A classical reactive potential for molecular clusters of sulphuric acid and water

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We present a two-state empirical valence bond (EVB) potential describing interactions between sulphuric acid and water molecules and designed to model proton transfer between them within a classical dynamical framework. The potential has been developed in order to study the properties of molecular clusters of these species, which are thought to be relevant to atmospheric aerosol nucleation. The particle swarm optimisation method has been used to fit the parameters of the EVB model to density functional theory (DFT) calculations. Features of the parametrised model and DFT data are compared and found to be in satisfactory agreement. In particular, it is found that a single sulphuric acid molecule will donate a proton when clustered with four water molecules at 300 K and that this threshold is temperature dependent.

I. INTRODUCTION

It has long been suspected that sulphuric acid plays an important role in atmospheric particle nucleation as a consequence of its affinity to water and its low volatility [1], though ammonia and organic species, as well as ions, are also likely to participate [2]. Considerable experimental advances in characterising nucleation phenomena in atmospherically relevant conditions, with particular emphasis on sulphuric acid, have been reported in recent years [3, 4]. The interpretation of such experimental data in order to understand behaviour over wider conditions is critically dependent on calculations of the free energies of clusters of the nucleating species. Such thermodynamic information is employed within a well-established theoretical framework of cluster growth and decay to predict rates of formation of stable clusters [5, 6]. Although further processes such as cluster coalescence or removal also play a role in particle formation [7], this kinetic and thermodynamic framework lies at the heart of our understanding of the phenomenon.

Cluster free energies, however, are not straightforward to calculate. Simple models of cluster thermodynamic properties have repeatedly been sought, but often such approaches rely on an extrapolation of the properties of larger droplets down to clusters consisting of only a few molecules [8–10]. The prime example of such a model is classical nucleation theory (CNT) [5, 11], based on the capillarity approximation. Caution is necessary when using such models if they suggest that the nucleation rate is sensitive to the properties of very small clusters, since accuracy is not to be expected [12], though surprisingly it is often observed.

More advanced models of molecular clusters can be used, of course, though at greater cost in computational effort. At the most fundamental level, molecular interaction models based on *ab initio* quantum mechanics are available. Indeed, very detailed studies have been conducted, even taking account of the quantum nature of the lighter nuclei present [13, 14] in addition to that of the electrons. In a structural study of the system that we consider in this paper, for example, Kakizaki *et al.* [13] concluded that nuclear zero point motion in clusters of sulphuric acid and water at 250 K gives rise to noticeably increased fluctuations and liquid-like behaviour. Sugawara *et al.* [14] studied the degree of hydration required for the dissociation of the sulphuric acid molecule, at the same level of theory [15]. Further evidence of small but significant effects of zero point motion in similar clusters was provided by Stinson *et al.* [16].

However, when computing free energies using *ab initio* methods, the harmonic oscillator approximation is commonly employed, based on identifying the lowest energy cluster configuration at zero temperature and estimating the vibrational entropic contributions to the free energy from a characterisation of the low temperature normal mode spectrum. Such an approach is likely to be accurate at temperatures where the cluster behaves as a vibrating solid-like structural network, but would seem to be less appropriate for liquid-like systems. A more general approach is then typically required, such as thermodynamic integration [17] where the free energy of a system is compared with that of a better understood reference system at the same temperature, through performing a series of canonical averages with interpolating Hamiltonians, often using Monte Carlo (MC) methods. Approaches based on nonequilibrium molecular dynamics (MD) simulation have also received attention [18, 19]. Methods of free energy computation are indeed rather numerous [20]. In many systems of interest, however, *ab initio* energy calculations are too expensive, and modelling necessarily proceeds on a more coarse grained, classical level.

A number of classical schemes have been employed to study clusters of sulphuric acid and water molecules. In an early study Kusaka *et al.* [21] developed a grand canonical MC model based on rigid molecules and concluded that the clusters are highly non-spherical and that bulk-like behaviour only emerges when there are at least 240 water molecules and $1 - 3$ molecules of sulphuric acid, or its dissociation product bisulphate, in the cluster. Later, Kathmann and Hale [22] presented a model based on rigid water and sulphate molecules and a free $H^{\delta+}$ ion, treated within an MC approach. Ding *et al.* [23] de-

veloped a flexible bonding model for sulphuric acid, bisulphate, hydronium and water species, which was employed by Toivola *et al.* [24] to study a quasiplanar liquid-vapour interface using clusters of 2000 molecules. Amongst other matters, they found that when the sulphuric acid mole fraction is less than 0.1, the acid molecules lie at the cluster surface and that the cluster structure is strongly dependent on the number of bisulphate ions present.

However, although mixtures of dissociated species were studied by Toivola *et al.* [24], the dynamics of the transfer of protons between species was not considered in the model. It is important to note that a classical potential suitable for free energy computations for clusters of sulphuric acid and water ought to be designed to describe the transfer of a proton from the acid to a water molecule. Without such a capability, it is not possible to allow proton transfer to take place naturally; instead, the degree of dissociation would have to be fixed by hand in a given simulation.

This brings us to the aim of this study, which is to develop and parametrise a classical potential that does offer this capability. Such a potential would allow us to test the harmonic approximation in calculations of the free energy in sulphuric acid/water clusters at relevant atmospheric temperatures. Using a classical potential that can describe the dynamics beyond structural vibrations is a crucial requirement.

There are a few classical schemes available which allow reactions to occur. These include the Gaussian Approximation Potential (GAP) [25] where a potential energy surface is constructed by fitting a Gaussian basis set to reference data following a Bayesian statistics procedure; the ReaxFF approach [26] which uses the bond order methodology; and the empirical valence bond (EVB) model [27] based on a superposition of underlying classical states of the system.

The EVB methodology is attractive for use in the sulphuric acid/water system since, as we shall see, it is based on classical potentials for each species plus mixing terms, and is relatively straightforward to implement into existing MC or MD schemes. The methodology was introduced by Aqvist and Warshel [28] and is reviewed by Kamerlin and Warshel [27]. It was first developed in order to model proton transfer between hydronium and water species. Schmitt and Voth [29] designed a so-called multi-state EVB (MS-EVB) model for the simulation of systems of water molecules containing excess protons. This work was further developed into the MS-EVB2 [30] and the MS-EVB3 [31] models. Our strategy is to use the MS-EVB3 model as a framework for constructing an EVB model for the sulphuric acid and water system. As a simplification, we limit the multiplicity of states to two (i.e. the proton may be attached either to a bisulphate or to the nearest appropriate water molecule) making it a two level EVB approach. Multiple potential proton transfers within the system are accommodated by employing the self-consistent iterative MS-EVB (SCI-MS-EVB) model, developed by Wang and Voth [32]

for water with excess protons. A recent summary of the EVB model in the context of modelling proton transfer in a water network is given by Knight and Voth [33].

We describe the basis of an EVB model in Section II. Section III is an account of the specific elements of the model developed here for sulphuric acid and water mixtures. A demonstration of the model is given in Section IV and in Section V we summarise and discuss future applications. The Appendix describes some technical aspects of the particle swarm optimisation (PSO) fitting procedure used to parametrise the model against *ab initio* calculations at the DFT level of theory.

II. THE EVB METHOD

A. EVB overview

In an EVB model the potential energy of the reactive system is constructed as an interpolation between energy surfaces defined for specific choices of bonding pattern. This is done in a fashion reminiscent of the quantum mechanics of a multilevel system, though it should be emphasised that the dynamics considered are entirely classical. The system is represented mathematically as a superposition of basis states, each representing a possible bonding pattern. For example, Figure 1 illustrates two basis states of a system corresponding to the possibility in this case that the central hydrogen atom can form part of either a sulphuric acid molecule on the left or a hydronium ion on the right.

Once the basis states of the system are specified, a matrix $\mathcal{H}$ that resembles a Hamiltonian is constructed as follows:

$$\mathcal{H}_{ij} = \langle i| H |j \rangle, \qquad (1)$$

where $\langle i| H |i \rangle$ is the potential energy of the system according to the bonding pattern defined by $|i\rangle$ and an associated classical potential. $\langle i| H |j \rangle$, where $i \neq j$, represents the coupling between basis states $|i\rangle$ and $|j\rangle$ responsible for mixing. In practice, $\langle i| H |j \rangle$ is specified by an empirical function chosen to reproduce the behaviour of a higher level theoretical model.

Once the $\mathcal{H}$ matrix has been constructed, the eigenvectors and eigenvalues are found. The eigenvector $|\Psi\rangle = \sum_i c_i |i\rangle$ with the lowest eigenvalue represents the ground state of the system, with coefficients c_i specifying the appropriate superposition of the basis states. The energy is given by $E = \boldsymbol{c}^T \mathcal{H} \boldsymbol{c}$ and the forces can be computed via the Hellmann-Feynman theorem

$$\mathbf{F}_n = -\langle \Psi| \frac{\partial H}{\partial \boldsymbol{x}_n} |\Psi \rangle = -\sum_{i,j} c_i c_j \frac{\partial \langle i| H |j \rangle}{\partial \boldsymbol{x}_n}, \qquad (2)$$

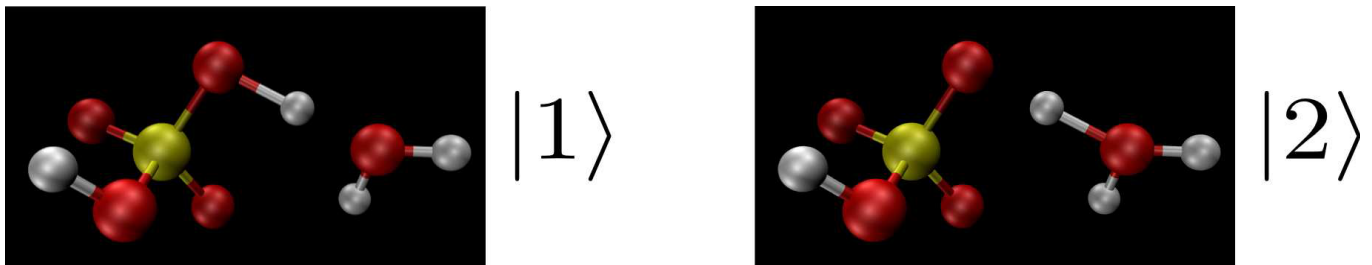where $\boldsymbol{x}_n$ and $\mathbf{F}_n$ indicate the position and the force, respectively, for atom n.

Figure 1. Illustration of two possible basis states of bonding for the same atomic configuration. State $|1\rangle$ is composed of a sulphuric acid and a water molecule whereas state $|2\rangle$ contains bisulphate and hydronium ions. The EVB approach provides an interpolation between the energy surfaces appropriate to each case.

B. The MS-EVB3 model of water systems with an excess proton

The MS-EVB3 model [31] was originally designed for simulating systems of water molecules with one excess proton. The key process of interest is the mobility of the excess proton across hydrogen bonds formed between water and hydronium. Diagonal elements of the matrix $\mathcal{H}$ are specified by a suitable potential for water and hydronium bonding patterns. Off-diagonal components of $\mathcal{H}$ are calculated in the following way:

$$\langle i | H | j \rangle_{i \neq j} = (V_{\text{const}}^{ij} + V_{\text{ex}}^{ij}) \cdot A(R_{\text{OO}}, \mathbf{q}), \qquad (3)$$

where R_{OO} is the oxygen-oxygen distance in the hydrogen bond that includes the transferring proton, V_{const}^{ij} is a constant and V_{ex}^{ij} is a representation of Coulombic interactions between the $H_5O_2^+$ Zundel cation consisting of the hydronium and water between which the proton is considered to be shared, and the remaining waters. It is given by

$$V_{\text{ex}}^{ij} = \sum_{m}^{7} \sum_{k}^{N_{\text{H}_2\text{O}} - 1} \sum_{n_k}^{3} \frac{q_{n_k}^{\text{H}_2\text{O}} q_m^{ex}}{R_{mn_k}}, \qquad (4)$$

where m is a label for the seven atoms in the Zundel cation, k is a label for the remaining water molecules ($N_{\text{H}_2\text{O}}$ is the total number of water molecules in the system) and n_k labels the three constituent atoms of each water molecule. $q_{n_k}^{\text{H}_2\text{O}}$ are the partial charges for the constituent atoms in the water molecule and q_m^{ex} are partial charges describing the Zundel cation. R_{mn_k} is the distance between atoms labelled by m and n_k.

The function $A(R_{\text{OO}}, \mathbf{q})$ has the form

$$A(R_{\text{OO}}, \mathbf{q}) = \exp(-\gamma \mathbf{q}^2) \cdot \left\{ 1 + P \exp\left[-\text{k}(R_{\text{OO}} - D_{\text{OO}})^2 \right] \right\}$$

$$\times \left\{ \tfrac{1}{2} \left\{ 1 - \tanh\left[\beta(R_{\text{OO}} - R_{\text{OO}}^0) \right] \right\} + \right.$$

$$\left. P' \exp\left[-\alpha(R_{\text{OO}} - r_{\text{OO}}^0) \right] \right\}, \qquad (5)$$

Table I. Parameters specifying the off-diagonal matrix elements of the Hamiltonian used in the MS-EVB3 model of water-hydronium transfer [31]; α, β and γ from [31], all others from [29].

V_{const}^{ij}	-23.1871874 kcal/mol	β	4.5 Å^{-1}
γ	1.85 Å^{-2}	R_{OO}^0	3.1 Å
P	0.2327246	P'	10.8831327
k	9.562153 Å^{-2}	α	15 Å^{-1}
D_{OO}	2.94 Å	r_{OO}^0	1.8136426 Å

where γ, P, k, D_{OO}, β, R_{OO}^0, P', α and r_{OO}^0 are empirical parameters (see Table I) and $\mathbf{q} = \frac{1}{2}(\mathbf{r}_{\text{O1}} + \mathbf{r}_{\text{O2}}) - \mathbf{r}_{\text{H}}$ where $\mathbf{r}_{\text{O1}}$, $\mathbf{r}_{\text{O2}}$ and $\mathbf{r}_{\text{H}}$ are the positions of the two oxygens and hydrogen, respectively, that participate in the hydrogen bond. The model is somewhat empirical in construction but was designed to have a number of desirable features [31].

C. The SCI-MS-EVB procedure

The EVB method has the capacity to model systems of $n > 1$ hydroniums (excess protons) with water, but this extension increases the size of $\mathcal{H}$ to order m^n where m is the size of the basis set for a single proton system. The SCI-MS-EVB model was developed by Wang and Voth [32] to improve the scaling of the procedure with respect to n. This is achieved by treating the system as n single excess protons in the presence of an environment with a given state of bond mixing. Employing a single proton EVB methodology, the state of mixing of the entire system is then given by a set of n eigenvectors each of length m. The eigenvectors are corrected iteratively as the effects of the other excess protons on the Hamiltonian matrix for each of the Zundel cations are taken into account. Essentially, the environment affects how the competing energy surfaces are specified. The problem of analysing one matrix of order m^n is hence reduced to the consideration of n matrices of size m. The number of iterations required to reach convergence in energy and forces is typically small. We similarly use this procedure for our system.

III. EVB MODEL FOR SULPHURIC ACID AND WATER

In the following subsections we describe in some detail the construction of an EVB model for a system containing sulphuric acid, bisulphate, hydronium and water species. It is a complex narrative, but a summary of the procedure is provided at the end in Subsection III G. In the discussion a naming convention is used where the `ground state` refers to the bonding pattern that has been identified as geometrically the most 'natural', based upon the configuration of the atoms. `Excited states` are bonding configurations that are identical to the `ground state` except for the repositioning of one bond as a consequence of a proton transfer. Therefore, it is possible to identify an `excited state` based upon the `ground state` and the two species involved in a proton transfer. The species are then referred to as a `donor` (the molecule to which the hydrogen atom is bonded in the `ground state` and which can either be a sulphuric acid molecule or a hydronium ion), and an `acceptor` (the molecule to which the hydrogen atom is bonded in the `excited state` and which can either be a bisulphate or a water). For clarity, the terms neutral and ionised are used to identify the state of the sulphur-bearing species (either as a neutral sulphuric acid or an ionised bisulphate).

A. Basis set size

The basis set size m for each transferable proton was chosen to be two, in order to keep the model as simple as possible, in line with the SCI-MS-EVB approach implemented for water and described in Section II C. This approach allows each donor and acceptor species in the system to be involved in a maximum of one proton transfer in a given configuration, but it is assumed that the possibility that such a species might be involved in two proton transfers simultaneously can be safely neglected. The small basis set leads to occasional ambiguities concerning which proton is considered to be shared but a modification of the off-diagonal term specified in Eq. (5) has been made to limit the impact of these issues and is described in Section III D 1.

Our focus here has been to develop the simplest possible scheme of the process of proton transfer between sulphuric acid and water, and for ease of implementation we have used a similar two-state model for the water network. Larger basis sets have previously been employed in studies of the water/hydronium system in order to capture effects such as the formation of highly correlated structures such as the $H_9O_4^+$ complex discussed in [33]. Our approach is less refined at present, but clearly a more elaborate model of state mixing within the water network could be implemented at a later stage alongside the two-state model of acid/water mixing in order to capture the finer details of proton transfer in the water sector. Our principal focus has been to describe the reactive behaviour of sulphuric acid in clusters containing relatively few water molecules.

B. Algorithms

A central part of the EVB methodology is the construction of appropriate basis states of the system, which is nontrivial as reactions can cause atoms to associate with different molecules in the course of a simulation. This section describes two algorithms which are applied at every time step in order to identify the ground state and excited states of the system by geometric arguments.

1. Ground state selector algorithm

An algorithm has been designed which constructs the `ground state` from a list of atomic positions. For convenience, four molecular lists are defined and are denoted by `SA` (sulphuric acid), `BS` (bisulphate), `HY` (hydronium) and `WA` (water) and an assignment refers to the identification of an atom as a constituent of a particular molecule. The algorithm is performed in the following way:

1. The four oxygens closest to each sulphur atom are identified. They are assigned to a sulphuric acid molecule (along with the sulphur atom) and placed in the `SA` list.

2. The remaining oxygen atoms are assigned to hydronium ions and added to the `HY` list.

3. Minimum numbers of hydrogen atoms are assigned to each molecular species. For each member of the `HY` list the *two* hydrogen atoms closest to the associated oxygen are identified and assigned to the list. The same process is used to assign *one* hydrogen to each member of the `SA` list.

4. The remaining hydrogen atoms are placed (in no particular order) in a temporary list named `H`. The closest oxygen to each of these hydrogens is identified and the hydrogen is assigned to the molecular species of which the oxygen is a constituent. The oxygen cannot be part of a molecule which has already accepted one of these remaining hydrogens and cannot be a member of the `SA` list that was assigned a bond to a hydrogen atom in step 3. If there is an attempt to assign a hydrogen where the bond length is greater than 1.2Å then this assignment is rejected and the atom is moved to the top of the `H` list. If the `H` list is rearranged at any time, then step 4 is immediately restarted using the modified `H` list. The hydrogens which went through a rejected assignment are no longer subject to the 1.2Å constraint, but if the bond length is over 2Å the hydrogen is again returned to the top of the `H` list. If problems with assignment persist, then the
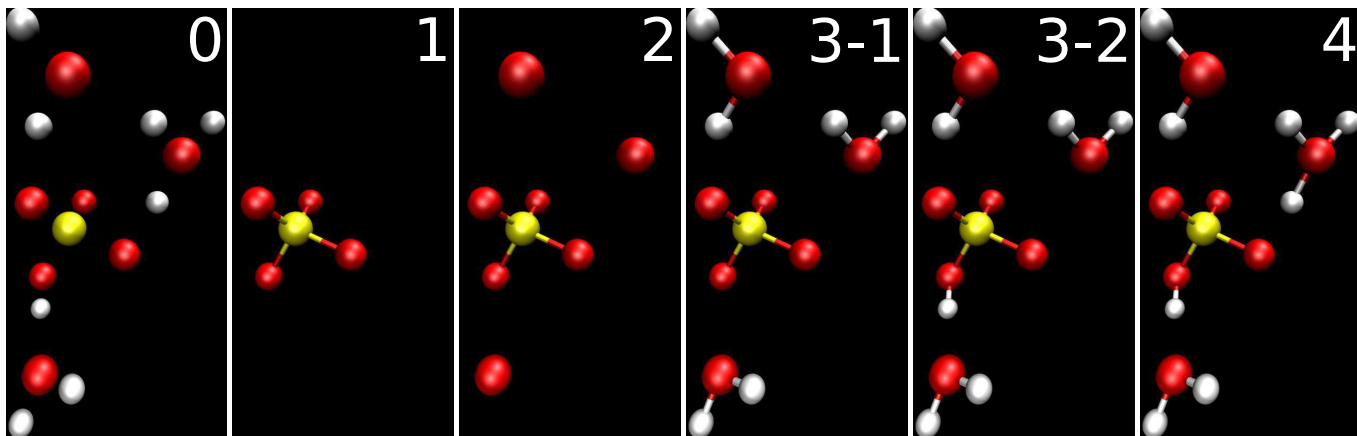
Figure 2. The ground state selector algorithm. Image zero shows the positions of atoms, and in subsequent steps bonds are inserted according to the procedure described in Section III B 1. Step three is shown in two parts; first, the attachment of two hydrogen atoms to each oxygen and second, the attachment of one hydrogen atom to each sulphate.

algorithm is run with the bond length check turned off. In practice, there is only need for these checks in the circumstances of proton transfer events, in which case the two state EVB mixing between the states will ensure that the appropriate forces are applied regardless of the assignment of the molecular species. This step is completed when all hydrogens in the H list have been assigned. The procedure followed in this step was found to work smoothly in trials of the model.

5. Any sulphuric acid molecule in the SA list for which only one hydrogen atom has been assigned is moved to the BS list. Similarly, any hydronium molecule in the HY list that does not have three assigned hydrogen atoms is moved to the WA list.

Figure 2 illustrates the steps of the algorithm as they are performed on a system. At the end of the procedure, the SA, BS, HY and WA lists represent the ground state of the system.

2. Excited state identification algorithm

As stated earlier, an excited state is defined as a change in the bonding assignment of one hydrogen in the ground state of a given configuration. An algorithm identifies the excited states in a system using the following steps:

1. The shortest distance between a hydrogen belonging to a donor species, and an oxygen belonging to an acceptor species is identified. The oxygen in a bisulphate ion which has an attached hydrogen is not considered here. If this distance is less than 2Å then an excited state may be constructed where the hydrogen is reassigned to the acceptor species.

2. Step 1 is repeated until either the shortest distance identified is greater than 2Å in length or there are
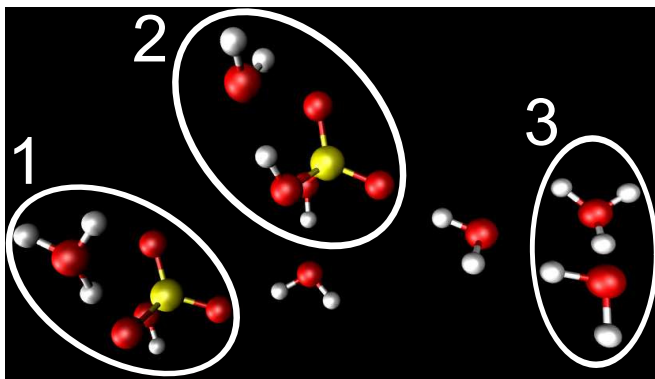

Figure 3. A simultaneous consideration of three potential proton transfer events. The groups labelled 1, 2 and 3 refer to [hydronium/bisulphate], [sulphuric acid/water] and [hydronium/water] proton transfer, respectively. One ground state (the bonding pattern shown) and three excited states (where the central hydrogen in each group is bonded differently) have therefore been identified.

no further acceptor or donor molecules for which it is possible to construct an O − H separation distance.

The ground state selector and the excited state identification algorithms produce one ground state and n excited states where n is the number of potential proton transfer events in the configuration under consideration. When $n = 0$ the system is in a non-reactive configuration. In the configuration shown in Figure 3, there are three groups where the bonding of a proton is unclear (ringed), such that a ground state and three excited states have been identified in this system.

C. Diagonal terms

The potentials needed to specify the diagonal elements of $\mathcal{H}$ are those developed by Loukonen et al. [34], and the SPC/EF potential is used for the water molecules [35]. The hydronium energy is represented by a set of harmonic angle potentials and Morse bond potentials as follows:

$$V_{\mathrm{hyd}} = \frac{1}{2} \sum_{i=1}^{3} k_\theta \left(\theta_i - \theta_0 \right)^2 + \sum_{j=1}^{3} D \left[1 - \mathrm{e}^{-\alpha(r_j - r_0)} \right]^2,$$
(6)

where i is summed over the three hydrogen-oxygen-hydrogen angles and j over the three oxygen-hydrogen bonds. The k_θ and θ_0 parameters are taken from Loukonen et al. [34]. The Morse potential is similar in form to the model used in Wu et al. [31], and employs the same value of D, but the α parameter has been changed so that the second order Taylor expansion around r_0 matches the strength of the harmonic spring used to represent the OH bond in Loukonen et al. [34], namely $\alpha = 2.327 \mathrm{Å}^{-1}$. The use of a Morse potential rather than a harmonic spring was found to improve the match between our model of hydronium and that used in the original MS-EVB3 model.

One of the diagonal terms is augmented by an energy shift, Δ, to account for the difference in zero temperature ground state energy between the sulphuric acid and water bonding pattern and the bisulphate and hydronium version. Ding et al. [23] calculated the value of this parameter to be 144.0 kcal/mol (602.5 kJ/mol), but for our purposes it was considered to be a free parameter and is fitted to higher level theory data.

D. Off-diagonal terms

The form chosen for the off-diagonal terms in the Hamiltonian describing sulphuric acid-water proton transfer is based upon the MS-EVB3 model (Eq. (5)), with two modifications. These relate to the expression involving the $\mathbf{q}$ parameter (Section III D 1) and the method for calculating V_{ex}^{ij} (Section III D 2).

1. The $\mathbf{q}$ dependence

There is a problem with using a limited basis set, especially when there are long-range off-diagonal terms in the Hamiltonian matrix. If configurational evolution brings about a change in identity of the species that might accept the proton from a given donor species, then the replacement of one energy surface by another will bring about an abrupt jump in energy that will need to be damped out by the thermostat. However, we have designed the two-state EVB scheme to avoid such jumps as much as possible. Mixing between bonding patterns will

only come about when the proton in question occupies a specific region between the donor and acceptor species. Outside this region, the interactions revert to those of a single pattern of bonding, and crucially, the energy surface is continuous at the boundary of the region. This is encoded in the specification of off-diagonal terms which vanish for proton positions outside an ellipsoidal volume centred on the mid-point between the donating and accepting oxygen atoms.

Specifically, the factor in Eq. (5) involving $\mathbf{q}$ becomes

$$\exp(-\gamma \mathbf{q}^2) \rightarrow \begin{cases} \left[\dfrac{\exp(-(\gamma \mathbf{q}_0^2 - 1)) - 1}{\mathrm{e} - 1} \right] & \mathbf{q}_0^2 \leq \gamma^{-1} \\ 0 & \mathbf{q}_0^2 > \gamma^{-1} \end{cases}$$
(7)

where $\mathbf{q}_0^2$ is related to $\mathbf{q}$ in the following way. The $\mathbf{q}$ vector is expressed in a new orthogonal coordinate system $\mathbf{q}'$ in which the x-axis is parallel to $\mathbf{r}_{\mathrm{OO}}$, where $\mathbf{r}_{\mathrm{OO}} = \mathbf{r}_{\mathrm{O1}} - \mathbf{r}_{\mathrm{O2}}$ is the vector separation between oxygens. The other two axes take arbitrary orientations. $\mathbf{q}_0^2$ is then defined as $\mathbf{q}_0^2 = \left(q_x'/\tau_x \right)^2 + \left(q_y'/\tau_{yz} \right)^2 + \left(q_z'/\tau_{yz} \right)^2$ where the τ_x and τ_{yz} are unitless scaling factors representing semi-major axes of an ellipsoid with respect to the x axis, and the y and z axes, respectively. In effect, a hydrogen atom experiences mixed bonding within an ellipsoidal volume between the two appropriate oxygen atoms. We find that this eliminates occasional ambiguities with regard to which oxygen pair is appropriate for the mixed bonding experienced by a particular hydrogen, introducing discontinuities in the potential energy landscape. The two variables τ_x and τ_{yz} are treated as additional fitting parameters. The form of Eq. (7) ensures two features: the expression is equal to unity at $\mathbf{q}_0^2 = 0$ and goes to zero on the surface of the ellipsoid at $\mathbf{q}_0^2 = \gamma^{-1}$, beyond which the off-diagonal term vanishes to enforce ordinary unmixed behaviour outside the ellipsoid.

In principle, a jump in energy can still occur if ellipsoidal mixing regions between two donor-acceptor pairs come into overlap as a consequence of configurational change. Such situations can occasionally arise during the molecular dynamics, but we have restricted the regions of mixing, through the parameters τ_x and τ_{yz}, specifically to avoid this. For most of the time there is no ambiguity in the choice of basis set to use for a configuration and few occasions when a jump in energy occurs according to our scheme. These jumps are unphysical, and a breakage of NVE conditions, but are the price to pay for the simplicity of the implementation.

2. Interpolated charges

The V_{ex}^{ij} parameter in Eq. (4) is also modified since the charges provided by the MS-EVB3 model for the calculation of this term are specific to the Zundel cation and do not transfer to a sulphuric acid and water model. We recall that it represents external electrostatic interactions for the group of atoms involved in the mixing

of bonding patterns. Our approach is to interpolate the charges of these atoms according to the c_i coefficients of the mixture. The procedure is as follows:

1. Initially the charges are assumed to be $q = \frac{1}{2}(q^{gs} + q^{es})$, where q^{gs} and q^{es} are the partial charges for that atom according to the classical potential provided, in accordance with whether the bonding is identified as the ground state or the excited state, respectively.

2. A self-consistent iteration is performed where q is updated according to $q = c_{gs}^2 q^{gs} + c_{es}^2 q^{es}$ where c_{gs} and c_{es} are the eigenvector coefficients for the ground state and excited state, respectively, obtained from the two-level Hamiltonian describing the mixing.

This procedure is performed alongside a separate self-consistent iterative process described in the next section, the purpose of which is to allow consideration of multiple proton transfers.

E.   Multiple proton procedure

The modelling of systems undergoing multiple proton transfers follows the SCI-MS-EVB procedure developed by Wang and Voth [32]. Figure 3 shows a system where this extension is required as it has three excited states available. The starting point in this procedure is to neglect overlap between two different excited states (i.e. $\langle i | H | j \rangle = 0$ where i and j represent two different excited states). This allows for the reduction of the EVB Hamiltonian matrix of the system, which is of order $n_d^{n_c}$, to n_d matrices of order n_c where n_d is the number of donor molecules being considered and n_c is the number basis states considered per donor molecule. An iterative procedure is then used to correct these matrices for the $\langle i | H | j \rangle$ contributions. The method can be described as follows:

1. We determine the eigenvector for each 2×2 matrix $\mathcal{H}$ corresponding to the ground state and an excited state. For clarity, n is used as a label such that $\mathbf{c}_n$ and $\mathcal{H}_n$ are defined for the nth excited state. In addition, n is used to label the donor and acceptor species that define the excited state.

2. Each $\mathcal{H}_n$ is then corrected for the effect of excited state m where $m \neq n$. This is performed by updating the intermolecular energy contributions to the diagonal terms in $\mathcal{H}_n$, i.e. $E_{\text{inter}}^{gs} \rightarrow \left(c_{gs}^2 E_{\text{inter}}^{gs} + c_{es}^2 E_{\text{inter}}^{es} \right)$ where c_{gs}^2 and c_{es}^2 are the squared coefficients of the $\mathbf{c}_m$ eigenvector representing the associated ground state and excited state. E_{inter}^{gs} and E_{inter}^{es} are the intermolecular energy contributions resulting from interactions between the acceptor/donor pair n and the

acceptor/donor pair m in the ground state and excited state of m respectively. The expression V_{ex}^{ij} in the off-diagonal term is updated in the same fashion; this includes recalculating the charges q according to the procedure in Section III D 2. The $\mathbf{c}_n$ values are then recalculated. This allows the coefficients $\mathbf{c}_n$ for the acceptor/donor pair n to be corrected for the intermolecular interactions arising from acceptor/donor pair m. This step is repeated until each $\mathbf{c}_n$ vector has been corrected for each acceptor/donor pair m (where $m \neq n$).

3. Step 2 is repeated until all $\mathbf{c}_n$ eigenvectors have converged. This is tested by defining $C_{\text{sum}} = \sum_n (\mathbf{c}_n^{\text{old}} - \mathbf{c}_n^{\text{new}})^2$ where $\mathbf{c}_n^{\text{old}}$ and $\mathbf{c}_n^{\text{new}}$ are the (normalised) $\mathbf{c}_n$ eigenvectors calculated before and after step 2 is performed. The system is considered to be converged when $C_{\text{sum}} < 10^{-5}$, or when step 2 has been cycled 10 times. In practice only a few iterations are required.

F.   Energy and force calculation

Once the self-consistency iterations have been performed, the energy of the system can be computed in the same fashion as in the SCI-MS-EVB method. Eq. (13) in reference [32] gives a deconstruction of the total energy of a system containing two excess protons in the form

$$E_{\text{total}} = E_{AA} + E_{BB} + E_{AB} + E_{AR} + E_{BR} + E_{RR}, \quad (8)$$

where E_{total} refers to the total energy of a system according to the EVB method. A and B refer to separate acceptor/donor pairs (see Figure 1 in reference [32]). E_{AA} and E_{BB} refer to the independent energy contributions of the acceptor/donor pairs and includes their off-diagonal contributions. E_{AB} describes the energy contribution due to interactions between A and B. R refers to the rest of the system, and there are three further contributions due to interactions between A and R, B and R and the independent energy contribution of R, referred to as E_{AR}, E_{BR} and E_{RR} respectively. Eq. (8) can be generalised to $E_{\text{total}} = E_{RR} + \sum_n \left(E_{nn} + E_{nR} + \sum_{m \neq n} E_{nm} \right)$ where n and m refer to the identified donor/acceptor pairs. Once E_{total} has been constructed it simply remains to apply the Hellmann-Feynman theorem to determine the force acting upon each atom within the system.

G.   Model overview

In summary, the model is an algorithm consisting of the following series of steps:

1. Construct a `ground state` from a set of atomic positions (Section III B 1).

2. Identify the `excited states` (Section III B 2).

3. Calculate the on-diagonal and off-diagonal terms of the 2×2 matrix $\mathcal{H}$ for each `excited state` (Sections III C and III D 1).

4. Optimise the $\mathbf{c}_i$ vectors for each `excited state` by performing a self-consistent iterative procedure which revises the off-diagonal terms and allows multiple proton transfers to be accommodated (Sections III D 2 and III E).

5. Calculate the energy of the system and the forces acting upon each atom (Section III F).

Once the parameters of the model have been selected, the procedure can be implemented in a classical molecular dynamics code, and we have done this using the DL_POLY 4.03 package [36].

IV. RESULTS

We have parametrised the EVB model against reference configurational energies calculated from a DFT approach using a particle swarm optimisation (PSO) fitting scheme, the details of which are described in the Appendix. We focus in this section on investigating various features of the parametrised model.

Figure 4 shows the potential energy of a sulphuric acid/water system as a function of the position of a transferring hydrogen atom, comparing the performance of the EVB model with a set of reference data. It is important to recognise that the EVB scheme does not operate for hydrogen positions beyond a distance $\pm 0.3\text{Å}$ in the $\mathbf{r}_{OO}$ direction starting from $\frac{1}{2}(\mathbf{r}_{O1} + \mathbf{r}_{O2})$, the mid-point between the oxygens atoms involved in the hydrogen bond, and so energies at hydrogen positions labelled $\pm 0.4\text{Å}$ in the $\mathbf{r}_{OO}$ direction are for unmixed bonding and are not affected by the EVB parametrisation scheme. The comparison demonstrates an overall correspondence between the EVB model and the DFT results. The scheme is limited in that it is only active for hydrogen positions lying in an ellipsoidal spatial region around the mid-point between the oxygens, that it only represents two possible bonding states per proton and that ultimately it is underpinned by a classical potential fit to the reference data and an empirical form for the off-diagonal term. Nevertheless, the EVB model seems to capture the shape of the energy surface experienced by the hydrogen atom.

Next, we demonstrate how the propensity for proton transfer from an acid molecule is affected by the extent of the surrounding water network. Figure 5 tracks the population of water molecules in various simulations of $[H_2SO_4] + [H_2O]_n$ with n = 2 − 4, over a time period of
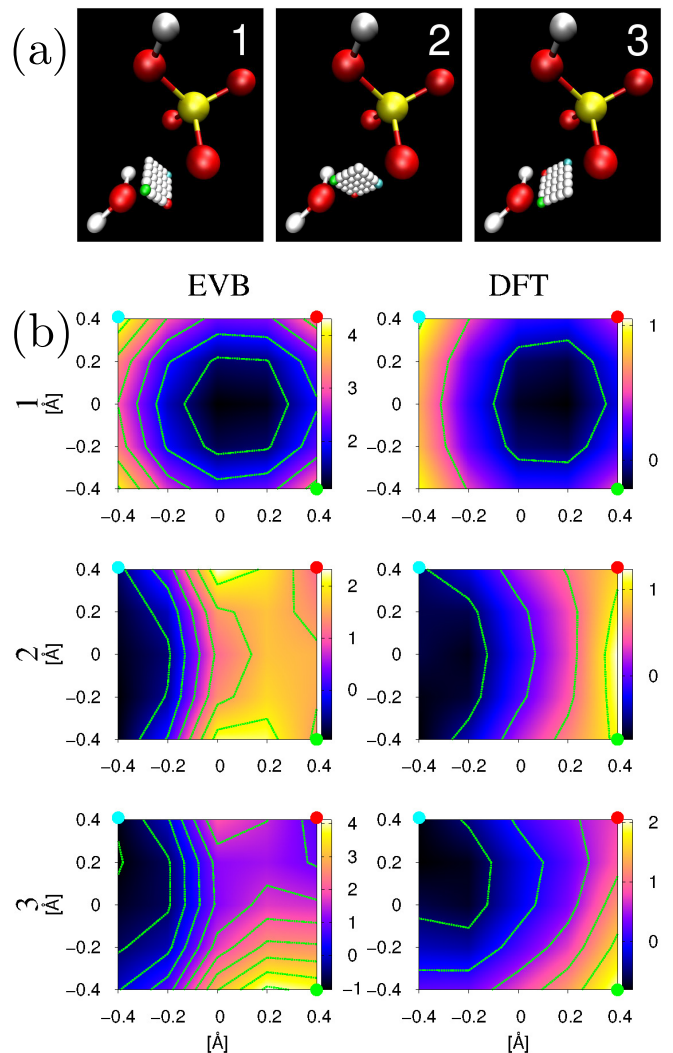

Figure 4. Sets of positions of a hydrogen atom in spatial regions of mixed bonding (a), together with corresponding contour plots of the potential energy in units of eV (b), for the I-n configuration (labelled according to reference [37]) of a sulphuric acid and a water molecule. The centre of the contour plots lies at the mid-point between the two participating oxygens and the labels 1, 2 and 3 in (b) refer to the arrays of points shown in (a). The cyan, red and green spheres in (a) match the equivalent top left, top right and the bottom right of each plot in (b), respectively. The energy when the hydrogen is at position $(-0.4\text{Å}, -0.4\text{Å}, -0.4\text{Å})$ relative to the mid-point is set to a reference point of zero for both the DFT and EVB calculations.

1 ns after a 20 ps equilibration period. The simulations employed a Langevin thermostat with target temperatures of 300 K or 200 K using a modified version of the DL_POLY 4.03 program [36]. There was no constraint on the centre of mass motion or the rotation of the clusters. The results show that at 300 K there is very little propensity for the proton to transfer to the closest water and remain there more than momentarily in the n = 2 and n = 3 cases. The hydrogen bond rarely
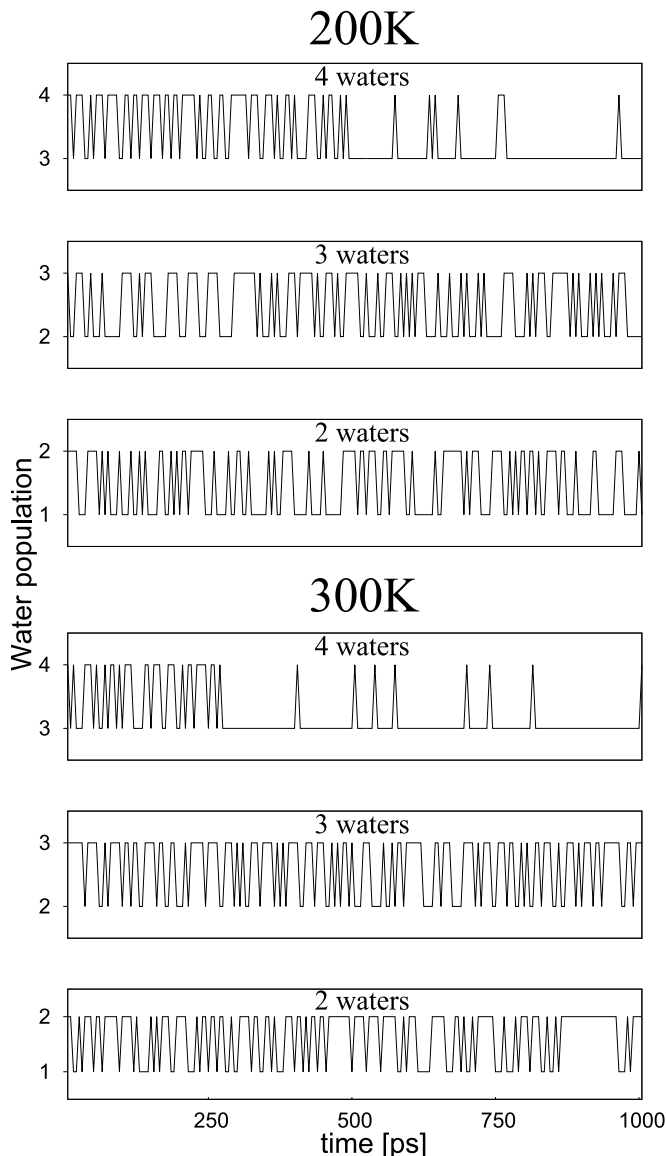
Figure 5. Evolution in the population of water molecules in simulations starting with the values indicated above each frame. A decrease of one in the water population indicates an ionisation event $[H_2SO_4] + [H_2O]_n \rightarrow [HSO_4]^- + [H_3O]^+ + [H_2O]_{n-1}$, and an increase by one refers to the reverse of this reaction. The simulations were performed at 200 K (top) and 300 K (bottom).

fluctuates to such an extent that the ground state configuration consists of a bisulphate/hydronium rather than the sulphuric acid/water bonding pattern. However, for the $n = 4$ case, the system spends the majority of its time in the dissociated state. Proton transfers are more frequent and quasistable. When the $n = 4$ simulation is run at 200 K, however, we see that it remains undissociated for a longer period of time suggesting that the dissociated state is less stable at lower temperature, which is to be expected. These conclusions are in agreement with

work performed at zero temperature using a higher level of theory [15, 37, 38], according to which the first dissociation event of a sulphuric acid molecule occurs when hydrated by between 3 and 6 water molecules.

When running the EVB model at 300 K we observe changes in configuration that involve intermolecular bond making and breaking, characteristic of the expected liquid-like nature of the system at relatively high temperatures. We also observe the Grotthuss mechanism where protons shuffle around the water network [39].

V. CONCLUSIONS

A two-state EVB model for the sulphuric acid, bisulphate, hydronium and water system has been presented, which is based upon the MS-EVB3 and SCI-MS-EVB models developed for hydronium/water alone [29, 30]. The approach essentially provides an interpolation between two energy surfaces corresponding to the choices of bonding pattern available to a proton in a particular spatial region between a bisulphate and a water. It involves a Hamiltonian represented in a basis of bonding patterns, with diagonal terms based on classical force fields, and off-diagonal terms constructed empirically and fitted to higher level calculations.

The limitation of the basis to two states implies that the model does not match the state of the art in the description of protonated water systems [33] but it provides the simplest scheme for representing proton transfer between sulphuric acid and water species, the focus of our attention here and a new application of the EVB framework. An extension to include more elaborate basis sets would be possible.

The parametrisation of the off-diagonal terms has been performed using the particle swarm optimisation (PSO) technique, with reference to DFT data for specific cases of sulphuric acid/water proton transfer events. The resulting scheme has been integrated into a modified version of the DL_POLY 4.03 MD code [36]. A quantitative comparison of the potential energy surface for the transferring proton within a geometry-optimised static configuration of one sulphuric acid and one water molecule gives good agreement. The level of hydration required for the first ionisation or dissociation of a single sulphuric acid molecule at 300 K has been investigated, revealing that a system with four water molecules is best described by a complex mixture between neutral and ionised bonding. At 200 K the four water case remains predominantly neutral, indicating that an increase in temperature promotes proton transfer, as would be expected. In highly hydrated structures, the proton becomes very mobile within the water network.

The main motivation for developing this model is to provide a tool for the fast simulation of cluster structures. The key performance details are as follows. The run time for a 1 ns simulation with six water molecules and one acid is 430 seconds on one Intel Core i5-460M

processor and it is, therefore, easily possible to generate trajectories several tens of nanoseconds in length for quite substantial systems using this model. The parametrisation procedure and tests we have reported give us confidence that the physics of proton transfer has been well captured by the scheme. Our computationally inexpensive method is suitable for performing calculations of the thermodynamic properties of clusters of water and sulphuric acid molecules at a range of temperatures relevant to the atmosphere. We shall report these results in future publications.

[1] R. Zhang, A. Khalizov, L. Wang, M. Hu and W. Xu, Chem. Rev. **112**, 1957 (2012).
[2] M. Kulmala, T. Petäjä, M. Ehn, J. Thornton, M. Sipalä, D. Worsnop and V.M. Kerminen, Annu. Rev. Phys. Chem. **65**, 21 (2014).
[3] J. Kirkby et al., Nature **476**, 429 (2011).
[4] F. Riccobono et al., Science **344**, 717 (2014).
[5] I.J. Ford, Proc. Inst. Mech. Eng., Part C: J. Mech. Eng. Sci. **218**, 883 (2004).
[6] V.I. Kalikmanov, *Nucleation Theory* (Springer, Heidelberg, 2013).
[7] M.J. McGrath, T. Olenius, I.K. Ortega, V. Loukonen, P. Paasonen, T. Kurtén, M. Kulmala and H. Vehkamäki, Atmos. Chem. Phys. **12**, 2345 (2012).
[8] S.L. Girshick and C.P. Chiu, J. Chem. Phys. **93**, 1273 (1990).
[9] A. Laaksonen, I.J. Ford and M. Kulmala, Phys. Rev. E **49**, 5517 (1994).
[10] V.I. Kalikmanov and M.E.H. van Dongen, J. Chem. Phys. **103**, 4250 (1995).
[11] H. Vehkamäki, *Classical Nucleation Theory in Multicomponent Systems* (Springer, Berlin, 2006).
[12] D. Brus, K. Neitola, A.P. Hyvärinen, T. Petäjä, J. Vanhanen, M. Sipilä, P. Paasonen, M. Kulmala and H. Lihavainen, Atmos. Chem. Phys. **11**, 5277 (2011).
[13] A. Kakizaki, H. Motegi, T. Yoshikawa, T. Takayanagi, M. Shiga and M. Tachikawa, J. Mol. Struc-THEOCHEM **901**, 1 (2009).
[14] S. Sugawara, T. Yoshikawa, T. Takayanagi, M. Shiga and M. Tachikawa, J. Phys. Chem. A **115**, 11486 (2011).
[15] C. Arrouvel, V. Viossat and C. Minot, J. Mol. Struc-THEOCHEM **718**, 71 (2005).
[16] J.L. Stinson, S.M. Kathmann and I.J. Ford, J. Chem. Phys. **140**, 024306 (2014).
[17] D. Frenkel and B. Smit, *Understanding Molecular Simulations: from Algorithms to Application*, 2nd ed. (Elsevier, Amsterdam, 2001).
[18] I.J. Ford and S.A. Harris, J. Chem. Phys. **120**, 4428 (2004).
[19] H.Y. Tang and I.J. Ford, Phys. Rev. E **91**, 023308 (2015).
[20] C. Chipot and A. Pohorille, (Eds.), *Free Energy Calculations* (Springer, Heidelberg, 2007).

[21] I. Kusaka, Z.G. Wang and J.H. Seinfeld, J. Chem. Phys. **108**, 6829 (1998).
[22] S.M. Kathmann and B.N. Hale, J. Phys. Chem. B **105**, 11719 (2001).
[23] C.G. Ding, T. Taskila, K. Laasonen and A. Laaksonen, Chem. Phys. **287**, 7 (2003).
[24] M. Toivola, I. Napari and H. Vehkamäki, Boreal Environment Research **14**, 654 (2009).
[25] A.P. Bartók, M.C. Payne and G. Csányi, Phys. Rev. Lett. **104**, 1 (2010).
[26] A.C.T. van Duin, S. Dasgupta, F. Lorant and W.A. Goddard, J. Phys. Chem. A **105**, 9396 (2001).
[27] S.C.L. Kamerlin and A. Warshel, Wiley Interdisciplinary Reviews: Computational Molecular Science **1**, 30 (2011).
[28] J. Aqvist and A. Warshel, Chem. Rev. **93**, 2523 (1993).
[29] U.W. Schmitt and G.A. Voth, J. Phys. Chem. B **102**, 5547 (1998).
[30] T.J.F. Day, A.V. Soudackov, M. Čuma, U.W. Schmitt and G.A. Voth, J. Chem. Phys. **117**, 5839 (2002).
[31] Y. Wu, H. Chen, F. Wang, F. Paesani and G.A. Voth, J. Phys. Chem. B **112**, 467 (2008).
[32] F. Wang and G.A. Voth, J. Chem. Phys. **122**, 144105 (2005).
[33] C. Knight and G.A. Voth, Acc. Chem. Res. **45**, 101 (2012).
[34] V. Loukonen, T. Kurtén, I.K. Ortega, H. Vehkamäki, A.A.H. Pádua, K. Sellegri and M. Kulmala, Atmos. Chem. Phys. **10**, 4961 (2010).
[35] J. Lopez-Lemus, G.A. Chapela and J. Alejandre, J. Chem. Phys. **128**, 174703 (2008).
[36] I.T. Todorov, W. Smith, K. Trachenko and M.T. Dove, J. Materials Chem. **16**, 1911 (2006).
[37] S. Re, Y. Osamura and K. Morokuma, J. Phys. Chem. A **103**, 3535 (1999).
[38] A.R. Bandy and J.C. Ianni, J. Phys. Chem. A **102**, 6533 (1998).
[39] A.Y. Lozovoi, T.J. Sheppard, D.L. Pashov, J.J. Kohanoff and A.T. Paxton, J. Chem. Phys. **141**, 044504 (2014).
[40] A. Banks, J. Vincent and C. Anyakoha, Nat. Comput. **6**, 467 (2007).
[41] A. Banks, J. Vincent and C. Anyakoha, Nat. Comput. **7**, 109 (2007).
[42] R. Poli, J. Artif. Evol. App. **2008**, 685175 (2008).

[43] Y. Shi and R. Eberhart, A modified particle swarm optimizer. in *Proceedings of the IEEE International Conference on Evolutionary Computation* (IEEE, New Jersey, 1998), pp. 69–73.
[44] J. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[45] S.J. Clark, M.D. Segall and C.J. Pickard, Z. Kristallogr. **220**, 567 (2005).

Appendix A: Parameter fitting procedure

The original MS-EVB3 model was parametrised to describe hydronium/water proton transfers [31]. We chose to employ slightly different classical force fields for the water molecule and hydronium ion, requiring us to revisit this parametrisation. The SPC/EF potential was employed for water (see Loukonen *et al.* [34]) as well as a modified version of the Morse potential in the MS-EVB3 model (see III C). Three parameters in the MS-EVB3 off-diagonal term for hydronium/water were refitted: these were $R_{OO}^0 = 2.7$Å, $P = 0.4$ and $D_{OO} = 2.65$Å and for this system we use $\tau_x = \tau_{yz} = 0.3$.

Two further proton transfer reactions are possible in the system under consideration, namely sulphuric acid/water and sulphuric acid/bisulphate but we disregard the latter as it is likely to be rare. We parametrised the new off-diagonal terms for sulphuric acid/water EVB mixing using the particle swarm optimisation (PSO) scheme [40, 41]. This technique has been employed in a variety of areas (reviewed in reference [42]) and we consider it to be sufficiently powerful for use in potential fitting as well.

The PSO method is used to perform a force matching parametrisation against DFT data. It employs a swarm of 'particles', each representing a choice of a set of parameters $\{\alpha\}$. The goodness of fit is assessed using a function, f, defined as

$$f(\{\alpha\}) = \sum \left(F_{ref} - F_{model}(\{\alpha\})\right)^2, \qquad (A1)$$

where F_{ref} denotes the reference forces for an atomic configuration, and $F_{model}(\{\alpha\})$ represents the model forces for the same configuration, given parameters $\{\alpha\}$. The square deviations are summed over a series of configurations to provide a global assessment of the fit between model and reference data.

The particles are allowed to explore parameter space according to a simple set of evolution equations for each parameter as described by Shi and Eberhart [43]:

$$v_{t+1}^i = \omega v_t^i + \varphi_1\beta_1(p_i - x_t^i) + \varphi_2\beta_2(p_g - x_t^i)$$
$$x_{t+1}^i = x_t^i + v_{t+1}^i \qquad (A2)$$

where x_t^i and v_t^i represent the 'position' and 'velocity', respectively, of particle i at iteration t. The terms proportional to φ_1 and φ_2 are 'forces' designed to guide the
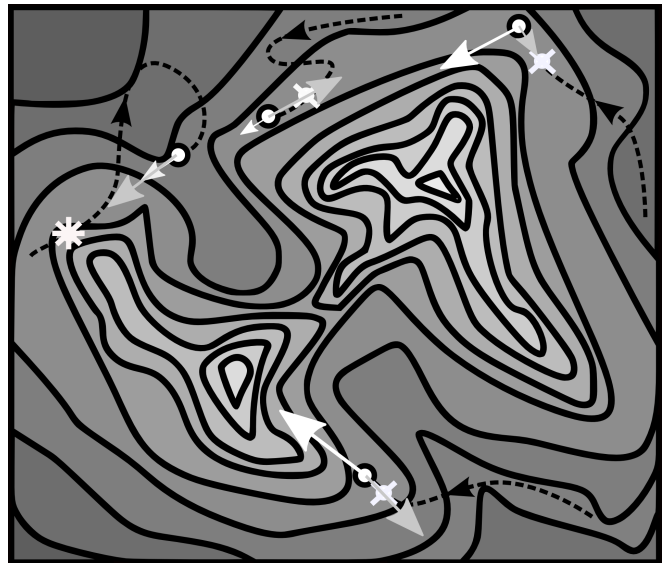
Key

Figure 6. Snapshot from a four 'particle' PSO procedure to optimise two parameters of a model. The darker shaded regions of parameter space represent a poor fit between model and data, while lighter shades represent a good fit (as determined by Eq. (A1)). The particles follow trajectories through parameter space influenced by 'forces' directed towards individual (p_i) and collective (p_g) best fit positions. The strength of the forces is influenced by noise introduced into the swarm through variables β_1 and β_2.

particle towards the positions in parameter space representing the previously found best fit parameter sets obtained locally by the particle in question (p_i) and globally by the entire swarm (p_g). β_1 and β_2 are uniformly distributed random numbers in the range $0 \le \beta_{1,2} \le 1$ designed to introduce stochasticity into the search. The values of φ_1 and φ_2 represent the relative importance that is given to the local and global best fits. The ω parameter is introduced to allow a further flexibility in the algorithm, to be described later. Figure 6 illustrates the evolution of a four particle swarm as it explores a two dimensional parameter space in search of a minimum in the fitting function.

The PSO approach requires data to which the model is to be fitted and also a numerical implementation specifying the number of particles in the swarm and the number of independent searches performed, amongst other matters.
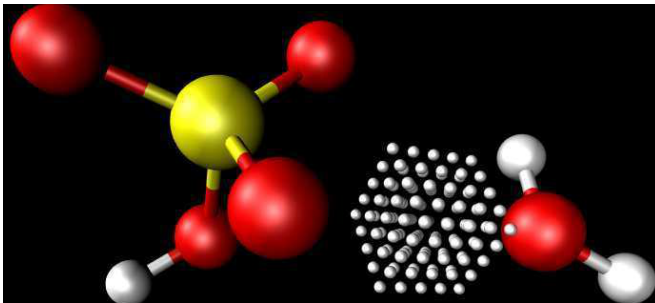
Figure 7. The grid of hydrogen positions in configuration I-n (in the terminology of reference [37]) used to generate reference force data for the PSO fitting procedure.

1. Reference data

The data against which the EVB model has been fitted was obtained using density functional theory (DFT) based on the PBE [44] functional with a plane wave basis set, a 550 eV cut off and a 15 Å box. The CASTEP 5.5 code [45] was used to determine forces on atoms in a given set of configurations. The configurations used in the dataset comprised:

1. Two molecular dynamics runs for trihydrated and tetrahydrated single sulphuric acid molecules in configurations described as Config H and SAQH in Stinson *et al.* [16].

2. A number of relaxed configurations designated I-n, II-n-a, III-n-a, III-n-b and III-i-a according to Re *et al.* [37]. For each of these structures a proton was selected for transfer between a sulphuric acid and a water molecule. This proton was positioned on a grid of points in a cube centred at the mid-point between the oxygens, $\frac{1}{2}(\mathbf{r}_{O1} + \mathbf{r}_{O2})$, with one axis of the cube parallel to the $\mathbf{r}_{OO}$ vector, and the other two axes orthogonal but arbitrary in direction. Grid points were separated by 0.2Å giving a total of 125 points per cube. Figure 7 illustrates the grid of points for the I-n configuration. For each grid point an energy and force calculation was performed.

From this reference dataset, 400 configurations were randomly selected for use in the PSO procedure.

2. Implementation of the PSO method

The PSO method was run 200 times using a swarm of 50 particles which was chosen as a compromise between computational expense and statistical noise. Each simulation was performed for 50 steps which was found to be sufficient for the parameters to have converged. During the simulation, the value of ω in Eq. (A2) was linearly scaled from 0.9 down to 0.4 as suggested by Banks *et al.* [40, 41]. φ_1 and φ_2 were both set equal to two.

Table II. Table of EVB parameters which were fitted using the PSO method. The 'Range' considered for each parameter is shown. During each PSO simulation the maximum permitted velocity of parameter change was linearly scaled from max to min values in each case. Units are as given in Table I, with τ_{yz} dimensionless and Δ in kcal/mol.

Param.	Range (max)	Range (min)	Vel. (max)	Vel. (min)	Fit
V_{const}^{ij}	0.0	-100.0	10.0	0.2	-72.20998
P	1.0	0.01	0.1	0.002	0.50743
k	30.0	1.0	3.0	0.06	15.64862
D_{OO}	8.0	0.1	0.8	0.016	4.18888
β	8.0	0.1	0.8	0.016	2.37963
R_{OO}^0	8.0	0.1	0.8	0.008	2.46345
P'	30.0	1.0	3.0	0.06	15.41834
α	30.0	5.0	3.0	0.06	17.42592
τ_{yz}	15.0	0.5	1.5	0.03	11.55606
Δ	800.0	400.0	20.0	0.05	558.40454

There are ten parameters of the model to be optimised, and details of the range searched for each parameter are given in Table II. Three parameters were not treated in this way. r_{OO}^0 was set to zero as it was noted to be redundant. The parameter γ was set to the value used in the MS-EVB3 model (see Table I). The parameter τ_x was chosen to be 0.3. The EVB model parameters were taken to be the averages of the parameter sets $\{p_g\}$ obtained from the 200 runs; this was seen as a fair compromise between computational expense and accuracy. The resulting optimised values are given in Table II.