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Kinetic Monte-Carlo simulation of network formation

I. Simulation method

Ján Šomvársky and Karel Dušek

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
162 06 Prague 6, Czech Republic

Summary

A Monte-Carlo simulation procedure of kinetically controlled structure growth including network formation determined by generalized Smoluchowski equations was described. In addition to intermolecular reactions affected by possible time and space long-range correlations, cyclization or degradation reactions can be considered. The kernel of these reactions can be a function of not only the numbers and types of the reactive groups but also of the composition and structure of the molecule. The random number generator selects a certain reaction event characterized by its rate out of all possible events at four decision levels, (1) reaction mechanism, (2) types of reacting groups, (3) selection of molecule and (4) its reaction partner.

Introduction

There exist three groups of theoretical methods of simulation of polymer network formation:

(1) Generation of structures from monomeric units or other structural fragments (Flory–Stockmayer theory, theory of branching processes (cascade theory), recursive theory, etc.);

(2) Evolution of structures viewed as a kinetic process and described by kinetic differential equations;

(3) Simulation of structure growth in d-dimensional space (lattice or off-lattice percolation).

As discussed elsewhere [1], the increase in connectivity of chemical structures (network formation) is primarily determined by bond formation between reactive sites in structure elements (units, molecules) but it can also be affected by long-range connectivity (time) correlations and spatial correlations. The long-range correlations are not inherent to group (1) theories because, by splitting the bonds existing between smaller fragments in molecules and recombining these fragments randomly, the information on long-range correlations (memory) is lost. The advantage of these approaches can be found in their simplicity and ability to describe various structural details. They may fail partly for complex reaction mechanisms (with initiation) and fully for strong spatial correlations – cyclization, excluded volume effects and specific diffusion control.

The simulation of network formation in space can in principle take into account both types of long-range correlations but at present it still suffers from the relatively unrealistic ways of doing so. The difficulty of introduction of a realistic mobilities (affected by bond formation), which drive the proper functional groups together close enough to make a bond, represents the main problem. The critical region has been the main domain of application of percolation techniques to polymer networks; it has been found that the critical exponents do depend on the dimensionality of space but not on the lattice type or details of the branching process [2, 3]. For modelling the structure growth throughout a wide conversion range, these "details" matter very much.

The kinetic generation occupies an intermediate position in that the long-range time (connectivity) correlations can be dealt with rigorously. In the classical kinetic theory, the rate constant of bimolecular combination of two molecules is proportional to the product of the numbers of groups in each molecule. However, one can go much farther and, by modifying the mass action law, get a reasonable approximation for the effects of spatial correlations as will be shown in more detail below. This modification is possible because one can make the respective rate constants dependent not only on the numbers and reactivities of the reacting functional groups, but also on other structural features of the reacting molecules like size, composition, symmetry, number of cycles, etc., i.e. the parameters that affect the reaction ability (apparent reactivity) of a given group. In such a way, one can simulate the excluded volume or limited diffusion effects in dependence on the structure evolution. Generalized kinetic equations describing structure evolution are called Smoluchowski coagulation equations and the generalized rate constant is called *kernel* of these equations.

Although conceptually the kinetic or coagulation differential equations belong to the mean-field category (average concentrations of molecules and thus groups they bear are considered), the non-mean-field effects are considered by modifying the reactivity of a group making it dependent on the structure of its carrier, e.g. its diffusivity. The effects of simple structure variations of the kernel were already investigated by several authors (cf. e.g. refs. 4–6). Delays in formation of an infinite cluster were observed or the formation of an infinite cluster was prevented. Important was also the fact that the non-classical kernels gave non-classical (non-mean-field) critical exponents the values of which, in some cases, were not far from the values of the percolation exponents.

The generalized kinetic theory thus seems to be suitable for description of non-ideal cases of network build-up. The relation between the forms of the kernels and the structure evolution will be investigated later. The purpose of this paper is to explain methods for solution of the generalized kinetic equations because it is known that the infinite systems of general kinetic differential equations can be solved neither analytically nor numerically. In this paper, we describe a Monte-Carlo method for simulation of structure evolution determined by differential equations of the Smoluchowski type. The simulation is performed in a system composed of a finite number of monomeric units. The simulation idea is based on the method used previously for a specific system and smaller number, by several orders of magnitude, of units [7]. In this communication, the methods of location of the critical point and determination of a few pregel and postgel parameters will be analyzed. For comparison, the exact results for the random trifunctional polycondensation will be used in Part II.

Kinetic (coagulation) equations

In the kinetic or coagulation theories, the structure evolution is described by sets of differential equations for temporal changes of concentrations of each distinguishable species. The criterion of distinctness depends on our choice and may go down to a full topological information on this species described by its adjacency matrix. For simplicity, in what follows, we will restrict ourselves to number of functional groups (vector $\mathbf{l}$) and building units (vector $\mathbf{x}$) and possibly bonds (vector $\mathbf{m}$) of distinguishable types.

In the course of a crosslinking reaction, the molecule $A(\mathbf{x},\mathbf{l})$ can be transformed into another species by a number of chemical reactions. The most typical are listed bellow:

Intermolecular combination (subscript I)

$$A(\mathbf{x},\mathbf{l}) + A(\mathbf{x}',\mathbf{l}') \xrightarrow{K_{\mathrm{I}}(l_j,l'_k;\mathbf{x},\mathbf{x}',\ldots)} A(\mathbf{x}+\mathbf{x}',\mathbf{l}+\mathbf{l}'-\mathbf{1}_j-\mathbf{1}_k) \tag{1}$$

where $\mathbf{1}_j$ and $\mathbf{1}_k$ are vectors the elements of which are zeros except for the j-th and k-th, respectively, which are unities.

Intramolecular (cyclization) reaction (C)

$$A(\mathbf{x},\mathbf{l}) \xrightarrow{K_{\mathrm{C}}(l_j,l_k;\mathbf{x},\ldots)} A(\mathbf{x},\mathbf{l}-\mathbf{1}_j-\mathbf{1}_k) \tag{2}$$

Degradation reaction (D) by splitting the r-th type bond

$$A(\mathbf{m};\mathbf{x},\mathbf{l}) \xrightarrow{K_{\mathrm{D}}(m_r;\mathbf{x},\mathbf{l},\ldots)} A(\mathbf{m}-\mathbf{m}'-\mathbf{1}_r;\mathbf{x}-\mathbf{x}',\mathbf{l}-\mathbf{l}') + A(\mathbf{m}';\mathbf{x}',\mathbf{l}') \tag{3}$$

The degradation reactions will not be considered hereinafter. However, depending on the reaction mechanism other formulations of the reaction balance are possible.

The quantities K_{I}, K_{C} and K_{D} are kernels (effective rate constants) which depend not only on the numbers and reactivities of the functional groups (bonds) but possibly also on the internal structure of the molecule.

Each of the transformation equations given above corresponds to a set of differential equations depending on the type of pairs of groups or bonds that react. The type of a group is determined not only by its chemical nature but also by its reactivity.

Thus, the rates of *transformation* (T) of the molecules $A(\mathbf{x},\mathbf{l})$ by reactions with all other molecules through the j-th and k-th groups, $v_{\mathrm{IT},jk}(\mathbf{x},\mathbf{l})$, is equal to

$$v_{\mathrm{IT},jk}(\mathbf{x},\mathbf{l}) \equiv c(\mathbf{x},\mathbf{l}) \sum_{\mathbf{l}',\mathbf{x}'} K_{\mathrm{I}}(l_j,l'_k;\mathbf{x},\mathbf{x}',\ldots)\, c(\mathbf{x}',\mathbf{l}') \tag{4}$$

where $c(\mathbf{x},\mathbf{l})$ is the concentration of the molecules $A(\mathbf{x},\mathbf{l})$. The right-hand side of this equation represents a sum of terms; each of them is decisive for selection of a pair of molecules for reaction (cf. the section on simulation).

The total rate of transformation of $A(\mathbf{x},\mathbf{l})$ molecules by all possible intermolecular reactions, $v_{\mathrm{IT}}(\mathbf{x},\mathbf{l})$, is given by

$$v_{\mathrm{IT}}(\mathbf{x},\mathbf{l}) = \sum_{j,k} v_{\mathrm{IT},jk}(\mathbf{x},\mathbf{l}) = \tag{5}$$

$$= c(\mathbf{x},\mathbf{l}) \sum_{j,k,\mathbf{l}',\mathbf{x}'} K_{\mathrm{I}}(l_j,l'_k;\mathbf{x},\mathbf{x}',\ldots)\, c(\mathbf{x}',\mathbf{l}') \tag{6}$$

Analogously,

$$\begin{aligned} v_{\mathrm{CT},jk}(\mathbf{x},\mathbf{l}) &= K_{\mathrm{C}}(l_j, l_k; \mathbf{x}, \ldots)\, c(\mathbf{x},\mathbf{l}) && (7)\\ v_{\mathrm{DT},r}(\mathbf{x},\mathbf{l}) &= K_{\mathrm{D}}(m_r; \mathbf{x}, \mathbf{l}, \ldots)\, c(\mathbf{m}; \mathbf{x},\mathbf{l}) && (8) \end{aligned}$$

From the balance eqs. (1)–(3), one can write for the time change of concentrations of the molecules $A(\mathbf{x},\mathbf{l})$:

For intermolecular combination

$$\begin{aligned} \frac{dc(\mathbf{x},\mathbf{l})}{dt} \equiv v_{\mathrm{I}}(\mathbf{x},\mathbf{l}) &= \frac{1}{2} \sum_{j,k,\mathbf{l}',\mathbf{x}'} K_{\mathrm{I}}(l_j - l'_j + 1, l'_k + 1; \mathbf{x} - \mathbf{x}', \ldots) \times \\ &\quad \times\ c(\mathbf{x} - \mathbf{x}', \mathbf{l} - \mathbf{l}' + \mathbf{1}_j)\, c(\mathbf{x}', \mathbf{l}' + \mathbf{1}_k) \\ &\quad - c(\mathbf{x},\mathbf{l}) \sum_{j,k,\mathbf{l}',\mathbf{x}'} K_{\mathrm{I}}(l_j, l'_k; \mathbf{x}, \mathbf{x}', \ldots)\, c(\mathbf{x}', \mathbf{l}') && (9) \end{aligned}$$

The first term on the right-hand side of eq. (9) means the rate of formation of the reaction product — the molecule $A(\mathbf{x},\mathbf{l})$ from two other (smaller) molecules. The rate of transformation of this molecule (i.e., the reaction in which the $A(\mathbf{x},\mathbf{l})$ molecule is active), $v_{\mathrm{IT}}(\mathbf{x},\mathbf{l})$, is characterized by the second term.

For the intramolecular reaction

$$\begin{aligned} \frac{dc(\mathbf{x},\mathbf{l})}{dt} \equiv v_{\mathrm{C}}(\mathbf{x},\mathbf{l}) &= -\sum_{j,k} K_{\mathrm{C}}(l_j, l_k; \mathbf{x}, \ldots)\, c(\mathbf{x},\mathbf{l}) \\ &\quad + \sum_{j,k} K_{\mathrm{C}}(l_j + 1, l_k + 1)\, c(\mathbf{x}, \mathbf{l} + \mathbf{1}_j + \mathbf{1}_k) && (10) \end{aligned}$$

The degradation equation giving $v_{\mathrm{D}}(\mathbf{x},\mathbf{l})$ can be formulated per analogiam.

The total change of $c(\mathbf{x},\mathbf{l})$ with time is given by the sum

$$dc(\mathbf{x},\mathbf{l})/dt = v_{\mathrm{I}}(\mathbf{x},\mathbf{l}) + v_{\mathrm{C}}(\mathbf{x},\mathbf{l}) + v_{\mathrm{D}}(\mathbf{x},\mathbf{l}) \tag{11}$$

The structure of the kernels K_{I}

$$K_{\mathrm{I}}(l_j, l'_k; \mathbf{x}, \mathbf{x}', \ldots) \tag{12}$$

adopted here is as follows: The rate depends primarily on the numbers of reacting groups in each reacting molecule, l_j and l'_k. Therefore, these more important quantities are placed to the left of the semicolon. On the right-hand side of the semicolon there are placed structural characteristics affecting the apparent reactivity of the j and k groups. Their reactivity can be modified by the size and composition of the molecules, $\mathbf{x}$, and other structural features, $(\ldots)$. Such formulation means that the apparent reactivity of a group in one molecule is dependent not only on its own reactivity and structure of its parent molecule but also on the structure of the reacting partner. This general dependence can be handled by the Monte-Carlo simulation. However, such complex dependence is usually not the case and one can factor out the effect of the internal structure of each reacting molecule in the following way:

$$K_{\mathrm{I}}(l_j, l'_k; \mathrm{x}, \mathrm{x}', \ldots) = k_{jk} F(K_{\mathrm{Im}}(l_j; \mathrm{x}, \ldots), K_{\mathrm{Im}}(l'_k; \mathrm{x}', \ldots)) \tag{13}$$

where the subscript m refers to molecule. F is a simple function of the molecular kernels, for instance a product $K_{\mathrm{Im}} \times K_{\mathrm{Im}}$, or a sum $K_{\mathrm{Im}} + K_{\mathrm{Im}}$, or combination of both. The form of K_{Im} can be of the exponent type

$$K_{\mathrm{Im}}(l_j; \mathrm{x}, \ldots) = l_j^a \tag{14}$$

where $a \equiv a(\mathrm{x}, \ldots)$ so that for product kernel

$$K_{\mathrm{I}}(l_j, l'_k; \mathrm{x}, \mathrm{x}', \ldots) = k_{jk}\, k(\mathrm{x}, \ldots)\, k(\mathrm{x}', \ldots) l_j^a l_k'^{a'} \tag{15}$$

or for sum kernel

$$K_{\mathrm{I}}(l_j, l'_k; \mathrm{x}, \mathrm{x}', \ldots) = k_{jk}[k(\mathrm{x}, \ldots)\, l_j^a + k(\mathrm{x}', \ldots)\, l_k'^{a'}] \tag{16}$$

The constant k_{jk} represents a reference intrinsic rate constant for a group j with a group k unaffected by the structure of the molecules they belong to.

Such simplification makes the simulation much less time-consuming since the number of operations necessary for evaluating the overall reaction rate is greatly reduced. According to our experience with simulation of random trifunctional polycondensation, the computing time for the type of kernel given by (13) is proportional to $N^{1.4}$ whereas for the interdependent kernel (eq. (12)) it is proportional to N^{γ}, where $\gamma \geq 2.4$.

Simulation procedure

The basic difference of the simulation procedure from the infinite sets of differential equations characteristic of the kinetic theories is the finiteness of the system. Therefore, no molecule can grow to infinity and no infinite structure exists beyond the gel point. In Monte-Carlo simulations, one does not work with concentrations of molecules $c(\mathbf{x}, \mathbf{l})$ but with numbers of molecules, $N(\mathbf{x}, \mathbf{l})$. The distribution $\{N(\mathbf{x}, \mathbf{l})\}$ at a given extent of reaction depends on the sequence of pseudorandom numbers generated in the given run and fluctuations in the distributions generated in different runs become smaller with increasing system size. The connection between the deterministic macroscopic kinetic process and stochastic mesoscopic simulation process is established by regarding

$$c_{\mathrm{f}}(\mathbf{x}, \mathbf{l}) = \frac{\langle N(\mathbf{x}, \mathbf{l}) \rangle}{V N_{\mathrm{A}}} \tag{17}$$

where V is the reaction volume, N_{A} is the Avogadro number and $\langle N(\mathbf{x}, \mathbf{l}) \rangle$ is expectation value or average of $N(\mathbf{x}, \mathbf{l})$ over ensemble of realizations of the simulation process. The concentrations $c_{\mathrm{f}}(\mathbf{x}, \mathbf{l})$ for the finite system is, however, not identical with $c(\mathbf{x}, \mathbf{l})$ because the former is limited by the maximum possible values $\mathbf{x}_{\mathrm{m}}$, $\mathbf{l}_{\mathrm{m}}$. A general formulation of this problem was offered by Breuer et al. [8].

In simulated (finite) systems, the distinguishable molecules (types) can be numbered and related quantities denoted by subscript $i = 1, \ldots, n_{\mathrm{type}}$, where the number of types n_{type} varies during evolution. Thus, the system is characterized by the numbers of molecules $N_i \equiv N(\mathbf{x}_i, \mathbf{l}_i)$. Evolution of the system is simulated by a sequence of single steps each consisting in choosing one reaction event characterized (1) by the number of participating molecules (one or two), (2) by types of reacting groups (j and k) and (3) by types of reacting molecules (i and possibly i'). The possibility of choosing a reaction is proportional to the rate of the reaction $v_{\mathrm{CT},jk}(i)$ for monomolecular and $v_{\mathrm{IT},jk}(i,i')$ for bimolecular reactions, given by the following equations:

$$v_{\mathrm{CT},jk}(i) = K_{\mathrm{C}}(l_{ij}, l_{ik}; \mathrm{x}_i, \ldots)\frac{N_i}{VN_{\mathrm{A}}} \tag{18}$$

$$v_{\mathrm{IT},jk}(i,i') = \begin{cases} K_{\mathrm{I}}(l_{ij}, l_{i'k}; \mathrm{x}_i, \mathrm{x}_{i'}, \ldots)\,\dfrac{N_i}{VN_{\mathrm{A}}}\,\dfrac{N_{i'}}{VN_{\mathrm{A}}} & \text{for } i \neq i' \quad (19\mathrm{a}) \\[2ex] K_{\mathrm{I}}(l_{ij}, l_{ik}; \mathrm{x}_i, \mathrm{x}_i, \ldots)\,\dfrac{1}{2}\,\dfrac{N_i}{VN_{\mathrm{A}}}\,\dfrac{N_i - 1}{VN_{\mathrm{A}}} & \text{for } i = i' \quad (19\mathrm{b}) \end{cases}$$

The rate of reaction of identical molecules ($i = i'$) given by eq. (19b) is proportional to $\frac{1}{2}N_i\,(N_i - 1)$ and not to $\frac{1}{2}N_i^2$, i.e., reactions of pairs of functional groups belonging to one molecule are excluded. The additional term corresponding to the rate of such "random" cyclization reactions

$$v_{\mathrm{CT(R)},jk}(i) \equiv K_{\mathrm{I}}(l_{ij}, l_{ik}; \mathrm{x}_i, \mathrm{x}_i, \ldots)\,\frac{1}{2}\,\frac{N_i}{VN_{\mathrm{A}}}\,\frac{1}{VN_{\mathrm{A}}} \tag{20}$$

approaches to zero in the limit of an infinite system for finite molecules (sol). For the infinite molecule, the gel, this rate is nonzero what can be demonstrated in the simple case $K_{\mathrm{I}}(l_{ij}, l_{ik}; \mathrm{x}_i, \mathrm{x}_i, \ldots) = k_{jk}l_{ij}l_{ik}$:

$$v_{\mathrm{CT(R)},jk}(i) = k_{jk}\frac{l_{ij}}{VN_{\mathrm{A}}}\,\frac{l_{ik}}{VN_{\mathrm{A}}}\,\frac{N_i}{2} \tag{21}$$

$N_i = 1$ for (one) gel molecule and l_{ij}/VN_{A} is its j-th type functional group concentration (averaged over the whole system)[1]. This corresponds to the Flory–Stockmayer theory, where bonds between functional groups of the gel are always formed and the gel structure is no longer tree-like; the probability of formation of an intramolecular bond in the gel is proportional to the product of concentrations of the groups in the gel. This means that the bond formation within a molecule is still considered as a bimolecular reaction proceeding with a rate proportional to the product of group concentrations.

The cyclization reactions distort the balance between l and x valid for a tree-like structure (which is, e.g. for an f-functional polycondensation, given by $l = x\,(f-2)+2$). The number of bonds in excess over that necessary for a tree, cycle rank ζ, is then given by

$$\zeta = \frac{x\,(f-2)}{2} - \frac{l}{2} + 1 \tag{22}$$

for a single component system, or

$$\zeta = \sum_s \frac{x_s\,(f_s-2)}{2} - \sum_t \frac{l_t}{2} + 1 \tag{23}$$

for a multicomponent one, where x_s is the number of monomeric units of functionality f_s and l_t is the number of unreacted functional groups of type t.

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[1] The factor 1/2 in eqs. (20) and (21) has been introduced because in subsequent summation, eq. (24), the reaction between a given pair of groups is counted twice (as jk and kj).

The technical principle of choosing the reaction event is as follows: First, the total rate v_{tot} is calculated by summing up the respective rates of reaction events

$$v_{\mathrm{tot}} = \sum_{j,k} \sum_{i=1}^{n_{\mathrm{type}}} v_{\mathrm{CT},jk}(i) + \sum_{j,k} \sum_{i=1}^{n_{\mathrm{type}}} \sum_{i'=1}^{n_{\mathrm{type}}} v_{\mathrm{IT},jk}(i,i') \tag{24}$$

A random number η is produced by a generator of pseudorandom numbers which are uniformly distributed over the interval $(0,1)$. Then the summation of increments $v_{\mathrm{CT},jk}(i)$ or $v_{\mathrm{IT},jk}(i,i')$ corresponding to eq. (24) is started in the defined order (Fig. 1) until the partial sum exceeds ηv_{tot}. The contributions to v_{tot} are hierarchically assembled in four levels. The highest level corresponds to the reaction mechanism (either monomolecular or intermolecular, bimolecular in this case), the second level to the types of groups that react (j and k), the third to the type of molecule selected (i) and, possibly, the fourth to its reaction partner (i'). Such hierarchy makes it possible to decide about a reaction event in $n_{\mathrm{re}} + n_{\mathrm{type}} + n_{\mathrm{type}}$ steps in contrast to random addition of the increments when the number of steps would be equal to $n_{\mathrm{re}} \times n_{\mathrm{type}} \times n_{\mathrm{type}}$.

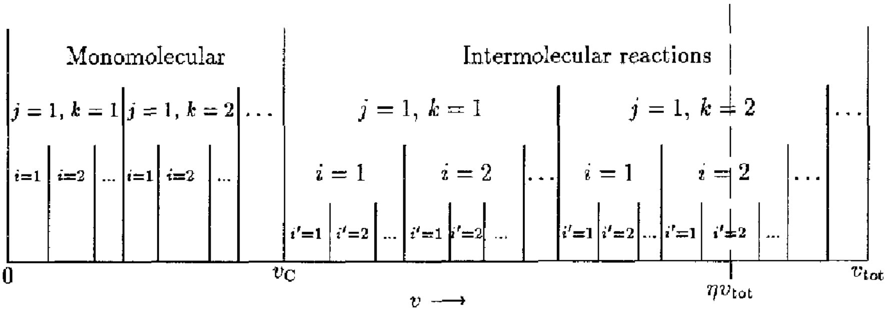

Figure 1: Connection between random number and reaction parameters. The horizontal axis is incremented by the rates of reactions characterized by (1) the mechanism (monomolecular or intermolecular), (2) types of reacting groups (j and k), (3) type of reacting molecule i and — in the case of intermolecular reaction — also (4) type of second reacting molecule i'. The increments are hierarchically assembled in four levels and separated by vertical lines of different height. The two largest compartments separated by the highest vertical line at $v = v_C$ correspond to total rates of all monomolecular and all intermolecular reactions, respectively, incremented at the second level (separated by the second highest vertical lines) by all reactions with fixed j and k, $\sum_i v_{\mathrm{CT},jk}(i)$ or $\sum_{i,i'} v_{\mathrm{IT},jk}(i,i')$. At the third and fourth levels also i ($v_{\mathrm{CT},jk}(i)$ or $\sum_{i'} v_{\mathrm{IT},jk}(i,i')$) and i' ($v_{\mathrm{IT},jk}(i,i')$) are fixed. In this figure, the random number η has chosen the intermolecular reaction with $j=1$, $k=2$, $i=2$ and $i'=2$

In the case of the general kernel, the simulation program is still rather slow and the computation time significantly increases with increasing size of system due to a high number ($\propto n_{\mathrm{type}}^2$) of increments contributing to v_{tot}. A dramatic improvement of the performance can be achieved if the restriction of functional form of the kernel given by eq. (13) is applied. In this case, the total rate and all necessary partial rates (corresponding to the three highest levels of our hierarchy scheme) can be expressed as simple combinations of terms like $\sum_i K_{\mathrm{Im}}(l_{ij}, \mathrm{x}_i, \ldots) N_i$ or $\sum_i K_{\mathrm{Im}}(l_{ij}, \mathrm{x}_i, \ldots) K_{\mathrm{Im}}(l_{ik}, \mathrm{x}_i, \ldots) N_i$. The number of operations in this case is proportional only to n_{type} and not to n_{type}^2. With the restricted form of kernel, a workstation-type computer can work with $\lesssim 10^8$ units.

Finally, the selected reaction has been executed and the vector characterizing the resulting molecule is computed according to reaction eqs. (1) and (2) by which the distribution $\{N(\mathbf{x}, \mathbf{l})\}$ is modified.

The scheme can be made more detailed. For instance, degradation can be included in the compartment of monomolecular reactions.

Conclusions

In this part, the differential equations governing the network formation process to be simulated have been formulated and the general features of the computer program have been characterized. In the second part, the efficiency and accuracy of the program will be tested as a function of the system size N and number of repetitions of the computer experiment.

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