ON A FIRST-PASSAGE TIME PROBLEM
IN CHEMICAL ENGINEERING

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August 1964

This study forms part of research carried out by this author jointly with R. Shinnar, School of Engineering, Princeton University, Princeton, N.J. and Technion, Israel Institute of Technology, Haifa, Israel. In its present form it will be delivered as an Invited Paper to a joint meeting of IMS and IASPS in Berne, Switzerland, September 1964. Results of this study will be incorporated in a paper jointly communicated by R. Shinnar and the author.

At the University of North Carolina the author's research was supported by the Office of Naval Research under Contract No. Nonr-655(09). Reproduction in whole or in part is permitted for any purpose of the United States Government.

ABSTRACT

The flow of particulate material through an agitated system is viewed as a manifestation of a birth and death process. It is shown that the models ordinarily considered in the technical literature - forward flow through a series of ideally mixed vessels on the one hand and diffusion-type flow on the other hand - represent special and/or extreme cases of the model considered here. The residence time of the material in the vessel is analyzed as a first-passage time. Laplace transforms (and second moments) of the residence time density function are presented for the general case and for cases with various specialized assumptions.
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1. Introduction

Chemical engineers are not infrequently concerned with the following problem:
A stream of particulate material enters a system which is made up of one or more
agitated vessels; each particle spends some time in the system and leaves at the
end of this residence time. By virtue of the agitation and mixing within the
system (i.e. in one or more of its component vessels) the residence time of a part-
icle is not constant. Rather it is a (non-negative) random variable and the
description and representation of its variability are of interest to the engineer.
It is ordinarily his purpose to attain one or more of the following objectives:
   a) to devise techniques for the experimental determination of the
      residence time distribution in a given system,
   b) to construct mathematical models of the flow and agitation of the
      particulate material, and
   c) to make inferences regarding the behavior of untested (and, possibly,
      as yet non-assembled) systems.

*At the University of North Carolina the author's research has been
 supported by O.N.R. Contract No. Nonr-855(09).
In principle the statistician can make contributions to all three areas of interest to the chemical engineer. However, in this study we are concerned with problems falling under the general heading of b): Construction and analysis of some models of particulate material flow under conditions of agitation and mixing.

As early as 1918, a paper was published under the names of Ham and Coe who obtained an interesting result: If material flows through n identical vessels connected in series under certain conditions (which were rather poorly specified in the original publication) the residence time follows a Gamma-distribution.* Subsequent studies published by chemical engineers - e.g. McMullin and Weber (1935), Gilliland and Mason (1949), Gilliland and Mason (1952) and, in particular, Danckwerts (1953) - clarified the concepts and created the nomenclature in present usage. While some facets of probability theory were utilized it is rather surprising to note that the concept of the Poisson process was not explicitly introduced in these studies. We shall see immediately that the earlier simple models of residence time distributions are - in effect - elementary manifestations of the Poisson process.

Consider a single agitated vessel. The stream has brought a particle into the vessel and on investigating the future course of the particle we make the following assumption: As soon as the particle has entered the vessel the prob-

* A historical remark seems not out of place: The notions of probability, distribution, etc., are not mentioned at all in this pioneering paper. The original version was written by Ham "...but the mode of presentation, which included the derivation of the formula by calculus, seemed somewhat too intricate." (Editor's Note). The Editor (or the Referee) must have been slightly suspicious of results derived by calculus since he continued as follows: "With Mr. Ham's approval we invited the cooperation of Mr. H.S. Coe, who confirmed the correctness of the premises and the computations." The nearest the paper gets to the notion of distribution is the following passage: "Different parts of the material are ... of different 'age' and the material passing out of the system comprises particles which have been subjected to agitation for different periods of time.
ability of its leaving in the outflow becomes independent of past history. This independence is the outcome of the intense agitation going on in the vessel. It characterizes the simplest type Poisson process with constant (i.e. time-independent) parameter and an immediate consequence is that the residence time within this single agitated vessel is exponentially distributed. If agitation of this nature is going on in a vessel it is referred to as an "exponential" or an "ideally mixed" vessel.

Now consider a system which is made up of several subsystems connected in series and the connection is such that (a) residence time realizations of a particle in the different subsystems are independent of each other and (b) particles can move forward within links between two successive subsystems. Clearly in this case the random variable "total residence time of a particle in the system" is the sum of independent (non-negative) random variables "residence times in subsystems" and the density of the total residence time is the convolution of all the component densities. In the particular case of all subsystems being ideally mixed vessels the residence time distribution turns out to be the so-called generalized Gamma-distribution and in the even more special case where all ideally mixed vessels (numbering \( n \), say) are of equal volume this becomes the Erlang distribution, that is, the (ordinary) Gamma-distribution with integral index. The squared coefficient of variation equal \( \frac{1}{n} \) in this case, that is the reciprocal of the number of agitated vessels. As the above specialized model of \( n \) identical exponential vessels - connected in series - was the first to be investigated in some detail by chemical engineers its associated indices serve as yardstick for actual systems under investigation and study even though they are not necessarily compartmentalized. Thus many authors use the concept of an "equivalent number" of vessels referring to the reciprocal squared coefficient of variation of the residence time, a quantity available from actual measurements.
We note, in passing, that a constant value (rather than one variable at random) of the residence time can be interpreted as a degenerate case of a random variable. Indeed this situation - described as plug flow - can be presented as a limiting case of the above simple model: Let the number $n$ of vessels tend to infinity and the size of each component exponential vessel tend to zero such that the expected residence time remains positive and finite; the limiting distribution is a unit step function and it pertains, of course, to the degenerate random variable.

The Poisson process can be characterized as a special case of a number of different, more general processes. For our purposes it is convenient to generalize it to the pure birth process. Indeed we have done so already in this Introduction by considering a model where particles flow through a series of (possibly) unequal exponential vessels. By introducing additional technical nomenclature we have not obtained new results. Rather we have gained a different viewpoint and new avenues of approach to further generalization are opened up.

The subdivision of the total system into smaller units may be representative of some (easily observable) physical reality; however, in many systems strict compartmentalization with clear-cut boundaries is impossible and this assumption serves only as a convenient artifice. A different approach has been taken by numerous researchers in order to circumvent this difficulty: it was assumed that agitation of the particles brought about a type of mixing and forward-backward motion along the direction of flow which could be described by a diffusion equation. Earlier work on this approach is comprehensively reviewed and original models are advanced in a paper by Levenspiel and Smith (1957) (see also van der Laan (1958)) and more recent diffusion approach studies will be mentioned later in this communication. It is important to note that it is not molecular diffusion which is under consideration. The mechanism envisaged is not on a molecular scale;
the particles under study are extremely large when compared with molecules though very small when measured against the total size of the particulate material in the system. It is assumed that some form of turbulent flow exists such that large hunks of material are violently agitated to and fro while at the same time a) neighboring molecules within such lumps do not typically change their relative positions, and b) an overall drift exists which moves new particles into the system and "aged" material out of it. Many terms have been used to describe this eddy diffusion phenomenon such as: longitudinal dispersion, axial mixing/et al. As stated before it is mathematically described by a diffusion-with-drift differential equation and the diffusion (or dispersion) coefficient is a constant representing the type of agitation under study. Starting from the diffusion-with-drift differential equation (and using the proper boundary conditions) it is possible to evaluate the residence time distribution of the particles either in some implicit form such as its Laplace transform or even in explicit (though approximate) fashion. Indeed this programme has been carried out almost simultaneously by Brenner (1962) and by Westerterp and Landsman (1962).

The basic statistical character of the diffusion equation has been well-known, of course, for many dozens of years together with the equivalence of results arrived at by a purely probabilistic approach and those attained by solving -- deterministically, as it were -- the differential equation with the appropriate boundary conditions. The authors mentioned above pursued the latter course; a minor purpose of this paper is to take the alternative course and to develop the diffusion model on probabilistic grounds. The major purpose of this communication is to construct a model of particulate flow possessing a character intermediate between the pure birth process and the diffusion-with-drift process. A birth and death process underlies the proposed model. It is then associated with a discrete state space and both the diffusion and the pure
birth processes present special and/or limiting cases. The model investigated here is more flexible than those dealt with by previous authors and in some sense is more general*. It is assumed here that agitated (exponential)/are connected in series. A particle starts its residence time in the system by entering the first vessel. It stays there for a random time and moves into the second vessel. After some additional random time has passed the particle moves either forward (into the third vessel) or backward (into the first vessel) with prescribed probabilities. This feature - the possibility of moving into either one of the two neighboring vessels - characterizes the process of the two neighboring vessels - and is common to all vessels except the first where forward movement only is possible. The last vessel, too, is unique: if a particle residing in it leaves in the forward direction it can no longer return to the system; it is absorbed, as it were. This is the termination of the process and in the nomenclature of birth and death (as well as diffusion) processes the time elapsing between entry into some state (in our case: the first vessel) and absorption on entering another state (in our case: a fictitious (n + 1)-th vessel from which no return to the n-th vessel is possible) is termed a first passage-time. Thus, for instance, in other areas of birth-and-death process applications the busy period of a server (in queueing theory), the time to first emptiness (in dam theory), etc., are first-passage times. The residence time of a particle in a system of connected agitated vessels is a first passage time and it is worthwhile to analyze it as such so as to make use of well-established theory and lines of research. We repeat an observation made before: The introduction of new technical terms does not - by itself - assure

*This latter statement has to be digested with some care; a diffusion-type process (or plug-flow, on the other extreme) is not a specialization of a birth and death process; rather it is a limiting form.
us of new results. All we have gained is a new viewpoint - old in other contexts may - and this/enable us to take over established techniques from other areas of application and make use of them in the present study.

2. Specification of Assumptions

A particle enters the system by being introduced into the first of n vessels which will be referred to as states. These are arranged in series and the particle moves from one to another in such a fashion that any transition involves neighboring states only. The sojourn time of a particle in a given state is an exponentially distributed random variable but the distributional parameters associated with the different states are not necessarily identical. The first state is somewhat different - a particle residing in it can move forward only into the second vessel. The last state too is somewhat set apart by virtue of the following property: If a particle sojourning in it moves backward (into the (n-1)th state) it is retained in the system. If, on the other hand, it moves forward (into a fictitious (n + 1)th state) it leaves the system and cannot return to it. We have then a particle performing a random walk on a line with a finite number of states; a reflecting barrier and a partly reflecting, partly absorbing barrier are associated with the first and the final state, resp. One problem of interest is the distribution of the first passage time from the instant of entry into the first state to the time of absorption in the (fictitious) (n + 1)th state.

Our microscopic model of particle motion has to be consistent with observable macroscopic properties of bulk flow. The total volume, V, of the system is a quantity which is fixed (though under "thought-experimental" control) and another constant - for a given experimental situation - is the (average) volume velocity, v say. The ratio of these two quantities determines the expected value of the residence time, E(t), for a very wide class of distributions (containing all the practical cases).
Next in our survey on a macroscopic scale consider the detailed balance of material flow at a boundary between two adjacent vessels. It is convenient to take the view that material transport occurs in a double link between such vessels; in one of these links material flows forward only whereas backward flow takes place in the other. If we ascribe the letters \( u \) and \( w \) to (average) forward and backward volume velocities and the subscript \( i \) to the \( i \)-th double link (i.e. to the double link connecting the \( i \)-th and the \((i+1)\)-th vessel) and furthermore, if we articulate the ordinarily implicit assumption that there are no regions of material accumulation within the system we immediately conclude that
\[
v = u_i - w_i \quad (i = 1,2, \ldots n-1)
\]

Let the volume of the \( i \)-th vessel be denoted by \( V_i \) \((i = 1,2, \ldots n)\). We obviously have then
\[
\sum V_i = V
\]
and the flow of material through the system may be described by the following diagram

![Diagram](image)

The average sojourn time\(^*\) of a particle in the \( i \)-th state is then equal to
\[
E(t_i) = \frac{V_i}{u_i + w_{i-1}} = \frac{V_i}{u_{i-1} + w_i}
\]

which holds for all \( i \) (that is: \( i = 1,2, \ldots n \)) if we define \( w_o = w_n = 0 \) and
\[
u_o = u_n = v.\] The reciprocal of this quantity

\(^*\)This holds for a single, uninterrupted sojourn of a particle in the \( i \)-th vessel; frequently a particle - in the course of its passage through the system - sojourns several times in some given vessel.
\[ \eta_i = \frac{1}{E(t_i)} \]  

(5)

is then the parameter of the exponential sojourn time distribution associated with the strongly agitated i-th vessel

\[ e_i(t) = \eta_i e^{-\eta_i t} \]  

(6)

The ratio of backward flow to total outflow from the i-th vessel - in other words: the fraction of backflowing material - may be identified with the probability \( p_i \) of a particle being transferred to the preceding (i-1)-th state on leaving the i-th state

\[ p_i = \frac{w_{i-1}}{u_i + w_{i-1}} \quad (i = 1, 2, \ldots, n) \]  

(7)

The complementary quantity, (1-\( p_i \)), refers, of course, to the probability of a particle to be transferred to the succeeding (i+1)-th state.

The specification of the assumptions as given in this Section enables us to proceed to the solution - in some implicit form - of the problem under consideration.

3. A General Model with Many Parameters

Let us fix attention on a particle in the i-th state and inquire into the characteristics of the random variable "future residence time (as measured from the present instant) of the particle in the system". This is analogous to the random variable "age of the particle in the system" and an obviously convenient and illustrative term to be used for the random variable under consideration is that of anti-age.

A little reflection shows that the density function, \( f_i(t) \), of the anti-age of a particle residing at present in the first state is identical with the density of the total residence time. It is connected with the density function of anti-
age in the second state through a simple convolutional relationship

\[ f_1(t) = e_1(t) \ast f_2(t) \] (8a)

The density function of anti-age in an intermediate state (i.e. other than the first and the last) is related to those of both its neighbors

\[ f_i(t) = p_i e_i(t) \ast f_{i-1}(t) + (1-p_i)e_i(t) \ast f_{i+1}(t) \quad (i = 2,3,\ldots,n-1) \] (8b)

The interpretation of the right hand side of equation (8b) is the following:
The duration of sojourn in the \( i \)-th state is associated with the density \( e_i \) regardless of the particle's future course; a transition to the \((i-1)\)-th state will take place with probability \( p \); and the additional future residence time (as measured from time of entry into that state) is governed by the density \( f_{i-1}(t) \); the alternative transition to the \((i+1)\)-th state possesses probability \((1-p_i)\) and in that case it is \( f_{i+1}(t) \) which represents the density of the future residence time.

Analogously the anti-age density function of the last state is given by

\[ f_n(t) = p_n e_n(t) \ast f_{n-1}(t) + (1-p_n)e_n(t) \] (8c)

We have then a set of \( n \) equations in \( n \) unknown functions. Let us now apply the Laplace transformation on the set (8); we define*

\[ L_i(s) = \int_0^\infty e^{-st}f_i(t) \, dt \] (9)

recall that

\[ \int_0^\infty e^{-st}e_i(t) \, dt = \eta \int_0^\infty e^{-(\eta+s)t} \, dt = \frac{\eta}{\eta + s} \] (10)

*For the purposes of this study \( s \) is a dummy variable defined in a suitable region.
and make use of the theorem that the Laplace transform of the convolution of two (or more) functions is the product of the Laplace transforms of the contributing functions*. By this device the set (8) has been transformed into a set of \( n \) linear equations in \( n \) unknowns

\[
L_1 = \frac{\eta_1}{\eta_1 + s} L_2
\]

\[
L_i = p_i \frac{\eta_i}{\eta_i + s} L_{i-1} + (1-p_i) \frac{\eta_i}{\eta_i + s} L_{i+1} \quad (i = 2, 3, \ldots n-1)
\]

\[
L_n = p_n \frac{\eta_n}{\eta_n + s} L_{n-1} + (1-p_n) \frac{\eta_n}{\eta_n + s}
\]

In principle this can be solved in an elementary fashion. However it cannot be expected that the solution will be cast in a form convenient for computational purposes.

Let the quantities \( \alpha_i \) and \( \alpha_i^* \) be defined as

\[
\alpha_i = (1-p_i) \frac{\eta_i}{\eta_i + s} \quad (12)
\]

\[
\alpha_i^* = p_i \frac{\eta_i}{\eta_i + s} \quad (13)
\]

The Laplace transform, \( L_1(s) \), of the first passage time density - the function of main interest - can be expressed in terms of the \( \alpha_i \)-s and \( \alpha_i^* \)-s

\[
L_1(s) = \frac{\prod \alpha_i}{1 - \sum \alpha_i \alpha_i^* + \sum_{i,j} \alpha_i \alpha_i^* \alpha_j \alpha_j^* - \sum_{i,j,k} \alpha_i \alpha_i^* \alpha_j \alpha_j^* \alpha_k \alpha_k^* + \cdots}
\]

\[
\binom{n-1}{1} \text{ terms} \quad j > i + 1 \quad \binom{n-2}{2} \text{ terms} \quad j > i + 1 \quad \binom{n-3}{3} \text{ terms} \quad k > j + 1
\]

*provided, of course, that their transforms exist.
The summations in the denominator are carried out over all suitable pairs, quadruplets, sextuplets, etc. Typically it is impossible to invert expression (14) into a function of closed form though, of course, approximations of the density may be presented and moments of any order can be precisely evaluated by the usual procedures associated with moment-generating functions of which the Laplace transform is a particular case.

The other unknowns \( L_i(s) \) \((i = 2,3,\ldots n)\) too can be derived in terms of the above quantities \( \alpha_i \) and \( \alpha_i^* \). It has been stated that it is the random variable "anti-age" of which an account is given by the density \( f_i(t) \) - the inverse transform of \( L_i(s) \). However, \( f_i(t) \) represents also the density of a residence time (first-passage time) in the system when it is assumed that the particle under study is injected into the \( i \)-th state from outside. This viewpoint may be of practical use when the properties of an experimental system are tested and explored.

We note, in passing, that the choice of the prospective random variable "anti-age of a particle" is arbitrary, to some extent, for the purpose of our investigation. An alternative course would be to subject the retrospective random variable "age of a particle" to the type of argument used in this Section. A set of relations analogous to (8) would be generated and the desired result - the residence time density (or rather its Laplace transform) - would be obtained in the "guise" of the age density in the last state. Equation (14) pertains to the Laplace transform of three conceptually different densities: residence time (or first-passage time), anti-age in the first state, and age in the last state. A little reflection confirms the logical identity of the three concepts.

The mathematical techniques used in our analysis are little more than a modification of Bachelier's methods - expounded, for instance, in Bachelier (1912) - combined with the application of the Laplace transformation. Alternative techniques for the (elementary) evaluation of first-passage time distributions are available not only in research papers but also in texts (e.g. Bharucha-Reid (1960)
Whether or not equation (14) can be made to be of practical use depends both on the precise purpose of the investigation and on the detailed knowledge of the $2n$ parameters involved. Typically $V$ and $v$ are known and the latter quantity can even by controlled and varied at the experimenter's discretion. But even if - in addition - compartmentalization of the system is clear-cut, thus providing us with the information about $(n-1)$ additional parameters, it may not be possible to make detailed statements about the quantities $u_1$. Still some value (or range of values) of the average forward flow velocity may be available from direct observation or otherwise. In other physically realizable systems we may be aware - in a qualitative way only - of the experimental fact that a general particle drift with forward and backward jumps exists but no detailed quantification of all required parameters is possible. For such and other contingencies it appears worthwhile to construct models which are flexible, mathematically (and/or computationally) tractable and yet retain the basic physical features described above. It is desirable that these models possess a small number of parameters and to that end it is necessary to introduce specializations into the present model. This will be done in the next Section.

4. A Birth and Death Model with Specialized Assumptions

An assumption usually made by chemical engineers in the investigation of pure birth process models is the equality of volumes of all participating vessels. A second simplifying assumption (specific to birth and death models) is that the velocities of forward flow between neighboring vessels are identical. This implies, of course, that all backward flow velocities, too, are identical. These are sweeping assumptions but typically they are not unrealistic. If the system is indeed physically made up of compartments, technical considerations of design simplicity,
etc., usually prescribe identical vessels and identical double links. Where the birth and death process is not more than a general delineation of the underlying physical process without laying claim to precise representation of reality sufficient flexibility of the model is retained even after the introduction of the simplifying assumptions.

At first sight it appears that there are still four parameters describing the specialized model:

1) the number of states, \( n \), in the system - this is a parameters' parameter, as it were;
2) the total volume of the system, \( V \);
3) the average drift velocity, \( v \);
4) the average forward flow velocity, \( u \), between two adjacent states.

Two only of these four parameters are non-trivial. No loss of generality is incurred if we set both \( V \) and \( v \) to equal 1. However some physical insight is gained if explicit use is made in our developments of all four parameters (and of other quantities dependent on them.)

We drop the general subscripts from the letters denoting various quantities in the last Section. The forward and backward flow velocities in any double link are denoted by \( u \) and \( w \), resp. The reciprocal sojourn times - the parameters of the pertaining exponential distributions - in all intermediate (i.e. other than first and last) vessels are identical and the use of the letter \( \eta \) will be retained for their description

\[
\eta = \frac{n(u + w)}{V}
\]  

(15)

For terminal vessels (both the first and the last) we introduce \( \xi \) as the reciprocal average sojourn time...
The probability, $p$, of a particle leaving an intermediate vessel in the backward direction is given by

$$ p = \frac{w}{u + w} = 1 - \frac{\xi}{\eta} $$

(17)

The analogous quantity in the first vessel equals zero. In the last vessel this probability will be denoted by $\Pi$; it is given by

$$ \Pi = \frac{w}{v + w} = \frac{w}{u} = \frac{p}{1 - p} = \frac{\eta}{\xi} - 1 $$

(18)

This can be rewritten as

$$ \frac{1}{p} - \frac{1}{\Pi} = 1 $$

(19)

which is convenient for some purposes. It is evident that restrictions on possible values of $\Pi$ are rather mild

$$ 0 < \Pi < 1 $$

(20)

whereas $p$ is rather constrained

$$ 0 \leq p < \frac{1}{2} $$

(21)

Physically (20) and (21) may be interpreted as follows: At the end of the system we can "reflux" any desired fraction of the material; however, the bulk of the material - located in the first and in the intermediate vessels - has to possess a forward drift movement ($1 - p > \frac{1}{2}$).

The expected residence time in the system (first-passage time) can be expressed in terms of the above quantities

$$ E(t) = \frac{v}{\nu} \xi v = \frac{nu}{\xi} = \frac{n}{\xi(1 - \frac{w}{u})} = \frac{n}{1 - \Pi} \frac{1}{\xi} $$

(22)
Next we shall derive the residence time density function by inversion of the Laplace transform in the simplest cases: \( n = 2 \) and \( n = 3 \).

In the first of these cases, \( n = 2 \), equation (14) is reduced to

\[
L_1(s) = \frac{\alpha_1 \alpha_2}{1 - \alpha_1 \alpha_2} = \frac{\left( \frac{\xi}{\xi + s} \right)^2 (1 - \pi)}{1 - \left( \frac{\xi}{\xi + s} \right)^2 \pi} = \frac{\pi^2 (1 - \pi)}{\pi^2 (1 - \pi) + 2\pi s + s^2} = \frac{\pi^2 (1 - \pi)}{[s + (1 + \sqrt{1 - \pi})^2][s + (1 - \sqrt{1 - \pi})]}
\]

The inverse, \( f(t) \), of this expression can be obtained by standard procedures

\[
f(t) = \frac{\xi (1 - \pi)}{2\sqrt{\pi}} \left( e^{-\xi (1 - \sqrt{\pi})} t - e^{-\xi (1 + \sqrt{\pi}) t} \right) = \frac{\xi (1 - \pi)}{\sqrt{\pi}} \xi^2 t \sinh (\xi \sqrt{\pi} t)
\]  

If we increase the number of states to the case \( n = 3 \) complexity is greatly increased but a closed expression for the density is still obtainable. Equation (14) becomes

\[
L_1(s) = \frac{\alpha_1 \alpha_2 \alpha_3}{1 - \alpha_1 \alpha_2 - \alpha_2 \alpha_3} = \frac{\left( \frac{\xi}{\xi + s} \right)^3 (1 - \pi)(1 - \pi')}{1 - \frac{\xi}{\xi + s} \pi - \frac{\xi}{\xi + s} \pi' + \left( \frac{\xi}{\xi + s} \right)^3 (1 - \pi')(1 - \pi'')}
\]

\[
= \frac{\xi^3}{(\xi + s)^3 (\pi + s)} (1 - \pi') = \frac{\xi^3 (1 - \pi')}{(\xi + s)((\xi + s) + s) - 2\xi^2 \pi'}
\]

\[
= \frac{\xi^3 (1 - \pi')}{(\xi + s)((\xi + s)(\pi + s) - 2\xi^2 \pi')} = \frac{\xi^3 (1 - \pi')}{(s + \xi)(s^2 + \xi(2 + \pi')+ \xi^2 (1 - \pi'))}
\]

\[
= \frac{\xi^3 (1 - \pi')}{(s + \xi) \left( s + \xi \frac{2 + \pi' + \sqrt{\pi' + \pi''}}{2} \right) \left( s + \xi \frac{2 + \pi' - \sqrt{\pi' + \pi''}}{2} \right)}
\]  

\[
\]
The inverse transform of (25) is given by

\[ f(t) = \frac{\xi(1-\Pi)}{2} e^{-\frac{\xi t}{2}} \left\{ e^{\frac{\xi t \Pi}{2}} \left[ \sinh \frac{\xi t}{2} \sqrt{\Pi + \frac{\Pi^2}{2}} \right] + \cosh \frac{\xi t}{2} \sqrt{\Pi + \frac{\Pi^2}{2}} - \frac{1}{\Pi} \right\} \]

(26)

Now when we proceed to higher values of \( n \), inversion of the Laplace transform into a closed form appears to be no longer possible. "Simple" invertibility depends on the factorizability of the denominator of (14); if \( n \geq 4 \) factorization cannot be carried out. Of course, as was stated before, approximations to the density functions can still be obtained and precise values of moments, cumulants, etc., can be made available by standard methods. We shall derive the variance (and other quantities of interest) of the residence time for a general \( n \) by using a variant of Bachelier's procedure:

Let the expected anti-age of a particle in the \( i \)-th vessel be denoted \( E(T_i) \). By considerations very similar to those made for deriving set (8) we obtain

\[ E(T_i) = E(T) = \frac{n}{1-\Pi} \frac{1}{\xi} \]

\[ E(T_i) = \frac{1}{\Pi} + p E(T_{i-1}) + (1-p) E(T_{i+1}) \ (i \neq 1,n) \]

(27)

\[ E(T_n) = \frac{1}{\Pi} + \Pi E(T_{n-1}) \]

The solution of (27) is given by

*Digressing we note that in a system composed of identical vessels and of identical double links symmetry considerations generate the following relation: Expected anti-age in \( i \)-th vessel = Expected age in \((n-i+1)\)th vessel. Actually the symmetry reaches farther - even the distributions are identical.

*Digressing we note that in a system composed of identical vessels and of identical double links symmetry considerations generate the following relation: Expected anti-age in \( i \)-th vessel = Expected age in \((n-i+1)\)th vessel. Actually the symmetry reaches farther - even the distributions are identical.
The expected anti-age $E(T)$ in the system (or, what is the same, the expected age in the system) is then equal to

$$E(T) = \frac{1}{n} \sum_{i=1}^{n} E(T_i) = \frac{1}{n^2} \left[ \frac{n\Pi}{1-\Pi} \frac{1-\Pi^2}{1-\Pi} + \ldots + \frac{n\Pi}{1-\Pi} \frac{1-\Pi^{n-1}}{1-\Pi} \right] =$$

$$\frac{E(t)}{n^2} \left[ \frac{n(n+1)}{2} + \frac{\Pi}{(1-\Pi)^2} \left( (n-1)n\Pi + \Pi^2 \right) \right] \quad (29)$$

Now it is known from Smoluchowski's work* (e.g. a paper published in 1915) that the expectation of anti-age (or age) and moments of residence time are related as follows

$$E(t) = \frac{E(t^2)}{2E(t)} = \frac{E(t)}{2} \left( 1 + \gamma^2 \right) \quad (30)$$

where $\gamma$ is the coefficient of variation of the residence time distribution.

Combination of (29) and (30) yields

$$\gamma^2 = \frac{1}{n} + \frac{2\Pi}{n^2 (1-\Pi)^2} \left[ (n-1)n\Pi + \Pi^2 \right] = \frac{1}{n} + \frac{2}{n^2} \left[ \Pi (n-1) + \Pi^2 (n-2) + \ldots + \Pi^{n-1} \right] \quad (31)$$

Since in many (but by no means all) engineering situations the performance of mixing equipment is judged by the variance** of the residence time distribution relation (31) is of some importance. A useful representation of (31) is obtained by drawing contours - that is, lines of equal $\gamma$ - on a graph whose

---

*The present notion of anti-age is identical with Smoluchowski's concept of "Erwartungszeit".

**We have noted before that the reciprocal of the squared coefficient of variation is defined as the "equivalent" number of vessels.
The flexibility of the present model can be demonstrated by examining special and extreme cases:

a) Let \( n \) equal 1; in this case there is no physical meaning to the notion of \( \Pi \) but even formal use of (31) with an arbitrary \( \Pi \) renders the correct result: \( \gamma^2 = 1 \). The present case simply represents the single exponential vessel.

b) Let \( n \) equal a fixed positive integer (other than 1) and assume that \( \Pi = 0 \); this corresponds to a pure birth process and indeed the correct value - \( \gamma^2 = \frac{1}{n} \) - of the dimensionless variance (i.e., the squared coefficient of variation) is obtained.

c) Let again \( n \) equal a fixed positive integer (other than 1) and let \( \Pi \) approach 1. Physically, it is meaningless to let \( \Pi \) be equal 1 (and \( n \) finite at the same time) since in that case material could not flow at all through the system. If, however, formally \( \Pi \) is made equal to 1, we obtain

\[
\gamma^2 = \frac{1}{n} + \frac{2}{n^2} \left[ (n-1) + (n-2) + \ldots + 1 \right] = \frac{1}{n} + \frac{2}{n^2} \left( \frac{(n-1)n}{2} \right) = 1
\]

i.e. that value of \( \gamma \) which is associated with a single exponential vessel. The physical interpretation to be attached to a situation where \( \Pi \) approaches 1 arbitrarily closely is the following: The birth and death model of particle flow through \( n \) vessels can be made to approach the single exponential vessel model as (arbitrarily) close as desired by making a judicious choice of the reflux parameter \( \Pi \).

*The quantity \( n \), originally conceived as a natural number can easily be thought of as (i.e., generalized to) a positive, not necessarily integral, number.
d) Let \( n \) tend to infinity and simultaneously both \( E(t) = \left( \frac{n}{1-\Pi} \right) \) and \( \Pi \) (\( \neq 1 \)) are held constant; clearly \( \psi^2 \to 0 \) and the case under consideration involves plug-flow.

e) As a final example consider the case where \( n \) tends to \( \infty \) and simultaneously \( \Pi \) approaches 1 such that

\[
n(1-\Pi) = \rho \tag{32}
\]

where \( \rho \) is positive and finite. This is the case of (eddy) diffusion and \( \psi^2 \) can be expressed as function of \( \rho \)

\[
\psi^2 = \frac{1}{n} + \frac{2}{[n(1-\Pi)]^2} \left\{ -1 + n(1-\Pi) + \left[ (1-(1-\Pi)) - \frac{1}{1-\Pi} \right] \right\};
\]

\[
n \to \infty , \Pi \to 1 , n(1-\Pi) \to \rho ;
\]

\[
= \frac{2[e^{-\rho} - (1-\rho)]}{\rho^2} \tag{33}
\]

Diffusion will be discussed in the next Section in some more detail.

5. A Model with Homogeneous Longitudinal Dispersion

The last paragraph of the preceding Section concerned itself with a situation where - with expected residence time held constant - the number of states in the system tended to infinity but agitation of the flowing material on a local scale persisted. This is a diffusion situation but we recollect that it is not molecular diffusion which is under consideration; rather the "to-and-fro" movement under study is carried out by lumps of material containing a huge number of atoms. We shall use the term "longitudinal dispersion" for this phenomenon. In this Section it will be shown that a pertinent description of longitudinal dispersion can be presented as a limiting case of the birth and death process model and that the same analytical approach can be used for the evaluation of the Laplace transform of the first-passage time density function. Alternative analytic approaches (with no explicit probability interpretation) have been used by Brenner (1962) and by Westerterp and Landsman (1962).
Equations (11) - associated with the birth and death process - may be regarded as a set of second order difference equations. If proper assumptions are made a second order differential equation in the desired Laplace transform (as a function of the location of the particle under observation) can be derived. First we make the homogeneity assumption, i.e. all vessel volumes are equal and all double links connecting adjacent vessels are identical. Next we define a variable $\theta$ depending on $i$ and $n$ by

$$\theta = \frac{i-1}{n}, \quad (0 \leq \theta < 1) \quad (34)$$

The (approximate) physical interpretation of $\theta$ is that a fraction $\theta$ of the path within the system has already been traversed by a particle located in the $i$-th vessel. Even without setting up the differential equation we can obtain the expected anti-age (or, by a simple transformation, the expected age) of a particle given that it is located on site $\theta$ within the interval $(0,1)$. We wish to insert (34) in (28) and then derive a result for the limiting case: $n \to \infty$, $\Pi \to 1$, $n(1-\Pi) \to \rho$. After some manipulation we obtain for the discrete case

$$E(T_i) = \frac{1}{n} \left[ (n-i+1) + (n-i+2)\Pi + \ldots + n\Pi^{i-1} + \frac{n\Pi^i}{1-\Pi} \right] =$$

$$= \frac{1}{n} \left[ (n-i) \frac{1-\Pi^i}{1-\Pi} + \frac{1 - (i+1)\Pi^i + i\Pi^i + 1}{(1-\Pi)^2} + \frac{n\Pi^i}{1-\Pi} \right] =$$

$$= E(t) \frac{1-\Pi}{n} \left[ \frac{(n-i)(1-\Pi^i) + n\Pi^i}{1-\Pi} + \frac{1 - (i+1)\Pi^i + i\Pi^i + 1}{(1-\Pi)^2} \right] =$$

$$= E(t) \left[ \frac{n-i}{n} (1-\Pi^i) + \Pi^i + \frac{1}{n} \frac{1-\Pi^i[1+(i+1)(1-\Pi)]}{1-\Pi} \right] \quad (35)$$

If now we carry out the limiting operations we get

$$E(T|\theta) = E(t) \left\{ (1-\theta)(1-e^{\theta}) + e^{-\rho\theta} + \frac{1}{\rho} \left[ 1-e^{-\rho\theta}(1+\rho\theta) \right] \right\} =$$
The physical meaning of (36) is the following: Consider the interval (0,1); site 0 is a reflecting barrier, site 1 is partly reflecting and partly absorbing. A particle enters the interval through site 0 and drifts forward under conditions of eddy diffusion. Given that at the present moment the particle is located on site 0, its expected anti-age is given by (36). The identical expression represents also the expected age of a particle located on site (1-θ).

The required second order differential equation will next be set up. Under the simplifying homogeneity assumption equation (11) reads (for \( i \neq 1, n \))

\[
L_i = p \frac{\eta}{\eta+s} L_{i-1} + (1-p) \frac{\eta}{\eta+s} L_{i+1}
\]

If we introduce (in obvious notation)

\[
\Delta \theta = \frac{1}{n} \quad (38)
\]

\[
\Delta L = L_{i+1} - L_i \quad (39)
\]

and

\[
\Delta (\Delta L) = L_{i+1} - 2L_i + L_{i-1} \quad (40)
\]

we can - on multiplying by (η+s) and rearranging terms - cast (37) into

\[
(1-p)\eta L_{i+1} - (\eta+s) L_i + p\eta L_{i-1} =
\]

\[
= [p\eta L_{i+1} - 2p\eta L_i + p\eta L_{i-1}] + [(1-2p)\eta L_i + (1-2p)\eta L_{i+1}] - s L_i =
\]

\[
= \frac{p\eta}{n^2} \frac{\Delta L}{\Delta \theta} + \frac{(1-2p)\eta}{n} \frac{\Delta L}{\Delta \theta} - s L_i = 0
\]

We take note that - on going to the limit - the coefficients \( \frac{p\eta}{n^2} \) and \( \frac{(1-2p)\eta}{n} \) tend to the following simple expressions

\[
\frac{p\eta}{n^2} = \frac{\Pi}{n^2} = \frac{1}{E(t)} \frac{\Pi}{n(1-\Pi)} \rightarrow \frac{1}{\rho E(t)}
\]

\[
\frac{(1-2p)\eta}{n} = \frac{1}{\rho E(t)}
\]
After multiplying (41) by $\rho E(t)$ the differential equations is established as

$$\frac{\partial L}{\partial \theta} + \rho \frac{\partial L}{\partial \theta} - \rho E(t) s \, L$$

(44)

and boundary conditions are set up as counterparts to the equations for $L_1$ and $L_n$ in the set (11)

$$\frac{dL}{d\theta} \theta = 0 = 0$$

(45)

$$\frac{dL}{d\theta} \theta = 1 + \rho L(\theta = 1) - \rho = 0$$

(46)

Equation (44) together with boundary conditions (45) and (46) can be solved by (lengthy) standard methods, details of which will not be presented here. Let a quantity $\sigma$ be defined as

$$\sigma = \sqrt{\rho^2 + 4\rho E(t)s}$$

(47)

We have then the following expression as the solution of equation (44)

$$L = \frac{e^{\frac{1}{2} \rho (1-\theta)} \left[ \rho \sinh \frac{\sigma \theta}{2} + \sigma \cosh \frac{\sigma \theta}{2} \right]}{\left( \rho + 2E(t)s \right) \sinh \frac{\sigma}{2} + \sigma \cosh \frac{\sigma}{2}}$$

(48)

This is the Laplace transform of the anti-age density given that the particle under consideration is located on site $\theta$ within the interval $(0,1)$. By virtue of arguments analogous to those used before, expression (48) is also the transform of the age density function of a particle located on site $(1-\theta)$; finally, it is the Laplace transform of the first-passage time density of a particle injected into the interval $(0,1)$ at location $\theta$. The residence time density is associated with the particular choice of the parameter $\theta = 0$. The inversion of the transform into a density of closed, simple form seems to be impossible, but again precise values of
all moments, cumulants etc., can be derived by standard (though cumbersome) procedures and approximations to the density function are readily established.

We note here that the formulation of first-passage time problems in terms of second order differential equations in the Laplace transform goes back to the work of Darling and Siegert (1953).

A dimensionless index used - by engineers and others - to describe mass and heat transfer problems is the Peclet number. Most frequently it is defined as

\[ Pe = \frac{v b}{D} \] (49)

where \( D \) is the diffusion coefficient and \( b \) a length characteristic of the system under study. It is not difficult to establish that the quantity \( \rho \) defined by (32) and used throughout this Section is actually the Peclet number of the present investigation. For some purposes this identification \( \rho \) with \( Pe \) may be useful.

6. Conclusion

The models advanced in this study should be of use if only for the reason that they provide a unified outlook on the various approaches to the analysis of turbulent particulate flow through a system of vessels. Whether or not a precise quantitative evaluation of a given engineering situation is obtained on using such a model depends not only - and even not necessarily - on a (hoped for) close correspondence between reality and the suggested model mechanism. To a great extent the usefulness of a model depends on the index (or indices) of performance deduced by its means; typically it is too much to expect complete agreement between the model-derived and the actual distributions. For practical purposes one identifies two distributions if they possess identical pertinent features, e.g. the coefficient of variation, the Peclet number*, etc., and it is hoped that the distributions do not

*The Peclet number of a system associated with a (homogeneous) birth and death process is given by the equivalent of 32: \( \rho = n(1-\Pi) = \frac{nv}{u} \)
diverge in their less important features. However, it is now widely felt that a single index of performance may characterize a system very poorly. Even if we were to accept a single index it is not at all clear which of several "candidates" is preferable. Thus, for instance, we may choose the coefficient of variation or the Peclet number; however systems possessing identical coefficients of variation may have different Peclet numbers and, of course, the converse statement holds as well. The homogeneous birth and death process model makes use of one additional parameter (or index); a large measure of flexibility is introduced and, at the same time, arbitrariness is kept at a minimum. Numerical tables of the distributions associated with the homogeneous birth and death process will be published together with the final version of this paper and a series of practical cases - as reported in the literature - will be examined with a view to the theory presented here.
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