

# Water-based superlubricity in vacuum

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**Abstract:** This study achieved water-based superlubricity with the lubrication of H<sub>3</sub>PO<sub>4</sub> solution in vacuum (highest vacuum degree <10<sup>-4</sup> torr) for the first time by performing a pre-running process in air before running in vacuum. The stable water-based superlubricity was sustainable in vacuum (0.02 torr) for 14 h until the test was stopped by the user for non-experimental factor. A further analysis suggested that the superlubricity may be attributed to the phosphoric acid–water network formed in air, which can efficiently lock water molecules in the liquid lubricating film even in vacuum owing to the strong hydrogen bond interaction. Such capability to lock water is strongly affected by the strength of hydrogen bond and environmental conditions. The realization of water-based superlubricity with H<sub>3</sub>PO<sub>4</sub> solution in vacuum can lead to its application in space environment.

**Keywords:** friction; water-based superlubricity; vacuum; phosphoric acid

## 1 Introduction

Due to their low mechanical noise, high lubricating stability, self-restoration capability, and insensitivity to environmental factors, liquid lubricants have been widely used to meet the long-term reliable and accurate operational requirements of space mechanisms [1–4]. Liquid lubricants can be divided into two types, i.e., oil-based and water-based. Given that rapid water evaporation occurs under low-pressure condition in space, water-based lubricants have not been used in space applications [4, 5]. However, water-based lubricants are one of the most promising lubricants because they are cost-effective, highly reproducible, and environmentally friendly [6]. In addition, water-based lubricating films have excellent fluidity even under high contact pressures and can usually generate friction-induced tribochemical reactions with tribopair surfaces, which creates favorable conditions for realizing

superlubricity [7–9]. Superlubricity, in which the friction coefficient between two contacting surfaces is less than 0.01, presents a unique advantage for saving energy, improving operation reliability, and increasing the working life of space mechanisms [10–13].

Previous studies have proposed different types of water-based superlubricants, such as ceramic materials with water, polymer brushes, glycerol solution with acid or polyhydric alcohol, and polysaccharide mucilage from plants [14–18]. The superlubricity of these systems is mainly attributed to the formation of a hydrated water layer between the tribopair surfaces with extremely low shear strength [19–21]. Chen et al. reported that environmental humidity has a significant effect on the lubrication behaviors of water-based superlubricants [22]. The experimental results showed that the water content in the liquid lubricating film played a key role in the superlubricity behavior. When the humidity is low, the water evaporation rate of the

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liquid lubricating film is higher than that of water absorption, which destroys the hydrated water layer and results in superlubricity failure. Therefore, in view of the severe low-pressure environment in space, strict control of the water content in liquid lubricating film has become an important method to achieve water-based superlubricity. To the best of our knowledge, until recently, no available information regarding the water-based superlubricity achieved in vacuum can be found in the previous literature. Thus, it is necessary to carry out the research on water-based superlubricity in vacuum to satisfy the increasing demands for high reliability and long-term requirements of space lubrication.

In the present work, the effect of vacuum environment on the lubrication behavior with  $\text{H}_3\text{PO}_4$  solution was investigated. After the phosphoric acid–water network was formed by performing the pre-running-in process in air, we found that the stable water-based superlubricity was sustainable in vacuum (0.02 torr) for 14 h until the test was stopped by user for non-experimental factor. The analysis suggested that the stable vacuum-superlubricity state may be attributed to the strong hydrogen bond interaction in the phosphoric acid–water network formed in air, which can efficiently lock water molecules in the liquid lubricating film. The results creatively overcome the difficulty in maintaining the water molecules in the liquid lubricating film in vacuum and provide new insights into the applications of water-based superlubricity in space.

## 2 Materials and methods

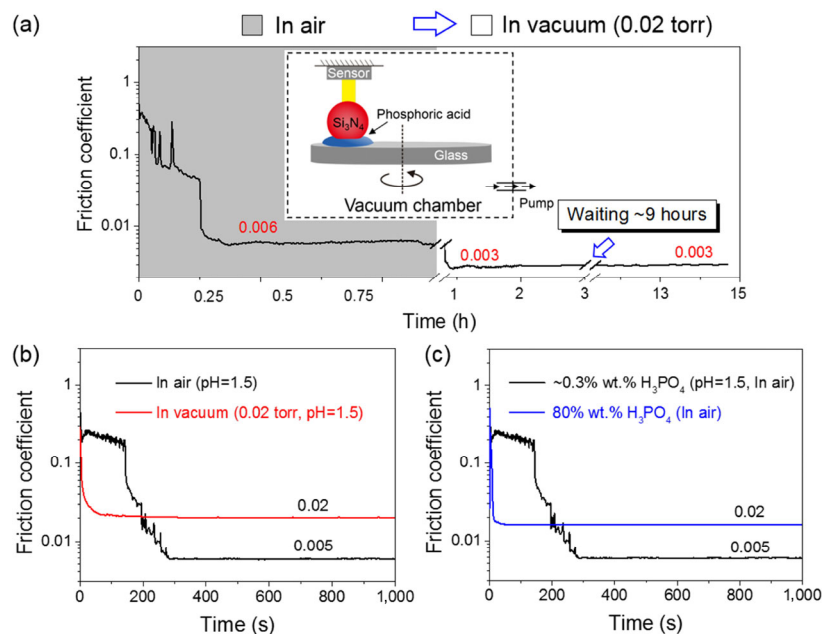
The liquid lubricant used in all friction tests was  $\text{H}_3\text{PO}_4$  solution with a pH of 1.5, which is measured by a standard pH meter after pre-calibration. It was diluted by a commercial product (purity greater than 99%) purchased from Sinopharm Chemical Reagent Co. Ltd. with a concentration of 85 wt.%. The tribopair consisted of  $\text{Si}_3\text{N}_4$  ball with a diameter of 4 mm and glass slide with a root mean square (RMS) roughness of approximately 0.5 nm over a  $400\ \mu\text{m}^2$  area. Before the friction tests, both the  $\text{Si}_3\text{N}_4$  ball and glass slide were ultrasonically cleaned in acetone, ethanol, and deionized water for 10 min in sequence to remove surface contamination, and then dried by pure nitrogen

gas. All the friction tests were performed using a universal micro-tribotester (UMT-V, Bruker, USA) with ball-on-disk mode, as illustrated in the inset of Fig. 1(a). When the tests were conducted in air, the relative humidity was controlled at  $50 \pm 1\%$ . To simulate the actual working environment of bearings that work inside the aircraft, the vacuum tests were performed in a vacuum chamber and the degree of vacuum was set at  $10^{-2}$  torr [23]. A drop (10  $\mu\text{L}$ ) of liquid lubricant was added between the  $\text{Si}_3\text{N}_4$  ball and glass substrate before test. During the whole tests, the applied normal load was 3 N, which provided a maximum contact pressure of 830 MPa based on the Hertzian contact theory [24], the liner speed was 0.2 m/s, and the temperature was controlled at  $25 \pm 2\ ^\circ\text{C}$ . In order to ensure the ultra-high measurement accuracy of friction, the measuring error could be reduced significantly by the pre-commission process. More details regarding this can be found in the previous literature [25].

## 3 Results and discussions

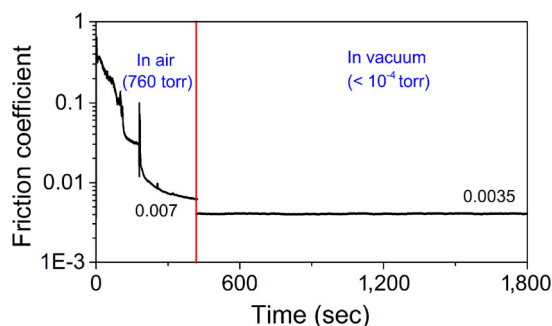
### 3.1 Water-based superlubricity achieved in vacuum

In order to investigate the effect of vacuum on the superlubricity behavior of  $\text{Si}_3\text{N}_4$ /glass pair with  $\text{H}_3\text{PO}_4$  solution, friction tests were performed in vacuum and the results are shown in Fig. 1(a). The friction test was divided into two steps: (I) achieve superlubricity state after the running-in process in air, and then suspend the experiment temporarily; (II) restart the test after the chamber is evacuated (0.02 torr). As shown in Fig. 1(a), the friction coefficient decreases to 0.006 after the running-in period of 200 s in air and then it stabilizes. Moreover, after restarting the test in vacuum, the friction coefficient further decreases to 0.003 without running-in process and the stable superlubricity state can be sustained for at least 14 h (including 9 h of standby time). Finally, the test was stopped by the user for non-experimental factor, and the superlubricity system was still effective at the end of test. Notably, the friction coefficient of the superlubricity state achieved in vacuum environment was lower than that in the atmosphere. Moreover, the superlubricity state is extremely stable in running and suspended stages. The morphologies of the wear



**Fig. 1** (a) Liquid superlubricity system with H<sub>3</sub>PO<sub>4</sub> solution remains effective in vacuum for 14 h (including 9 h of standby time) after the pre-running-in process in air. The inset shows the schematic illustration of friction measurement system with ball-on-disk mode. (b) Friction coefficient measured in vacuum without pre-running-in process in air. The result of test performed in air is also plotted as a comparison. (c) Effect of water content in liquid lubricating film on the lubrication behavior of H<sub>3</sub>PO<sub>4</sub> solution.

tracks on the tribopair surfaces in vacuum and ambient environments are shown in Fig. S1 in the Electronic Supplementary Material (ESM). There is little difference in the wear depth of wear tracks on tribopair surfaces, which indicates that the vacuum environment has little effect on the wear behavior between the Si<sub>3</sub>N<sub>4</sub> balls and glass substrates. Furthermore, a wear test was conducted under higher vacuum degree ( $<10^{-4}$  torr), and the superlubricity state could also be maintained, as shown in Fig. 2. Similar to the results obtained at 0.02 torr, the friction coefficient further decreased from 0.007 to 0.0035 in the vacuum. Previous studies pointed



**Fig. 2** Superlubricity state with H<sub>3</sub>PO<sub>4</sub> solution maintains in higher vacuum degree condition ( $<10^{-4}$  torr) after the pre-running-in process in air.

out that the superlubricity mechanism in air may be attributed to the hydrated water layer with hydrogen bond network among H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, and H<sub>2</sub>O [19]. The results suggest that the phosphoric acid–water network formed in air can be barely destroyed and it even presents a better superlubricity performance in vacuum, which may be attributed to the more compact hydrogen bond network induced by structural transformations in vacuum [26].

However, when the test was performed in vacuum without the pre-running-in process in air, the superlubricity state cannot be achieved until the end of test, and the friction coefficient can just enter traditional hydrodynamic lubrication state ( $\mu = 0.02$ ), as shown in Fig. 1(b). Superlubricity failure in vacuum may be attributed to the accelerated water evaporation. Thus, the friction tests under the lubrication of H<sub>3</sub>PO<sub>4</sub> solution with different concentrations were performed in air to verify the aforementioned process, as shown in Fig. 1(c). The evolution of friction coefficient in vacuum is similar to that under the lubrication of 80 wt.% H<sub>3</sub>PO<sub>4</sub> solution in air, which is also consistent with the results by Li et al. [27]. Above results reveal that the pre-running-in process in air plays an

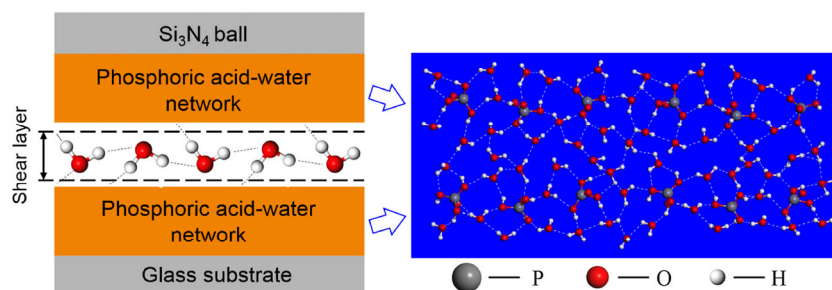
important role in the subsequent vacuum-superlubricity, and the main reason for superlubricity failure in vacuum may be similar to that under the lubrication of  $\text{H}_3\text{PO}_4$  solution with high concentration. A free water layer is necessary because it provides a low shearing strength to lower the friction force, which is the origin of superlubricity [19]. However, too much free water will restrain the formation of starvation state and hydrogen bond network [28]. It can be speculated that the loss of free water in lubricating film caused by rapid water evaporation leads to an insufficient running-in process, as well as lack of time for the tribochemical reaction to occur, thereby resulting in the failure of vacuum-superlubricity [27]. Therefore, stable superlubricity is unachievable when the test is performed in vacuum without pre-running-in process in air, but it can be realized after the formation of phosphoric acid-water network in air. This work introduces new insights into achieving water-based superlubricity in vacuum, which provides the possibility for the application of water-based superlubricants in space.

### 3.2 Mechanism of water-based superlubricity achieved in vacuum

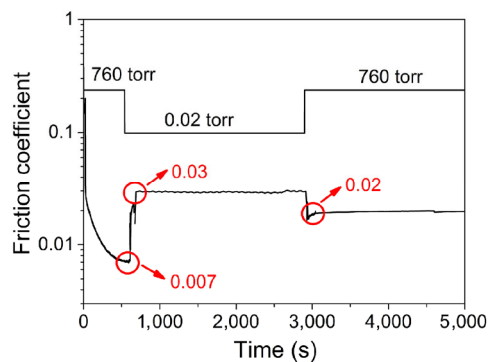
A large number of studies have shown that there is a complex interaction between phosphate groups and water molecules [29, 30]. Since  $\text{H}_3\text{PO}_4$  molecules contain high-density  $\text{P}=\text{O}$  bonds and  $\text{OH}$  groups, the hydrogen bond interaction between  $\text{H}_3\text{PO}_4$  and water molecules can be formed in various combinations according to the formation conditions of hydrogen bonds [31]. Moreover,  $\text{H}_3\text{PO}_4$  and water molecules can also form a strong hydrogen bond network with each other. In many stable configurations,  $\text{H}_3\text{PO}_4$  and

water molecules are not only the providers of proton but also their acceptors [32]. Thus, they tend to form a multi-cyclic structure with abundant hydrogen bonds and reduce the distance between the molecules [33]. This synergistic effect results in a considerable stability of the hydrogen bond network, which is also conducive to develop a strong hydrogen bond interaction between  $\text{H}_3\text{PO}_4$  and water molecule. Figure 3 shows the possible molecular model of phosphoric acid-water network, more details about the tribochemical reaction processes can be found in the previous literatures [19, 22, 26, 28, 34]. For the vast majority of liquid lubricants in vacuum, water molecules in lubricating film would rapidly evaporate, but no water can be absorbed back. However, the phenomenological results show that, even in vacuum environment, the phosphoric acid–water layer with strong hydrogen bond interaction may efficiently lock the water molecules in the lubricating film and further prevent superlubricity failure.

In order to understand the influence of hydrogen bond strength in hydrated water layer on water-based superlubricity behavior in vacuum, the same experiments were performed with the lubrication of mixture of glycerol ( $\text{C}_3\text{H}_8\text{O}_3$ ) and  $\text{H}_3\text{PO}_4$  solutions, which was obtained by mixing the  $\text{H}_3\text{PO}_4$  solution with  $\text{C}_3\text{H}_8\text{O}_3$  solution (20% v/v) and the pH value was controlled at approximately 1.5. In addition to the liquid lubricant, other experimental parameters kept the same as mentioned above. Figure 4 shows that the superlubricity state is achieved after the running-in process in air, which is attributed to the hydrogen bond network formed by  $\text{C}_3\text{H}_8\text{O}_3$  and water molecules with low shear strength [35]. However, the friction coefficient immediately increases from 0.007 to 0.03 when the



**Fig. 3** Schematic illustration of the liquid lubricating film between two friction surfaces (left) and the possible molecular schematic representation of phosphoric acid-water network (right) [19].



**Fig. 4** Effect of the hydrogen bond strength in hydrated water layer on water-based superlubricity behavior in vacuum. The friction coefficient is measured under the lubrication of mixture of glycerol and  $\text{H}_3\text{PO}_4$  solutions, and the other experimental parameters are the same as those in Fig. 1.

chamber pressure is pumped to 0.02 torr. After the experimental environment is returned to the atmosphere condition, some free water in air may come into the lubricant and induce a little reduction in friction coefficient but the superlubricity state is still not restored. We also repeated that experiment with the lubrication of mixture of glycerol and  $\text{H}_2\text{SO}_4$  solutions, whose pH value was also controlled as 1.5, as shown in Fig. S2 in the ESM. The results show that the effect of the type of acids on superlubricity failure in vacuum can be ignored. The above results indicate that the glycerol-water network cannot effectively prevent water loss in the liquid lubricating film under low-pressure condition, which results in irreversible superlubricity failure. Since the  $\text{H}_3\text{PO}_4$  molecule has a higher density of hydroxyl or carboxyl groups (approximately 74 mol/L for 94 wt.% solution) than  $\text{C}_3\text{H}_8\text{O}_3$  molecule (approximately 41 mol/L for 92 wt.% solution). Therefore, the tetrahedral structure ( $\text{H}_3\text{PO}_4$ ) could form a more compact molecular configuration with water molecules compared with the chain structure ( $\text{C}_3\text{H}_8\text{O}_3$ ), and the hydrogen bond strength in phosphoric acid–water network is much stronger than that in glycerol–water network [33]. Thus, the superlubricity state in vacuum may be attributed to the phosphoric-water network formed in the pre-running-in process which could efficiently lock the water molecules in the lubricating film. Moreover, the capability of lubricant molecules to lock water is strongly affected by the hydrogen bond strength and environmental conditions (vacuum degree). According

to our results, strong hydrogen bond network is conducive in achieving a stable liquid superlubricity in vacuum. Therefore, the molecular structure with high-density functional groups, which can form compact hydrogen bond networks (such as hydroxyl, carboxyl, and amidogen groups) should be considered in the future design of water-based superlubricity in vacuum. The results present in this paper may open a door to the liquid superlubricity in vacuum environment.

## 4 Conclusions

This work demonstrates water-based superlubricity in vacuum (highest vacuum degree  $<10^{-4}$  torr) for the first time. After the phosphoric acid–water network was formed by performing the pre-running-in process in air, the stable water-based superlubricity state was sustainable in vacuum for at least 14 h. The phosphoric acid–water network may hold the water molecules in vacuum by the strong hydrogen bond interaction. Moreover, the capability to lock water is strongly affected by the hydrogen bond strength and environmental conditions.

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