Mathematical Foundation of Kinetic Monte Carlo

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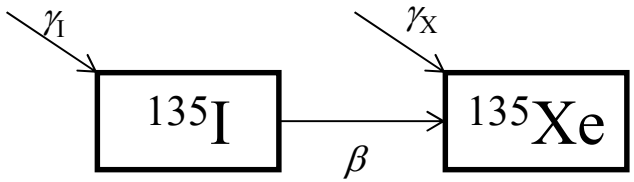
Problem: Depletion Eq. for Xe-135

- A simple decay chain of I-135 & Xe-135 can be shown as below.



- And the corresponding deletion equations can be written by

$$\frac{dN_I}{dt} = \gamma_I \Sigma_f \phi - \lambda_I N_I, \qquad \text{(A.1)}$$

$$\frac{dN_X}{dt} = \gamma_X \Sigma_f \phi + \lambda_I N_I - (\lambda_X + \sigma_X \phi) N_X \qquad \text{(A.2)}$$

- And from initial conditions of the clean state at t=0, the two nuclide densities can be obtained by

$$N_I(t) = \frac{\gamma_I \Sigma_f \phi}{\lambda_I}\left(1 - e^{-\lambda_I t}\right) \qquad \text{(A.3)}$$

$$N_X(t) = \frac{\gamma_X \Sigma_f \phi + \gamma_I \Sigma_f \phi}{\lambda_X + \sigma_X \phi}\left(1 - e^{-(\lambda_X + \sigma_X \phi)t}\right) - \frac{\gamma_I \Sigma_f \phi}{\lambda_X + \sigma_X \phi - \lambda_I}\left(e^{-\lambda_I t} - e^{-(\lambda_X + \sigma_X \phi)t}\right) \qquad \text{(A.4)}$$

Densities of I-135 & Xe-135

- For simplicity, Eqs. (A.1) & (A.2) can be rewritten by

$$\frac{dN_I}{dt} = k_I^C - \kappa_I^D N_I, \qquad \text{(A.5)}$$

$$\frac{dN_X}{dt} = k_X^C + \kappa_I^D N_I - \kappa_X^D N_X \qquad \text{(A.6)}$$

- Solve Eqs. (A.5) & (A.6) under the following conditions[*] by the kinetic Monte Carlo method.

$$k_I^C = \gamma_I \Sigma_f \phi = (0.056) \times \left(3 \times 10^{-3}\,\text{cm}^{-1}\right) \times \left(10^4\,\text{cm}^{-2}\,\text{sec}^{-1}\right) = 1.68\,/\,\text{cc} \cdot \text{sec}$$

$$\kappa_I^D = \lambda_I = 2.9 \times 10^{-5}\,/\,\text{sec}$$

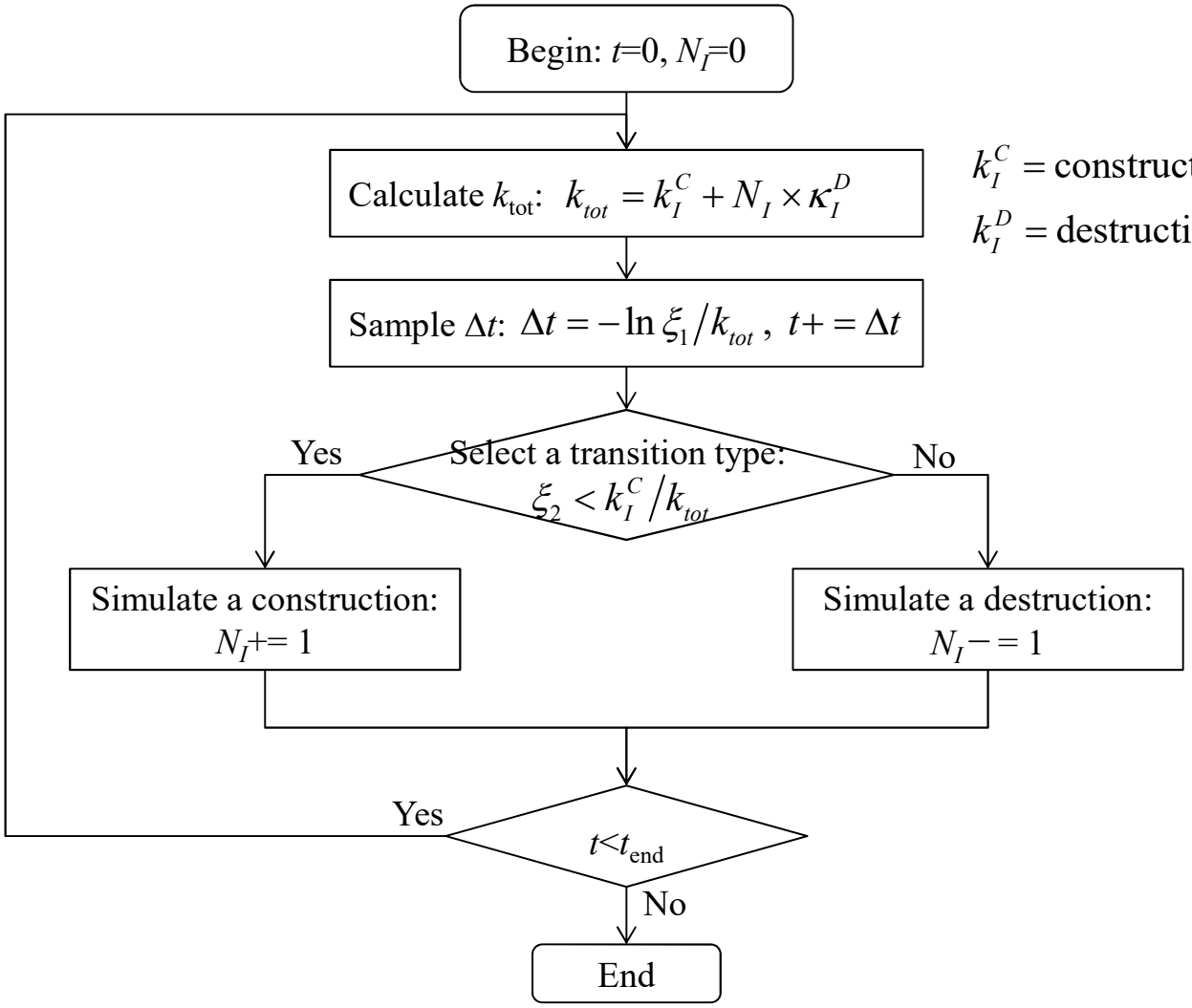
$$k_X^C = \gamma_X \Sigma_f \phi = (0.003) \times \left(3 \times 10^{-3}\,\text{cm}^{-1}\right) \times \left(10^4\,\text{cm}^{-2}\,\text{sec}^{-1}\right) = 9 \times 10^{-2}\,/\,\text{cc} \cdot \text{sec}$$

$$\kappa_X^D = \lambda_X + \sigma_X \phi = 2.1 \times 10^{-5}\,\text{sec}^{-1} + \left(3.5 \times 10^{-18}\,\text{cm}^2\right) \times \left(10^4\,\text{cm}^{-2}\,\text{sec}^{-1}\right)$$

$$= 2.1000000035 \times 10^{-5}\,/\,\text{sec}$$

[*] D. L. Hetrick, *Dynamics of Nuclear Reactors*, American Nuclear Society, Inc., La Grange Park, IL (1993).

CASE #1: Density of I-135 – Algorithm



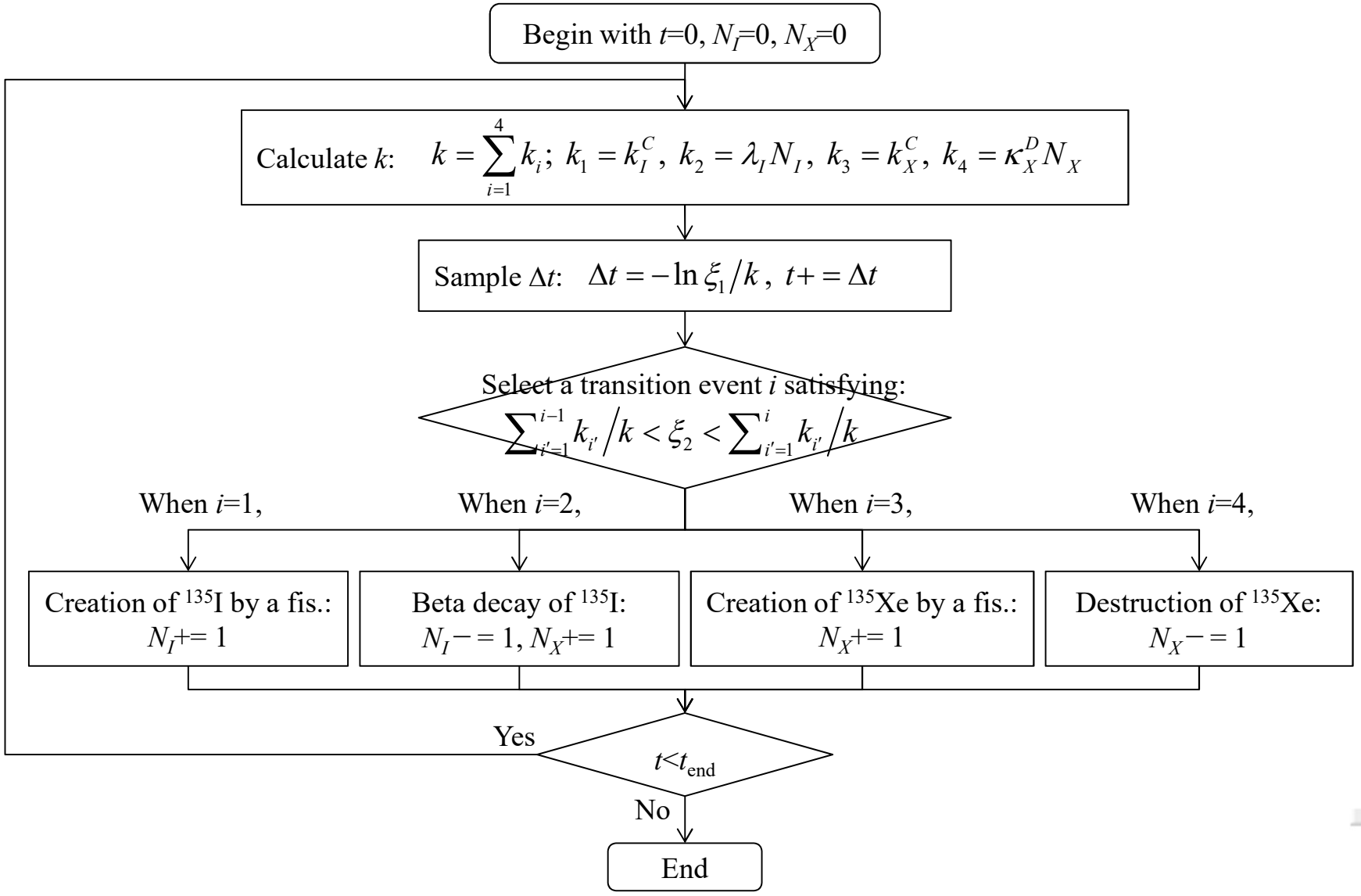
k_I^C = construction rate of ^{135}I=1.68 / cc · sec,

k_I^D = destruction rate of ^{135}I=2.9×10^{-5} / sec

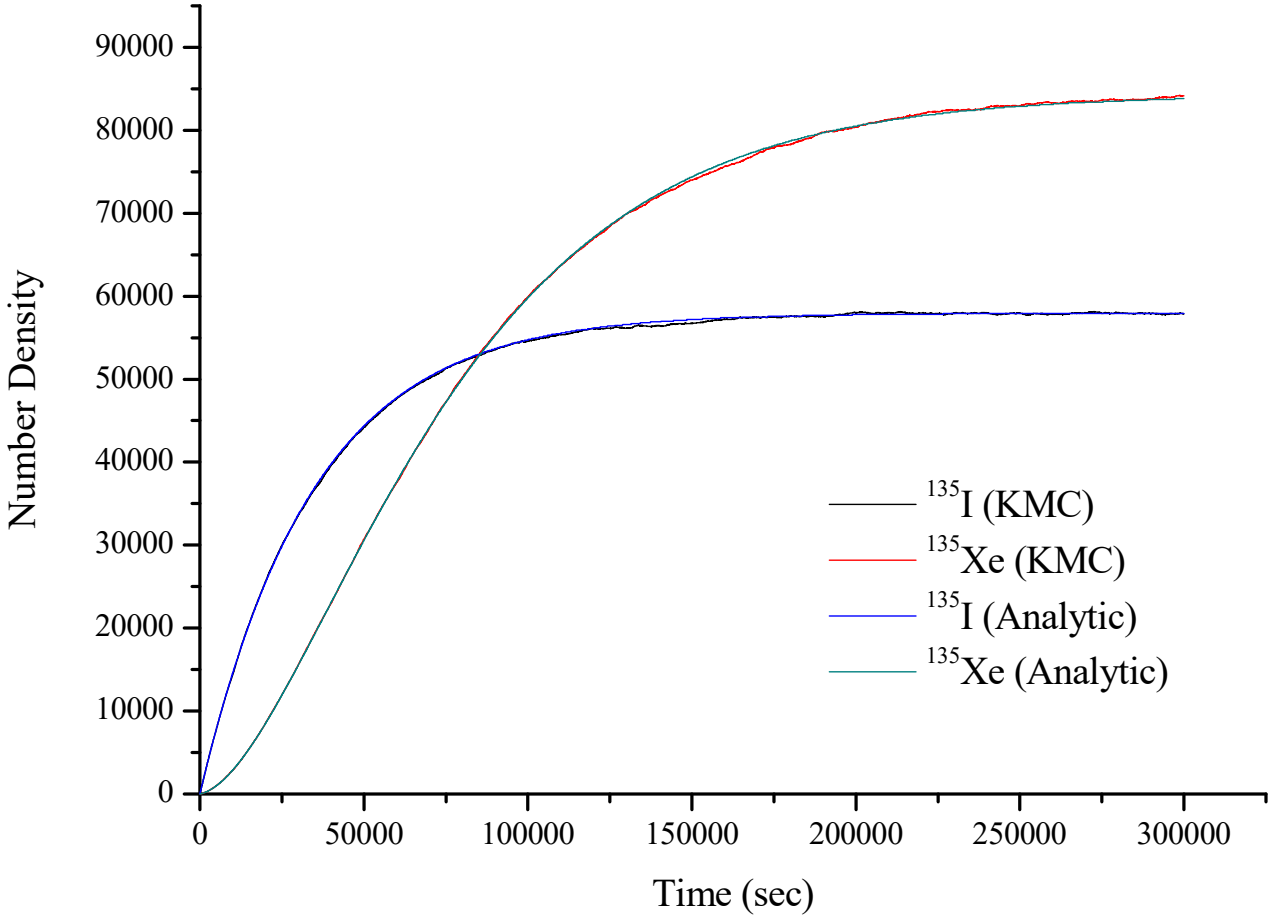
CASE #1: Density of I-135 – Implementation

```
do {
    //Calculate the total conversion rate
    totalLambda = genRateI + lambdaI*amountI;

    //Sample delta_time
    deltaT = -log(RNG.GetRN())/totalLambda;

    //Select a conversion type
    if(RNG.GetRN()<genRateI/totalLambda) {
        //Simulate a generation of I-135
        amountI += 1.;
    }
    else {
        //Simulate a destruction of I-135
        amountI -= 1.;
    }

    //Update time
    time += deltaT;

    if(time>=chkTime) {
        out<<setw(10)<<time<<setw(15)<<amountI<<endl;
        chkTime += binTime;
    }

    //Check the end of simulation time
    if(time > 1.e-3) bEnd = true;
}while(!bEnd);
```

Algorithm for Xe-135



Numerical Results



Mathematical Foundation of Kinetic Monte Carlo Method

Kinetic Monte Carlo vs. Poisson Process

- K. A. Fichthorn and W. H. Weinberg [1] presented the theoretical basis for a dynamical Monte Carlo method in terms of the theory of Poisson process.
- They showed that if
  1. A "dynamical hierarchy" of transition probabilities is created which also satisfy the detailed-balance criterion;
  2. Time increments upon successful events are calculated appropriately;
  3. The effective independence of various events comprising the system can be achieved,

  then Monte Carlo methods may be utilized to simulate the Poisson process.

[1] K. A. Fichthorn and W.H Weinberg, "Theoretical Foundations of Dynamical Monte Carlo Simulations," *J. Chem. Phys.*, **95**(2), 1090 (1991).

Kinetic Monte Carlo vs. Poisson Process (Contd.)

- They stated that under a dynamical interpretation, the Monte Carlo method provides a numerical solution to the Master equation:

$$\frac{\partial P(\mathbf{X},t)}{\partial t} = \sum_{\mathbf{X}'} K(\mathbf{X}' \to \mathbf{X}) P(\mathbf{X}',t) - \sum_{\mathbf{X}'} K(\mathbf{X} \to \mathbf{X}') P(\mathbf{X},t) \qquad \cdots\cdots (1)$$

where $\mathbf{X}$ and $\mathbf{X}'$ are successive states of the system.

$P(\mathbf{X},t)$ is the probability that the system is in state $\mathbf{X}$ at time t.

$K(\mathbf{X}' \to \mathbf{X})$ is the probability per unit time that the system will undergo a transition from state $\mathbf{X}'$ to state $\mathbf{X}$.

- The kinetic Monte Carlo method is explained as
  - The solution of the Master equation is achieved computationally by choosing randomly among various possible transitions with appropriate probabilities.
  - Upon each successful transition, time is typically incremented in integral units of Monte Carlo steps.

Mathematical Foundation of KMC

- We are going to derive a mathematical formulation corresponding to the kinetic Monte Carlo method from the general kinetic equation as

$$\frac{\partial P(\mathbf{X},t)}{\partial t} = \sum_{\mathbf{X}'} k_{\mathbf{X}'\to\mathbf{X}} P(\mathbf{X}',t) - \sum_{\mathbf{X}'} k_{\mathbf{X}\to\mathbf{X}'} P(\mathbf{X},t), \qquad (2)$$

and the initial condition at t=0 given by

$$Q(\mathbf{X}) \equiv P(\mathbf{X},0) \qquad (3)$$

- For simplicity, we rewrite Eq. (2) as

$$\frac{\partial P(\mathbf{X},t)}{\partial t} + k_{\mathbf{X}} P(\mathbf{X},t) = S(\mathbf{X},t); \qquad (4)$$

$$k_{\mathbf{X}} = \sum_{\mathbf{X}'} k_{\mathbf{X}\to\mathbf{X}'}, \qquad (5)$$

$$S(\mathbf{X},t) = \sum_{\mathbf{X}'} k_{\mathbf{X}'\to\mathbf{X}} P(\mathbf{X}',t). \qquad (6)$$

Derivation of KMC Algorithm

- Equation (4) with the initial condition of Eq. (3) is seen to be a first-order linear partial differential equation which has a unique solution. By introducing an integrating factor, Eq. (4) becomes

$$\frac{\partial}{\partial t}\left[e^{k_{\mathbf{X}}t}\cdot P(\mathbf{X},t)\right]=e^{k_{\mathbf{X}}t}\cdot S(\mathbf{X},t) \qquad \text{(7)}$$

- Then an integration of Eq. (7) from t=0 yields

$$P(\mathbf{X},t)e^{k_{\mathbf{X}}t}-Q(\mathbf{X})=\int_0^t e^{k_{\mathbf{X}}t'}\cdot S(\mathbf{X},t')dt'$$

$$\Rightarrow\quad P(\mathbf{X},t)=Q(\mathbf{X})e^{-k_{\mathbf{X}}t}+\int_0^t e^{-k_{\mathbf{X}}(t-t')}\cdot S(\mathbf{X},t')dt' \qquad \text{(8)}$$

- Eq. (8) implies that the probability of state **X** is made up of the state appeared in the previous time multiplied by the attenuation factor of $e^{-k_{\mathbf{X}}(t-t')}$.

Transition Probability Equation

- The transition probability can be defined by

$$\Psi(\mathbf{X},t) \equiv k_{\mathbf{X}} P(\mathbf{X},t) \qquad \text{(9)}$$

- Then by multiplying $k_{\mathbf{X}}$ on the both sides of Eq. (8), it can be expressed as

$$\Psi(\mathbf{X},t) = k_{\mathbf{X}} e^{-k_{\mathbf{X}} t} Q(\mathbf{X}) + \int_0^t k_{\mathbf{X}} e^{-k_{\mathbf{X}}(t-t')} \cdot S(\mathbf{X},t')dt' \qquad \text{(10)}$$

- By introducing the time-flight kernel, T defined by

$$T(t' \to t \mid \mathbf{X}) = k_{\mathbf{X}} e^{-k_{\mathbf{X}}(t-t')} \qquad \text{(11)}$$

Eq. (10) becomes

$$\Psi(\mathbf{X},t) = \hat{Q}(\mathbf{X},t) + \int_0^t T(t' \to t \mid \mathbf{X}) \cdot S(\mathbf{X},t')dt'; \qquad \text{(12)}$$

$$\hat{Q}(\mathbf{X},t) = T(0 \to t \mid \mathbf{X}) Q(\mathbf{X}) \qquad \text{(13)}$$

$\hat{Q}(\mathbf{X},t)$ is named the first transition source.

Transition Density Equation (Contd.)

- And we define another kernel named the event kernel as

$$C(\mathbf{X}' \to \mathbf{X}) = \frac{k_{\mathbf{X}' \to \mathbf{X}}}{k_{\mathbf{X}'}} \qquad \text{(14)}$$

- Using the event kernel C and the transition probability Ψ, $S(\mathbf{X},t)$ of Eq. (6) can be expressed as

$$\begin{aligned} S(\mathbf{X},t) &= \sum_{\mathbf{X}'} k_{\mathbf{X}'} C(\mathbf{X}' \to \mathbf{X}) P(\mathbf{X}',t) \\ &= \sum_{\mathbf{X}'} C(\mathbf{X}' \to \mathbf{X}) \Psi(\mathbf{X}',t) \end{aligned} \qquad \text{(15)}$$

- The introduction of Eq. (15) into Eq. (12) yields

$$\Psi(\mathbf{X},t) = \hat{Q}(\mathbf{X},t) + \int_0^t \sum_{\mathbf{X}'} K(\mathbf{X}',t' \to \mathbf{X},t) \Psi(\mathbf{X}',t') dt' \qquad \text{(16)}$$

$$K(\mathbf{X}',t' \to \mathbf{X},t) = T(t' \to t \mid \mathbf{X}) \cdot C(\mathbf{X}' \to \mathbf{X}) \qquad \text{(17)}$$

Series Solution

$$\Psi(\mathbf{X},t) = \hat{Q}(\mathbf{X},t) + \int_0^t \sum_{\mathbf{X}'} K(\mathbf{X}',t' \to \mathbf{X},t)\Psi(\mathbf{X}',t')dt' \quad \cdots\cdots (16)$$

- Let's consider the solution of Eq. (16) obtained by iteration; thus

$$\psi_0(\mathbf{X},t) = \hat{Q}(\mathbf{X},t)$$

$$\psi_1(\mathbf{X},t) = \int_0^t \sum_{\mathbf{X}'} K(\mathbf{X}',t' \to \mathbf{X},t)\psi_0(\mathbf{X}',t')dt'$$

$$\vdots \qquad\qquad \vdots$$

$$\psi_n(\mathbf{X},t) = \int_0^t \sum_{\mathbf{X}'} K(\mathbf{X}',t' \to \mathbf{X},t)\psi_{n-1}(\mathbf{X}',t')dt'$$

Clearly ψ_0 is the first-transition source. ψ_1 means the transition probability from the second-transition state. Similarly, ψ_2 indicates the contribution of the third-transition state, and so on. If the series $\sum_{j=0}^{\infty} \psi_j(\mathbf{X},t)$ converges, it represents a solution to Eq. (16).

Neumann Series Solution

$$\Psi(\mathbf{X},t) = \hat{Q}(\mathbf{X},t) + \int_0^t \sum_{\mathbf{X}'} K(\mathbf{X}',t' \to \mathbf{X},t)\Psi(\mathbf{X}',t')dt' \qquad \text{(16)}$$

- The solution of Eq. (16) can be expressed by the Neumann series:

$$\Psi(\mathbf{X},t) = \sum_{j=0}^{\infty} \psi_j(\mathbf{X},t); \qquad \text{(18)}$$

$$\psi_j(\mathbf{X},t) = \int_0^t dt_0 \sum_{\mathbf{X}_0} K_j(\mathbf{X}_0,t_0 \to \mathbf{X},t)\hat{Q}(\mathbf{X}_0,t_0), \qquad \text{(19)}$$

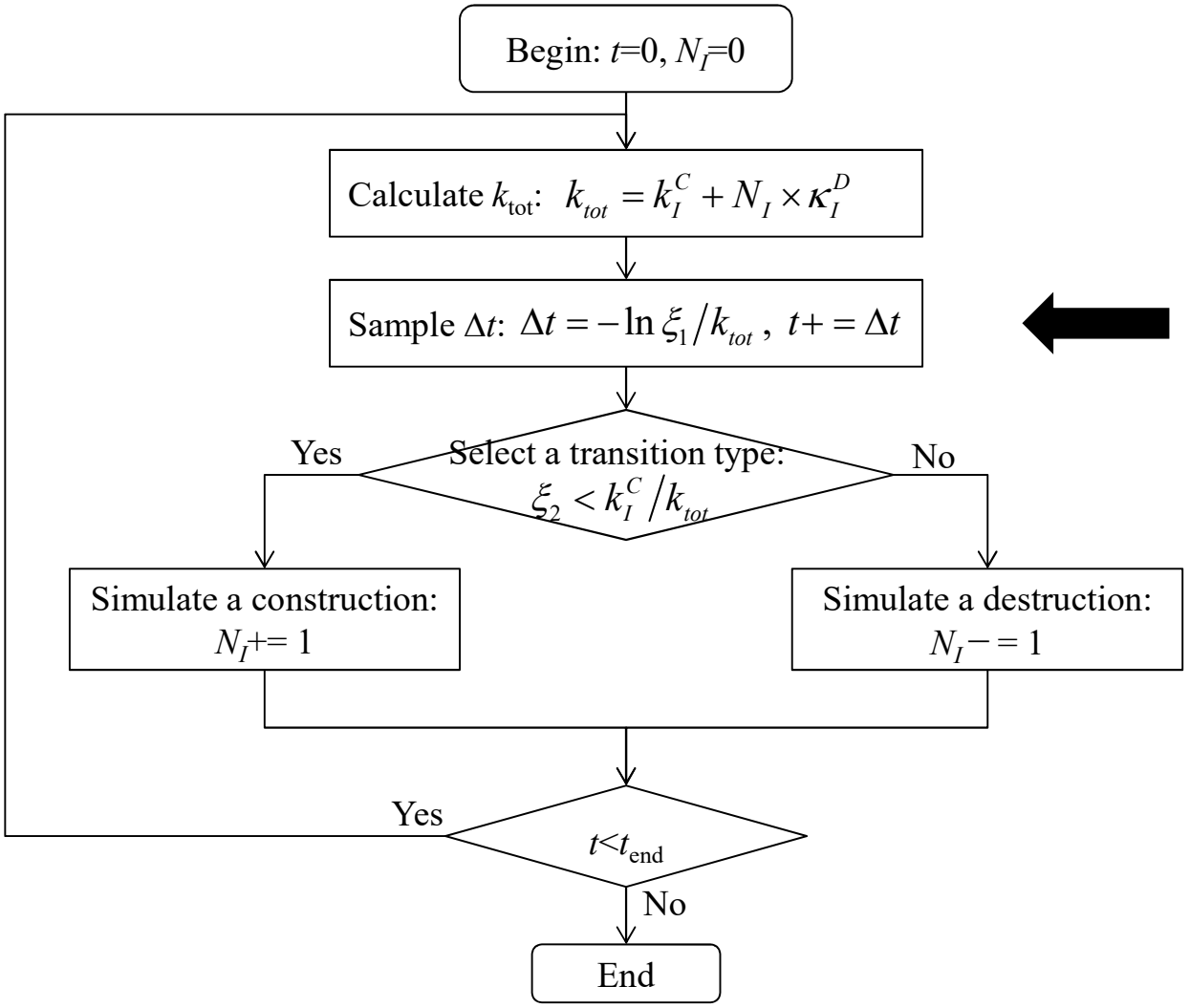
$$K_0(\mathbf{X}_0,t_0 \to \mathbf{X},t) = \delta(\mathbf{X}_0 - \mathbf{X})\delta(t_0 - t),$$
$$K_1(\mathbf{X}_0,t_0 \to \mathbf{X},t) = K(\mathbf{X}_0,t_0 \to \mathbf{X},t),$$
$$K_2(\mathbf{X}_0,t_0 \to \mathbf{X},t) = \int_{t_0}^t dt_1 \sum_{\mathbf{X}_1} K(\mathbf{X}_1,t_1 \to \mathbf{X},t)K(\mathbf{X}_0,t_0 \to \mathbf{X}_1,t_1),$$
$$\vdots$$
$$K_j(\mathbf{X}_0,t_0 \to \mathbf{X},t) = \int dt_1 \sum_{\mathbf{X}_1} \cdots \int dt_{j-1} \sum_{\mathbf{X}_{j-1}} K(\mathbf{X}_{j-1},t_{j-1} \to \mathbf{X},t)K(\mathbf{X}_{j-2},t_{j-2} \to \mathbf{X}_{j-1},t_{j-1}) \cdots K(\mathbf{X}_0,t_0 \to \mathbf{X}_1,t_1)$$

(20)

From Eq. (18), we can find that the transition probability is the sum of the contributions from transition at ($\mathbf{X}$,t) first and after a transition or more.

- The Monte Carlo kinetic analysis is based on Eqs. (18) & (19).

Interpretation of KMC by MC Sim. of Series Sol.



$$T(\tau) = k_{tot} e^{-k_{tot}\tau} \Rightarrow \int_0^{\tau} k_{tot} e^{-k_{tot}\tau'} d\tau' = \xi_1$$
$$\Rightarrow \tau = -\frac{\ln \xi_1}{k_{tot}}$$

$$C(\mathbf{X}' \rightarrow \mathbf{X}) = \frac{k_{\mathbf{X}' \rightarrow \mathbf{X}}}{k_{\mathbf{X}'}}$$