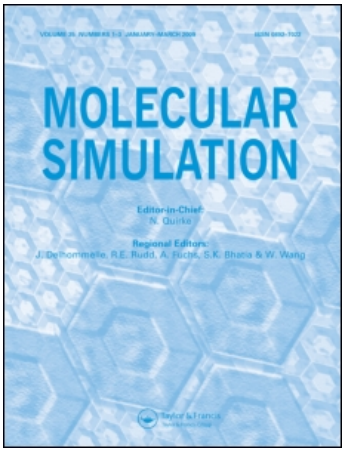

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Simulation of Restricted Self-diffusion

L. Coppola[a]; S. Di Gregorio[a]; G. A. Ranieri[a]; G. Rocca[a]
[a] Dept. of Chemistry, Dept. of Mathematics, University of Calabria, Italy

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SIMULATION OF RESTRICTED SELF-DIFFUSION

L. COPPOLA, S. DI GREGORIO, G.A. RANIERI and G. ROCCA

Dept. of Chemistry, Dept. of Mathematics, University of Calabria, I-87036 Arcavacata di Rende (CS), Italy

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In this paper the simulation of restricted self-diffusion is developed using the formal support of Cellular Automata so that it is described as a local interactions based system with discrete time and space.

The main topic concerns the solvent self-diffusion in some lyotropic mesophases. In the model the lyotropic aggregates are assumed immovable, impenetrable and perfectly reflecting. The simulation data presented is in good accord with Pulsed Field Gradient NMR measurements. Finally the simulation results for motion restricted by single lamella are compared with those obtained by a purely theoretical investigation.

KEY WORDS: Self-diffusion, simulation, brownian motion, lyotropic mesophases.

1. INTRODUCTION

The self-diffusion in lyotropic liquid mesophases has been extensively studied by Pulsed Field Gradient Nuclear Magnetic Resonance (PFG–NMR) technique, to obtain information on the solvent "restricted motion" in organized structures [1]. This problem is important in elucidating transport processes occurring in systems of biological relevance (vescicles, liposomes, tissues, etc.).

In systems without thermodynamic gradients, the apparent self-diffusion coefficient, according to Brownian motion theory, can be defined through the relation:

$$D(t) = \langle r^2 \rangle / (6 \cdot t) \tag{1}$$

where $\langle r^2 \rangle$ is the particles mean square displacement and t is the observation time.

In an isotropic and unrestricted situation, the mean square displacement $\langle r_0^2 \rangle = n \cdot b^2$ defines a free self-diffusion coefficient through the relation [2]:

$$D_0 = n \cdot b^2 / (6 \cdot t) \tag{2}$$

where n is the number of impacts in the observation time and b^2 is the mean square distance between two subsequent impacts. This situation corresponds to a complete lack of correlation between individual impacts.

The solvent self-diffusion in lyotrophic mesophases is strongly restricted by ordered molecular aggregates with various shapes (lamellae, cylinders, ribbons etc.) arranged in randomly oriented domains.

The reduction in solvent mobility in these systems has been attributed to the structural obstruction according to different models. Such an effect is made manifest through comparing the completely free self-diffusion to the self-diffusion restricted by

obstacles; it is measured by:

$$f = \langle r^2 \rangle / (n \cdot b^2) \tag{3}$$

the so called "structural factor" with range between 0 (completely restricted self-diffusion) and 1 (free self-diffusion).

In restricted situation the term $\langle r^2 \rangle$, and so the self-diffusion, can involve many computational difficulties when we consider particular restrictions given by obstacles to the motion, whose geometrical shape effect can be hardly described in terms of differential equations.

According to the methodologies of the Computational Physics [3] we attempt, in this paper, a new approach using Cellular Automata (C.A.) as *formal* support in order to implement simulation algorithms: the aim is to provide a new tool for computing the values of $\langle r^2 \rangle$, and then f, in some lyotropic mesophases.

A Cellular Automaton (C.A.) can be seen as a d-dimensional space, the cellular space, partitioned into cells of uniform size, each one embedding an identical Moore elementary automaton (e.a.) [4].

Input for each elementary automaton is given by the states of the elementary automata in the neighbouring cells, where neighbourhood conditions are determined by a pattern invariant in the time/space and are equal for each cell.

At the time $t = 0$, the elementary automaton are in arbitrary states and the C.A. evolves changing state of elementary automaton at discrete times, according to the transition function of the elementary automaton.

C.A. capture the peculiar characteristics of systems which evolve exclusively according to the local interactions of their constituent parts, and have been used for modelling and simulating high complexity systems such as self reproducing machines, parallel computing, fluid-dynamics, and so on [3–5]; they guarantee computational universality, furthermore applied aspects have been widely investigated from a theoretical viewpoint.

The first simulations were performed for trivial cases in order to evaluate roughly the validation limits of such an approach; the second step considered well known but more complex cases and good results were obtained by introducing some secondary refinements; the last simulations concerned situations hardly tractable by standard approaches. Laboratory data fitted very well to the computer data and furthermore the visual control of the evolution of the simulated phenomenon gave useful suggestions as to the interpretation.

2. $A_{(\text{self-diffusion})}$

The main idea which led to the choice of the particular C.A. is the following: the unrestricted brownian motion, the self-diffusion motion can be described by the random displacement of particles in a regular d-dimensional lattice between contiguous sites; the computation is better approximated the smaller is the lattice distance compared to mean square displacement [7].

In our approach we follow the general methods of self-diffusion simulation developed by users of the C.A.M.6, the Cellular Automata Machine [3], with obvious differences suggested by the particularities of the problem and the computer implementation choices.

A bidimensional C.A. is adopted for the problem of restricted self-diffusion,

without loss of generality in spite of the spatial character of the phenomenon; each cell is a point of the bidimensional lattice, the neighbouring cells are the same cell and the lattice contiguous sites, giving a cross pattern.

Each elementary automaton state represents the physical conditions of a piece of "experimental environment" [3] and describes if there are particles to be moved, an obstacle or it is free and so on.

Of course it is wasteful to use all the particles in the simulation, so we consider a small number of "representative" ones enough to get meaningful data; in this context, in order to capture the evolution of the phenomenon, we need to consider only collisions of "representative" particles between themselves. The collisions of "representative" particles and other ones are implemented using a transition function, which introduces random changes of motion direction for the particles at each step and represents the collisions for each mean displacement.

The particle-obstacle interaction is described by "stopping" the particle in the cell; it is equivalent to bouncing back.

More precisely:

$$A_{(\text{self-diffusion})} = (R^2, S, B, \sigma)$$

where

— $R^2 = \{(x, y) \mid x, y \in N, 0 \leqslant x \leqslant L_x, 0 \leqslant y \leqslant L_y\}$ is the set of cells identified by the points with integer coordinates in the finite region, where the phenomenon evolves; N is the set of natural numbers.

— S is the finite set of states of the elementary automaton; it is specified by the two sets Phys and Prob. The former set Phys $= \{o, q, p_1, p_2, ..., p_s\}$ represents respectively the physical conditions obstacle, no particle or quiescent, one particle, two particles, ..., s particles; the latter set Prob $= \{$"up", "down", "left", "right"$\}$ represents the motion directions; $S = \{o, q\}\ Up_1 \cdot \text{Prob}\, Up_2 \cdot \text{Prob}^2\ U, ...,\ Up_s \cdot \text{Prob}^s$.

— $B = \{(0,0), (0,1), (1,0), (-1,0), (0, -1)\}$ is the pattern of neighbourhood, the so called von Neumann neighbourhood [3,4]. Neighbouring cells are the ordered set given by summing the vector (i, j) of the cell coordinates to the vectors of B in order.

— σ: $S^5 \to S$ is the state transition function and satisfies our introductory statements about brownian motion; a cell in the state obstacle doesn't change in the time; for cells in other states are determined the number of particle inside and directions at the next step according to the following rules:

a) all the particles in the neighbouring cells $(0, -1)$, $(-1, 0)$, $(0,1)$, $(1,0)$ with motion direction toward $(0,0)$ are counted,

b) if a neighbouring cell is in the state obstacle, the particles in the neighbouring cell $(0,0)$ with motion direction toward the obstacle are counted,

c) the number n, sum of the particles counted in a) and b), determines the substate $p_n \in$ Phys; a value of Prob is associated to each particle by a stochastic function.

The initial conditions of C.A. are specified giving substates "particle" in plane positions, where we want to be at the beginning particles to be diffused, giving substates "obstacle" in the plane positions, where we want to be obstacles, and giving "quiescent" substates otherwise.

3. SIMULATION RESULTS

In this paragraph are reported the numerical results of the structural factor simulation for the cases at lamellar and hexagonal mesophases. Similar results are also obtained experimentally by NMR diffusion technique.

Table 1 Results of simulations for different geometrical restrictions and comparison with experimental data. f, in the simulation data, are the tridimensional average value calculated by assuming f_z component equal to unity.

A: unrestricted motion.
B: ideal lamellar (repetition 30 · b).
C: ideal hexagonal (repetition 30 · b and diameter 20 · b).
D: lamellae containing holes. Holes are 10 % of the lamellar surface and randomly arranged but with repetition 40 · b.
E: lamellae containing holes. The amount of holes is as D case but their distribution is regular (stacked).
F: lamellae containing holes. Conditions as D case, but with repetition equal to 20 · b and regular distribution.

Restriction type	*Simulation data*			*Laboratory data*	*Refer.*
	f_x	f_y	f	f	
A	0.995	0.993	0.996	1	
B	1.022	0.005	0.657	0.66	[8]
C	0.657	0.611	0.762	0.75	[9]
D	0.915	0.212	0.709	-	[10]
E	0.915	0.221	0.707	-	[10]
F	0.921	0.291	0.737	-	[10]

Basic assumptions of the simulation model follow:

(a) the aggregates are immovable, impenetrable and reflecting, so that the self-diffusion is due only to motion of solvent phase.

(b) Lamellar and cylinder aggregates are infinite. Self-diffusion is assumed isotropic and non restricted along the z-axis.

(c) The simulation is carried only in the x, y-plane for long enough observation times.

The values of output parameters in simulation are $f_x = 2 \cdot \langle x^2 \rangle / (n \cdot b^2)$ and $f_y = 2 \cdot \langle y^2 \rangle / (n \cdot b^2)$ with $r^2 = x^2 + y^2$. Constant structural factors are observed at long enough observation time because the solvent has an opportunity to repeatedly sample all of the different environments.

Some values, approximated to the third digit and computed with 20000 molecules and $n = 20000$, are reported in Table 1 for different restriction conditions; f is the tridimensional averaged value calculated assuming $f_z = 1$.

Be aware that f is the unique parameter comparable to experimental measurements because all the lyotropic liquid crystals are arranged in random oriented domains.

At beginning we wanted to test the program and the random function without restriction and obtained correctly structural factor values next to unity. Subsequently we simulated ideal lamellar obstructions such as impenetrable walls parallel to x, z-plane and we obtained $f = 0.67$, in accordance with experimental results of the Potassium Palmitate and water mixture [8].

Simulations of structures composed by infinite cylinders arranged in hexagonal symmetry, as in Figure 1, offer the best accordance with the experimental results of the mean structural factor [9]: the results $f_x = 0.67$ and $f_y = 0.61$, give a little asymetry in the x, y-plane.

Finally imperfect lamellar structures with holes were considered and rather complex data were obtained; the results indicate that the structural factors depend strongly on distribution of holes in space. The lack of such structural data for

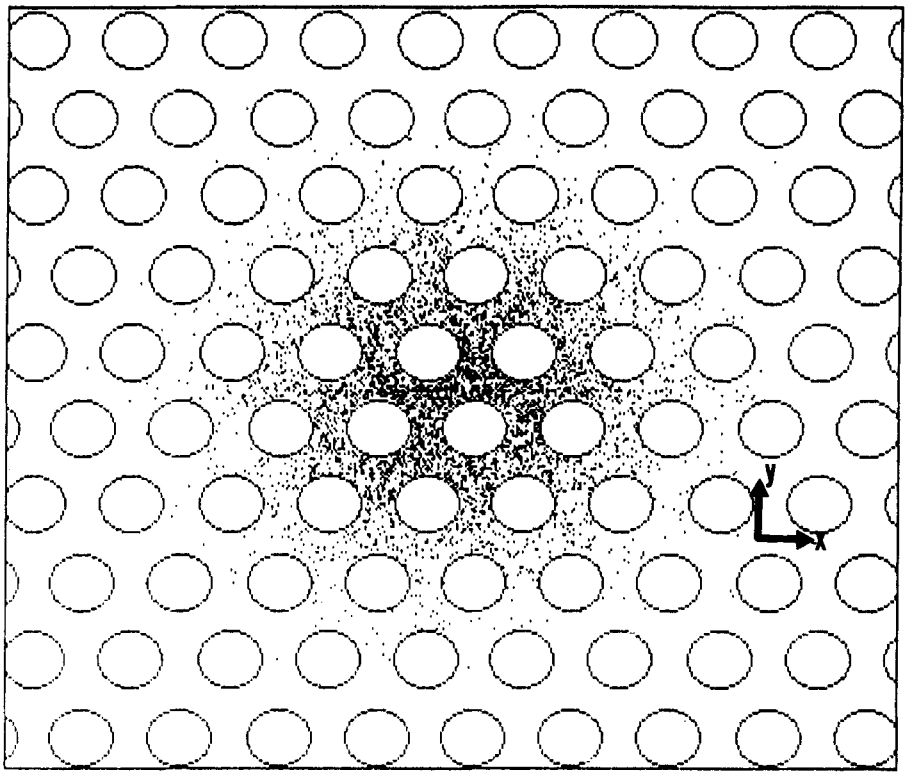

Figure 1 Simulation of particle self-diffusion in the x,y-plane for systems composed of infinitely long cylinders arranged in hexagonal arrays. The particles at the start are distributed randomly in cells, constituting the elementary structure of the lyomesophase, at the center of the figure. The z-axis is parallel to the cylinders.

fractured lamellar mesophases does not permit an immediate comparison between experimental and simulation data, but shows the incompleteness of the model produced in [10].

For a further validation of such results we analyzed the contribution to the obstruction of an ideal single lamella (Figure. 2); then we realized that self-diffusion in anisotropic systems may be described by effective reflexions of probability clouds, according to previous theoretical results [11,12].

In the bidimensional case the probability, that a particle arrives a distance r after n displacements with a reflecting barrier along y-axis at d distance, is given by:

$$W(r, n; d) = \frac{1}{A}\left[\exp - \frac{x^2 + y^2}{B} + \exp - \frac{x^2 + (y - 2d)^2}{B}\right] \quad (4)$$

with $A = \pi \cdot n \cdot b^2$ and $B = n \cdot b^2$.

Consequently the bidimensional mean square displacement can be obtained by:

$$\langle r^2 \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{u} (x^2 + y^2) \cdot W(r, n; d)\, dy\, dx \quad (5)$$

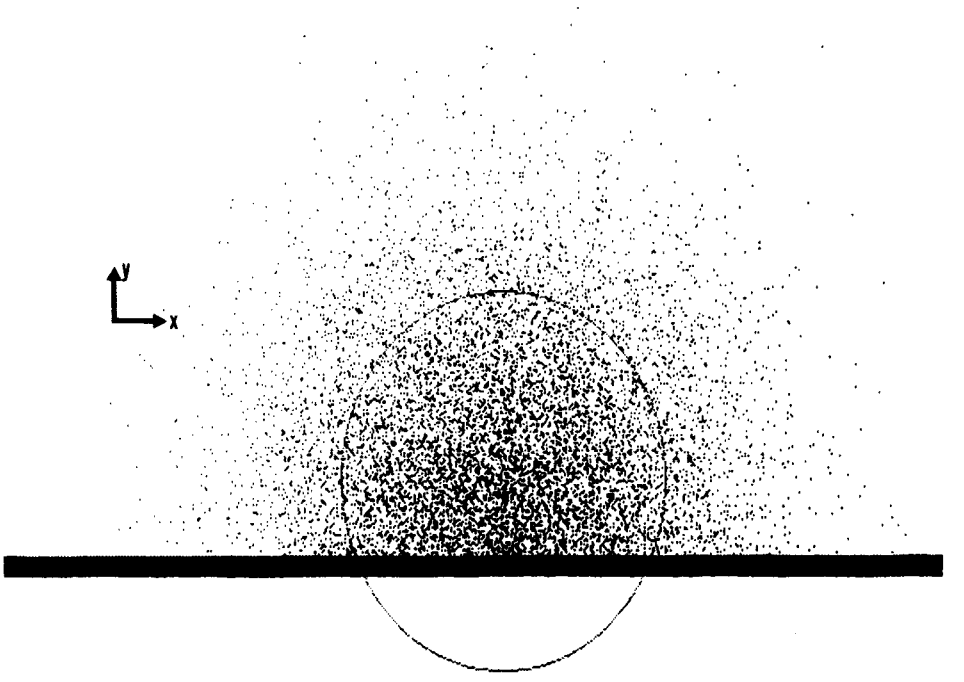

Figure 2 Simulation of particle self-diffusion in the x,y-plane having a reflecting wall parallel to the x-axis. All the particles start from a unique cell with distance d from the lamella; such a cell is the center of the circle with radius $n^{1/2} \cdot b$, the root mean square displacement in unrestricted conditions.

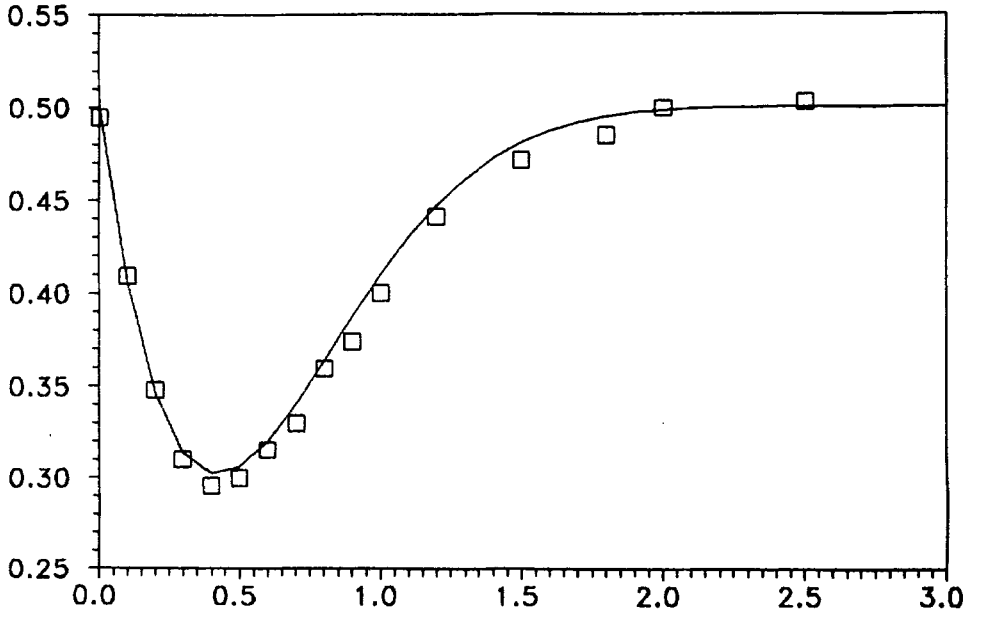

Figure 3 Plot of $f_y/2 = \langle y^2 \rangle / (n \cdot b^2)$ of Equations (4) and (6) versus $d/(n^{1/2} \cdot b)$. Full squares refer to values obtained from simulation in analogue restricted conditions.

The mean square displacement along y-axis is given by:

$$\langle y^2 \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{d} y^2 \cdot W(r, n; d)\, dy\, dx \tag{6}$$

Calculus of $f_y = 2\langle y^2 \rangle / (n \cdot b^2)$ through the previous formula and the corresponding simulation values are represented as functions of $d/(n^{1/2} \cdot b)$ in Figure 3; in this case all the particles start from unique cell with distance d from the lamella. The best agreement between theoretical and simulation results is shown clearly in this simplified case.

We are encouraged by this combination of results to generalize the validity of such a method to further cases, where an analytical approach appears intractable because of the great number of obstacles.

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