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# New techniques for modelling glass dissolution

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**Abstract**

Due to the large increase in computation power, new methods for modelling glass dissolution are becoming available. We give a short description of two classes of such methods. For each method, we first explain where it is based on, then we list existing applications in glass dissolution and finally, we discuss what it could provide to glass dissolution modelling. The first class of models consists of molecular modelling. These are methods with a solid mathematical basis, like ab initio calculations, molecular dynamics or Monte Carlo simulations. These methods are complementary, not only to one another but also to existing analytical or geochemical models, which will not become superfluous. Instead, one method can provide input for another method, either by calculating values or by confirming its basic assumptions. The second class of models consists of soft computing techniques like neural networks, fuzzy systems or genetic algorithms. These methods, which can be viewed as complementary to traditional methods, are more empirically based and can be useful for modelling systems that are ill defined or not completely understood yet.

## 1. Introduction

Reliable predictions of the corrosion behaviour of glasses in aqueous solutions or in disposal media can only be obtained by the combination of theoretical models and experiments. Up to now, almost all models used for predicting glass dissolution are: (1) analytical models, (2) geochemical models or (3) a combination of both. Due to the still increasing computation power in recent years, new modelling methods have become available. These methods, which are still barely used for modelling glass dissolution, will definitely lead to an enormous increase in what modelling can provide in understanding and predicting glass dissolution. In this paper, we will present some of these new modelling methods. For each method, we will explain: (1) what it is, (2) existing applications and (3) what it can provide to glass dissolution modelling.

Before presenting new modelling methods, we briefly reconsider the existing approaches. Extensive recent reviews of existing models are given in [1,2]. The first type consists of analytical models. Existing analytical models are based on the Grambow rate law [3] and/or diffusion. The basis of the Grambow rate law is that the glass dissolution rate is equal to the dissolution rate of the main glass component, silica. Next, the silica dissolution rate is supposed to be a linear function of the concentration of dissolved silica in solution so that (1) the rate is maximal when the silica concentration in solution is zero and (2) the rate is zero at the so-called 'silica saturation concentration'. To comply with experiments according to which the glass dissolution rate is not zero at silica saturation, one sometimes adds a constant rate (the so-called final saturation rate) to the Grambow rate law. In models like Lixiver [4,5] or the Grambow model [3], the Grambow rate law is combined with the diffusion of silica through a gel layer. Other models [6,7] join the Grambow rate law and sodium diffusion. A major advantage of analytical models is that they allow to make extrapolations to very long times. A problem is that the basic assumptions of these models are not always correct and that the model parameters are often obtained only by fitting (sometimes there is no independent way to

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measure them). Geochemical models (e.g., [8,9]) take into account most of the glass components. They describe glass dissolution as a function of a variable called 'reaction progress'. The major problem here is to link this variable with time. Traditional geochemical models also consider only lowest energy states, so they are not able to describe kinetics. Now, modern geochemical codes that are able to handle mixed kinetic and equilibrium problems exist. Assuming that the necessary input data are available, these codes can consider precipitation/dissolution reactions. Expressing the dissolution rate as a function of time is also impossible in thermodynamic models (e.g., [10–12]), that make predictions as a function of glass composition.

How do these models compare with experiments? Because (1) during glass dissolution several processes occur simultaneously and (2) the values of (at least) some model parameters are obtained by fitting, an experiment does not always allow to determine unambiguously which model is right. Two models, based on completely different basic assumptions can both lead to a good fit of the same dissolution data [1]. This indicates that one needs to be very careful with the interpretation of experimental results, which sometimes needs to be refined. As an illustration, after experiments by Chick and Pederson [13] there was a consensus that a protective layer does not develop on the glass surface. However, some years later, the same experiments for the same glass but with a higher (glass) surface to (solution) volume ratio, contradicted this [14]. Similarly, recent experiments [15–17] contradict the Grambow rate law. The major (long time) process for glass dissolution should be diffusion through the gel layer [15], which should not behave as a protective barrier only in the initial phase of the glass dissolution. The experimentally observed restructuring of the gel layer [18,19] can make it protective after some time. So, the value of macroscopic parameters like those of the Grambow rate law or a diffusion coefficient through the gel may change as a function of time. Summarising, there is still no complete consensus on the basic mechanisms of glass dissolution. Also the validity of the basic assumptions of the existing analytical models is still uncertain. There is only an agreement [2] that any model for glass dissolution should be consistent with transition state theory [20]. In this paper, we will introduce modelling methods, which allow testing the basic assumptions of the existing models. Those modelling methods can also address structure related factors (like silica condensation [19,21], a percolation transition [22,23] or the openness of the glass surface [24]) affecting glass dissolution, which cannot be taken into account in analytical or geochemical models.

Two classes of new modelling methods for glass dissolution will be presented. The first class consists of molecular modelling methods: (1) ab initio calculations, (2) molecular dynamics and (3) Monte Carlo simulations. These types of methods have a solid mathematical basis. They try to model the glass dissolution through a better understanding of the basic mechanism and more accurate representation of the process. The second class consists of soft computing methods. These methods are more empirically based and do not require a full mathematical description of the system. As an illustration, most skilled car drivers handle their car without knowing or solving the mathematical equations of car behaviour. Examples of such methods are neural networks, fuzzy systems and genetic algorithms. Soft computing methods are used for controlling many industrial processes (see [25] for some examples), including a nuclear reactor [26–28]. For some problems (e.g., [29]), soft-computing methods perform better than 'hard' computations. After the presentation of the new modelling methods, we explain in our conclusion how they can be integrated to obtain a better understanding, and possibly real predictive capacity, of glass dissolution.

## 2. Ab initio calculations

### 2.1. What is it?

The driving force for all chemical reactions is the interaction between the atoms in a system. If one knows the variation of the energy in a system as a function of the positions of the atoms, one can calculate the forces on the atoms. Therefore, one must solve Schrödinger's time-independent equation

$$H\psi = E\psi \tag{1}$$

with $H$ the Hamiltonian, $\psi$ the wave function and $E$ the eigenvalue (energy). In the Born–Oppenheimer approximation, the positions of the nuclei are fixed and one looks for the wave functions of the electrons. This approximation is justified because the mass of an electron is much lower than a nucleus mass and thus electrons move faster. In this approximation, the Hamiltonian $H$ is given by the sum of the kinetic and potential energy of the electrons as well as the nucleus–nucleus electrostatic repulsion:

$$H = T + V, \tag{2}$$

$$T = -\frac{h^2}{8\pi^2 m}\sum_{i=1}^{N_{\mathrm{elec}}}\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right), \tag{3}$$

$$V = -\sum_{i=1}^{N_{\mathrm{elec}}}\sum_{n=1}^{N_{\mathrm{nucl}}}\frac{Z_n e^2}{r_{in}} + \sum_{i=1<j=1}^{N_{\mathrm{elec}},N_{\mathrm{elec}}}\frac{e^2}{r_{ij}} + \sum_{n=1<p=1}^{N_{\mathrm{nucl}},N_{\mathrm{nucl}}}\frac{Z_n Z_p e^2}{R_{np}}, \tag{4}$$

with $h$ the Planck constant, $m$ the mass of an electron, $(x_i, y_i, z_i)$ its position, $Z_n$ and $Z_p$ the dimensionless charge of nucleus $n$ and $p$, $N_{\mathrm{elec}}$ the number of electrons in the system, $N_{\mathrm{nucl}}$ the number of nuclei in the system, $r_{in}$ the distance between electron $i$ and nucleus $n$, $r_{ij}$ the distance between electron $i$ and electron $j$ and $R_{np}$ the distance between nuclei $n$ and $p$. Solving (1)–(4) allows calculating the energy $E$ as a function of the distance $R$ between two nuclei. By knowing $E(R)$ accurately, it is possible to predict the detailed atomic forces and the chemical behaviour of the system. It is also possible to carry out a minimisation of the cluster geometry and to compute the optimal equilibrium geometry by solving

$$\frac{\partial E}{\partial x_i} = 0 \qquad (5)$$

for each of the $N_{\mathrm{nucl}}$ nuclei in the system. Evidently, one has to check whether the configuration found is a true minimum by calculating the second derivatives of the energy $E(R)$. Similarly, one can also calculate the maxima and find the activation energy.

The agreement between calculated bond length and experimental bond lengths for several compounds is impressive (see Fig. 1). However, one must remain careful with the interpretation of ab initio results. These depend on the accuracy used for calculating the wave function (which is strongly related to the basis set) and also on (the size of) the configuration, which must be representative for the bulk or surface structure. Due to the potential energy operator (4), it is obvious that (at present) ab initio calculations are possible only for small clusters of small elements.

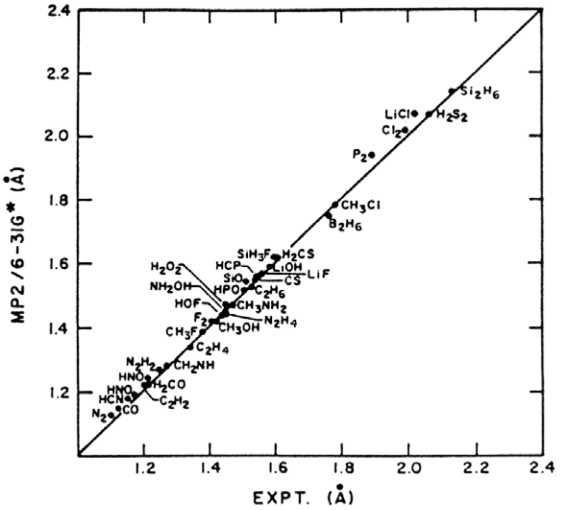

Fig. 1. Comparison of experimentally measured bond lengths with those calculated by ab initio methods in the basis set MP2/6-31G* (from [69]).

### 2.2. Existing applications in glass dissolution

Very relevant for glass dissolution is the ab initio calculation of the activation energy for breaking Si–O–Si or Si–O–Al bonds by water, hydrogen or a proton [30,31]:

| Reaction | Activation energy |
|---|---|
| $\equiv$Si–O–Si$\equiv$ + $H_2O$<br>$\rightarrow$ $\equiv$Si–OH + $\equiv$Si–OH | 29 kcal/mol |
| $\equiv$Si–O–Al$\equiv$ + $H_2O$<br>$\rightarrow$ $\equiv$Si–OH + $\equiv$Al–OH | 26 kcal/mol |
| $\equiv$Si–O–Si$\equiv$ + $H_3O^+$<br>$\rightarrow$ $\equiv$Si–OH + $\equiv$Si–$OH_2^+$ | 24 kcal/mol |
| $\equiv$Si–O–Al$\equiv$ + $H_3O^+$<br>$\rightarrow$ $\equiv$Si–OH + $\equiv$Si–$OH_2^+$ | 16 kcal/mol |
| $\equiv$Si–O–Si$\equiv$ + $OH^-$<br>$\rightarrow$ $\equiv$Si–OH + $\equiv$Si–$O^-$. | 19 kcal/mol |

In fact, the final reaction is a two-step process, of which we have only mentioned the highest activation energy. These results indicate a catalytic effect of hydrogen and a proton on the breaking of Si–O–Si bonds. Experimentally, for a borosilicate glass, Knauss et al. [32] find indeed that the glass dissolution is slowest at neutral pH. For the R7T7 nuclear glass, Advocat [33] finds that the dissolution rate is highest at high pH. Measuring only the pH values larger than 4, he does not observe an increasing dissolution rate at low pH.

Experiments show that alkalis in solution also have a rate enhancing effect on the dissolution rate of glass and quartz [34,35]. Ab initio calculations by Strandh et al. [36] show at high pH a weakening of the Si–O–Si bond in the presence of alkalis. The calculations for low pH do not entirely correspond with experiments, which is attributed to the choice of the configuration.

At least in some circumstances, diffusion through the gel is crucial in glass dissolution. This means that also the structure of the gel (glass) is extremely important. The gel (glass) contains small pores [37] and the size of these pores determines how fast elements can diffuse through them [38,39]. Such pores can be considered as the hole of a ring formed by glass formers. Tossell and Saghi-Szabo [40] performed ab initio calculations for such rings of four tetrahedrally co-ordinated atoms connected by bridging oxygens. Their results show that the Si · Al · Si · Al configuration is more stable than Si · Si · Al · Al (this is the Loewenstein rule). However, the incorporation of a proton or $Ca^{+2}$ makes the Si · Si · Al · Al configuration more stable than Si · Al · Si · Al. Similar calculations are executed for boron instead of aluminium. More specific for dissolution of sodium aluminosilicate glasses, their calculations show that the reaction of $H_2O$ with

$Si_2Al_2O_{12}H_8Na_2$, which can be considered as a simple simulation of ion exchange, does not lead to the hydrolysis of the Si–O–Al bond. Instead, the water molecule sits near to the sodium.

### 2.3. Potential applications for glass dissolution

It is obvious that ab initio calculations alone will never be able to model the entire glass dissolution process. However, they can provide essential input for other modelling methods and allow additional understanding of experiments.

An asset of ab initio is its ability to calculate the catalytic effect. In this way, they could allow, e.g., (1) a better understanding and modelling of effects of solution composition (including pH) on the glass dissolution rate, (2) more accurate estimates of the activation energy for silica dissolution (up to now the values found in the literature diverge considerably) or (3) a better understanding of the mixed alkali effect. Another application is in the development of waste packages. Including or leaving out some components of a package can lead to much slower dissolution and a better immobilisation of the waste. Of course, this can be tested by experiments, but (at least in some years) calculations will be easier and cheaper. Concerning the link with other modelling methods, ab initio methods can provide (1) the potential energy functions used in molecular dynamics or (2) the activation energies or equilibrium constants needed for Monte Carlo modelling or (3) equilibrium constants which can be compared with those in geochemical databases.

## 3. Molecular dynamics

### 3.1. What is it?

Molecular dynamics allows to describe the behaviour of nanometer-sized volumes of atomic systems by calculating explicitly the trajectories of all the atoms [41,42].

In any molecular dynamics calculation, the first step consists of choosing the analytical functions that will be used to calculate the forces on each of the atoms of the represented volume. One could use ab initio methods to calculate these, but mostly one uses standard potentials from which the parameters are determined by fitting certain material properties (e.g., structure factor, elastic constants, etc.). The interaction potentials used for nuclear glasses take into account the particular chemical nature of bonds (ionic and covalent bonds). They are generally constituted by Born–Mayer–Huggins terms completed by three body terms [43,44].

Now, it is possible to write explicitly the (classical) Hamiltonian $H$ of the atomic system:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + E_{\text{pot}}(q_1, \ldots, q_N) \tag{6}$$

with $n$ the number of atoms in the system, $p_i$ the kinetic moment of every atom, $m_i$ its mass, $q_i$ its position and $E_{\text{pot}}(q_1, \ldots, q_N)$ the total potential energy.

Solving the classical movement equations

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \tag{7}$$

where the dot stands for the derivative with respect to time, allows the trajectory of each atom to be obtained. The atomic paths are calculated step by step on a time interval on the order of 100 ps. The choice of this time step determines the accuracy level of the total energy configuration. In general, one asks an energy conservation of about 0.05%. In the case of a constant volume simulation, the most used algorithm is Verlet's [45].

Because they do not take into account the electrons of atoms and often work with two particles potentials (instead of potential energy surfaces), molecular dynamics are less accurate than ab initio calculations. On the other hand, they allow the time-dependent behaviour of systems up to the order of some hundred thousands of particles to be described.

### 3.2. Existing applications in glass dissolution

For nuclear waste glasses, molecular dynamics studies focus on describing the glass structure. The initial point of any study of long term glass behaviour is to improve the knowledge on the structure of the glass. Molecular dynamics is one of the most successful tools to describe at the atomic level the characteristics of glasses (structure, some thermodynamic data, etc.) such as the structural organisation of the basic matrix (calculations with four, five and six oxides) of the French nuclear waste glass [43,44,46,47]. On a short range, one can determine the co-ordination of the atoms, their interatomic distances and the angular distributions (see Fig. 2). The medium range organisation is obtained from the angular distribution between cations (Si–O–Si, Si–O–Al, etc.), the distribution of rings of the network and its polymerisation (number of non-bridging oxygens, average silica co-ordination (connectivity) number $Q_n$). These papers show the particular role of alkalis and the earth-alkalis in the glass structure [48]. The changes by irradiation (nucleus recoil) [49–52] of the surrounding glass structure is also described by molecular dynamics. Finally, this technique also allows us to determine migration parameters for mobile atoms (e.g., sodium) [46].

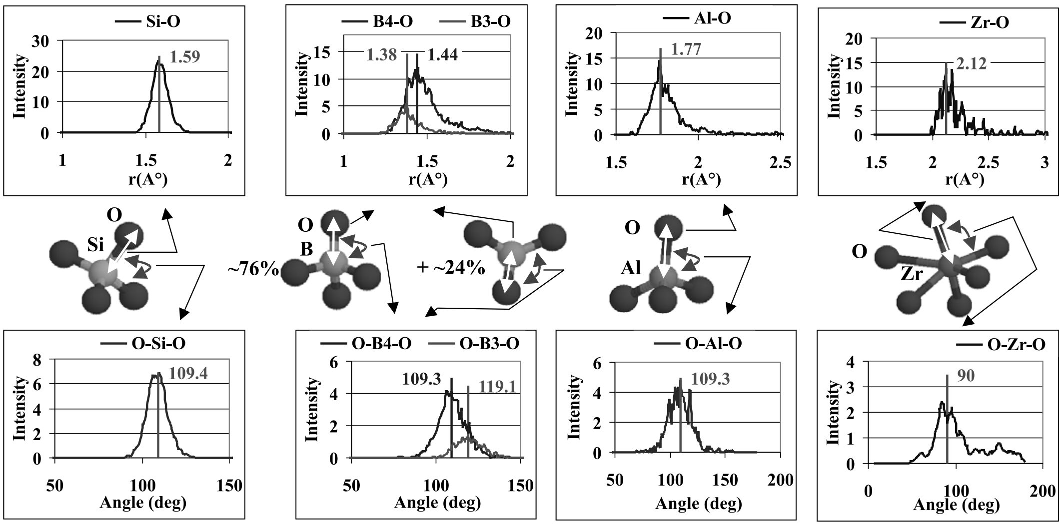

Fig. 2. Short range structure of a nuclear glass as determined by molecular dynamics [43,44]. The curves represent the radial and angular distributions. The maximum of each distribution is indicated by a line. About 76% of the boron particles are in the $B_4$–O coordination. The remaining part (24%) is $B_3$–O.

Concerning the glass dissolution process itself, molecular dynamics studies on the hydration of silica glasses already exist for simple glasses [53,54].

### *3.3. Potential applications for modelling glass dissolution*

The major strength of molecular dynamics is its possibility to model the structure of atomic systems. It is also a tool to study phenomena with dynamics on the order of picoseconds.

Due to its ability to describe the glass structure, molecular dynamics are excellent to study structure related factors affecting glass dissolution. Examples are: (1) influence of the glass (gel) structure on the diffusion of each element (in particular (mixed) alkali diffusion), (2) the modification, structure and stability of the gel, (3) the glass structure modification introduced by a surface, (4) the possible change in dissolution behaviour caused by the modified glass (gel) structure due to irradiation, etc.

The potential energy functions used in molecular dynamics can be related to ab initio calculations as well as to Monte Carlo methods. Ab initio molecular dynamic calculations (e.g., Car Parinello calculations [55]) can permit adjustments to the parameters of the classical molecular dynamics potentials. Similarly, a combination of ab initio and molecular dynamics could form a database of the main mechanisms, their probability and consequences on the mobility of species and the resulting influence on the gel structure. This database could be used as input for Monte Carlo models.

## 4. Monte Carlo simulations

### *4.1. What is it?*

Monte Carlo methods are based on probabilities. The idea is that by repeating a stochastic process many times, one gets a clear average. In this way, Monte Carlo methods can be used, e.g., to calculate numerically definite integrals.

Another possibility, more relevant for glass dissolution modelling, is to apply a Monte Carlo method for solving the mathematics of transition state theory [20]. Consider for instance the simple chemical reaction

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}^* \rightarrow \mathrm{D}, \qquad (8)$$

where the reactants A and B are forming the activated complex $C^*$, which decays to the product D. The reaction kinetics of (8) are described by two parameters, e.g., the equilibrium constant and the activation energy. Those two parameters can be transformed in two probabilities: (1) a probability $P^+$ to transform a couple of neighbouring $(\mathrm{A},\mathrm{B})$ particles in a D particle and (2) a probability $P^-$ for the reverse reaction. The Monte Carlo method now consists of transforming at every time step all couples of neighbouring $(\mathrm{A},\mathrm{B})$ particles in a D particle with probability $P^+$. Simultaneously, all D particles are transformed in a couple of $(\mathrm{A},\mathrm{B})$ particles with the probability $P^-$. In this way, one solves the reaction kinetics in a stochastic way. The result is the same when one would solve the reaction kinetics analytically. But, analytical solutions are only available for simple systems. For complicated systems, with several reactions and geometrical constraints, a Monte Carlo method is a convenient way to solve the mathematics of transition state theory (see [56] for more details).

Comparing the Monte Carlo method from the previous paragraph with molecular dynamics, it is clear that the interaction potential from molecular dynamics is replaced by some discrete values (probabilities). This is not necessarily so. It is also possible to perform Monte Carlo simulations with the full interaction potential, but that case is more complicated than applying it on discrete lattices. Approximating the amorphous glass structure by a discrete lattice obviously leads to a decrease in accuracy. On the other hand, this also allows simulations to be performed on larger time scales. Typically, molecular dynamics perform simulations on the order of picoseconds. Monte Carlo methods can obtain results on the order of hours to days.

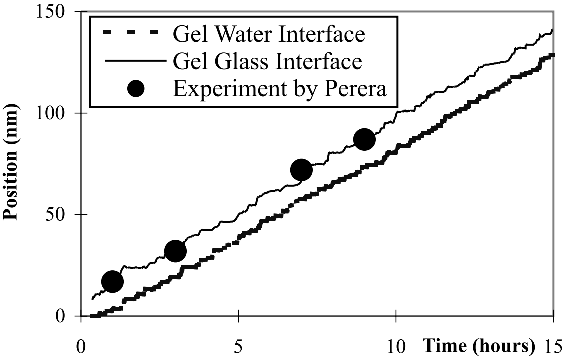

Fig. 3. Comparing the experimentally measured [24] retreat of the Corning 015 soda lime glass (composition: 72.2% $SiO_2$, 21.4% $Na_2O$, 6.5% CaO, mol%) at 50°C and pH 7 with a Monte Carlo simulation result (sodium fraction in the glass of 0.25, $P^+ = 3.9 \times 10^{-14}$, $\ln(P^+/P^-) = -6$, $P_{\mathrm{diff}} = 1000\ P^-$, $P_{\mathrm{ion}} = P^-$).

### *4.2. Existing applications in glass dissolution*

Simulating glass dissolution by a Monte Carlo method was introduced by Aertsens [56–59]. He divides all glass components in (1) easily dissolving components and (2) slowly dissolving, solubility limited components. For simplicity, he calls the first class of elements sodium and the second class silica. All the elements (including water) are supposed to be on a lattice. He chooses a diamond lattice because it best represents the tetrahedral co-ordination of silica. The glass structure is approximated as being a random mixture of silica and sodium. Initially, the glass water surface is flat. Next, water can penetrate the glass. Water can exchange places with sites bearing a sodium particle (according to some probability $P_{\mathrm{ion}}$) or break silica (in fact Si–O–Si) bonds. The silica dissolution reaction is modelled as consisting of four elementary reactions, where in each elementary reaction one Si–O–Si bond is broken. If all Si–O–Si bonds are broken, then a silica particle is considered dissolved and it can diffuse with a probability $P_{\mathrm{diff}}$ over water bearing sites. This diffusion goes on until (1) the silica particle reaches the water solution or (2) it is trapped again by another silica particle. Since in every elementary reaction a Si–O–Si bond is broken, it is reasonable to characterise all these reactions by the same parameters $P^+$ and $P^-$ (see previous section). Aertsens performs simulations for a zero (glass) surface to (water) volume ratio, as well as for non-zero surface to volume ratios. In the second case, the silica concentration in solution can increase from zero until some maximal level. It is also important to know that the parameters used in the simulations can be related to experimental values [58] and that for simple cases, simulation results can be compared quantitatively with experiments (see Fig. 3).

The simulations from Aertsens are used to test the basic assumptions (e.g., congruent dissolution) of analytical models. For a zero surface to volume ratio and no silica in solution, the simulations show that the dissolution of glass is closely related to a percolation transition. For low sodium contents, sodium cannot leach out of the glass unless silica dissolves first. So, dissolution is congruent and slow. For higher sodium contents, connected pathways of sodium exist. So, sodium can leach out of the glass by these paths which can lead to noncongruent, faster dissolution with extensive surface layers. In this case, sodium leaching can go on at silica saturation. Below the percolation threshold, sodium leaching stops at silica saturation. The thickness of the surface layer depends on the sodium content of the glass (more sodium leads to thicker layers) and on the probabilities $P$ (a higher ratio $P^+/P_{\mathrm{ion}}$ leads to thinner layers). On a qualitative level, these simulations agree with the types of surface layer characterised by Hench and Clark [60]. Similarly, the profiles of sodium in the gel agree qualitatively with experimentally measured SIMS profiles [56].

The general belief that transition state theory does not lead to a protective layer formation is contradicted by the simulations. In simulations with silica saturated concentrations, dissolved silica from solution is trapped again by the gel. This leads to an increase of the silica concentration at the gel/solution interface. These silica particles partially or completely block the way out for sodium particles. This result is a lower leach rate in silica saturated solutions than in solutions containing no silica. Besides, consistent with experiments [18,19], the simulations show silica condensation. This means that more silica bonds need to be broken for dissolution. Thus, the overall silica dissolution rate should decrease as a function of time. Again, this is consistent with recent experiments [15], showing that dissolution is slower for glass that has already leached before. Experiments [15] and simulations [58] also show that the second parameter of the Grambow rate law, the 'silica saturation concentration' does not remain constant during glass dissolution. Thus, it is not surprising that the simulations do not agree with the Grambow rate law [58].

Other Monte Carlo simulations, similar to those of Aertsens, are performed by a French group from Palaiseau [61,62]. Major differences between both simulation models are that the Palaiseau group: (1) works on a square or a cubic lattice, (2) uses different dynamics, (3) allows three kinds of glass components and (4) does not consider silica diffusion. On a qualitative level, the simulation results from the Palaiseau group agree in general with those from Aertsens. Due to different basic assumptions and parameter values, there are also limited differences. As an example, some simulations of Aertsens [58] lead to silica concentrations higher than the final silica concentration, while the Palaiseau group does not report such behaviour.

A common problem of both the simulations of Aertsens and Palaiseau is that, especially below the percolation threshold, at silica saturation, the gel layer finally rearranges to a state where no 'sodium' can leach out. Experimentally, leaching can go on due to solid state diffusion or diffusion by small pores [7,37,63]. A better representation of the glass structure (e.g., different bond lengths for sodium and silica) could possibly solve this problem.

Finally, Monte Carlo simulations for glasses are also performed on a continuum instead of a lattice. Results of these should be available soon [64].

### *4.3. Potential applications for modelling glass dissolution*

Monte Carlo simulations are a powerful tool to model glass dissolution on experimentally relevant time scales. Because Monte Carlo models take a three-dimensional (simplified) glass structure into account, they can describe structure-related phenomena like a percolation transition, phase separation, silica condensation, the changing size of the microscopic glass surface, the openness of the structure, etc. None of these phenomena can be included in a natural way in analytical models. Monte Carlo methods are also an excellent way to test the basic assumptions of simpler models (e.g., analytical models).

The present Monte Carlo models are still too simple, especially in how they model the glass structure. Besides, the discussion about how to implement glass dissolution microscopically is still open. As a result, one must remain careful with the interpretation of the simulations. The major challenge for the existing Monte Carlo models is to take into account in a more realistic way the glass structure while still keeping computation times acceptable.

## 5. Neural networks

### *5.1. What is it?*

Artificial neural networks are based on how our brain works. In our brain, a biological neuron consists of a cell body, which is connected to other neurons by synapses (see Fig. 4). Electrical pulses coming from other neurons are transmitted by the synapses to the cell body. If the sum of these pulses exceeds a certain threshold, the neuron fires an electric pulse to the other neurons to which it is connected. An artificial neuron works in the same way. Its input is the output $x_i$ of other neurons, multiplied by a corresponding weight $w_i$, which reflects the strength of the connection. These weighted inputs are then combined, usually by a simple summation

$$S = \sum_i w_i x_i. \tag{9}$$

This summation is further processed by a transfer function to produce the output of the neuron. Initially, this transfer function was a step function, but other functions like the sigmoidal function $f(x) = 1/(1 + \exp(-x))$ resulted in better performances.

Network of neurons can be constructed in all kinds of configurations, but usually they are built by a sequence of layers, where each layer consists of a number of neurons which are fully or partly connected to successive layers (see Fig. 5). Most neural networks have two layers with connections to the outside world: an input layer, where data are submitted to the network, and an output layer, which presents the response. The other layers are called hidden layers.

Once the configuration is fixed, the neural net can be trained. Training can be compared with fitting in conventional models. One presents to the net input and/or output data. Simultaneously, the weights are changed according to some 'learning rules'. The aim is that, after the training phase, the neural net provides correct answers (output) for a given input. Hereby it is essential that the network not just memorises the training data, but that it manages to extract the features of the problem for which it is trained. To make sure that this is the case, it is possible to present the neural network data

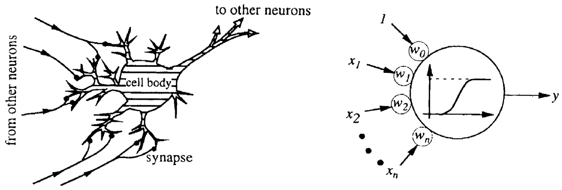

Fig. 4. A biological neuron (left) and an artificial neuron (right) (from [25]).

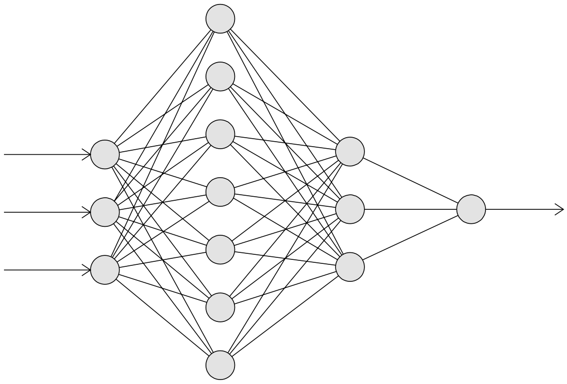

Fig. 5. Neural network architecture for the prediction of stress corrosion cracking. The input layer (left) consists of three neurons. The output layer (right) has one neuron.

that are not included in the training set and see that the output corresponds with the desired one. If this is satisfactory, the network is ready to be used.

As an illustration, we present a specific case [65], where a neural network is used to predict stress corrosion cracking in boiling water nuclear reactors. The network is learned to recognise the combined effect of temperature, chloride and oxygen concentration on the occurrence of stress corrosion cracking. It has three input neurons (see Fig. 5): one for temperature, a second for chloride concentration and a third for oxygen concentration. There is one output neuron. During the training phase, the output neuron is given a value of one if stress corrosion occurs for the corresponding input data. If not, the output neuron has a zero value. For predictions, the value of the output neuron varies gradually between zero and one. If the probability for stress corrosion increases, the value of the output neuron increases as well.

For this particular case, the predictions correspond well with the input data. During the learning phase, conflicting input data have been inserted in the network. Indeed, similar input data sometimes lead to stress corrosion cracking and sometimes not. It is up to the neural network to generalise this contradictory information in a reliable way. To put it in a simple way, the neural network provides a kind of fitting without needing a well-defined fit function. Note also that (similar to conventional fitting) it remains possible that other parameters (e.g., the stress level) which are not taken into account, can also effect stress corrosion cracking.

### *5.2. Existing and potential applications for glass dissolution*

We do not know if any existing neural network is helping to model glass dissolution. But, efforts are going on to use neural networks for predicting interactions in cement/waste systems [66,67]. We do not see any reason why it is not possible to develop a similar program for interactions in glass/waste systems, where many experimental data for many types of glass are available.

## 6. Fuzzy systems and genetic algorithms

### *6.1. What is it?*

The basis of fuzzy systems is fuzzy set and fuzzy logic, in which fuzzy rules are most popular. Assuming that in nature, change is not sudden but gradual, the boundary of such rules is not sharp but fuzzy. As a result, the system output from one rule area to the next rule area changes gradually. Depending on the area (of input points) each rule has a weight. The total system output is calculated by taking the weighted average of the output of every individual rule. Contrary to traditional logic, which only considers the values zero (for false) and one (for true) fuzzy logic uses values between zero and one. In this way, fuzzy logic allows for a better description of concepts like large, fast, etc.

Takagi [25] gives a good introduction to genetic algorithms.

### *6.2. Existing and potential applications for glass dissolution*

We do not know any existing applications concerning glass dissolution. Fuzzy systems possibly combined with genetic algorithms or neural networks are a good alternative for modelling systems that are not fully understood yet.

## 7. Conclusion

Due to the large increase in computation power, new microscopic modelling methods like ab initio, molecular dynamics or Monte Carlo simulations, will definitely enhance the capabilities of modelling. These microscopic modelling methods are complementary: not only to one another, but also to the existing analytical and geochemical models. In fact we can view mathematical models as a kind of hierarchy. On top is a very accurate method (ab initio) which is however so computationally expensive, that it can only be used for very few small elements. Going down the hierarchy to molecular dynamics and Monte Carlo simulations, one looses accuracy each time. But, simplifications also lead to lower computation times. This means that one can proceed to bigger systems and larger times. At the bottom of this hierarchy are analytical methods. These are the only ones capable of predictions on very long time scales.

However, these predictions depend on assumptions that are not necessarily correct. During glass dissolution, several processes are going on simultaneously, so experiments cannot always confirm or negate simple basic assumptions. Therefore, microscopic methods are extremely helpful; they can test which (or under which circumstances) assumptions or experimental determined values make sense. For such things, simulations are much more versatile, much easier to use and (in the future) also much cheaper, than experiments. Similarly, in the just sketched hierarchy, higher level simulation methods can provide essential information to lower levels.

Soft computing methods provide a way to model phenomena that are not completely understood yet. In this way, they can be combined with hard mathematical models. Neural networks are a fast way to obtain predictions. Since these predictions are not based on understanding the problem, we do not recommend relying only on them for extrapolations. On the other hand, the glass dissolution literature shows many examples of fit functions and models, for which there is no or a questionable theoretical basis (e.g., the Grambow rate law). We do not see much reason why such a prediction should be more reliable for extrapolation than a neural network.

Finally, keeping in mind that despite great advances in science, predicting the future is still very hard. As an example, testing five hydrogeological models showed that all of them failed to accurately predict the future behaviour of the system [68]. In any field, more reliable predictions are only possible by a better understanding of the system. Although they still need improvement, it is obvious that for glass dissolution microscopic modelling will provide much of this understanding.

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