

Simulation for memory effect of Fick's first law[†]

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Abstract. The memory effect of the Fick's first law, expressed by $\tau(\partial J/\partial t) = -J - D\text{grad}c$, was confirmed by means of the 3D Monte Carlo simulation, where τ is the relaxation time, J is the flux of the diffusing particles, D is the diffusion coefficient, and c is the concentration of the particles. The delay has been observed by chronoamperometry at a pair electrode. It behaves as if it were due to a slow electron transfer reaction. A diffusion model was composed of two cubic cells with different volumes in contact with each other by their faces, which worked as the boundary for the flux. Each cell contained one diffusing particle and solvent molecules for a given concentration. The particle moved randomly in the 3D lattice until it traversed the boundary. The number of the random steps before the traverse was equivalent to the relaxation time. It was proportional to ca 2/3 powers of the number of solvent molecules or was inversely proportional to 0.63 powers of the concentration. The relaxation time was roughly equivalent to the lapse of taking for the particle to visit every lattice site impartially.

Keywords. Fick's first law; memory effects; relaxation time; second sound; Monte Carlo simulation.

1. Introduction

Diffusion is a spontaneous, irreversible process of smoothing a sharp concentration variation.¹ It is expressed by the Fick's first law, $J = -D\text{grad}c$, where J is the flux of the diffusing particle, D is the diffusion coefficient and c is the concentration. The Fick's first law states that the flux should be simultaneously caused by the concentration gradient. The gradient is a cause while the flux is an effect. An effect does not take place generally until a cause.² This logic leads to the prediction that the flux is followed by the gradient with a delay. The simultaneous occurrence of the flux and the gradient in the Fick's law may be an approximation for a long term response. The approximation has been challenged theoretically and been resolved by the concept of the second sound or the memory effect in the field of heat transport.^{3–5} The concept was applied to the electrochemical diffusion problem⁶ to propose the form of $J(\tau + t) = -D\partial c(t)/\partial x$, which included the relaxation time, τ . This equation can be reduced to after the Taylor expansion

$$\tau(\partial J/\partial t) = -J - D(\partial c/\partial x). \quad (1)$$

The relaxation time was measured by chronoamperometry at a pair electrode as a delay of the

propagation from the conventional diffusion to be of the order of 1 ms.⁷

Now we consider a physical meaning of the delay by exemplifying 1 mM diffusing species in water. The molar ratio of the diffusing species to water is 1/55,500. We define the cell as an assembly of one diffusion molecule + 55,000 water molecules. When the diffusing molecule finds that neighbouring cells have lower concentrations than its concentration, it begins to diffuse toward the lower concentration cell. In other words, the onset of diffusion requires comparison of concentrations at neighbouring cells for the diffusing molecule. The comparison is not completed at least until the molecule collides with 55,500 water molecules in the cell. Therefore, the flux may be delayed by the collision period. This prediction agrees with the observation that lower concentrations have revealed longer delays.⁷

This report is devoted to modelling of the memory diffusion of one Brownian particle, to carrying out Monte Carlo (MC) simulation, and to estimating a quantitative relation between τ and the concentration. Monte Carlo simulation has recently been applied to voltammetric study on diffusion,^{8,9} adsorption associated with inter-molecular interactions,^{10–12} propagation in polymer,^{13–16} and metal deposition.^{17–20} It plays a vital role in estimating random behaviour of diffusion, accidental adsorption, and catastrophic crystal growth.

[†]Dedicated to the memory of the late Professor S K Rangarajan

2. Model and MC process

The diffusion model was a cubic cell, which contains one diffusing molecule. Location of the molecule is restricted to at a site of the grid of the cubic lattice. The other sites in the cell were occupied by solvent molecules (figure 1(a)). The use of the 3D-lattice structure allowed us to carry out digitally random walk to reduce the computation time. Another square pillar cell (b) in figure 1 came in contact with the cubic cell (a), forming the interface through which the molecules passes by random walk to yield the flux.

A molecule was located initially at arbitrary site of the lattice in each cell. It was transported randomly in the x -, y -, z -direction step-by-step. The number of steps, m , was counted until the molecule traversed the interface. The number of steps multiplied by the period of each step, t_{step} , is equivalent to the relaxation time, $\tau = mt_{\text{step}}$. Figure 1 shows examples of trajectories for $m = 6$ by the zigzag arrows. The boundaries of the cell normal to the interface had periodic conditions for the transport, i.e. the particle traversing the boundary came into the cell from the opposite boundary. The upper and the lower boundaries parallel to the interface worked as a reflection wall.

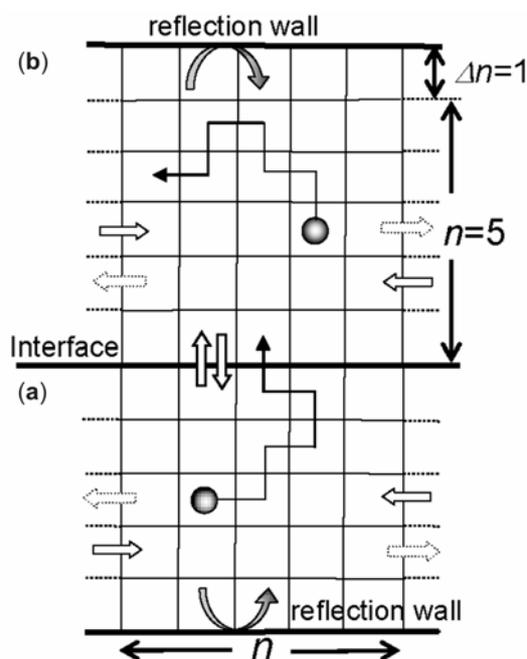


Figure 1. Diffusion domains composed of two lattice cells, A and B, between which the cell interface is present. Each cell has a diffusing particle, which moves randomly in the lattice step-by-step.

The above procedure was carried out by the Monte Carlo simulation with a personal computer of 3.2 GHz cpu. Controlled variables were the number of the grids, n , on the side of the cubic cell A, the number of the extra grids of the longer side, $n + \Delta n$, of the square pillar cell B, and the number of the MC iteration, K . An example of the value of n is $(55.5 \text{ M}/1 \text{ mM})^{1/3} = 38$ at $c = 1 \text{ mM}$ of the diffusing species in water solvent. Values of Δn were 1 or 2. The output variables were the total number of the traverse from cell A to B, j_{AB} , that from B to A, j_{BA} , and the number of steps, m , until the particle traverses the interface. The normalized and net flux is given by

$$J = (j_{AB} - j_{BA}) / (j_{AB} + j_{BA}). \quad (2)$$

3. Results and discussion

Values of m were obtained for $10 \leq n \leq 60$ at the maximum iterative run of 15000. For example, the maximum value of m was 1642 at $n = 20$, corresponding to 1642/20 times going back and forth in average within the cell before traversing the interface. The minimum value of m was 1, that occurred when the particle initially located next to the interface traverses the interface by just one step. Longer trajectories (large m) occurred less frequently. We define the frequency, $f(m)$, as the number of the trajectories with m steps. For example, a data set of $m = 5, 4, 9, 4, 5, 4$ gives $f(4) = 3$, $f(5) = 2$ and $f(9) = 1$. The frequency is equivalent to the probability of causing the traverse (flux) for a given m ,

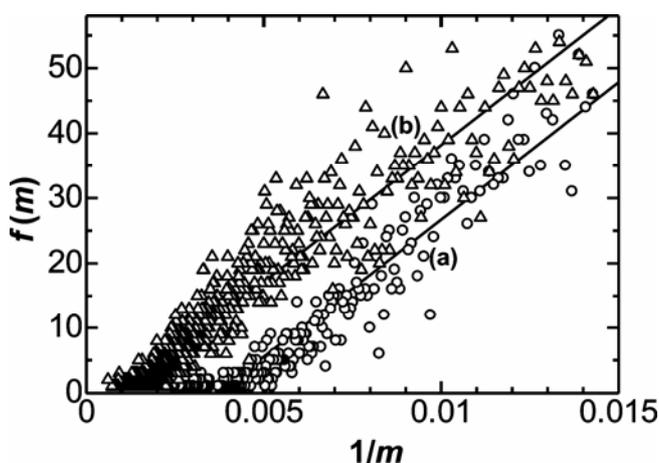


Figure 2. Variations of the frequency of the flux with the inverse of the number of steps reaching the interface for $n =$ (a) 10 and (b) 20. The y -axis corresponds to J , whereas the x -axis does to $-\partial J / \partial t$.

e.g. $2/(2+2+1)$ at $m=2$. According to the definition of m , the period of terminating the trajectory for one unit flux ($j_{AB} = 1$ or $j_{BA} = 1$) is equivalent to m . Thus $\partial J/\partial t$ or $\Delta J/\Delta t$ should be proportional to $1/m$ because of $|J| = 1$ and $t = mt_{\text{step}}$. The plot of f against $1/m$ may be approximated as the plot of J against $-\partial J/\partial t$ in (1). Figure 2 shows this plot for $m > 60$ at two values of n . Linear variations hold, indicating the validity of (1). The large scatter is due to the characteristics of MC simulations. The slope is proportional to τ , according to (1). The shift of curve (b) from (a) is ascribed to the different values of $\partial c/\partial x$.

We denote by m_{av} a value of m averaged over the number of the MC iteration (K), and plotted m_{av} against n on the logarithmic scale in figure 3. A linear relation was found, suggesting $m_{\text{av}} = 0.45 n^{1.9}$ for $n > 10$. In order for the diffusing molecule to recognize concentrations not only in its own cell but also in both neighbouring cells, $0.45(3n)^{1.9}$ steps are needed. Thus we have

$$\tau = 0.45(3n)^{1.9} t_{\text{step}} = 3.6 n^{1.9} t_{\text{step}}. \quad (3)$$

Combination of (3) with the proportionality of n with $c^{-1/3}$ states that τ should decrease with an increase in the concentration, obeying the relation $\tau = 3.6L^{-1.9}c^{-0.63}t_{\text{step}}$. This tendency has been demonstrated experimentally in the measurement of propagation times at the pair electrode.⁷ When the recognition process is not taken into account ($n = 1$ in (3)), the relaxation time can be of the order of pico second.²¹ If the diffusion domain is assumed to

be limited to a one-dimensional space, the relaxation time may be very short.

We estimate τ approximately from (3) under the chronoamperometric conditions, taking into account the concentration-variation in the diffusion layer. The period, t_{step} , of stepping a distance, $L = 0.3$ nm, between two closest neighbouring solvent (water) molecules is given by $0.3 \text{ nm} = (Dt_{\text{step}})^{1/2}$. Then we obtain $t_{\text{step}} = 0.1$ ns for $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. We use the conditions of 1 mM bulk concentration of the redox species and the thickness of the diffusion layer, $\delta = 10 \mu\text{m}$, which corresponds to 0.1 s electrolysis. Then one redox molecule in the bulk lies in a solvent cube, the side length of which is $a = 11.8$ nm (from $10^{-3} N_A/10^3 \text{ cm}^3 = a^{-3}$ for the Avogadro constant, N_A). We assume that the concentration of the redox species by potential step chronoamperometry varies linearly from zero at the electrode to the bulk value. Then the concentration at a position x from the electrode is given by $(1 \text{ mM})(x/\delta)$. The integration from $x = 0$ to b becomes $(1 \text{ mM})(b^2/2\delta)$. The number of the redox molecules contained in the volume a^2b is $(10^{-3} N_A/10^3 \text{ cm}^3)(a^2b^2/2\delta)$. The unit cell can be defined as the volume in which this number becomes unity. The value of b for the unit cell is $0.49 \mu\text{m}$, which is equivalent to $n = 1600$ by dividing by L . Inserting the values of n and t_{step} into (3), we obtain $\tau = 0.9$ ms. This value is in the ranges (0.05–1.05 ms) obtained from chronoamperometry at the pair electrode.⁷

Figure 4 shows variations of the net flux with K (number of the iterative runs). Fluctuation of the flux for $K < 2000$ was large because the difference

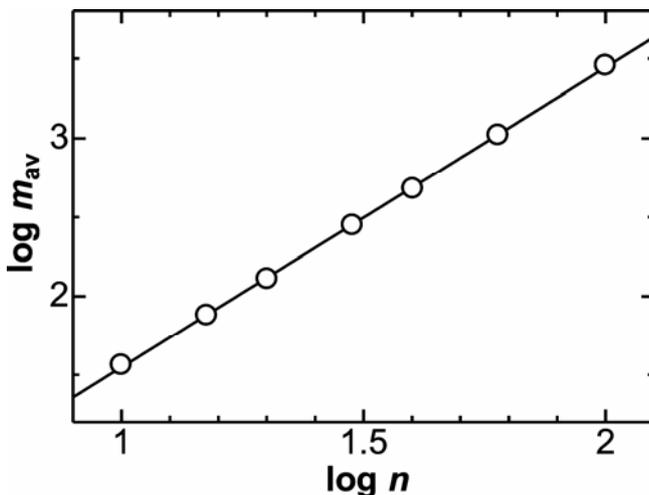


Figure 3. Logarithmic variations of the averaged m with n .

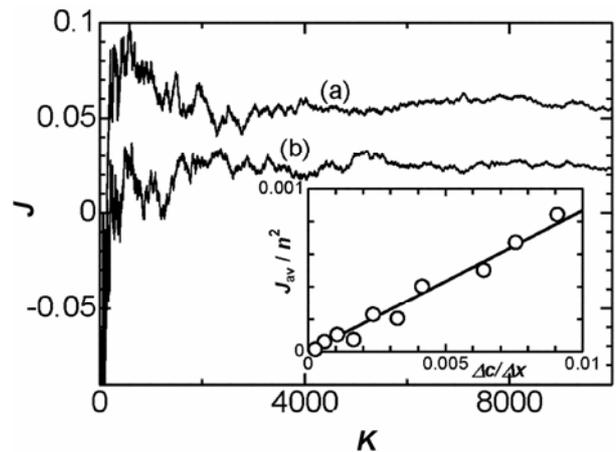


Figure 4. Convergence of J with the increase in K for $n =$ (a) 15 and (b) 40 at $\Delta n = 1$. The inset is the dependence of thus obtained J_{av} on $\Delta c/\Delta x$.

between j_{AB} and j_{BA} for small values of j_{AB} and j_{BA} was emphasized to J (see (2)). Since K increases both j_{AB} and j_{BA} , the fluctuation decreases, and the flux reaches the average value, J_{av} . The flux per area L^2 was plotted against the concentration gradient, $\Delta c/\Delta x$ in the inset of figure 4, where the gradient was evaluated from $n^{-3}-n^{-2}(n+\Delta n)^{-1}$. The averaged or long term flux was proportional to the gradient, implying the conventional Fick's first law.

When a molecule passes through the interface, a cell gains or loses the molecules by thermal fluctuation. According to the theory of the fluctuation of numbers 22, $N^{1/2}$ particles are fluctuated in a cell containing N particles. Therefore, a cell containing nominally one molecule has actually zero, one or two molecules. A cell containing less than one molecule becomes substantially larger than the cell with n^3 solvent molecules in the bulk. The cell size might get infinity for zero-particle. Therefore, an actual value of n may be larger than that in (3).

The present approach contains limitations of (i) equi-volume of the diffusion particle and solvent molecules, (ii) the lattice structure of the diffusion space, and (iii) a loss of consideration of a depleted concentration in the diffusion layer for the MC simulation. Limitation (i) cannot be neglected for diffusion of (ferrocenylmethyl) trimethylammonium ion (FcTMA) in water,⁷ in which diffusion coefficients of FcTMA range from 0.69 to $0.75 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$,^{7,22} and that of water is $2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.²³ According to the Stokes–Einstein's relation, the ratio of the diameters of the two molecules is 3 times. Therefore, it is not appropriate to discuss in detail the agreement of the experimental values of τ with the simulated one. Although the lattice structure is invalid in liquid (limitation (ii)), it can provide a suitable hint to estimate experimental results. Extension of the lattice model to a spatially continuous MD simulation belongs to future work. A solution of limitation (iii) needs extremely large computation time, and will be realized in connection with MD simulation.

It is well known that diffusion is caused microscopically by random walk, regardless of recognition of concentration for a diffusing particle. For example, the existing probability of a diffusing particle at x and $t + \Delta t$ is a sum of the probability at $(x + \Delta x, t)$ with the left step by Δx for Δt , and that at $(x - \Delta x, t)$ with the right step by Δx , i.e.

$$p(x, t + \Delta t) = \{p(x + \Delta x, t) + p(x - \Delta x, t)\}/2, \quad (4)$$

where a half means the equi-probability of going to the positive or the negative step by Δx . The Taylor expansion of (4) around (x, t) yields the Fick's second law, $\partial p/\partial t = D(\partial^2 p/\partial x^2)$ for $D = (\Delta x)^2/2\Delta t$. Equation (4) includes no delay or no concept of recognition of concentrations. This is because the probability is an averaged result just by calculation without the experience of collisions with solvent molecules which can give rise to diffusion.

4. Conclusion

The linear variation of $\partial J/\partial t$ with J in (1) was demonstrated to be valid by the variation in figure 2 which was carried out by MC simulation. The point is the presence of the intercept in the linear relation of f or J with $1/m$ or $-\partial J/\partial t$ as the delay. The delay term, $\tau(\partial J/\partial t)$, is caused by the drift of the diffusing molecule in the cell before the molecule traverses the interface. The number of steps of the drift was proportional to $n^{1.9}$ or $c^{-0.63}$. The delay is more remarkable for lower concentrations. The relaxation time estimated from both the simulation and the depleted concentration in the diffusion layer was close to the experimental values by chronoamperometry.

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