Electronic Supporting Information

Neural Network Molecular Dynamics Simulations of Solid-Liquid Interfaces: Water at Low-Index Copper Surfaces

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## 1 Atom-Centered Symmetry Functions

There are two types of symmetry functions used in the description of the atomic environments, namely, radial ($G^{rad}$) and angular ($G^{ang}$) symmetry functions [1]. They are of form

$$G_i^{rad} = \sum_j e^{-\eta(R_{ij}-R_s)^2} \cdot f_c(R_{ij}) \tag{1}$$

and

$$G_i^{ang} = 2^{1-\zeta} \sum_{j,k\neq i}^{all} (1+\lambda\cos\theta_{ijk})^{\zeta}\ e^{-\eta(R_{ij}^2+R_{jk}^2+R_{ki}^2)}\ f_c(R_{ij})\ f_c(R_{ik})\ f_c(R_{jk}), \tag{2}$$

where

$$f_c(R_{ij}) = \begin{cases} 0.5\left(\cos\frac{\pi R_{ij}}{R_c}+1\right) & \text{for } R_{ij} \leq R_c \\ 0 & \text{otherwise.} \end{cases} \tag{3}$$

$G_i^{rad}$ is the radial symmetry function for atom $i$, which is a sum of Gaussian functions, one for each neighbour $j$, multiplied by a cutoff function $f_c(R_{ij})$. The cutoff function $f_c(R_{ij})$ tells the neural network to stop considering an atom $j$, which is beyond the cutoff radius ($R_c$) from atom $i$. The parameter $\eta$ controls the width of the Gaussians and $R_s$ shifts the Gaussians along the radial direction. $G_i^{ang}$ is the angular symmetry function for atom $i$ which includes sums of angular information between any two atom neighbours $j$ and $k$ and Gaussians for describing the radial part along with respective cutoff functions. $\lambda$ shifts the angular part of the function by 180 $^\circ$ and $\zeta$ controls the width of the angular part.

**Table 1** Parameters of all symmetry functions for hydrogen atom used in fitting the potential. The radial and angular symmetry functions are given by type 2 and 3, respectively.

| Type | Element 2 | Element 3 | $\eta$ [bohr$^{-2}$] | $R_s$ [bohr] | $\lambda$ | $\zeta$ | $R_c$ [bohr] |
|---|---|---|---|---|---|---|---|
| 2 | H/O/Cu | | 0.001 | 0.0 | | | 12 |
| 2 | H/O/Cu | | 0.010 | 0.0 | | | 12 |
| 2 | H/O/Cu | | 0.030 | 0.0 | | | 12 |
| 2 | H/O/Cu | | 0.060 | 0.0 | | | 12 |
| 2 | O/Cu | | 0.150 | 0.9 | | | 12 |
| 2 | H | | 0.150 | 1.9 | | | 12 |
| 2 | O/Cu | | 0.300 | 0.9 | | | 12 |
| 2 | H | | 0.300 | 1.9 | | | 12 |
| 2 | O/Cu | | 0.600 | 0.9 | | | 12 |
| 2 | H | | 0.600 | 1.9 | | | 12 |
| 2 | O/Cu | | 1.500 | 0.9 | | | 12 |
| 2 | H | | 1.500 | 1.9 | | | 12 |
| 3 | O | Cu | 0.001 | | -1.0 | 1 | 12 |
| 3 | H/O/Cu | Cu | 0.001 | | 1.0 | 1 | 12 |
| 3 | H/O/Cu | Cu | 0.001 | | 1.0 | 2 | 12 |
| 3 | O | O | 0.001 | | -1.0 | 4 | 12 |
| 3 | O | O | 0.001 | | 1.0 | 4 | 12 |
| 3 | O | Cu | 0.003 | | -1.0 | 1 | 12 |
| 3 | H/O/Cu | Cu | 0.003 | | 1.0 | 1 | 12 |
| 3 | Cu | Cu | 0.003 | | 1.0 | 2 | 12 |
| 3 | O | Cu | 0.007 | | -1.0 | 1 | 12 |
| 3 | H | Cu | 0.007 | | 1.0 | 1 | 12 |
| 3 | H | Cu | 0.010 | | 1.0 | 1 | 12 |
| 3 | H | O | 0.010 | | -1.0 | 4 | 12 |
| 3 | H | O | 0.010 | | 1.0 | 4 | 12 |
| 3 | H | Cu | 0.015 | | 1.0 | 1 | 12 |
| 3 | H/O | O | 0.030 | | -1.0 | 1 | 12 |
| 3 | H/O | O | 0.030 | | 1.0 | 1 | 12 |
| 3 | H | O | 0.070 | | -1.0 | 1 | 12 |
| 3 | H | O | 0.070 | | 1.0 | 1 | 12 |
| 3 | H | O | 0.200 | | 1.0 | 1 | 12 |

**Table 2** Parameters of all symmetry functions for oxygen atom used in fitting the potential. The radial and angular symmetry functions are given by type 2 and 3, respectively.

| Type | Element 2 | Element 3 | $\eta$ [bohr$^{-2}$] | $R_s$ [bohr] | $\lambda$ | $\zeta$ | $R_c$ [bohr] |
|---|---|---|---|---|---|---|---|
| 2 | H/O/Cu | | 0.001 | 0.0 | | | 12 |
| 2 | H/O/Cu | | 0.010 | 0.0 | | 12 | |
| 2 | H/O/Cu | | 0.030 | 0.0 | | | 12 |
| 2 | H/O/Cu | | 0.060 | 0.0 | | | 12 |
| 2 | H/Cu | | 0.150 | 0.9 | | | 12 |
| 2 | O | | 0.150 | 4.0 | | | 12 |
| 2 | H/Cu | | 0.300 | 0.9 | | | 12 |
| 2 | O | | 0.300 | 4.0 | | | 12 |
| 2 | H/Cu | | 0.600 | 0.9 | | | 12 |
| 2 | O | | 0.600 | 4.0 | | | 12 |
| 2 | H | | 1.500 | 0.9 | | | 12 |
| 2 | O | | 1.500 | 4.0 | | | 12 |
| 3 | O | Cu | 0.001 | | -1.0 | 1 | 12 |
| 3 | H/O/Cu | Cu | 0.001 | | 1.0 | 1 | 12 |
| 3 | H/O/Cu | Cu | 0.001 | | 1.0 | 2 | 12 |
| 3 | H/O | O | 0.001 | | -1.0 | 4 | 12 |
| 3 | H/O/Cu | O | 0.001 | | 1.0 | 4 | 12 |
| 3 | H/O/Cu | Cu | 0.003 | | 1.0 | 1 | 12 |
| 3 | Cu | Cu | 0.003 | | 1.0 | 2 | 12 |
| 3 | H/Cu | Cu | 0.007 | | 1.0 | 1 | 12 |
| 3 | H | Cu | 0.010 | | 1.0 | 1 | 12 |
| 3 | H | H | 0.010 | | -1.0 | 4 | 12 |
| 3 | H | H | 0.010 | | 1.0 | 4 | 12 |
| 3 | H | Cu | 0.015 | | 1.0 | 1 | 12 |
| 3 | H | H | 0.030 | | -1.0 | 1 | 12 |
| 3 | H/O | O | 0.030 | | -1.0 | 1 | 12 |
| 3 | H | H | 0.030 | | 1.0 | 1 | 12 |
| 3 | H/O | O | 0.030 | | 1.0 | 1 | 12 |
| 3 | H | H | 0.070 | | -1.0 | 1 | 12 |
| 3 | H | H | 0.070 | | 1.0 | 1 | 12 |

**Table 3** Parameters of all symmetry functions for copper atom used in fitting the potential. The radial and angular symmetry functions are given by type 2 and 3, respectively.

| Type | Element 2 | Element 3 | $\eta$ [bohr$^{-2}$] | $R_s$ [bohr] | $\lambda$ | $\zeta$ | $R_c$ [bohr] |
|---|---|---|---|---|---|---|---|
| 2 | H/O | | 0.001 | 0.0 | | | 12 |
| 2 | H/O/Cu | | 0.010 | 0.0 | | | 12 |
| 2 | H/O/Cu | | 0.030 | 0.0 | | | 12 |
| 2 | H/O/Cu | | 0.060 | 0.0 | | | 12 |
| 2 | Cu | | 0.100 | 0.0 | | | 12 |
| 2 | H/O | | 0.150 | 0.9 | | | 12 |
| 2 | Cu | | 0.200 | 0.0 | | | 12 |
| 2 | Cu | | 0.200 | 1.0 | | | 12 |
| 2 | H/O | | 0.300 | 0.9 | | | 12 |
| 2 | H/O | | 0.600 | 0.9 | | | 12 |
| 2 | H | | 1.500 | 0.9 | | | 12 |
| 3 | H | H | 0.001 | | -1.0 | 1 | 12 |
| 3 | O | O | 0.001 | | -1.0 | 1 | 12 |
| 3 | H | H/O/Cu | 0.001 | | 1.0 | 1 | 12 |
| 3 | O | O | 0.001 | | 1.0 | 1 | 12 |
| 3 | O/Cu | Cu | 0.001 | | 1.0 | 1 | 12 |
| 3 | H | O/Cu | 0.001 | | 1.0 | 2 | 12 |
| 3 | O | O/Cu | 0.001 | | 1.0 | 2 | 12 |
| 3 | Cu | Cu | 0.001 | | 1.0 | 2 | 12 |
| 3 | H | O/Cu | 0.003 | | -1.0 | 1 | 12 |
| 3 | O/Cu | Cu | 0.003 | | -1.0 | 1 | 12 |
| 3 | H | H/O/Cu | 0.003 | | 1.0 | 1 | 12 |
| 3 | O | O/Cu | 0.003 | | 1.0 | 1 | 12 |
| 3 | Cu | Cu | 0.003 | | 1.0 | 1 | 12 |
| 3 | H | O | 0.003 | | -1.0 | 2 | 12 |
| 3 | Cu | Cu | 0.003 | | -1.0 | 2 | 12 |
| 3 | H | H/O | 0.003 | | 1.0 | 2 | 12 |
| 3 | Cu | Cu | 0.003 | | 1.0 | 2 | 12 |
| 3 | H | H/O | 0.007 | | 1.0 | 1 | 12 |
| 3 | Cu | Cu | 0.007 | | 1.0 | 1 | 12 |
| 3 | H | H | 0.010 | | 1.0 | 1 | 12 |

## 2 Composition of the Reference Set

**Table 4** A summary of bulk water and ice geometries present in the reference data set.

| Type | $N$(H) | $N$(O) | Structures | | K-points |
|---|---|---|---|---|---|
| | | | Training | Test | |
| Ice | 20 | 10 | 207 | 23 | 6×6×6 |
| Ice/bulk | 32 | 16 | 2799 | 313 | 4×4×4 |
| Bulk | 64 | 32 | 814 | 86 | 2×2×2 |
| Bulk | 128 | 64 | 1114 | 153 | 1×1×1 |
| Bulk | 256 | 128 | 1748 | 191 | 1×1×1 |

**Table 5** A summary of bulk copper geometries present in the reference data set.

| Size | K-points | $N$(Cu) | Structures | |
|---|---|---|---|---|
| | | | Training | Test |
| 1×1×1 | 12×12×12 | 4 | 297 | 29 |
| 1×1×2 | 12×12×6 | 8 | 21 | 3 |
| 1×1×3 | 12×12×4 | 12 | 22 | 2 |
| 1×2×2 | 12×6×6 | 16 | 19 | 5 |
| 1×2×3 | 12×6×4 | 24 | 23 | 1 |
| 2×2×2 | 6×6×6 | 32 | 24 | |
| 1×3×3 | 12×4×4 | 36 | 22 | 2 |
| 3×2×2 | 4×6×6 | 48 | 21 | 3 |
| 2×3×3 | 6×4×4 | 72 | 23 | 1 |
| 3×3×3 | 4×4×4 | 108 | 17 | 1 |

**Table 6** A summary of bulk cuprous oxide geometries present in the reference data set.

| Size | K-points | $N$(O) | N(Cu) | Structures | |
|---|---|---|---|---|---|
| | | | | Training | Test |
| 1×1×1 | 12×12×12 | 2 | 4 | 187 | 21 |
| 1×1×2 | 12×12×6 | 4 | 8 | 6 | |
| 1×1×3 | 12×12×4 | 6 | 12 | 5 | 1 |
| 1×2×2 | 12×6×6 | 8 | 16 | 6 | |
| 1×2×3 | 12×6×4 | 12 | 24 | 4 | 2 |
| 2×2×2 | 6×6×6 | 16 | 32 | 5 | 1 |
| 1×3×3 | 12×4×4 | 18 | 36 | 4 | 2 |
| 3×2×2 | 4×6×6 | 24 | 48 | 6 | |

**Table 7** A summary of copper-water interfacial geometries present in the reference data set.

| $N$(H) | $N$(O) | $N$(Cu) | Structures | | Description |
|---|---|---|---|---|---|
| | | | Training | Test | |
| 32 | 16 | 40 | 79 | 6 | 5 layered (4×2) Cu(100) |
| 42 | 21 | 42 | 176 | 19 | 7 layered (3×2) Cu(110) |
| 44 | 22 | 42 | 62 | 5 | 7 layered (3×2) Cu(110) |
| 44 | 22 | 90 | 18 | 3 | 7 layered (4×4) Cu(111) with missing rows (24 atoms) |
| 46 | 23 | 45 | 91 | 9 | 5 layered (3×3) Cu(111) saw-toothed |
| 46 | 23 | 60 | 38 | 2 | 5 layered (3×4) Cu(111) surface |
| 50 | 31 | 89 | 63 | 5 | Cu2O adlayer I on 5 layered (4×4) Cu(111) |
| 52 | 32 | 89 | 20 | 3 | Cu2O adlayer II on 5 layered (4×4) Cu(111) |
| 54 | 27 | 40 | 54 | 10 | 5 layered (2×4) Cu(100) |
| 54 | 27 | 90 | 8 | 3 | 6 layered (4×4) Cu(111) with 6 surface vacancies |
| 54 | 33 | 89 | 24 | 3 | Cu2O adlayer III on 5 layered (4×4) Cu(111) |
| 56 | 34 | 89 | 41 | 5 | Cu2O adlayer IV on 5 layered (4×4) Cu(111) |
| 66 | 33 | 42 | 65 | 7 | 7 layered (3×2) Cu(110) |
| 66 | 38 | 64 | 7 | | 5 Oxygen adatoms on 4 layered (4×4) Cu(111) |
| 68 | 34 | 76 | 22 | | 5 layered (3×5) Cu(111) with missing rows |
| 70 | 35 | 78 | 270 | 30 | 5 layered Cu(110) with missing rows |
| 70 | 36 | 64 | 6 | 2 | 1 Oxygen adatom on 4 layered (4×4) Cu(111) |
| 74 | 37 | 60 | 333 | 28 | 5 layered (3×4) Cu(111) surface |
| 74 | 37 | 61 | 43 | 8 | 5 layered (3×4) Cu(111) surface + 1 ad atoms |
| 74 | 37 | 64 | 260 | 28 | 5 layered (3×4) Cu(111) surface + 4 ad atoms |
| 134 | 67 | 140 | 14 | 1 | 4 layered (5×2) step on 4 layered (5×5) Cu(110) base |
| 144 | 72 | 99 | 73 | 8 | 3 layered (3×3) step on 2 layered (6×6) Cu(111) base |
| 158 | 79 | 88 | 21 | 6 | Flat copper cluster with 88 atoms in water |
| 188 | 94 | 181 | 19 | 1 | 5 layered (6×6) Cu(111) with an adatom |
| 194 | 97 | 43 | 57 | 3 | copper nano particle in water |

## 3 Probability Distribution of Atoms

The probability distribution along $Z$ direction shown in Fig. 3 (a) and (b), Fig. 10, Fig. 12, Fig. 13 and Fig. 14 are computed according to

$$\rho(Z_{ab}) = \frac{1}{\rho_{bulk}\, N} \sum_{i=1}^{N} \sum_{j=1}^{n} f(Z_{ij}, Z_a, Z_b)$$

$$f(Z_{ij}, Z_a, Z_b) = \begin{cases} 1, & \text{if } Z_{ij} \geq Z_b \;\&\; Z_{ij} < Z_a \\ 0, & \text{otherwise} \end{cases},$$

where, $\rho(Z_{ab})$ is the probability density of finding an atom between $Z_a$ and $Z_b$, $\rho_{bulk}$ is the corresponding density in pure bulk water simulation, $N$ is the number of trajectory frames used, $n$ is the number of respective atom whose distribution is being computed, $f(Zij;Z_a;Z_b)$ is a binary function which gives 1 if an atom of the specified type is present between $Z_a$ and $Z_b$, else 0. For computing these distributions, $Z$ lattice dimension between 0 Å and 60 Å is split into 1000 small units. From every 1 ns NVT trajectory, 10,000 frames are extracted with a time spacing of 100 fs and used for this computation.

## 4 Radial Distribution Function

The oxygen-oxygen radial distribution functions in the bulk region of the simulation cell plotted in Fig.5 and Fig. 6 are computed as

$$g_{OO}(r) = \frac{n(r)}{4\,\pi\, r^2\, \Delta r},$$

where, $g_{OO}(r)$ is the radial distribution function, $n(r)$ is the average count of oxygen atoms in a spherical shell of width $\Delta r$ at a distance $r$ from the reference oxygen atom given by

$$n(r) = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{\rho} \sum_{j=1}^{n} f(Z_{ij}, Z_a, Z_b) \sum_{k \neq j}^{n} f(R_{jk}, r).$$

In the above equation, $N$ is the number of frames used, $\rho$ is the number of oxygen atom per unit volume in the selected bulk region, $n$ is the total number of oxygen atoms in a frame of the trajectory. $f(Z_{ij}, Z_a, Z_b)$ allows for computing RDF only for the oxygen atoms ($j$) within $Z_a$ and $Z_b$ (selected bulk region) of the simulation cell (defined as in previous section), $R_{jk}$ is the distance of the oxygen atom $k$ from the reference oxygen atom $j$. $f(R_{jk}, r)$ is a binary function that gives a 1 if $R_{jk}$ is within $r$ and $r + \Delta r$ and 0 otherwise.

The maximum value of $r$ is chosen as 10.0 Å in these calculations and it is split into 250 equidistant bins for numerical counting.

## 5 Choice of Cu(111) Cell for Comparison Study

We use the matrix representation of Park and Madden[2] where the supercell vectors are written as linear combinations of the non-orthogonal primitive vectors. If $\mathbf{x}_s$ , $\mathbf{y}_s$ and $\mathbf{x}_p$ , $\mathbf{y}_p$ are the translation vectors of supercell and the primitive cell, respectively then

$$\mathbf{x}_s = a\,\mathbf{x}_p + b\,\mathbf{y}_p \tag{4}$$

$$\mathbf{y}_s = c\,\mathbf{x}_p + d\,\mathbf{y}_p \tag{5}$$

are the translation vectors of the supercell. The supercell can then be represented in a matrix notation

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix}.$$

It can be further simplified as (a,b)×(c,d).

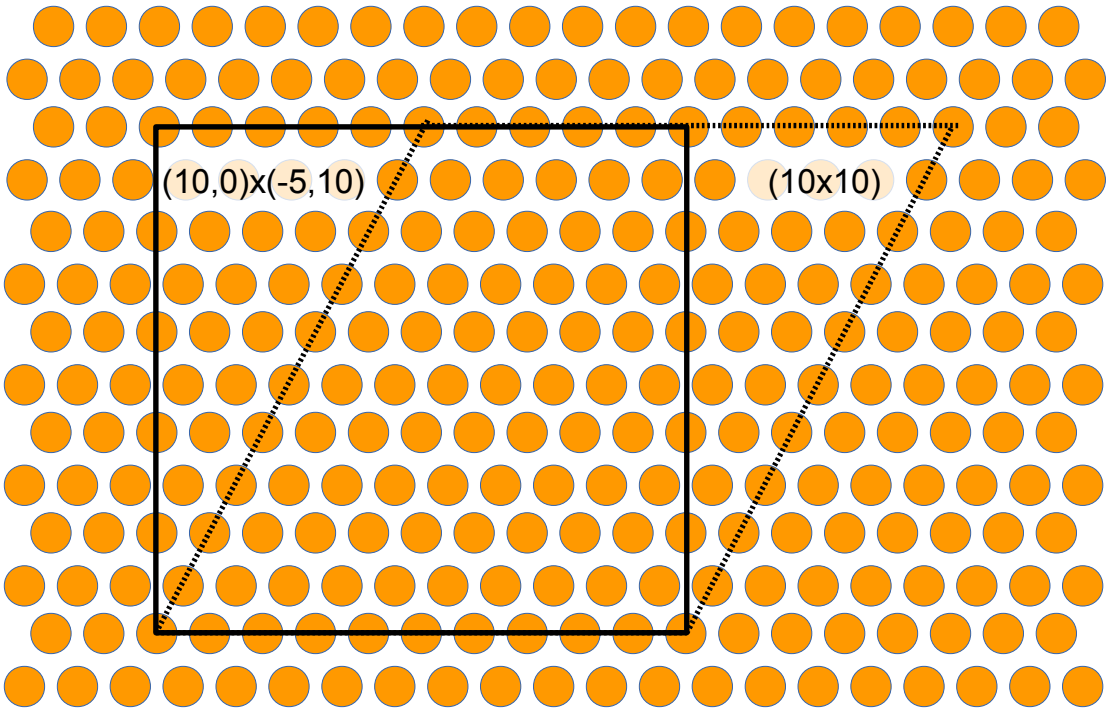


**Figure 1** The supercell representing Cu(111) surface in the comparison studies (i.e. the (10,10)×(-5,10) supercell) is given by the solid lines, whereas the surface cell symmetry, (10×10) is given by dotted lines.

## References

[1] J. Behler, *J. Chem. Phys.*, 2011, **134**, 074106.

[2] R. L. Park and H. H. Madden, *Surf. Sci.*, 1968, **11**, 188.