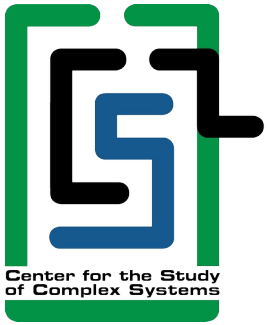

Tribological Properties of Selected Vanadium Oxide Stoichiometries Studied with Reactive Molecular Dynamics

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Outline of the talk

A) Introduction

- A1) Overview of vanadium-doped hard coatings
- A2) Our study on vanadium oxide lubricants
- A3) Methods applied and simulation setup

B) Key results

- B1) Tribological properties of V_xO_y lubricants
  - B1.1) Sliding force F_x vs. applied normal load F_z
  - B1.2) Coefficient Of Friction (COF) and offset F_x^0
- B2) Structural analysis of V_xO_y lubricants
  - B2.1) Coordination numbers (CN) of V, O, V^*
  - B2.2) Bond (V-O) length
  - B2.3) Tribological properties-structure relation: F_x vs. CN_v

C) Conclusions

Introduction

- Overview of major types of lubricants

  Friction and wear cause a loss of approximately 1/4 of the global energy production
  → serious need for using lubricants to decrease friction and prevent wear

- Depending on operating conditions (*temperature/pressure, presence of oxygen*):

  (1) non-demanding conditions (*not high temperature/pressure, oxygen present*)

  → **liquid lubricants:**

  - water
  - petroleum-based oils
  - ionic liquids

  (2) demanding conditions (*high temperature/pressure, vacuum or oxygen present*)

  → **solid lubricants:**

  - carbon-based (graphite, DLC (diamond-like carbon) coatings)
  - TMD (transition metal dichalcogenides)

- However, both carbon-based and TMD solid lubricants degrade in conditions of high temperature in oxidative environments due to their oxidation!

Vanadium-doped hard coatings

- Achieving effective lubrication under high temperature/pressure and under oxidation is highly relevant for various industrial applications (e.g., turbomachinery – turbines and compressors, cutting tools etc.)

→ **design of adequate coatings is needed**

- **Solution:**

→ **oxidation-resistant hard coatings**

- Those are binary of ternary films: **Cr-N**, **Ti-N**, **Cr-Al-N**, **Ti-Al-N** doped with a lubricious agent: **vanadium (V)**, **silver (Ag)**

- Operation of vanadium-doped hard coatings:

→ Vanadium diffuses to the coating's surface, reacts with oxygen and forms a lubricious oxide with a stoichiometry generally labeled as $\mathbf{V_xO_y}$

- **Vanadium oxides melt** at relatively low temperatures (under 700°C under atmospheric pressure in case of V_2O_5) **enabling liquid lubrication**

Our study on vanadium oxide lubricants

- **Study's main goal:**

  → research on tribological properties of selected V_xO_y lubricants

- **Length-scale and time-scale:** [nm] and [ns]

- **Number of atoms:**

  - vanadium: $N_v = 144$
  - oxygen: $N_o = y/x * N_v$

- Taking into account length- and time- scale, number of atoms, as well as the need for treating chemical bonding between the atoms (i.e., atomic reactivity)

  → adequate method: reactive molecular dynamics with ReaxFF

Key information regarding the method

- We investigated tribological properties of five different stoichiometries V_xO_y, selected based on available experimental studies:

$$V_2O_3,\ V_3O_5,\ V_8O_{15},\ V_9O_{17},\ VO_2$$

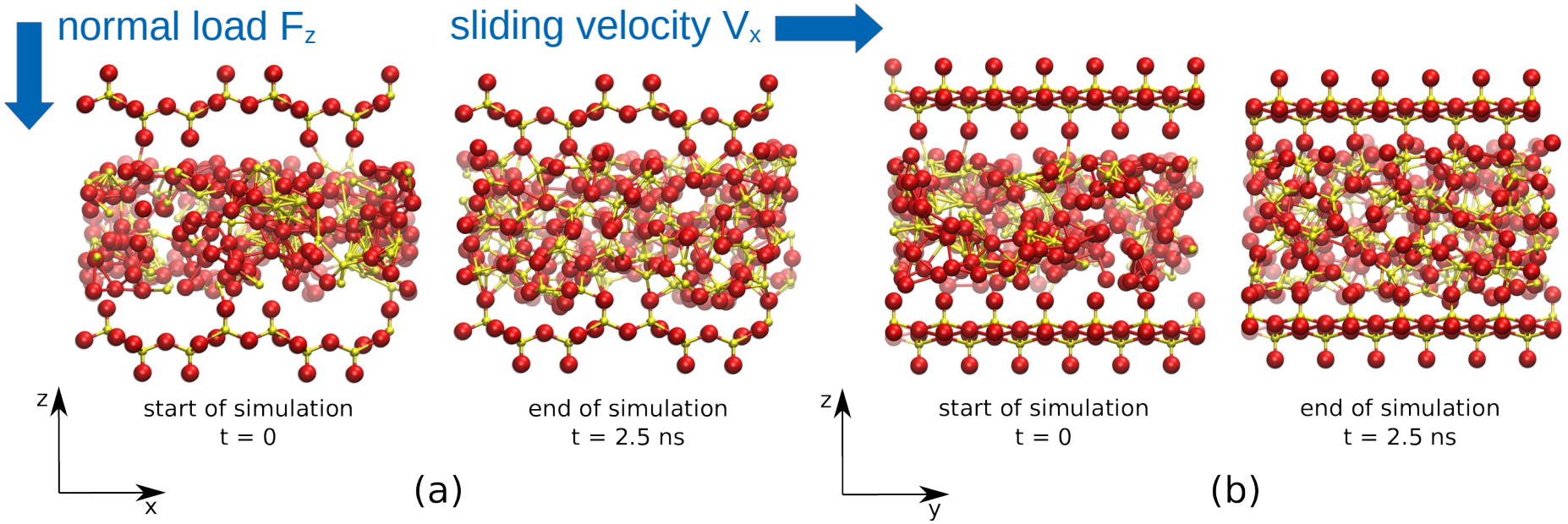
- We used the "*Chenoweth et al.*" ReaxFF parametrization [*J. Phys. Chem. A* 2008, 112, 5, 1040–1053]

- All reactive molecular dynamics simulations were run using:
  → **reax/c** package of the **LAMMPS** code

- <u>Study parameters:</u>
  - stoichiometry V_xO_y
  - applied normal load F_z = {0, 1, 2, 3, 4} [GPa]
  - temperature T = {600, 800, 1000} [K]

Simulation setup

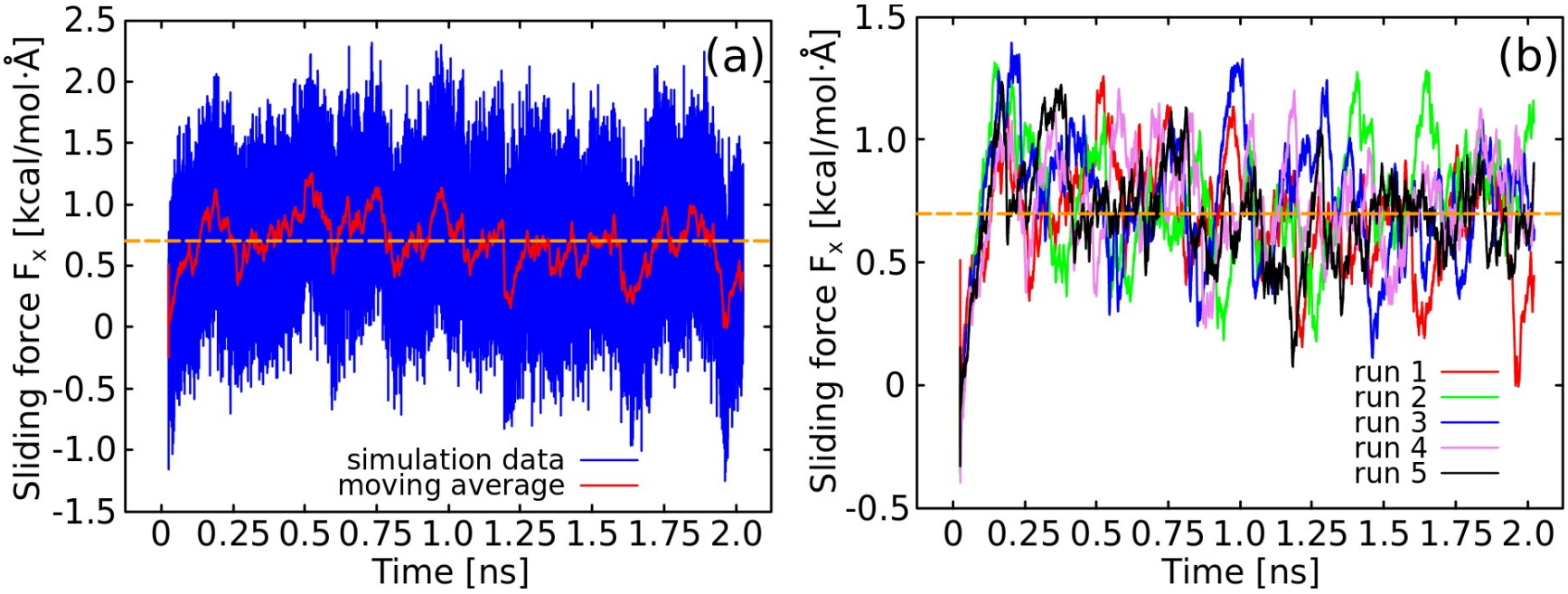
- Configuration snapshots (**V atoms** and **O atoms**)



➔ <u>Simulation segments:</u>

- Randomly arranged V and O atoms (according to V_xO_y) between two fixed V_2O_5 layers
- Melting (at target normal load F_z) and quenching (to target temperature T)
- Melt-quench gives amorphous V_xO_y → system equilibration (at target temperature T)
- Sliding of the top fixed V_2O_5 layer (at target sliding velocity V_x)

Averaging of the sliding force F_x



- Time evolution of the sliding force F_x acting on top V_2O_5 layer (case: stoichiometry V_3O_5/pressure 4 GPa/temperature 1000 K) during 2 ns of sliding

(a) blue line: simulation data
red line: moving average at 1000 points
orange line: average value of moving average curves for 5 independent initial random configurations (run 1 to run 5)

(b) averaging of moving average curves in case of 5 independent runs
orange line is mutual for panels (a) and (b)

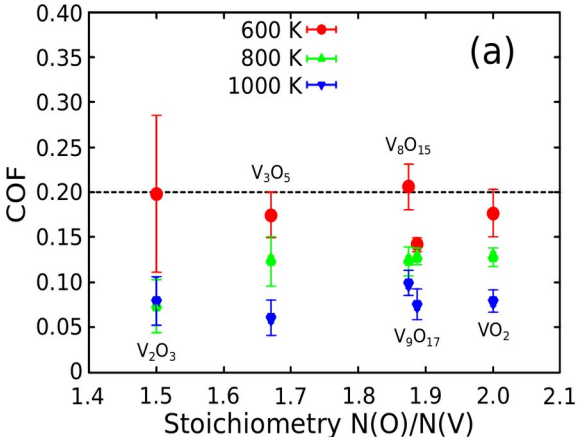
Tribological properties of V_xO_y lubricants

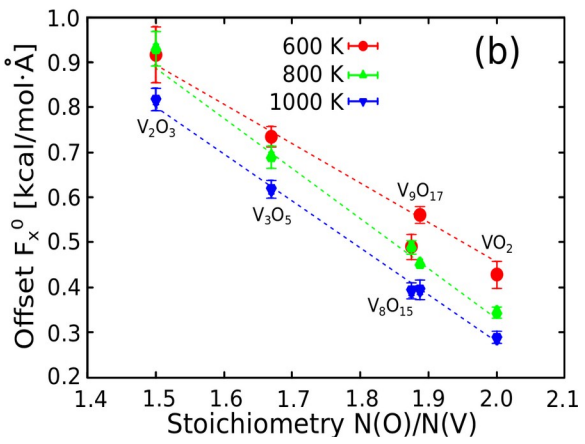
Sliding force F_x vs. normal load F_z
for all stoichiometries V_xO_y and temperatures T

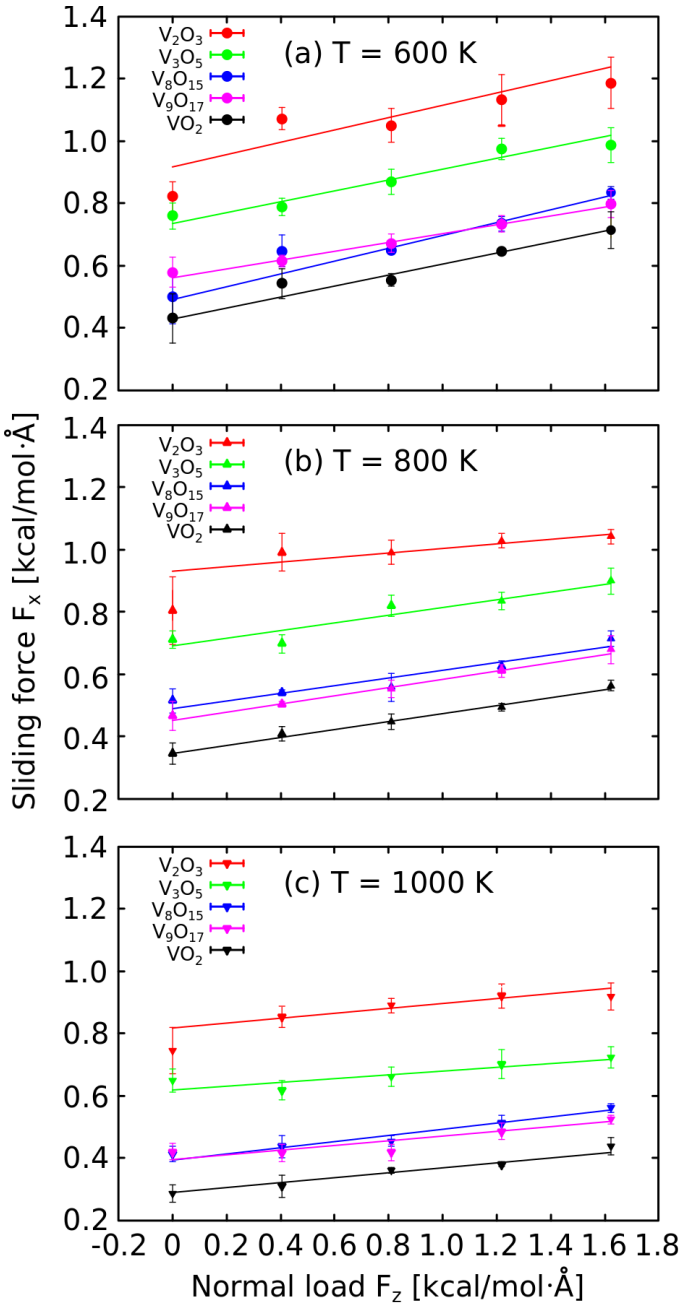
Linear fit:

$$F_x = COF \cdot F_z + F_x^0$$

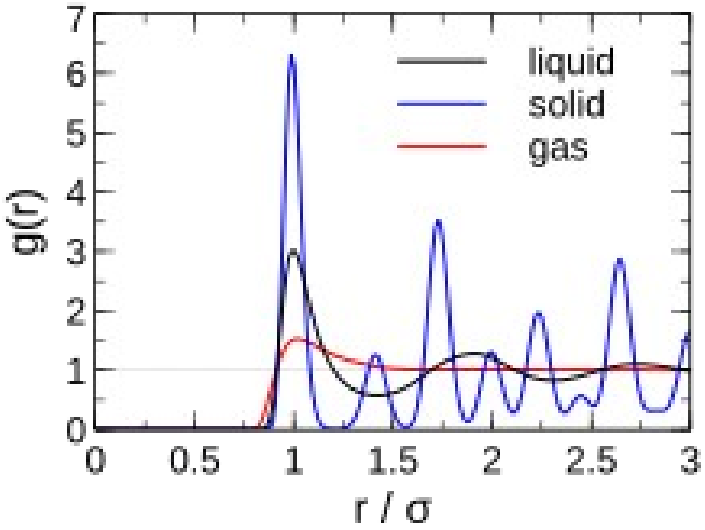
Slope (COF) and offset (F_x^0)
obtained via linear fitting





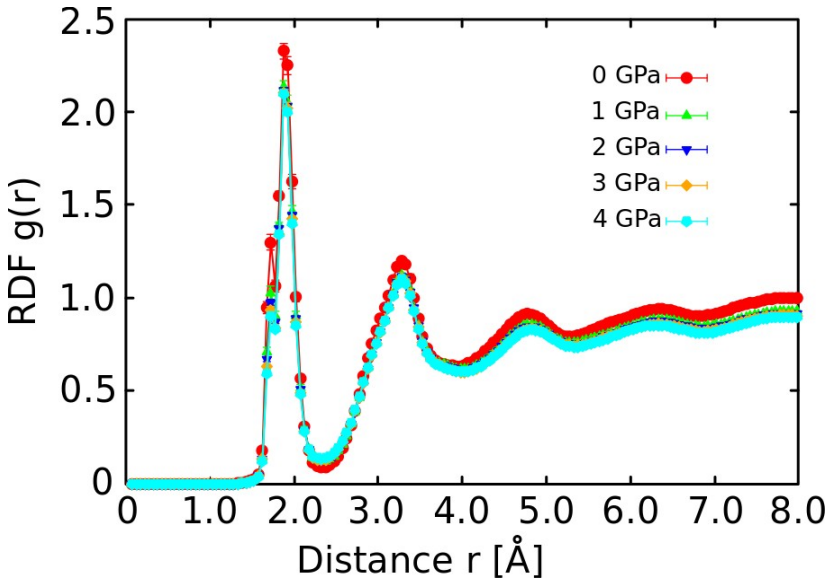


Structural analysis of V_xO_y - RDF

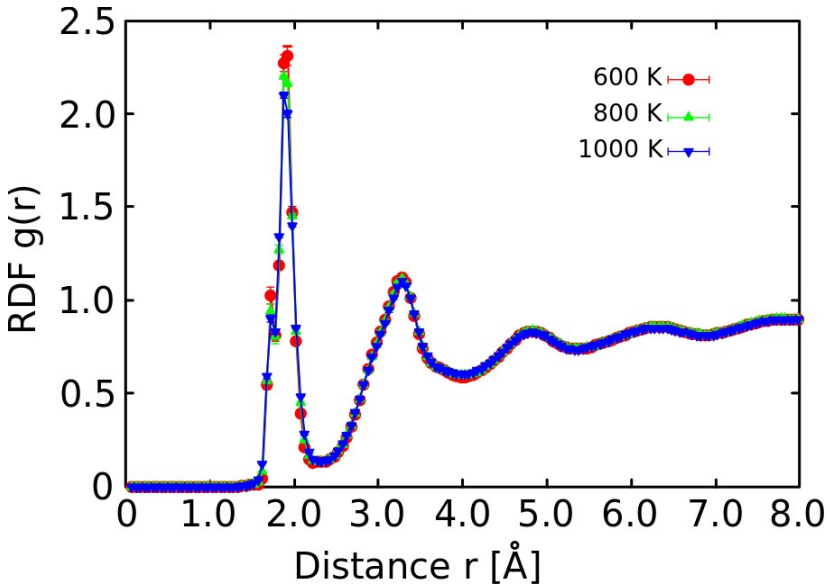


- Example:
  Comparison of RDF (Radial Distribution Function) for a solid, liquid and gas

- We computed RDF regarding V-V, O-O, V-O and total (their sum)



Total RDF of V_2O_3 at 1000 K



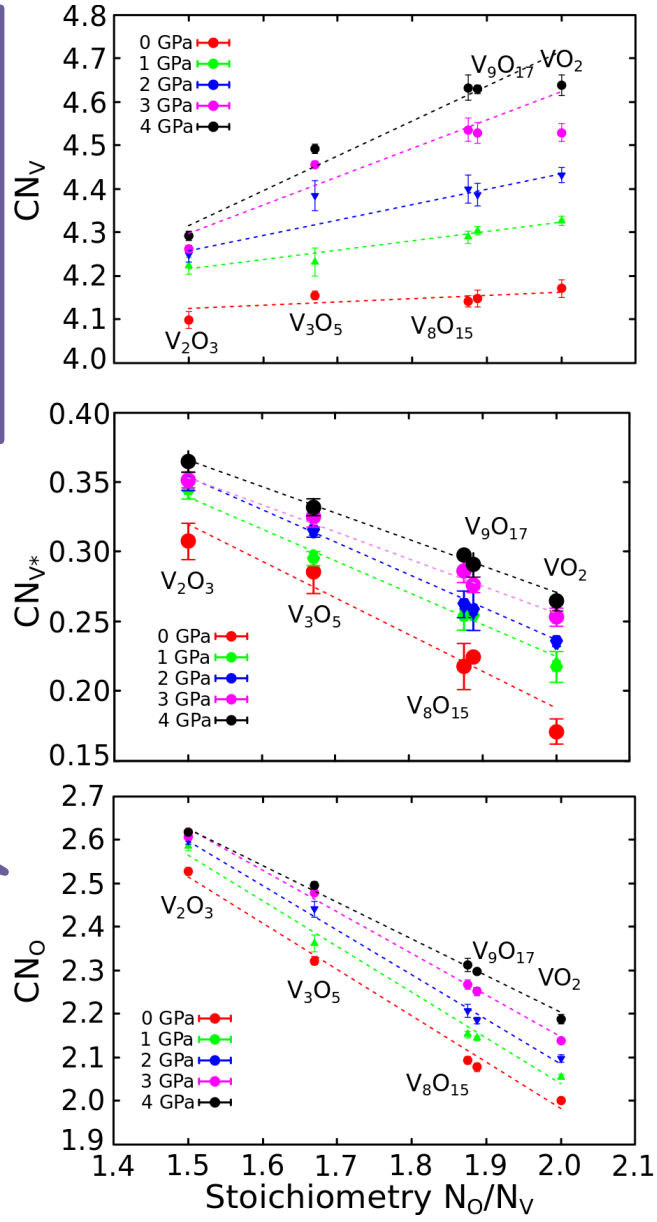
Total RDF of V_2O_3 at 4 GPa

Structural analysis of V_xO_y – Coordination Numbers (CN)

- CN (coordination number) represents average number of formed bonds of a certain atomic type

- CN_v → coordination number of V
- CN_o → coordination number of O
- CN_{v^*} → coordination number counting bonds between V atoms in V_xO_y and O atoms in V_2O_5

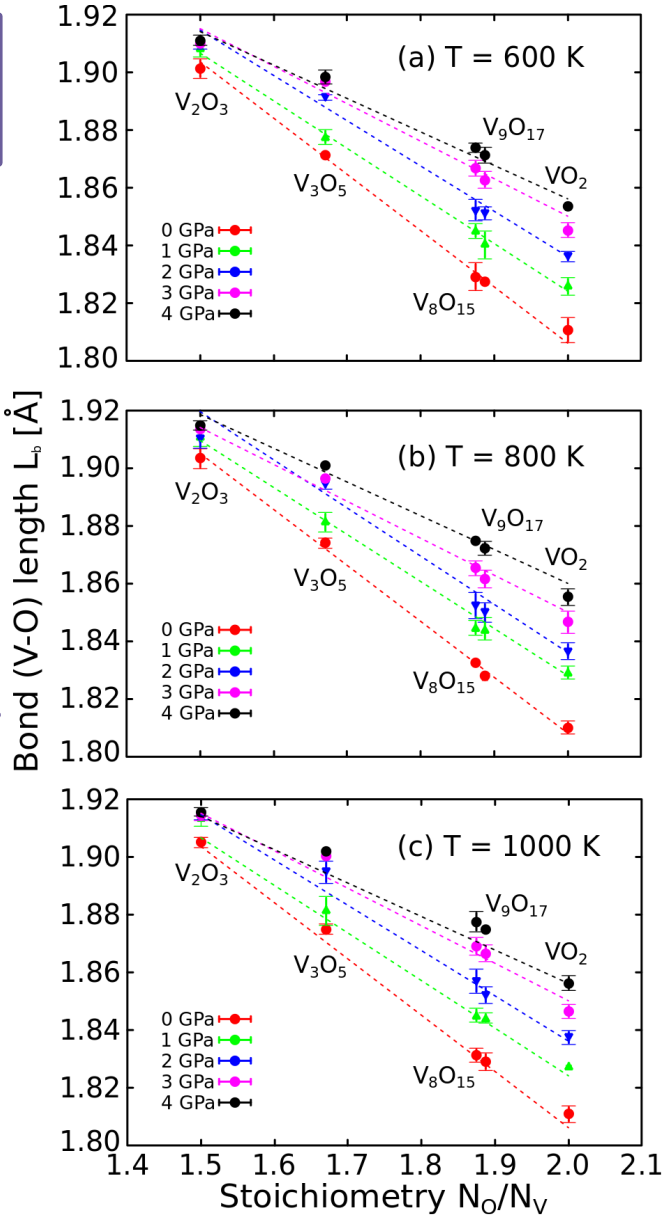
- CN_V, CN_{V^*} and CN_O depending on stoichiometry N_O/N_V for all normal loads F_z at T = 1000 K



Structural analysis of V_xO_y – Bond (V-O) length

- We computed average bond (V-O) length L_b
  → insight into amorphous V_xO_y network connectivity

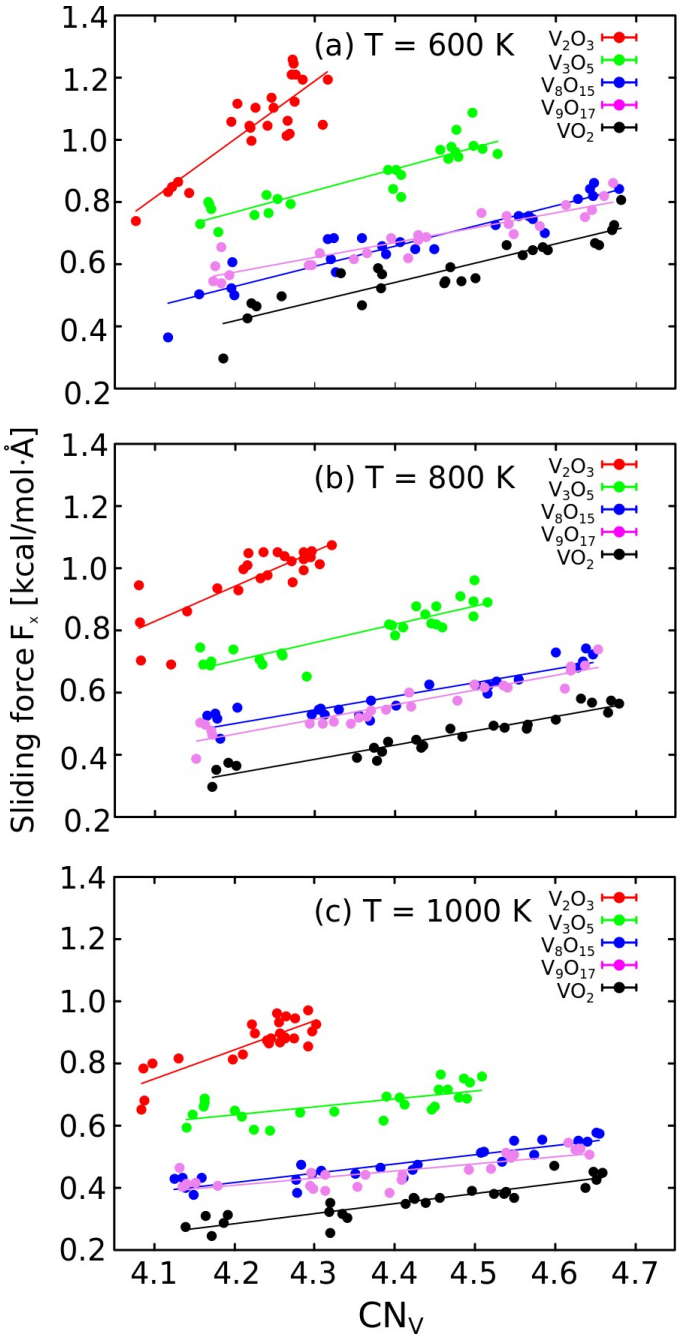
- Bond (V-O) length L_b depending on stoichiometry N_O/N_V for all normal loads F_z and temperatures T



Tribological properties-structure relation – F_x vs. CN_v

- Sliding force F_x vs. coordination number CN_v for all stoichiometries V_xO_y and temperatures T

- Separation of results depending on stoichiometry
- Linear increase of F_x with the increase of CN_v
- More or less pronounced grouping of points depending on the normal load F_z



Conclusions

- Considering different oxides with a fixed N_v = 144, and N_o computed according to stoichiometry, models realistic conditions of oxidative environments with different content of oxygen

- Tribocontact of two fixed V_2O_5 layers and thermalized V_xO_y lubricant between them:
  → Under high temperature/pressure all V_xO_y lubricants are amorphous, which is a preferable structural property, since they can effectively provide lubrication and friction reduction

- Effectivity of V_xO_y lubricants: how low is COF and does it depend on stoichiometry?

→ Each of the considered V_xO_y stoichiometries enables lubrication with a low friction coefficient (COF < 0.2 at T = 800 and 1000 K; COF ~ 0.2 at T = 600 K)

→ We obtained that COF decreases with increase of temperature T and it weakly depends on stoichiometry V_xO_y

- We explained the dependence of offset F_x^0 (related to the adhesion component of friction force) on stoichiometry V_xO_y with structural analysis based on the coordination number CN_{v^*}

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contact: igor@ipb.ac.rs (expressions of interest); mdasic@ipb.ac.rs
website: ultimate-i.eu

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THANK YOU FOR YOUR ATTENTION!

ХВАЛА НА ПАЖЊИ!