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Modeling Chlorine Decay in Pipes using Two-State Random Walk Approach

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Abstract-As water moves through a distribution network, maintaining residual chlorine is essential to prevent the regrowth or recontamination of pathogens and inactivate harmful micro-organisms that might be present. On the other hand, chlorine should be kept below a certain level because of concerns about formation of carcinogenic disinfection by-products within the distribution system. In this paper, a stochastic model is proposed as a tool to offer a cost-effective way to study the spatial and temporal variation of a number of water quality constituents, including chlorine. Under a known set of hydraulic conditions and source input patterns, a two state random walk model is developed to simulate the decay of chlorine in a single pipe by solving the advective-transport equation. The model predicts how the concentration of dissolved chlorine varies with time and space throughout the flow. Linear non-equilibrium particle transfer from water bulk phase (state 1) to pipe wall phase (state 2) is handled using stochastic analogue of two-state Markov-chain process with absorbing state. The model is verified by comparison with experimental observations available in the literature, EPANET 2 (Time- driven method) and other models.

Index Term- chlorine decay, Markov-chain, Random walk, pipes, stochastic, Transport equation.

I. INTRODUCTION

The aim behind constructing a water distribution system is to deliver sufficient quantities of water where and when it is needed at an acceptable level of quality. Throughout the distribution system, transformation of the quality of the water may occur after leaving the treatment facilities with acceptable level of quality. In most cases, the quality is related to the presence of microbiological and other toxic substance growing through the system. In the past, the concern was focused mainly on the basis of hydraulic reliability and economics. But at present, because of health related issues, attention has been paid more to the quality of the water through the distribution system [1]. Monitoring data along the water distribution system is considered to be the most important action that the water suppliers should satisfy. On the other hand, it is the most difficult. Even in medium-sized cities, the thousands kilometers of pipe makes it impossible to have a widespread monitoring in a reasonable time.

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It is almost impractical to examine the entire distribution system by seeing how changes in pumping schedules, storage facility operations, or treatment methods affect the quality of water received by the consumer. Therefore, mathematical modeling of water-quality behavior in distribution systems has become the best choice for mentoring. This option has effectively reduced the cost of studying the spatial and temporal variation of a number of water quality constituents including chlorine [1]. Most mathematical models are based on some assumptions such as first-order decay, second order decay, power-law decay (n^{th} order) and exponential decay or reacting balance equation to simulate the decay of chlorine concentration throughout the water distribution system like Liou and Kroon [2], Clark et al. [3, 4, 5], Rossman et al. [6], Clark et al. [7], Rossman et al.[8], Islam et al. [9], Clark and Sivaganesan [10], Ucak and Ozdemir[11], Leeuwen et al.[12]. Musz et al. [13] established a review paper that presents the most popular computer models of water quality in distribution systems used in environmental engineering practice. They concluded that these models have disadvantages which can prevent a proper assessment of water quality in the whole system of water distribution or limiting their usage only to small networks as well as simulating changes in fixed hydraulic conditions [13]. Biswas et al. (1993) derive an analytical solution of a two-dimensional (2-D) steady-state for the chlorine transport equation under turbulent flow. This radial diffusion model described chlorine decay in turbulent flow regime with good accuracy if the wall decay coefficient is relatively small. By neglecting the high order terms in the analytical solution of Biswas, Hund-Der Yeh et al. [14] provide more accurate approximate solution of the 2-D steady-state chlorine transport equation under the turbulent condition when dealing with small or large wall decay coefficient. In addition, they developed a methodology to combine simulated annealing (optimization algorithm) with this new approximate solution to determine the wall decay parameter [14]. This paper presents a method to solve the advection transport equation based on a stochastic approach that is called as a discrete particle-tracking model. The basic idea of this model is related to the random-walk method (RWM) which is a lagrangian based approach. The model algorithm is as follows: the transported quantity of solute mass is discretized by a set of moving particles say N. Each particle is carrying part of the mass of the solute that is equal to the total mass divided by the number of particles. The particles are moving in the pipe under the influence of advection by the flow.

The transport of the solute (cloud of the particles) should be carried out in such a way that it simulates the transport that is described microscopically by the equation. The mass reduction to each particle of the solute is estimated according to the mass decay process. The concentration is estimated back through a scaling up process to determine the concentration of the solute. In our case, the method will allow us to track changes in chlorine concentration depending on time and localization throughout the water distribution system. This case is a two-state random walk defined as a one in which a particular particle can be in one of two states for certain period of time. Each particle has the same transition probability to change from one state to another. These two states are transient state, representing the particle in the water bulk phase (state 1), and absorbing state (state 2), representing the particle on pipe wall phase. The movement of the chlorine particles between the two states is a linear non-equilibrium process from water bulk to pipe wall states. The process of state-changes is handled using the concept of stochastic analogue of two-state Markov-chain process with absorbing state [15]. Unlike the regular Markov chain, for which the transition matrix P is primitive ($p_{ii} < 1$) and the chains never get stuck in a particular state, Markov- chain with absorbing state must have at least one absorbing state say i with $p_{ii} = 1$ and $p_{ij} = 0$ for all $j \neq i$. The transition is to be from non- absorbing states to absorbing states. Therefore, a two-state Markov-chain transition matrix may have the following canonical form:

$$p = \begin{array}{c} \\ TR \\ ABS \end{array} \begin{array}{c} \begin{array}{cc} TR & ABS \end{array} \\ \begin{bmatrix} p_{11} & p_{12} \\ p_{21} & p_{22} \end{bmatrix} \end{array} \qquad (1)$$

Where P is the transition matrix, p_{11} is the probability of having a particle stay in transition state TR and it is determined by subtracting p_{12} from one.; p_{12} is the probability of having a particle transfer from TR to absorbing state ABS; p_{21} is the probability of having a particle transfer from ABS to TR; and p_{22} is the probability of having a particle stay in ABS. in our case, the sum of p_{11} and p_{12} will equal 1, $p_{21} = 0$ and $p_{22} = 1$. More explanation of the process and how to apply it to our case will be in details in methodology. Figure 1 shows the conceptual model of particle transfer between state 1 and 2.

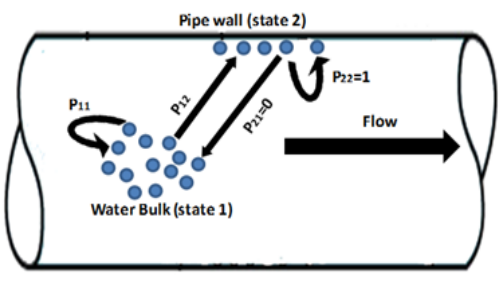

Figure 1: conceptual model of particle transfer between water bulk and pipe wall.

The application of RWM offers an alternative to classical solution methods to the transport equation. Within the last two decades, many authors have demonstrated it as a more computational efficient method than traditional numerical methods such as finite element, finite difference, and characteristic methods when solving the traditional second-order advection-dispersion equation (ADE). As an advantage over these methods, the RW particle tracking approach does not need spatial discretization and it does not suffer the numerical dispersion problem. Moreover, these standard numerical techniques are especially apparent when one simulates solute transport using regional-scale and high-resolution numerical models. In addition, the random-walk approach does not modify the target partial differential equations and the nature of the physical problem. Furthermore, the stability and convergence analysis which are required by the traditional numerical methods are not needed within this approach. Most importantly, the approach cannot only solve the PDE, but also improve our understanding about the physical process by providing a description of the dynamics underlying the target PDE [17].

II. METHDOLOGY

The 1-D steady-state classical advection equation to describe the decay of free chlorine concentration in the water flowing though pipe, neglecting the axial dispersion and diffusivity of chlorine solution, is written as:

$$\frac{\partial c_i}{\partial t} = -u_i \frac{\partial c_i}{\partial x} \pm R(c_i) \qquad (2)$$

Where, c_i is the concentration of constituent in pipe i (mg/l) as a function of distance x and time t; u_i is the mean flow velocity in pipe i (m/s); and $R(c_i)$ is the reaction rate expression, equals zero for conservative constituent [13, 18]. In the current paper, some theories were adopted to formulate the chlorine decay process governed by Equation (2). A random walk method is used together with Markov chain theory with absorbing state. The following lines shall explain how these theories are formulated in an algorithm to be implemented in a spreadsheet. A special case of random-walk scheme given in Eq. (3) is employed to solve the local-scale advection transport equation (2) for the reactive compound (chlorine) and tracking the chemical [15, 16].

$$X_{t+\Delta t} = X_t + [u(X_t) \cdot \Delta t] \qquad (3)$$

Where; $X_{t+\Delta t}$ is the tagged particle position at time $t+\Delta t$; X_t is the particle position at time t; $u(X_t)$ is the velocity of the water at position X_t at time t.

The longitudinal dispersion is usually not an important transport mechanism under most operating conditions. This means there is no intermixing of mass between adjacent parcels of water traveling down a pipe [19, 21].

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Linear non-equilibrium particle transfer from state 1 (water bulk) to state 2 (pipe wall) is to be handled. Consider a particle between two states: the aqueous state 1 and the absorbing state 2. At any instant of time, the particle can be transferred from state 1 to state 2. This can be handled by stochastic analogue of the two-state Markov-chain with absorbing state. This chain has state space {1, 2}. The rates at which the particle leaves states 1 to state two 2 are k_f (mass transfer coefficient). Since chlorine is not conservative, the mass of its particles can be represented by the first order decay function of the form [20]:

$$M_p(t) = M_p(0)\exp(-k_b \cdot t) \quad (4)$$

Where $M_p(t)$ is the Mass of chlorine particle at time t (M); $M_p(0)$ is the Mass of chlorine particle at time zero (M); and k_b is the bulk decay constant (1/T).

The probability of having a particle transferred from state 1(water bulk phase) to state 2 (pipe wall phase) is represented by the modified equation [15]:

$$p_{12} = \lambda \cdot \frac{4}{D} \cdot \Delta t \quad (5)$$

Where p_{12} is the probability at which the chlorine particle will move from State 1, transition state, to State 2, the absorbed state and get decayed. Whenever p_{12} value is determined, it will be introduced along with p_{11}, p_{21} and p_{22} to Markov chain transition matrix to set a linear non-equilibrium absorption or particle transfer from water bulk (state1) to pipe wall (state 2) as in eq. 1. λ is the global wall coefficient (L/T):

$$\lambda = \frac{k_w k_f}{(k_w + k_f)} \quad (6)$$

Where k_w is the wall decay constant (L/T); k_f is the mass transfer coefficient (L/T).

$$k_f = 0.0149 \frac{d}{D}\left(\frac{\nu}{d}\right)^{\frac{1}{3}} \mathrm{Re}^{0.88} \quad (7)$$

Where d is the molecular diffusivity of the chlorine in water (1.21×10^{-9} m2 /s); D is the diameter of the pipe (L); ν is the kinematic viscosity of the water (10^{-6} m2/s); and Re is the Reynolds number of the flow:

$$\mathrm{Re} = \frac{4Q}{\pi D \nu} \quad (8)$$

Where Q is the flow rate of water in the pipe (L3/T).

The four values in the matrix in eq. 1 will be introduced into the Markov chain cumulative transition matrix as,

$$\mathbf{P} = \begin{bmatrix} p_{11} & p_{11} + p_{12} \\ 0 & 1 \end{bmatrix} \quad (9)$$

for realization of states in the random walk process.

An Excel spreadsheet is developed to implement the algorithm. The idea is to generate random numbers between 0 and 1 by the built in function (RAND()). In order to realize a state of a particle each time step, a random number is drawn and if the number exists in the range between 0 and p_{11} (<1), indicate that a particular particle will stay in the bulk flow, other than that it will be transfer to wall state. In reality, lab test examination for several samples, taken at the same moment, will not give the same result when analyzed. There should be a slight difference between the results because of several affecting factors one of them is that this process is more stochastic than to be deterministic. RWM is following the same principle. Each simulation result will be considered to be a one realization and it is slightly different from the next realization depending on the resolution of the chlorine dose applied. If the resolution is high, (high number of particles per chlorine dose) the differences between each realization are low indicating an Inverse relationship. Therefore, high resolution and averaging realization implemented in the simulation using RWM.

III. CASE STUDY AND DISCUSSION: EXPRIMENTAL RESEARCH

To represent the decay of chlorine concentration, the first-order reaction kinetic, Eq. (4), is usually used. Bulk decay coefficient k_b and wall decay coefficient k_w can be determined by appropriate mathematical model or measured chlorine concentration data [14]. In 2006, Rossman conducted an experiment at US EPA's test and evaluation facility in Cincinnati, Ohio. He used a distribution system simulator, which consists of a 27 m long loop with 0.15 m diameter of unlined ductile iron pipe, a recirculation pump, and heat exchanger cooling system. The purpose of this experiment is to measure the reaction rate of chlorine concentration in a simulated pipe for water treated by different forms of advanced treatment, conventional treatment + reverse osmosis RO, conventional treatment (sedimentation + filtration) CON and conventional treatment + ozonation O_3. Throughout the experiment, a steady state condition is maintained with a flow velocity of 0.3 (m/s). The axial distance from the inlet along the pipe, X, is equal to the flow velocity multiplied by the flow time in the pipe [14]. The time series of chlorine measurements made for each experiment to estimate the first-order kinetic parameters k_b and k_w for chlorine decay are shown in Table 1 [20]. The residual chlorine concentration at the beginning of the experiment is 1 mg/L.

TABLE 1. Values of k_b and k_w for three sorts of lab-tested water [21].

Treatment	k_b (1/s)	k_w (m/s)
RO	8.10×10^{-8}	4.66×10^{-7}

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CON	1.09×10^{-7}	6.73×10^{-7}
O_3	5.56×10^{-7}	1.30×10^{-6}

For Biswas's and Hund-Der Yeh's studies, k_w was determined from the experiment-observed data based on their approximate solution and presented in table 2[14, 22]. Notice that k_w values for these two approximate solutions slightly differ from those given by Rossman [14, 21] because they take radial diffusion factor into account in their determination.

TABLE 2. Values of k_b and k_w for three sorts of lab-tested water for Biswas [22] and Hund-Der Yeh [14]

Treatment	k_b (1/s)	k_w (m/s) (Biswas)	k_w (m/s) (Hund-Der Yeh)
RO	8.10×10^{-8}	4.20×10^{-7}	4.50×10^{-7}
CON	1.09×10^{-7}	6.43×10^{-7}	6.52×10^{-7}
O_3	5.56×10^{-7}	1.53×10^{-6}	1.33×10^{-6}

The simulated results obtained from applying RWM is verified by the experimental data [21]. Simulated results of the lagrangian Time Driven Method (TDM) incorporated in EPANET 2 and two analytical approximate solutions for Biswas et al. [22] and Hund-Der Yeh et al. [14] are compared with RWM. Figure 2, 3 and 4 show experiment-observed data [21] and simulated results of the average of ten realizations of RWM , TDM (EPANET 2), Biswas et al.'s approximate solution and Hund-Der Yeh et al.'s approximate solution for lab-tested water treated by reverse osmosis RO, conventional treatment CON[14, 22], and ozonation O_3, respectively. The figures indicate a good agreement between the simulated result of the average of ten realizations of RWM and the experimental data by Rossman [21], along with the other three methods. But, the simulated result of Biswas et al.'s approximate solution [22] is discordant in the case of the lab-tested water treated by ozonation with greater k_w values. According to Hund-Der Yeh et al. [14], this problem may be attributed to the fact that the chlorine concentration is inversely proportional to the quadratic of wall decay constant in Biswas et al.'s approximate solution as expressed in the equations of the dimensionless cup-mixing average concentration of the pipe at any cross-section and the fractional error. To evaluate the four models in a quantitative manner, the root mean square error (RMSE) is estimated between model results and observations. The results are shown in Table 3. It might be concluded that the RW method gives relatively good results with higher values of k_b and k_w (water treated by ozonation O_3) when comparing with models' results of TDM method and Biswas approximate solution.

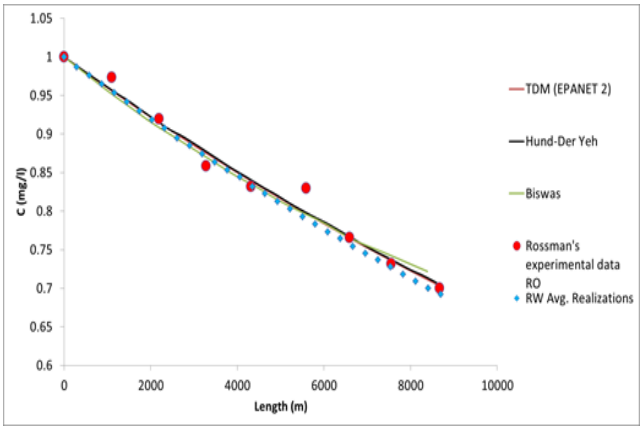

Figure 2: The experimental observation [21], simulated results of Hund-Der Yeh et al's approximate solution[14], Biswas et al.'s approximate solution[14], TDM (EPANET 2) and the average behavior of ten realizations of RWM for water that is treated by reverse osmosis RO.

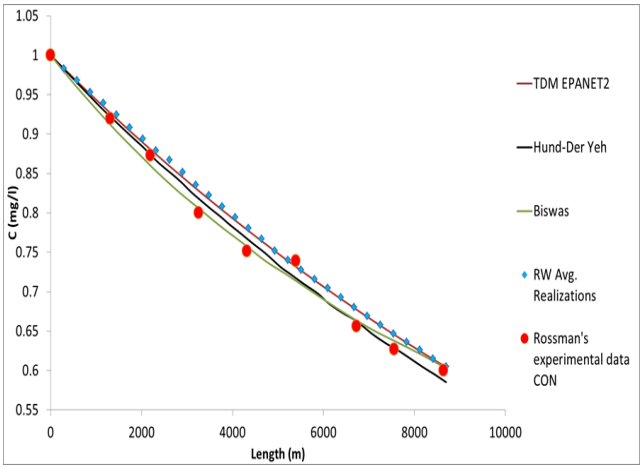

Figure 3: The experimental observation [21], simulated results of Hund-Der Yeh et al's approximate solution[14], Biswas et al.'s approximate solution[14], TDM (EPANET 2) and the average behavior of ten realizations of RWM for water that is treated by conventional treatment CON.

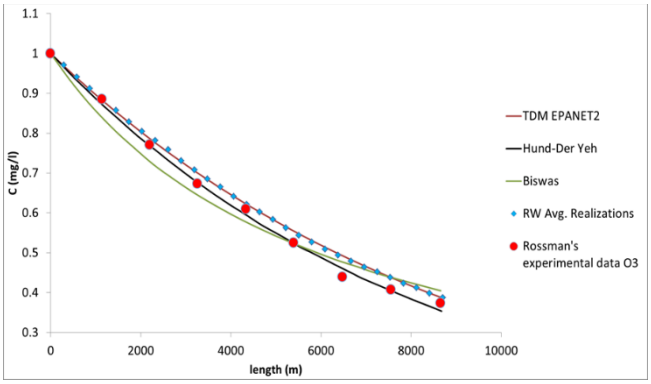

Figure 4: The experimental observation [21], simulated results of Hund-Der Yeh et al's approximate solution [14], Biswas et al.'s approximate solution [14], TDM (EPANET 2) and the average behavior of ten realizations of RWM for water that is treated by ozonation O_3.

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TABLE 3. Root mean square error between simulated results of Biswas et al.'s approximate solution[14], Hund-Der Yeh et al's approximate solution [14], TDM (EPANET 2), the average behavior of ten realizations of RWM and The experimental observation [21] for water that is treated by RO, CON and O_3.

Method	RMSE RO	RMSE CON	RMSE O_3
Biswas	0.01558	0.01181	0.03161
Hund-Der Yeh	0.01465	0.01184	0.01165
TDM	0.01461	0.01769	0.02604
RW	0.01637	0.02007	0.02527

Because of it randomness, Random Walk Method depends highly on the resolution of the chlorine cloud presented in the flow. Since we are dealing with the mass of the chlorine particle, increasing the number of particles per chlorine cloud (dose) will lead to less fluctuation around the average of number of realizations and more accurate determination for the decay of chlorine though out the flow. Figure 5 shows a high fluctuation around the values of both the average of ten realizations of RWM simulated result and the simulated result of TDM (EPANET2). In figure 6, increasing the number of particles per chlorine cloud from 100 in figure 5 to 1000, leads to low fluctuation and better agreement for the average of ten realizations of RWM with TDM (EPANET2)'s simulated result. It is even better than the values of the average in figure 5 when compared with TDM (EPANET 2) simulated result.

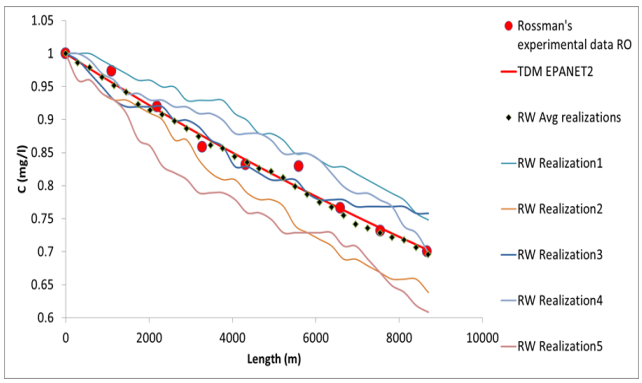

Figure 5: Example of two realizations with high fluctuation of RWM (with 100 particles per chlorine dose) compared with RWM average behavior of ten realizations and TDM (EPANET 2)'s simulated results.

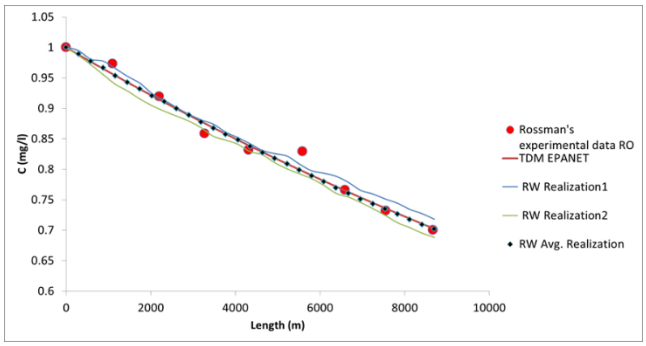

Figure 6: Example of two realizations with low fluctuation of RWM (high resolution with 1000 particles per chlorine dose) compared with RWM average behavior of ten realizations and TDM (EPANET 2)'s simulated results.

IV. CONCLUSION

The need for a more reliable and more efficient mathematical m0odel to simulate the actual transient behavior of chlorine concentration in water distribution system, has been driving researchers to conduct comparison, coupling or developing techniques to obtain more stability and accuracy in the model or increase the level of convergence. This paper introduces a numerical Lagrangian Random-Walk Method to numerically simulate the chlorine decay in water flow through a single pipe by solving the advective-transport equation for dynamic water-quality modeling. Linear non-equilibrium particle transfer from water bulk to pipe wall state is handled using stochastic analogue of two-state Markov-chain process with absorbing state. The model is verified by a good agreement with experiment-observed data [21], and simulated results of TDM (EPANET 2), Biswas et al.'s approximate solution [14,22] and Hund-Der Yeh et al.'s approximate solution [14], for water treated by different forms of advanced treatment.

V. ACKNOWLEDGMENT

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APPENDIX I. NOTATION

The following symbols are used in this paper:
ABS: absorbing state;
C: point value of chlorine concentration in any location of the pipe (M /L^3);
CON: conventional treatment (sedimentation + filtration);
D: diameter of the pipe;
d: molecular diffusivity of the chlorine in water (L^2/T);
k_b: bulk decay constant (1/T);
k_f: mass transfer coefficient (L/T);
k_w: wall decay constant (L/T);
M_p (0): mass of chlorine particle at time zero (M);
M_p (t): mass of chlorine particle at time t (M);

O_3: conventional treatment + ozonation;
P: Markov chain transition matrix;
P: Markov chain cumulative transition Matrix;
Q: flow rate of water though pipe (L^3/T);
Re: Reynolds number;
RO: conventional treatment + reverse osmosis;
RWM: random-walk-method;
TR: transition state;
t: time (T);
TDM: time-driven-method;
u: mean flow velocity of water (L/T);
v: kinematic viscosity (L^2/T);
X: position of the particle (L);

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