Obtaining the Evolving Concentration Distribution Curves During Binary Disintegration of Macromolecules

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A general numerical procedure is developed to solve the integro-differential equation that describes the binary disintegration of macromolecules. The key step in this procedure is the application of the Method of Lines to convert the integro-differential equation into a set of ordinary differential equations which are then integrated using commercial scientific computing software. This procedure is applied to a number of progressively more complex disintegration kinetics and for arbitrary initial concentration distribution. Its performance and potential for generalization are briefly discussed.
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Introduction

In many chemical, biochemical, and industrial processes, macromolecules are cleaved by different means and for different purposes into a collection of smaller fragments of assorted sizes. For example, in thermal cracking of petroleum fractions, large hydrocarbon molecules are split into smaller ones by exposure to elevated temperatures. In bioprocessing and biochemical reactions, complex polysaccharides are frequently hydrolyzed by enzymes into a collection of oligosaccharides and/or sugars. In the recycling of waste plastics, large polymer molecules are converted into short-chain hydrocarbons by sonification, thermal, or chemical degradation. In all these processes an important factor is, of course, the rate at which the disintegration reaction takes place, but of equal importance is the concentration distribution of the products formed. While the rate of disintegration is controlled by some appropriately defined average rate constant of the reaction, the shape of the concentration distribution curve (CDC) and its evolution with time depend on the relative ease with which the various chemical bonds in a macromolecule can be cleaved. Thus the concentration distribution depends not on a single kinetic parameter but on a large number of parameters each describing the rate at which a particular chemical bond in the macromolecule is cleaved. An added complication is that the rate of disintegration associated with a particular chemical bond is, in general, not only a property of the chemical bond itself but may depend on the location of that bond within the macromolecule. Thus the task of computing the CDC and its evolution is not a trivial exercise even for the simplest macromolecules.

For this reason such curves have only been reported for a restricted number of cases in which the kinetic parameter associated with a particular bond is assumed to be a simple function of the overall molecular weight and/or of the location of that bond within the molecule (consequently a function of the molecular weight of the products formed). Even with these restrictions, the computation of CDC very often

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requires mathematics and numerical analysis that may not be familiar to investigators of macromolecule disintegration. The aim of this investigation is to develop a simple and yet general computer-based numerical procedure for obtaining CDC that is not restricted to simple disintegration kinetics. The procedure will make full use of the flexibility of the scientific computing software currently on the market so as to keep the effort of computer code development to a minimum. This procedure will be demonstrated by a number of examples, and where possible, the resulting CDC will be compared against that reported in the open literature.

Continuous Kinetics and Disintegration Rate

The molecular weight of a typical macromolecule will be denoted by m and the minimum and maximum molecular weight encountered in a disintegration process will be denoted by $m_{\min}$ and $m_{\max}$, respectively. Typically, $m_{\max}$ is of the order of 10^6 or 10^7 or larger and $m_{\min}$, depending on the extent of the disintegration reaction, can be several orders of magnitude smaller than $m_{\max}$. For such a large variation in m, it is physically realistic and computationally convenient to treat the molecular weight as a continuous variable between the limits $m_{\min} \le m \le m_{\max}$.[1] The composition of a mixture of macromolecules undergoing disintegration is described, at anytime, by its concentration distribution in the form $c(m, t)$, where $c(m, t)\ \delta m$ represents the concentration of macromolecules with molecular weight between the interval $m - \delta m/2 \le m \le m + \delta m/2$. Given an arbitrary initial composition, i.e., $c(m, 0)$, the following numerical procedure described will compute the evolving concentration distribution $c(m, t)$ for $t > 0$.

The governing equation for $c(m, t)$ is[2]

$$\begin{aligned}\frac{\partial c(m,t)}{\partial t} &= -\int_{m_p=m_{\min}}^{m} k\,(m,m_p)c(m,t)dm_p + 2\int_{m_r=m}^{m_{\max}} k(m_r,m)c(m_r,t)dm_r \\ &= -\left\{\int_{m_p=m_{\min}}^{m} k\,(m,m_p)dm_p\right\}c(m,t) + 2\int_{m_r=m}^{m_{\max}} k(m_r,m)c(m_r,t)dm_r \qquad (1)\end{aligned}$$

In some textbooks this is referred to as a population balance equation. This equation implicitly assumes that the macromolecules is essentially linear and is homogeneous along its entire length and utilizes the symmetry resulting from this. k is the kinetic "constant" of the disintegration. See the following discussion regarding its variation with molecular weights and some of the assumptions involved. The first integral on the right-hand side (RHS) gives the rate of disappearance of macromolecule m as a result of its disintegration into smaller macromolecules m_p and $m - m_p$ (where $m_p \le m$). The second integral gives the rate of formation of macromolecule m arising from the disintegration of larger macromolecules m_r into m and $m_r - m$ (where $m_r \ge m$). The numerical coefficient 2 associated with this integral is a consequence of the assumption that the two ways that this disintegration can take place occur at the same average rate. Together the two integrals give the net rate of formation of m. Apart from some differences in notation, this is the equation used by Ziff and McGrady[2] in their study of polymer degradation. The term $c(m, t)$ in the first integral is independent of the variable of integration m_p and can therefore be taken out of the integral sign. This leads to slight simplification in the subsequent computation.

In arriving at Eq. 1, it is assumed that the binary disintegration of a macromolecule m_r

$$m_r \rightarrow m_p + (m_r - m_p) \qquad (2)$$

is essentially first order with respect to $c(m_r, t)$, i.e.,[1]

$$\frac{dc(m_r)}{dt} = -k(m_r,m_p)c(m_r,t) \qquad (3)$$

$k(m_r, m_p)$ is the first-order rate "constant" for this particular binary disintegration. It is, in general, not a constant but depends on the molecular weight of the entity undergoing binary disintegration and that of the products formed. This is emphasized by writing the first-order rate "constant" as a general function of two independent variables $k(m_r, m_p)$. The first variable in $k(m_r, m_p)$ is the molecular weight of the entity undergoing binary disintegration and the second variable is that of one of the products. To be consistent with Eq. 1, the condition $k(m_r, m_p) = k(m_r, m_r - m_p)$ has to be met. The way k varies with m_r and m_p characterizes the binary disintegration behavior of a macromolecule. For the purpose of computing the evolving $c(m, t)$ it is assumed that, for any combination of m_r and m_p in the range $\{m_{\min}, m_{\max}\}$, the numerical value of $k(m_r, m_p)$ is known. These values are either measured experimentally or obtained via some theoretical considerations. The inverse problem of deducing $k(m_r, m_p)$ from observed $c(m, t)$ data is also of great practical interest. However, both mathematically and computationally this is an entirely different problem requiring a completely different solution procedure.[3] This problem will not be considered in this investigation.

In all the computation reported in this article, Eq. 1 is first made dimensionless by defining the following dimensionless quantities: kinetic parameter K, molecular weight M, and concentration distribution C,

$$K(M_r,M_p) = \frac{k(m_r,m_p)}{k_{\max}}, \quad M = \frac{m - m_{\min}}{m_{\max} - m_{\min}}, \quad C = \frac{c}{c_{\max}} \qquad (4)$$

In these expressions, $k_{\max}$ is the maximum value of the function $k(m_r, m_p)$ for m_r in the range $m_{\min} \le m_r \le m_{\max}$. $c_{\max}$ is the maximum value of the initial concentration distribution, i.e., $c_{\max} = \mathrm{Max}(c(m,0))$. In terms of these dimensionless quantities, Eq. 1 takes the form

$$\frac{\partial C(M,\tau)}{\partial \tau} = -\left[\int_{M_p=0}^{M} K(M,M_p)dM_p\right]C(M,\tau) + 2\int_{M_r=M}^{1} K(M_r,M)C(M_r,\tau)dM_r \qquad (5)$$

In this equation τ is the dimensionless time defined as $\tau = k_{\max}(m_{\max} - m_{\min})t$. The dimensionless molecular weight varies within the range $0 \leq M \leq 1$ and this greatly simplifies the numerical solution of Eq. 5 and the presentation of results.

Solution by the Method of Lines

The unknown $C(M, \tau)$ appears as a first order partial derivative on the left-hand side (LHS) of Eq. 5 and also within the integral in the second term on the RHS. This makes Eq. 5 an integro-differential equation for $C(M, \tau)$. There does not appear to be a general procedure for dealing with this type of equations. Only a small number of analytical solutions for $C(M, \tau)$, for selected and relatively simple $K(M_r, M_p)$, have been reported in the literature.[2,4–7] There is also a dearth of numerical solution technique for $C(M, \tau)$ for arbitrary but physically realistic disintegration kinetics and initial molecular weight distribution.[8] A possible cause for this is that integro-differential equations have not been investigated as extensively as differential equations and integral equations of various kinds.[9] In this investigation, the Method of Lines (MoL) will be applied to solve Eq. 5 for $C(M, \tau)$. This is an adaptation of the MoL that is regularly used to solve parabolic partial differential equations numerically The performance of MoL in handling integro-differential equations is not discussed in standard reference books on MoL.[10]

To apply MoL, the independent variable M is discretized into N_k points, $M_1 = 0, M_2, M_3, \ldots, M_i, \ldots, M_{N_k} = 1$. Typically N_k is set between 201 and 801 points. Following from this, the unknown $C(M, \tau)$ at these discretization points is represented by a finite collection of unknown functions, of a single independent variable τ, defined by $C_i(\tau) \equiv C(M_i, \tau)$, for $i = 1$ to N_k. Upon substitution into Eq. 5, the integro-differential equation becomes a set of simultaneous first-order ordinary differential equations (ODEs) for the $C_i(\tau)$. These ODEs take the general form

$$\frac{dC_i}{d\tau} = -\left\{\sum_{j=1}^{i} \alpha_{ij} K_{ij}\right\} C_i \Delta M + 2\left\{\sum_{q=i}^{N_k} \beta_{iq} K_{qi} C_q\right\} \Delta M \quad \text{for} \quad i = 1 \text{ to } N_k \qquad (6)$$

In these equations, $K_{ij} \equiv K(M_i, M_j)$ and $K_{qi} \equiv K(M_q, M_i)$ are the discretized first-order kinetic parameters. The two integrals in Eq. 5, approximated by numerical quadrature, now appear as the two finite sums on the RHS of Eq. 6. ΔM is the discretization step size. α_{ij} and β_{iq} are known numerical coefficients that depend on the method of quadrature used. For example, if the trapezoidal rule is used to approximate the integrals then α_{ij} and β_{iq} are 1/2 for the upper and lower limits of the integrals and 1 for all the interior discretization points. If the Simpson's rule is used, they become 1/3 for the two limits, 2/3 for the odd interior points, and 4/3 for the even interior points.[9]

Equation 6 is a set of linear simultaneous first-order ODEs. The number of equations may be large, of the order of several hundreds, but they can be integrated numerically with relative ease using any of the many standard numerical routines, such as fourth-order Runge-Kutta, for handling ODEs. Such numerical routines can be found in most scientific computing software and they normally come with numerical error estimation and automatic adjustment of integration step size (in τ). All these make the integration of these ODEs a particularly simple task. In the results reported below integration of the ODEs was performed using the ODE solver in the commercial software Mathematica. No numerical or computation complications were encountered.

Results

Typical $C(M, \tau)$, for different assumed kinetics $K(M_r, M_p)$ and initial concentration distribution $C(M, 0)$, obtained by the application of MoL to Eq. 5 are reported later. As mentioned earlier, some of these will be verified against published results. Besides showing the reliability of these numerical results, the other key objective is to demonstrate the versatility and the ease with which this procedure can be applied to these and other more general kinetics. Apart from the remarks in passing regarding the physical meaning of the four cases of $K(M_r, M_p)$ considered later, discussion of the practical significance of the resulting $C(M, \tau)$, in the absence of experimental data, will be kept to a minimum.

Constant disintegration kinetics with uniform initial distribution

This example deals with the simplest first-order disintegration kinetics, i.e., $K(M_r, M_p) = 1$. This corresponds to a disintegration rate that is independent of the size of the macromolecule undergoing cleaving and of that of the binary products. To further simplify the computation, the macromolecules will be assumed to be uniformly dispersed initially, i.e., $C(M, 0) = 1$.

Typical results of the MoL computation are plotted as continuous curves in Figure 1. They show the variation of $C(M, \tau)$ with τ for $M = (0, 0.2, 0.4, 0.6, 0.8, 1.0)$. These curves show that larger macromolecules, M greater than about 0.6, decrease monotonically while the smaller ones increase initially reach a peak and then decrease. The smallest molecule, of course, increases monotonically. This simple case has been investigated by Kehlen et al.[5] and they reported an exact solution of the form

$$C(M, \tau) = \left[1 + 2(1 - M)\tau + \frac{(1 - M)^2 \tau^2}{2}\right] e^{-M\tau} \qquad (7)$$

For comparison, their results are shown as discrete points in Figure 1. There is essentially no difference between the MoL results and their exact analytical results. For this kinetics the concentration changes relatively slowly with M and also with τ. It was found that the MoL results, even with N_k as low as 51, are already indistinguishable from the exact analytical solution. The results shown in Figure 1 are for $N_k = 301$.

Kinetics proportional to reactant size

Another disintegration kinetics that is regularly reported in the literature is $K(M_r, M_p) = M_r$. This corresponds to the simple but physically plausible assumption that the larger macromolecules will disintegrate faster than the smaller

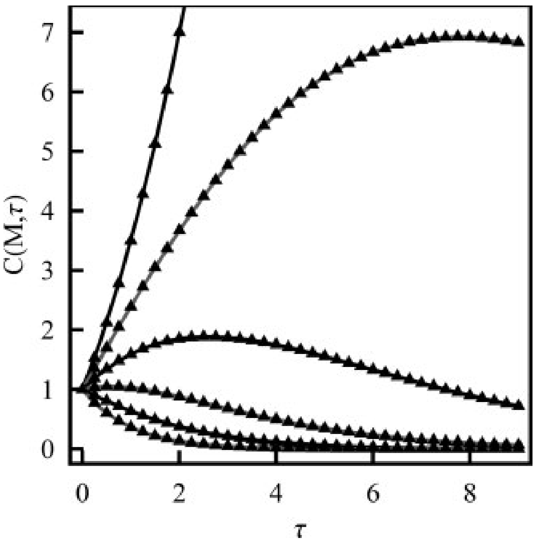

Figure 1. Variation of concentration with time for uniform kinetics and uniform initial dispersion.

The curves are from MoL computation and the discrete points are exact solution.[5] $M = 0$ (uppermost), 0.2, 0.4, 0.6, 0.8, 1.0 (lowest).

ones. As K is independent of the size of the products M_p and $M_r - M_p$, this kinetics implies that a macromolecule is equally likely to disintegrate at any location within its structure, i.e., the case of random scission. This may be a realistic assumption for linear macromolecules with uniform structure along its entire length.

To demonstrate the flexibility of MoL in coping with Eq. 5 with arbitrary but physically realistic initial concentration distribution, it will be applied to this kinetics for a collection of macromolecules that are nonuniformly dispersed. The initial $C(M, 0)$ considered here is shown in Figure 2a. It is in the form of a beta function given by $C(M, 0) = 962{,}219.8157(1 - M)^6 M^{19}$. The numerical coefficient is a consequence of normalization. The functional form of this distribution is irrelevant to the MoL procedure as it only requires the values of $C_i(\tau = 0)$ at the discretization points of M. This initial distribution will be used in all the subsequent MoL computation.

The $C(M, \tau)$ curves generated by MoL for this case are shown as continuous curves in Figure 2b. Instead of plotting the $C_i(\tau)$ curves for selected i, the values of $C_i(\tau)$ for $i = 1$ to N_k at a selected τ are computed and the points are then joined up to yield a complete $C(M, \tau)$ curve for the selected τ. For N_k sufficiently large, greater than 201 or thereabout, the resulting $C(M, \tau)$ appears as smooth curves. The curves in Figure 2b are for $\tau = (0, 1, 2, 5, 8)$ with $N_k = 301$. They show clearly that the peak exhibited by $C(M, \tau)$ moves toward lower M as τ increases, and as expected, the larger macromolecules are disappearing at a significantly higher rate than the smaller ones. For the range of τ covered in Figure 2b, macromolecules smaller than ~0.6 increase monotonically. The concentrations of these smaller fragments have greatly increased even for the relatively small τ covered in Figure 2b.

As in the previous example, the results of MoL computation are checked against the following exact solution:

$$C(M,\tau) = [C(M,0) + 2\tau \int_{M_p=M}^{1} M_p C(M_p,0) dM_p] e^{-M^2\tau} \quad (8)$$

This is based on the solution reported by Ziff and McGrady.[4] The integral on the RHS can be evaluated explicitly for the initial distribution in Figure 2a. However, the resulting expression for $C(M, \tau)$ is too lengthy to print out in full and does not shed much light on the general trend of how the concentration distribution change with M and with τ. Instead this expression is stored in computer memory to be retrieved and evaluated numerically when required. The $C(M, \tau)$ given

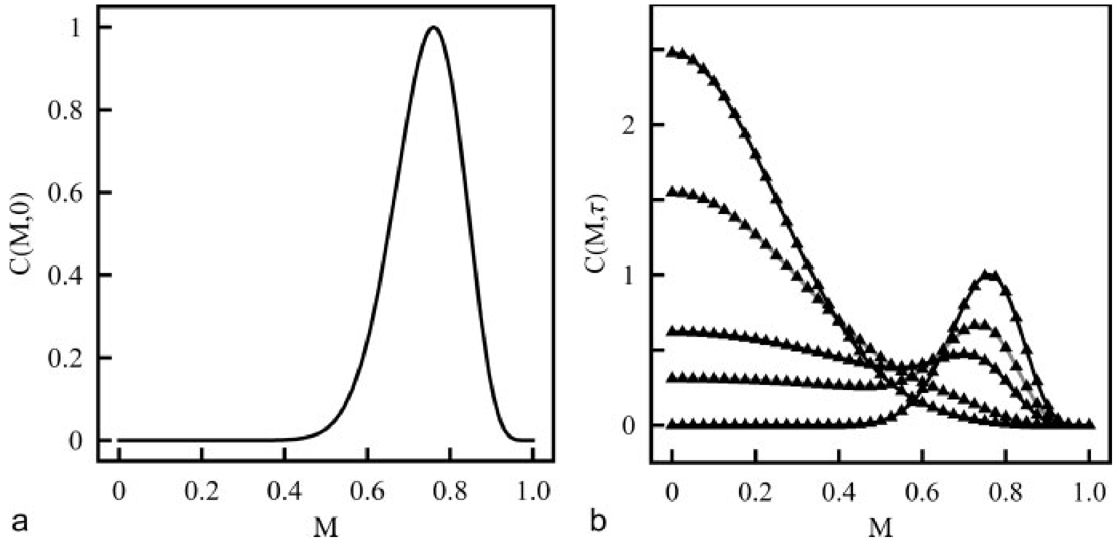

Figure 2. (a) Arbitrary initial concentration distribution used in MoL computation. (b) Concentration distribution curves for kinetics proportional to reactant size.

The curves are from MoL computation and the discrete points are the exact solution.[4] $\tau = 0$ (lowest at $M = 0$), 1, 2, 5, 8 (uppermost).

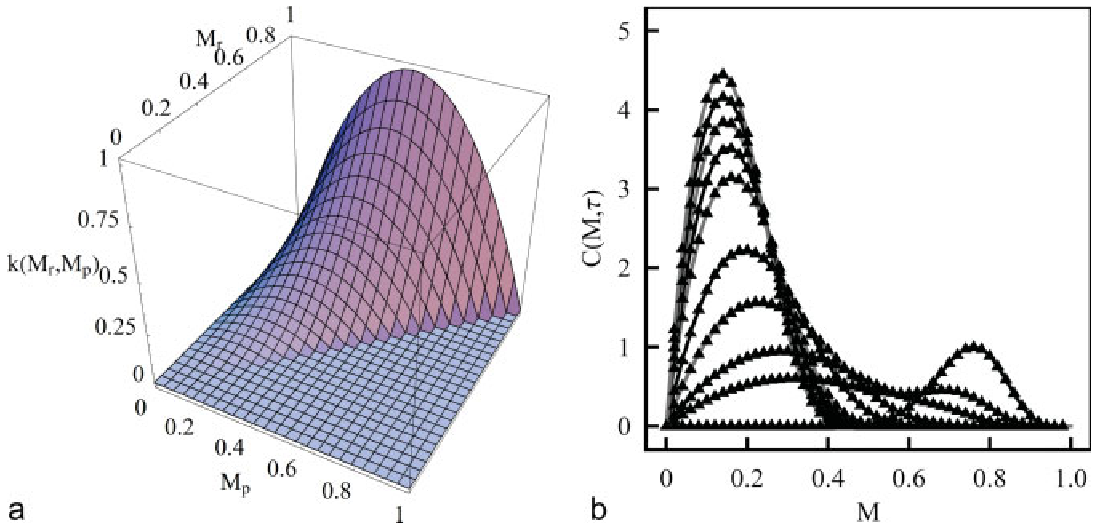

Figure 3. (a) Variation of kinetic parameter with molecular weights. Rate of disintegration is proportional to M_r (reactant) and to M_p and $M_r - M_p$ (products). (b) Concentration distribution curves for the kinetics shown in Figure 3a.

The curves are from MoL computation and the discrete points are the exact solution.[7] $M^* = 0, 5, 10, 25, 50, 100, 125, 150, 175, 200$. The maximum in concentration moves from right (at $M \approx 0.8$) to left ($M \approx 0.15$) as τ increases. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

by this exact expression are shown as discrete points in Figure 2b. Again these are indistinguishable from the MoL results.

Kinetics proportional to reactant and product molecular weights

It is frequently theorized that not only are larger macromolecules more likely to disintegrate than smaller ones and that when they disintegrate they are more likely to break closer to the midpoint of the macromolecule than near to the two ends. For example, experimental data of mechanically and ultrasonically induced disintegrations appear to conform to this kinetics.[11,12] This general kinetic behavior can be captured by a relatively simple kinetic function of the form

$$K(M_r, M_p) = 4M_rM_p(M_r - M_p) \tag{9}$$

According to this dimensionless expression, the rate of disintegration is directly proportional to the size of the reactant M_r and also to that of the binary products M_p and $M_r - M_p$. A plot of this kinetic function is shown in 3D in Figure 3a. The numerical factor of 4 that appears in Eq. 9 arises from the way it have been made dimensionless so that its maximum value is unity. It is clear from this expression that, for any M_r, the disintegration rate is at a maximum at the midpoint of the macromolecule and decreases to zero toward the two ends. Thus not only are the products of disintegration more likely to be made up of two mid-sized fragments than a relatively large fragment accompanied by a very small one, but also the rate of formation of small fragments approaches zero as the size gets smaller.

The MoL results for the disintegration according to Eq. 9 are shown in Figure 3b. These are presented in the same format as that in Figure 2b and are for the same initial distribution as in Figure 2a. There are very significant differences between the $C(M, \tau)$ in Figure 2b and that in Figure 3b. For the present kinetics, the $C(M, \tau)$ for small M do not increase as rapidly as those in Figure 2b. This can be seen in Figure 3b that, for small M, the values of $C(M, \tau)$ remain moderate even for τ that are an order of magnitude larger than those covered in Figure 2b. In fact, according to the MoL results, the concentration of the smallest disintegration product, $M = 0$, does not increase at all with time and remains at zero. While all these observations are consistent with the disintegration kinetics described by Eq. 9, the extent to which they reflect the behavior of real macromolecular systems can be checked by solving the inverse problem of disintegration kinetics. In this problem the starting point is a set of experimentally measured $C(M, \tau)$ data at a sequence of increasing τ. The problem is then one of deducing from these data the form of $k(m_r, m_p)$ and the constants associated with it. This is mathematically a very different problem and is not considered in this investigation.

Browarzik and Kehlen[7] reported an exact solution of $C(M, \tau)$ for this particular kinetics for a monodisperse initial distribution. Through linear superposition this solution can be used to generate the analytical expression for $C(M, \tau)$ for the initial distribution shown in Figure 2a (see also Ref. 6). As in the previous examples, these exact analytical results are shown in Figure 3b as discrete points and there is no noticeable difference between them and the MoL curves. It should be pointed out that the expression for the exact $C(M, \tau)$ is far too complicated and lengthy to be handled manually or printed out. The use of scientific computing software with symbolic manipulation capability becomes absolutely essential to generate and evaluate this exact expression. In fact the computing requirements to handle and evaluate this expression for the initial distribution in Figure 2a are not much less than that for generating the numerical solution using MoL.

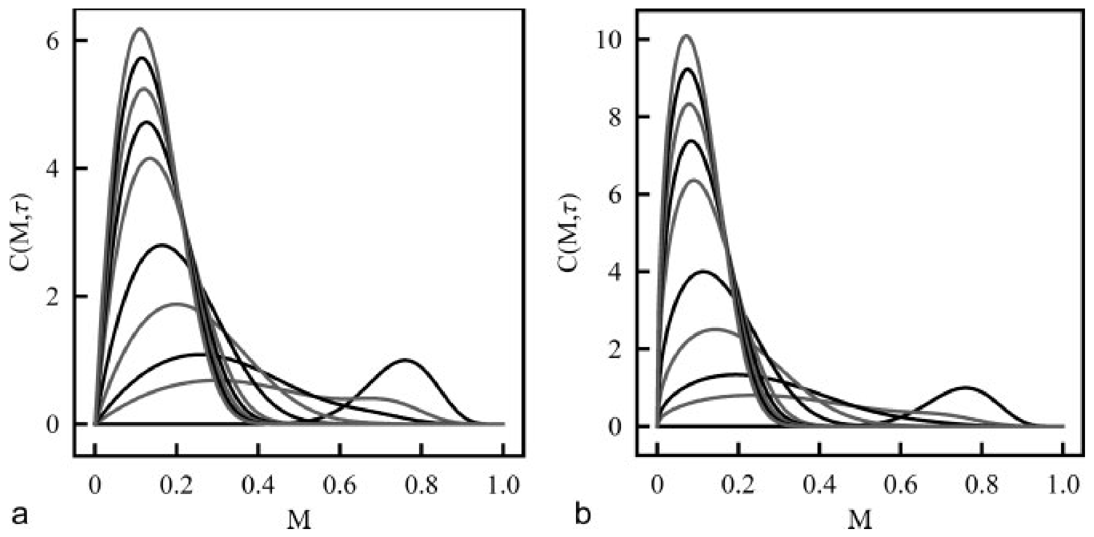

Figure 4. Concentration distribution curves for power-law kinetics. (a) (α, β) = (0.5, 1.0); (b) (α, β) = (1.0, 0.5). From right to left: τ = 0, 5, 10, 25, 50, 100, 125, 150, 175, 200.

Power-law kinetics

The following disintegration kinetics is a direct generalization of that in Eq. 9:

$$K(M_r, M_p) = 4(M_r)^{\alpha}(M_p)^{\beta}(M_r - M_p)^{\beta} \qquad (10)$$

where α and β can be regarded as empirical power-law indices. Kinetic expression of this general form has been explored by various investigators.[13] To be consistent with the assumptions implicit in Eq. 1, the power-law indices associated with the two products have to take on the same numerical value. By varying these indices the nature of the disintegration kinetics can be altered. Setting $\alpha < 1$, for example, means that the size of the macromolecules undergoing cleaving becomes more important in determining the rate of disintegration. On the other hand setting $\beta < 1$ increases the influence of the binary products on the disintegration rate. $K(M_r, M_p)$ can become unbounded for negative α or β and will require special treatment in the MoL solution process. In the absence of physical justification of negative indices, MoL computation for such indices has not been attempted.

Typical outcomes of the MoL computation for the power-law kinetics are shown in Figures 4a, b. These are for the combinations $(\alpha, \beta) = (0.5, 1)$ and $(1, 0.5)$, respectively. The general shape and trend of the $C(M, \tau)$ curves for these two combinations of indices, as well as those for others, appear similar but their disintegration rates are quite different. A search of the literature has failed to locate analytical solutions for these or other arbitrary combinations of the indices. The reliability of these numerical results can, however, be checked by examining the plots of the first moment of $C(M, \tau)$ i.e., $M \times C(M, \tau)$ vs. M for different τ. These are shown in Figures 5a, b, again for the combinations $(\alpha, \beta) = (0.5, 1)$

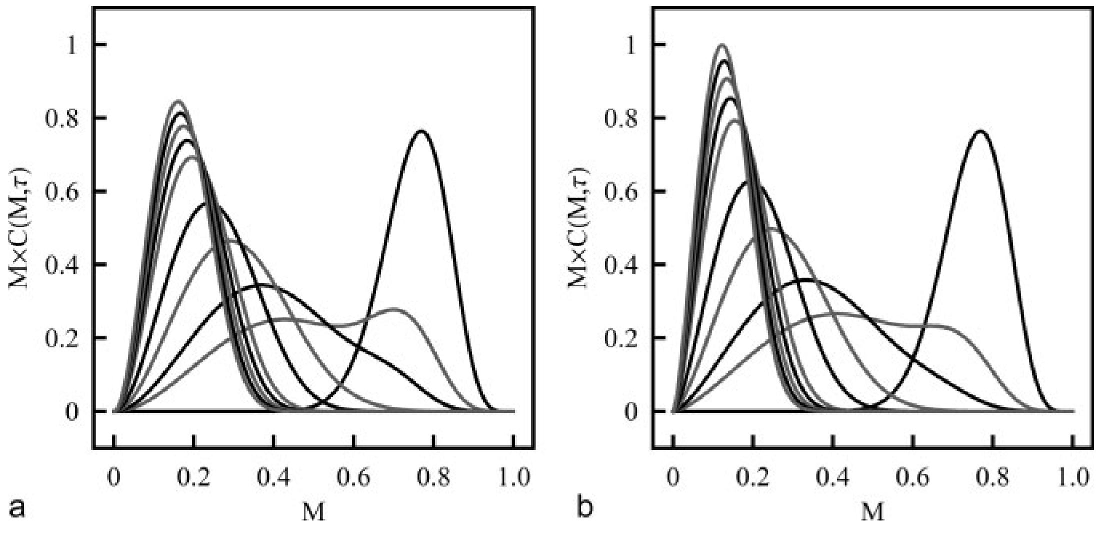

Figure 5. First moment of concentration for power-law kinetics. (a) (α, β) = (0.5, 1.0); (b) (α, β) = (1.0, 0.5). From right to left: τ = 0, 5, 10, 25, 50, 100, 125, 150, 175, 200.

and (1, 0.5), respectively. The area under each of these curves represents the total mass of the macromolecules undergoing disintegration and should therefore remain constant for all τ. With $N_k = 601$, this is indeed so for all the curves in Figures 5a, b and serves as a partial check of the reliability of the MoL results. In general, if $C(M, \tau)$ is required for large τ, when the distribution curves have shifted significantly toward the left of the M axis and the $C(M, \tau)$ curve has become narrowly dispersed then a larger N_k will be required. This is to keep the errors incurred by the approximation of the two integrals in Eq. 5 by numerical quadrature under control. Ensuring that the area under the first moment curves remains constant has in fact been used to check and guide the selection of N_k in all the MoL results reported earlier.

Discussion

The evolution of the CDC $C(M, \tau)$ of macromolecule disintegration is described by an integro-differential equation. This equation does not have a general solution and the small number of the solutions reported in the literature, both analytical and numerical, are for special cases of simple disintegration kinetics. It is also restricted to simple, such as uniformly dispersed or monodisperse, initial concentration distribution. It is true that the governing integro-differential equation is linear in $C(M, \tau)$ and so the principle of linear superposition can be applied to cope with arbitrary initial molecular weight distribution. However, the resulting analytical solution obtained by superposition can be quite unmanageable. Examination of the solution procedures of the integro-differential equation for $C(M, \tau)$ reported in the literature confirms that most of these procedures assume a level of training in mathematics and numerical analysis that does not match up with that of most of their would-be users. There is clearly a need for an easy to apply general solution technique that can cope with most physically realistic disintegration kinetics and initial conditions.

Adaptation of the MoL to convert the integro-differential equation into a set of first-order ODEs, admittedly a large set, is just such a general method. When MoL is combined with the numerical routines for handling simultaneous ODEs implemented on commercial scientific computing software it becomes particularly simple to implement and to apply. This simplicity as well as its reliability has been demonstrated by the selected examples. In this investigation it was found that a typical set of 301–601 simultaneous ODE of the form given Eq. 6 can be solved using Mathematica in no more than 3–5 min on a 1 GHz PC. While this computation time is far from excessive and can be speeded up if so desired, the greatest attraction of MoL is the ease with which this scheme can be implemented and run routinely requiring only knowledge of numerical methods covered in most science and engineering courses.

The four cases investigated here are just some of the most widely discussed disintegration kinetics. There are a few other popular kinetics proposed in the literature.[5,14,15] Some of which have been solved analytically and for others only limited solutions, such as for some specific initial concentration distributions, or approximate solutions are available.[2,14–18] Because the MoL technique is independent of the functional form of the kinetics it is equally applicable for all these kinetics models. More importantly, it is likely that experimentally determined disintegration kinetics is only known numerically with no known or convenient functional form. For such cases analytical solution is clearly not feasible. The MoL technique which does not require the kinetics to be described explicitly in functional form should remain applicable for such a situation, provided the kinetics data can be interpolated numerically. The same can be said regarding the initial concentration distribution. The MoL remains applicable if the measured initial concentration distribution cannot be represented in functional form.

Implicit in the derivation of Eq. 1 is the assumption that the binary disintegration of macromolecules is first order in terms of the concentration of the cleaving entity. It is also assumed that the disintegration is essentially irreversible, i.e., smaller macromolecules do not recombine to form larger ones. Relaxation of these assumptions will require the integro-differential equation (Eq. 1) to be modified, for example, by the inclusion of another integral to describe the recombination kinetics. As this integral is likely to involve the product of the concentrations of the two recombining entities, this makes the integro-differential equation nonlinear.[19] Analytical solution to such an equation is even more difficult to come by. In contrast, the MoL procedure described in this article remains applicable. It can still be applied to convert the nonlinear integro-differential equation into a set of ODEs. The only difference is that these ODEs will now be nonlinear. Furthermore these ODEs can still be, in principle at least, integrated by Runge-Kutta or other ODE solvers. The main issue will then center on whether nonlinearity is likely to introduce numerical problems for the ODE solver and how these can be overcome. These issues can best be investigated when specific and realistic nonlinear kinetics of recombination can be found. This problem has not been attempted.

For all the results reported above, the integrals in Eq. 5 were approximated using the trapezoidal rule. This was done with the sole aim of keeping the computer code simple. The limited numerical experimentation in which the Simpson's Rule was used did not show up any significant improvement in accuracy or saving in computing time. Investigations of alternative ways of approximating these integrals, such as collocation or finite element methods, are currently in progress. The closely related issue of numerical error propagation in the MoL discretization step is also under investigation. Interested readers should consult Brunner[20] concerning these and many other issues associated with the numerical solution of integro-differential equation in general.

Conclusion

The MoL coupled with a standard ODE solver implemented in most scientific computing software provides an efficient mean of obtaining the evolving molecular weight distribution curves of macromolecule disintegration. The method is simple to apply, is applicable to arbitrary initial dispersion of macromolecules, and is not restricted to simple binary disintegration kinetics. The numerical nature of this approach also means that it has the potential of being extended to cope with the nonlinearity associated with reversible disintegration.

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