Temperature Effects of Water-Metallic Interface Energies and Their Influence on Contact Angle Test for Surface Cleanliness: A Combined Experimental and Molecular Simulation Study

Yilan Jiang

China Academy of Engineering Physics

Longfei Niu

China Academy of Engineering Physics

Guorui Zhou

China Academy of Engineering Physics

Haibin Lv

China Academy of Engineering Physics

Xinxiang Miao

China Academy of Engineering Physics

Caizhen Yao

China Academy of Engineering Physics

Wen Qian (✉ davidqian1943@gmail.com)

China Academy of Engineering Physics <https://orcid.org/0000-0002-4260-4625>

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Abstract

To ensure the effectiveness of the high-power-laser facilities, the cleanliness of metal parts is of significance. In this paper, molecular modelings combined with contact angle tests were performed, in order to investigate the temperature effects of water-metallic interface energies and their influence on the tests for surface cleanliness. As results, the attractive forces were found between water and metallic surfaces, in which van der Waals forces contribute most, and the energies raised with elevated temperatures from 291 K to 303 K; meanwhile, the contact angle tests show both the Al and Fe components are hydrophilic, and the contact angle reduced with elevated temperatures; furthermore, correlations can be found between the energy change and the contact angle at varying temperatures. These conclusions are helpful in the accurate testing of surface cleanliness for optical scientific facilities.

Introduction

Surface cleanliness is a major challenge for optic scientific facilities, including high-power-laser facility which contains both expensive optics and large proportion of metal parts. In the laser devices, the metal parts often take more than 80 % of the whole device, and may directly contact with the optics, reducing the damage threshold of the optics if there is any contaminant on the surface. Thus the surface cleanliness of these metal parts is of great importance for the function and service-life of the whole facility [1].

The commonly-used metal parts in high-power-laser devices are made of the stainless steel 304 or aluminum alloy 6061, with main elements Fe or Al. The contact angle tests are used to determine the surface cleanliness of these metals [2, 3]. The surface cleanliness is related to the wetness degree of water on the surfaces, and the angle between the tangent line of gas-liquid interface and solid-liquid boundary, namely the contact angle, can determine the wetness [4–7]. For example, if the contact angle is less than 90° , the materials are hydrophilic and expected to be clean; otherwise they are hydrophobic materials which may be polluted by oil and other impurities [8]. The interface interactions are believed to cause the differences [9], which can be easily changed with thermodynamic temperatures. As results, temperature effects should be considered in order to investigate the interface interactions, as well as to obtain precise cleanliness test results [10].

In recent years, theoretical methods including molecular modelings show great ability in the investigation of solid-liquid interfaces, such as water-metallic interfaces, and the stable interface structures, as well as interface energies have been well represented using density functional theory [11] or molecular dynamics [12–15]. In this paper, a combined strategy of molecular modeling and surface experiment was carried out to find the temperature effects of water-metallic interface energies and their influence on the cleanliness tests. The results are helpful for ensuring the effectiveness and accuracy of the metal parts in high-power-laser facilities.

Methodology

Molecular simulations

In order to investigate the interface interaction energies for water on the metals at the temperatures 291–303 K, water-metallic interface models were constructed as shown in Fig. 4. The amorphous cells (AC) of water (H_2O) were established with a density of 1.0 g/cm^3 , where the short lines between H and O atoms represent the chemical bonds in the water molecule; we use the crystalline structure of main element Al or Fe to represent the metallic samples, where Al crystal is in *fcc* stacking style, *fm-3m* space group, with cell parameters $a = b = c = 0.405 \text{ nm}$, $\alpha = \beta = \gamma = 90^\circ$ [16]; and Fe crystal is in *bcc* stacking style, *im-3m* space group, with cell parameters $a = b = c = 0.28664 \text{ nm}$, $\alpha = \beta = \gamma = 90^\circ$ [17]. The neighbour atoms have metallic bonds are represented with the atomic interactions in the potential field, considering the existence of H_2O molecular system, the COMPASS force-field [18, 19] was applied, which can cover the interactions between H, O, Fe, and Al elements. Considering the anisotropy of the metallic crystals, the supercells of $5 \times 5 \times 5$ Al and $10 \times 10 \times 10$ Fe were cut along (1 0 0), (1 1 0), (1 1 1), respectively. The amorphous cells containing 200 H_2O molecules were put onto each metallic surface to form water-metallic (liquid-solid) interface models, along with 2 nm vacuum layer on the top to overcome the influence of the upper interface. The interface models were optimized using molecular mechanics (MM) [20, 21], and then molecular dynamics (MD) simulations were carried out under COMPASS force-field using NVT ensemble (constant particle number, volume and temperature), with varying temperatures 291 K, 296 K, 297 K, 298 K, 299 K, 300 K, 301 K, 302 K and 303 K. Nosé method was used to control the temperatures [22–24]. The van der Waals forces were summed by atom-based method, while the electrostatic forces were summed by Ewald method [25, 26]. For each system, three replica simulations are carried out to reduce random errors. Each MD simulation lasts 500 ps to ensure the equilibrium of both temperature and energy.

Experimental tests

The contact angle tests were carried out on the metal parts, in order to validate the surface interactions and to determine the surface cleanliness of these components [27–30]. The portable contact angle tester (MobileDrop, KRÜSS GmbH) was used in all the test, which is accurate, portable and efficient. The tester has its own injector to drop liquid on the surface of the sample, with accuracy of $2 \mu\text{l}$. The stainless steel 304 (with main element Fe) and aluminum alloy 6061 (with main element Al) are chosen as the samples of the tests to simulate the components of high power laser device, and both samples are in the same dimension of $100 \times 100 \times 10 \text{ mm}$. Before the surface tests, clean treatment process was carried out on each sample, firstly the sample was infiltrated in high-pressure water for 10 min, and in cleaning agent for another 10 min; then it was washed under high-pressure water for 3 times, dried under ethyl alcohol, and dried by heating for 4 hours. Finally, the surface test experiments are carried out on the treated samples under various temperatures as same as the molecular simulations from 291–303 K at a constant humidity of 40 % RH. As results, the contact angles at elevated temperatures were obtained [31, 32].

Results And Discussion

Anisotropy of interface interactions

The equilibrium trajectories were used to analyze the interaction energy (E_{inter}), which is the difference between the energy of the total system (E_{total}) and the divided systems including the metallic surface (E_{metal}) and the water AC (E_{water}), normalized by the contact surface area (S) (Eq. 1), and the contributions of van der Waals force (vdW) and Electrostatic force (ES) were also calculated as shown in Fig. 2. From the results of three replica simulations for each system, it can be seen that the calculated energies remain the same for each system at specific temperature and pressure.

$$E_{inter} = [E_{total} - (E_{metal} + E_{water})] / S.....(1)$$

It can be concluded from Fig. 2 that, the water molecules have attractive interactions with the metallic surfaces, in which the van der Waals forces contribute most [33–36], while the electrostatic forces also contribute mainly for H₂O molecular systems. For different metals, the interactions are different, in which water on Fe template are stronger, for Fe surfaces the absolute values of interaction energies are all lager than 60 kcal/mol per nm², while that of the Al surfaces are all smaller than 50 kcal/mol per nm². For the same metal, the interactions show anisotropy along different crystalline directions, for water on Al (1 0 0)>(1 1 0)>(1 1 1), while for water on Fe (1 0 0)>(1 1 0)>(1 1 1). Above all, the attractive forces between water and Al or Fe metallic surfaces are strong, making the samples a kind of hydrophilic materials, and the surface tension and contact angle between water and these materials are expected to be small [37].

Temperature effects on interaction energies

It should be noticed that, the absolute values of interaction energies raised with the temperature from 291 K to 303 K [10]. The energy gradients at elevated temperatures can be found by correlating interaction energies with temperatures (Fig. 3). The values of energy gradient for each system are summed in Table 1, from which it can be seen that the energy gradients for water on both Al and Fe show anisotropy.

Table 1

Interaction energy gradient at elevated temperatures from 291–303 K

System	Energy gradient [kcal/(mol·nm ² ·K)]	System	Energy gradient [kcal/(mol·nm ² ·K)]
H ₂ O-Al (1 0 0)	0.4824	H ₂ O-Fe (1 0 0)	0.1880
H ₂ O-Al (1 1 0)	0.2355	H ₂ O-Fe (1 1 0)	0.2813
H ₂ O-Al (1 1 1)	0.2216	H ₂ O-Fe (1 1 1)	0.1643

Correlation interface interactions to contact angles

From the results of the contact angle tests at various temperatures from 291 K to 303 K and a constant humidity 40 % RH, it can be seen that, for each sample, two different test points on the surface were

chosen to do *in situ* tests; for each point, 10 parallel tests of contact angle were performed to reduce the random error, and the average value of the results were calculated as shown in Fig. 4.

As results, for both Al and Fe samples, the contact angles are all small ($< 60^\circ$), in the range for hydrophilic materials, which match with the calculation results of strong surface energies. In addition, for both samples, the contact angles reduce with elevated temperatures from 291 K to 303 K. Linear relationship can be found for each test with correlation coefficients all larger than 0.90, and the slope values which represent the contact angle gradient at elevated temperatures are as shown in Table 2. It can be seen that the contact angle gradients for Al sample and Fe sample are all around the value of $-2.4^\circ/\text{K}$, with slight changes caused by the different test points. The changes of contact angle also match with the surface energy gradients, proving that with elevated temperature, the atomic and molecular movements exacerbated, and surface energy rose, causing the reducing of surface tension and contact angle [38]. It can be concluded that, the experiments consisted with the computations.

Table 2
Contact angle gradient at elevated temperatures from 291–303 K

System	Contact angle gradient [$^\circ/\text{K}$]	System	Contact angle gradient [$^\circ/\text{K}$]
Al sample 1	-2.3737	Fe sample 1	-2.4020
Al sample 2	-2.4187	Fe sample 2	-2.3819
average	-2.3962	average	-2.3920

Conclusions

Combined methods of experimental tests and molecular simulations were carried out to investigate the temperature effects of interface interactions for water on metallic surfaces. Conclusions can be found as follows:

Firstly, there are strong attractive forces between water molecules and the metallic surfaces; for different metals, the interactions are different, where the interaction energies between water and Fe are stronger than that of Al; for the same metal, the interactions show anisotropy along different crystalline directions.

Moreover, the absolute values of interaction energies raised with temperatures, and the energy gradient at elevated temperatures are anisotropic.

Meanwhile, the experimental tests show that the contact angle are relatively small, proving the metallic surfaces to be hydrophilic; what's more, the contact angle reduce with elevated temperatures, and the contact angle gradient versus temperatures can also be calculated and related to the energy gradient.

The above show the temperatures have positive effects on water-metallic interface energies, which should be considered in accurate contact angle tests for cleanliness of high-power-laser facilities.

Declarations

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The authors have no conflicts of interest to be declared.

Availability of data and material

All raw data are available from the authors upon reasonable request.

Code availability

The calculations were performed using Materials Studio Release 6.1. provided by Accelrys Software Inc.

Author contributions

All authors designed the project; Y.J., L.N., H.L., G.Z. and C.Y. did the surface cleanliness tests; W.Q., Y.J. and X.M. did the calculations, data collections and analysis; W.Q. and Y.J. contributed to the writing of the manuscript.

References

1. Emmett JL, Krupke WF, Simmons WW (1999) NIF Technology Review. Technology Resource Group of the NIF Council
2. Wenzel RN (1936) Resistance of solid surfaces to wetting by water. *Industrial Engineering Chemistry* 28(8):988–994
3. Koga K, Tanaka H (2005) Phase diagram of water between hydrophobic surfaces. *J Chem Phys* 122:104711
4. Fürstner R, Barthlott W, Neinhuis C, Walzel P (2005) Wetting and self-cleaning properties of artificial superhydrophobic surfaces. *Langmuir* 21(3):956–961
5. Loudet JC, Yodh AG, Pouligny B (2006) Wetting and contact lines of micrometer-sized ellipsoids. *Phys Rev Lett* 97(1):018304
6. Kumar G, Prabhu KN (2007) Review of non-reactive and reactive wetting of liquids on surfaces. *Advances in Colloid Interface Science* 133(2):61–89
7. Alloul H, Roques-Carmes T, Hamieh T, Razafitianamaharavo A, Barres O, Toufaily J, Villieras F (2013) Effect of chemical modification on surface free energy components of Aerosil silica powders determined with capillary rise technique. *Powder Technol* 246:575–582

8. Johnson RE, Dettre RH (1964) Contact angle hysteresis I. study of an idealized rough surface. *Contact Angle, Wettability and Adhesion* 43: 112–135
9. Israelachvili JN (2011) *Intermolecular and Surface Forces*, 3rd edition, Academic Press
10. Chau TT, Bruckard WJ, Koh PTL, Nguyen AV (2000) A review of factors that affect contact angle and implications for flotation practice. *Adv Coll Interface Sci* 150:106–115
11. Curtin W (1987) Density-functional theory of the solid-liquid interface. *Phys Rev Lett* 59:1228
12. Li R, Zhong Y, Huang C, Tao X, Ouyang Y (2013) Surface energy and surface self-diffusion of Al calculated by embedded atom method. *Physica B* 422:51–55
13. Hoyt J, Asta M, Karma A (2001) Method for computing the anisotropy of the solid-liquid interfacial free energy. *Phys Rev Lett* 86:5530
14. Broughton JQ, Gilmer GH (1986) Molecular dynamics investigation of the crystal-fluid interface. VI. Excess surface free energies of crystal-liquid systems. *J Chem Phys* 84:5759–5768
15. Luo W, Hu W, Su K, Liu F (2013) The calculation of surface free energy based on embedded atom method for solid nickel. *Appl Surf Sci* 265(1):375–378
16. Cai J, Ye YY (1996) Simple analytical embedded-atom-potential model including a long-range force for fcc metals and their alloys. *Phys Rev B* 54:8398–8410
17. Sun D, Asta M, Hoyt J (2004) Crystal-melt interfacial free energies and mobilities in fcc and bcc Fe. *Phys Rev B* 69:174103
18. Sun H (1998) COMPASS: an ab initio forcefield optimized for condensed-phase applications- overview with details on alkane and benzene compounds. *J Phys Chem B* 102:7338
19. Sun H, Ren P, Fried JR (1998) The COMPASS forcefield: parameterization and validation for polyphosphazenes. *Comput Theor Polym Sci* 8:229
20. Verlet L (1967) Computer experiments on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules. *Phys Rev* 159:98–103
21. Ermer O (1976) Calculation of molecular properties using force fields. Applications in organic chemistry. *Struct Bond* 27:161–211
22. Nosé S (1984) A molecular dynamics method for simulations in the canonical ensemble. *Mol Phys* 52:255–268
23. Nosé S (1984) A unified formulation of the constant temperature molecular dynamics methods. *J Chem Phys* 81:511–519
24. Nosé S (1991) Constant temperature molecular dynamics methods. *Prog Theor Phys Suppl* 103:1–46
25. Ewald PP (1921) Die Berechnung optischer und elektrostatischer Gitter potentiale (The calculation of optical and electrostatic lattice potentials). *Ann Phys Leipzig* 64:253
26. Karasawa N, Goddard WA (1989) Acceleration of convergence for lattice sums. *J Phys Chem* 93:7320–7327

27. Stalder AF, Kulik G, Sage D, Barbieri L, Hoffmann P (2006) A snake-based approach to accurate determination of both contact points and contact angles. *Colloids Surfaces A: Physicochemical Engineering Aspects* 286(1):92–103
28. Lee B, Ravindra P, Chan E (2008) A critical review: surface and interfacial tension measurement by the drop weight method. *Chem Eng Commun* 195(7):889–924
29. Stalder AF, Melchior T, Müller M, Sage D, Blu T, Unser M (2010) Low-bond axisymmetric drop shape analysis for surface tension and contact angle measurements of sessile drops. *Colloids Surfaces A: Physicochemical Engineering Aspects* 364(1):72–81
30. Matykina E, Garcia I, Damborenea JJD, Arenas MA (2011) Comparative determination of TiO_2 surface free energies for adhesive bonding application. *International Journal of Adhesion Adhesives* 31(8):832–839
31. Li XM, Reinhoudt D, Crego-Calama M (2007) What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces. *Chem Soc Rev* 36(8):1350–1368
32. Hung YL, Chang YY, Wang MJ, Lin SY (2010) A simple method for measuring the superhydrophobic contact angle with high accuracy. *Rev Sci Instrum* 81(6):065105
33. Oss CJV, Chaudhury MK, Good RJ (1988) Interfacial Lifshitz-van der Waals and polar interactions in macroscopic systems. *Chem Rev* 88(6):927–941
34. Kwok DY (1999) The usefulness of the Lifshitz-van der Waals/acid-base approach for surface tension components and interfacial tensions. *Colloids Surfaces A: Physicochemical Engineering Aspects* 156(1):191–200
35. Oss CJV (2002) Use of the combined Lifshitz-van der Waals and Lewis acid-base approaches in determining the apolar and polar contributions to surface and interfacial tensions and free energies. *Journal of Adhesion Science Technology* 16(6):669–677
36. Zhao YP (2002) Morphological stability of epitaxial thin elastic films by van der Waals force. *Arch Appl Mech* 72(1):77–84
37. Mitroy J, Zhang JY (2007) Long-range dispersion interactions. II. Alkali-metal and rare-gas atoms. *Phys Rev A* 76:032706
38. Rubio F, Rubio J, Oteo JL (2000) Effect of the measurement temperature on the dispersive component of the surface free energy of a heat treated SiO_2 Xerogel. *Journal of Sol-Gel Science Technology* 18(2):115–118

Figures

Figure 1

Atomic model for water-metallic interface [H₂O-Fe(1 0 0)] is taken for an example, and Fe, H, O atoms are represent using purple, white, and red respectively]

Figure 2

Interaction energies for water on different metallic surfaces

Figure 3

The interaction energies as functions of temperatures for different surfaces

Figure 4

The experimental contact angle as functions of test temperatures

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