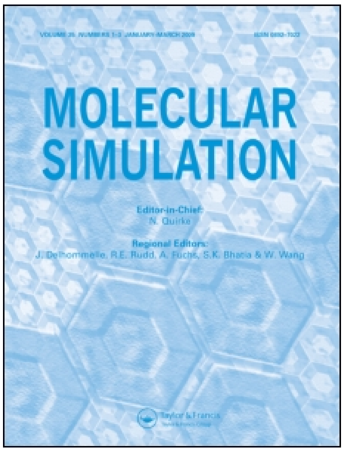

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Kinetic Lattice Model for Long-Time Chemical Phenomena: Introduction of Time-Scale into Monte Carlo Simulation

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KINETIC LATTICE MODEL FOR LONG-TIME CHEMICAL PHENOMENA: INTRODUCTION OF TIME-SCALE INTO MONTE CARLO SIMULATION

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The kinetic lattice model (KLM) has been proposed, as a model of the slow dynamics in chemical systems, where the molecular diffusion can be treated and the time notion can be introduced within the Monte Carlo (MC) simulation scheme by combining Stokes-Einstein relation and Einstein's formula for the diffusion coefficient D of the solute molecule. Then, its mean square displacement calculated *via* MC simulations, brings about directly a time-scale per 1 MC step. For a model chemical system consisting of a spherical molecule with a radius of 10 Å in such a solvent with the coefficient of viscosity η of toluene, 1 MC step was found to correspond to the order of 100 ps for both 2-dimensional and 3-dimensional KLM. At the same time, the temperature dependence and the dimensionality were discussed within the present KLM. It was established that the KLM should be a plausible and unique tool to understand the long-time chemical phenomena which have been, for a long time, difficult problems that can not be dealt by any direct microscopic methods.

Keywords: Kinetic lattice model; Monte Carlo simulation; diffusion constant; Stokes-Einstein relation; Einstein's formula

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1. INTRODUCTION

Recent computational methods, not only quantum mechanical but also statistical mechanical simulations, have been becoming very powerful tools for understanding the complex systems where simple analytical methods can not be straightforwardly applicable [1]. Under the circumstances, understanding the microscopic mechanism of the nucleation process and the crystallization process in solution, is now a fascinating and fundamental problem from both experimental and theoretical points of view [2]. For example, the crystal resolution process of racemate in solution is one of recent hot topics, since it should lead directly to important techniques for separating optical isomers in chemistry and biochemistry [3].

For this purpose, the molecular mechanics (MM) and molecular orbital (MO) calculations can be and have been very useful tools for dealing with the problem since these can make it possible to discuss the microscopic origin in molecular interaction and can propose some directions from the synthetic chemical viewpoint [4]. However, even now, there exists much difficulty in direct application of MM and MO approaches in treating the nucleation process and the crystallization process in solution, since their realistic applications are still restricted due to the complexity of the system. Therefore, only static treatments can be usually examined. Although the molecular dynamics (MD) simulation where the intermolecular interaction is approximated by Coulomb and Lennard-Jones (LJ) potentials, can examine the dynamic motions of molecules, the time-scale of such slow dynamics as nucleation and crystallization should be much longer than that of the standard MD simulation. Accordingly, it is difficult to study the dynamic property of these phenomena as well as the protein folding problem, *i.e.*, another popular problem relating to slow dynamics.

Therefore, we have proposed the kinetic lattice model (KLM), which assumes that solute and solvent molecules should be located only on lattice sites and might be ruled by some effective interaction hamiltonians [5, 6]. Even for the 2-dimensional (2D) model, it is important to note that this hamiltonian should include not only the first nearest neighbor (1stNN) interaction but also the second nearest neighbor (2ndNN) one [7]. This is such a crucial point that most of all discussions on the basis of MM and MO have never mentioned usually. Further, for the 3-dimensional (3D) model, the third nearest neighbor (3rdNN) interaction might take also some important roles for discussing these phenomena. On the other hand, an essential and important feature of KLM is the introduction of the time-scale to the MC procedure. Usually, the MC simulation is considered to be capable of treating not the dynamic behavior of the systems but the statistical properties in equilibrium, since each microscopic state is only generated by some stochastic methods in no relation to the law of causality. However, for such discrete systems as the Ising spin model, it has been common to treat it numerically by the MC method [5, 6] and also well-known that, for example, the kinetic Ising model has been proposed for treating the diffusion dynamics of spins within the MC scheme, *i.e.*, Kawasaki dynamics [8]. Therefore, to construct the KLM and apply it to the slow dynamics in chemical phenomena, is not a show-off but an "egg of Columbus" for treating the dynamic properties of the molecular systems over a long time range. In the KLM, first, the diffusion coefficient D is evaluated by combining Stokes-Einstein relation [9, 10] with the experimental value of the coefficient of viscosity η. Second, assuming an appropriate lattice constant, the mean square displacement (MSD) for some finite MC steps is calculated directly *via* the MC simulations for one solute molecule in solvent. Finally, the effective time length for 1 MC step is estimated by equating the diffusion constant in Stokes-Einstein relation [10] with that obtained by the MC simulation through Einstein's formula [10].

In this paper, for a model chemical system consisting of a spherical molecule with a radius of 10 Å in such a solvent with the coefficient of viscosity η of toluene, we have reported, for the first time, a numerical realization of the relation between 1 MC step and the real time-scale within both the 2D and 3D KLMs. The effective time per 1 MC step is evaluated at several temperatures.

The Section 2 introduces precisely the way of thinking in KLM and explains its real computational procedures in relation to chemical situations. In Section 3, results and discussion are given for the present model examples. Finally, the conclusions are presented in Section 4.

2. METHOD OF CALCULATION

A. Effective Interaction Hamiltonian and Kinetic Lattice Model (KLM)

In KLM for the 2D model, the following effective interaction hamiltonian is presently assumed:

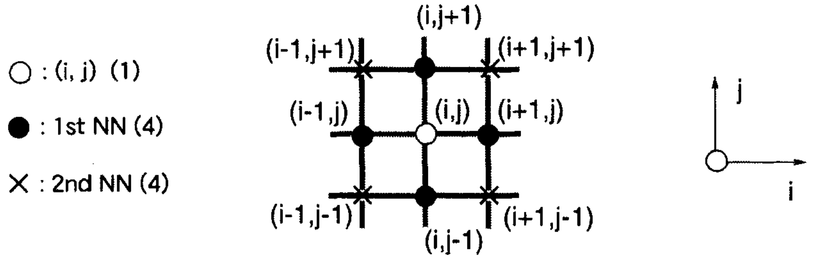
$$H_{\text{int}} = \frac{1}{2}\sum_{i,j,I,J} \mathbf{s}_{ij}^{t}\mathbf{J}\mathbf{s}_{IJ} \tag{1}$$

where $\mathbf{J}$ ($= \mathbf{J}^t$) is the interaction matrix defined as a sum of the 1stNN and 2ndNN interaction matrix, *i.e.*, $\mathbf{J}^{(1)}$ and $\mathbf{J}^{(2)}$:

$$\begin{aligned}\mathbf{J} &\equiv \mathbf{J}^{(1)} + \mathbf{J}^{(2)}\\ &\equiv \begin{pmatrix} J^{(1)}_{\mathrm{LL}} & J^{(1)}_{\mathrm{LS}} \\ J^{(1)}_{\mathrm{SL}} & J^{(1)}_{\mathrm{SS}} \end{pmatrix} \cdot (\delta_{Ii}\delta_{Jj\pm1} + \delta_{Ii\pm1}\delta_{Jj})\\ &+ \begin{pmatrix} J^{(2)}_{\mathrm{LL}} & J^{(2)}_{\mathrm{LS}} \\ J^{(2)}_{\mathrm{SL}} & J^{(2)}_{\mathrm{SS}} \end{pmatrix} \cdot \delta_{Ii\pm1}\delta_{Jj\pm1},\end{aligned} \tag{2}$$

$\mathbf{s}^t_{ij}$ denotes a 2D state vector on the site (i,j) on the 2D lattice (Fig. 1a), which takes one of the two states, *i.e.*, (1 0) or (0 1), corresponding to the occupation of a solute (L) or a solvent (S) molecule, respectively. Each elemental effective interaction $J_{\mathrm{MM}'}$ ($\mathrm{M}, \mathrm{M}' = \mathrm{L}$ or S) can be obtained microscopically by MM or MO methods by being interpreted as the

(a) 2 dimensional case



(b) 3 dimensional case

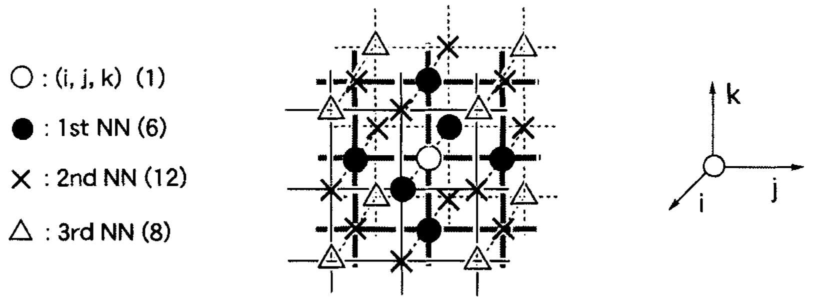


FIGURE 1 (a) The 2-dimensional lattice and the 1stNN and 2ndNN sites relative to the lattice site (i,j) (○), which are denoted as ● and ×, respectively. The site number is 1, 4 and 4 for ○, ● and ×, respectively. (b) The 3D lattice and the 1stNN, 2ndNN and 3rdNN sites relative to the lattice site (i,j,k) (○), which are denoted as ●, × and △, respectively. The site number is 1, 6. 12 and 8 for ○, ●, × and △, respectively.

appropriate Boltzmann-weighted average interaction energy between the M and M′ species [11]:

$$J_{\mathrm{MM'}} = \frac{\iint E_{\mathrm{MM'}}(\omega,\omega')\exp(-\beta E_{\mathrm{MM'}}(\omega,\omega'))d\omega d\omega'}{\iint \exp(-\beta E_{\mathrm{MM'}}(\omega,\omega'))d\omega d\omega'} \tag{3}$$

where $E_{\mathrm{MM'}}(\omega,\omega')$ is the microscopic interaction energy between the M and M′ species that are placed with a certain separation at the orientations ω and ω' and $d\omega = d\chi \cdot d\phi \cdot d\theta \sin\theta$.

For all initial configurations in the present model for a single molecule diffusion, a solute molecule (L) is always located at the center of the 2D (100 × 100) tetragonal lattice sites and solvent molecules (S) are filled on the other 9999 lattice sites. For the MC procedure, each configuration was generated by replacing a species on a lattice site, which is selected in order, with one of its four 1stNN sites (● in Fig. 1a). This procedure was originally proposed by Kawasaki, to conserve the order parameter for the Ising spin systems [8].

Similarly in the 2D KLM, we can easily extend Eqs. (1) and (2) to the 3D form. The effective interaction hamiltonian takes the following form similar to Eq. (1):

$$H_{\mathrm{Int}} = \frac{1}{2}\sum_{i,j,k,I,J,K} \mathbf{s}^{t}_{ijk}\mathbf{J}\mathbf{s}_{IJK}. \tag{4}$$

Here, $\mathbf{J}$ $(= \mathbf{J}^{t})$ is the interaction matrix defined as a sum of the 1stNN, 2ndNN, and 3rdNN interactions, *i.e.*, $\mathbf{J}^{(1)}$, $\mathbf{J}^{(2)}$ and $\mathbf{J}^{(3)}$:

$$\begin{aligned}
\mathbf{J} &\equiv \mathbf{J}^{(1)} + \mathbf{J}^{(2)} + \mathbf{J}^{(3)} \\
&\equiv \begin{pmatrix} J^{(1)}_{\mathrm{LL}} & J^{(1)}_{\mathrm{LS}} \\ J^{(1)}_{\mathrm{SL}} & J^{(1)}_{\mathrm{SS}} \end{pmatrix} \cdot (\delta_{Ii}\delta_{Jj}\delta_{Kk\pm1} + \delta_{Ii}\delta_{Jj\pm1}\delta_{Kk} + \delta_{Ii\pm1}\delta_{Jj}\delta_{Kk}) \\
&\quad + \begin{pmatrix} J^{(2)}_{\mathrm{LL}} & J^{(2)}_{\mathrm{LS}} \\ J^{(2)}_{\mathrm{SL}} & J^{(2)}_{\mathrm{SS}} \end{pmatrix} \cdot (\delta_{Ii}\delta_{Jj\pm1}\delta_{Kk\pm1} + \delta_{Ii\pm1}\delta_{Jj}\delta_{Kk\pm1} + \delta_{Ii\pm1}\delta_{Jj\pm1}\delta_{Kk}) \\
&\quad + \begin{pmatrix} J^{(3)}_{\mathrm{LL}} & J^{(3)}_{\mathrm{LS}} \\ J^{(3)}_{\mathrm{SL}} & J^{(3)}_{\mathrm{SS}} \end{pmatrix} \cdot \delta_{Ii\pm1}\delta_{Jj\pm1}\delta_{Kk\pm1},
\end{aligned} \tag{5}$$

$\mathbf{s}^{t}_{ijk}$ denotes a 2D state vector on the site (i,j,k) on the 3D lattice (Fig. 1b), which takes also one of the two states, *i.e.*, (1 0) or (0 1), corresponding to the solute (L), or solvent (S) molecule, respectively.

In the same way as in 2D KLM, for all initial configurations, a solute molecule (L) is always located at the center of the 3D (30 × 30 × 30) cubic lattice sites (Fig. 1b) and solvent molecules (S) are filled on the other 26999 lattice sites. For the MC procedure, each configuration was generated by replacing a species on a lattice site, which is selected in order, with one of its six 1stNN sites (● in Fig. 1b).

For both 2D and 3D KLMs, under the periodic boundary condition, the Metropolis sampling scheme was executed for generating new configurations.

B. Relation between MC Step and Real Time

For introducing the relation between an MC step and real time-scale, first, by combining Stokes' low [9, 12],

$$f = 6\pi c\eta \tag{6}$$

and Einstein's relation [10, 12],

$$f = k_B T/D, \tag{7}$$

the diffusion coefficient D for a solute molecule was evaluated by

$$D = k_B T/6\pi c\eta. \tag{8}$$

Here, in Eq. (6), f is the friction coefficient, c is the radius of a spherical solute molecule and η is the coefficient of viscosity of solvent [12, 13]. Equation (6) holds under the approximation that Reynolds number

$$R = cu/v \tag{9}$$

is not too large, where u is the solute velocity and v is the dynamic coefficient of viscosity as follows,

$$v = \eta/\rho \tag{10}$$

ρ denoting the density of solvent [13]. In more realistic cases, the shape of solute molecule may also be elliptical [12]. In these cases, f should be scaled properly according to the ratio of the long axis to the short axis. When 2a and 2b are the lengths of the long and short axis, respectively, c in Eq. (6) should take $(ab^2)^{1/3}$ for an oblate ellipsoid and $(a^2b)^{1/3}$ for a prolate ellipsoid. Further, for example, if the ratio (a/b) is 2, a corrected f can be obtained as a product of a correction coefficient 1.04 and f by Eq. (6) [12]. In Eq. (7), k_B is the Boltzmann constant and T is the absolute temperature.

On the other hand, as Einstein developed in his famous paper for Brownian motion [10], the diffusion constant D can be connected to MSD of the Brownian particle [10]. The equation is now called Einstein's formula. Therefore, second, for estimating the diffusion constant D in another way, the MSD for the one solute molecule in the solvent is calculated *via* MC simulations. It should be noted that, when only one solute is immersed in solvent, all the generated configurations are accepted in the Metropolis method. Finally, by using Einstein's formula in the 2D case [10],

$$D = \lim_{t\to\infty} \frac{1}{4t} \langle |\mathbf{r}(n_{\mathrm{MC}}) - \mathbf{r}(0)|^2 \rangle, \tag{11}$$

the effective time-scale per a 1 MC step, *i.e.*, t_{MC}, can be estimated by equating in Eq. (11) with that in Eq. (8), as follows:

$$t_{\mathrm{MC}} = \frac{t}{n_{\mathrm{MC}}} \tag{12a}$$

$$= \frac{\langle |\mathbf{r}(n_{\mathrm{MC}}) - \mathbf{r}(0)|^2 \rangle}{d \cdot D} \tag{12b}$$

$$= \frac{\langle \mathbf{r}(n_{\mathrm{MC}}) - \mathbf{r}(0)|^2 \rangle}{d \cdot k_B T / 6\pi c \eta} \tag{12c}$$

with the dimensional factor d equal to 4. For the 3D case, the following relation should be used instead of Eq. (11),

$$D = \lim_{t\to\infty} \frac{1}{6t} \langle |\mathbf{r}(n_{\mathrm{MC}}) - \mathbf{r}(0)|^2 \rangle \tag{13}$$

and d must be equal to 6 for Eq. (12c).

3. RESULTS AND DISCUSSION

The effective time-scale per 1 MC step was estimated for 11 temperatures in the range of 273.15–413.15 K. The coefficient of viscosity of toluene in the range of 0.768–0.199 kg·m^{-1}·s^{-1} [14] was used as η in Eq. (6) accordingly at each temperature, as shown in Table I. In order to determine the lattice constant in both 2D and 3D KLMs, the radius of toluene was estimated using the GAUSSIAN94 program package [15]. After geometry optimization was done at the HF/6-31G* level, the radius of toluene was then obtained to be 4.0 Å with the VOLUME keyword. Consequently, the lattice constant was taken to be 8 Å, which is twice the radius of toluene, for both 2D and 3D KLMs. The shape of the model solute molecule was presently assumed to be spherical and have a radius of 10 Å, which is larger than that of toluene.

The number of lattice sites in each side of the unit cell is 100 for the 2D model, and 30 for the 3D model, respectively. For each initial configuration in the MC runs, one spherical solute molecule was placed at the center of the unit cell surrounded by solvent molecules and the MC simulation was done under the KLM scheme. 100 independent simulations, which started from different initial random numbers, were performed for 10,000 MC steps. One MC step includes 10,000 ($= 100 \times 100$) configurations for the 2D model or 27,000 ($= 30 \times 30 \times 30$) configurations for the 3D model, respectively. For each simulation, the solute coordinate (i,j) for the 2D KLM and (i,j,k) for the 3D KLM, were stored at every 100 MC steps, taking the effect of the periodic boundary condition into consideration. Using these coordinates, the MSD of the solute position was calculated at every 100 MC steps for a range of 0-10000 MC steps.

In Figure 2, the MSD of the solute molecule whose radius is 10 Å, is plotted for the MC step for the 2D model. It is found that the MSD increases linearly in proportion to the MC step. The MSD per 1 MC step (Eq. (12)) can be obtained from the slope of the plot. Then, the least square fitting was applied and the slope was calculated to be 122.24 ($Å^2$/MC step). On the other hand, in Figure 3, shown is the MSD plot for the solute molecule in the 3D model. A linear increase of the displacement is also found and it leads to the slope, 139.15 ($Å^2$/MC step), obtained also from the least square fitting, which is almost similar to that in the 2D model, *i.e.*, 122.24 ($Å^2$/MC step).

In Table I, those effective time-scales per 1 MC step for both 2D and 3D models, t_{MC}, are tabulated for 11 temperatures (from 273.15 to 413.15 K) in the third and fourth lines, respectively. The coefficients of viscosity of toluene [14] and estimations of diffusion constant by Eq. (8) are also listed at the first and second lines, respectively. In the present models where the only one solute is solvated in the cell, all the generated configurations are accepted in the Metropolis method. Consequently, it must be noticed that the displacement of the solute should not be influenced explicitly by the

TABLE I The coefficient of viscosity of toluene[14)], the calculated diffusion coefficients, and the calculated time-scales t_{MC} corresponding to 1 MC step in the 2D or 3D model at various temperatures

T (/K)	273.15	283.15	293.15	303.15	313.15	323.15	333.15	353.15	373.15	393.15	413.15
η (/kg · m^{-1} · s^{-1})	0.768	0.667	0.586	0.522	0.466	0.420	0.381	0.319	0.271	0.231	0.199
D (/10^{-10} m^2 · s^{-1})	2.61	3.11	3.66	4.25	4.92	5.64	6.40	8.11	10.1	12.5	15.2
t_{MC} (/10^{-10} s) (2D)	11.7	9.83	8.34	7.18	6.21	5.42	4.77	3.77	3.03	2.45	2.01
t_{MC} (/10^{-10} s) (3D)	8.90	7.46	6.33	5.45	4.71	4.12	3.62	2.86	2.30	1.86	1.53

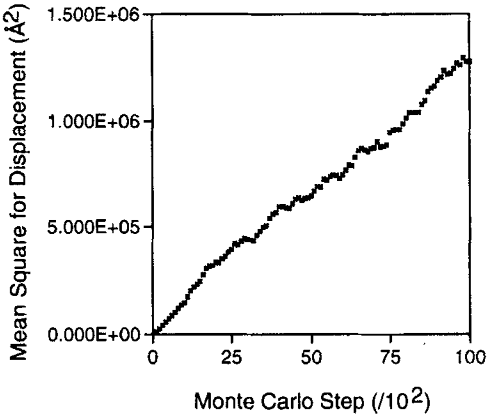


FIGURE 2 The plot of the mean square displacement (Å^2) for the solute molecule for the 2-dimensional lattice. 1 MC step = 100 x 100 = 10,000 configurations.

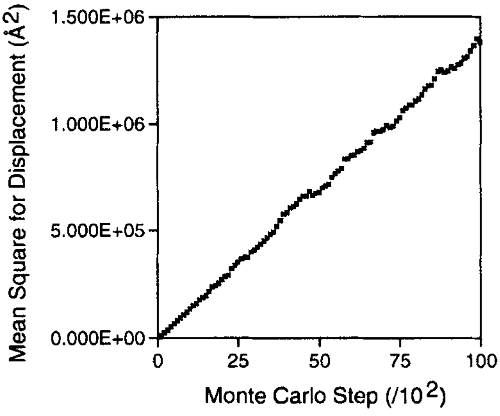


FIGURE 3 The plot of the mean square displacement (Å^2) for the solute molecule for the 3-dimensional lattice. 1 MC step = 30 x 30 x 30 = 27,000 configurations.

temperature that is set up for the MC simulation and then the results are just influenced indirectly through T and in Eq. (8). Therefore, the slope from Figure 2 or 3 was always used for calculating the effective time-scale corresponding to 1 MC step at each temperature. Those time-scales for the 3D model are found to be slightly shorter than the corresponding 2D ones. This difference is attributed to the difference in Eqs. (11) and (13). However, strictly speaking, since Stokes' law, Eq. (6), is correct only for the 3D model and if the correct "Stokes' law" in the 2D model can be replaced in Eq. (8), the difference could disappear by cancellation of the dimensional differences in Eqs. (11) and (13) and those in Stokes' law, and then a unique time-scale might be obtained in no relation to the dimensionality.

Incidentally, for both the model systems, the effective time-scales corresponding to 1 MC step become shorter as the temperature increases. From the viewpoints of fundamental laws of physics, this is a reasonable observation because the motion of a solute molecule should become more extensive as the temperature, namely, the kinetic energy per one degree of freedom, increases. As an example of such observation, two typical numerical realizations are shown in Figure 4, where the loci of the solute molecule for the same time duration of 6.33×10^{-8} s are depicted at two temperatures, (a) 293.15 and (b) 413.15 K. As listed in Table I, the effective time-scale corresponding to 1 MC step at 293.15 K is 6.33×10^{-10} s, which is about 4 times longer than that at 413.15 K (*i.e.*, 1.53×10^{-10} s). As a result, whereas 100 MC steps correspond to the time duration of 6.33×10^{-8} s at 293.15 K, 414 MC steps can be updated for the same time duration at 413.15 K. Thus, Figure 4 has clearly demonstrated that the solute can move more frequently and extensively at a higher temperature. It should be noticed that all the time-scales listed are found almost in the same order of 100 ps. Namely, it means that the present KLM can treat suitably the dynamic motion of molecules occurring in or over such a time scale as 100 ps in this temperature range. This order of time is much longer than that treated in usual MD simulations.

Therefore, it should be noted that our KLM scheme can be applied to the situation where a number of solute molecules diffuse in solvent at the same

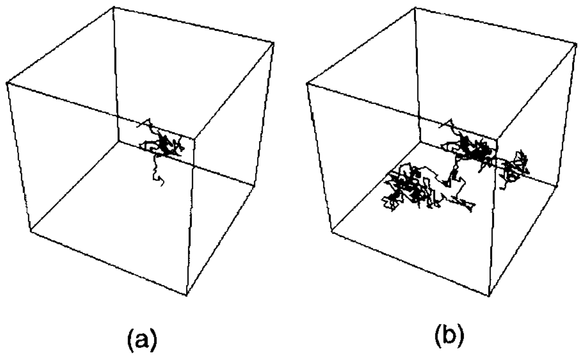


FIGURE 4 The plot of loci of the solute molecule for the 3D lattice, for the constant time interval of 6.33×10^{-8} sec at 293.15 and 453.15 K; (a) 293.15 K (100 MC steps); (b) 413.15 K (414 MC steps). Each side of the boxes is 240 Å.

time. In this case, the interaction between solute and solvent molecules should be considered explicitly since a lot of generated configurations can be rejected within the Metropolis sampling scheme. The research in this direction is now in progress [16].

4. CONCLUSIONS

In the present article, we have proposed and constructed, for the first time, the KLM scheme where the slow dynamics of chemical systems can be treated in the MC simulation. In the present KLM scheme, the effective time-scale per 1 MC step was introduced and the diffusion motion of a solute molecule in solution was discussed. Further, for both the 2D and 3D models, time-scales were estimated and the diffusion processes are simulated for a relatively long time. One MC step was found to correspond to the time-scale of 100 ps if one spherical solute molecule with a radius of 10 Å shows diffusion in solvent with the coefficient of viscosity of toluene. This indicates that KLM can deal with the molecular motion occurring through a longer time range than usual MD simulations.

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References

[1] Miyashita, S., Imada, M. and Takayama, H. Eds. (1991). *Computational Approaches in Condensed-Matter Physics*, Springer-Verlag, Berlin.

[2] Nagaoka, M., Suenobu, K. and Yamabe, T., "Kinetic Lattice Model for Long-Time Phenomena: Crystal Resolution Dynamics of Racemate in Solution", in preparation.

[3] Jacques, J., Collet, A. and Wilen, S. H. (1994). *Enantiomers, Racemates, and Resolutions*, Krieger Publishing Co.: Malabar, FL.

[4] Kimoto, H., Saigo, K. and Hasegawa, M. (1990). "The Potential Energy Calculation for Conglomerate Crystals", *Chem. Lett.*, pp. 711–714.

[5] Heermann, D. W. (1990). *Computer simulation methods*, 2nd ed., Springer-Verlag, Berlin.

[6] Binder, K. and Heermann, D. W. (1992). *Monte Carlo Simulation in Statistical Physics*, 2nd rev. ed., Springer-Verlag, Berlin.

[7] Ogita, N., Ueda, A., Matsubara, T., Matsuda, H., Yonezawa, F. (1969). "Computer Simulation of Order-Disorder Phenomena", *J. Phys. Soc. Jpn.*, **26**, 145–149.

[8] (a)Kawasaki, K. (1966). "Diffusion Constants near the Critical Point for Time-Dependent Ising Models. I", *Phys. Rev.*, **145**, 224–230; (b) Kawasaki, K., (1972). "Kinetic of Ising Models" In: *Phase Transitions and Critical Phenomena*, Vol. 2, Domb, C. and Green, M. S. Eds., Academic Press, pp. 443–501.

[9] Stokes, G. G. (1851). "On the effect of the internal friction of fluids on the motion of pendulums", *Trans. Camb. Phil. Soc.*, **9**, 8–106.

[10] Einstein, A. (1905). "Über die von der molekular kinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen", *Ann. Phys.*, **17**, 549–560.

[11] Salem, L., Chapuisat, X., Segal, G., Hiberty, P. C. and Minot, C., Leforestier, C. and Sautet, P. J. (1987). "Chirality Forces", *J. Am. Chem. Soc.*, **109**, 2887–2894.

[12] Atkins, P. W. (1990). *Physical Chemistry*, 4th ed., Oxford University Press.

[13] Landau, L. D. and Lifshitz, E. M. (1987). *Fluid Mechanics*, 2nd ed., Pergamon Press.

[14] The Chemical Society of Japan, *Kagaku Binran Kisohen II*, 4th rev. ed., Maruzen (1993).

[15] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T. A., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C. and Pople, J. A. (1995). *Gaussian 94* (Revision C.3), Gaussian, Inc., Pittsbrugh PA.

[16] Nagaoka, M., Suenobu, K. and Yamabe, T., in preparation.