A numerical model for studying glass dissolution in water

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Abstract   Glass, a multicomponent vitreous system, can be considered as a random mixture of the constituent oxides Due to random local environment, the binding energy of silica in the solid is expected to be randomly distributed Dissolution of this random solid in water is modeled *via* a Monte Carlo (MC) algorithm Time evolution of such a system under normal conditions shows that the system becomes rough to porous with the formation of dry silica gel layer It is found that the chemical reaction of corrosion occurs at a constant speed in the steady state As an effect, a self-established potential gradient is established and the system evolves into a critical state

1. Introduction

Since multicomponent silicate glasses are used as the disposal media for radioactive and toxic wastes [1], it is important to understand the dynamics of corrosion or dissolution of glass in an aqueous solution. Glass, a multicomponent vitreous system, can be considered as a random mixture of the constituent oxides with random binding energy of silica in the solid. Such a solid could be called as a random solid. A random solid is then a multicomponent vitreous system in which, due to random local chemical environment, the binding energies of the constituent molecules of the solid are randomly distributed. If such a solid is in contact with an aqueous solution, the solid element dissolves at a slow rate and forms a complex with the solution. The complex breaks almost instantaneously and the solid element in the solution is available for redeposition on the rough or irregular solid surface exposed to the solution. As the process continues, the solution penetrates into the solid and the solid becomes porous. A self-established potential gradient drives the solution molecules inside the solid with a constant drift velocity. The solution molecule

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forms cluster of different sizes inside the solid At the non-equilibrium steady state a power law distribution of the cluster size is found This is then a self-organized critical state between a random solid and an aqueous solution driven by a self-established potential gradient Below, we will present the model and discuss the results obtained

2. The model

In order to study the time evolution of a random solid in contact with an aqueous solution a numerical model of corrosion or dissolution is developed in 2 dimensions (2D) In this model, it is assumed that the random binding energy is uniformly distributed between 0 and 1 The solid shown in Figure 1(a) is a dense structure of elements with random binding energy r_i The solid of width L is infinitely long in the y-direction The aqueous solution, infinite in volume, is placed at the bottom of the semi infinite solid The white space in Figure 1 represents the solution The initial solid-solution interface is marked by a thick line Random solid element R dissolves slowly in the solution S, makes a compound RS and the compound breaks instantaneously into R and S The chemical reaction of dissolution could be represented as

$$R + S \rightarrow RS \rightarrow R + S \qquad\qquad (1)$$

The solid element R in the solution is now available for redeposition on the interface Assuming diffusion of the solid element R is very fast in the solution, redeposition is made at a randomly chosen site on the externally accessible perimeter with unit probability Generally, dissolution is a slow process and redeposition is faster It is mimicked here by considering no further dissolution during redeposition The slowest possible dynamics of the system then involves dissolution and redeposition processes together with reconstruction of the rough interface at the single particle level This is usually the case of glass dissolution in aqueous solutions in the macroscopic scale [2] Different physical processes involved in a single Monte Carlo (MC) step are explained with the help of Figure 1 The process are (i) extraction of externally accessible perimeter of the solid, (ii) dissolution of the site with minimum random number (minimum binding energy) on the perimeter with unit probability (in Figure 1(b), it is r_3), (iii) modification of the external perimeter, (iv)
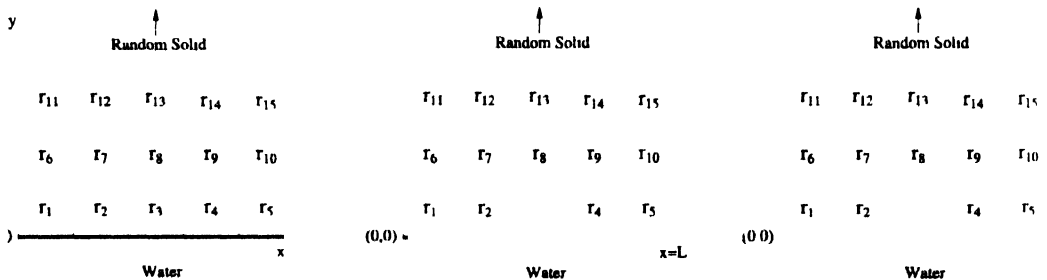

Figure 1. A single MC step is represented here (a) The arrangement of random numbers r_i represents a random solid, (b) r_3 is identified as minimum random number on the solid-solution interface and it is dissolved, (c) the solid element is redeposited at a randomly chosen site r_1 of the modified solid surface A new random number r_α is assigned with the redeposited site The process is then repeated

redeposition of the solid element present in the solution on a randomly chosen site of the modified external perimeter (r_1 in Figure 1(c)), (v) assignment of a new random number r_u to the redeposited site The whole process is then repeated and time is increased from t to $t+1$ Note that the total number of particles is conserved and the system evolves at equal solid to liquid and liquid to solid flux rate (one particle per time step) throughout the simulation

In Figure 3, the system morphology is shown for a system of width $L = 64$ at time steps $t = 2^{11}$ The solution is represented by light gray scale and the random solid is represented by dark gray scale The black dots represent the perimeter sites It can be seen that the interface becomes rough and the solution has penetrated into the solid leaving behind a restructured solid like a dry silica gel as observed in glass alteration experiments [2] It should be noted here that in the study of self-stabilized etching of random solids by finite etching solution [3] (infinite solid and finite solution) final stable morphology obtained was fractal as it was observed by Balazs in the corrosion of thin metal films [4]

$t = 2^{11}$

Figure 2. Morphology of the random solid system at $t=2^{11}$ Dark gray scale represents the random solid and the light gray scale represents the solution Black dots are the externally accessible perimeter sites in contact with the solution The solid line represents the lattice boundary at $t=0$

3. Results and discussion

Simulations have been performed on the square lattice of widths ranging from $L = 64$, 128 and 256 Data are averaged over maximum 1000 samples It is seen from the system morphology that the solution molecules enter into the system The solution molecules

inside the solid form clusters and move collectively In order to characterize the motion of the solution molecules inside the solid, the profile of solution molecules are calculated as a function of the penetration depth along y The solution profile is defined as the average number of solution molecules per row $N_w(y)$ and plotted in Figure 3(a) against y the coordinate of rows It can be seen that the solution molecules move inside the solid as a Gaussian profile leaving behind a restructured solid To distinguish the restructured solid from the original random solid, the average energy per row $< r(y) >$ has been calculated as a function of y In Figure 3(b) $< r(y) >$ is plotted against y It can be seen that a gradient in the average energy has developed spontaneously The region of higher potential corresponds to the restructured solid whereas lower potential region corresponds to the unexplored random solid with average energy 0 5 Note that the solution profile is just in front of the potential gradient It seems that the spontaneously developed potential gradient pushing the solution profile deeper and deeper into the solid with time
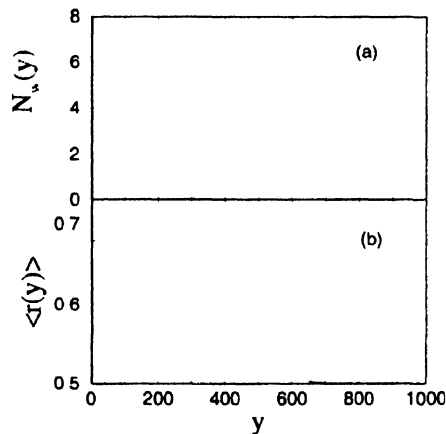

Figure 3 (a) Water profile number of water molecules per row as a function of y the row index inside the solid (b) Plot of average energy $<r(y)>$ *versus* y A self-established potential gradient is observed in the system

The motion of solution profile can be studied measuring the average peak position $<y>$ of the profile with time Peak positions of the solution profile is the distance of the peak from the initial interface at $t = 0$ It is measured as a function of time t for $L = 64,128$ and 256 In Figure 4, $<y_p>$ is plotted against scaled time t/L Different symbols correspond to the system sizes circle for $L = 64$, squares for $L = 128$, and triangles for $L = 256$ It should be noticed that the data for different width of the systems collapse onto a single curve when t is scaled as t/L The time scale of the system is thus proportional to the width L of the system The solid line represents a straight line with slope one It can be seen that the data in double logarithmic scale is parallel to the solid line Thus, $<y_p>$ the mean displacement is proportional to time t This means that the solution profile is drifted by the potential gradient into the solid with a constant velocity $v = d <y_p>/dt$ [5] Therefore in the $t \to \infty$ limit, the whole random solid will dissolve completely leaving a pure silica gel

During the motion of solution molecules through the random solid, the solution molecules occupy nearest neighbour sites and form clusters The clustering of solution molecules occur on its own due the dynamics of the system without fine tuning of any parameter of
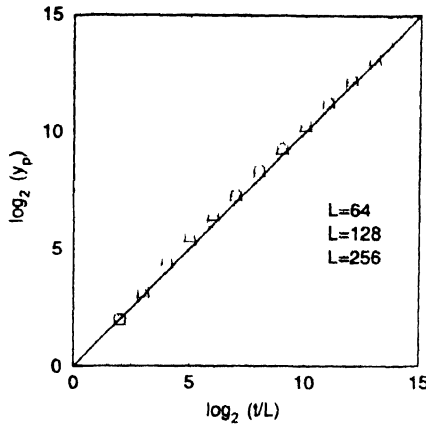

Figure 4. Plot of average peak position of the solution profile $<y_p>$ inside the solid as a function scaled time t/L Different symbols corresponds to different system sizes circle for $L=64$, squares for $L=128$, and triangles for $L=256$ The solid line represents a straight line with slope one It is found the profile is drifted with a constant velocity into the solid

the system from outside The size of a cluster s is defined as the number of solution molecules connected by nearest neighbour bonds The probability to have a cluster of s number of solution molecules (size s) at time t for a given system size L is given by

$$P_s(t) = n_s(t)/N_{tot}(t) \tag{2}$$

where $n_s(t)$ is the number of clusters of size s out of $N_{tot}(t)$ clusters at time t The probability distribution $P_s(t)$ of cluster size is plotted in Figure 5 for a system size $L = 1024$ Different symbols correspond to different time steps circle for $t = 2^{18}$, square
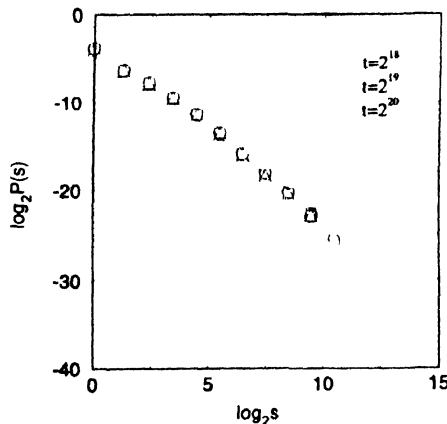

Figure 5. Plot of cluster size distribution $P_s(t)$ against s Different symbols correspond to different time steps circle for $t = 2^{18}$, square for $t = 2^{19}$, and triangle for $t = 2^{20}$ The solid line represents a straight line with a slope -2 A power law distribution of cluster size is observed

for $t = 2^{19}$, and triangle for $t = 2^{20}$. The solid line represents a straight line with a slope −2. It can be seen that the cluster size has a power law distribution $P_s(t) \sim s_s^{-r}$ with an exponent $\tau_s \approx -2$. It should be mentioned here that the exponent obtained here is close to that of the cluster size distribution in the case of percolation [6]. The system driven by a self-established potential gradient thus evolves into a critical state through the self clustering of solution molecules This demonstrates self-organized criticality [7] in the process of dissolution of a random solid in a solution driven by a self-established potential gradient. This is a new observation.

4. Conclusion

The process of glass dissolution in a solution is modeled considering the glass as a random solid The molecules in solution penetrate the solid at a constant speed A self established potential gradient develops in the system which drives the solution profile deep into the solid. During the drift of the solution profile it is found that there is self-clustering of solution molecules The cluster size distribution is found to be a power law with an exponent approximately −2. The non-equilibrium steady state is then a self-organized critical state of a random solid and an aqueous solution driven by a self-established potential gradient

Acknowledgment

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