Supplementary Material

Attraction induced frictionless sliding of rare gas monolayer on metallic surfaces: An efficient strategy for superlubricity

Junhui Sun,[†, §, //] Yanning Zhang,[⊥] Zhibin Lu,*,[†] Qunji Xue,[†] and Liping Wang*,[†,‡]

[†]State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China

[‡]Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, P. R. China

[⊥]School of Energy Science and Engineering, University of Electronic Science and Technology of China, Chengdu 611731, China

[§]University of Chinese Academy of Sciences, Beijing 100039, P. R. China

[//]Institute of Nanoscience and Nanotechnology, School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, P. R. China

*E-mail: zblu@licp.cas.cn (Z. L.); lpwang@licp.cas.cn (L. W.)

Computational method

The pressure dependence of friction for matched commensurate sliding system of Xe/Cu(111), Xe/Pd(111) and Ar/Cu(111) in the attractive regime are investigated via a van der Waals (vdW) corrected density functional theory (DFT) approach. The Xe monolayer was represented by a lattice of Xe on the Cu(111) ($\sqrt{3}\times\sqrt{3}$)R30° surface (lattice mismatch~2%) and a lattice of Xe on the (3×3) Pd(111) ((lattice mismatch~4.7%)), depicting in Fig.1 and Fig.S1, respectively, and a lattice of Ar on the (3×3) Cu(111) surface (lattice mismatch~3.8%). The metal surfaces were simulated using a slab of five atomic layers. For the sake of simplicity as done by Silva *et al.* [1], we performed the interaction energy calculations (for different relative perpendicular and lateral relative position) with the atoms of the metal substrate fixed at ideal surface positions, since the adsorbate-induced substrate rumpling is negligible [1-4]. The present results for Xe/Cu(111) are consistent with our previous theoretical studies from fully relaxed model [5], justifying the present treatment. We performed first-principles the energy plane-wave calculations within the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [6] augmented with

the Tkatchenko-Scheffler vdW (TS-vdW) correction [7,8] for Xe/Cu(111) and Ar/Cu, and Grimme-vdW [9] for Xe/Pd(111) (For TS method for DFT-D corrections the Pd elements are not parametrized), using CASTEP code [10]. The sliding of periodic models is simulated with a vacuum of 20 Å in the perpendicular direction to ensure negligible interaction between their periodic images. The cut-off energy of 500 eV was adopted for the plane-wave expansion and the k-point of Brillouin zone was sampled by 9×9×1 Monkhorst–Pack grid. The convergence for energy was chosen as 2×10^{-6} eV/atom between two steps. The calculated values were obtained at 0 K.
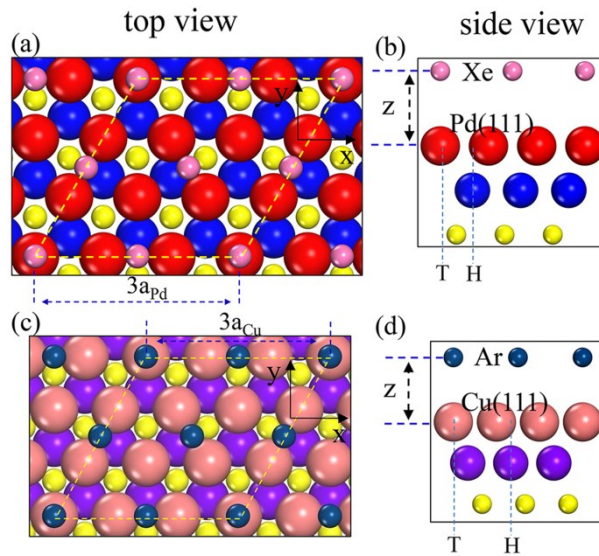

Figure S1 The top and side views of the atomic sliding model for **(a, b)** Xe/Pd(111) and **(c,d)** Ar/Cu(111) sliding systems with quasi-commensurate contacts. Yellow parallelogram in (a) and (c) shows the 3×3 unit cell (lattice parameter a_{Pd}=2.751 Å and a_{Cu}=2.556Å).
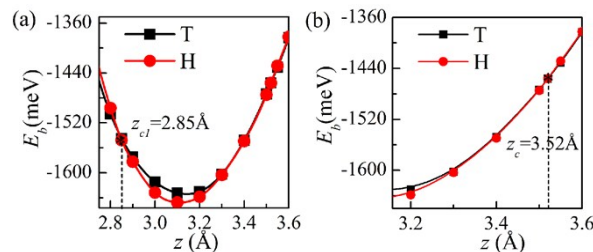

Figure S2 (a) The crossings of the binding energy distance $E_b(z)$ curves of T and H sites for Xe/Pd(111). **(b)** The potential crossing at z_c=3.52Å in the far-surface region. The crossing at z_{c1}=2.85Å in the near-surface region is consistent with previous

investigation of Silva *et al.*[1], justifying the present results. The relatively small energy difference between T and H sites suggests quasi-commensurate sliding friction for Xe/Pd(111) system shown in Fig. S1(a).
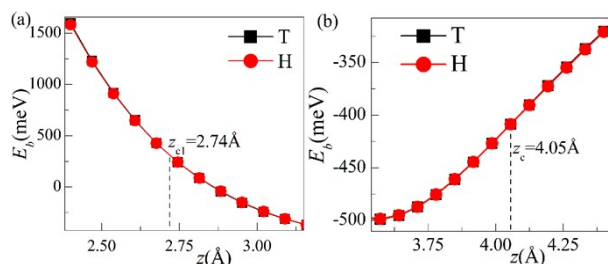

Figure S3 (a) The crossings of the binding energy distance $E_b(z)$ curves of T and H sites for the quasi-commensurate sliding friction systems of Ar/Cu(111) in the near-surface region of z_1=2.74Å, which is consistent with previous investigation of Righi *et al.*[11]. **(b)** The potential crossing in the far-surface region at z_c=4.05Å.
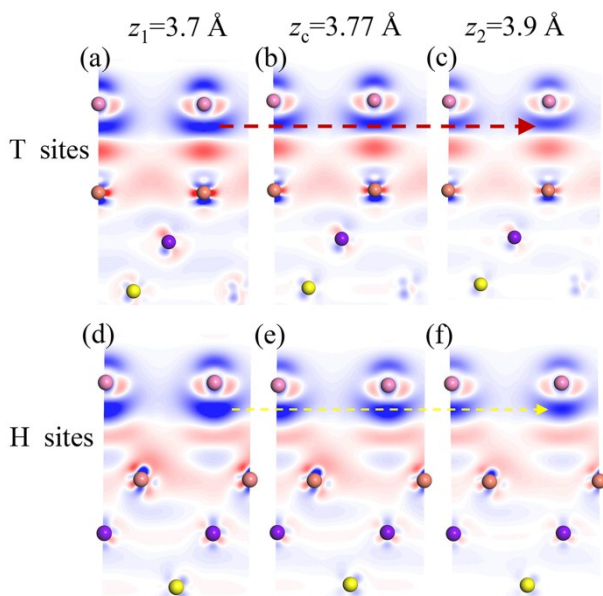

Figure S4 Electron density difference of Xe/Cu(111) in T (a, b, c) and H (e, f, g) sites under different separation (a, d) z_1=3.7Å, (b, e) z_c=3.77Å and (c, f) z_c=3.9Å shown in planes perpendicular to the surface within the range of ±0.003e/Å³. The light red (gray) and dark blue (gray) represent electron accumulation and depletion, respectively. The red (thick) and yellow (fine) dashed lines indicate the recede of redistribution of electronic density for T sites and H sites, respectively. The contrasts between the two lines manifest that the fade of charge polarization of T sites is more quickly than H sites.

The separation-dependent redistribution of electronic density

Fig.S4 shows the electron-density differences between the Xe/Cu and the clean

Cu(111) substrate combined with the Xe monolayer $[\Delta\rho(z) = \rho_{Xe/Cu}(z) - \rho_{RG}(z) - \rho_{Metal}(z)]$. As expectation from interacting energy in Fig.2a, around equilibrium separation at z_1=3.7 Å, plots of $\Delta\rho$ show that, in agreement with previously investigation [12], the electron-density redistribution (depletion centered about the Xe atom while accumulation between the Xe atom and the topmost layer of Cu surface together with a slight accumulation around the center of the Xe atom) is stronger for T site (Fig.S4a) than for H site (Fig.S4d). These result in the T site a more attractive potential, thus making energetically favored compared to the H site due to the polarization effects [13,14]. With increasing separation z from z_1=3.7 Å (Figs. S4a and S4d), crossing z_c=3.77 Å (Figs. S4b and S4e), to z_2=3.9 Å (Figs. S4c and S4f), there is a clear weakening tendency of electron-density (depletion and accumulation) redistribution. Meanwhile, note that, there is a significant difference for T and H sites: the reduction rate of T site is larger than that of the H site, as marked with red thick and yellow fine lines shown in Fig.3. And therefore, the depletion of electron-density redistribution (charge polarization) is clearly stronger for H site (Fig.S4f) than for T site (Fig.S4c) at z_2=3.9 Å to induce a much larger attractive effects, and result in the H site being energetically favored, which in line with the behavior of transformation between anti-corrugated (z_1=3.7 Å) and corrugated potential (z_2=3.9 Å), revealing the details of potential crossing at z_c=3.77 Å.

References

1. J. L. F. Da Silva, C. Stampfl, and M. Scheffler, Xe adsorption on metal surfaces: First-principles investigations. *Phys. Rev. B* **72,** 075424 (2005).

2. Y. N., Zhang, F., Hanke, V., Bortolani, M. Persson, and R.Q. Wu. Why Sliding Friction of Ne and Kr Monolayers Is So Different on the Pb(111) Surface. Phys. Rev. Lett. **106,** 236103 (2011).

3. E. Abad, Y. J. Dappe, J. I. Martnez, F. Flores, and J. Ortega. C_6H_6/Au(111): Interface dipoles, band alignment, charging energy, and van der Waals interaction. J. Chem. Phys. **134,** 044701 (2011).

4. A. Tkatchenko and M. Scheffler. Accurate Molecular Van Der Waals Interactions

from Ground-State Electron Density and Free-Atom Reference Data. Phys. Rev. Lett. 102, 073005 (2009).

5. Y. N. Zhang, V. Bortolani, and G. Mistura, Determination of corrugation and friction of Cu(111) toward adsorption and motion of Ne and Xe. *Phys. Rev. B* **89,** 165414 (2014).

6. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77,** 3865 (1996).

7. V. G. Ruiz, W. Liu, E. Zojer, M. Scheffler, A. Tkatchenko. Density-Functional Theory with Screened van der Waals Interactions for the Modeling of Hybrid Inorganic-Organic Systems. Phys. Rev. Lett. 108, 146103 (2012).

8. Marom, N., Bernstein, J., Garel, J., Tkatchenko, A., Joselevich, E., Kronik, L. & Hod, O. Stacking and registry effects in layered materials: The case of hexagonal boron nitride. Phys. Rev. Lett. **105,** 046801 (2010).

9. S. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J. Comp. Chem. **27,** 1787 (2006).

10. S. J. Clark *et al.*, Z. Kristallogr.−Cryst. Mater. **220,** 567 (2005).

11. Righi, M. C. & Ferrario, M. Pressure induced friction collapse of rare gas boundary layers sliding over metal surfaces. *Phys. Rev. Lett.* **99,** 176101 (2007).

12. P. L. Silvestrelli, A. Ambrosetti, S. Grubisiĉ, F. Ancilotto, Adsorption of rare-gas atoms on Cu(111) and Pb(111) surfaces by van der Waals corrected density functional theory. Phys. Rev. B **85,** 165405 (2012).

13. D.-L. Chen, W. A. Al-Saidi, and J. K. Johnson. Noble gases on metal surfaces: Insights on adsorption site preference. Phys. Rev. B **84,** 241405(R) (2011).

14. J. L. F. Da Silva and C. Stampfl, Trends in adsorption of noble gases He, Ne, Ar, Kr, and Xe on Pd(111) ($\sqrt{3}\times\sqrt{3}$)R30°: All-electron density-functional calculations. Phys. Rev. B **77,** 045401 (2008).