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Molecular dynamics study on thermal dehydration process of epsomite (MgSO₄·7H₂O)

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Water vapour sorption in salt hydrates is one of the most promising means of compact, low loss and long-term solar heat storage in the built environment. Among all, epsomite (MgSO₄·7H₂O) excels for its high-energy storage density and vast availability. However, in practical applications, the slow kinetics and evident structural changes during hydration and dehydration significantly jeopardise the heat storage/recovery rate. A molecular dynamics (MD) study is carried out to investigate the thermal properties and structural changes in the thermal dehydration process of the epsomite. The MD simulation is carried out at 450 K and a vapour pressure of 20 mbar, in accordance with experimental heat storage conditions. The study identifies the dehydration as multiple stages from the initial quick water loss and collapse of the crystal framework to the adsorption of water molecules, which inhibits complete dehydration. Further, the anisotropic diffusion behaviour supports the important role of the porous matrix structure in the heat and mass transfer process. The enthalpy changes, partial densities, mass diffusion coefficients of water and radial distribution functions are calculated and compared with corresponding experimental data to support the conclusions.

Keywords: molecular dynamics simulation; diffusion coefficient; magnesium sulphate; thermal dehydration

1. Introduction

Compact heat storage is widely used in various applications. For example, in seasonal heat storage systems, the energy consumption in the built environment in winter can be cut down by recovering the solar heat stored in the summer. Recent studies suggested using salt hydrates as long-term thermo-chemical heat storage materials for their high storage capacity, low environmental impact and low heat loss.[1] In summer, dry hot air from solar collectors is blown into the reactor to dry up the hydrates to charge the storage tank; in winter, humid air is absorbed by anhydrous salts to extract heat from the storage tank. A recent study identified epsomite (MgSO₄·7H₂O) as one of the most promising thermo-chemical heat storage materials,[2] and subsequent studies were carried out to improve its thermal properties.[3] Epsomite is cost-effective, non-toxic, non-corrosive and has a large storage capacity of 2.8 GJ/m³ when fully dehydrated. Preliminary measurements showed that sensible heat losses only comprise about 10% of the total energy stored. However, in applications, clotting and expansion during hydration and formation of powdery particles during dehydration can block the air flow or reduce the effective area of adsorption; melting of the heptahydrate during dehydration may reduce the connectivity of the pores, change the internal surface structure and block the air flow through the reactor. These practical issues increase the difficulty in the reactor design, which relies on a detailed understanding of the vapour transport by diffusion and convection.

The thermal dehydration process of epsomite was extensively studied by experiments. One crucial step is the opening of wider channels and cracks, which allows the transportation of water molecules, while the formation of cracks is then influenced by the rate of dehydration and the growth of superficial textures.[4] The dehydration rate and pathways are further dependent on the water vapour pressure.[5,6] The structural changes during dehydration are identified and possible metastable states at different temperatures and vapour pressures are characterised.[7–10] These give better understandings and predictions about the dehydration process at larger scales. Van Essen et al.[2] measured the heat flux during dehydration at 23 mbar vapour pressure according to experimental heat storage conditions, which laid the foundation and brought our interest to the present work. However, the vapour transport process, especially on powder/grain scale, is still unclear, and at these small scales, detailed local properties such as diffusion coefficients remain difficult to be directly studied through experiments. A molecular-scale investigation into the dehydration process seems necessary in order to unveil these details and to identify the factors that affect the diffusion through the surface layers. Iype et al.[11] quantified the energies of distinct magnesium sulphate hydrates[11] and identified various hydrogen-bonding networks[12] from density functional theory (DFT) calculations. These calculations show that there is no
significant charge transfer during the dehydration process, which opened up the possibility of performing a large-scale non-reactive molecular dynamics (MD) simulation. MD techniques were used to study the dehydration from other inorganic crystalline structures [13,14]; however, such techniques have not been applied to epsonite yet.

In this study, we present the results of MD simulations on the dehydration of epsonite at 450 K (177°C) and approximately 20 mbar of water vapour pressure. We report various thermodynamic properties including energy, partial densities, radial distribution functions (RDFs) and diffusion coefficients. The dehydration process and the water transport by diffusion are investigated based on molecular observations as well as on quantitative analyses.

2. Methodology
2.1 Molecular dynamics

Computer simulations, and in particular non-equilibrium molecular dynamics methods based on non-equilibrium thermodynamics (NET), offer a valuable tool for the study of transport properties of materials. One key assumption of the NET theory is that any small element of a system can be considered to be in a state of local equilibrium. This enables the calculation of dynamic properties in non-equilibrium states. In this study, a general-purpose GROMOS53A6 force field [16] additionally optimised for hydration and solvation was selected in the energy minimisation and MD simulations. Simple point charge (SPC) water model [17] was adopted because of its good approximation in liquid–vapour coexistence. [18] The total potential energy in the molecular model is

\[
E_{\text{pot}} = \sum_{\text{bonds}} \frac{1}{4} k_{\text{bond},ij} \left( r_{ij}^2 - r_{0,ij}^2 \right)^2 + \sum_{\text{angles}} \frac{1}{2} k_{\text{angle},ijk} (\cos \theta_{ijk} - \cos \theta_{0,ijk})^2 + \sum_{\text{non–bonded}} \left( \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} \right) + \sum_{\text{non–bonded}} f \frac{\text{erfc}(\beta r_{ij})}{r_{ij}^6} q_i q_j + E_{\text{long–range}},
\]

where the first three terms represent the S–O bond energy in the sulphate dianion, the O–S–O bond angle energy in the sulphate dianion and the non-bonded Lennard-Jones potential within the cut-off radius, respectively. The last two terms are for the electrostatic interactions within the cut-off radius and the long-range corrections using the smoothed particle mesh Ewald (PME) summation method. [19]

2.2 Simulation details

To simulate the dehydration of MgSO₄·7H₂O from a perfect crystalline surface, we took the crystalline structure from a neutron diffraction study [20] at 2 K. A cuboid simulation box consisting of 5 × 5 × 6 cells, each of which contained 4 Mg²⁺ dications, 4 SO₄²⁻ dianions and 28 H₂O molecules, was constructed with periodic boundary conditions in all directions, and was equilibrated under 1 bar and 450 K using a Berendsen barostat and thermostat [21] for a sufficient time of 500 ps. This was to prevent thermal expansion in the later constant NVT simulation. After equilibration, the crystal was cleaved at the (001) surfaces. The cleaved crystal slab had 5 × 5 × 3 cells, which summed up to 300 Mg²⁺, 300 SO₄²⁻ and 2100 H₂O entities. The 2.036 nm thick slab was then attached to two vacuum spaces of 50 nm in thickness, as illustrated in Figure 1. We first applied a steepest descent energy minimisation on this newly generated configuration before the MD simulation was started.

GROMACS4.5.4 [22] was used to carry out the MD simulation. Short-range electrostatic interactions and van der Waals interactions were cut off at 2.5 nm. Long-range electrostatic interactions were calculated using PME [19] with 20 × 20 × 340-sized meshes. A correction term was added in z-direction to produce a pseudo 2D summation, in prevention of slab–slab interactions. [22] Initial velocities of the particles were generated according to a Boltzmann distribution at 450 K. In this simulation, the temperature was

Figure 1. (Colour online) The periodic simulation cuboid contains a crystal slab cleaved at the (001) surfaces and two vacuum spaces attached onto both sides of the crystal.
kept at 450 K using a Berendsen thermostat with a time constant $\tau = 0.1$ ps. The constant temperature simulation ensures a correct energy calculation. After 300 ns of simulation time, the temperature was instantly raised to 600 K for another 25 ns, and then raised to 800 K for the final 75 ns, to completely dehydrate the crystal.

Water molecules in the slab-vacuum system were labelled as ‘free’ if they are at least 1 nm away from the crystal slab surface or ‘confined’ if otherwise. Note that assuming the ideal gas law, a single water molecule in the vacuum space will result in 17.4 mbar of vapour pressure, assuming the ideal gas law, a single water molecule in the crystal slab surface or ‘confined’ if otherwise. Note that usually $t$ should be much larger than it $t_0$ to ensure a correct result since the MSDs show an asymptotic behaviour. In our work, the diffusion coefficients were obtained by fitting the linear region of MSDs over time, which no longer requires a large $(t - t_0)$.

Local partial densities are uniform in $x$ and $y$ directions in early dehydration stages. Therefore, the partial densities as functions of $z$ give very useful information on the dehydration behaviours. The local partial density is calculated as:

$$\rho_A = \frac{1}{(t_1 - t_0) V \Omega} \int_{t_0}^{t_1} \sum_{i \in A, r \in \Omega} m_i \, dt,$$  \hspace{1cm} (4)

where $V$ is the volume of the local region and $m$ is the mass.

RDFs provide information on the structural changes and are calculated as:

$$g_{AB}(r) = \frac{\langle \rho_B(r) \rangle}{\langle \rho_B \rangle_{\text{local}}} = \frac{\langle V_{\text{effective}} \rangle}{V_{\text{nominal}}},$$  \hspace{1cm} (5)

where $\rho$ represents density, $\delta$ is the Dirac delta function, $r$ is the scalar radius and $i$ and $j$ are atoms that belong to chemical species A and B, respectively. The angle brackets denote the ensemble averages. The RDF of slab-like geometries is corrected by the global/local density ratio $C$ during normalisation, which is equivalent to the effective/nominal volume ratio. The nominal volume is the volume of the simulation box, and the effective volume is the actual volume occupied by the slab structure, which is calculated by the enclosed contact and re-entrant surfaces.[25]

The stages throughout the dehydration process are characterised by the composition ratio $n$, which is the molar ratio between water molecules and MgSO$_4$ ions in a local or global region. In case of global $n$ value, the ratio is taken between the number of confined water molecules $N_{\text{conf}}$ and the number of MgSO$_4$ ions $N_{\text{MgSO}_4}$, which is a constant of 300 as mentioned earlier. Note that the initial global $n$ value is 7.0, and $n = 0$ indicates complete dehydration.

To validate the energy terms in the simulation, normal mode analyses were used to correct the classical simulation results following harmonic approximation. [26] This method was well validated through the heat capacity calculation of a metal system. [27] The corrected equations:

$$D_{xyz} = \frac{1}{6(t - t_0)} \sum_{i \in A, r \in \Omega} \|\mathbf{r}_i(t) - \mathbf{r}_i(t_0)\|^2,$$  \hspace{1cm} (2)

$$D_z = \frac{1}{2(t - t_0)} \sum_{i \in A, r \in \Omega} \|\mathbf{r}_i(t) - \mathbf{r}_i(t_0)\cdot \mathbf{n}_z\|^2,$$  \hspace{1cm} (3)

where $\mathbf{r}_i$ is the position of atom $i$, $i$ represents all atoms belonging to chemical species A, $\Omega$ is a local region, $t$ is the time, $t_0$ is the time level at which a molecule enters the local region, $\mathbf{n}_z = [0 \ 0 \ 1]^T$ is the unit vector in $z$-direction, $D_{xyz}$ is the 3D diffusion coefficient and $D_z$ is the $z$ component of the diffusion coefficient. Note that usually $t$ should be much larger than it $t_0$ to ensure a correct result since the MSDs show an asymptotic behaviour. In our work, the diffusion coefficients were obtained by fitting the linear region of MSDs over time, which no longer requires a large $(t - t_0)$.
total energy can be obtained from

$$\begin{align*}
   H_{QM} &= H_{CL} + k_B T \sum_{i=1}^{N_{conf}} \left( \frac{1}{2} x_i^2 - \frac{x_i}{e^{x_i} - 1} \right),
\end{align*}$$

(7)

where \(H_{QM}\) and \(H_{CL}\) are quantum mechanical and classical enthalpies, \(x_i = h v_i / k_B T\), and \(v_i\) are vibration frequencies of normal modes calculated from the normal mode analyses. The summation is over all degrees of freedoms except for 3 coming from the centre of mass motion.

3. Results and discussions

3.1 Dehydration process

In the endothermic dehydration simulation, the total potential energy in the simulation box increased with time while the total number of water molecules decreased, as illustrated in Figure 2. In the early stage of dehydration (0–15 ns), a rapid evasion of surface layer water molecules was observed from the simulation, and the number of confined water molecules \(N_{conf}\) quickly dropped from an initial value of 2100 to around 1650. In around 15–25 ns, the dehydration slowed down, followed by a temporary reacceleration, before it eventually detained. The reacceleration could be the result of the Smith–Topley [28] effect, which stated that the water molecules adsorbed on the surfaces could serve as catalyst for dehydration. Further investigation is needed to support this statement. After 300 ns of simulation, the dehydration was not complete, and the composition ratio \(n\) was decreased to approximately 1.2 (\(N_{conf} = 355, \text{ Figure 3}\)), compared with an experimental value of 0.8 from thermogravimetric analysis.[2]

The total potential energy \(E_{pot}\) with respect to \(N_{conf}\) is plotted in Figure 3. The total potential energy jumps when temperature is increased. Assuming a linear dependence of potential energy on the water number, by linear regression of the 450 K curve, the slope is \(-36.34 \pm 0.09\) kJ/mol with a 95% confidence level. This value can be viewed as the average binding energy per water molecule into the crystal slab. Considering a complete dehydration process from MgSO\(_4\)·7H\(_2\)O to anhydrous MgSO\(_4\), and taking the above average binding energy value, the total reaction enthalpy for complete dehydration is estimated to be 254.38 \(\pm\) 36.34 kJ/mol, compared with an experimental value of 354.0 kJ/mol.[2] Note that the experimental result is measured using a differential scanning calorimetry heat flux technique during the heating up process, while the simulation is carried out at a constant temperature scheme. To further validate the simulation result, supplementary equilibrium MD simulations of bulk epsomite were carried out at 300 and 450 K. Both NpT simulations consisted of 64 epsomite molecules, in combination with periodic boundary conditions. After energy minimisation and equilibration, the ensemble averages of the classical enthalpies from the 500 ps trajectories (500 configurations) are calculated. It is worth mentioning that both NpT simulations lead to structurally stable systems. Then we took the resultant configurations for a thorough energy minimisation by a combined conjugate gradient and steepest descent method, before calculating the Hessian matrix for normal mode analyses. The corrected enthalpy difference according to Equation (7) between 300 and 450 K was then obtained to be 84.58 \(\pm\) 3.22 kJ/mol. According to Hess’ law, this adds up to 339.0 \(\pm\) 13.9 kJ/mol of dehydration energy, close to the experimental value of 354.0 kJ/mol.
3.2 Partial densities

Partial densities of water and MgSO₄ components were calculated separately according to Equation (4). In the early dehydration stages, the local densities were less dependent on \( x \) and \( y \) coordinates. To study the local density changes in \( z \)-direction, local regions were defined as sliced bins stacked along \( z \)-direction, each 0.005 nm wide. Then the densities are averaged from 1000 configurations within 100 ps of simulation. The results are shown in Figure 4. Throughout the thermal dehydration process, several distinct density profiles can be recognised as representations of different dehydration stages. The numbering below is in accordance with that in Figure 4.

(a) At the initial stage, there are evident periodic peaks that indicate a crystalline structure. The average bulk density is 1560 kg/m³, as compared with an experimental value of 1670 kg/m³ at atmospheric temperature and pressure.

(b) The water near or on top of the crystal surface quickly evaded into the vacuum. Within 5 ns, one seventh of the water molecules were removed from the system, and in another 25 ns, another seventh of water molecules were removed. The partial density profiles show that the loss of water starts from the surface layer, forming a gradient in water number towards the centre. Under the attraction forces, the crystal began to shrink, and two peaks in the MgSO₄ partial density appeared. The periodic peaks of the crystalline structure are no longer evident under the rapid loss of water, which is possibly due to the collapse of the crystal framework and formation of amorphous phases. [7,8] However, a rough symmetry around the central plane is still existent.

(c) The two peaks in the MgSO₄ density grow higher and begin to move towards the centre. The thickness of the slab continues to decrease. The partial density of water near the centre approximately remains unchanged while the surface water partial density keeps decreasing.

(d) The peak of the water partial density near the centre is leveled off, accompanied with a slowdown of the dehydration rate. The two peaks in the MgSO₄ density have merged and become indistinguishable. In this stage, the thickness of the crystal slab is no longer uniform, and the slab surface is no longer flat. The superficial texture and the geometry of the slab are not symmetric about the central plane. The thinnest part of the slab approaches to zero, prior to the formation of hollow regions. Therefore, the

![Figure 4](image_url)

Figure 4. (Colour online) (a) to (e) Local partial densities of water (blue) and MgSO₄ (red) in \( z \)-direction as the composition ratio \( n \) changes from 7.0 to 0.1. The dashed lines are referenced bulk densities of MgSO₄ and MgSO₄·7H₂O at ambient conditions. (f) Top view snapshot taken at \( t = 400 \) ns at the end of the simulation.
partial density of water in the centre part shown in the figure is partly contributed by water adhered on the internal surfaces.

(e) The final density profile when the temperature was raised to 800 K does not reach that of bulk anhydrous MgSO₄, because of the hollow regions formed, probably because of surface tension. This is illustrated in the top view screenshot in Figure 4(f). These hollow regions can also be identified as initial cracks from volume shrinkage in micro grain particles, which develop into a porous structure.

A further understanding of the slowdown of the dehydration rate ascribes to the analysis of local composition ratios shown in Figure 5. Although the dehydration process is characterised by the systems composition ratio n, the local ratios may differ from the average value. To give a general tendency of the ratio curve without loss of the details, Figure 5 presents both bin-wise ratios and trend lines which are fitted by fourth power polynomials, symmetric to the centre plane that passes through the systems mass centre. The higher local n values near the surfaces come from the adhered surface water molecules, where no MgSO₄ ions are present. In the centre part, local n values do not change much in the early stages of dehydration (n = 7.0, 5.0) and a gradient in n is formed. At later stages (n = 3.0, 1.5, 0.1), n in the centre region decreases and the gradient in the n profiles decreases accordingly.

### 3.3 Radial distribution functions

The structural changes throughout the dehydration are characterised by RDFs. To make a good comparison with simulated bulk crystals, the calculated RDFs of the slab structures are multiplied with factor C, as described in Equation (6), to ensure that the local densities are the averaged densities within the slab structures. In Figure 6, four sets of RDFs are plotted, with \( \text{Mg} \), \( \text{O}_\text{W} \), \( \text{O}_S \), \( \text{O} \), \( \text{S} \) and \( \text{H} \) representing magnesium dications, oxygen atoms in SPC water molecules, oxygen atoms in sulphate dianions, all oxygen atoms, sulphur atoms and hydrogen atoms, respectively. The RDFs of crystalline \( \text{Mg}_2\text{SO}_4\cdot7\text{H}_2\text{O} \) and \( \text{MgSO}_4 \) are represented by thick lines in Figure 6. These are calculated from equilibrium NpT MD simulations of bulk crystals at 450 K with initial configurations generated from neutron diffraction data.[20,29] The simulation for epsomite consisted of 180 molecules and for \( \text{MgSO}_4 \), 480 molecules. Both simulations lasted for 500 ps with 500 configurations sampled. The RDFs of the final configuration at 800 K and 400 ns when n = 0.1 are also plotted as a reference.

Accompanied with water loss, the RDF peaks change in both height and position. One evident shift is recognised in the second peak in Figure 6(c), which corresponds to the \( \text{H} \cdot \cdot \cdot \text{O} \) hydrogen bonds. The increasing average \( \text{H} \cdot \cdot \cdot \text{O} \) bond length is confirmed by DFT calculations.[12] The decrease in the first peak in \( \text{Mg} \cdot \cdot \cdot \text{O}_\text{W} \) (Figure 6(b)) and the increase in the first peak in \( \text{Mg} \cdot \cdot \cdot \text{O}_S \) (Figure 6(a)) support the loss of water and the clustering of magnesium and sulphate ions. This is also concluded from the density analysis as presented in the previous section.

Note that the discrepancies in RDFs calculated from bulk and slab simulations are expected, because the RDFs in the slab geometries will converge to the effective/nominal volume ratio \( C \) in Equation (6). This geometry effect underestimates the intensity of the peaks at larger \( r \) but keeps correct peak intensity at smaller \( r \). The disagreement between the \( n = 7.0 \) curve with the crystalline epsomite (Figure 6(a–d)) curve comes from the geometry effect mentioned above on the one hand and from the surface rearrangement during energy minimisation and initial MD steps on the other hand. The RDF profiles in the final configuration differ from the RDF profiles of crystalline \( \text{MgSO}_4 \) (Figure 6(a),(d)), indicating that the newly formed anhydrous \( \text{MgSO}_4 \) possesses a disordered structure and therefore has a different RDF. Both van Essen et al. [2] and Ruiz-Agudo et al. [30] mentioned a recrystallisation process of the dehydrated amorphous precursor. However, this possibly slow reorganisation of the lattice structure was not observed in the simulation. It is not fully clear whether there are intermediate products (hexa-, tetra-, di- and mono-hydrate), as no sharp characteristic peaks are observed.
3.4 Mass diffusion of water

Based on the density analyses, after the quick removal of surface water molecules, the dehydration process is governed by the slow diffusion of water from the inner layers to the surface. Compared with water, the MgSO$_4$ ions are less mobile and act as the framework of the structure. Therefore, we quantify the mass transfer in the dehydration process by the local diffusion coefficient of water molecules.

To obtain good ensemble averages, trajectories of 100 ps length are selected in the calculations. Local regions are defined by slicing the slab into many pieces, analogous to the density calculations. The bin widths are chosen to be 0.50 nm, larger than the mean free path of liquid water. Note that the data points are only 0.10 nm apart but represent the diffusion coefficients in a 0.50-nm wide region. In this way, the particles that are oscillating around a bin surface will be included in the calculation of the adjacent bin. Whether a water molecule is counted into the diffusion calculation of a certain region is determined by its duration of stay in this region. The choice of the minimum duration of stay $t_m$ below which the molecule is not counted depends on the specific system of interest. Shinoda et al. [31] argued that the diffusion coefficient of water was not sensitive to the choice of duration in the range of 2–10 ps in lipid bilayer systems. Meanwhile, Taylor et al. [32] selected 2 ps in his study of nanometer water films. In this study, the diffusion coefficients in centre regions are not influenced by the choice of $t_m$, as the water molecules are trapped in the crystal for a longer timescale. However, near surface regions, they can be affected, because of the fast evasion movement of surface water molecules into the vacuum space. To determine the optimal $t_m$ in the diffusion coefficient calculation, we compared different MSD curves in a local region near the surface. This is illustrated in Figure 7. We tested the cases when $t_m$ equals to 5, 3 and 2 ps. Only the molecules that stay longer than $t_m$ are included in the MSD calculation. The trajectories of these molecules are divided into segments of length $t_m$ and are considered as molecules that have newly entered the local region. For instance, suppose a water molecule enters the local region at the 7th picoseconds and exits at the 12th picoseconds of the selected 100 ps long trajectory. We define $t_0$ as the moment at which a water molecule enters the local region. With $t_m = 2$ ps, its moving path will be divided into three segments: 7–9, 9–11 and 11–12 ps. Then the first two
averaged bulk densities.

Figure 7. (Colour online) Mean square displacements (MSDs) of water molecules within a local region near the solid slab surface by different molecule selection criteria (minimum duration of stay $t_0$) and the number of water molecules $N_{\text{local}}$ that stays in the local region for a period of time greater than $(t - t_0)$, where $t_0$ is the moment a water molecule enters the local region. Black dots labels a dynamic averaging scheme counting all molecules that are present at time $(t - t_0)$.

segments are included in the MSD calculation as two independent molecules with $t_0 = 7$ ps and $t_0 = 9$ ps, and the third segment is discarded. In case of the dynamically averaged MSD (Figure 7, black dots), the mean value is taken over all molecules that are present at time $(t - t_0)$ without segmentation. Note that $N_{\text{local}}$, the number of water molecules that stay in the local region longer than $(t - t_0)$, decays with $(t - t_0)$ significantly. After about 2.3 ps, the dynamically averaged MSD stops increasing, as the slower molecules then come into play. Since any choice for the value of $t_m$ will exclude a number of molecules that stays less than $t_m$ into the MSD calculation, the question to be addressed now is till what $t_m$, will the selected molecules best represent the excluded ones ($t_m$ as short as possible), while at the same time, the trajectory segments are still long enough to ensure a reliable linear fit. From Figure 7, it can be seen that $t_m = 5$ ps or 3 ps are not good choices. The linear fit of these two curves (0.8–5 and 0.8–3 ps) gives lower diffusion constants than that from $t_m = 2$ ps (fitted from 0.8 to 2 ps). This is because the selected molecules that stay longer than 5 ps or 3 ps are much slower and cannot represent those excluded faster molecules. However, the choice of $t_m = 2$ ps is reasonably better, as its curve has a good agreement with the dynamically averaged MSD plots. Therefore, we identify 2 ps as a proper choice of $t_m$ to best preserve the diffusion properties without underestimation of the diffusion coefficients. We sorted out all water molecules that stayed longer than 2 ps in the selected trajectories, and divided the trajectories of individual water molecules according to the aforementioned segmentation rule. The diffusion coefficients are then calculated by fitting the linear region in the MSD curve from 0.8 to 2.0 ps.

In Figure 8, the 3D and directional diffusion coefficients of water $D_{\text{xyz}}$ and $D_z$ are plotted as functions of the $z$-coordinate for several global $n$ values. Both $D_{\text{xyz}}$ and $D_z$ are higher at surface regions regardless of $n$, as illustrated in Figure 8. In the centre region, both $D_{\text{xyz}}$ and $D_z$ are less dependent of the $z$-coordinate. Also, $D_{\text{xyz}}$ and $D_z$ seem to increase with decreasing $n$. However, this could be partially contributed by the uneven slab surfaces that locate near centre regions, given that the diffusion coefficients are higher at the surface regions. The diffusion coefficients in the centre are in the order of $10^{-10}$ m$^2$/s, while those near surface are in the order of

Figure 8. (Colour online) (a) Local diffusion coefficients $D_{\text{xyz}}$ and (b) $z$ components of local diffusion coefficients $D_z$ within the solid slab at various dehydration stages. The error bars represent the standard deviations of linear regression. The dashed and dash-dot lines label the coordinates of the slab surfaces at $n = 7.0$ and $n = 2.0$. The surfaces are defined by the locations where the density is 20% of the averaged bulk densities.
10^{-9} \text{m}^2/\text{s}. This falls into the same order of magnitude of a very recent research on the dehydration of MgCl_2·6H_2O at the same temperature, which gives values ranging from 8.5 \times 10^{-10} to 3.7 \times 10^{-9} \text{m}^2/\text{s}.\text{[33]} For comparison, the diffusion coefficient of saturated SPC liquid water at the same temperature (450 K, 890.35 kg/m^3) is also computed to be 18.9 \pm 0.6 \times 10^{-9} \text{m}^2/\text{s} in the same order of magnitude but higher than that of the water molecules on the slab surfaces. This may lead to discussions on the role of the presence of MgSO_4 ions. The higher diffusion rates of the surfaces come from the breakdown of the hydrogen-bonding network\text{[32]} and the collapse of the lattice frameworks.\text{[7,8]} The slow diffusion kinetics in the centre region seems to limit the dehydration rate and, therefore, the dehydration process can be characterised as a diffusion-driven process. In the $n = 2.0$ plot in Figure 8(b), $D_z$ is no longer evidently larger in the surface regions but approximately shows a constant value. This indicates that the diffusion in $z$-direction has almost reached a steady state, and further dehydration is more difficult.

Another aspect of the mass diffusion of water is its anisotropic behaviour. This is most evident on the surface regions where $D_{xyz}$ values are much larger than $D_z$ values. The water molecules have more mobility along the surface than perpendicular to the surface. This conclusion suggests that the internal porous structure and the surface/volume ratio are crucial to the vapour transport by diffusion in the dehydration process.

4. Conclusions

MD simulations have been applied to investigate the thermodynamic and diffusion properties as well as structural changes during the thermal dehydration of a cleaved epsomite ($\text{MgSO}_4·7\text{H}_2\text{O}$) crystal. In this study, the enthalpy change during dehydration and the bulk densities are calculated and compared with experimental values that validated the method. It is discovered that the dehydration process exhibits multiple stages. The initial quick dissociation and loss of surface water caused the high initial dehydration rate, accompanied by the collapse of the crystal framework and formation of amorphous phases. Following the loss of surface water, a density gradient of water is formed and the partial density of MgSO_4 is raised near the two surfaces. Subsequently, the rate of dehydration is seemingly controlled by the diffusion of water from the centre part to the slab surfaces. Eventually, the surface adsorption of water further inhibited the diffusion of water to the surfaces, and the diffusion in $z$-direction gradually reaches the steady state. The exothermic adsorption process can be reduced by increasing the simulation temperature. Superficial texture changes were observed during the simulation and evolved into hollow regions due to the volume shrinkage. It is also noted that the diffusion of water is anisotropic, suggesting that the internal porous matrix structures in the porous epsomite reactant play an important role in the water transport. Recrystallisation is not observed in this simulation owing to the slow lattice reorganising kinetics. The results obtained in this study agreed with corresponding experiments, and led to more insight into the thermal dehydration process of epsomite.

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References

[8] Brotton SJ, Kaisen RI. In situ Raman spectroscopic study of gyspum ($\text{CaSO}_4·2\text{H}_2\text{O}$) and epsomite ($\text{MgSO}_4·7\text{H}_2\text{O}$) dehydration utilizing an ultrasonic levitator. J Phys Chem Lett. 2013;4:669–673.


