BENG0091 Coursework 1

To be submitted on Moodle by 15-Feb-2019

Chemically reactive mixtures of molecules can exhibit intriguing behaviour that stems from the stochasticity in the occurrence of reaction events. For small system sizes, containing only a few reactive molecules, the stochastic fluctuations can be significant. Kinetic Monte Carlo simulation can be used to study such systems, and a suitable algorithm for this purpose was proposed by D. T. Gillespie back in 1977.

The algorithm keeps track of the number of molecules that exist in the system at all times. New molecules can appear in the system as reactions occur. It can also happen that molecules are consumed by certain reactions. The waiting times for reaction events to occur are modelled by exponentially distributed random variables. Moreover, in the case where there is more than one reaction, the algorithm uses a discrete random variable to select the reaction to occur; each reaction has probability of occurrence that is proportional to the so-called propensity of this reaction. The propensity can be calculated easily from the numbers of molecules and the kinetic constant of the reaction (which will be assumed to be a known parameter). Pseudocode for the Gillespie algorithm is given below:

Gillespie algorithm

---

1. Perform initialisation procedures
   1.1. Input values for kinetic constants c_j, j = 1…m
   1.2. Input initial concentrations of all species X_i, i = 1…n
   1.3. Specify the maximum time t_{max} that the simulation will run for, as well as the maximum allowed number of steps nmax
   1.4. Initialise the time t = 0, and the reaction counter cnt = 0
   1.5. Initialise uniform pseudo-random number generator
2. Loop while $t < t_{max}$ and cnt < nmax
   2.1. Calculate the reactions' propensity functions: $\alpha_j(X) = c_j \cdot h_j(X)$ for $j = 1,2,\ldots,m$
   2.2. Calculate the total propensity: $\alpha_0(X) = \sum_{j=1}^{m} \alpha_j(X)$
   2.3. Generate two uniformly distributed pseudo-random numbers r_1 and r_2.
   2.4. Calculate the time for the next reaction: $\tau = \frac{1}{\alpha_0} \cdot \ln\left(\frac{1}{r_1}\right)$
   2.5. Find which reaction μ will be next by solving: $\sum_{j=1}^{\mu-1} \alpha_j < r_2 \cdot \alpha_0 \leq \sum_{j=1}^{\mu} \alpha_j$
   2.6. Realize the reaction:
      2.6.1. Update time $t = t + \tau$
      2.6.2. Update species concentrations X_i to reflect the occurrence of reaction R_μ
      2.6.3. Update reaction counter cnt = cnt + 1
3. Stop

If you are interested to know more about the Gillespie algorithm you can consult Ref. [1].

For this coursework you are asked to do the following:

1. Code (in Matlab or similar) the Gillespie algorithm that simulates the radioactive decay reaction:

$$\mathrm{X} \xrightarrow{c_{rd}} \varnothing$$

Your algorithm will keep track of the number of molecules of species X over time. This number of molecules can take the values X = 0, 1, 2, … Use the following values for the kinetic constant c_{rd} and the initial population, X_0:

$$c_{rd} = 0.5$$
$$X_0 = 1000$$

The h-factor and the propensity are given as:

$$h(X) = X$$

$$\alpha(X) = c_{rd}\, h(X) = c_{rd}\, X$$

Plot the time evolution of the system as propagated by your stochastic algorithm along with the deterministic solution of the exponential decay:

$$X = X_0 \exp\left(-c_{rd}\, t\right) \qquad \textbf{[20]}$$

2. Now, let's model a more interesting system devised by Schlögl [2] as a model for non-equilibrium phase transitions. The following four reactions are possible in this system (with the last two being the forward and reverse steps of a reversible reaction):

$$\mathrm{A} \xrightarrow{c_1} \mathrm{X}$$

$$\mathrm{X} \xrightarrow{c_2} \mathrm{B}$$

$$2\mathrm{X} + \mathrm{C} \underset{c_4}{\overset{c_3}{\rightleftharpoons}} 3\mathrm{X}$$

We assume that species A, B, and C exist in high concentrations and any changes to their numbers are negligible. Therefore, your algorithm will only focus on the population of species X. Use the following parameters to run your code:

$$c_1 = 4.7876 \cdot 10^5$$
$$c_2 = 9.9800 \cdot 10^3$$
$$c_3 = 7.0739 \cdot 10^3$$
$$c_4 = 16.544$$

The h-factors and the propensities are given as:

$$h_1(X) = 1$$

$$h_2(X) = X$$

$$h_3(X) = \frac{X(X-1)}{2}$$

$$h_4(X) = \frac{X(X-1)(X-2)}{6}$$

$$\alpha_j(X) = c_j\, h_i(X) \quad \text{for} \quad j = 1, \ldots, 4$$

Plot the time evolution of the system starting from an initial population of $X_0 = 1$, and setting $t_{max} = 10$ and $nmax = 10^8$. **[20]**

Take samples of the process over constant time intervals of $\Delta t = 0.001$ time units, and plot the histogram of the population of species X. **[20]**

Out of the samples taken over these constant time intervals, calculate the mean and the standard deviation of the population of species X. Is the mean representative of the population and why (or why not)? **[20]**

Comment on the results: look closely at the transients (X versus time) and explain the observed behaviour on the basis of the reactions you are modelling. **[10]**

Present your Matlab codes as Appendixes to your report. **[10]**

References

[1] Gillespie, D. T. (1977). "Exact Stochastic Simulation of Coupled Chemical Reactions". The Journal of Physical Chemistry. **81** (25): 2340-2361. doi: 10.1021/j100540a008

[2] Schlögl, F. (1972). "Chemical reaction models for non-equilibrium phase transitions." Zeitschrift fur Physik A: Hadrons and Nuclei **253**(2): 147-161. doi: 10.1007/BF01379769