et al. 1992; Wise and Charbeneau 1994). Note that the averaging in (5.52) is over the realizations of travel time at a certain point in x_1-space, and not over the deterministic measure of travel time $T(x_1)$ itself. That is, the average in the right-hand side of (5.52) is exactly the streamtube (or streamfilament) ensemble average, as is demonstrated on substitution of (5.57):

$$\begin{aligned} c_f(t,x_1) &= \int_0^\infty c(t,\tau)p(\tau;x_1)d\tau = \int_0^\infty c(t,\tau)\langle\delta(\tau - T(x_1))\rangle d\tau \\ &= \left\langle \int_0^\infty c(t,\tau)\delta(\tau - T(x_1))d\tau \right\rangle = \langle c(t,T(x_1))\rangle \end{aligned} \tag{5.58}$$

Returning to a discrete ensemble of streamtubes as might be generated by means of deterministic simulation, each indexed with subscript i [i.e., each with a corresponding travel- time function $T_i(x_1)$], then the expectation takes the form of a sum over solutions $C(\tau_i, t)$, where τ_i is the value of the function $T_i(x_1)$ evaluated at a certain point x_1. These solutions are weighted by their corresponding travel-time frequencies, as in

$$c_f(t,x_1) = \langle c\rangle(t,\tau) = \sum_k c(t,\tau_k)p(\tau_k;x_1) \tag{5.59}$$

Here $p(\tau_k, t)$ is the discrete probability for the occurrence of $T_k = \tau_k$ at x_1; that is, the relative flux contribution of streamtubes with average travel time τ_k.

Note also that the travel-time distribution function may be recast as a distribution over any relevant integrable space. One useful example is seen when the streamtubes all emanate from points **a** within a source domain **A**—in this case, streamtubes (or streamfilaments, associating them with the differentials within the integration) may be counted of a given travel time by indexing their particular start location **a** with the Dirac-δ function as in:

$$p(\tau;x_1) = \frac{\int_{\mathbf{a}\in A_o} q_x(\mathbf{a})\delta(\tau - T(x_1;\mathbf{a}))d\mathbf{a}}{\int_{\mathbf{a}\in A_o} q_x(\mathbf{a})d\mathbf{a}} \tag{5.60}$$

This form will be used in the later section, Travel-Time Distribution Function Estimation, to relate the conventional Lagrangian stochastic-analytic representation of the streamtube ensemble as indexed by starting location **a** to the general flux accounting by equation (5.53). For instance, downstream breakthrough mass flux of mixed solutes emanating from start locations **a** in $\mathbf{A}_o$ can be written in terms of the elemental areal water flux at the start location $q_x = \theta V_o(\mathbf{a})d\mathbf{A}_o$, times the volumetric mass density of the solute emanating from **a** downstream, integrated over $\mathbf{A}_o$. This is done by parameterizing travel time on start location **a**, via $T(\mathbf{a})$ (Dagan et al. 1992):

$$c_f(x_1,t) = \int_{\mathbf{a}\in \mathbf{A}_o} \theta c^k(t, T(\mathbf{a})) V_1^o(\mathbf{a})\, d\mathbf{a} \tag{5.61}$$

where $T(\mathbf{a})$ is the travel time for solute mass originating at $\mathbf{a}$. The travel-time argument may now be formally expanded toward (5.60) by introducing the Dirac-δ generalized function to collocate elements $d\mathbf{a}$ with the same travel-time value τ,

$$c_f(x_1,t) = \int_{\mathbf{a}\in \mathbf{A}_o} \theta \left[\int_0^\infty \delta(\tau - T(\mathbf{a})) c^k(\tau, t)\, d\tau \right] V_1^o(\mathbf{a})\, d\mathbf{a} \tag{5.62}$$

rotating the order of integration,

$$c_f(x_1,t) = \int_0^\infty c^k(\tau, t) \left[\int_{\mathbf{a}\in \mathbf{A}_o} \delta(\tau - T(\mathbf{a})) \theta V_1^o(\mathbf{a})\, d\mathbf{a} \right] d\tau \tag{5.63}$$

combining the velocity and porosity for the flux $q(\mathbf{a})$,

$$c_f(x_1,t) = \int_0^\infty c^k(\tau, t) \left[\int_{\mathbf{a}\in \mathbf{A}_o} \delta(\tau - T(\mathbf{a})) q(\mathbf{a})\, d\mathbf{a} \right] d\tau \tag{5.64}$$

which for unit initial flux by (5.60) is simply

$$c_f(x_1,t) = \int_0^\infty c^k(\tau, t) p(\tau; x_1)\, dt \tag{5.65}$$

Therefore, by means of the generalized ensemble averaging operator defined in (5.60), the averaging of ensemble concentrations can be related by essentially any parameterization of travel time back to the form involving a relative flux distribution p.

Convolution Forms: Use and Limitations

Travel time defined in (5.18) determines the mapping of the variable velocity along a streamtube onto an equivalent (constant) velocity field for an equivalent one-dimensional system with distance coordinate x_1. Therefore, the travel-time distribution p is experimentally observed as the conservative tracer breakthrough curve at the control plane at x_1 in response to a unit Dirac-δ input of inert tracer. Alternatively, the distribution function may be deconvolved from the observed response to other input functions of inert tracers, as variously described in Rainwater et al. (1987), Wise and Charbeneau (1994), Ginn et al. (1995), and Skaggs et al. (1998), by means of the exploitation of the linearity of the flux-averaging, when the boundary conditions are known. Linearity allows solutions for arbitrary input functions c_o to be represented as convolutions of the solution to the Dirac-δ solution, by means of the superposition principle. That is, the single streamfilament (or dispersionless streamtube) breakthrough curve response to any positive input of inert tracer $c_o(t_o)$ can be written as the convolution

$$c_f(t; x_1) = \int_0^t c_o(t - \tau) p(\tau; x_1) d\tau \tag{5.66}$$

and then deconvolution techniques may be applied to estimate p from observed breakthrough c_f with knowledge of the boundary condition c_o. For instance, if c_o is a unit-concentration pulse of unit duration, (5.66) becomes

$$c_f(t; x_1) = \int_{t-1}^{t} p(\tau; x_1) d\tau = \int_0^t p(\tau; x_1) d\tau - \int_0^{t-1} p(\tau; x_1) d\tau \tag{5.67}$$

which can be rearranged and differentiated to write a simple (but not robust) recursive deconvolution involving differentiation of c_f (Ginn et al. 1995):

$$p(t; x_1) = p(t-1; x_1) + \left.\frac{\partial c_f}{\partial t}\right|_t \tag{5.68}$$

This form fails to discriminate the causes of travel-time distribution, that is, convective differences between streamtubes versus diffusive/dispersive mixing within streamtubes. This issue will be returned to in the section, Travel-Time Distribution Function Estimation.

An alternate approach is used in Wise and Charbeneau (1994) and Rainwater et al. (1987), where streamtube ensemble transport conveying solutes from an injection well to a production well is associated with the measured cumulative inert breakthrough (termed there the "fractional breakthrough," which is the integral of our travel-time distribution function).

Convolution relations can be developed using the principle of superposition that allows the expression of breakthrough curve (flux-averaged) concentrations for inert solute transport arising from steady or transient (see Streamtube Invariance: Use and Limitations) flow fields, involving both initial distributions of solute (initial value problems) or boundary injections of solutes (boundary value problems). Such solutions for inert or passive tracer transport appear as transfer function solutions in terms of convolutions between the input distribution and the travel-time distribution function (Raats 1975, 1978; Simmons 1982; Jury and Roth 1990).

However, the convolution representation, although convenient, is not intrinsically required in the streamtube averaging, and in fact is an overly restrictive approach to dealing with multicomponent and/or nonlinear solute interactions. Because the convolution representation requires the solution of the reactive transport model in the one-dimensional lth-streamtube $c_l^k(t, \tau)$ to be stationary in the difference $t - \tau$; that is, because it requires $c_l^k(t, \tau)$ to be expressible as $c_l^k(t - \tau)$, it prevents incorporation of most realistic (in particular, nonstationary) kinetic transformation processes, including (purely physical) longitudinal diffusion/dispersion, along a streamtube. The general integral form (5.65) allows treatment of multi-component, nonlinear interactions as well as the incorporation of mixing longitudinally within streamtubes.

Streamtube Invariance: Use and Limitations

The solution of the streamtube system (5.52) representing breakthrough curves of reacting solutes requires the determination of the full surface $c_l^k(t,\tau)$ for component k in streamtube l. In the discrete streamtube case, (5.59) requires calculation of each of the surfaces $c^k(T_i,t)$ for each realization of travel-time function $T_i(x_1)$. In the case of the availability of canonical solutions (Ginn et al. 1995), this is accomplished by simply rescaling the travel-time axis of the canonical solution $C(T, t)$ to the indicated $T_i(x)$. However, in many cases, canonical solutions are not available, and one needs to solve for $c^k(\tau, t)$ over a real finite ensemble of one-dimensional streamtubes. This is in general much more tractable a computation than solving the full three-dimensional reactive transport model, and a demonstration calculation is shown in the section, A Computational Example, using the example from the Introduction.

The accuracy of the representation will depend partly on the level of approximation involved in the use of the CVE to express $c^k(x_1, t)$ as $c^k(\tau, t)$, which in turn relies on the validity of the streamtube invariance conditions underlying the CVE. General streamtube invariance issues were discussed previously in Streamtube Ensemble Formulation. However, for analysis of streamtube invariance requirements in particular cases, it is instructive to revisit the formulation for the simple case of coupled reactive transport in one dimension involving a single mobile and single immobile component. Consider a purely convective transport in a nonuniform velocity $v(s)$ along the streamtube coordinate $s(\mathbf{x})$, with reaction terms explicitly dependent on space, time, and solute concentration. This template fits various nonequilibrium sorption, decay, precipitation, biodegradation, and multidomain mass transfer processes. The governing differential equations for this single streamtube model (without yet invoking the CVE) are

$$\frac{\partial c^1}{\partial t} + v(x)\frac{\partial c^1}{\partial x} = -\sum_{j=1}^{J} r_j(x, t, \bar{c})$$

$$\frac{\partial c^2}{\partial t} = \sum_{j=1}^{J} r_j(x, t, \bar{c}) \tag{5.69}$$

Details of methods for analytical solution to variations of such systems are given in Lassey (1988), Toride et al. (1993), Simmons et al. (1995), and Ginn et al. (1995) among other articles. Here, this representative reactive transport system is investigated to identify streamtube invariance conditions required for the applicability of the simple average given in (5.52).

Next, the conditions required for representing the solutions to this system in the time and travel time space are sought, and the streamtube invariance of such solutions are studied. Also considered in turn are the cases where information propagates from the time boundary (boundary value problems) and from the space boundary (initial value problems) as per Simmons et al. (1995). A case involving mixed boundary conditions, where one reactant is initially uniformly distributed along the spatial coordinate and another along the temporal, is discussed in Ginn et al. (1995).

Boundary value problems. When the boundary condition is Dirichlet on the time ordinate, that is,

$$\begin{aligned} c^1(x=0,t_o) &= c_o^1(t_o) \\ c^2(x=0,t_o) &= 0 \end{aligned} \tag{5.70}$$

the system (5.69) and (5.70) is a boundary value problem. Perform the change of variables

$$d\tau = \frac{dx}{v_1} \tag{5.71}$$

for $\tau \in [0, T]$ and $x \in [0, x_1]$, defining a travel-time function as usual as

$$\tau(x;0) = \int_0^x \frac{dx'}{v(x')} \tag{5.72}$$

and under the assumption of positive v, the inverse function determining position is

$$x = \xi(\tau;0) \tag{5.73}$$

which gives position x as a function of τ, measured from the origin. In the simple case where the velocity does happen to be uniform within the streamtube, then $\tau(x; 0) = x/v$ and $\xi(\tau; 0) = v\tau$. Equation (5.71) may be used to convert the system to the time and travel-time space as follows:

$$\begin{aligned} \frac{\partial c^1}{\partial t} + \frac{\partial c^1}{\partial \tau} &= -\sum_{j=1}^{J} r_j(\xi(\tau;0),t,\bar{c}) \\ \frac{\partial c^2}{\partial t} &= \sum_{j=1}^{J} r_j(\xi(\tau;0),t,\bar{c}) \end{aligned} \tag{5.74}$$

$$\begin{aligned} c^1(x=0,t_o) &= c_o^1(t_o) \\ c^2(x=0,t_o) &= 0 \end{aligned} \tag{5.75}$$

The system (5.74) and (5.75) then provides a formulation dictating a solution $\bar{c}(\tau, t)$ entirely as a function of time and travel time. The boundary conditions in this boundary value problem are independent of any streamtube-specific velocity-based function, and so are invariant with streamtube. However, the reactions term requires the generally streamtube-specific inverse travel-time function, $\xi(\tau; 0)$, to express the position dependence of the rate of reaction; this renders the governing equation, and thus the solution, streamtube variant, because the rates of reaction depend on the velocity nonuniformity through $\xi_l(\tau; 0)$,where the subscript l denotes streamtube l. Therefore, when the reaction terms involve spatial dependence, the solution is dependent on the particular velocity nonuniformity. In this case the solution for a given l^{th} streamtube may be denoted with label l as $\bar{c}(l, \tau, t)$, and any flux-averaging of the streamtube contributions from the ensemble must be done with regard to not only the distribution of travel time but also the distribution of inverse travel time functions $\xi_l(\tau; 0)$ contributing flux given a particular τ. That is the averaging defined in (5.52) must be recast as

$$c_f(t,\mathbf{x}) = \left[\int_0^\infty q(\tau;\mathbf{x})\,d\tau\right]^{-1} \int_0^\infty c_g(t,\tau)q(\tau;\mathbf{x})\,d\tau \tag{5.76}$$

where c_g is a pre-averaged concentration weighted by the relative occurrence of fluxes corresponding to streamtubes l within the sub-ensemble of streamtubes with travel time τ:

$$c_g(t,\tau) = \left[\sum_l q(l;\tau,x)\right]^{-1} \sum_l c(l,t;\tau)q(l;\tau,x) \tag{5.77}$$

Put another way, the streamtube invariance conditions for the use of the averaging in (5.52) are that the reaction terms and boundary conditions be streamtube invariant, which here means they must not depend on the nonuniform velocity function characterizing convective transport along a streamtube.

Initial value problems. In the initial value specification, the boundary condition data usually takes the form of Dirichlet condition along the space coordinate; that is,

$$\begin{aligned} c^1(x_o,0) &= 0 \\ c^2(x_o,0) &= c_o^2(x_o) \end{aligned} \tag{5.78}$$

Again do the change of variable

$$d\tau = \frac{dx}{v_1} \tag{5.79}$$

as before, with travel time defined as in (5.72), including the particular case

$$\tau(x_o;0)=\int_0^{x_o}\frac{dx'}{v(x')} \tag{5.80}$$

and the same inverse function determining position (5.73), including the particular case

$$x_o=\xi(\tau_o;0) \tag{5.81}$$

which gives position x_o as a function of τ_o, measured from the origin. The new system is constructed as in the boundary value case, but with the initial values converted as well:

$$\begin{aligned}\frac{\partial c^1}{\partial t}+\frac{\partial c^1}{\partial \tau}&=-\sum_{j=1}^{J} r_j(\xi(\tau;0),t,\bar{c})\\ \frac{\partial c^2}{\partial t}&=\sum_{j=1}^{J} r_j(\xi(\tau;0),t,\bar{c})\end{aligned} \tag{5.82}$$

$$\begin{aligned}&c^1(\xi(\tau_o;0),0)=0\\ &c^2(\xi(\tau_o;0),0)=c_o^2(\xi(\tau_o;0))\end{aligned} \tag{5.83}$$

For instance, in the constant velocity case, the initial condition becomes

$$c_o^2(\xi(\tau_o;0))=c_o^2(v\tau_o) \tag{5.84}$$

Therefore, as in the case of the boundary value problem, it is seen that the solution to this system with nonuniform velocity may be cast in the time and travel time space. However, it can only be used in the averaging scheme of (5.52) if the reaction rates and initial distribution of reactant are invariant with the inverse travel-time function $\xi(\tau;0)$.

In summary, the streamtube invariance conditions for allowing the use of averaging in (5.52) are that the reactions term and boundary conditions be independent of the inverse travel-time function used to identify spatial coordinate. When these conditions are satisfied, the solution $c^k(t,\tau)$ is invariant with the particular form of the nonuniform velocity function involved in the governing differential equations, as long as the travel time for that velocity function, when evaluated at x_1, yields the value τ. This means that any velocity function $v(x)$ satisfying

$$\tau(x_1;0)=\int_0^{x_1}\frac{dx'}{v(x')} \tag{5.85}$$

at a specified observation location x_1 can be used in getting the solution to the governing system, including the constant velocity $v(x)=U=x_1/\tau$. That is, the streamtube solutions can be calculated using a CVE of representative streamtubes.

There are some cases that defy description by means of the CVE used here. These include the case of colloid or bacterial transport when aqueous- and solid-phase partitioning is governed by filtration theory (Rajagopalan and Tien 1976) so that the reaction rate is linear in porewater velocity v, the low-Peclet case where errors involved in the approximate representation of dispersion/diffusion may be important, and the case of nonuniform initial distribution of solid-phase reactant.

Chemical/Biologic Heterogeneity in Immobile Species

It was noted previously that the streamtube invariance conditions require among other things uniformity of the initial distribution of immobile and mobile reactants. *Evolving* nonuniformity in reactants along a streamtube poses no difficulty as this is captured in the differential equation governing reactive transport within a streamtube; however, the general case of arbitrary initial geochemical heterogeneity complicates the calculations. If appreciable heterogeneity appears in the initial distribution of solid-phase reactants, then the solute response will depend on particular streamtube index l as well as independent travel time, thus breaking streamtube invariance and making it necessary to characterize Eulerean geochemical properties (e.g., $\mathbf{z}$) along each streamtube and to incorporate this information in the reactive transport solution. This additional burden is avoidable under some conditions as demonstrated by a simplified example, involving the case where $\mathbf{z}$ is factorable into one function that represents spatio-temporal dependencies and another that reflects the multicomponent dependencies. The overall approach is to treat reactivity as velocity has been treated and to replace it with a cumulative reactivity in the streamtube solution. Doing so allows one to introduce an effective constant reactive rate and thus to divide up the streamtube corresponding to a particular travel time into a series of conditional streamtubes covering a range of reactivities. In this case, one may introduce the distribution of flux over not only travel time, but also over reactivity, as depicted in Figure 5-4, which is simply a two-dimensional probabilistic extension of Figure 5-3. Conditions for which this may be achieved are not yet fully known, because the existence of a constant reactivity ensemble depends to some degree on the form of the reactions and the nature of the initial nonuniformity in solid-phase properties.

For this reason, the simple case of a single mobile reactive species and how it is affected by chemical heterogeneity in the solid phase will be considered.

Factorable kinetic forms. In many cases, heterogeneity in the reaction term $z_j(\mathbf{x}, t, \mathbf{c})$ appears multiplicatively through a space-time weight function $z_j^o(\mathbf{x}, t)$, which for simplicity will be taken as independent of time, and an often nonlinear kinetic rate modulation term $h(\mathbf{c})$, such as (for the simplified case)

$$z_j(\mathbf{x}, t, \mathbf{c}) = z_j(\mathbf{x}, c) = z_j^o(\mathbf{x})h(c) \tag{5.86}$$

where z_j^o is the spatially nonuniform reactivity function representing the effects of geochemical heterogeneity and where the kinetic term h represents modulation of

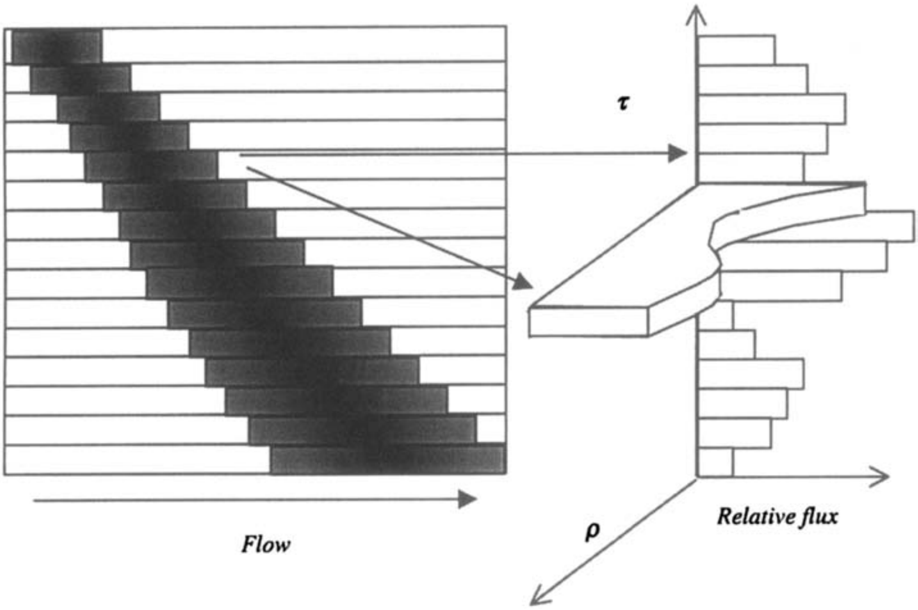

Figure 5-4. Constant velocity streamtube ensemble of Figure 5-3, depicted now with distribution of flux over not only travel time τ, but also effective constant reactivity ρ. Conceptual distribution is shown in section for given τ over ρ.

the reaction to some order in aqueous species c. This form is generally representative of single-species heterogeneous-reaction (e.g., aqueous solid phase) kinetics including biodegradation with negligible growth, kinetic sorption of arbitrary order, and colloid filtration, among others. Incorporating (5.86) into the streamtube equation before commitment to the CVE (for generality),

$$\frac{\partial c^k}{\partial t} + V_1(x)\frac{\partial c^k}{\partial x} - d_U\frac{\partial^2 c^k}{\partial x^2} = \sum_{j=1}^{J}(S^T)_{k,j}z_j(\mathbf{x}, \mathbf{c}) \tag{5.87}$$

gives

$$\frac{\partial c^k}{\partial t} + V_1(x)\frac{\partial c^k}{\partial x} - d_U\frac{\partial^2 c^k}{\partial x^2} = \sum_{j=1}^{J}(S^T)_{k,j}z_j^o(\mathbf{x})h(c) \tag{5.88}$$

For simplicity ignoring dispersive/diffusive flux, and then executing the conversion to travel time for this particular streamtube's velocity function $V_1(x)$ [e.g., from (5.42)], makes from (5.88):

$$\frac{\partial c^k}{\partial t} + \frac{\partial c^k}{\partial \tau} = \sum_{j=1}^{J}(S^T)_{k,j}z_j^o\{\mathbf{x}[s(x_1(\tau))]\}h(c) = \zeta_l^o(\tau)h(c) \tag{5.89}$$

where ζ_l^o is defined as (lth streamtube dependent) reactivity function that includes all terms in the sum in (5.88) and is in terms of time and travel time, and in terms of index l. The index may alternately be introduced in a continuous measure. In either case, the streamtube dependence (e.g., streamtube variance as opposed to invariance) of (5.89) on l requires one to condition the solution on l, and so the solution to (5.89) is denoted as $c_l(\tau, t)$. Within this notation, the solution can be expressed in terms of its analytical form according to the method of characteristics approach (Ginn et al. 1995). Consideration of the characteristics of the first-order partial differential equation (5.89) gives rise to a pair of ordinary differential equations describing the transport trajectory and the change in solute concentrations along that trajectory, respectively:

$$dt = d\tau \qquad \frac{dc}{h(c)} = \zeta_l^o dt \tag{5.90}$$

Integrating the first to obtain the path

$$\tau(x_1; 0) - \tau(x_o; 0) \equiv \tau(x_1; x_o) = t - t_o \tag{5.91}$$

and subsequently the second along the path described by the first gives, for the combined result, the formal integral solution

$$\int_{c_o(t_o)}^{c(t;t_o,c_o(t_o))} \frac{dc}{h(c)} = \int_{t_o}^{t} \zeta_l^o(t')dt' = \int_{0}^{\tau} \zeta_l^o(\tau')d\tau' \equiv Z_l^o(\tau) \tag{5.92}$$

where the penultimate step is obtained by using the path in (5.91) and the last step defines the cumulative reactivity $Z_l^o(\tau)$ of streamtube l in terms of travel time alone. Representing the left-hand side using integral notation as $F(c; c_o) \equiv F(c(t; t_o)) - F(c_o(t_o))$, (5.92) can be expressed as the implicit relation, giving c as a function of travel time and of boundary concentration c_o. The dependence on time is implicit in the dependence of c_o on t_o where t_o involves t by its restriction to obey (5.84). That is, the solution $c_l(\tau, t)$ is given in the form

$$F(c_l; c_o) = Z_l^o(\tau) \tag{5.93}$$

The method of characteristics approach is here essentially a separation of variables that has allowed one to functionally separate cumulative reactivity as an integral in travel time alone. In the form given by (5.93), just as in the case of a constant velocity representation for travel time discussed in the section, Streamtube Ensemble Formulation, the integral over the lth streamtube dependent reactivity (before it was the lth streamtube dependent reciprocal velocity) is equally given by any reaction function ζ_l^o that yields the same cumulative reactivity $Z_l^o(\tau)$ for a particular travel time τ (before it was a cumulative travel time for a particular x-coordinate x_1). Notice