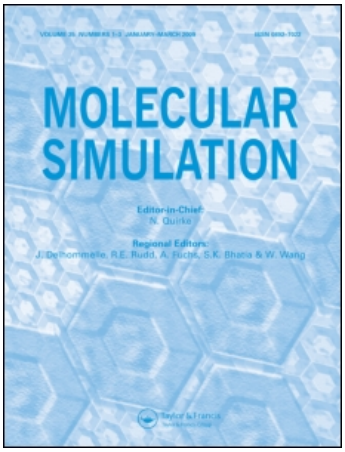

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Simulating Dehydration: A Novel Hybrid Molecular Dynamics Method

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This paper describes the development of an atomistic simulation method which can model and predict the water content and structural behaviour of complex framework systems undergoing dehydration. The procedure uses constant-pressure molecular dynamics (MD) and involves calculation of individual potential energies of adsorbed water molecules and comparison of these with their average kinetic energies. An "escape probability" is defined for water trapped in the channels and cages of host structures. Thermo-gravimetric (experimental) data are used to scale and validate the method. The corresponding structural variations (framework, cations) are compared with X-ray diffraction (XRD) data obtained from an ion-exchanged zeolite, Na- and Cs–clinoptilolite (CLI).

Keywords: Dehydration; Clinoptilolite; Modelling; Forcefields

INTRODUCTION

Although there have been several studies of hydrodynamic systems very little work has been reported on modelling of dehydration, which is the concern of this study. Existing Grand Canonical Monte Carlo (GCMC) procedures allow random creation and destruction of particles, in addition to translation and rotation, in an ensemble at constant chemical potential, volume and temperature. However, we need to be able to model framework dynamics, in the absence of cell constraints, together with other features such as framework model charge redistribution and diffusion, using realistic computational resources. This points towards the development of time-dependent (rather than stochastic) methods with an alternative procedure for removing water molecules, but retaining GCMC as a complementary and bench-marking technique. However, molecular dynamics (MD) simulations are generally computationally intensive. A real time dehydration of a large heterogeneous system would represent a challenging simulation for even the most powerful computing resources. Instead, we combine a simple routine, based on the total non-bonded energies of individual water molecules, with a sequence of NPT (constant pressure) simulations. The overall aim is to provide a tractable and accurate solution to modelling dehydration with realistic computing resources.

We illustrate this hybrid method with an examination of dehydration in an ion-exchanged zeolite, clinoptilolite (CLI), comprising porous frameworks, mobile extra-framework cations and water. CLI has an alumino-silicate framework, with pore sizes of <1 nm, represented by a unit cell composition of $Si_{30}{\cdot}Al_6{\cdot}O_{72}{\cdot}(M^{+}{\cdot}(1/2)M^{2+})_6{\cdot}10{-}20\,H_2O$. It has been used as a general adsorbent and ion exchanger, particularly for trapping and containing ions from low and intermediate level nuclear waste. As it is a widely occurring natural zeolite, it has also been the subject of interest for the disposal of toxic materials in major geological repositories [1]. The sodium–exchanged form (Na–CLI) is often a starting material in the treatment of radioactive effluent, in which competing Cs^+ ions from a contaminated stream replace the incumbent Na^+ ions. We have simulated the dehydration and structural behaviour of both the sodium and caesium (Cs–CLI) exchanged forms and compare the output with experimental data from thermo-gravimetric analysis (TGA) and X-ray diffraction (XRD).

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FORCEFIELDS

The simulations reported in this paper use inter-atomic potentials in which the energy is expressed as a sum of bonded (valence) and non-bonded terms. The methodology described here has been tested with two alternative sets of potentials: The first, denoted F1, includes valence components to model explicitly the covalent characteristics of extended frameworks, but limited to bond distance and angle terms with an additional distance term between two atoms bonded to a common (third) atom. This is a modified form of the "universal" forcefield of Rappé and Goddard [3]. A full list of the potential parameters are given by Johnson *et al.* [2] and details of the derivation are also given by Rappé and Goddard [3]. The second set, F2, involves no valence terms for the framework and could be described as "ionic". It is adapted from the augmented form of the CVFF [4] forcefield, using fixed reduced charges (for a justification see van Beest *et al.* [5]) with a dielectric constant of unity.

The TIP3P [6] model of the water molecule is used in conjunction with Dreiding [7] van der Waals terms and simple harmonic bond and angle functions to provide flexibility. The explicit form of the function used to calculate the *non-bonded* H_2O energy is

$$E_{H_2O} = E_{LJ} + E_{Coulomb} = D\left[\left(\frac{r_0}{r_{ij}}\right)^{12} - 2\left(\frac{r_0}{r_{ij}}\right)^{6}\right] + C\frac{q_i q_j}{\varepsilon r_{ij}} \qquad (1)$$

where D is the potential well depth at r_0, the corresponding inter-atomic separation, q_i is the charge on centre i, r_{ij} is the distance between the water molecule and other species, j, ε is the dielectric constant and C a constant conversion factor. The repulsive van der Waals interactions are calculated by the direct method (which decay as the standard Lennard–Jones 12th power form) and are negligible beyond distances of a few angstroms. The electrostatic and attractive van der Waals interactions are calculated by the Ewald method which splits the calculation into a short real space part and a Fourier sum for the remaining periodic lattice. Since quantum calculation of electronic states is not feasible for dynamic simulations on large collections of atoms, the rapid charge equilibration (Qeq [8]) procedure of Rappé and Goddard has been used to calculate partial charges in the F1 forcefield. This is based on the electro-negativity of an atom, which can be associated with the average of the ionisation potential and the electron affinity. Qeq uses experimental atomic ionisation potentials and electron affinities as well as additional information on atomic radii, and estimates of the shielded electrostatic interactions between charges, to construct atomic chemical potentials. The equalisation of potentials within the system then leads to an equilibrium charge distribution dependent on the geometry. This method has been applied to a wide range of organic and inorganic systems, and has been used here to recalculate the partial charges for the extended zeolite framework after water removal and at the start of each new temperature cycle.

DEVELOPMENT OF THE HYBRID MD METHOD

Before describing the new hybrid method, the context of its intended use first needs to be explained. The 3-dimensional (3D) system of channels and cages within a zeolite offers an extensive surface area on which guest molecules can adsorb. Disordered water in these structures is presented with many sorption sites, effectively potential wells whose depth and location within the structure both change with temperature. Thus a desorption event can be associated with an activation energy, E_d, and an Arrhenius-like dependence for the desorption rate k_d:

$$k_d = A\exp\left(-\frac{E_d}{RT}\right) \qquad (2)$$

where A represents a frequency factor; a complicating issue is the further dependence of E_d on sorbate coverage (i.e. degree of hydration). The exponential term can be identified with the probability of desorption of a molecule in a potential well of depth PE at a temperature T, and the kinetic energy components, KE, of a guest water molecule act to overcome this binding potential and increase the likelihood of exiting the host structure. Using the classical equi-partition of kinetic energy with each degree of freedom, $k_BT/2$, leads to a total contribution of $3k_BT$ for the case of a non-linear tri-atomic molecule such as water possessing both translational and rotational degrees of freedom (we can neglect vibrational components for T within the dehydration regime). We can then assign a probability, p, to an individual water molecule for its removal from the host structure based on its total energy ($KE + PE$):

$$p = \min\left[1; A\exp\left(\frac{KE + PE}{RT}\right)\right] \qquad (3)$$

where A is a proportionality constant which is discussed below. In addition to the other simplifying assumptions made, one can question whether these degrees of freedom are always fully available for desorption. However, the approach adopted here is to deal with these aspects in a probabilistic fashion using the Monte Carlo procedure inspired by Metropolis *et al.* [9] for making an unfavourable change in configurational energy. Thus if p, in Eq. (3), is larger than

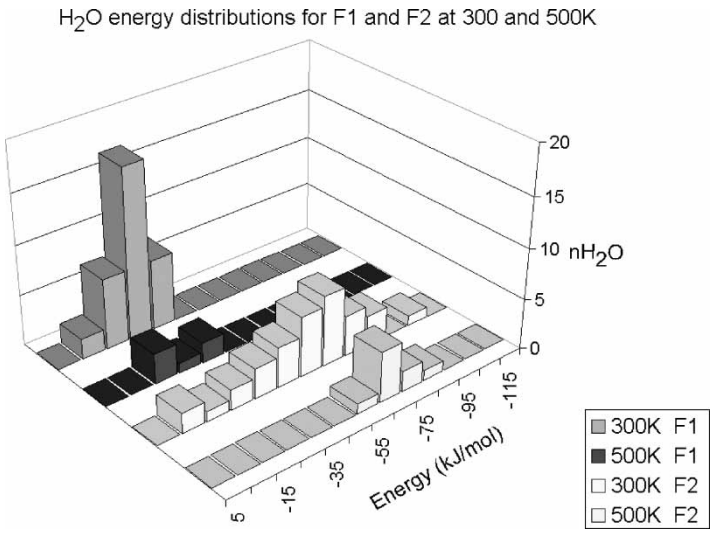

FIGURE 1 Water energy distributions in Na–clinoptilolite at 300 and 500 K using the F1 and F2 forcefields. (Colour version available online.)

a random number ξ uniformly distributed in the interval (0,1), then the molecule will be removed. For our temperatures, the degrees of freedom are effectively constant, while the distribution of potential wells shifts towards shallower values as T increases.

The pre-exponential factor A in Eq. (3) can assume a useful significance, effectively to normalise the algorithm for a given potential to dehydration rates that are consistent with experimental data. The importance for such normalisation can be easily appreciated when we note that calculated sorption energies for water in zeolites differ significantly when using different forcefields, mainly due to the treatment of charges; experimental values also vary widely ($\sim$20–60 kJ/mol and even as high as 100 kJ/mol at low coverage [10]). Figure 1 shows the distribution of binding energies for water in Na–CLI obtained using the two forcefields F1 and F2 (higher values with the "ionic" model F2) and how these change with temperature from 300 to 500 K.

The first step is to calculate the mean binding energy, E_{ave}, for the chosen forcefield (e.g. -24.60 ± 7.5 kJ/mol for F1 or -53.97 ± 20.9 kJ/mol for F2 in Na–CLI at 300 K). We then require an estimate for a parameter T_ω, the approximate temperature by which dehydration of the material is complete. At T_ω we define the probability of desorption for the average molecule to be unity, with the corresponding assumption that the average well-depth (E_{ave}) and kinetic energy ($KE = 3RT_\omega$) are equal. The inverse probability at this point, A as given by Eq. (4), can then be used to adjust any deviation from ideality by scaling all the calculated probabilities given by the exponential term in Eq. (3).

$$A = \frac{1}{p_\omega} = \exp\left(\frac{|E_{\text{ave}}| - KE}{RT_\omega}\right) \tag{4}$$

Sets of A-values have been calculated for the example used here and shown in Fig. 2 for a range of dehydration temperatures, T_ω, and average well depth, E_{ave}. It can also be pointed out that E_{ave} does not actually remain constant. However, we can see from Fig. 1 that it does not change far from its reference value for either forcefield. One could refine further this general method by making A a non-linear, temperature-dependent function, though in its constant form described here it has the virtue of being associated with a simple physical interpretation (an average energy and its assumed dehydration point) and attracts negligible computational overheads in its implementation.

The testing and benchmarking of this hybrid method against experimental data has been undertaken using primarily thermo-gravimetric and structural (rather than calorimetric) data; these provide a fairly exacting test of the method: TGA essentially charts the water content (from the total mass of the sample) as a function of temperature, as the model material is heated. From these data either $\Delta N/\Delta T$, the change in water content with temperature for any interval ΔT, or the dehydration temperature, T_ω, can be obtained and used. If we use the former (i.e. $\Delta N/\Delta T$) then the hybrid method effectively determines not *how many* but *which* water molecules should be lost over a given interval. This is done by calculating the probabilities and applying the routine $p >$ rnd until the required ΔN molecules have been removed; i.e. it is not necessarily just the least negative ΔN water molecules that are removed at each step. Equation (5) links the experimental and simulation data via the constraint $\Delta N_{\text{sim}} = \Delta N_{\text{exp}}$:

$$\Delta N_{\text{sim}} = \sum_{N=1}^{N=\Delta N_{\text{exp}}} \max\left[1; (p > \text{rnd})\right] \tag{5}$$

where p is given by Eq. (3) and the inequality term indicates that the summation only includes water

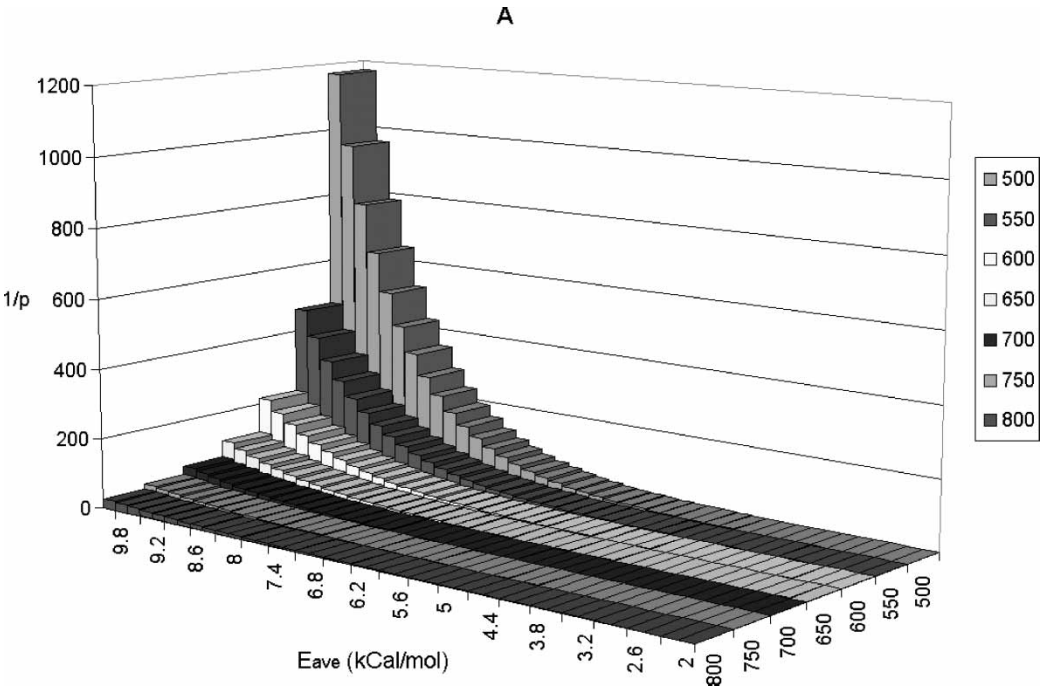

FIGURE 2 Plots of calculated *A*-values for different average water well depths, E_{ave} and dehydration temperatures, T_ω. (Colour version available online.)

molecules for which $p >$ rnd is satisfied. However, the alternative and more general approach is to predict $\Delta N/\Delta T$ using only an experimental estimate for T_ω. It follows that the experimental data on water loss, and resulting structural changes, then become an exacting test of the method. This is the approach used in the remainder of this study.

It is important to distinguish this hybrid method from those using conventional ensembles: although the hybrid method bears some similarity to the GCMC method by using a probabilistic removal step, there are significant differences in that the hybrid method does not hold the volume constant, has no need for a probabilistic insertion step and does not attempt to achieve reversibility. Rather the method is aimed at reproducing experimental data, particularly TGA, where the gaseous environment content is not in equilibrium with the sample (except possibly after complete dehydration) and where typical dehydration rates are sufficiently high that temporary (water) re-adsorption events can be ignored. Further the method is intended to cater for irreversible changes that can occur with zeolite dehydration, such as extensive bonding rearrangements, framework transformations and eventually framework collapse.

The flexible NPT simulation is necessary to ensure proper exchanges between sorbate molecules, ions and the framework. Consequently there is a reorganisation of energy levels and sorption sites after each simulation stage. Ideally, an incremental sequence of NPT simulations should employ infinitesimal adjustments in N and T in order that the system remain in equilibrium at constant atmospheric pressure. However, real simulations conducted with finite computational resources are obliged to use more substantial adjustments such as the $\Delta N \sim 1$–3 and $\Delta T \sim 10$–20 K used here. In this study, the framework structures, such as Na/Cs–CLI, appeared to remain stable throughout dehydration with cell parameters remaining within expected values.

Another issue that requires consideration is the representation of disorder in the water positions. Although the use of periodic boundaries is acceptable for modelling bulk crystalline materials, its use for water within a framework runs a risk of imposing excessive order on the system. This risk can be reduced by using a larger simulation cell, but the cost would be severe in terms of feasible simulation times. A compromise configuration for the CLIs consisted of two unit cells containing, at full hydration, approximately 30 water molecules (depending on ion type) and in excess of 300 atoms. Figure 3 illustrates such a simulation cell for Cs–CLI. Apart from the aluminium "defects" which are responsible for the inclusion of mobile charge-balancing cations, the framework is identically distributed about a horizontal (020) mirror plane.

IMPLEMENTATION OF THE HYBRID MD METHOD

Software development was structured around a flexible, cross-platform, modular approach. Program

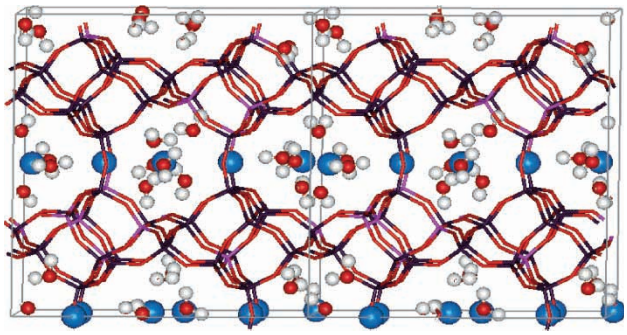

FIGURE 3 Two simulation cells (four crystallographic cells) of caesium clinoptilolite showing mobile Cs ions (blue) and water (O, red; H, white) as spheres and the framework as sticks (Si, black; Al, pink; O, red). The view is looking down the *c*-axis which clearly illustrates the larger 10- and smaller 8-ring channels; another 8-ring channel (not seen in this view) runs along the *a*-axis. (Colour version available online.)

logic, file manipulation, data analysis and image processing were designed and written as a collection of Tcl modules. The MD and static energy calculations were called as external routines. A minimal amount of platform-specific shell programming was also required. The prototype was originally run on an SGI Octane, and the MSI/Accelrys C^2·Dynamics module used to perform the MD and energy calculations. The program flow, for the key elements of the process, is as follows:

- Read in a structure (e.g. Bish [11] for CLI) and an experimentally determined composition and water content (which, in the absence of definitive positions can be distributed in the framework with an NVT MC).
- Read in the required forcefield functions and parameters. If using charge equilibration, calculate the framework charges. Keep the counter-ion and TIP3P charges constant. Check for overall charge neutrality.
- Set up the key run-time parameters (all temperatures are given in Kelvin):
  - T_{min}, the starting temperature is typically 300
  - T_{max}, the maximum temperature is at least up to the end of a TGA scan, ~850
  - ΔT, an acceptable temperature increment is 10 or 20 K
  - Δt, a time step of at most 0.001 ps
  - A, the pre-exponential correction factor
- Relax the atoms at constant volume (NVT), check the total energy and system temperature; typically 5–10 ps.
- Change to the constant pressure (NPT) ensemble and relax the entire structure. Check that the atom and unit cell parameters are still consistent with the experimental values as validation for the forcefield used.
- Runtime: the remainder of the simulation is conducted in the NPT ensemble. Progress from T_{min} to T_{max} incrementing in steps of ΔT. At each temperature run the MD until equilibration is achieved; usually a minimum of 5–10 ps.
- After equilibration has been reached run the dehydration routine:
  - loop over the remaining water molecules
  - calculate the potential energy PE of each molecule
  - sum the energy terms, i.e. $\Sigma = ((PE + KE)/RT)$
  - if $\Sigma \geq 0$, designate the H_2O molecule for removal
  - if $\Sigma < 0$ calculate the removal probability, $p = A \times \exp(\Sigma)$
  - compare p with a random number ξ uniformly distributed in the interval (0,1)
  - if $p > \xi$, designate the molecule for removal
- Remove the designated H_2O molecules.
- If appropriate, recalculate the framework partial charges for the new structure.
- Increment by ΔT and loop until $T = T_{max}$.

When there are no remaining water molecules, the routine continues with a sequence of NPT simulations up to the desired termination point.

RESULTS AND DISCUSSION

(a) *Na–CLI*: Figure 4 compares the experimental water loss profile for Na–CLI (by TGA) with the simulated profile obtained by the method described above using the F1 forcefield and 20 K temperature intervals with 10 ps per point. Both the trend and actual values are well reproduced. Detailed examination of the structure files indicate that the least bound water molecules, found in the large main channel system, leave early leading to a slight reduction in the cell volume which stabilises as the simulation continues. The water molecules in the small cages are more strongly bound and occasionally get trapped in positions which screen cations from their full repulsive interactions with each other or the framework; some persist to quite high temperatures [1,12]. The Na-cations are initially distributed in the mirror (020) plane, shielded from each other and the framework by water, as illustrated in Fig. 5. As water desorbs, the cations begin to experience both framework attraction and inter-ionic repulsion and migrate to explore the cage and channel system and framework surfaces, as indicated in Fig. 6 which shows a simulation snapshot after equilibration at 580 K.

The Na-cations in the small channel have redistributed themselves into potential minima vertically above and below the mirror plane and in the process have induced a vertical elongation of the small channel cross section. This process induces a corresponding horizontal elongation in the large channel. Experimental data subsequently collected at 300°C on

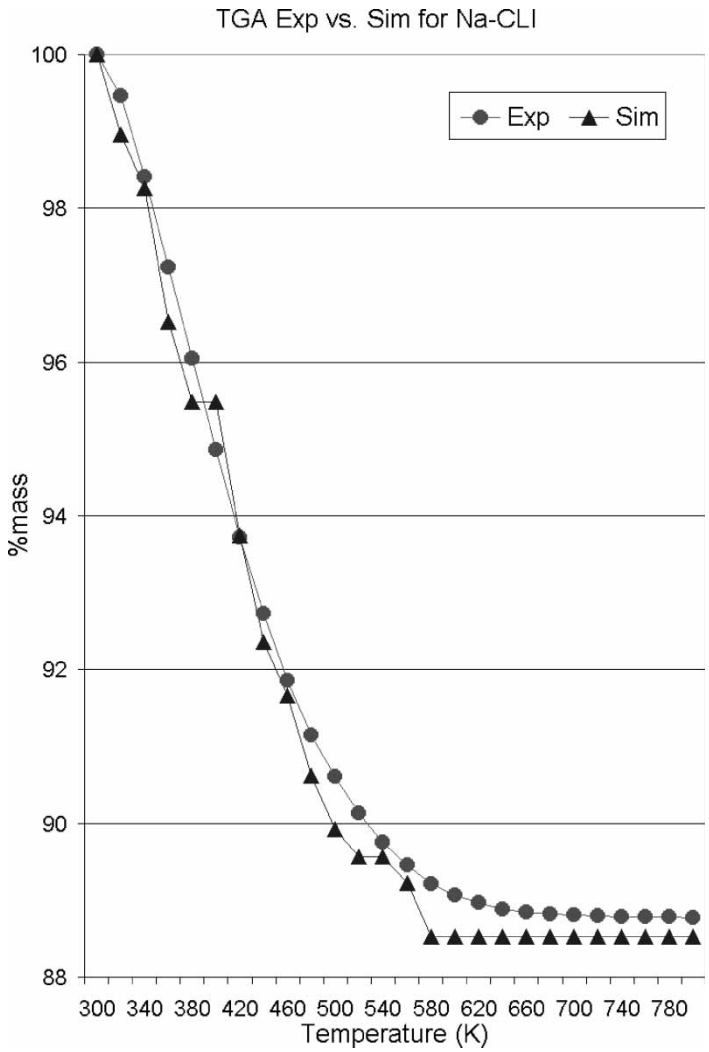

FIGURE 4 Comparison of experimental (Exp) and simulated (Sim) TGA (thermo-gravimetric analysis) data for the dehydration of Na–clinoptilolite during calcination up to 800 K. (Colour version available online.)

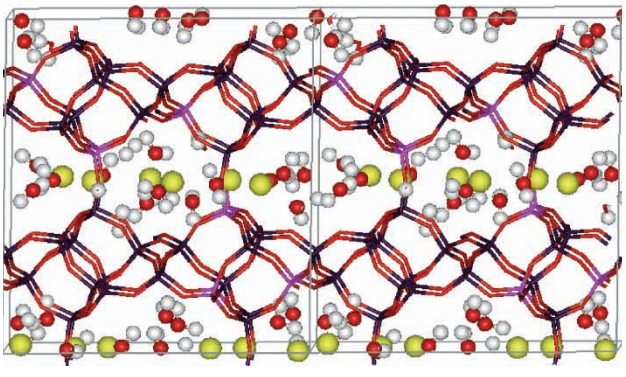

FIGURE 5 Simulation snapshot (two full cells for clarity) of hydrated Na–clinoptilolite at 300 K (Na, yellow, otherwise colour scheme is as in Fig. 3). (Colour version available online.)

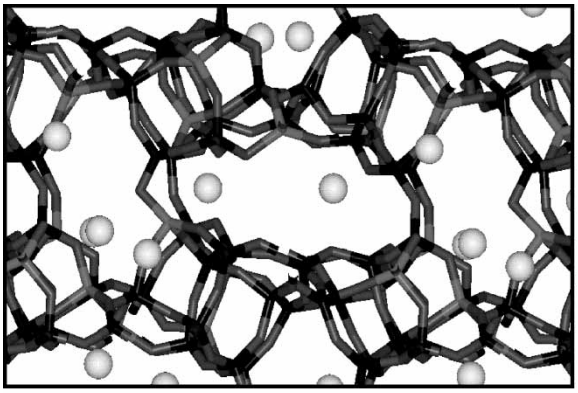

FIGURE 6 Simulation snapshot (nearly 2 cells' worth for clarity) of hydrated Na–clinoptilolite at 580 K which can be compared with the experimental data (Fig. 7). The Na-cations in the smaller channel are noticeably displaced from the central mirror (020) plane inducing a more elliptical cross section to the channel. (Colour version available online.)

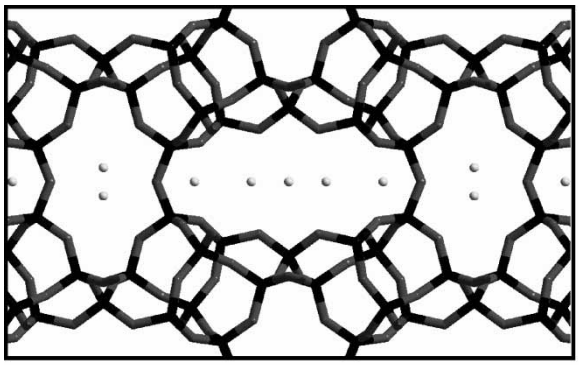

FIGURE 7 Experimentally determined framework and Na (partial) occupancies derived from micro-crystal X-ray diffraction studies (after Johnson *et al.* [2] and reproduced with permission of the American Chemical Society). (Colour version available online.)

the Daresbury Laboratory SRS synchrotron (described in detail elsewhere [2]) verify this structural prediction (Fig. 7; note this shows the partial cation sites which are not therefore simultaneously occupied).

(b) *Cs–CLI*: Figure 8 similarly compares the experimental and simulated water loss profiles for Cs–CLI using again 20 K temperature intervals with 10 ps per point and an estimation of $T_\omega = 650$ K. Again the trend is well reproduced although a slightly less aggressive desorption simulation could be achieved by using a higher T_ω value. However, the pattern of water loss was consistent with the Na case, with water departing from the main channel before finally exiting the lowest energy sites in the small channels. The simulation structural snapshots (Fig. 9) show the Cs-cations remaining largely in the mirror plane, with some migration during the intermediate dehydration phase while adjusting to the reduction in electrostatic screening. This is completely consistent with the corresponding experimental data (Fig. 10) where the off-mirror sites have very low occupancies. Continued simulation after the dehydration regime indicates greater structural integrity for the Cs-exchanged form than the Na-form, which is related to the different

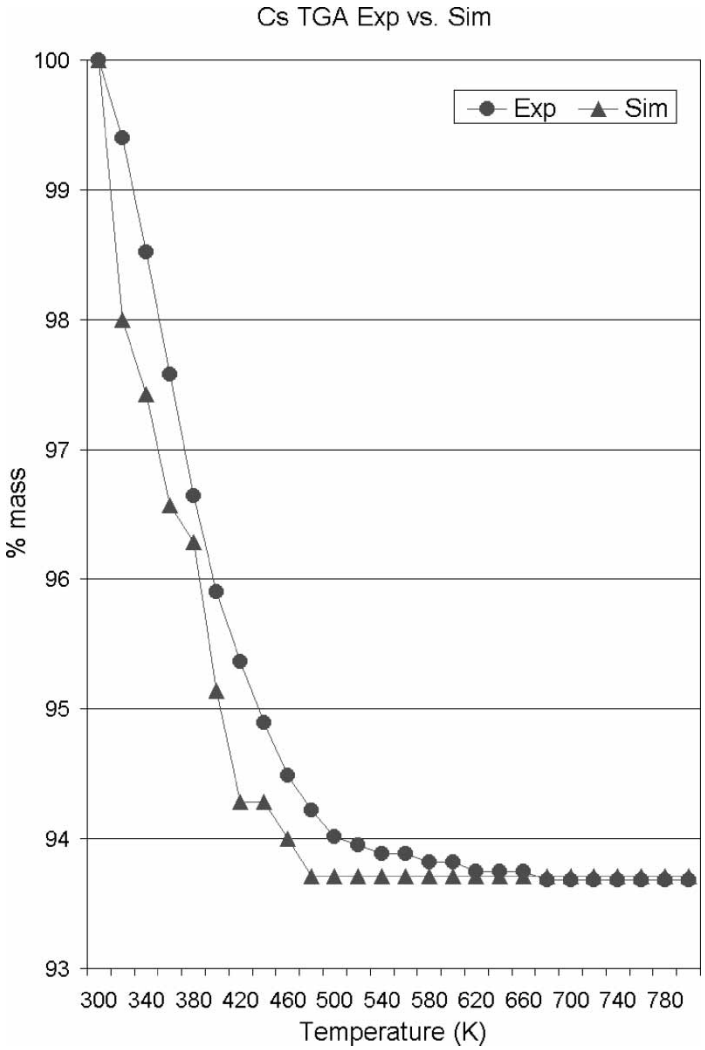

FIGURE 8 Comparison of experimental (Exp) and simulated (Sim) TGA (thermo-gravimetric analysis) data for the dehydration of Cs–clinoptilolite during calcination up to 800 K. (Colour version available online.)

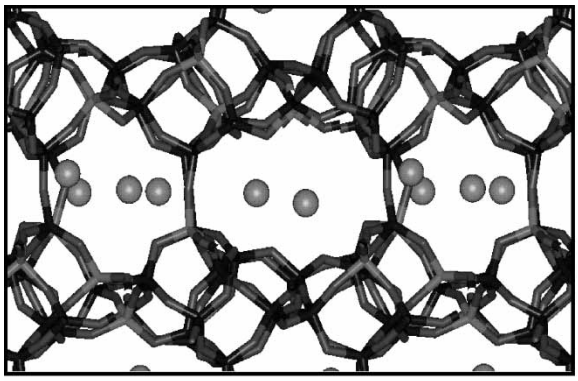

FIGURE 9 Simulation snapshot (nearly 2 cells' worth) of hydrated Cs–clinoptilolite at 580 K which can be compared with the experimental data (Fig. 10). The Cs-cations (blue) remain close to the central (020) mirror plane and the channel cross sections remain approximately constant. (Colour version available online.)

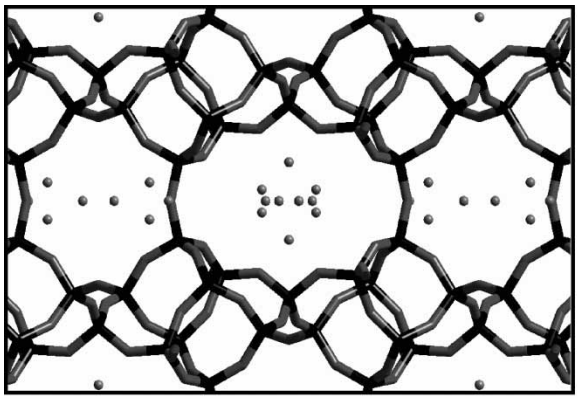

FIGURE 10 Experimentally determined framework and Cs sites (blue) derived from micro-crystal X-ray diffraction studies at 573 K. The Cs-sites shown have very low occupancies away from the central (020) mirror plane (after Johnson *et al.* [2] and reproduced with permission of the American Chemical Society). (Colour version available online.)

behaviour of Na and Cs and subsequent framework response. Unit cell parameter data showed an overall volume decrease, consistent with expectations from water loss; otherwise there was little overall change in unit cell dimensions (typically 1–3% reduction in volume over this temperature range) which is largely consistent with experimental data [13].

CONCLUSION

A simple hybrid MD method has been developed to model dehydration in framework structures possessing mobile cations. The method performs well in describing and predicting thermo-gravimetric water loss; cation positions and framework structural behaviour. In computational terms the procedure is relatively inexpensive and permits the incorporation of various levels of experimental information into the modelling process. The atomistic approach allows examination of the behaviour of individual molecules and ions, whilst the probabilistic feature is consistent with the statistical nature of macroscopic data. The semi-covalent model with framework charge recalculation, F1, is found to be simple and effective, whereas the alternative ionic model, F2, led to an excessively robust structure that did not display the experimentally observed framework transformation with Na–CLI. The flexible NPT simulations provide realistic modelling of energy transfer mechanisms and a fluctuating 3D zeolitic pore structure in which the water molecules and cations move. Despite the simplicity and success of this approach, the recommendation for subsequent improvement would be to use a high performance parallel architecture to achieve a bigger simulation cell, smaller temperature increments and more frequent charge recalculation. This would also permit extended simulations for the estimation of diffusion constants and vibrational properties. The method is applicable to other systems, such as ceramics, cementitious materials and pharmaceutical compounds, for which structure and performance depend critically on water content and behaviour.

Acknowledgements

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SPECIAL APPENDIX: SIMULATION METHODOLOGY

The main simulation details are listed in the "Implementation of the hybrid MD method" section. These are:

(a) *Hamiltonian/Potentials*: The Molecular Dynamics employs the standard classical (Newtonian) form of equations of motion using the Verlet "leapfrog" method of solution. The intermolecular 'F1" potentials used in the results shown here have been reported by Johnson *et al.* [2].

(b) *Algorithm used*: The algorithm consists of a standard NPT Molecular Dynamics (as in (a)) plus a dehydration routine which is the main subject of the paper and which is detailed in the "Implementation of the hybrid MD method" section.

(c) *Averages*: The Energy and Probability calculations are the main subject of the publication with further details in the "Implementation of the hybrid MD method" section.

(d) *Comparisons*: The following checks/comparisons are utilised: (i) Structural behaviour of the models under NPT simulation is compared with crystallographic data (unit cell parameters in the case of powder diffraction data, and atomic positions in the case of high quality single crystal diffraction data); (ii) The water energies are checked to be approximately comparable with experimental values as given in the literature (e.g. Ref. [1]); (iii) The water content is compared with experimentally determined TGA data by the authors.

(e) *Simulation parameters*: These are given explicitly in the "Implementation of the hybrid MD method" section.

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