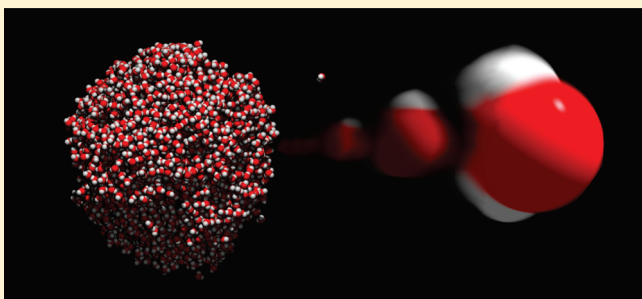


# Molecular Dynamics Study on the Microscopic Details of the Evaporation of Water

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**ABSTRACT:** Molecular dynamics simulations were conducted on a drop of water (containing 4890 TIP3P waters) at 350 K. About 70 evaporation events were found and characterized in enough detail to determine significant patterns relating to the mechanism of evaporation. It was found that in almost all evaporation events that a single, high-energy state immediately preceded the evaporation event. In  $\sim 50\%$  of the cases, this high-energy state involved a short oxygen–oxygen distance, suggesting a van der Waals collision, whereas in the remaining cases, a short hydrogen–hydrogen distance was found, suggesting an electrostatic “collision”. Of the high-energy states that led to evaporation, about half occurred when the coordination number of water was 1, and about half, when the coordination number was 2. It was found that the 1-coordinated waters ( $\sim 1\%$  of the surface waters) and 2-coordinated waters (6% of the surface waters) were responsible for almost all the evaporation events.



## INTRODUCTION

Naturally, for life forms on a planet covered 2/3 with water, and with a range of temperatures and pressures that make all three phases of water possible, the properties of water are of pervasive interest. For instance, evaporation alone is of direct relevance to the hydraulic architecture of trees<sup>1</sup> and the desiccation of living cells;<sup>2</sup> is of widespread interest to climate scientists,<sup>3,4</sup> both here and elsewhere in the solar system;<sup>5</sup> and, of course, is relevant for simple physical properties, such as heat flow.<sup>6</sup> Although there has been experimental work done on the rates of evaporation<sup>7,8</sup> and the evaporation/condensation equilibrium, which is key in many aspects of atmospheric chemistry,<sup>9</sup> there has been comparatively little done on the microscopic details of the evaporation event. In part, this is due to the limited techniques that can observe elements as small as a water molecule and the limited number of techniques that can observe kinetic events as quick as water evaporation (an event that, as is shown below, typically is due to a single collision of two water molecules and takes place in  $\sim 0.1$  ps).

Molecular dynamics has a good track record of accurately describing structural and dynamical properties of water,<sup>10–12</sup> and it is this technique that is used here to examine the evaporation of water. Although there have been previous interesting MD studies that have addressed evaporation, they have focused on aspects other than its microscopic mechanism; for example, the cooling/structural effects of evaporation<sup>13</sup> or the effect of solutes on the rate of evaporation.<sup>14,15</sup> The mechanism of evaporation of water is pragmatically difficult to study by MD by virtue of the fact that it occurs from a surface population and that these events occur only rarely, but when they do occur, they happen very quickly.

Previous studies have looked at the energetics of evaporation from small water clusters (2–10 molecules) without actually

examining the detailed mechanism of evaporation.<sup>16</sup> The mechanism of evaporation from a large water droplet with a relatively flat radius of curvature has not been examined. To gain information on a large number of water evaporation events using an “off the shelf” MD simulation package, it is necessary to run long simulations, saved frequently (hence, leading to very large file sizes), and then mine this to gain data on enough evaporation events to draw a meaningful conclusion. In practice, this means, as will be shown below, that 20 Gb of simulation will yield information on only about 100 evaporation events.

Superficially, the process of water evaporation appears trivial in that for a water to evaporate, it must gain enough energy to separate itself from the droplet. However, the surface of a droplet is a population of states with each water molecule interacting with multiple other waters, and so although it is expected that the fewer the number of waters a molecule is interacting with, the lower the energy required to escape from the drop, it is also true that the molecule is interacting with a fewer number of water molecules; hence, there are fewer potential “evaporation energy” donors to the central water.

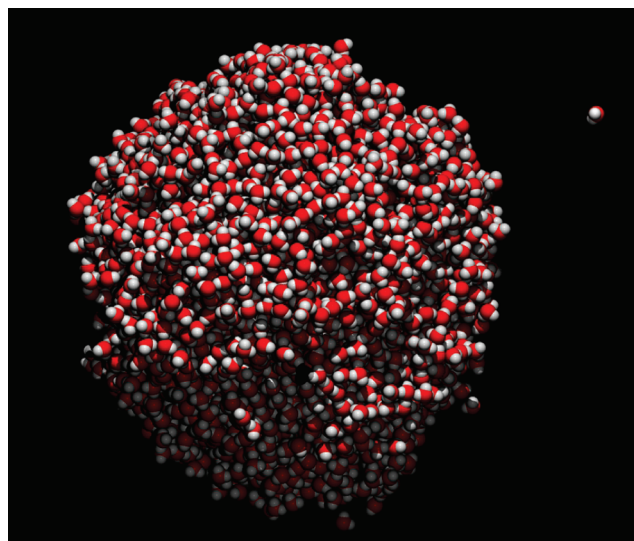
This paper examines  $\sim 70$  evaporation events to characterize the general attributes of water evaporation by MD, such as at what level of the surface does the evaporation occur, and how many waters on average is the water in contact with when the “escape energy” is given to the evaporating water molecules? Although it would be possible to examine if polarizability has a

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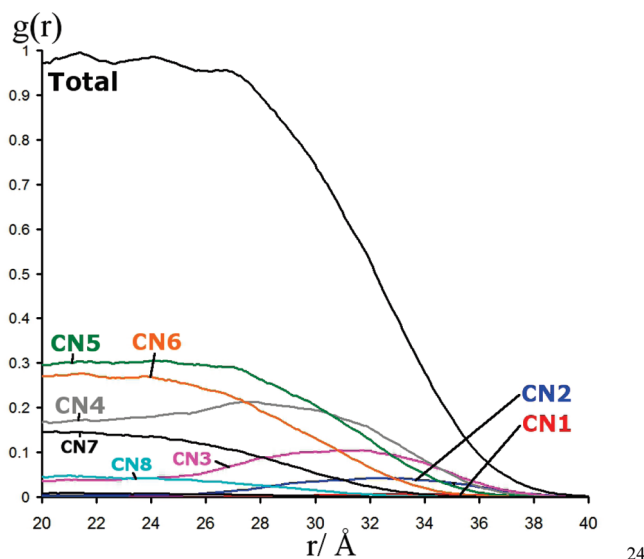
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**Figure 1.** The water drop of TIP3P water used in this simulation. The water drop is  $\sim 65$  Å in diameter and an evaporating water molecule is shown in the top right-hand corner. Clearly, the surface of the droplet is a complicated population of states. This figure was produced with the aid of VMD.<sup>23,24</sup>

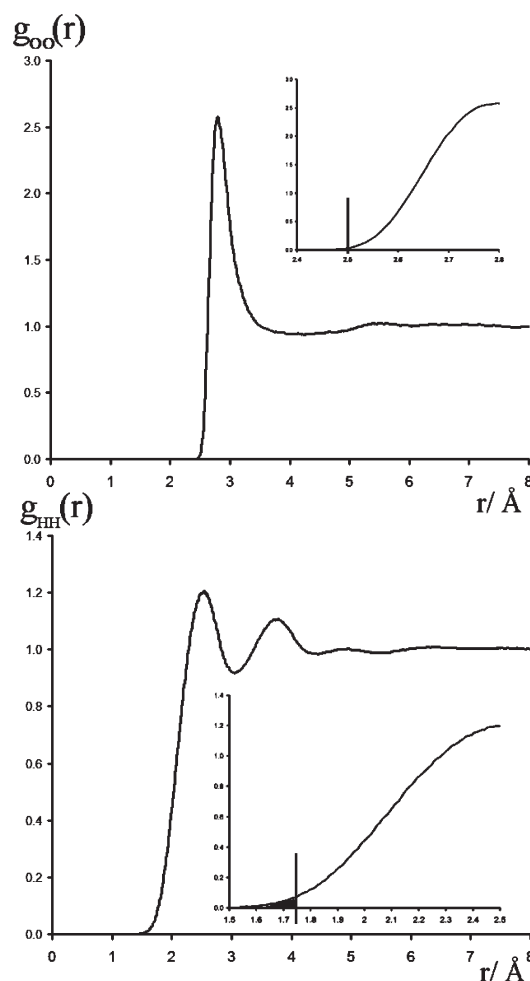


**Figure 2.** The  $g(r)$  of the water droplet (based on water oxygens). Total is shown in black. The components of the total that are constituted of the various coordination numbers are labeled in various colors. Notably, CN 1 and 2 peak just below the surface at  $\sim 34$  Å).

significant effect on evaporation (using models such as those proposed by Guillot et al.<sup>17</sup>), in this first study, polarization, which may affect both the rates and thermodynamics of evaporation, is not included.

## EXPERIMENTAL SECTION

A neutral and periodic cubic system (90 Å) was created containing 4890 independent, modified TIP3P<sup>18</sup> water molecules forming a spherical droplet about 65 Å in diameter. The simulation was performed using the CHARMM program<sup>19</sup> with all bonds to hydrogen kept fixed using SHAKE,<sup>20</sup> a time step of 1 fs, and with



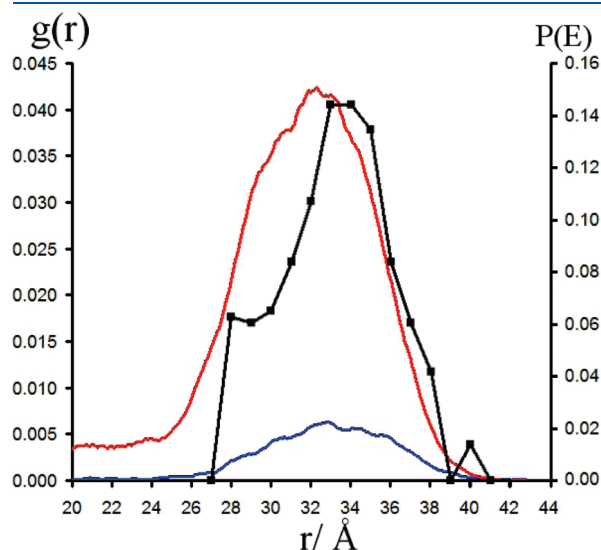
**Figure 3.** The  $g(r)$ 's of the oxygens and hydrogens within this water droplet. Shown in the insert in each case is an expansion of the low probability states characterized by short OO or HH distances. Only  $\sim 0.3\%$  of oxygens have an OO distance  $< 2.5$  Å, and 2% of hydrogens have an HH distance  $< 1.75$  Å.

the coordinates being saved every 5 fs. All van der Waals and electrostatic interactions were smoothly truncated on a group basis using switching functions from 14.5 to 16.5 Å. Initial velocities were assigned from a Boltzman distribution (350 K), followed by 50 ps of equilibration dynamics with the velocities reassigned every 0.2 ps. The simulation was then equilibrated for 0.5 ns with an additional 0.5 ns (with no further velocity reassignment) used for analysis. Due to the high saved frame rate necessary to capture evaporation events in sufficient detail, even this 0.5 ns simulation required  $\sim 20$  Gb storage as a binary file. The basic spherical geometry was chosen to have comparable populations of both surface and interior waters (in the current case,  $\sim 45\%$  interior to 55% “surface” (waters between 28 and 40 Å)) and because a droplet is arguably of more relevance to atmospheric chemistry.

## RESULTS

The water drop used in this simulation was about 65 Å in diameter (Figure 1). Two analyses were performed on this simulation: first, with regard to the properties of the water drop; and second, with regard to the evaporating waters. The  $g(r)$  of the water oxygens within the drop is shown in Figure 2, with this broken down into the subcomponents of the  $g(r)$  for water with a

coordination number (CN, the number of water oxygens within 3.5 Å of the water in question) of 0, 1, 2, 3, etc. The  $g(r)$ 's for the oxygens ( $g_{OO}(r)$ ) and hydrogens ( $g_{HH}(r)$ ) on water in this drop are shown in Figure 3 and are comparable to those found in the literature.<sup>10</sup> The average CN of O up to 3.5 Å was  $\sim 5.5$ . Evaporation events were identified by custom-written computer code, and the depth at which the evaporation event occurred was



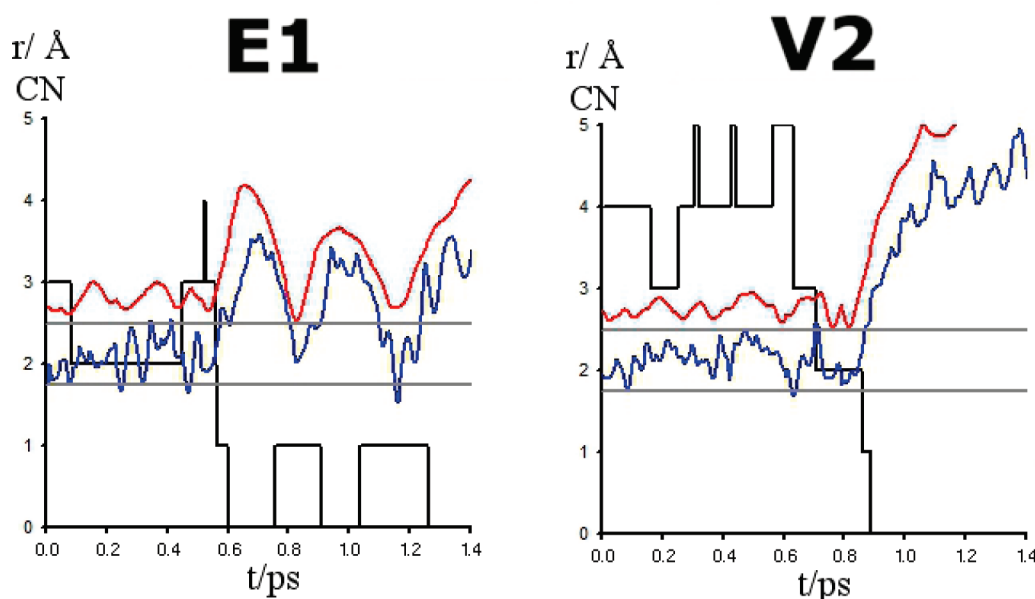
**Figure 4.** The left scale is the fraction of the total  $g(r)$  composed of CN 1 and 2 (blue and red lines, respectively). The right scale is the probability of evaporation and corresponds to the black line. The  $x$ -axis is the distance from the center of mass of the droplet. Clearly, there is a strong correlation between the populations of CN 1 and 2 and the probability of evaporation. Both the blue population and the red population produce comparable numbers of evaporation events.

recorded. About 70 evaporation events were identified, and a histogram of the depth at which they occurred was constructed (Figure 4). For each of these events, a time series of the CN, the shortest distance of the evaporating water oxygen to an oxygen in the water drop and the shortest distance between the evaporating water hydrogen and a hydrogen in the water drop, was calculated. For each of the evaporation events, a high energy configuration was identified by a short either OO or HH distance (a configuration found only  $\sim 1\%$  of the time; see below for details) almost immediately prior to evaporation, and each evaporation event was characterized by the CN of the evaporating water at this time and if the high energy state was due to an unusually short OO or HH distance.

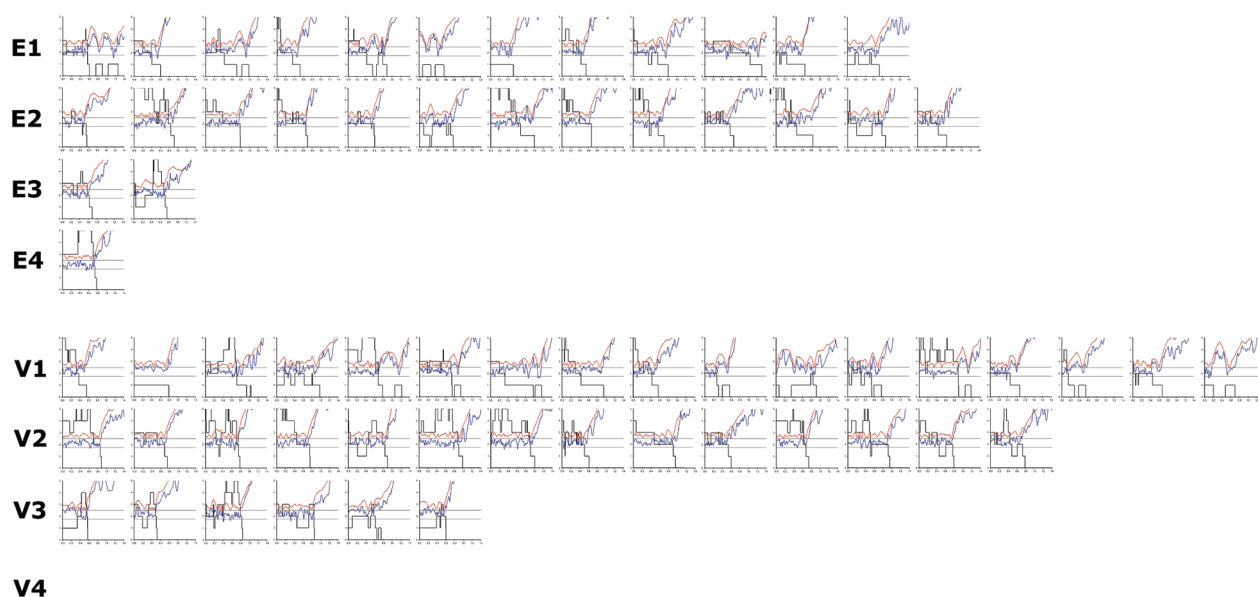
## DISCUSSION

In principal, water evaporation should be a straightforward process, in that a water molecule has three translational and three rotational modes of freedom, all containing equal amounts of energy. For a water to evaporate, it must gain enough energy from an interaction with another water molecule to overcome its interaction with the drop. It is expected that the lower the coordination number of the water, the lower this barrier, but also, the fewer the number of waters there are available to transfer the “escape energy” to the water. It is also expected that there will be a population of states on the surface of the droplet and that the surface waters will try to maximize their interaction with their neighbors, and thus, it is not clear which coordination state of water will produce the most evaporation events. However, whereas a total  $g(r)$  is a common way of characterizing a surface,<sup>21,22</sup> it was clear in this case that such a metric concealed some of the extant structure of the surface (Figure 2).

Indeed, inspection of Figure 1 readily shows that the surface was actually a population of 1-, 2-, 3-, etc. coordinated states that only average out to the Gaussian-type decline in density at the



**Figure 5.** Some enlargements of two typical time-series of evaporation events. The right scale serves both for the CN of the evaporating water molecule (black) and the shortest distance of the oxygen of the evaporating water molecules to an oxygen (red) or of a hydrogen of an evaporating water molecule to another hydrogen (blue). The two gray lines are the “low probability cutoffs”, in that only 2% of water have a HH distance  $< 1.75$  Å, and only 0.3% of oxygens have an OO distance of  $< 2.5$  Å.



**Figure 6.** The time-series of all the evaporation events in this study. They are classified by whether the high energy state immediately prior to evaporation was characterized by either a short HH distance (E) or a short OO distance (V). In both cases, the CN of that “high-energy state” is given by the number.

surface seen in Figure 2. When this total  $g(r)$  is broken down into its various subcomponents of 1-, 2-, 3-, etc. coordinated waters, a wealth of structure is found with the peaks of CN 1, 2, 3, and 4 occurring at 33, 33, 31, and 27 Å, respectively (or 7, 7, 9, and 13 Å below the “surface” (the point where the density drops below 1/1000th of the bulk)). If the surface is defined as the region between 27 and 40 Å, then it is found that CN 1, 2, 3, 4, ... 7, etc. have fractional populations of 1, 6, 16, 26, 26, 16, and 7%, respectively. By inspection of the evaporation events, it was clear that immediately prior to ejection, an unusually short either oxygen–oxygen or hydrogen–hydrogen distance was found. This implies that the energy transfer required for a water to eject from the droplet is typically characterized by a single collision.

To quantitate this, the oxygen–oxygen  $g(r)$  was calculated, and it was found that only  $\sim 0.3\%$  of the waters had an oxygen–oxygen distance shorter than 2.5 Å (Figure 3) and that only  $\sim 2\%$  of waters had a hydrogen–hydrogen distance of shorter than 2.75 Å (Figure 3). Although the use of simple distance criteria does somewhat ignore the asymmetry of the molecule, in van der Waals terms, the molecule is essentially spherical with only tiny perturbations for the hydrogens. Within the MD simulation, the prime reason for the low population (high energy) of the short O–O distance is the van der Waal repulsion, and the prime reason for the low population (high energy) of H–H distance is the electrostatic repulsion of the hydrogens. Therefore, to a first-degree approximation, the evaporation of water can be broken down into van der Waals or electrostatic type evaporation events. Further, these can be categorized into the CN of the high-energy state immediately prior to evaporation.

Figure 6 shows the  $\sim 70$  evaporation events examined in this study broken down by these categories (e.g., V1 = “van der Waals” evaporation for which the high energy state prior to evaporation was characterized by a short OO distance and the CN of the evaporating water was 1, or E3 = “electrostatic” evaporation, for which the high energy state prior to evaporation was characterized by a short HH distance and the CN of the evaporating water was 3). Because of the problems of defining concise states, these categorizations were done manually, and in about 3/4 of the cases, the

categorization was unambiguous; however, in the remaining 25% of cases, there was some ambiguity as to if the evaporation event should be categorized as E or V. Taking this practical classification difficulty into account, it was found that comparable numbers of “electrostatic” and “van der Waals” evaporation events were observed (Figure 6). It was found that for both modes of evaporation, there were comparable numbers of events when the high energy state resulted from CN of 1 and 2. The fractional composition of the surface waters with CN 1 and 2 was about 7%, yet these populations account for  $\sim 90\%$  of the water evaporation events. A strong correlation was found between the depth at which evaporation events occurred and the population of water with CN 1 and 2 (Figure 4). It was found that although the population distributions of CN 1 and CN 2 waters with depth were similar in profile, the population of CN 2 was about 10 times higher than CN 1. Given that both CN 2 waters and CN 1 waters produce comparable numbers of evaporation events, it seems reasonable to suggest that CN 1 waters are  $\sim 10$  times as likely to evaporate as CN 2 waters.

## CONCLUSIONS

From the examination of a MD simulations of a water droplet ( $\sim 65$  Å in diameter, 350 K) containing nonpolarizable, essentially “hard sphere” waters, the surface of water was found to be a population of states with both CN 1 and 2 having maximum probabilities about 7 Å below the “surface” (the point where the probability of finding a water is 1/1000 that of the bulk). The populations of CN 1 and 2 correlate strongly to the probability of evaporation with depth. Examination of the time series immediately prior to and after evaporation showed that in most cases there was a “high-energy event” characterized by a uncommonly short OO (“van der Waals evaporation”) or HH distance (“electrostatic evaporation”) with about half the evaporation events falling into each of these categories. In almost all cases, this “high energy state” occurred when the water had CN 1 or 2, even though the fraction of CN 1 and 2 waters on the surface was only  $\sim 1$  and 6%, respectively. That is, the CN 1 and 2 states which constitute only  $\sim 10\%$  of the surface states produce  $\sim 90\%$



of the evaporation events. This result is consistent with recent experimental results from Smith et al.,<sup>7</sup> who found that a rate-limiting barrier impeded evaporation.

## ■ ACKNOWLEDGMENT

This work was initiated back in early 2007 in Prague by a chance meeting between Victoria Buch (during her sabbatical with Pavel Jungwirth at the Academy of Science of the Czech Republic) and me in which we decided on some of the conceptually interesting aspects of water evaporation. Although we did not actively pursue the work at that time, it seemed fitting to investigate those attributes we discussed and report them in a journal dedicated to her memory.

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