical and empirical information that is available for p and A_1 can be used to provide first estimates for $\hat{\alpha}$.

When equations (5.2-13) and (5.2-14) hold then (5.2-11) becomes

$$\frac{d^2 g}{d\hat{r}^2} + \left(\frac{1}{\hat{r}} + \hat{r} \right) \frac{dg}{d\hat{r}} + (4 - \hat{\alpha}) g = -2 \left(\frac{df}{d\hat{r}} \right)^2 \quad (5.2 - 15)$$

The boundary conditions for (5.2-11) arise from requirements of axial symmetry and a decay of σ_c^2 to zero at large radial distances:

$$\frac{dg}{d\hat{r}} = 0 \text{ at } \hat{r} = 0, \quad g \rightarrow 0 \text{ at } \hat{r} \rightarrow \infty \quad (5.2 - 16)$$

We must remark here that boundary effects, which would complicate not only the formulation of boundary conditions but also the appropriate choice for \hat{r} , are not considered in the above analysis. Therefore this approach is formally valid for unbounded domains. Furthermore, for an elevated source, the existence of ground effects imposes an "external" length scale on the dispersion process. This "destroys" the conditions necessary for self similar characteristics of the physical problem, at least until far downwind where the source height becomes negligible compared to the distance traveled and a second range of self similarity is expected. Hence, the present self-similar model formulation will be a reasonable approximation only as long as boundary effects are not very significant, i.e. relatively close to the source.

The general solution of (5.2-15) can be shown to be

$$g(\hat{r}) \equiv g_*(\eta) = g_1(\eta) \int \frac{f_*(\eta)g_2(\eta)}{W(\eta)} d\eta - g_2(\eta) \int \frac{f_*(\eta)g_1(\eta)}{W(\eta)} d\eta \quad (5.2-17)$$

where $\eta = -(\hat{r}^2/2)$, $f_*(\eta) \equiv f(\hat{r})$, and

$$g_1(\eta) = {}_1F_1(\hat{a}, 1; \eta) \equiv \sum_{k=0}^{\infty} \frac{\Gamma(\hat{a} + k)}{\Gamma(\hat{a})\Gamma(1 + k)} \frac{\eta^k}{k!} \quad (5.2-18a)$$

$$g_2(\eta) = {}_1F_2(\hat{a}, 1; \eta) \equiv -\frac{1}{\Gamma(\hat{a})} \sum_{k=0}^{\infty} \frac{\Gamma(\hat{a} + k)}{\Gamma(\hat{a})\Gamma(1 + k)} \frac{\eta^k}{k!} [\psi(\hat{a} + k) - 2\psi(1 + k) + \ln \eta] \quad (5.2-18b)$$

$$\psi(x) \equiv \frac{\Gamma'(x)}{\Gamma(x)}$$

$$W(\eta) = W[{}_1F_1(\hat{a}, 1; \eta), {}_1F_2(\hat{a}, 1; \eta)] = -\frac{\exp(\eta)}{\eta\Gamma(\hat{a})} \quad (5.2-18c)$$

and

$$\hat{a} = \frac{(4 - \hat{\alpha})}{2}$$

${}_1F_1(\hat{a}, 1; \eta)$, ${}_1F_2(\hat{a}, 1; \eta)$ are confluent hypergeometric functions of the first and second kind respectively (Abramowitz and Stegun, 1964; Lebedev, 1965) and are linearly independent. $W(\eta)$ is their Wronskian determinant and $\psi(x)$ is the logarithmic derivative of the Gamma function. The constants of the integrations in (5.2-17) have to be calculated so as to satisfy the conditions of (5.2-16).

Alternatively, the boundary value problem defined by (5.2-15,16) can be solved numerically for specific values of $\hat{\alpha}$. Csanady (1967, 1973) pursued this approach for the isotropic case assuming Gaussian $f(\hat{r})$, and presented typical $g(\hat{r})$ profiles together with the relative intensity of stream segregation $I_s \equiv \sigma_c^2 / \langle c \rangle^2 = g \langle c_0 \rangle^2 / \langle c \rangle^2$. These calculations show that while the variance σ_c^2 (which is proportional to $g(\hat{r})$) decreases from the center of the plume to the fringes, by analogy to the mean concentration, the relative intensity of segregation – describing the degree of micromixing of the plume with the ambient – increases at the fringes. Near the plume centerline both quantities have very small gradients and thus can be considered approximately constant in a

“core region”. For different values of $\hat{\alpha}$ different profiles of $g(\hat{r})$ are obtained. The center value $g(0)$ is a rapidly varying function of $\hat{\alpha}$. For $\hat{\alpha} > 4$ the origin becomes a saddle point (because $d^2g/d\hat{r}^2$ turns positive) and a full section across the plume will show a double-peaked profile for σ_c^2 , a situation which is experimentally observed in free jets (Fischer et al., 1979; List, 1982). The physical reason is that the maximum rate of production occurs in the region of steepest gradients (around $\hat{r} = 1$) from where σ_c^2 diffuses both inwards and outwards. High diffusion and low dissipation (i.e., a low value of $\hat{\alpha}$) quickly smoothes the two peaks out resulting in a single peak at $\hat{r} = 0$. The problem in the development of self-similar solutions relies to a very large extent on the proper estimation of $\hat{\alpha}$. Csanady (1973) compared his approach to the experimental observations of Becker et al. (1966) by fitting $g(0)$ to the data. With the value of $g(0)$ obtained in this way, calculated profiles simulated measurements to a satisfactory degree with corresponding values of $\hat{\alpha}$ in the range 2.5 to 3.0. These values clearly are in very good agreement with the estimate $\hat{\alpha} = A_1/p$; indeed, for the theoretical values $p = 0.5$ and $A_1 = 1.5$, one obtains $\hat{\alpha} = 3.0$.

In conclusion, direct application of the self-similarity concept to the σ_c^2 transport problem, although it offers an integral representation of the solution of (5.2-11), does not lead to results appropriate for routine calculations (e.g. in conjunction with the common Gaussian solutions for $\langle c \rangle$). Indeed, the uncertainty in the parameters involved in (5.2-17) and the restricted range of conditions to which it applies would not justify the computational burden involved in its use. However, the conditions associated with the existence of self-similarity that are derived here are useful for reducing the complexity of the mathematical description of the fluctuations problem. These conditions will be further used in the next section combined with a scheme that is more appropriate for routine use than equation (5.2-15).

5.3 THE LOCALIZED PRODUCTION OF FLUCTUATIONS MODEL

In the following we present a new model that fulfills the need for simplicity by providing closed form analytical expressions for $\sigma_c^2(x_1, y_2, y_3)$, using a limited number of parameters. This "Localized Production of Fluctuations (LPF) Model" is based on the knowledge on the nature of the terms of (5.2-11) and of its solutions, already discussed in the previous sections. Self-similarity of σ_c^2 profiles is not an a priori assumption in the development of this model; however, when assumed to hold, it simplifies further the structure of the final equations.

To avoid excessive notational complexity in this section we adopt a (x, y, z) coordinate system and drop the subscript R from the dispersion parameters; however it must be kept in mind that throughout the following discussion (x, y, z) are coordinates relative to the meandering plume centerline and K 's, σ 's, as well as $\langle c \rangle$ and σ_c^2 , describe relative dispersion.

5.3.1 Model Formulation

The solutions of (5.2-11) can in general be expressed in terms of the Green's function G of the corresponding non-dissipative equation (containing only terms (i) and (iii)), through

$$\begin{aligned} \sigma_c^2(x, y, z) = & \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^x G(x, y, z | x', y', z') \Pi_c(x', y', z') \times \\ & \times \exp \left[-\frac{1}{\bar{u}} \int_{x'}^x \frac{dx''}{t_d(x'')} \right] dx' dy' dz' \end{aligned} \quad (5.3-1)$$

where $\Pi_c(x', y', z')$ is the spatial distribution of variance production, given by (5.2-5).

Since production of σ_c^2 is of important magnitude, relevant to the other processes contributing to the balance of σ_c^2 , mainly in the immediate vicinity of the source (where boundary effects can be neglected), an estimate of Π_c formulated in terms of a mean concentration field $\langle c \rangle$ for an unbounded flow should be a satisfactory

approximation. Considering for simplicity the isotropic case (*) with

$$K_{R_y}(x) = K_{R_x}(x) = K(x), \quad \sigma_{R_y}(x) = \sigma_{R_x}(x) = \sigma(x) = \sigma_0 x^p$$

one has

$$\Pi_c(x, r) = 2K(x) \left[\left(\frac{\partial \langle c \rangle}{\partial x} \right)^2 + \left(\frac{\partial \langle c \rangle}{\partial r} \right)^2 \right] = \Pi_x + \Pi_r \quad (5.3-2)$$

where

$$r = \sqrt{y^2 + z^2}$$

$$\Pi_x = 2K(x) \left(\frac{\partial \langle c \rangle}{\partial x} \right)^2, \quad \Pi_r = 2K(x) \left(\frac{\partial \langle c \rangle}{\partial r} \right)^2$$

In general, studies of (5.2-11) have implicitly neglected production of σ_c^2 due to gradients of $\langle c \rangle$ in the x -direction. In fact, *locally* (at a given point (x, r)) this term can be important; however, the *total* generation of fluctuations due to these gradients is small compared to the generation of gradients of $\langle c \rangle$ in the r -direction. Indeed, for Gaussian mean instantaneous concentration distributions in the meandering frame of reference:

$$\langle c(x, r) \rangle = \langle c_0(x) \rangle \exp\left(-\frac{r^2}{2\sigma^2}\right) = \frac{S}{2\pi\bar{u}\sigma^2(x)} \exp\left(-\frac{r^2}{2\sigma^2}\right)$$

the ratio

$$\frac{\Pi_r}{\Pi_x} = \frac{2x^2 r^2}{p^2 (r^2 - 2\sigma^2)^2}$$

is not necessarily much larger than unity for arbitrary (x, r) .

Consider, however, the overall cross-wind fluctuations production at a given x from gradients of $\langle c \rangle$ in the r and x directions:

$$\Xi_r(x) = \int_0^\infty \int_0^{2\pi} r \Pi_r(x, r) d\phi dr = \frac{p}{x} \frac{S^2}{2\pi\bar{u}\sigma^2(x)} \quad (5.3-3)$$

(*) These results are directly extendable to the anisotropic case by an appropriate transformation of coordinates.

$$\Xi_x(x) = \int_0^\infty \int_0^{2\pi} r \Pi_x(x, r) d\phi dr = \frac{2}{\exp 2} \sigma_0^2 p^3 x^{2p-3} \frac{S^2}{\pi \bar{u} \sigma^2(x)} \quad (5.3-4)$$

Statistical diffusion theory for small travel times demands that $p = O(1.0)$ for both the processes of absolute and relative diffusion. Thus, in the vicinity of the source $\Xi_r(x)/\Xi_x(x) = O(1/\sigma_0^2)$, which typically is much larger than unity and therefore the production of fluctuations due to gradients of $\langle c \rangle$ in the x direction can be neglected. Thus, finally, for the overall cross-flow production of fluctuations

$$\Xi(x) = \int_{-\infty}^\infty \int_{-\infty}^\infty \Pi(x, y, z) dy dz$$

one can write $\Xi(x) \simeq \Xi_r(x)$ with $\Xi_r(x)$ given by (5.3-3).

The formulation of the LPF model consists of two steps. The first step utilizes the fact that at every cross-flow plane the production of fluctuations is strongly localized around its maximum value which is attained at $r = \sigma$. Figure 5-3 shows the dimensionless distribution of radial production of fluctuations, $1/4 x \Pi_r(x, r) (\bar{u})^{-1} p^{-1} \langle c_0(x) \rangle^{-2}$, with respect to r/σ , for arbitrary x . It is reasonable therefore to approximate the distribution of production along a given radius by a delta function with strength estimated from (5.3-3). The optimal location of this delta function on each radius will be slightly off the value $r = \sigma$ since the production extends asymptotically to infinity; thus, for given ϕ , we fix this location at

$$r^* = \frac{\int_0^\infty r \Pi_r(x, r) r dr}{\int_0^\infty \Pi_r(x, r) r dr} = \Gamma \left(\frac{5}{2} \right) \sigma = \frac{3}{4} \sqrt{\pi} \sigma \quad (5.3-5)$$

i.e. at the "center of mass" of the actual production distribution. The complete locus of these delta functions at any x will be a ring of radius r^* .

Thus (for the isotropic case)

$$\Pi_c(x, r) = \Xi_r(x) \delta(r - r^*, \phi - \phi_s) \quad \text{with } r^* = \frac{3}{4} \sqrt{\pi} \sigma \quad (5.3-6)$$

where ϕ_s arbitrary in the interval 0 to 2π .

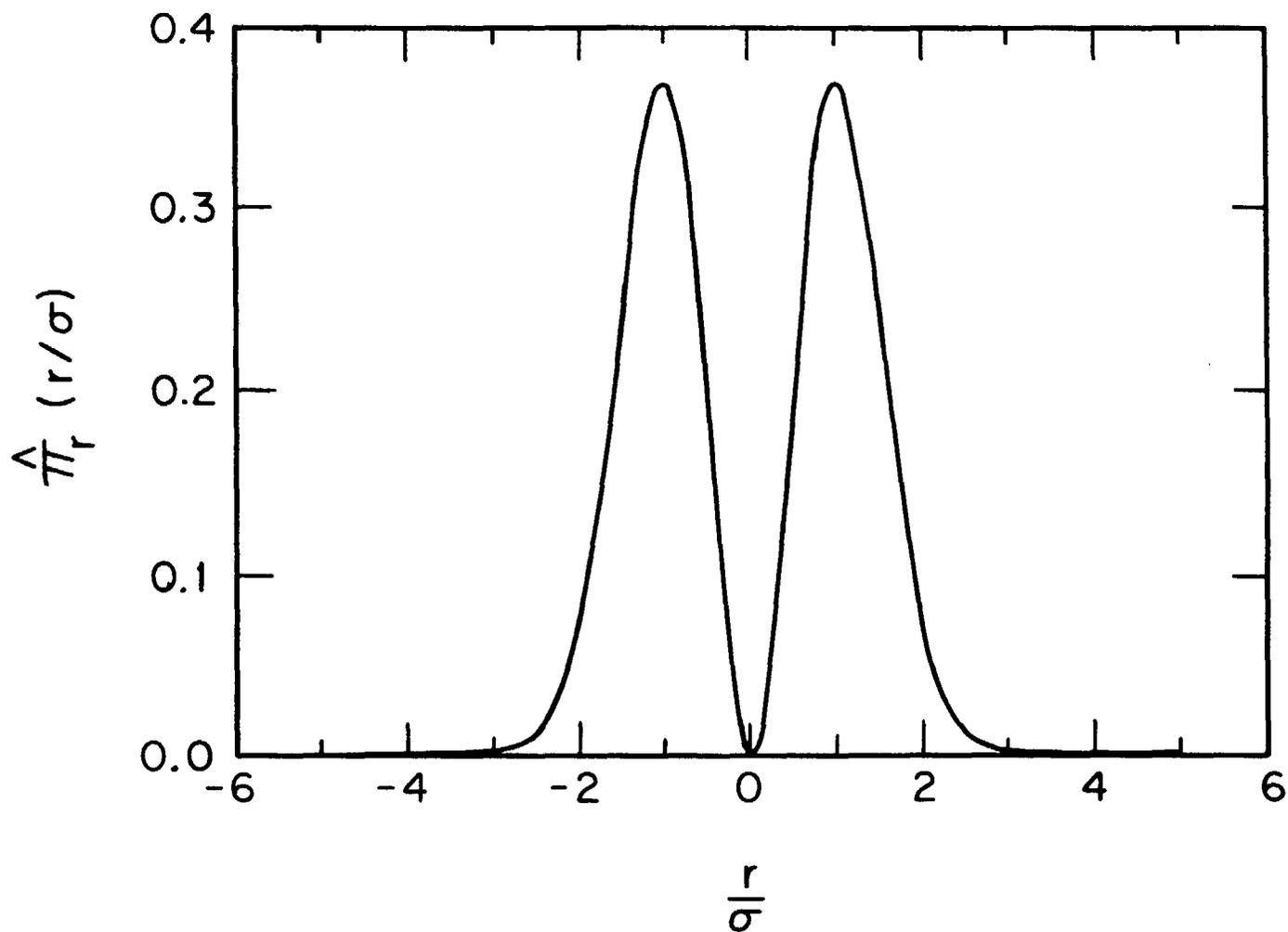


Figure 5-3

Dimensionless Radial Distribution of Fluctuation Production

at any Cross-Flow Plane

$$(\hat{\Pi}_r(r/\sigma) = (1/4)x\Pi_r(x, r/\sigma)(\bar{u})^{-1})$$

This Π_c can be introduced in (5.3-1). However, (because of the nature of the Gaussian solution of $\langle c \rangle$) production of fluctuations is infinite at $x = 0$ and the integral would diverge. Of course, this is just an artifact created from the assumed ideal "point" character of the source producing the theoretical Gaussian solution that creates a singularity at the origin. Since in reality the maximum field concentration is not infinite, it is justifiable to start the integration not at $x = 0$ but at some point \hat{x}_0 . To apply (5.3-1), one should actually have to estimate \hat{x}_0 from available data so that it simulates measurements in a satisfactory manner. However, no general a priori estimate of it should be expected since it encompasses a variety of source and initial flow characteristics, specific to each particular application. Another major problem that inhibits direct integration of (5.3-1) is the changing character of the relative dispersion process with downwind distance. Thus, fundamental two-particle dispersion theory predicts three asymptotic values for the exponent p and even if one hypothesizes step changes and constant values in between there is significant uncertainty regarding the location of these changes; similar uncertainties are associated with the σ_0 's. We circumvent these problems by introducing the second step in the formulation of the LPF model. Applying the mean value theorem of Lagrange to the isotropic form of (5.3-1) for the integration with respect to x , one has

$$\begin{aligned} \sigma_c^2(x, y, z) = \hat{\Xi}(\xi, x) \int_0^\infty \int_0^{2\pi} \frac{1}{r'} \delta(r' - r^*) \delta(\phi' - \phi_s) G(x, r, \phi | \xi, r', \phi') r' d\phi' dr' \\ \times \exp \left[-\frac{1}{\bar{u}} \int_\xi^x \frac{dx_1}{t_d(x_1)} \right] \end{aligned} \quad (5.3 - 7)$$

with

$$\hat{\Xi}(\xi, x) = \frac{S^2}{4\pi\bar{u}\sigma_0^2} 2p\xi^{-2p-1}(x - \hat{x}_0) \quad (5.3 - 8a)$$

where ξ is some point between \hat{x}_0 and x (fixed for given \hat{x}_0, x). Setting $\xi = \omega x$, with $0 < \omega \leq 1$, and assuming that $x \gg \hat{x}_0$ one can further write

$$\hat{\Xi}(x) = \frac{pS^2}{2\pi\bar{u}\sigma_0^2\xi^{2p}} \frac{x}{\xi} = \frac{\omega p S^2}{2\pi\bar{u}\sigma^2(\omega x)} \quad (5.3 - 8b)$$

So, the problem of estimating \hat{x}_0 , or, more generally, integrating (5.3-1), is essentially transferred to the problem of choosing the appropriate value (between 0 and 1) of the dimensionless *localization parameter* ω (that can possibly vary, within these limits, with distance x). Now, (5.3-7) associates σ_c^2 at x to the dispersion parameters corresponding only to x and to another single ωx . In this way all the different kinds of uncertainty implicit in (5.3-1) are now collectively lumped in one parameter, i.e. in the unknown value of ω .

5.3.2 Analytical Solutions

Equation (5.3-1) can now be used, through its reduced form (5.3-7), to obtain approximate closed solutions to the variance transport (5.2-11).

For an unbounded flow (and $\sigma_c^2 \rightarrow 0$ as $y, z \rightarrow \infty$) the corresponding Green's function of (5.2-11) (without terms (iv) and (ii)), is

$$G(x, y, z | x', y', z') = G(x - x', y - y', z - z') = \frac{1}{2\pi \sigma_y(x - x') \sigma_z(x - x') \bar{u}} \exp \left[-\frac{(y - y')^2}{2\sigma_y^2(x - x')} - \frac{(z - z')^2}{2\sigma_z^2(x - x')} \right] \quad (5.3 - 9)$$

when dispersion is assumed negligible compared to advection in the x direction and the σ 's are related to the K 's through (5.2-4).

Using (5.2-9) one obtains

$$\int_{x'}^x \frac{dx''}{t_d(x'')} = A_1 \bar{u} [\ln(x + x_0) - \ln(x' + x_0)]$$

and

$$\exp \left[-\frac{1}{\bar{u}} \int_{x'}^x \frac{dx''}{t_d(x'')} \right] = \left(\frac{x' + x_0}{x + x_0} \right)^{A_1} \quad (5.3 - 10)$$

Consider the general anisotropic (orthotropic) case, where the source of fluctuations takes the form of an elliptical ring (of infinitesimal thickness) located at $x = \xi$ with semiaxes a , b such that

$$a = 3/4 \sqrt{\pi} \sigma_y(\xi), \quad b = \kappa a$$

where $\kappa = \sigma_z(\xi)/\sigma_y(\xi)$. We define

$$w^2 \equiv ab \quad \text{and} \quad \sigma^2(x) = \sigma_y(x) \sigma_z(x)$$

and introduce the new variables

$$y_1 = \kappa^{1/2} y \quad \text{and} \quad z_1 = \kappa^{-1/2} z$$

The transformation $(y, z) \mapsto (y_1, z_1)$ has a Jacobian equal to unity and therefore preserves areas. The phenomenal variance source coordinates will transform to

$$y_{1s} = w \cos \phi_s, \quad z_{1s} = w \sin \phi_s$$

where ϕ_s is now the polar angle of point (y_{1s}, z_{1s}) in the new coordinate system. The Cartesian form of (5.3-7) in this system will be

$$\begin{aligned} \sigma_c^2 &= \frac{\hat{S}(\xi)}{2\pi\bar{u}\sigma^2(x-\xi)} \left(\frac{\xi + x_0}{x + x_0} \right)^{A_1} \\ &\times \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left[-\frac{(y_1 - y'_1)^2 + (z_1 - z'_1)^2}{2\sigma^2(x-\xi)} \right] \delta(y'_1 - y_{1s}) \delta(z'_1 - z_{1s}) dy'_1 dz'_1 \end{aligned}$$

where

$$\hat{S}(\xi) = \frac{pS^2}{2\omega\pi\bar{u}\sigma_y(\xi)\sigma_z(\xi)}$$

Introducing polar coordinates

$$r_1 = \sqrt{y_1^2 + z_1^2}, \quad y_1 = r_1 \cos \phi, \quad z_1 = r_1 \sin \phi$$

the integral in the above relation becomes

$$\int_0^{\infty} \int_0^{2\pi} \frac{1}{r'_1} \delta(r'_1 - w) \delta(\phi' - \phi_s) \exp \left(-\frac{R^2}{2\sigma^2(x-\xi)} \right) r'_1 d\phi' dr'_1$$

where

$$R^2 = (y_1 - y'_1)^2 + (z_1 - z'_1)^2 = r_1^2 + r'_1{}^2 - 2r_1 r'_1 \cos(\phi - \phi')$$

Thus,

$$\sigma_c^2 = \frac{\hat{S}(\xi)}{2\pi\bar{u}\sigma^2(x-\xi)} \left(\frac{\xi+x_0}{x+x_0}\right)^{A_1} \exp\left(-\frac{r_1^2+w^2}{2\sigma^2(x-\xi)}\right) \times \int_0^{2\pi} \exp\left[\frac{r_1 w \cos(\phi' - \phi_s)}{2\sigma^2(x-\xi)}\right] d\phi'$$

which finally gives

$$\sigma_c^2 = \frac{\hat{S}(\xi)}{2\pi\bar{u}\sigma^2(x-\xi)} \left(\frac{\xi+x_0}{x+x_0}\right)^{A_1} \exp\left(-\frac{r_1^2+w^2}{2\sigma^2(x-\xi)}\right) I_0\left(\frac{r_1 w}{\sigma^2(x-\xi)}\right) \quad (5.3-11)$$

where $I_0(\cdot)$ is the modified Bessel function of order zero.

For $x, \xi \gg x_0$ (5.3-11) becomes

$$\sigma_c^2(x, r_1; \xi) = \left(\frac{S}{2\pi\bar{u}}\right)^2 \frac{p\omega(x)^{A_1-1}}{\sigma^2(\xi)\sigma^2(x-\xi)} \exp\left(-\frac{r_1^2+w^2}{2\sigma^2(x-\xi)}\right) I_0\left(\frac{r_1 w}{\sigma^2(x-\xi)}\right) \quad (5.3-12)$$

Now, a sufficient condition for self similarity of the σ_c^2 profiles for a given x -range (where p, A_1 are assumed constant) is that ω is a constant in this range. In this case

$$\sigma(\xi) = \omega^p \sigma(x), \quad \sigma(x-\xi) = (1-\omega)^p \sigma(x), \quad w = 3/4\sqrt{\pi}\omega^p \sigma(x)$$

and σ_c^2 becomes

$$\sigma_c^2 = \langle c_0(x) \rangle^2 g\left(\frac{r_1}{\sigma(x)}\right) = \langle c_0(x) \rangle^2 g(0) \exp\left(\frac{-1}{2\bar{\omega}^{2p}} \frac{r_1^2}{\sigma^2}\right) I_0\left(\frac{3\sqrt{\pi}\omega^p r_1}{4\bar{\omega}^{2p} \sigma}\right) \quad (5.3-13)$$

where $\bar{\omega} = 1 - \omega$ and $g(\cdot) = I_s\langle c \rangle^2 / \langle c_0 \rangle^2$ is the dimensionless absolute intensity of internal fluctuations. On the plume centerline $g(0)$ will be

$$g(0) = \frac{p\omega^{A_1-2p-1}}{(\bar{\omega})^{2p}} \exp\left(-\frac{9\pi\omega^{2p}}{32\bar{\omega}^{2p}}\right) \quad (5.3-14)$$

When experimental information for this quantity is available it can be used in conjunction with information on parameters p and A_1 to estimate ω values (see next section).

Returning to the y, z coordinates, (5.3-12) takes the form

$$\begin{aligned} \sigma_c^2(x, y, z; \xi) = & \left(\frac{S}{2\pi\bar{u}} \right)^2 \frac{p\omega(x)^{A_1-1}}{\sigma_y(\xi)\sigma_z(\xi)\sigma_y(x-\xi)\sigma_z(x-\xi)} \exp\left(-\frac{y^2}{2\sigma_y^2(x-\xi)}\right) \exp\left(-\frac{z^2}{2\sigma_z^2(x-\xi)}\right) \times \\ & \times \exp\left(-\frac{ab}{2\sigma_y(x-\xi)\sigma_z(x-\xi)}\right) I_0\left(\frac{\sqrt{a^2z^2+b^2y^2}}{\sigma_y(x-\xi)\sigma_z(x-\xi)}\right) \end{aligned} \quad (5.3-15)$$

Equations (5.3-13) and (5.3-15) constitute basic, usable, forms of the LPF model when boundary effects can be assumed negligible, as in the immediate vicinity of the source.

When the dispersion field cannot be assumed unbounded, one must take into account the boundary condition of (5.2-10), i.e.

$$\sigma_c^2 \rightarrow 0 \text{ at } z(=y_3) = -b_3$$

where, because of meandering effects b_3 is a random variable. Far downstream, where meandering is negligible and boundary effects most significant, one can obtain the following result, assuming that the plume centerline is at a constant height h from the boundary (notice that now the coordinates origin is fixed on the boundary):

$$\begin{aligned} \sigma_c^2(x, y, z; \xi) = & \left(\frac{S}{2\pi\bar{u}} \right)^2 \frac{p\omega(x)^{A_1-1}}{\sigma_y(\xi)\sigma_z(\xi)\sigma_y(x-\xi)\sigma_z(x-\xi)} \exp\left(-\frac{y^2}{2\sigma_y^2(x-\xi)}\right) \times \\ & \times \exp\left(-\frac{ab}{2\sigma_y(x-\xi)\sigma_z(x-\xi)}\right) \left[\exp\left(-\frac{(z-h)^2}{2\sigma_z^2(x-\xi)}\right) I_0\left(\frac{\sqrt{a^2(z-h)^2+b^2y^2}}{\sigma_y(x-\xi)\sigma_z(x-\xi)}\right) \right. \\ & \left. - \alpha \exp\left(-\frac{(z+h)^2}{2\sigma_z^2(x-\xi)}\right) I_0\left(\frac{\sqrt{a^2(z+h)^2+b^2y^2}}{\sigma_y(x-\xi)\sigma_z(x-\xi)}\right) \right] \end{aligned} \quad (5.3-16)$$

The parameter α appearing in the above equation equals unity for a "perfectly absorbing" boundary i.e., σ_c^2 actually equal to 0 at the surface. However, the effects of dissipation might not be so strong, and a lower value for α may be more appropriate.

5.4 MODEL TESTING AND DISCUSSION

The LPF model is a simple formulation for the internal concentration variance that is directly derived from the physics of the point release problem, starting from "rigorous" equations and utilizing empirical information and approximations to simplify the analysis. The required inputs reduce to a set of "physical" parameters and a "model specific" one. The "physical" parameters are the relative dispersion σ 's (which are assumed to obey simple power laws, at least locally) and a factor relating dispersion time to the local dissipation time scale t_d . The "model specific" or "localization" parameter ω actually defines the location of an effective source of fluctuations. As already mentioned, uncertainties associated with a variety of factors such as source size, flow conditions, and the relative dispersion process itself, are "lumped" into ω . Introduction of ω reduces the uncertainty associated with the physical parameters since, instead of their complete – and unknown – variation with downstream distance, only estimates of their local values are needed.

The problem of estimating ω is facilitated by two facts: (1), the often observed validity of self similarity, which is expressed by (5.2-12); (2), the observation that $g(0)$ is "at most a weak function of the distance from the source" – even for the total fluctuations variance (Sawford et al., 1985). This $g(0)$ for given flow conditions tends to a constant value after a certain distance (Becker et al., 1966; Fackrell and Robins, 1982ab; Wilson et al., 1982ab, etc). These facts, although deduced from observations that do not cover the entire range of possible conditions encountered in laboratory and environmental flows, suggest that adequately reliable estimates of ω are possible, at least for specified ranges of the dispersion, even without a complete understanding and analysis of all the mechanisms that affect the level of $g(0)$. It is therefore often justified to treat $g(0)$ as an empirical constant typical of given flow conditions. In this simplified approach ω is completely determined from the physical parameters (including $g(0)$) of the problem. Of course in order to be able to construct

empirical estimates of, say, typical values of $g(0)$ (and therefore ω) for ambient turbulence of various Reynolds numbers, many more experimental data bases than they are currently available are needed. In a more fundamental approach $g(0)$ or closely related functions have been modeled theoretically, in terms of statistical correlations of the turbulent flow field, for source configurations that create mean concentration fields approximately equivalent to that of the continuous "point" source. Numerical simulations and analytical expressions that in general involve a measure of effective source size are available (Durbin, 1980, 1982; Sawford, 1983). However, because of the existing uncertainties and limitations in the formulation of the theoretical models, it presently seems reasonable to confine this discussion to the previously mentioned simplified approach.

As far as atmospheric dispersion is concerned, present knowledge suggests that for neutral stability the far field value of $g(0)$ is of order unity (for elevated sources), and use of the typical ("theoretical") values $p = 0.5$ (for the "far field"), $A_1 = 1.5$ to 2.5 seems to offer a qualitatively acceptable simulation of many available relevant field and wind tunnel data sets. (For example, see Figure 5-6). However the scatter, the resolution and the uncertainty of these data often make quantitative comparisons meaningless or impossible. The problems are even more severe in cases of more complicated atmospheric conditions.

The measurements most appropriate for comparing with and testing LPF model calculations are those of Becker et al. (1966) for point source dispersion in homogeneous, quasi-isotropic, pipe flow turbulence. Indeed, in the conditions of these experiments meandering was insignificant and the structure of the turbulent flow, being relevant to the conditions for which (5.2-8) was suggested, reduces the uncertainty regarding the proper choice of A_1 ; further, $p = 0.5$ fits accurately the entire range of the data. Thus, the uncertainty regarding the physical parameters is minimum. Self similarity of σ_c^2 profiles and a constant value of $g(0)$ are observed in all these experiments. Comparisons of LPF calculations with reported absolute and relative intensities of internal fluctuations are shown in Figures 5-4a, 5-4b, 5-4c and 5-5. The

parameter ω is estimated directly (for $A_1 = 1.5$) from the centerline value $g(0)$, whose square root value, for all the flows studied, lies in the range 1.0 ± 0.2 . The agreement obtained by using solely the centerline value to "adjust" ω , while p and A_1 are pre-set equal to their theoretical values, must be considered very satisfactory (Somewhat different values of A_1 , can improve slightly the success of the simulation, especially near $r/\sigma = 0.75$ where the difference between predictions and observations seems higher).

A comparison with atmospheric field data is also shown in Figure 5-6. The data are of Ramsdell and Hinds (1971) and the typical values $p = 0.5$, $A_1 = 1.5$ were used while ω is determined directly by the centerline intensity. Although the uncertainty of the data is very significant the agreement can be considered satisfactory in this case too.

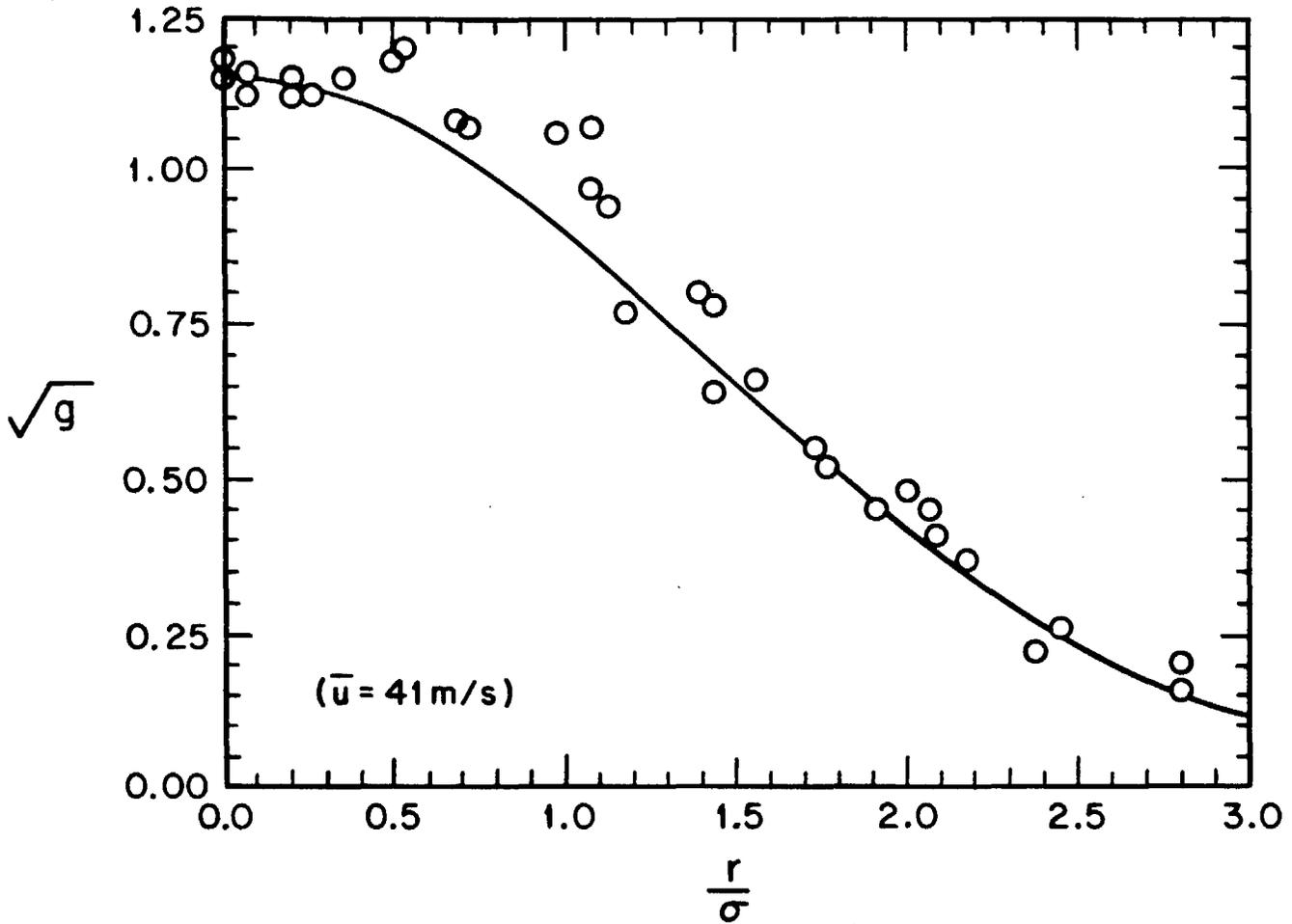


Figure 5-4a

Dimensionless Absolute Square Root Intensity of Segregation, $\sqrt{g(r/\sigma)}$
 as Predicted by the LPF Model, Compared with Data from Becker et al., (1966)

Data (at five downstream distances) for Centerline Velocity 41 m/s

LPFM Calculations for $p = 0.5$, $A_1 = 1.50$ ($g(0) = 1.15$)

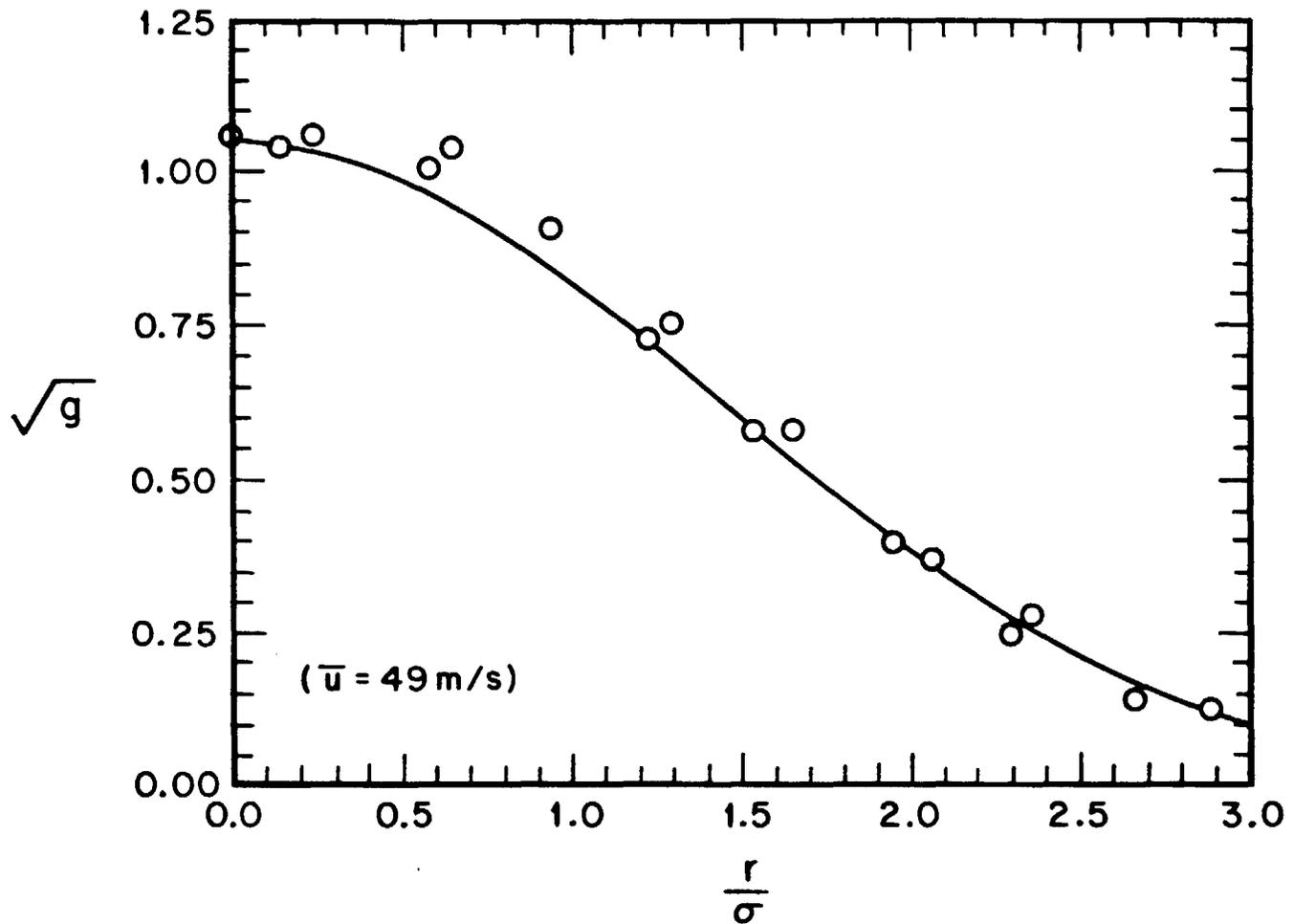


Figure 5-4b

Dimensionless Absolute Square Root Intensity of Segregation, $\sqrt{g(r/\sigma)}$
 as Predicted by the LPF Model, Compared with Data from Becker et al., (1966)

Data (at two downstream distances) for Centerline Velocity 49 m/s

LPFM Calculations for $p = 0.5$, $A_1 = 1.50$ ($g(0) = 1.05$)

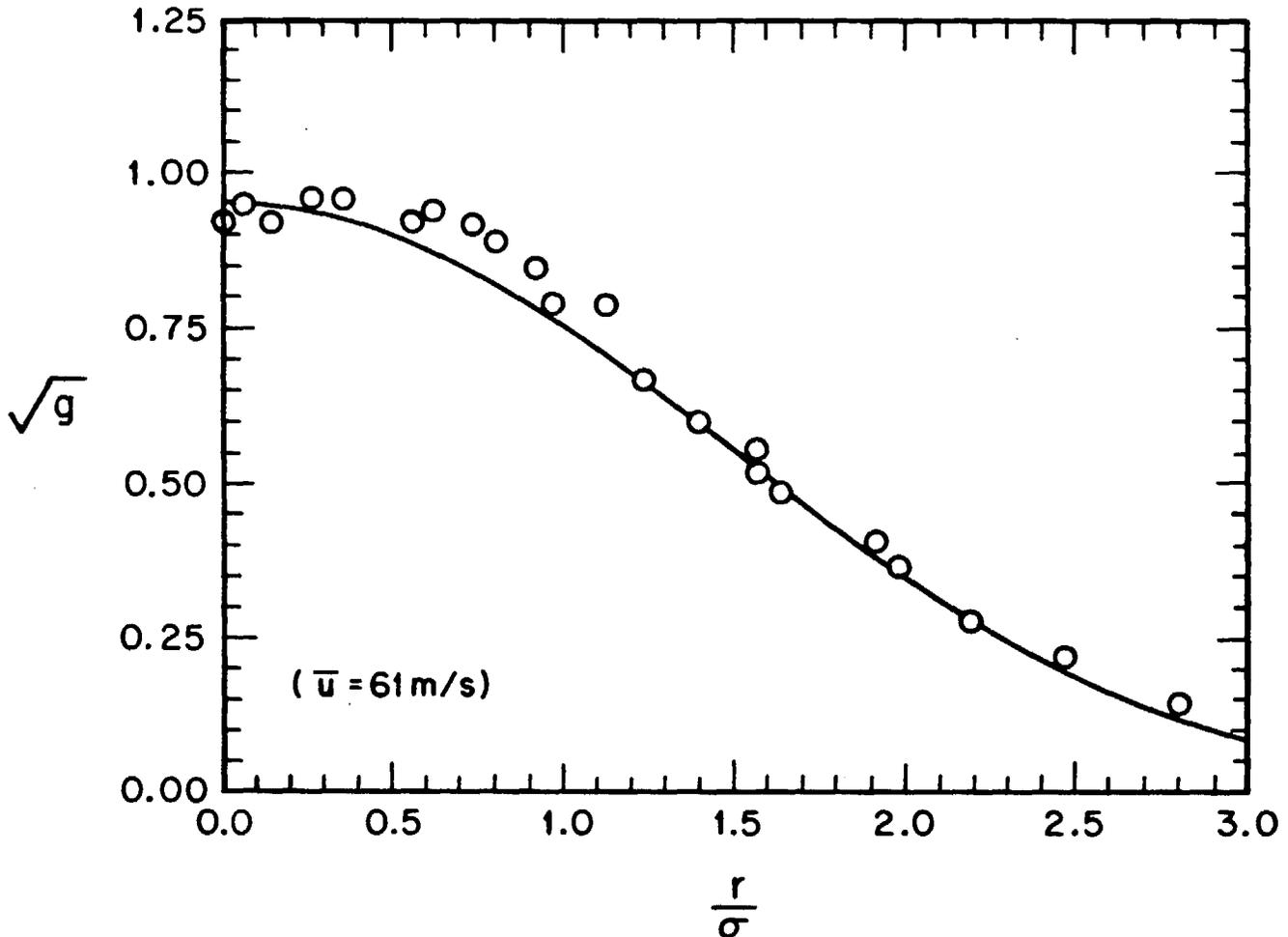


Figure 5-4c

Dimensionless Absolute Square Root Intensity of Segregation, $\sqrt{g(r/\sigma)}$
 as Predicted by the LPF Model, Compared with Data from Becker et al., (1966)

Data (at four downstream distances) for Centerline Velocity 61 m/s

LPFM Calculations for $p = 0.5$, $A_1 = 1.50$ ($g(0) = 0.95$)

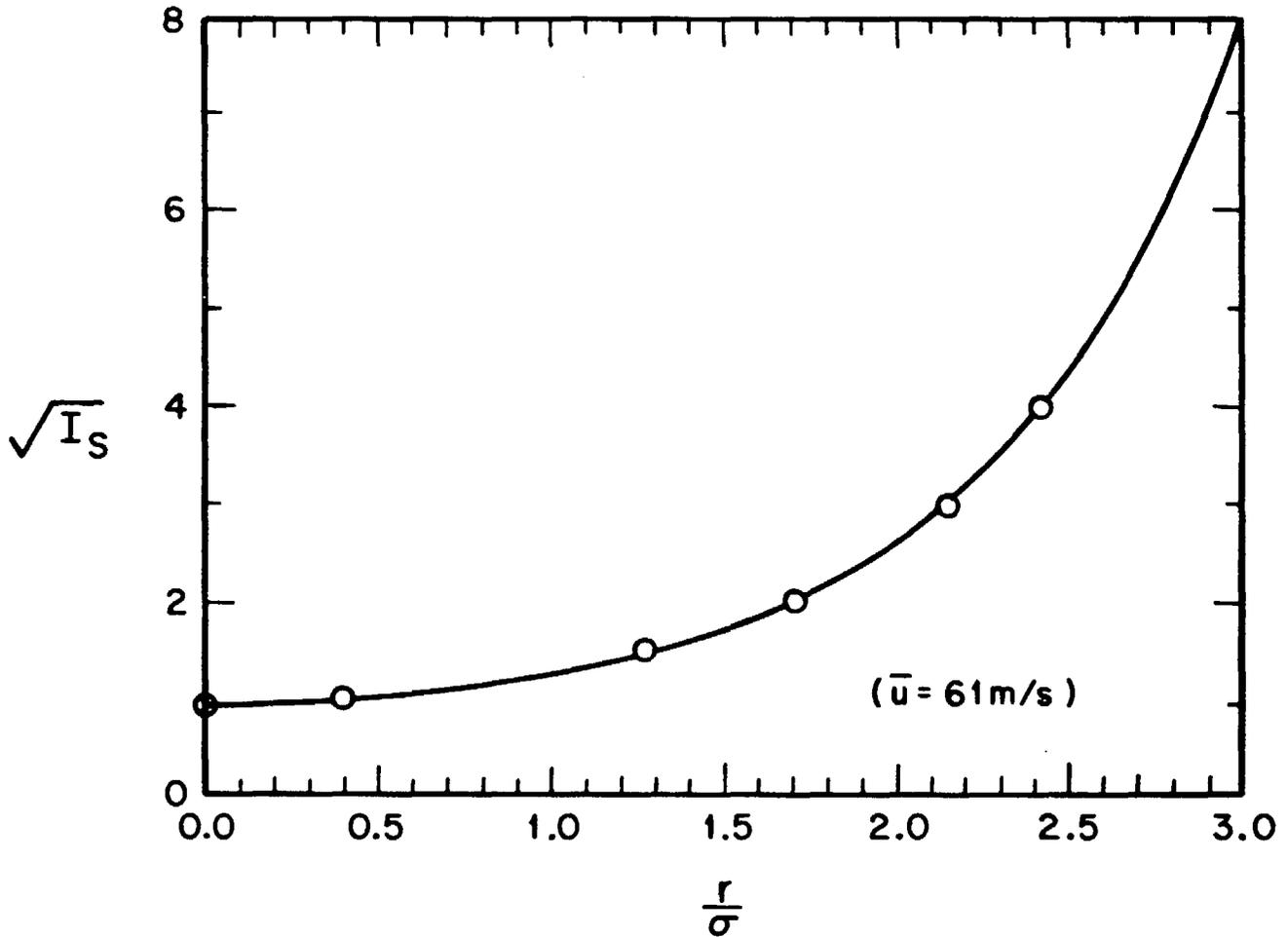
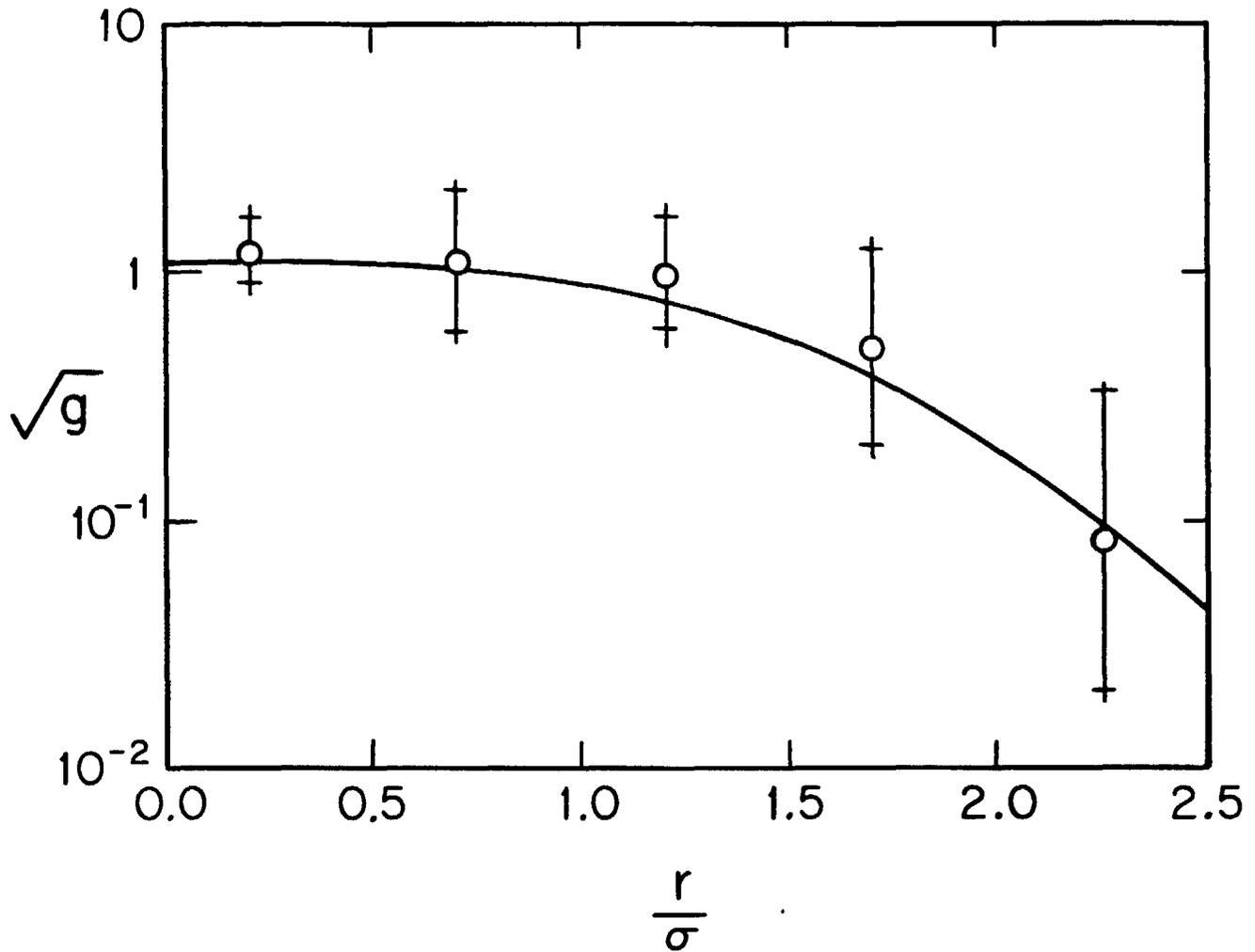


Figure 5-5

Dimensionless Square Root Relative Intensity of Segregation, $\sqrt{I_s}$

as Predicted by the LPF Model, Compared with Data from Becker et al., (1966)

(The data were obtained at five downstream distances for centerline velocity 61 m/s and the points shown correspond to the experimental curve in Figure 7 of Becker et al. (1966) (note that in that figure $\sqrt{I_s}$ is plotted versus $r/r_{1/2}$); LPFM calculations for $p = 0.5$, $A_1 = 1.50$.)

**Figure 5-6**

Dimensionless absolute intensity of segregation, $\sqrt{g(r/\sigma)}$

as Predicted by the LPF Model

Compared with Atmospheric Field data from Ramsdell and Hinds (1971)

(LPFM calculations for $p = 0.5$, $A_1 = 1.5$)

5.5 CONCLUSIONS

Knowledge of statistical properties of point-source plume concentrations, such as the variance σ_c^2 or the intensity of segregation, is essential in many situations calling for plume modeling (e.g. in assessing the impact of releases of pollutants in the environment), and in particular in estimating the effects of local turbulent mixing on relatively fast nonlinear chemistry. Although recent experimental and theoretical work has enhanced significantly the available information on the behavior of σ_c^2 , this had not resulted in the development of practical predictive methods, especially with regard to fine scale in-plume fluctuations – as opposed to total observed fluctuations that encompass bulk motion effects (meandering) which do not interact with the chemical processes.

A new model for the “internal” σ_c^2 , at a level of sophistication analogous to that of the Gaussian formulas for the mean concentration field, has been developed here, starting from the Eulerian transport equation for σ_c^2 . A series of approximations utilizing existing experimental and theoretical information for the processes involved, combined with the Localized Production of Fluctuations (LPF) scheme allowed the construction of closed analytic expressions for σ_c^2 , directly from its governing equation. The capability of this “LPF model” to simulate the variance profile was successfully tested against available data on point source plume concentrations.

In conclusion, the model developed in this work provides a rational, yet computationally simple, means for describing concentration fluctuations and the corresponding intensity of segregation inside instantaneous plume boundaries. Although its applicability is restricted by assumptions such as the uniform mean flow (or “mild” mean plume motion), and slender plumes, this model can serve as a first approximation to a wide range of point source dispersion problems. Further experimental information will be useful to provide accurate estimates of its parameters for specific flows.

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APPENDIX A5.1

**Concentration Probabilities:
Summary of Basic Concepts
and Definitions**

The main volume of work relevant to air pollutant concentration statistical characteristics is concerned with defining concentration distributions and estimating extreme value statistics for use with air quality standards; in this perspective the air pollution system is typically viewed as a "black box" although in some approaches physical reasoning have been invoked to explain qualitatively the statistical results (see Chapter 8). The aforementioned work is directed primarily towards statistically describing long-time averages (usually 1 hr and upwards) of concentration. Thus it must be remembered that (empirical) results relevant to this work cannot be applied directly in the study of very short term ("instantaneous" up to a few minutes averages) fluctuations in a rapidly changing concentration field that results from an isolated source. In the following we summarize certain basic concepts related to the probabilistic properties of instantaneous concentration fields.

The (cumulative) probability distribution associated with the random concentration c at the fixed space-time point (\mathbf{x}, t) of the flow field is defined as

$$F(C, \mathbf{x}, t) = \text{Prob} \{c(\mathbf{x}, t) \leq C\} \quad (\text{A5.1} - 1)$$

The moments of c are defined formally by the relations

$$E^n \{c\} \equiv \langle c^n(\mathbf{x}, t) \rangle = \int_{F=0}^1 C^n dF(C, \mathbf{x}, t) \quad (\text{A5.1} - 2)$$

$$E^n \{c'\} \equiv \langle c'^n(\mathbf{x}, t) \rangle = \int_{F=0}^1 (C - \langle c \rangle)^n dF(C, \mathbf{x}, t) \quad (\text{A5.1} - 3)$$

In particular we set $E^1 \{c\} \equiv \langle c \rangle$, $E^2 \{c'\} \equiv \sigma_c^2$.

In steady state cases, i.e. in continuous plumes (which are of interest in this work) the distribution (and of course moments of all orders) become independent of time.

The probability density function (pdf) $p(C, \mathbf{x}, t)$ of $c(\mathbf{x}, t)$ is defined as

$$p(C, \mathbf{x}, t) = \frac{dF(C, \mathbf{x}, t)}{dC} \quad (\text{A5.1} - 4)$$

for all C for which F is continuous. For certain C , F may not be continuous. In fact $c(\mathbf{x}, t) = 0$ usually occurs with finite probability, at least for certain (\mathbf{x}, t) , and thus arises a discontinuity of $F(C, \mathbf{x}, t)$ at $C = 0$. (This is the only case of discontinuity of F that will concern us here.)

Various functional forms can be assigned to the distribution of the non-zero fraction of the ensemble of concentration values. In practice, such a distribution must be determined by appropriate statistical treatment of data at a fixed point. Experience has shown that skewed distributions such as the lognormal are usually a satisfactory choice for the non-zero fraction ("subensemble") of concentration values in atmospheric plumes. Semi-Gaussian or "clipped-Gaussian" (i.e. linear combinations of Gaussian functions, defined over bounded ranges of values, and Dirac deltas), exponential, and other types of distributions have been used to fit the entire range of concentration values, especially at points close to the average boundaries of the plume.

A variety of theoretical methods for determining *a priori*, from physical principles, is available in the literature for both conserved and reactive scalars (see, e.g., Hill, 1976; Pope, 1982, 1985). However most of these methods are either limited to highly idealized turbulent scalar fields and are formulated for very specific flows, or represent formulations so general that are of little practical use (see, e.g., O'Brien, 1980). Analogous formulations for the moments of c are in general much more tractable and these are pursued in Chapter 5.

An *intermittency factor* or *function* $\gamma_c(\mathbf{x}, t)$ can be introduced, specifying the fraction of the ensemble in which the concentration is not zero (i.e. the subensemble conditioned by $c \neq 0$):

$$1 - \gamma_c(\mathbf{x}, t) = F(0, \mathbf{x}, t) \quad (\text{A5.1 - 5})$$

The *complementary intermittency factor*, defined through

$$\tilde{\gamma}_c = 1 - \gamma_c(\mathbf{x}, t) = F(0, \mathbf{x}, t) \quad (\text{A5.1 - 5a})$$

is also used by some authors.

We will not elaborate here on the subtle and important concept of intermittency in turbulent fields; for an illuminating discussion of both physical and mathematical aspects of this property one may consult the monograph of Mandelbrot (1983).

With the introduction of γ_c one can express the probability density function for all the members of the concentration ensemble as

$$p(C, \mathbf{x}, t) = \gamma_c(\mathbf{x}, t) p_*(C, \mathbf{x}, t) + [1 - \gamma_c(\mathbf{x}, t)] \delta(C) \quad (\text{A5.1 - 6})$$

where $p_*(C, \mathbf{x}, t)$ is the "conditioned" pdf that describes the subensemble $\{c_*\}$ of nonzero concentrations and $\delta(C)$ is the Dirac delta.

$F(C, \mathbf{x}, t)$ is a result of absolute diffusion; so is $\gamma_c(\mathbf{x}, t)$. However, a "decomposition" of the results of relative diffusion and meandering is sometimes necessary in the study of the plume dispersion phenomenon, as it has already been discussed. To study relative diffusion effects one can consider a reference frame attached to the center of mass of a diffusing cloud (for an instantaneous release of material) or "following" through parallel translation the line defined by the infinite sequence of the centers of mass of "thin cross-wind slices" of a continuous plume (the centerline of the plume). An extensive discussion of the description of turbulent dispersion in this frame can be found in Chapter 6 of the present work.

Thus let \mathbf{y} be the distance of a fluid particle from the origin of this meandering frame (for uniform wind $\mathbf{y} = (y_1, y_2, y_3)$ reduces to a two dimensional vector $\mathbf{y} = (x_1, y_2, y_3)$, with the origin taken at x_1 , since it is always perpendicular to the wind vector). Let also $\mathbf{b}(t)$ be the position of the center of mass of the cross-section relative to which \mathbf{y} is measured: $\mathbf{y} = \mathbf{x} - \mathbf{b}$. Then if

$$F_r(C, \mathbf{y}, \mathbf{b}, t) = \text{Prob} \{c(\mathbf{x}, t) = c_r(\mathbf{y}, \mathbf{b}, t) \leq C\} \quad (\text{A5.1} - 7)$$

moments of c_r , a pdf p_r , an intermittency function γ_{rc} and a conditioned pdf p_{r*} can be defined exactly as for the c -field.

The general functional form of p_{r*} is expected to display the same typical characteristics as p_c (a skewed distribution) and experience shows that lognormal type distributions again offer successful fit (Csanady, 1973). However, γ_{rc} is expected now to behave in a more predictable manner than γ_c because the effect of meandering has been removed and $F_r(C, \mathbf{y}, \mathbf{b}, t)$ characterizes the process of relative diffusion alone. Of course the spatial distribution of both γ_c and γ_{rc} is in general unknown for most cases; however in a frame moving with the centerline of a continuous plume, $\gamma_{rc}(\mathbf{y})$ is known to be near unity in the center portion of the plume and to be zero outside the plume, its distribution across the plume being probably like that of the intermittency of turbulent velocities across a jet (see Townsend, 1976; compare also with Eidsvik, 1980). In a fixed frame of reference $\gamma_c(\mathbf{x})$ can be as low as 0.65 even at the axis of the plume (Csanady, 1973) and much lower at the fringes, showing the pronounced effect of meandering (see also Fackrell and Robins, 1982; Jones, 1983). The fact that in a moving frame formulation the intermittency factor is likely to be near unity for much of the field is a certain advantage of this description. Indeed, when using a frame of reference attached to the centerline of the plume, $\gamma_{rc} \simeq 1$ everywhere is an acceptable first approximation. In this way we assign all intermittency effects to meandering: they assumed "bulk intermittency" effects. Seeing this from an alternative viewpoint, we *define* the instantaneous plume through the condition $\gamma_{rc} = 1$.

Plume meandering is described by the spatial probability density function of the position of the center of mass:

$$P_k(\mathbf{x}, t) = \text{Prob} \{ \text{at time } t, \mathbf{b}(t) \text{ has its endpoint in the volume element } d\mathbf{x} \text{ surrounding } \mathbf{x} \}$$

$P_k(\mathbf{x}, t)$ and $F_r(C, \mathbf{b}, \mathbf{x}-\mathbf{b}, t)$ are statistically independent in general and thus the following *convolution* relation connects F , F_r , and P_k :

$$F(C, \mathbf{x}, t) = \int_{\text{all } \mathbf{b}} F_r(C, \mathbf{x}, \mathbf{x}-\mathbf{b}, t) P_k(\mathbf{b}, t) d\mathbf{b} \quad (\text{A5.1-8})$$

As a consequence of this general relationship, we have a similar connection between pdf's (for continuous F_r 's) and non-central moments of the ensembles $\{c\}$ and $\{c_r\}$:

$$\langle c^n(\mathbf{x}, t) \rangle = \int_{\text{all } \mathbf{b}} \langle c_r^n(\mathbf{x}, \mathbf{x}-\mathbf{b}, t) \rangle P_k(\mathbf{b}, t) d\mathbf{b} \quad (\text{A5.1-9})$$

As far as $P_k(\mathbf{x}, t)$ is concerned, this pdf is typically approximated by the probability density function for a fluid particle's location at time t , in a turbulent field, $\bar{\psi}(\mathbf{x}, t)$. (See Chapter 6). Thus $P_k(\mathbf{x}, t)$ can be expressed as the product of:

- the pdf that the center of mass was at \mathbf{x}' at t' , $P_k(\mathbf{x}', t')$, integrated over all possible starting points \mathbf{x}' .
- the transition probability density for a fluid particle in the turbulent field under consideration $Q(\mathbf{x}, t|\mathbf{x}', t') = \text{Prob}\{\text{if the particle is at } \mathbf{x}' \text{ at } t' \text{ it will undergo a displacement to } \mathbf{x} \text{ at } t\}$. (This probability will be introduced formally and discussed in more detail in Chapter 6 where it is denoted by G .)

$$P_k(\mathbf{x}, t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^t Q(\mathbf{x}, t|\mathbf{x}', t') P_k(\mathbf{x}', t') d\mathbf{x}' dt'$$

Invoking initial conditions (at $t' = t_0 = 0$) for a *point source* located at \mathbf{x}_0 we have

$$P_k(\mathbf{x}, t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^t Q(\mathbf{x}, t|\mathbf{x}', t') \delta(\mathbf{x}' - \mathbf{x}_0) d\mathbf{x}' dt'$$

and therefore

$$P_k(\mathbf{x}, t) = \int_0^t Q(\mathbf{x}, t|\mathbf{x}_0, t') dt'$$

The analytical form of the transition probability density $Q(\mathbf{x}, t|\mathbf{x}', t')$ has been one of the main concerns of the Lagrangian methodology for describing turbulent diffusion and extensive discussions are presented elsewhere (see Chapter 6 and Monin and Yaglom, 1975). Gaussian type distributions are the typical choice for Q ; such a choice is theoretically founded for stationary and homogeneous turbulence where, after a certain time has passed, can be deduced formally if the turbulent velocity fluctuations are assumed normally distributed (Seinfeld, 1983). In this case $P_k(\mathbf{x}, t) = P_k(\mathbf{x})$ for a steady plume will also be a Gaussian distribution in \mathbf{x} . Then, relations (A5.1-8), (A5.1-9) define convolution transforms with Gaussian kernel; these are known as *Weierstrass transforms* (see, e.g., Zemanian, 1968).

Finally, we must note that equations (A5.1-8) and (A5.1-9) relating the statistics of the c and c_r fields should not be misinterpreted as providing relations connecting analogous statistical characteristics of the c and c_* fields. Although it is possible to identify the sets of c_r and c_* values by limiting appropriately the range of the spatial variable \mathbf{y} for c_r , the information "carried" by each set is not equivalent. (See also Fackrell and Robins, 1982, their Section 5.2.) To obtain statistics of c from c_* (and vice versa), the spatial (and perhaps the temporal) dependence of γ_c is needed. Then it can be shown that from equation (A5.1-6) follows

$$\langle c \rangle = \gamma_c \langle c_* \rangle \quad (\text{A5.1-10})$$

and

$$\sigma_c^2 = \gamma_c \langle c_*'^2 \rangle + \gamma_c (1 - \gamma_c) \langle c_* \rangle^2 \quad (\text{A5.1-11})$$

References
for Appendix A5.1

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APPENDIX A5.2

Discussion of
Earlier Work on Plume Concentration Fluctuations
and the Empirical Model of Wilson et al. (1982ab)

Experimental measurements of short term fluctuation statistics in plumes under conditions met in cases of interest to air pollution (either in situ or in wind tunnels simulating the atmospheric boundary layer) are relatively limited. Most of these works have been reviewed by Csanady (1973) and Hanna (1984). Useful information of closely related nature can be found in the substantial fluid-mechanical literature about momentum jets and buoyant plumes (see e.g., the reviews of List, 1982, and Gebhard et al., 1984).

A brief chronological survey of results that are of direct interest to the present analysis follows:

An early investigation of concentration probability distributions was carried out by Gosline (1952) who measured "instantaneous" (10 s averages) ground level NO and NO₂ concentrations downwind of a 24 m tall chimney at distances of 5 to 10 chimney heights. His measurements showed the importance of intermittency effects (he noted that only 14 to 34% of the time there was a measurable concentration at the site chosen). Also the duration of each NO bearing eddy at a given site was between 30 and 90 s. The non-zero measurements were found to obey a log-normal distribution to a very good approximation.

Becker et al. (1966) studied plume dispersion and fluctuations in pipe flow. Their experiments show self-similarity of σ_c^2 profiles up to significant dispersion times. The specific characteristics of these profiles varied significantly with changing properties of the ambient turbulent flow. Self-similarity of fluctuation intensities was also clearly observed in experiments involving diffusing dye plumes in the Great Lakes, reported by Csanady (1966) and Murthy and Csanady (1971).

Lognormal curves were found to fit successfully the non-zero data from the Fort Wayne experiments reported in Csanady (1973). An instantaneous line source was considered in this case.

Barry (1971) reported on the continuous monitoring of argon-41 emitted from a reactor stack, his basic data being in the form of 6-minute averages. From his data Barry deduced a probability density for these concentration time averages that is of exponential form. The same density was suggested by Csanady for instantaneous fluctuations from the experiments of Becker et al. (1966).

Ramsdell and Hinds (1971) made limited measurements of short term (38.4 s averages) field

concentration values in the wake of a continuous near ground level (at 1m) point source of krypton gas. Near zero readings occupied from 35 to 80% of the time at the locations investigated (200 and 800 m from the source). A replot of the non-zero readings again approximated a lognormal distribution.

Eidsvik (1980) presented data from transverse line sampling of continuous plumes 500 m from the source. He indicated that concentration distributions at fixed transverse location relative to the center of gravity of the plume are well described by a log-normal curve for the non-zero measurements. The parameters of the log-normal distribution are given as functions of the distance r from the centerline in a cross wind plane. Thus the concentration pdf is of the form

$$p(C) = \frac{1}{\sqrt{2\pi}\sigma_*(r)C(r)} \exp \left\{ -\frac{1}{2\sigma_*^2(r)} [\ln C(r) - \ln C_0(r)]^2 \right\}$$

where $C_0(r)$ is the measured time average concentration that was found to have a nearly Gaussian profile and $\sigma_*(r)$ is estimated to increase from approximately $\sigma_*(0) \simeq 1$ at the center to $\sigma_*(r) \simeq 1.5$ at the boundaries of the mean cloud). Eidsvik stressed the fact that the transverse concentration fluctuation profile was dominated by large scale variations. He also estimated the probability of zero concentrations $F(0, r)$; he found it to be of the order of only 1% in the interior of the mean cloud and increase rapidly near the edges.

The most extensive experimental work directly related to atmospheric plume situations – yet still confined mainly to studies of non-buoyant plumes in neutrally stable environments – is carried by the research team under Fackrell and Robins for CEGB, UK (see Fackrell, 1978, 1980; Fackrell and Robins, 1981, 1982ab; Robins, 1978, 1979; Robins and Fackrell, 1979). Their research reveals a large amount of useful information which we use extensively in the following sections, in our critical examination of the transport equation for σ_c^2 to suggest or justify approximation schemes and simplifications of the mathematical analysis. Some of this work has been incorporated in an empirical model developed by Wilson et al. (1982a,b, 1985) which is briefly discussed in the following.

To summarize briefly the experimental results of Fackrell and Robins, their major conclusions were:

- (i) Meandering is the most significant source of fluctuation in the near field.
- (ii) Production of fluctuations is in general significant only very close to the source.
- (iii) The variance of concentrations from ground level sources exhibits profiles that are approximately self-similar in both the horizontal and vertical directions; further, it does not show significant dependence on source size.
- (iv) The same variance for elevated sources initially shows dependence on source size which is eventually "forgotten." Horizontal profiles of σ_c^2 are again approximately self-similar, but vertical profiles show a more complicated behavior: In the immediate vicinity of the source they are self-similar;

then, as the effect of the ground is felt by the dispersing material, they differentiate. In the far field, however, these profiles become again self-similar, resembling those of a ground level source.

- (v) The power law distribution resulting from Gifford's fluctuating plume model (see Section 5.7) seemed to provide the best fit to experimentally measured pdf's in most cases. Log-normal pdf's offered the best fit to sets of non-intermittent data.

Other sets of instantaneous plume concentrations measurements are presented by Kimura et al. (1981) and Jones (1983); in general, the nature of these data is consistent with the observations mentioned above. In particular, Jones' (1983) data reveal an exceptionally strong effect of the meandering processes, even for downwind, as the total intensities of fluctuations reported are consistently almost an order of magnitude larger than the respective in-plume intensities.

The theoretical study of the σ_c^2 dynamics was originated in the works of Corrsin (1952, 1964) and Batchelor (1959). Since then, various approaches have been followed in dealing with the statistics, especially $\langle c \rangle$ and σ_c^2 , of scalar fields in turbulent flows (see, e.g. Monin and Yaglom, 1971, 1975; Hinze, 1975; Bradshaw, 1978; Libby and Williams, 1980).

As far as the specific atmospheric plume situation is concerned, the three major approaches commonly employed in modeling the mean field, i.e. *Eulerian and Lagrangian statistical methods* and *dimensional (similarity) analysis* (see, e.g., Pasquill, 1974; Seinfeld, 1975) can also be used to model second moments. In addition, *heuristic* models focusing on particular characteristics of the fluctuation problem and *empirical* schemes, utilizing the information embodied in experimental data, have been developed and applied in various cases.

Eulerian modeling for the atmospheric plume fluctuations has been pursued mainly by Csanady (1967, 1973); some relevant work can also be found in Harris (1979) (see, e.g., Thomas, 1979). Csanady (1967) formulated a model for the mean-square fluctuation of concentration (variance of the concentration field) as a solution of the transport equation for this quantity, in the case of a continuous point source in a uniform wind, for axisymmetric conditions of spreading. He avoided the problem of accounting for meandering effects (large scale turbulence effects) by formulating his description in a reference frame attached to the centerline of the plume, assuming intermittency effects to be negligible in this reference frame. The crucial assumptions in Csanady's model are the validity of a (modified) gradient transfer-type theory for the transport of both the mean and the mean-square concentration field and self-similarity for both these fields. As already mentioned the latter assumption has been evaluated to some extent against experiments; for the first see also the works of Nettetville and Wilson (1980) and Wilson et al. (1982a,b). Csanady's approach has been extended to less restrictive conditions in Chapter 5.

Lagrangian modeling has been given more attention in recent years (Chatwin and Sullivan, 1979;

Durbin, 1980; Lamb, 1981; Sawford, 1982, 1983, 1984, 1985; see also Weil, 1985). A particularly clear exposition of the concepts and methods related to this approach, together with a critical review of the work on the subject, can be found in Sawford (1983). To summarize briefly, in the works mentioned σ_c^2 is typically related to the joint probability density for particle-pair displacements. Lamb (1980) and Durbin (1980) used systems of coupled Langevin equations to model the particle pair velocities. Sawford (1983) showed that the predicted behavior of σ_c^2 in dispersing puffs depended critically on the form of the probability density for particle separations; he further showed that Gaussian densities for these separations are not realistic because they smooth out the internal structure of the cloud and the relative fluctuations, thus leaving meandering as the only source for randomness. For further information, the interested reader should consult Sawford (1983, 1984).

Variances of scalars in the surface atmospheric layer can also be studied through dimensional analysis following the Monin-Obukhov theory (see, e.g., Panofsky and Dutton, 1984). In a study more closely related to the point source case Chatwin and Sullivan (1979) used dimensional analysis and simplifying assumptions to deduce, from the fundamental transport equations, results concerning the relative dispersion of a puff from instantaneous emissions that had an initial linear dimension. Their analysis concludes that, in the bulk of the cloud $\sigma_c^2 \sim Q^2/\sigma^3\sigma_0^3$, where σ and σ_0 respectively are the current and the initial linear dimensions of the puff and Q is the source strength, whereas in a central core region, which decreases with time, fluctuations are of greater magnitude, that is, of order Q^2/σ_0^6 i.e., conditioned by the initial puff size. Extensions of this model were proposed and applied by Hanna (1984).

Among the heuristic formulations, Gifford's (1959) fluctuating plume model still remains the single most influential work in the field. Gifford (1959) formulated a model of a meandering Gaussian plume such that fluctuations in concentration are produced *only* by the random displacements (meandering) of sections of the plume, ignoring fluctuations within each section. One cannot deduce predictions for the detailed structure of the fluctuating concentration field from a model such as Gifford's, however, some of its more general conclusions may be sufficient approximations under certain conditions and have been tested against experiments (see, e.g. Fackrell, 1978). Thus in the immediate vicinity of the source, where meandering is the more dominant source of fluctuations, it is a valid approximation and can offer reasonable estimates of the total σ_c^2 . Two major conclusions of the model are that on the plume axis the pdf of the concentration should obey a simple power law (see also Appendix A5.3), and that the "peak to mean" ratio, which is often used to represent observational studies of atmospheric diffusion along with the mean concentration (the "peak" value of a random variable can be specified precisely as a high quantile of the probability distribution of concentration), tends to unity for large distances (see Gifford 1960, Csanady 1973).

Extensions of the original model have also been presented in the literature (see, e.g., Scriven, 1965; Diamante et al., 1976). Other formulations that are related to the spirit of Gifford's model have been developed by Vencatram (1979, 1983) and Hanna (1984); however, in general the latter schemes deal with averaged and not instantaneous-pointwise concentrations.

Finally, empirical models utilizing the experimental results of Fackrell and Robins (1979, 1982ab) have been developed by Wilson et al. (1982ab, 1985) in the form of closed algebraic expressions for ground level and elevated sources. The general model equations are

$$\langle c'^2 \rangle = \left(\frac{\tilde{q}(x)}{B\bar{u}\sigma_y(x)\sigma_x(x)} \right)^2 G \left(\frac{y}{\sigma_y} \right) F \left(\frac{z}{\sigma_x} \right)$$

where

$$B = 2\pi$$

for an elevated source, and

$$B = \frac{4 \ln \sqrt{2} \pi \Gamma(1/m)}{m(\ln 2)^{1/m+1/2}}$$

for a ground level source. The dimensionless functions F , G are

$$G \left(\frac{y}{\sigma_y} \right) = \frac{1}{2} \left\{ \exp \left[- \left(\frac{y}{\sqrt{2}\sigma_y} - \beta\sqrt{\ln 2} \right)^2 \right] + \exp \left[- \left(\frac{y}{\sqrt{2}\sigma_y} + \beta\sqrt{\ln 2} \right)^2 \right] \right\}$$

and

$$F \left(\frac{z}{\sigma_x} \right) = \exp \left[- \ln 2 \left(\frac{z - h_v}{\sqrt{2 \ln 2} \sigma_x} \right)^m \right] - \alpha \exp \left[- \ln 2 \left(\frac{z - h_v}{\sqrt{2 \ln 2} \sigma_x} \right)^m \right]$$

where $m = 2.0$ for an elevated source and $m = 1.7$ for a ground level source. h_v is defined through

$$h_v = \sigma_x \left[\left(\frac{h}{\sigma_x} \right)^2 + 2 \ln 2 \beta^2 \right]^{1/2}$$

h being the source height. The "source" function $\tilde{q}(x)$ and the constants α , β are estimated so as to fit the observations. This model, although its structure is partially defended by physical reasoning, is definitely an empirical formulation constructed so as to describe specific sets of available data. This reliance on the aforementioned sets of data can be seen as a relative advantage (an "a priori validation") of the model; nevertheless, it limits significantly arguments for its applicability in situations not closely resembling the conditions corresponding to these measurements. Further, even for these conditions (i.e., neutral atmospheric stability), its parameters are estimated under the condition $\sigma_y \sim \sigma_x \sim x^{0.5}$ which limits the validity of the model to dispersion times (i.e., downwind distances from the source) large enough for this assumption to hold to a sufficient approximation. However, the major disadvantage of this model is that from the nature of its source data it estimates values of σ_c^2 that

contain contributions from both internal fluctuations and partially "filtered" random meandering (a portion of meandering processes related to very large time scales is "cut off" as the measurements are typically 1hr averages). Actually, Fackrell and Robins (1982ab), commenting on the data on which the model is based, say that their analysis "shows meandering to be the main source of fluctuations." This fact about the model does not allow its application to situations where only internal fluctuations effects must be considered, as, for example, in modeling nonlinear chemical processes in plumes. Far downwind however, where internal fluctuations dominate the value of σ_c^2 the model could be an acceptable scheme for such applications.

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for Appendix A5.2**

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APPENDIX A5.3

**A New, Simple, Model
for the Probability Density
of Instantaneous Plume Concentrations**

The (experimentally supported) lognormality of instantaneous plume concentrations in the meandering frame of reference can be directly combined with the closed form solutions that we now have available for both $\langle c_r \rangle$ (the Gaussian type formulas) and $\sigma_{c_r}^2$ (from the LPF model), to produce pdf curves for the concentration, at each point inside the instantaneous plume. Indeed, the parameters of the log normal pdf

$$p_r^L(C) = \frac{1}{C\sigma_L(2\pi)^{1/2}} \exp \left[-\frac{(C - \mu_L)^2}{\sigma_L^2} \right] \quad (\text{A5.3-1})$$

are directly related to $\langle c_r \rangle$, $\sigma_{c_r}^2$, at each point, through

$$\mu_L = 2 \ln \langle c_r \rangle - \frac{1}{2} \ln \left(\langle c_r \rangle^2 + \sigma_{c_r}^2 \right) \quad (\text{A5.3-2})$$

$$\sigma_L^2 = \ln \left(\langle c_r \rangle^2 + \sigma_{c_r}^2 \right) - 2 \ln \langle c_r \rangle \quad (\text{A5.3-3})$$

Thus, substituting (A5.3-2), (A5.3-3) in (A5.3-1), one has $p_r^L(C)$ as a function of position (relative to the moving frame) inside the instantaneous plume:

$$p_r^L(C) = p_r^L(C; x, y_r, z_r)$$

For ranges of the downwind distance x where the profiles of $\langle c_r \rangle$ and $\sigma_{c_r}^2$ are self-similar p_r^L becomes independent of x with the introduction of the transformation

$$X_r = \frac{C}{\langle c_0 \rangle_r} \quad (\text{A5.3-4})$$

where $\langle c_0 \rangle_r$ is the expected concentration at the instantaneous centerline. Then

$$p_r^L(X_r; y_r, z_r) = \langle c_0 \rangle_r p_r^L \left(\frac{X_r}{\langle c_0 \rangle_r}; x, y_r, z_r \right) \quad (\text{A5.3-5})$$

Introducing the relations (5.2-12) (Chapter 5) one obtains

$$p_r^L(X_r; \hat{r}) = \frac{1}{\sqrt{2\pi} X_r \ln \left(\frac{f^2 + g}{f^2} \right)} \exp \left\{ -\frac{\left[\ln \left(\frac{X_r \sqrt{f^2 + g}}{f^2} \right) \right]^2}{2 \left[\ln \left(\frac{f^2 + g}{f^2} \right) \right]^2} \right\} \quad (\text{A5.3-6})$$

where $f(\hat{r})$, $g(\hat{r})$ are estimated through the Gaussian and the LPF Models respectively (Chapter 5, Section 5.3). For this choice of f and g the form of the resulting pdf is shown in Figure A5.3-1 at dimensionless distances $\hat{r} = 0, 0.5, 1.0$ and 2.5 from the instantaneous plume centerline. The parameters used to calculate g are the "most typical ones" (i.e., $p = 0.5$, $A_1 = 1.5$) and a centerline value of g of order unity is assumed. The figure shows the increasing probability of near-zero χ_r , and the corresponding movement of the mode of the distribution, equal to $\exp(\mu_L - \sigma_L^2)$, towards zero, as one moves from the centerline to the edges of the instantaneous plume.

The rate of the relative dispersion process (i.e., the value of the exponent p) is the most important factor in determining the shape of the pdf at a given dimensionless distance from the centerline. This results from the fact that the overall production of fluctuations up to a given downwind distance is an increasing function of p . So, intuitively, one expects the resulting pdf to show "increasing randomness" for the values χ_r for increasing p . This indeed appears in Figure A5.3-2 where the pdf at $\hat{r} = 0.0$ is shown for the three different values that, according to the theory of two-particle dispersion, are assumed by the exponent p at the different stages of dispersion, i.e., $p = 1.0, 1.5$, and 0.5 . For increasing p the tails of the pdf cover more extensive area in the $p_r^L - \chi_r$ graph and values of χ_r very close to zero (as well as values $\chi_r \gg 1$) become more probable than for lower p . If p could approach zero the most probable values of χ_r would occur in the vicinity of its deterministic expected value.

The LPF model parameters ω has an effect that is roughly the opposite of p . Figure A5.3-3 shows the effect of changing the value of ω on the pdf at the centerline. Low values of ω result in increased randomness and the probability of near zero values of χ_r rises. For larger values of ω the pdf mode moves towards the expected centerline value ($\chi_r = 1$) and for $\omega \rightarrow 1$ the pdf reduces to a delta function at $\chi_r = 1$ (since for this value of ω the LPF model "places" the production of fluctuations exactly at the point where the calculation is performed, thus no fluctuations have diffused to the centerline). These results are easily extended to the behavior of the pdf at points not on the centerline. It must be made clear at this point that, whereas the dependence of the pdf on the value of p reflects the physical mechanism by which fluctuations are produced and transported, the respective dependence on the values of ω results simply from the structure of the LPF model and the artificial description of the physical processes embodied in it. Knowledge of this dependence, however, allows the proper choice and adjustment of this parameter for a given physical situation when some experimental information regarding the pdf is available.

The general convolution relation (A5.1-8) can now be used for the estimation of probability densities for the instantaneous concentration C observed with respect to a fixed frame of reference. For convenience we define the dimensionless fixed frame concentration at (x, y, z) by

$$\chi = \frac{C}{\langle c_0 \rangle_r} \quad (\text{A5.3-7})$$

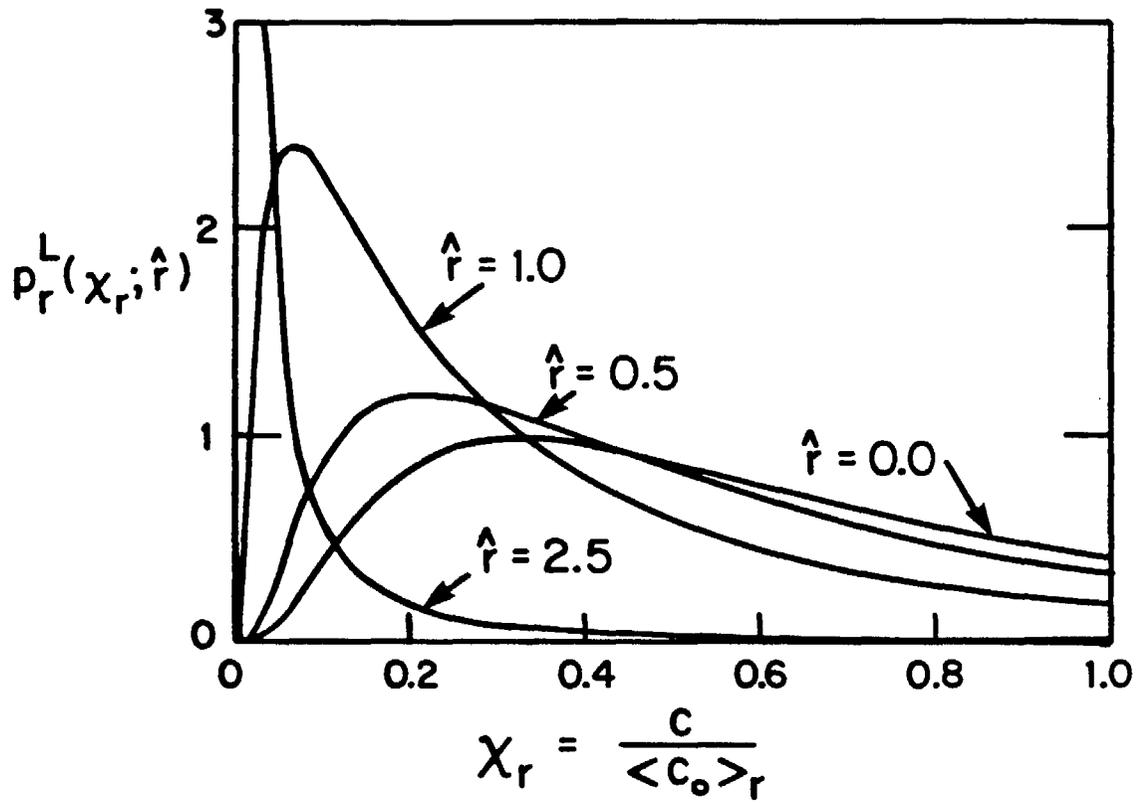


Figure A5.3-1

Probability p_r of the instantaneous dimensionless concentration x_r
 in the meandering frame of reference
 at dimensionless crosswind distances $r/\sigma = 0.0, 0.5, 1.0, 2.5$ from the instant. centerline

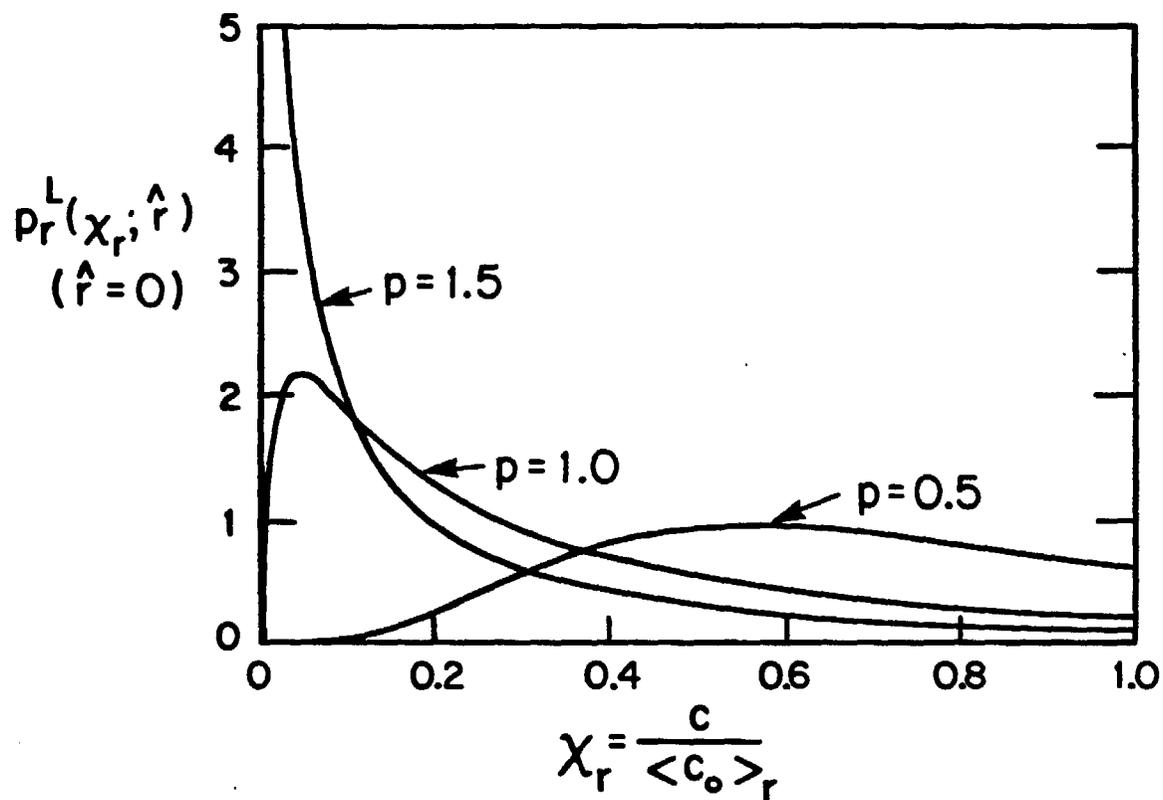


Figure A5.3-2

Effect of dispersion intensity (expressed via the parameter p)
 on the probability p_r
 (calculations for $r = 0$)

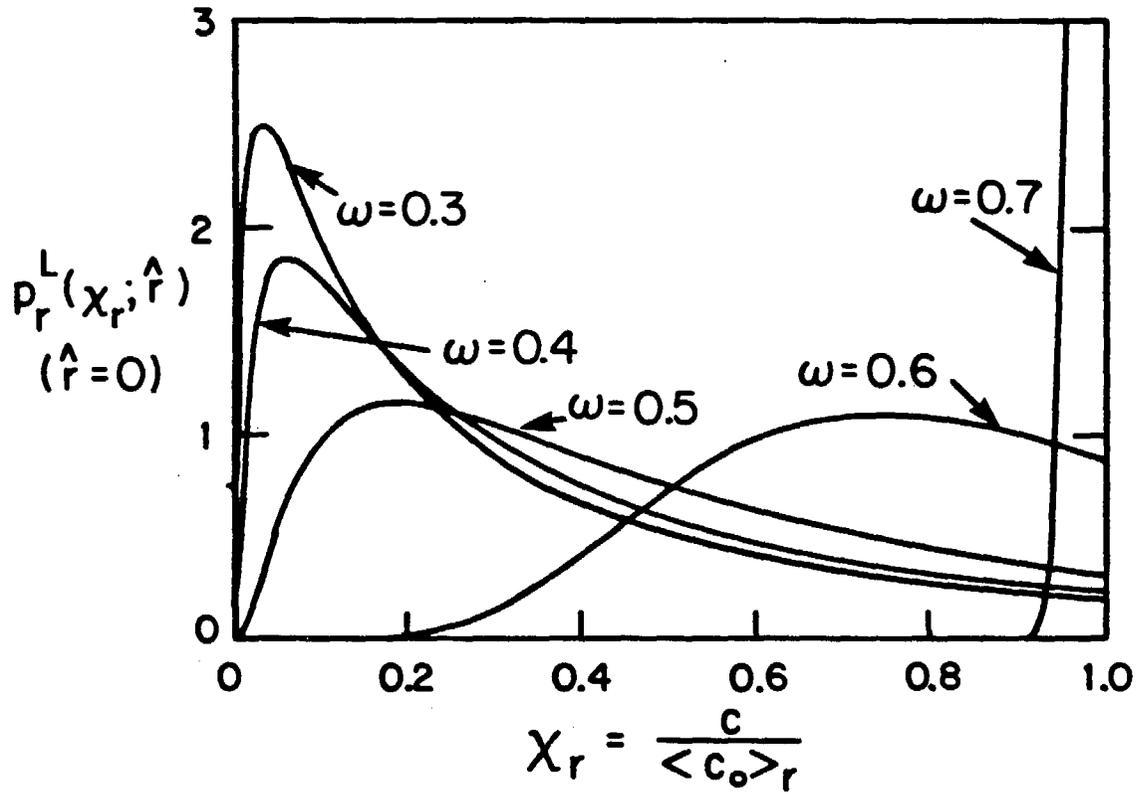


Figure A5.3-3

Effect of the parameter ω on the probability p_r
 (calculations for $r = 0$)

(Notice that the concentration scale adopted above is again the expected concentration at the instantaneous centerline and not at the mean centerline.)

To apply (A5.1-8) we consider for simplicity the isotropic case with relative dispersion parameters $s_y = s_x = s$ and meandering parameters $m_y = m_x = m$. Then, for Gaussian $P_k(b_y, b_x)$ it can be shown that (A5.1-8) becomes

$$p^L(\chi; \hat{R}) = \frac{1}{2\pi} \int_0^\infty \int_0^{2\pi} \hat{B} \exp\left(-\frac{\hat{B}^2}{2}\right) p_r^L(\chi; \hat{R}, \hat{B}, \phi) d\phi d\hat{B} \quad (\text{A5.3-8})$$

where

$$\hat{B} = \frac{\sqrt{b_y^2 + b_x^2}}{m}, \quad \hat{R} = \frac{\sqrt{y^2 + z^2}}{m}$$

and the argument \hat{r} of f, g is

$$\hat{r} = \left(\frac{m}{s}\right) \sqrt{\hat{R}^2 + \hat{B}^2 - 2\hat{B}\hat{R}\cos\phi}, \quad 0 \leq \phi < 2\pi$$

Thus, (A5.3-8) gives the pdf of instantaneous concentrations in plumes relative to a fixed frame, at the dimensionless distance \hat{R} , accounting for both the effects of meandering and internal plume fluctuations.

The estimates provided by (A5.3-8) can be compared directly to the results of Gifford's (1959) fluctuating plume model where all the randomness in the concentration field is attributed exclusively to the process of meandering. In the case of Gifford's model the pdf of instantaneous concentrations in the moving frame corresponds to a delta function located at the expected value of C (since in this frame the concentration is assumed equal to its expected value in all realizations):

$$p_r(C; x, y_r, z_r) = p_r^\delta(C; x, y_r, z_r) = \delta(C(x, y_r, z_r) - \langle c_r(x, y_r, z_r) \rangle) \quad (\text{A5.3-9})$$

For this (most ideal) choice of p_r , equation (A5.3-8) can be integrated analytically to give, for isotropic dispersion and unbounded atmosphere,

$$p^\delta(\chi; \hat{R}) = \left(\frac{s}{m}\right)^2 \chi^{(s/m)^2 - 1} \exp\left(-\frac{\hat{R}^2}{2}\right) I_0\left(\frac{s}{m} \sqrt{2 \ln\left(\frac{1}{\chi}\right)}\right) \quad (\text{A5.3-10})$$

This relation on the mean centerline reduces to

$$p^\delta(\chi; \hat{R} = 0) = \left(\frac{s}{m}\right)^2 \chi^{(s/m)^2 - 1} \quad (\text{A5.3-11})$$

The above equations, directly derived through the present formalism, are exactly the classical results of Gifford (1959).

Figures A5.3-4 and A5.3-5 show the estimates of the classic fluctuating plume model and of the combined lognormal internal pdf-fluctuating plume model, with parameters provided by the LPF formulation, for $m/s = 2.0$ and $m/s = 1$, respectively, on the mean plume centerline. As expected, the integrated model "adds randomness" to the concentration characteristics predicted by the simple fluctuating plume model for $m/s = 2.0$, thus giving higher probabilities for near-zero values of χ and reducing the probabilities for near-expected ($\chi = 1$) values. The effect is more pronounced as $m/s \rightarrow 1.0$; for $m = s$ Gifford's model gives equal probability to all values of χ . Clearly in this limit the internal fluctuations are dominant in determining the probabilistic characteristics of the plume concentration field, and Gifford's model is insufficient. For $s \gg m$ the LPF model can be used to predict total randomness on a "stand alone" basis.

References for Appendix A5.3

- Gifford, F.A. (1959) "Statistical Properties of a Fluctuating Plume Dispersion Model," in *Adv. in Geophys.*, 6, 117-137

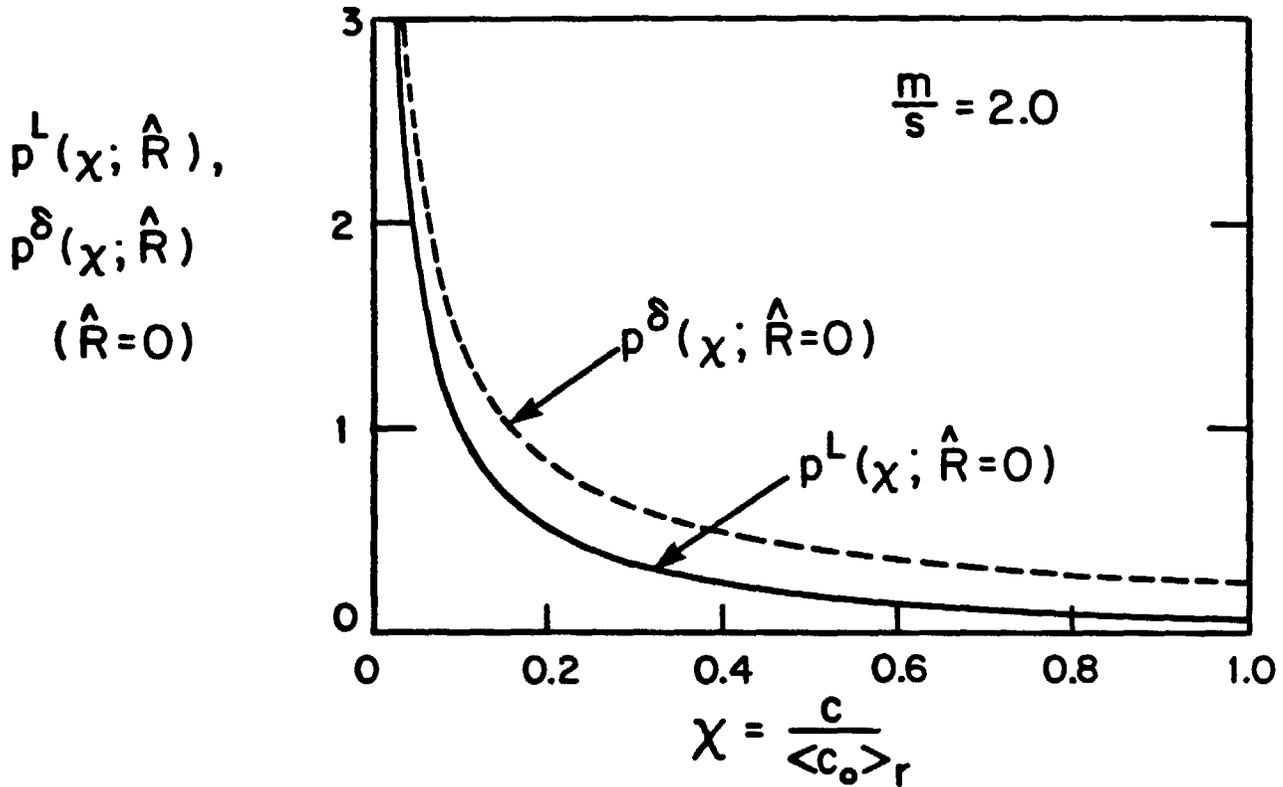


Figure A5.3-4

Probability density p of the instantaneous dimensionless concentration χ
 in the fixed frame of reference on the mean centerline for $m/s = 2$
 (solid line: calculations using the LPF-lognormal model)
 (dashed line: calculations using Gifford's fluctuating plume model)

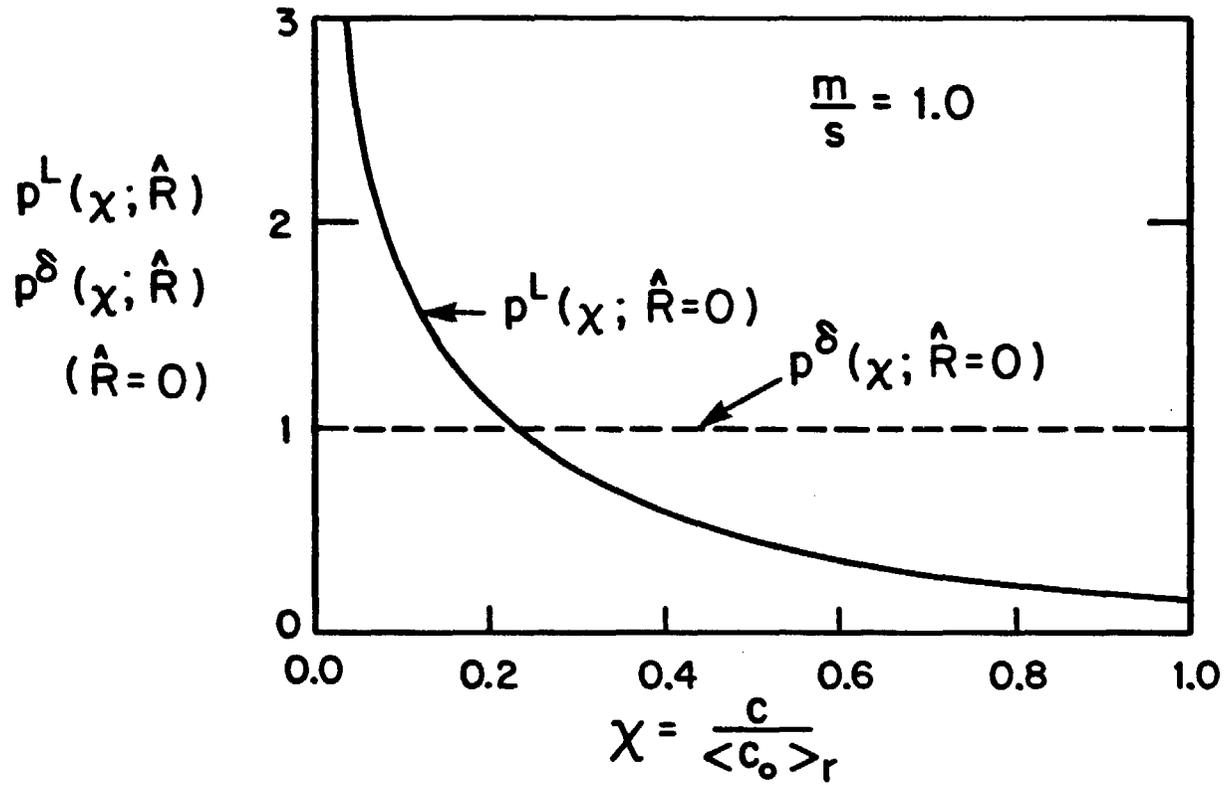


Figure A5.3-5

As in Figure A5.3-4 for $m/s = 1$