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Multiscale Sampling of a Heterogeneous Water/Metal Catalyst Interface using Density Functional Theory and Force-Field Molecular Dynamics

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Cover Letter

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Dear Dr. Phillip Steindel:

Thank you for sending the Editorial and Reviewer comments on our manuscript JoVE59284. Please find our revised manuscript as well as a letter providing detailed responses to each comment enclosed with this submission. We have supplied the manuscript file as a Microsoft Word docx file with track changes turned on, as requested. Further, we have highlighted 2.75 pages of the protocol to indicate the portion that we propose be filmed, also as requested. If you or the Reviewers would like a non-marked-up version, please let me know, as I will be happy to supply one.

We are also supplying a zip file that includes the software, scripts, and input files used in this protocol. These files can additionally be found on the Getman Group github page at https://github.com/getman-research-group/JoVE_article.

Thank you again for handling our manuscript.

Sincerely,

Rachel Getman

TITLE:

Multiscale Sampling of a Heterogeneous Water/Metal Catalyst Interface using Density Functional Theory and Force-Field Molecular Dynamics

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KEYWORDS:
density functional theory, molecular dynamics, aqueous phase, water/solid interface, heterogeneous catalysis, transition metal surface, configurational sampling, force field, ab initio molecular dynamics, quantum mechanics/molecular mechanics

SUMMARY:

The goal of the protocol presented here is to generate and sample trajectories of configurations of liquid water molecules around catalytic species on a flat transition metal surface. The sampled configurations can be used as starting structures in quantum mechanics-based methods.

ABSTRACT:

A significant number of heterogeneously-catalyzed chemical processes occur under liquid conditions, but simulating catalyst function under such conditions is challenging when it is necessary to include the solvent molecules. The bond breaking and forming processes modeled in these systems necessitate the use of quantum chemical methods. Since molecules in the liquid phase are under constant thermal motion, simulations must also include configurational sampling. This means that multiple configurations of liquid molecules must be simulated for each catalytic species of interest. The goal of the protocol presented here is to generate and sample trajectories of configurations of liquid water molecules around catalytic species on flat transition

metal surfaces in a way that balances chemical accuracy with computational expense. Specifically, force field molecular dynamics (FFMD) simulations are used to generate configurations of liquid molecules that can subsequently be used in quantum mechanics-based methods such as density functional theory or *ab initio* molecular dynamics. To illustrate this, in this manuscript, the protocol is used for catalytic intermediates that could be involved in the pathway for the decomposition of glycerol ($C_3H_8O_3$). The structures that are generated using FFMD are modeled in DFT in order to estimate the enthalpies of solvation of the catalytic species and to identify how H_2O molecules participate in catalytic decompositions.

INTRODUCTION:

Modeling molecular phenomena involved in heterogeneous catalysis under liquid conditions is necessary for understanding catalytic function; however, this remains challenging because it requires a fine balance between chemical accuracy and computational expense. In general, since catalysis involves the breaking and forming of chemical bonds, quantum mechanics must be used to at least some degree; however, long simulations are challenging in quantum mechanics, as they require significant computer resources. Since molecules in the liquid phase are under constant thermal motion, simulations must also include configurational sampling, i.e., they must incorporate multiple spatial arrangements of the liquid molecules, as each different spatial arrangement (i.e., each configuration) has a different energy. This means that multiple configurations of liquid molecules must be simulated for each catalytic species of interest. These needs – to use quantum mechanics and to perform multiple calculations per catalytic species – can render modeling in heterogeneous catalysis under liquid phase computationally intractable. The purpose of the method described herein is to enable computationally tractable simulations of phenomena in heterogeneous catalysis under liquid phase.

We are particularly interested in heterogeneously catalyzed reactions that are carried out under liquid water. Water molecules have significant influence on catalytic phenomena, such as interacting with catalytic species (e.g., via dispersion forces and hydrogen bonding)[1-23], participating in catalytic reactions[1,7-9,15,21,22,24-27], and influencing reaction pathways and/or catalytic rates[1,11,12,15,18,23,25,27-31]. Modeling of these phenomena has been performed using QM and/or *ab initio* molecular dynamics (AIMD)[1,2,6,7,14,22,25,27,28,32-34], force field molecular dynamics (FFMD)[35], and quantum mechanics/molecular mechanics (QM/MM)[10]. In AIMD and FFMD, the atoms in the system are moved pursuant to Newton's equations of motion according to the forces acting upon them. In AIMD, the system energy and forces are calculated with quantum mechanics, whereas in FFMD, the system energy and forces are calculated using force fields, which are algebraic expressions that are parameterized based on experimental or QM data. In QM/MM, the portion of the system where the bond breaking and forming occurs is calculated with QM, and the remainder of the system is calculated with MM, which employs force fields. Because they directly employ QM, AIMD and QM/MM are better suited for capturing the bond breaking and forming that occurs in aqueous phase heterogeneous catalysis; however, FFMD is significantly more computationally tractable and thus better suited for generating the configurations of liquid H_2O molecules. The method presented in this protocol balances chemical accuracy and computational expense by employing a combination of QM and FFMD.

Specifically, this method uses FFMD simulations for generating configurations of liquid H_2O and QM to calculate system energies. FFMD is carried out using LAMMPS.[36] The force fields used in FFMD in this work employ Lennard-Jones + Coulomb (LJ+C) potentials, where the LJ parameters have been taken from the TIP3P/CHARMM model[37] for H_2O, the universal force field[38] (UFF) for Pt, and the OPLS-AA force field[39] for catalytic species, and the Coulomb parameters have been taken from the TIP3P/CHARMM[37] model for H_2O and the OPLS-AA force field[39] for catalytic species. The Coulomb parameters for Pt atoms have been set to 0. QM calculations are performed using the VASP code[40-42], which is a density functional theory (DFT) code. Water molecule insertions are performed with a code developed in-house called Monte Carlo Plug-in for Quantum Methods (MCPliQ). File conversions from VASP to LAMMPS in this protocol are performed with the Visual Molecular Dynamics (VMD) software[43].

The protocol is intended to generate configurations of liquid water molecules around catalytic species on flat transition metal surfaces at low coverage. Coverage is denoted θ and defined as the number of adsorbates per surface metal atom (i.e., the number of surface adsorbates normalized by the number of metal atoms in the topmost layer of the metal slab in the catalyst model). In this manuscript, low coverage is defined as $\theta \leq 1/9$ monolayer (ML), where 1 ML means one catalytic species per surface metal atom. The catalyst models should be placed in periodic simulation boxes. The simulation boxes do not have to be cubes. This manuscript demonstrates the use of the protocol for generating configurations of liquid H_2O that can be used to calculate quantities of interest in aqueous phase heterogeneous catalysis.

This protocol requires that the user has access to installed and working versions of the VASP, MCPliQ, LAMMPS, and VMD software. More information about VASP (https://www.vasp.at/), LAMMPS (https://Lammps.sandia.gov/), and VMD (https://www.ks.uiuc.edu/Research/vmd/) are available on their respective websites. The MCPliQ software is documented at https://github.com/getman-research-group/JoVE_article, along with all input files and Python scripts mentioned in this protocol. This protocol assumes that the executables and scripts mentioned within will be run on a high-performance research computer and are installed in a directory that is in the user's $PATH variable. If an executable or script is placed in a location that is not in the user's $PATH, then the path to the executable must be included to execute it. Executables and scripts are executed in steps 2.1.2, 2.2.1, 2.2.8, 3.1, 4.2, 5.2, and 6.1.2. For example, to execute the MCPliQ code in step 2.1.2 from a directory that is not in the user's $PATH, the user would type **$PATHTOMCPLIQ/mcpliq** at the command-line interface instead of **mcpliq**, where $PATHTOMCPLIQ is the location where the mcpliq executable has been stored (e.g., $PATHTOMCPLIQ might be ~/bin). Before starting this protocol, all executables and scripts should be given executable permissions (e.g., in Linux, this could be done by typing **chmod +x mcpliq** at the command-line interface from the directory where the mcpliq executable is stored). Further, any modules required by any of the software or scripts should be loaded (these dependencies will be specific to individual installations of the various software and the computer where the simulations will be run).

PROTOCOL:

1. Generate the adsorbate structure

1.1. Create a VASP POSCAR file comprising a supercell with periodic boundary conditions, as you would if you were performing simulations of adsorbates on metal surfaces under vacuum. The supercell should include an initial guess of the adsorbate structure and the metal surface as well as vacuum space above the adsorbate for adding H_2O molecules. Details on how to do this are provided in previous work[35,44].

NOTE: It is important that the height of the vacuum space be at least 12 Å above the top of the adsorbate.

1.2. Relax the structure and minimize its energy using the VASP code. Details on how to do this are provided in previous work[35,44]. This will produce a file called CONTCAR, which will be used in the next section.

2. Add explicit H_2O molecules

2.1. Add N water molecules to the vacuum space in the CONTCAR created in step 1.2 using the MCPliQ code, where $N = \rho V$, ρ is the density of water, and V is the volume of the vacuum space above the adsorbate.

NOTE: ρ should be taken as the density of water as determined by the TIP3P/CHARMM water model at the simulation temperature. V will be refined in the next step.

2.1.1. Specify the following information in the MCPliQ master_input.txt file: The number of H_2O molecules to add (N) by changing the first argument in line 28, the path to the water.txt file by changing the second argument in line 28, and the minimum and maximum height of the supercell that can be occupied by water molecules by changing the **Minimum z-coordinate** in line 11 and the **Maximum z-coordinate** in line 12.

2.1.2. Execute the MCPliQ code by typing **mcpliq** from the command-line interface to insert water molecules into the CONTCAR file. The code will output one or more files with the file extension of .POSCAR.

NOTE: If more than one POSCAR files are produced, they will be named POSCAR_n.POSCAR. Select the file where n is largest.

2.2. Generate the LAMMPS input files for an NPT simulation and equilibrate the cell volume using FFMD in the NPT ensemble in LAMMPS.

2.2.1. Execute the script lmps_bond_angle.py on the .POSCAR file generated in step 2.1.2 by typing **lmps_bond_angle.py $filename.POSCAR** at the command-line interface, where $filename is the name of the .POSCAR file generated in step 2.1.2. This script creates a file called $filename.POSCAR.bond_angle_info.txt which lists bonds and angles that will be used in the

LAMMPS data file.

2.2.2. Open VMD and select **File** > **New Molecule** in the main window to open the **Molecule File Browser** window. Select VASP_POSCAR from the **Determine File Type** dropdown menu. Click **Browse** and navigate to the $filename.POSCAR file. Click **Load** to open the $filename.POSCAR file.

2.2.3. Open the Tk Console within VMD by selecting **Extensions** > **Tk Console** from the VMD Main window.

2.2.4. Execute the following command in the Tk console: **topo writelammpsdata $WDPATH/data.myadsorbate full**, where $WDPATH is the directory on the computer where VMD will write the LAMMPS data file and data.myadsorbate is the name of the LAMMPS data file.

2.2.5. Delete the **Bonds** section at the bottom of the data.myadsorbate file. Then, append the bond and angle lists in the file $filename.POSCAR.bond_angle_info.text into data.myadsorbate.

NOTE: The indexes for the O-H bond type and H-O-H angle type for the water molecules in the $filename.POSCAR.bond_angle_info.txt file are both set to 1. Thus, bond and angle types for adsorbates should start counting at 2.

2.2.6. Edit the data.myadsorbate file by adding the Lennard-Jones parameters to the **Pair Coeffs** section and the Coulomb parameters to the **Atoms** section. Lennard-Jones and Coulomb parameters for the H_2O molecules, adsorbate atoms, and metal surface atoms need to be added.

NOTE: The Lennard-Jones parameters for Pt atoms, water molecules, and adsorbate atoms in this protocol are obtained from the UFF[38], TIP3P/CHARMM[37], and OPLS-AA[39] force fields, respectively. Coulomb parameters for water molecules and adsorbates atoms are obtained from the TIP3P/CHARMM[37] and OPLS-AA[39] force fields, respectively. Coulomb parameters for Pt atoms are set to 0 in this protocol. Alternatively, calculated partial charges could be used for the Coulomb parameters for adsorbate atoms and Pt atoms.

2.2.7. Copy the LAMMPS input file input.equil into the directory $WDPATH. Edit the group variable on line 34 to indicate the atom type indexes for the water oxygen and water hydrogen atoms and the group variable on line 35 to indicate the atom type indexes for the Pt and adsorbate atoms.

2.2.8. Execute the LAMMPS software by typing **mpiexec -n XX lmp_mpi < input.equil** at the command-line interface, where XX is the number of CPU cores to use, and lmp_mpi is the name of the LAMMPS executable. Doing this will run an energy minimization to refine the H_2O configuration, followed by a FFMD simulation performed at constant number of H_2O molecules (*N*), volume (*V*), and temperature (*T*) to bring the water to the simulation temperature, followed by a FFMD simulation run at constant *N*, pressure (*P*), and temperature (*T*) to determine the physically correct height of the simulation box. Output files that will be used in section 3 are called data.myadsorbate_npt and log.myadsorbate.

NOTE: The duration of the NPT simulation should be long enough to comprise an “equilibration” run, where the volume of the supercell comes to steady state, and a “production” run, which is used to sample the ensemble averages (here, the height of the supercell). During the equilibration run, the volume of the supercell when plotted against time should level off to a steady state value. Once this occurs, the NPT simulation can be said to be in its production run. Verify equilibration of the NPT simulation by ensuring that the fluctuations in the height of the supercell (lz) are minimal or have converged to a steady value. If large fluctuations occur, then re-generate a H_2O configuration by decreasing the timestep on line 92 in the input.equil file and repeating step 2.2.8 or starting again from step 2.1.1 .

3. Extract the proper height of the supercell

3.1. Execute the script get_npt_lz.py on the log.myadsorbate file by typing **get_npt_lz.py log.myadsorbate** at the command-line interface. This script outputs the average supercell height from the “production” run portion of the NPT simulation in the avg_lz.txt file.

NOTE: The get_npt_lz.py script assumes that LAMMPS writes the length of the cell z-dimension (lz) to the log.myadsorbate file every 1000 fs (customizable at line 20 of the get_npt_lz.py script), which is the default in the provided input.equil LAMMPS input file. The get_npt_lz.py script detects and discards the first 2 ns (customizable at line 19 of the get_npt_lz.py script) worth of lz values in the log.myadsorbate file, as they comprise the equilibration portion of the simulation, while the remaining 3 ns comprise the “production” portion and are thus used by the get_npt_lz.py script to compute the average z-dimension length. In addition to the avg_lz.txt file, the get_npt_lz.py script outputs a file called npt_data.txt, which provides values of lz as a function of the timestep, as well as a file called npt_plot.png, which plots the same data. The plot can be used to verify equilibration of the NPT simulation.

3.2. Reconstruct the supercell using the average height determined in NPT.

3.2.1. Copy the data.myadsorbate_npt file into a new directory, referred to here as $WD2PATH, and rename it data.myadsorbate.

3.2.2. Edit the new data.myadsorbate file so that the lz height is equal to the average value output from the get_npt_lz.py script by changing the zlo and zhi arguments in the data.myadsorbate file such that zlo is 0.0 and zhi is the lz value from the avg_lz.txt file produced in step 3.1.

4. Generate configurations of H_2O molecules

4.1. Copy the LAMMPS input file input.prod into $WD2PATH. Edit the group variable on line 32 to indicate the atom type indexes for the water oxygen and water hydrogen atoms and the group variable on line 33 to indicate the atom type indexes for the Pt and adsorbate atoms.

4.2. Execute the LAMMPS software by typing **mpiexec -n XX lmp_mpi < input.prod** into the command-line interface, where XX is the number of CPU cores to use, and lmp_mpi is the name of the LAMMPS executable. Doing this will run a constant NVT simulation on the H_2O molecules. The key output file from this simulation is the dump.myadsorbate.lammpstrj file.

NOTE: The duration of the NVT simulation should be long enough to comprise an equilibration run, where the energy of the system comes to steady state, and a production run, from which the ensemble averages (here, the spatial positions of the water molecules) are sampled. During the equilibration run, the energy of the system when plotted against time should level off to a steady state value. Once this occurs, the NVT simulation can be said to be in its production run.

5. Determine the hydrogen bond lifetime for proper time sampling

5.1. Edit the hb_lifetime_dist.py script to specify: the timestep of the first frame of the dump.myadsorbate.lammpstrj file by changing the actualStart variable on line 22, how often frames are written to the LAMMPS trajectory file by changing the timestep variable on line 23, the first and last timesteps the script should consider (i.e., the production portion of the trajectory) by changing the N_first and N_last variables on lines 24 and 25, whether consecutive frames are considered or frames are skipped by changing the nevery variable on line 26, and the number of lines per frame section of the trajectory file by changing the frameLine variable on line 27. Additionally, edit lines 31 through 35 to specify which atom types within the data.myadsorbate file belong to the adsorbate and which atom types belong to the H_2O molecules.

NOTE: The hb_lifetime_dist.py script analyzes the H_2O configurations in the production run and determines if any H_2O molecules are hydrogen bonded to the adsorbate. It then counts the simulation time that each hydrogen bond remains intact and reports this information as a distribution of hydrogen bond lifetimes in units of ps. The specific version of the script that is provided with this protocol assumes that LAMMPS writes the configuration of H_2O molecules to the dump.myadsorbate.lammpstrj file every 1000 fs, which is the default in the provided input.prod LAMMPS input file. It detects and discards the first 2 ns worth of configurations in the the dump.myadsorbate.lammpstrj file, as they comprise the equilibration portion of the simulation, and uses the remaining 3 ns to calculate hydrogen bond lifetimes.

5.2. Execute the script hb_lifetime_dist.py on the dump.myadsorbate.lammpstrj file by typing **hb_lifetime_dist.py** at the command-line interface. Doing this will produce a file called distribution_HB_lifetime.dat.

5.3. Plot the data in the distribution_HB_lifetime.dat file to view the distribution of hydrogen bond lifetimes that occurred during the NVT simulation.

5.4. Determine the time increment to use for the time sampling interval based on the calculated hydrogen bond lifetimes. The best choice is the maximum hydrogen bond lifetime; alternatively, a value that would capture the 95% confidence interval can be used.

6. Sample configurations of liquid H_2O molecules

6.1. Determine the number of configurations from the production run of the NVT FFMD trajectory for further calculations. The number of configurations should be selected so that the minimum time between configurations is equal to or greater than the time sampling interval identified in section 5.

6.1.1. Edit the default value for the num_frames variable on line 21 of the lammps_frames.py script to specify the number of configurations to extract.

6.1.2. Execute the script lammps_frames.py on the file dump.myadsorbate.lammpstrj by typing **lammps_frames.py** at the command-line interface. Doing this will output a list of simulation times corresponding to the configurations that should be extracted from the dump.myadsorbate.lammpstrj file. These configurations can be used as starting structures in AIMD or QM simulations.

NOTE: 1) The lammps_frames.py script automatically detects the LAMMPS log and dump files as well as the production portion of the trajectory within the dump file and divides the number of configurations within the dump file into 10 groups. Alternatively, the user can specify the log file, the dump file, and the number of configurations from the command-line interface using the -l, -d, and -n options, respectively. To do so, the user should type **lammps_frames.py -n XX -l $logfilename -d $dumpfilename** at the command-line interface, where XX is the desired number of configurations, $logfilename is the name of the LAMMPS logfile, and $dumpfilename is the name of the LAMMPS trajectory (dump) file. The simulation times that are output refer to the median times in each group. 2) If the configurations will be calculated in VASP with the LDIPOLE flag turned on, a small layer of vacuum space should be added to the top of the supercell above the water layer. This will facilitate convergence of the electronic structure in the VASP calculation. Adding an additional 3 Å of vacuum space above the H_2O molecules has been successful in the simulations discussed below.

REPRESENTATIVE RESULTS:

One use of this protocol is to calculate the energies of interaction between the liquid water and catalytic species, i.e., ΔE_{int}[35]:

$$\Delta E_{\text{int}} = E_{\text{Catalytic species+H}_2\text{O}} + E_{\text{Clean catalyst surface}} - E_{\text{Catalytic species}} - E_{\text{Clean catalyst surface+H}_2\text{O}}$$

where $E_{Catalytic\ species+H2O}$ is the energy of a configuration of H_2O molecules around a catalytic species on a metal surface, $E_{Clean\ catalyst\ surface}$ is the energy of the clean catalyst surface in vacuum, $E_{Catalytic\ species}$ is the energy of the catalytic species on a metal surface in vacuum, and $E_{Clean\ catalyst\ surface+H2O}$ is the energy of the configuration of H_2O over the catalyst surface with the catalytic species removed. The positions of the H_2O molecules used to calculate $E_{Catalytic\ species+H2O}$ and $E_{Clean\ catalyst\ surface+H2O}$ should be identical. All values of E are calculated using the VASP code. The quantity ΔE_{int} includes all of the physical and chemical interactions between all of the molecules in the liquid water structure and the catalytic species and gives a reasonable estimate of the enthalpy of solvation of the catalytic species, which is needed to calculate its free energy of solvation and total free energy. **Table 1** provides values for ΔE_{int} calculated for species on a Pt(111) catalyst surface with chemical formulas equal to $C_xH_yO_z$ in units of eV (1 eV = 96.485 kJ/mol). The values were calculated at coverages ≤1/9 ML.[35,48] The values reported are the averages taken over 10 configurations of liquid H_2O, and the uncertainties are reported as standard deviations. All the values are negative, indicating favorable interactions with water.

Another application of this protocol is to generate starting structures for AIMD. Movie 1 is a movie of an AIMD trajectory that was started from a configuration generated by this protocol. At the start of this movie, a COH adsorbate is shown on a Pt(111) surface under a structure of liquid H_2O. One H_2O molecule is emphasized, which formed a hydrogen bond with COH. Over the course of the movie, this H_2O molecule abstracts the proton from the COH adsorbate and deposits a second hydrogen atom on the Pt(111) surface. The H_2O molecule thus helps to catalyze the reaction $COH^* + {}^* \rightarrow CO^* + H^*$, where the *s indicate catalytic sites. This simulation highlights the main strength and the main purpose of the multiscale sampling method described herein. Numerous configurations of H_2O molecules are generated with FFMD, due to its strength in computational tractability. However, a limitation of FFMD is that it cannot capture bond breaking and forming unless a reactive force field is implemented. AIMD uses quantum mechanics to calculate energies and thus can capture bond breaking and forming. However, AIMD is too computationally demanding to generate all of the configurations of H_2O molecules necessary to ensure sufficient sampling has been achieved. Thus, this protocol combines the two methods.

The structures of liquid H_2O molecules generated by this procedure are dependent on input settings. Setting these improperly can have unintended influences on the water structures. For example, when the intermolecular distances become too small or when other parameters in the molecular dynamics input files are set improperly or take on unphysical values, the water structure can become unreasonable. Under these circumstances, the structure of water will “blow up” unintendedly during the FFMD trajectory. **Figure 1** shows an example of this. The snapshot on the left-hand side is the starting structure for a FFMD run, and the snapshot on the right-hand side is a snapshot taken within 1 ps of starting the simulation. As can be seen, the H_2O molecules have moved far away from the surface. This is caused by improper settings made in the simulation input files and is not a structure that is likely to occur in reality.

FIGURE AND TABLE LEGENDS:

Figure 1: Example of a negative result. The force field molecular dynamics simulation “blows up” due to an unphysical setting or value. Left hand image: The starting geometry of the Pt(111) surface, adsorbate, and liquid water structure. Right hand image: The geometry of the Pt(111) surface, adsorbate, and liquid water structure less than 1 ps later. In the right-hand image, the H_2O molecules have separated from the surface due to unphysically large forces.

Movie 1: *Ab initio* molecular dynamics (AIMD) simulation initiated from a configuration generated in multiscale sampling. A H_2O molecule that is originally hydrogen bonded to a COH adsorbate on a Pt(111) surface abstracts the proton from COH and deposits a second hydrogen on the Pt(111) surface. This bond breaking and forming event can be captured by AIMD but not with force field molecular dynamics (FFMD) unless a reactive force field is used. The initial configuration of H_2O molecules used in this AIMD simulation was generated using FFMD as described in this manuscript.

Table 1: Water-catalytic species interaction energy results. Interaction energies in eV calculated for eight $C_xH_yO_z$ adsorbates on Pt(111). Values reported are the averages taken over multiple configurations of liquid H_2O. The uncertainties are the standard deviations of the averages. 1 eV = 96.485 kJ/mol.

DISCUSSION:

The method as presented was selected for its ease of implementation, but multiple customizations could be made. For one, the force fields used in the FFMD simulations can be modified. Changing the force field parameters and/or potentials can be done by editing the LAMMPS input and data files. Similarly, solvents other than H_2O could be employed. To make this modification, the desired solvent molecule would need to be inserted starting from step 2.1.1, and the LAMMPS input files would need to be edited to incorporate the appropriate potentials and parameters. Inserting the new solvent molecule would also require supplying the internal coordinates of the solvent molecule in a .txt file analogous to the water.txt file.

Another modification that could be made is to modify the area of the surface slab. The results discussed in this manuscript employed 3 Pt x 3 Pt or 4 Pt x 4 Pt surface slabs, which have surface areas less than 120 $Å^2$. As the slab surface area increases, the computational expense also increases. Computational expense has the largest impact on section 5 of this protocol. If the data processing steps in section 5 become computationally prohibitive, big data post processing strategies such as those discussed in Li et al. 2018[45] can be employed.

Possible sources of uncertainty for this procedure include the force field employed, the sampling method, and the sampling frequency. The water structure is determined by the force field that is used, meaning that the choice of force field could influence the specific configurations of H_2O molecules. Our group has assessed how the choices of force field for H_2O molecules and Pt atoms influence the interaction energies calculated in FFMD and found that the choice of force field contributes less than 0.1 eV to this interaction energy. Another source of uncertainty is the sampling method, which influences the specific configurations that are used to calculate a quantity of interest. Our group has compared the performance of the "time sampling" method presented in this protocol with an "energy sampling" method, which is biased to lower energy configurations of H_2O molecules, on the interaction energies calculated in DFT and found both of these sampling methods give statistically equal values[35,46]. The sampling frequency can also influence the results. We have assessed how increasing the number of configurations from 10 to 30,000 influences the average interaction energies calculated in FFMD for 40 different $C_3H_xO_3$

adsorbates and found that the sampling frequency contributes less than 0.1 eV to the average interaction energy[44].

The main limitation to this method is that the adsorbates are approximated by the structures under vacuum during the FFMD simulations. In reality, the adsorbates would exhibit conformational changes (bond stretches, angle bends, torsional motions, etc.) due to normal thermal movements, including interactions with solvent molecules. Attempts to include conformational changes of adsorbates into the FFMD simulations would require detailed development of force fields for catalytic surface adsorbates, i.e., which comprise terms that describe bond stretches, angle bends, and torsional terms, amongst others. As a future direction of this protocol, we are developing such force fields for adsorbates at solid surfaces, which we will use to determine the extent to which using rigid adsorbates influences the results.

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The authors disclose no conflicts of interest.

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Figure 1

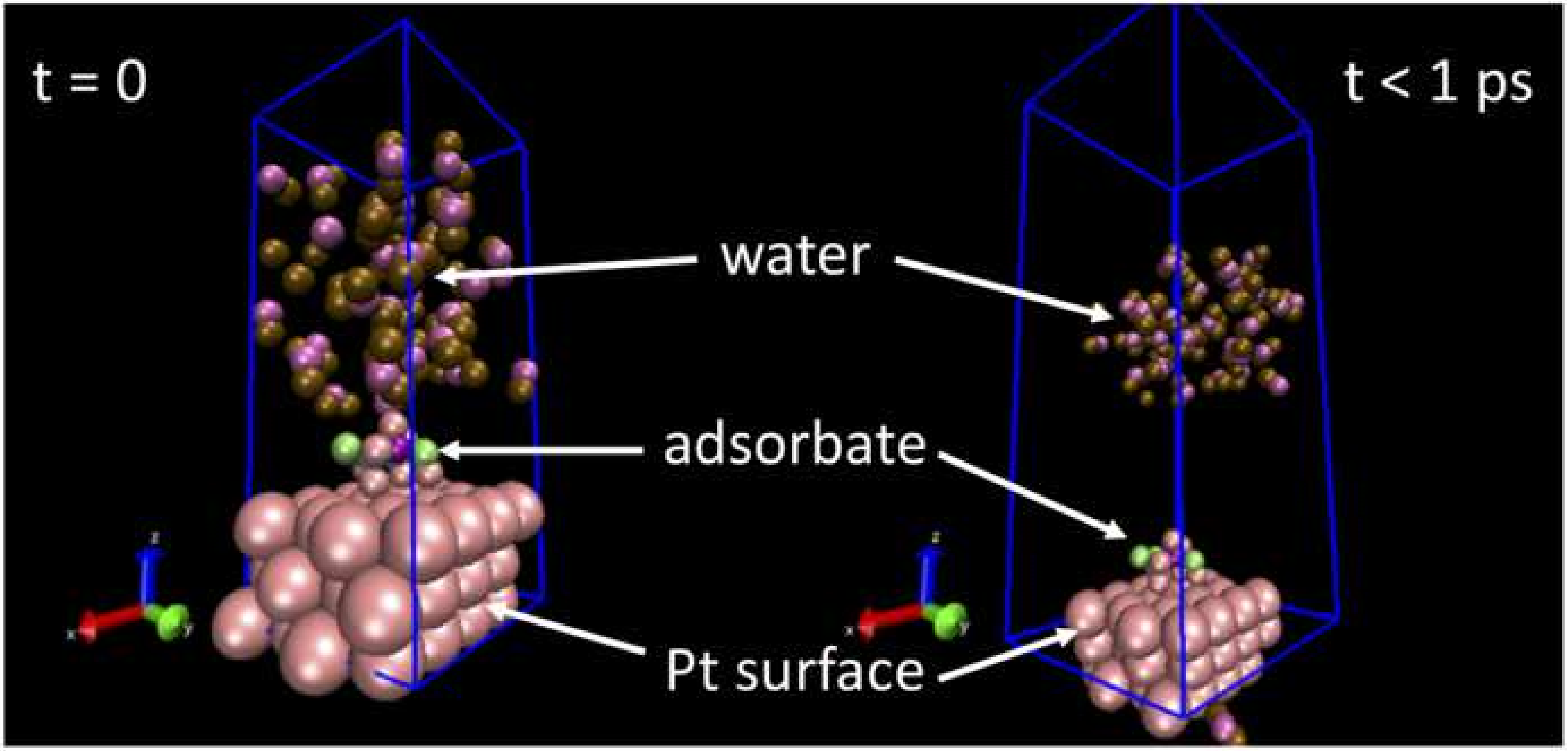

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Table 1

Catalytic Species	ΔE_{int} (eV)
COH	-0.70 ± 0.07
CO	-0.03 ± 0.03
CH_2OH	-0.64 ± 0.12
CHO-CHOH-CH_2OH	-0.93 ± 0.22
COH-COH-CH_2OH	-0.87 ± 0.23
COH-CHOH-COH	-1.72 ± 0.26
CHOH-COH-CO	-1.57 ± 0.25
CHO-CO-CO	-0.31 ± 0.19

Name of Material/ Equipment	Company	Catalog Number
VASP software	Computational Materials Physics, Dept. of Physics, University of Vienna	vasp.5.4.4
LAMMPS software	Sandia National Laboratory	31Mar17-dp
VMD software	Theoretical and Computational Biophysics Group, University of Illinois at Urbana-Champaign	1.9.3
MCPliQ software	Getman Research Group, Dept. of Chemical and Biomolecular Engineering, Clemson University	
JoVE article scripts	Getman Research Group, Dept. of Chemical and Biomolecular Engineering, Clemson University	
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Comments/Description
Standard parallel VASP executable in the newest version.
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Standard VMD executable in the newest version.
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We added the following text to Steps 1.1 and 1.2: "Details on how to do this are provided in References 35 and 48." As Step 1.3 was a simple re-naming step, we edited the master_input.txt file employed in Step 2.1 to read the original file. We thus deleted Step 1.3 from the protocol.

2. 2.1.2: Where in this file, exactly, are these parameters modified?

This is now Step 2.1.1. We rephrased Step 2.1.1 to read "Specify the following information in the MCPliQ master_input.txt file: The number of H_2O molecules to add (N) by changing the first argument in line 28, the path to the water.txt file by changing the second argument in line 28, and the minimum and maximum height of the supercell that can be occupied by water molecules by changing the "Minimum z-coordinate" in line 11 and the "Maximum z-coordinate" in line 12."

3. 2.2.1, 3.1, 5.2, 6.3: How exactly are these scripts/programs executed on the command line; e.g., how are they modified for different files? Including the exact command used (as in 2.2.4) may help.

We included more information in the protocol header: "This protocol requires that the user has access to installed and working versions of the VASP, MCPliQ, LAMMPS, and VMD software. More information about VASP (https://www.vasp.at/), LAMMPS (https://lammps.sandia.gov/), and VMD (https://www.ks.uiuc.edu/Research/vmd/) are available on their respective websites. The MCPliQ software is documented at https://github.com/getman-research-group/JoVE_article, along with all input files and Python scripts mentioned in this protocol. This protocol assumes that the executables and scripts mentioned within will be run on a high-performance research computer and are installed in a directory that is in the user's $PATH variable. If an executable or script is placed in a location that is not in the user's $PATH, then the path to the executable must be included to execute it. Executables and scripts are executed in Steps 2.1.2, *2.2.1, 2.2.8, 3.1, 4.2, 5.2, and 6.1.2. For example, to execute the MCPliQ code in Step 2.1.2 from a directory that is not in the user's $PATH, the user would type "$PATHTOMCPLIQ/mcpliq" at the command-line interface instead of "mcpliq", where $PATHTOMCPLIQ is the location where the mcpliq executable has been stored (e.g., $PATHTOMCPLIQ might be ~/$USER/bin). Before starting this protocol, all executables and scripts should be given executable permissions (e.g., in Linux, this could be done by typing chmod +x mcpliq at the command-line interface from the directory where the mcpliq executable is stored). Further, any modules required by any of the software or scripts should be loaded (these dependencies will be specific to individual installations of the various software and the computer where the simulations will be run)."*

We additionally rephrased the following Steps:

Step 2.1.2: "Execute the MCPliQ code by typing "mcpliq" from the command-line interface to insert water molecules into the CONTCAR file. The code will output one or more files with the file extension of .POSCAR."

Step 2.2.1: "Execute the script lmps_bond_angle.py on the .POSCAR file generated in Step 2.1.2 by typing "lmps_bond_angle.py $filename.POSCAR" at the command-line interface, where $filename is the name of the .POSCAR file generated in Step 2.1.2. This script creates a file called $filename.POSCAR.bond_angle_info.txt which lists bonds and angles that will be used in the LAMMPS data file."

Step 3.1: "Execute the script get_npt_lz.py on the log.myadsorbate file by typing "get_npt_lz.py log.myadsorbate" at the command-line interface. This script outputs the average supercell height from the "production" run portion of the NPT simulation to the screen."

Step 5.2: "Execute the script hb_lifetime_dist.py on the dump.myadsorbate.lammpstrj file by typing "hb_lifetime_dist.py" at the command-line interface. Doing this will produce a file called distribution_HB_lifetime.dat."

Step 6.3 is now Step 6.1.2 and reads: "Execute the script lammps_frames.py on the file dump.myadsorbate.lammpstrj by typing "lammps_frames.py" at the command-line interface. Doing this will output a list of simulation times corresponding to the configurations that should be extracted from the dump.myadsorbate.lammpstrj file. These configurations can be used as starting structures in AIMD or QM simulations."

4. 2.2.2: How exactly is this file opened?

We rephrased Step 2.2.2 to: "Open VMD, and select File → New Molecule in the Main window to open the Molecule File Browser window. Select VASP_POSCAR from the Determine File Type dropdown menu. Click Browse and navigate to the $filename.POSCAR file. Click Load to open the $filename.POSCAR file."

5. 2.2.8, 4.2: How exactly is LAMMPs software executed?

We rephrased the following steps:

Step 2.2.8: "Execute the LAMMPS software by typing "mpiexec -n XX lmp_mpi < input.equil" into the command-line interface, where XX is the number of CPU cores to use, and lmp_mpi is the name of the LAMMPS executable. Doing this will run an energy minimization to refine the H_2O configuration, followed by a FFMD simulation performed at constant number of H_2O molecules (N), volume (V), and temperature (T) to bring the water to the simulation temperature, followed by a FFMD simulation run at constant N, pressure (P), and temperature (T) to determine the physically correct height of the simulation box. Output files that will be used in Step 3 are called data.myadsorbate_npt and log.myadsorbate."

Step 4.2: "Execute the LAMMPS software by typing "mpiexec -n XX lmp_mpi < input.prod" into the command-line interface, where XX is the number of CPU cores to use, and lmp_mpi is the name of the LAMMPS executable. Doing this will run a constant NVT simulation on the H_2O molecules. The key output file from this simulation is the dump.myadsorbate.lammpstrj file."

Highlighting:

1. There is a 10 page limit for the Protocol, but there is a 2.75 page limit for filmable content. If revisions cause the highlighted portion to be more than 2.75 pages, please highlight 2.75 pages or less of the Protocol (including headers and spacing) that identifies the essential steps of the protocol for the video, i.e., the steps that should be visualized to tell the most cohesive story of the Protocol.

We have modified the highlighting so that it is 2.75 pages.

2. 6.1, 6.2: These appear to be mostly vague calculation steps and cannot be filmed.

These steps are now 6.1.1. and 6.1.2. We have eliminated the vague calculation instructions from these steps. The steps now read:

Step 6.1.1: "Edit the num_frames variable on line 26 of the lammps_frames.py script to specify the number of configurations to extract."

Step 6.1.2: "Execute the script lammps_frames.py on the file dump.myadsorbate.lammpstrj by typing "lammps_frames.py" at the command-line interface. Doing this will output a list of simulation times corresponding to the configurations that should be extracted from the dump.myadsorbate.lammpstrj file. These configurations can be used as starting structures in AIMD or QM simulations."

References:
1. Please ensure references have a consistent format.

We have edited the references so that they all follow the same format.

Table of Materials:
1. Please ensure the Table of Materials has information on all materials and equipment used, including software and computational equipment.

We have filled out the Table of Materials, including software. It is included with this re-submission.

Other:
1. Please include, if possible, any software you have developed in your revised submission (this can be included as a single .zip file).

We are including with our re-submission a zip file that contains the MCPliQ software as well as all of the scripts and input files that are used in this protocol.

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Reviewers' comments:

Reviewer #1:

Manuscript Summary:

This manuscript provides approach and necessary software (and scripts) to set up condensed phase simulations for catalytic systems. The manuscript provides the approach in great detail and it will be helpful for the community especially new graduate and undergraduate students in the fields. The protocol and scripts are easy to use and are well documented. The manuscript is well written and can be accepted for publications. Authors may want to revise the manuscript as some parts were highlighted (remove highlighting) prior to acceptance.

We thank the Reviewer for their favorable review. With apologies to the Reviewer, we did not remove the highlighting. This is because the editor has requested that we use highlighting to indicate the portion of the protocol that we would like to be filmed.

Reviewer #2:

Manuscript Summary:

The overall purpose of the manuscript, sampling solvent degrees of freedom in quantum chemical simulation of heterogeneous catalysis, is of broad interest. The authors present a computational protocol, combining QM and MM methods in different steps, to address this challenge.

We thank the Reviewer for their interest into our protocol.

Major Concerns:

1) The protocol is far from ideal. The manuscript explains how to perform a complex simulation on a computer in many small steps, while the purpose of computers is exactly the opposite: they should handle many tedious steps, so that human beings don't have to bother with them. Many of the small steps in the presented protocol can be carried out by an overarching driver script, such that the user of this protocol does not have to worry about getting all the little steps right. To quote Steve Jobs: "Computers

are bicycles for the mind". In this paper, the computer becomes a treadmill for the mind. Having control over all small steps is useful for research, but this does not imply that a large amount of tedious work is necessary. On the contrary, you want to free your mind of having to deal with all the tediousness, so there is some room to think about what really matters. Most of it can be replaced by a software implementation of the presented steps, which the authors should consider. With such a software implementation, I doubt there would be much left for publication or video presentation.

The reviewer is correct that we could have written a piece of software to carry out many of the steps in this protocol. We instead chose to write a protocol, which, as the reviewer also points out, allows flexibility that is useful for research. As we have written a protocol, we have submitted it for publication in the Journal of Visualized Experiments, which, according to its website (https://www.jove.com/about/) allows "educators and students to see the intricate details of cutting-edge experiments."

2) It is very difficult to make quantitative predictions with quantum chemical calculations of heterogeneous catalysis, also with the presented protocol. Can the authors reveal how well the example calculations compare to experiment? In addition, can they make error estimates, other than just sampling uncertainties (vide infra), in case no experimental data would be available?

This protocol describes how to obtain configurations of liquid molecules at the interface of a heterogeneous catalyst surface that can be used in quantum chemical calculations, so while skepticism of quantum chemical calculations is acknowledged, it pertains to an application of the protocol rather than to the protocol itself.

To answer the Reviewer's questions:

Can the authors reveal how well the example calculations compare to experiment?

We assume that the Reviewer is asking about the calculated interaction energies. To our knowledge, there is no experimental method available for measuring these values. It would be plausible to compare observations from kinetic experiments to those from microkinetic modeling. From a computational standpoint, this would require that the interaction energies of many catalytic species be calculated and that the results be input to a microkinetic model, an endeavor that could comprise a protocol in itself.

In addition, can they make error estimates, other than just sampling uncertainties (vide infra), in case no experimental data would be available?

Going back to the response above about comparing with experiment, Heyden's group has developed a method of Uncertainty Quantification that can be used to determine how uncertainty in quantum chemical values can propagate into results from microkinetic modeling (Walker, Ammal, Terejanu, Heyden, "Uncertainty Quantification Framework Applied to the Water-Gas Shift Reaction over Pt-Based Catalysts," Journal of Physical Chemistry C, 2016, 120, 10328-10339, DOI: 10.1021/acs.jpcc.6b01348.)

For the protocol written in this manuscript, we have added the following paragraph to the Discussion section: "Possible sources of uncertainty for this procedure include the force field employed, the sampling method, and the sampling frequency. The water structure is determined by the force field that is used, meaning that the choice of force field influences the specific configurations of H_2O molecules. Our group has assessed how the choices of force field for H_2O molecules and Pt atoms influence the interaction energies calculated in FFMD and found that the choice of force field contributes less than 0.1 eV to the interaction energy. Another source of uncertainty is the sampling method, which influences the specific configurations that are used to calculate a quantity of interest. Our group has compared the performance of the "time sampling" method presented in this protocol with an "energy sampling" method, which is biased to lower energy configurations of H_2O molecules, on the interaction energies calculated in DFT and found both of these sampling methods give statistically equal values.[35,50] The sampling frequency can also influence the results. We have assessed how increasing the number of configurations from 10 to 30,000 influences the average interaction energies calculated in FFMD for 40 different $C_3H_xO_3$ adsorbates and found that the sampling frequency contributes less than 0.1 eV to the average interaction energy.[48] The specific installation of any of the executables can also contribute to uncertainty in the calculated configurations and values. The influence on the calculated interaction energies is expected to be small (i.e., on the order of meV). This source of uncertainty can be minimized by properly equilibrating the H_2O configuration in FFMD."

3) The authors should elaborate more on potential sources of error. Currently missing is e.g. the limited accuracy of the force field, such that not the (most) relevant configurations are sampled in the molecular dynamics simulation. Could there be more sources of uncertainty?

We have included discussions of potential sources of error in the Discussion section (see our response to Reviewer #2's Major Concern 2 above).

4) The protocol is not described in sufficient detail to produce a calculation. The authors should improve the description of the input and options for each script and which output is produced. Even better would be to write the protocol in Python, instead of plain English.

The Editor also commented on this. To address this concern, we added the exact commands for executing the scripts in Steps 2.1.1, 2.1.2, 2.2.1, 2.2.2, 2.2.8, 3.1, 4.2, 5.2, 6.1.1, and 6.1.2 (see our responses to the Editor's comments above). We have also made the following edits:

Added the following text to Step 1.2: "This will produce a file called CONTCAR, which will be used in the next Step."

Edited Step 2.2.4: "Execute the following command in the Tk console to generate the LAMMPS data file: "topo writelammpsdata $WDPATH/data.myadsorbate full," where $WDPATH is the directory on the computer where VMD will write the LAMMPS data file and data.myadsorbate is the name of the LAMMPS data file."

5) The protocol description omits technical details on how the scripts written by the authors work, which may confuse the reader or user of the protocol. For example. take the script get_npt_lz.py in step 3. How does it determine which part of the NpT simulation comprises the production run? Usually, when computing such averages, the first N iterations of the MD trajectory are omitted because these are not representative for the equilibrium state. Does the script figure out which part is in equilibrium? Also, just to make this script more helpful, it would be good to let it also estimate the error on the average, e.g. using the block-averaging algorithm. This could be helpful to judge the convergence of the MD simulation.

We added notes to the following steps, which describe how the scripts that we supply with this protocol work:

Step 3.1: "The get_npt_lz.py script assumes that LAMMPS writes the length of the cell z-dimension (lz) to the log.myadsorbate file every 1000 fs (customizable at Line 10 of the get_npt_lz.py script), which is the default in the provided input.equil LAMMPS input *file. The get_npt_lz.py script detects and discards the first 2 ns (customizable at Line 9 of the get_npt_lz.py script) worth of lz values in of the the log.myadsorbate file, as they comprise the equilibration portion of the simulation, while the remaining 3 ns comprise the "production" portion and are thus used by the get_npt_lz.py script to compute the average z-dimension length. In addition to the avg_lz.txt file, this script outputs the npt_data.txt file, which includes the timestep and lz data from the NPT portion of the LAMMPS trajectory, and the npt_plot.png file, which is a timestep vs. lz plot from the same data. The plot can be used to verify equilibration of the LAMMPS simulation."*

Step 5.1: "Note: The hb_lifetime_dist.py script analyzes the H_2O *configurations in the production run and determines if any* H_2O *molecules are hydrogen bonded to the adsorbate. It then counts the simulation time that each hydrogen bond remains intact and reports this information as a distribution of hydrogen bond lifetimes in units of ps. The specific version of the script that is provided with this protocol assumes that LAMMPS writes the configuration of* H_2O *molecules to the dump.myadsorbate.lammpstrj file every 1000 fs, which is the default in the provided input.prod LAMMPS input file. It detects and discards the first 2 ns worth of configurations in the the dump.myadsorbate.lammpstrj file, as they comprise the equilibration portion of the simulation, and uses the remaining 3 ns to calculate hydrogen bond lifetimes. "*

Step 6.1.2: "Note: The lammps_frames.py script automatically detects the LAMMPS log file and dump file as well as the production portion of the trajectory within the dump file and divides the number of configurations within the dump file into 10 groups. Alternatively, the user can specify the log file, the dump file, and the number of configurations from the command-line interface using the -l, -d, and -n options, respectively. To do so, the user should type "lammps_frames.py -n XX -l $logfilename -d $dumpfilename" at the command-line interface, where XX is the desired number of configurations, $logfilename is the name of the LAMMPS logfile, and $dumpfilename is the name of the LAMMPS trajectory (dump) file. The simulation times that are output refer to the median times in each group."

Minor Concerns:

- The first two sentences of "long abstract" and "introduction" are identical. Lack of creativity?

We edited the text in the long abstract to read: "A large number of heterogeneously-catalyzed chemical processes occur under liquid conditions, but learning about how catalysts function under such conditions is challenging when it is necessary to include the solvent molecules. The bond breaking and forming processes modeled in these systems necessitate the use of quantum chemical methods."

- line 64: "arragement". Use a spelling checker to fix mistakes in the manuscript.

We corrected this typo.

- line 77: "In AIMD and FFMD ..." -> "In MD", the remainder of the sentence is valid, independent of how the forces are computed. QM/MM could also be used.

The sentence prior compares three methods: AIMD, FFMD, and QM. The sentence in question discusses two of those. We agree with the reviewer that since both methods include MD, we could generalize; however, we feel as if the text is clearer as written.

- line 86: Order of words in "significantly more computationally tractable"? E.g. "Computationally significantly more efficient"

We discussed the two ways of wording and feel that the original version is clearer.

- line 91: "Force fields used in FFMD employ Lennard-Jones + Coulomb (LJ+C) potentials, ..." This is formulated as a general statement for all force fields, but it mainly applies to the force field used in this work. In general, force fields can also use other functional forms for the van der Waals interactions.

We changed this sentence to read, "The force fields used in FFMD in this work employ…"

- line 110: "period simulation boxes" => "periodic simulation boxes"

We corrected this typo.

- line 132: "optimize its energy" => "minimize its energy"

We made this change.

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