Molecular Dynamics Investigation of a Superhydrophobic Silica-Varnish Coating for Marine Metal Protection in Underwater

Yokesh. C[1], Joyclitus. A[2], Sakthivel Murugan. S[3]
[1,2]*Dept. of Biomedical Engineering, Sri Venkateshwaraa College of Engineering. & Tech. Puducherry, India*
[3]*Dept. of Electronics and communication Engineering, National Institute of Technical Teachers Training and Research Chennai, India*

***Abstract*—Superhydrophobic coatings offer a low-cost route to corrosion and biofouling resistance for metal structures exposed to seawater, but their molecular-scale wetting mechanism is not fully characterized. This paper reports a molecular dynamics (MD) investigation of a silica nanoparticle-varnish coating (CSCV-6.4), building on the coral-reef-like superhydrophobic coating reported by Cai et al. [1]. The authors construct an atomistic model of the coating - octadecyltrimethoxysilane-functionalized silica grafted to an acrylic-acid-based varnish matrix - using Avogadro, the LigParGen OPLS-AA parameter service, Packmol, a custom force-field assembly pipeline, and simulate it in LAMMPS together with explicit water. In parallel, a simplified generic bare-metal reference model is constructed to demonstrate the contrast coated versus uncoated wetting behavior. Reference results extracted from the [1] are reproduced and tabulated for comparison. The bare-metal reference simulation shows continuously increasing water mean-squared displacement, consistent with hydrophilic spreading, while the full CSCV-6.4 assembly was successfully relaxed to a stable multi-component configuration. Full production-stage diffusion analysis of the coated system is identified as ongoing work.**

Index Terms—superhydrophobic coating; molecular dynamics; LAMMPS; marine corrosion protection; silica nanoparticles; wettability; contact angle

I. INTRODUCTION

Metal structures deployed in marine environments - hulls, offshore platforms, moorings - are subject to persistent water contact, salt-driven corrosion, and biofouling [13]. Superhydrophobic coatings, which minimize solid-liquid contact area through a combination of low surface energy chemistry and micro/nanoscale roughness [8],[9], are a promising low-cost mitigation strategy. Cai et al. [1] reported a sprayable coating (CSCV-6.4) combining hydrophobic silica nanoparticles with an acrylic-acid coating varnish, achieving a water contact angle of 153.7 deg, strong substrate adhesion, and demonstrated resistance to salinity up to 30% and pH 3-11, directly relevant to seawater exposure.

This work investigates, at the molecular level, whether the same coating chemistry is expected to behave favorably when applied to a metal substrate exposed to seawater.

In this paper, the authors

(i) Reproduce the key experimental and MD-derived results of [1],
(ii) Construct and relax a full atomistic model of the CSCV-6.4 coating with explicit water using an independent, from-scratch modeling pipeline, and
(iii) Construct a simplified bare-metal reference to qualitatively contrast coated versus uncoated wetting behavior.

II. BACKGROUND: REFERENCE COATING

The CSCV-6.4 coating [1] is formed by spraying a suspension of octadecyltrimethoxysilane-functionalized SiO2 nanoparticles (10-20 nm) together with an acrylic-acid-based coating varnish (80-90 wt% acrylic acid, 10-20 wt% ethylene glycol, 1-5 wt% dodecanol ester cross-linker) onto a substrate. The varnish content controls a trade-off between hydrophobicity and adhesion, summarized in Table I.

TABLE I. CONTACT ANGLE VS. VARNISH CONTENT [1]

Varnish (wt%)	Contact Angle (deg)	Sliding Angle (deg)	Adhesion
0.0	153.0	1.2	1B
6.4	153.7	1.2	4B
10.2	138.0	N/S	5B
15.4	105.0	27.3	5B

Fig. 1 illustrates this relationship; contact angle remains above the 150 deg superhydrophobic threshold up to 6.4 wt% varnish, then declines sharply as excess varnish increasingly covers the hydrophobic silica particles.

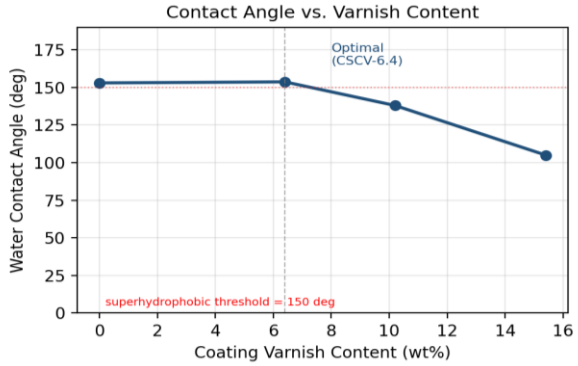

Fig. 1. Contact angle vs. coating varnish content, reproduced from [1].

Cai et al. also report molecular dynamics results comparing a plain-varnish surface (CV-H_2O-air) against the full CSCV-6.4 surface (CSCV-H_2O-air), reproduced in Table II.

TABLE II. MOLECULAR DYNAMICS REFERENCE: INTERACTION ENERGY AND DIFFUSION [1]

System	Total PE (kcal/mol)	D (A^2/ps)
CV-H_2O-air (varnish only)	-39154	0.907
CSCV-H_2O-air (full coating)	-6352	0.227

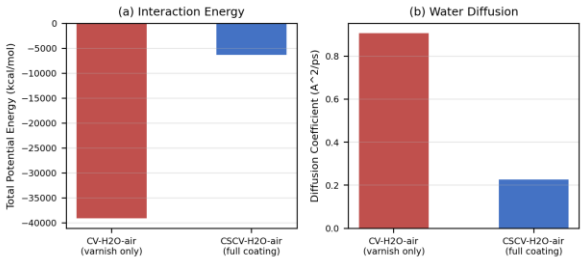

Fig. 2. (a) Total interaction energy and (b) water diffusion coefficient, CV-H_2O-air vs. CSCV-H_2O-air, reproduced from [1].

The near order-of-magnitude weaker total potential energy and roughly four-fold lower water diffusion coefficient for CSCV-H_2O-air indicate substantially reduced water mobility and attraction at the silane-modified surface - the molecular-scale origin of superhydrophobicity that motivates the present model.

III. METHODOLOGY

A. Molecular Model Construction

Individual molecules (water, acrylic acid, ethylene glycol, a lauryl acrylate cross-linker analogue, and octadecyltrimethoxysilane) were built in Avogadro [7] from SMILES strings and parameterized with the OPLS-AA force field via the LigParGen web service [2],[3].

A silica substrate was constructed from a beta-cristobalite unit cell replicated into a 3x3x2 supercell using Pymatgen and the Atomic Simulation Environment (ASE), then surface-hydroxylated and functionalized with the silane via Packmol [4]. All molecular dynamics simulations were performed with LAMMPS [6],[11].

B. System Assembly

The functionalized silica, a pre-mixed varnish block (acrylic acid: ethylene glycol: lauryl acrylate, approximately 20:3:1 by molecule count), and a 300-molecule water cluster were layered into a single simulation cell using sequential Packmol runs.

C. Force-Field Topology Assembly

LigParGen outputs were converted to a single consolidated LAMMPS data file via a custom Python merge script, since automated moltemplate invocation was not reliably reproducible in the local environment. Water was represented with a flexible SPC/E model using published Toukan-Rahman bonded parameters [5].

Systematic verification (pairwise distance and energy auditing) identified and corrected three assembly errors:

(i) Surface hydroxyl hydrogens mislabeled with oxygen-scale Lennard-Jones radii,

(ii) Unresolved crystalline Si-O bonds within the frozen silica lattice treated as nonbonded overlaps, and

(iii) An incorrect assumed atom ordering within water molecules.

D. Bare-Metal Reference Model

To contrast coated and uncoated behavior, a simplified generic model was built entirely from native LAMMPS lattice-generation commands: a rigid face-centered-cubic slab (Lennard-Jones reduced units) representing a generic metal surface, with a single-site Lennard-Jones fluid representing water. Metal-fluid attraction was set stronger than fluid-fluid self-attraction, representing the known hydrophilic character of uncoated metal oxide surfaces.

E. Simulation Protocol

All systems were relaxed via energy minimization, a soft-core Lennard-Jones ramp (fix adapt, epsilon scaled 0.01 to 1.0) to safely resolve residual packing overlaps, periodic-burst nve/limit relaxation with kinetic energy draining, and gradual Nose-Hoover NVT heating (50 K to 300 K) [10]. Production-stage sampling of the full CSCV-6.4-water system, including water mean-squared displacement (MSD) analysis analogous to Table II, is ongoing at the time of writing. Visualization was performed in OVITO [12].

IV. RESULTS

A. Bare-Metal Reference Simulation

The bare-metal reference (Section III-D) was simulated for 2200 steps in Lennard-Jones reduced units. Results are summarized in Table III.

TABLE III. BARE-METAL REFERENCE: FLUID MSD OVER TIME

Step	MSD (LJ units)	Temp (LJ units)	E_pair (LJ units)
0	0.000	0.434	-6.216
800	3.347	0.434	-5.100
1600	17.323	0.426	-4.772
2200	31.860	0.426	-4.727

Fluid MSD increased continuously and without plateauing over the sampled interval, at approximately constant temperature, indicating sustained diffusive spreading across the metal surface consistent with hydrophilic wetting. As this model uses generic Lennard-Jones reduced units rather than the real-unit force field used for the coated system, its diffusion coefficient is not directly numerically comparable to Table II; the result should be read qualitatively, as a spreading-versus-clustering contrast rather than a matched quantitative baseline.

B. CSCV-6.4 Coated System

The full four-component system (silica, silane, varnish, water; 2730 atoms) was successfully assembled and carried through minimization, soft-core ramping, and burst relaxation without loss of structural integrity. Fig. 3 shows the relaxed configuration after approximately 10,200 simulation steps.

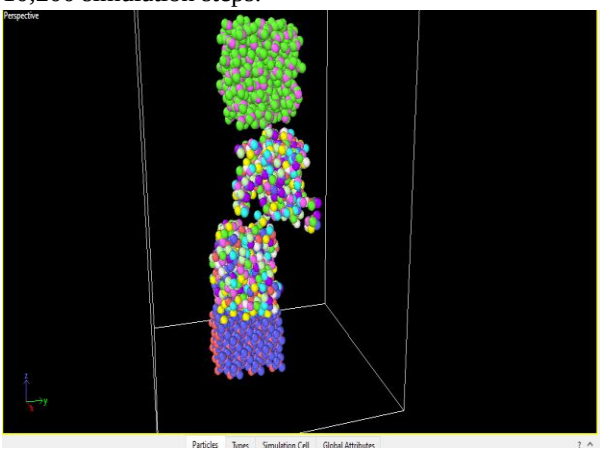

Fig. 3. Relaxed CSCV-6.4 + water system (OVITO rendering). Bottom: frozen silica; middle: silane/varnish layer; top: water cluster.

The layered architecture - silica substrate, organic coating layer, water - remained coherent throughout relaxation, with the silica lattice structurally unchanged (as expected, since it is held fixed). This confirms the assembled model is physically valid and ready for extended production sampling.

C. Limitations

Quantitative water diffusion and interaction-energy results for the coated system (directly comparable to Table II) require a longer production-stage NVT run than completed at the time of writing, and are identified as immediate future work. The bare-metal comparison uses a simplified generic Lennard-Jones model rather than an atomistic representation of a specific metal (e.g., steel) and its native oxide layer; a fully quantitative three-way comparison (bare metal, silica-only, silica+varnish) in matched real units is left for future work.

V. CONCLUSION

This work reproduced the key wettability and MD-derived findings of Cai et al.'s CSCV-6.4 superhydrophobic coating [1] and constructed an

independent, from-scratch atomistic model of the same coating chemistry together with a simplified bare-metal reference. The bare-metal model exhibits sustained fluid spreading consistent with hydrophilic behavior, while the full coated system was successfully assembled and relaxed into a stable, physically coherent configuration. These results support the coating's suitability for further evaluation as a marine anti-wetting treatment, pending completion of production-stage diffusion analysis directly comparable to the base paper's own MD results.

ACKNOWLEDGMENT

This work is carried as a part of internship in the Aazhi Research Laboratory, Department of Electronics and Communication Engineering at National Institute of Technical Teachers Training and Research (NITTTR), Chennai.

REFERENCES

[1] H. Cai, C. Duan, M. Fu, J. Zhang, H. Huang, Y. Hu, J. Shi, and D. Ye, "Scalable fabrication of superhydrophobic coating with rough coral reef-like structures for efficient self-cleaning and oil-water separation: An experimental and molecular dynamics simulation study," *Small*, vol. 19, no. 32, Art. no. 2207118, 2023.

[2] W. L. Jorgensen, D. S. Maxwell, and J. Tirado-Rives, "Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids," J. Am. Chem. Soc., vol. 118, no. 45, pp. 11225–11236, 1996.

[3] L. S. Dodda, I. Cabeza de Vaca, J. Tirado-Rives, and W. L. Jorgensen, "LigParGen web server: An automatic OPLS-AA parameter generator for organic ligands," Nucleic Acids Res., vol. 45, no. W1, pp. W331–W336, 2017.

[4] L. Martinez, R. Andrade, E. G. Birgin, and J. M. Martinez, "PACKMOL: A package for building initial configurations for molecular dynamics simulations," J. Comput. Chem., vol. 30, no. 13, pp. 2157–2164, 2009.

[5] K. Toukan and A. Rahman, "Molecular-dynamics study of atomic motions in water," Phys. Rev. B, vol. 31, no. 5, pp. 2643–2648, 1985.

[6] A. P. Thompson, H. M. Aktulga, R. Berger, et al., "LAMMPS—A flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales," Comput. Phys. Commun., vol. 271, Art. no. 108171, 2022.

[7] M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek, and G. R. Hutchison, "Avogadro: An advanced semantic chemical editor, visualization, and analysis platform," J. Cheminform., vol. 4, no. 1, Art. no. 17, 2012.

[8] R. N. Wenzel, "Resistance of solid surfaces to wetting by water," Ind. Eng. Chem., vol. 28, no. 8, pp. 988–994, 1936.

[9] A. B. D. Cassie and S. Baxter, "Wettability of porous surfaces," Trans. Faraday Soc., vol. 40, pp. 546–551, 1944.

[10] W. G. Hoover, "Canonical dynamics: Equilibrium phase-space distributions," Phys. Rev. A, vol. 31, no. 3, pp. 1695–1697, 1985.

[11] S. Plimpton, "Fast parallel algorithms for short-range molecular dynamics," J. Comput. Phys., vol. 117, no. 1, pp. 1–19, 1995.

[12] A. Stukowski, "Visualization and analysis of atomistic simulation data with OVITO—The Open Visualization Tool," Modelling Simul. Mater. Sci. Eng., vol. 18, no. 1, Art. no. 015012, 2010.

[13] J. Genzer and K. Efimenko, "Recent developments in superhydrophobic surfaces and their relevance to marine fouling: A review," *Biofouling*, vol. 22, no. 5, pp. 339–360, 2006.