基于结构导向集总、量子化学和分子动力学的生成抗磨损膜的摩擦化学动力学模型

Lubricant - Chemistry Kinetic Model of Antiwear Film Formation by SOL and quantum chemical molecular dynamic approach

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动机　Motivation

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- 润滑抗磨添加剂用于控制摩擦部件磨损以满足可持续发展目标，特别是碳达峰和碳中和的需求

  Lubricant antiwear additives are used to control the wear of rubbing parts and thus meet sustainable development goals, in particular carbon peak and carbon neutral needs

- 抗摩擦膜的形成和去除是复杂的摩擦化学反应过程，涉及到众多参与物分子和各种边界润滑条件

  Antiwear film formation and removal are complex tribochemical reaction processes, which involve both of considerable molecular compositions of participating materials and various boundary lubrication conditions.

- 受限于试验方面无法直接观察到基本的摩擦化学反应途径，生成抗摩擦膜的机理还不能完全理解

  Mechanisms of film formation are poorly understood because they arise within a sliding contact that cannot readily be directly probed and observed experimentally

- 基于时间空间多尺度机械、材料、热和化学变量间相互作用数值模型能确定性模拟这些膜的生成

  Completely deterministic modeling of such films is possible based on the complex interactions between the numerous mechanical, material, thermal, and chemical variables over disparate magnitudes of time and length scales

方法　Methods

结构导向集总方法

Structure oriented lumping (SOL) approach

- 结构导向集总(SOL)方法的基本概念是任何摩擦化学的分子能被一组特定的结构特征或组合描述和表现。SOL方法将这系列组合成其元素代表特定结构特征数量的向量。由于每个元素都是作为一个完整分子的增量部分存在而不是单独存在，这些向量元素被称为结构增量。基于参加物材料的分子块和摩擦化学反应规则，边界润滑的润滑剂-化学动力学模型能在分子水平描述复杂的摩擦化学反应过程和预测抗磨损膜的形成和移除。

The basic concept of the SOL approach is that any tribochemical molecule can be described and represented by a set of certain of structural features or groups. The SOL approach organizes this set as a vector, with the elements of the vector representing the number of specific structural features. These vector elements are referred as structural increments, because each element exists as an incremental part of a complete molecule, and not by itself. Molecules are built from these increments. Based on the molecular lump of participating materials （e.g., lubricants, additives, tribopairs, debris, intermediate and final products）and rules of tribochemical reaction, the lubricant-chemistry kinetic model of boundary lubrication can describe the processes of complex tribochemical reaction on molecular level and predict antiwear film formation and removal.

参与摩擦化学反应分子组成的SOL表征

SOL Characterization of participating molecular compositions in tribochemical reactions

- 构建结构导向集总的第一步是把参与分子组成转换成它的分子矩阵，它是化学计量矩阵，可以被计算机通过结构向量识别和读取。

The first step to build the structure-oriented lumping is to transform participating molecular composition into its molecular matrix, which is stoichiometric matrix and can be identified and read by computers, through structure vectors

- 边界润滑膜的形成和去除的润滑剂-化学是复杂的有大量参加物和生成物的化学反应系统，非常详细地分析分子组成和研究摩擦化学反应动力学不可能允许包括所有分子和基础处理.

lubricant-chemistry of antiwear film formation and removal is the complex reaction systems, which have so large number of both reactants and reactions that measuring the molecular composition and studying the kinetics in sufficient detail are not possible to allow a complete molecular and fundamental treatment

- 分子集总中的结构向量表征分子中有什么结构而不是它的细节，每个结构向量有它相应的向量符号, 选择一系列的种子分子让化学反应产生覆盖属性和成分范围的产物。根据可能的参与物材料的分子结构扩大种子分子族，通过合并一些具有相似的化学反应特征和结构特征的分子以确定最终的种子分子。

The structure vector s in molecular lumps represent what structures are present in a molecule, but not its arrangement, Each structure vector has its corresponding vector symbol, A set of seed molecules are chosen to allow chemical transformations to generate products that populate the property and composition ranges, According to the possible molecular structures of participating materials, the above classes of seed molecules are extended, and the final seed molecules are determined by merging some molecules with similar reaction characteristics or structural characteristics.

摩擦化学反应机理和规则
Mechanisms and rules of tribochemical reaction

- 参与物和边界润滑条件决定摩擦化学反应机理，给定边界润滑系统中摩擦化学反应机理的所有信息是重要的。

Mechanisms of tribochemical reaction depend on participating materials and boundary lubrication condition, it is important to understand thoroughly all the information on mechanisms of tribochemical reactions for a given boundary lubrication system.

- 采用有限的结构组描述上千个成份能应用有限的化学反应规则建立相当多的构成混合物复杂反应网络的反应。反应规则是判断反应物分子矩阵转换到产物分子矩阵的基础, 它包括确定分子是否有反应必需的增量的选择规则和通过简单的数学算法把反应结构向量转换到产物结构向量并确定边界膜生成和移去位置的规则。反应规则需要由逻辑结构表征使计算机能识别。

Using a limited set of structural groups to describe thousands of components enables the use of a limited set of reaction rules to establish the rather large number of reactions that constitutes the complex reaction networks of mixtures. Reaction rules are the basis for judging the transition of the reactant molecular matrix to the product molecular matrix. It includes reactant selection rules, which determine if a molecule has the increment(s) necessary for the reaction, and product generation rules, which convert the reactant structure vector to the product structure vector through a simple mathematical operation and determine the locations of antiwear film formation and removal. The reaction rules need to be characterized by logical constructs for the convenience of computer recognition.

- 建立反应规则的基本原则是采用深度学习策略在给定摩擦化学系统的边界膜生成和移去过程中忽略次要的反应和保持关键的反应。

the basic principle of formulation of the reaction rules is ignoring minor reactions and retaining key reactions based on the antiwear film formation and removal processes of the given tribochamical systems using deep learning.

反应速度常数 – Arrhenius法则

Reaction rate constants – Arrhenius form

一些反应速度常数能通过文献或实验获得，但是许多不符合求解上述微分方程的要求。反应速度常数能由下列的**Arrhenius**法则和过渡态理论计算得到：

Some reaction rate constants could be obtained from the literatures or by experiments, but maybe far from the standard to solve such differential equations. The reaction rate constants can be calculated by the Arrhenius law and the transition state theory:

$$k = \frac{k_B T q^*}{h q^A} exp\left(-\frac{\Delta E}{RT}\right)$$

- k_B – 玻尔茨兹曼常数　Boltzmann constant；h – 为普郎克常数　Planck constant；R – 理想气体常数 ideal gas constant；T – 温度　　local temperature；　q^*，q^A– 分别为过渡态和反应物的分子配分函数 molecular partition function of transition state and reactant respectively；ΔE – 过渡态和反应物的摩尔能垒 molecular energy barrier；
- MS软件中的量子化学分析DMol³模块和具有化学反应势的大规模原子分子并行模拟器LAMMPS软件可以求解 q^*，q^A和ΔE

q^*，$q^A$and ΔE can be obtained by using QM Materials Studio DMol³ software and MD LAMMPS with ReaxFF potential

摩擦化学反应的反应网络和动力学微分方程

Reaction network and kinetic differential equation

- 用每个反应规则作为外循环、每个结构向量组作为内循环对混合物的所有成分施加反应规则，产生表征化学过程的整个反应网络。生成整个网络计算机程序用分类处理以自动构成模型的微分速率和动力学平衡方程。

Application of all rules to all components of the mixture by using each reaction rule as the outer loop and each structure vector group as the inner loop generates the entire reaction network representing the chemistry of the process. Computer programs generating the entire network use sorting procedures to automatically construct the differential rate and energy balance equations for reactor modeling.

- 由于所有的反应都假设为一阶不可逆，反应网络等价于分子集总的简单运动微分方程，该方程可用等效于传统的4-5阶Runge-Kutta法且非常适合解SOL系统动力学模型的方法求解。

Because all reaction is assumed as first order irreversible, the reaction network is equivalent to simple kinetic differential equations of the molecular lumps, which are solved with the approach, which is equivalent to the classical fourth-and fifth-order Runge-Kutta method and is very suitable for solving the dynamic model of SOL system .

- 这个方法中计算效率是关键的优先级，没有有效的算法，这种类型的建模可能不可行，更不实际。对给定的摩擦化学反应系统，优化模型的计算以能更详细地分析分子成分和在某种程度上减少计算的复杂性。

Computational efficiency is a key priority in this work, without an efficient approach, this type of modeling may not be feasible, much less practical. For a given tribochemical reaction system, model calculation is optimized in order both to ensure a more detailed description of the molecular compositions, but also and reduce the computational complexity to a certain extent.

分子集总的摩擦化学反应的动力学微分方程

Kinetic differential equations of the molecular lumps

$$\begin{bmatrix} \frac{dy_1}{dt} \\ \vdots \\ \frac{dy_n}{dt} \end{bmatrix} \times \begin{bmatrix} \sum_{i=1}^{n} k_{i,i\in\Omega_{11}} & \cdots & \sum_{i=1}^{n} k_{i,i\in\Omega_{n1}} \\ \vdots & \ddots & \vdots \\ \sum_{i=1}^{n} k_i, i \in \Omega_{1n} & \cdots & \sum_{i=1}^{n} k_{i,i\in\Omega_{nn}} \end{bmatrix} = \begin{bmatrix} y_1 \\ \vdots \\ y_n \end{bmatrix}$$

y_i is the concentration of molecule i,

k_i is the reaction rate constant for rule i,

Ω_{ij} is the associative set of k_i corresponding to molecule i and j

混合量子化学分子动力学和机器学习方法

Hybrid quantum chemical molecular dynamic and machine learning approach

- MS软件中密度泛函理论量子力学分析模块DMol^3　　QM Materials Studio DMol^3 software

第一性原理的密度泛函理论方法，广义梯度梯度近似下的 PW91交换关联函数, 零点校正，采用完全线性同步/二次线性同步方法搜索反应的过渡状态。

First principles DFT, the exchange-correlation energy functions were deduced in terms of spin-polarizaed Perdew-Wang (PW91) of the generalized gradient approximation (GGA), Zero-point vibrational energy correction (ZPE), complete linear synchronous transit and quadratic synchronous transit.

- 具有化学反应力场的分子动力学分析软件LAMMPS　　MD LAMMPS with ReaxFF force field

最小化和动力学模拟采用LAMMPS软件，所有原子间的化学反应作用由ReaxFF力场描述，模型先做能量最小化处理，然后做分子动力学分析。

Minimization and dynamics simulations were performed with the LAMMPS simulation package, all atomic interactions were modeled by ReaxFF force field. The model was energy minimized, then dynamics were run.

- 机器学习算法　　Machine learning technique

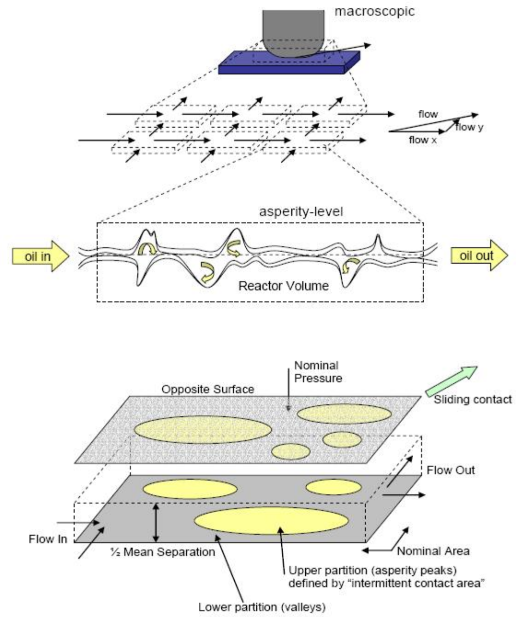
用混合量子化学分子动力学模拟和试验产生用于机器学习训练、验证、试验和预测的高通量合成数据，进行深度学习以了解微观结构特征与多尺度特性间的因果关系。

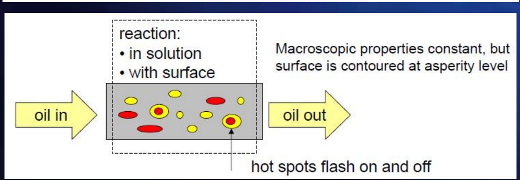
Both hybrid quantum chemical molecular dynamics simulations and experiments were conducted to generate high-throughput synthetic data for machine learning training, validation, testing and prediction. Deep learning was exploited to understand the causality between the microstructural features and the multiscale properties.

模型阐述 Model formulation

反应控制体及其空间分区

Reactor volume and spatial sub-partition





考虑二表面a和b，表面a和b的间歇接触面积分别是$A_{i,a}$和 $A_{i,b}$，真实和名义接触面积分别是A_r和A_n，名义接触面积上任意接触点落在间歇接触面积a和b上的概率分别等于 $A_{i,a}/A_n$ 和$A_{i,b}/A_n$，则在该点的接触概率等于联合概率：

For two surfaces a and b, $A_{i,a}$ and $A_{i,b}$ are the intermittent contact areas of surfaces a and b. A_r and A_n are the real and nominal contact areas. The probabilities that the point falls within the intermittent contact areas of surface a and b are equal to $A_{i,a}/A_n$ and $A_{i,b}/A_n$. Then the probability of contact at this point is then equal to the joint probability:

$$P[a \in i, b \in i] = \left(\frac{A_{i,a}}{A_n}\right)\left(\frac{A_{i,b}}{A_n}\right)$$

2D/3D表面形貌仪测得的表面形貌、扫描电镜、原子力显微镜测得的数据由深度卷积生成式对抗网络处理以获得间歇接触面、名义接触面积上任意接触点落在间歇接触面上的概率及联合概率。

The surface profiles measured by 2D/3D surface profilometers, SEM, conductive atomic force microscopy (AFM) are treated by deep convolutional generative adversarial networks DCGANs in deep learning for $A_{i,a}$, $A_{i,b}$, A_r, A_n, $A_{i,a}/A_n$, and $A_{i,b}/A_n$.

反应控制体的时间分区

Temporal sub-partition of reactor volume

估计上表面分区的一个点实际上与相反表面接触时间的总分数是必要的。计算对应于给定时间步长的平均闪温时，仅考虑上表面分区和实际接触持续的时间。为达到表面间的力平衡使瞬间和滑动间保持一致，真实接触的部分时间必须等于真实接触面积与间隙接触面积之比。这能以动量守恒来表征：

It is necessary to estimate the overall fraction of time that a point on the upper surface partition actually spends in contact with the opposite surface. Then, when an average flash temperature is calculated for a given time step, it will only be applied to the upper surface partition, and only for the duration of actual contact. In order for the force balance between the surfaces to remain consistent between the instantaneous and sliding cases, the fractional duration of real contact must be equal to the ratio of real to intermittent contact areas. This can be shown in terms of conservation of momentum:

$$\overbrace{\underbrace{P_{nom}A_{nom}}_{\text{macroscopic}}dt = P_{asp}A_{real}dt}^{\text{static or instantaneous}} = \overbrace{P_{asp}\underset{\uparrow\,\text{discretized}}{A_{intermittent}}t_{contact}}^{\text{time averaged}}$$

which implies that:

$$\frac{A_{real}}{A_{intermitted}} = \frac{t_{real}}{t_{nom}}$$

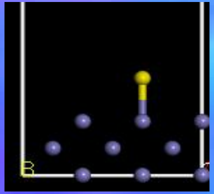
P_{nom}和P_{asp} 分别是名义和平均接触压力，由深度卷积生成式对抗网络处理以获得.

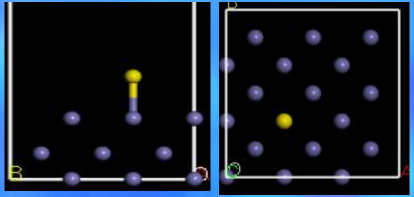
P_{nom} and P_{asp} are the nominal and average contact pressures. deep convolutional generative adversarial networks DCGANs for P_{nom} and P_{asp}.

初步结果和讨论
Preliminary results and discussion

结果1 – 气相环境中S原子和PO分子在Fe(100)，Al(100)和Cu(100)面的吸附构型和吸附能。黄色–S，棕褐色–Fe，橘黄色–Cu，粉红色–Al，暗红色–P，括号内值是吸附能（单位：kJ·mol^{-1}）

Results 1 - Optimized adsorption configurations and energies of S atom and PO molecule on Fe(100) , Al(100) , Cu(100) surfaces in gas phase (IT: Initial-Top; Yellow - S, brown - Fe, orange - Cu, and pink - Al。 Value in parenthesis is adsorption energy (unit: kJ·mol^{-1}))


Initial-Top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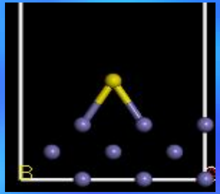
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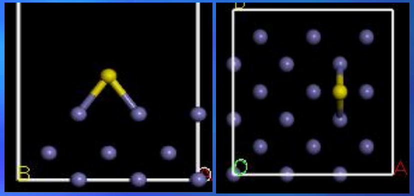
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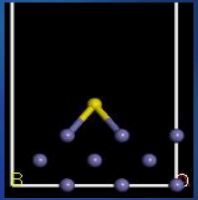
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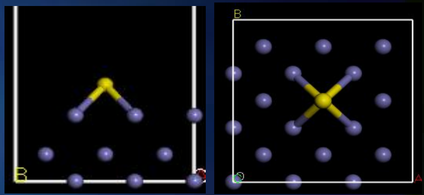
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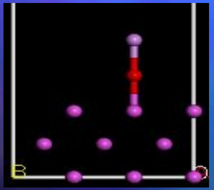
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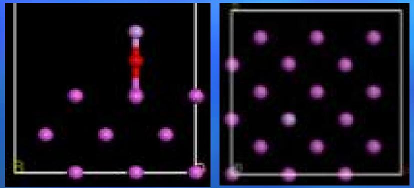
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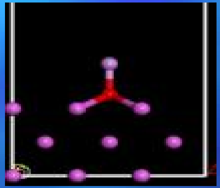
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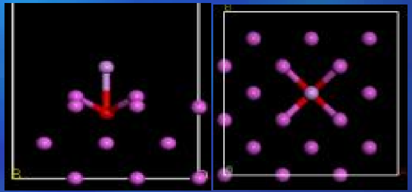
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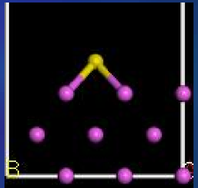
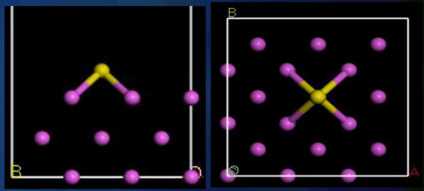

Initial-4-F hollow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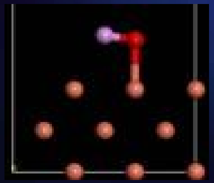
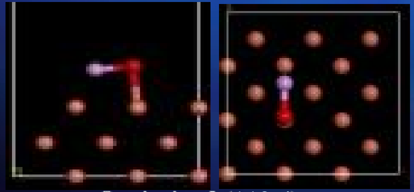

Initial-Top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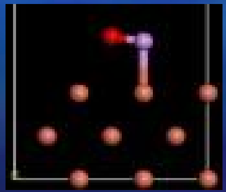
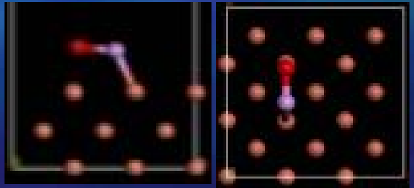

IT Cu-P-O angle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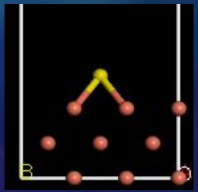
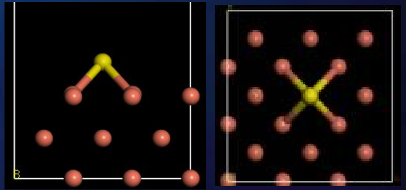
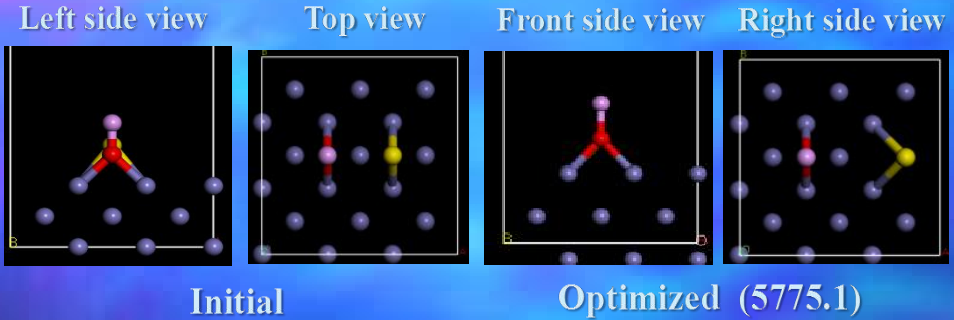

Initial-4-F hollow

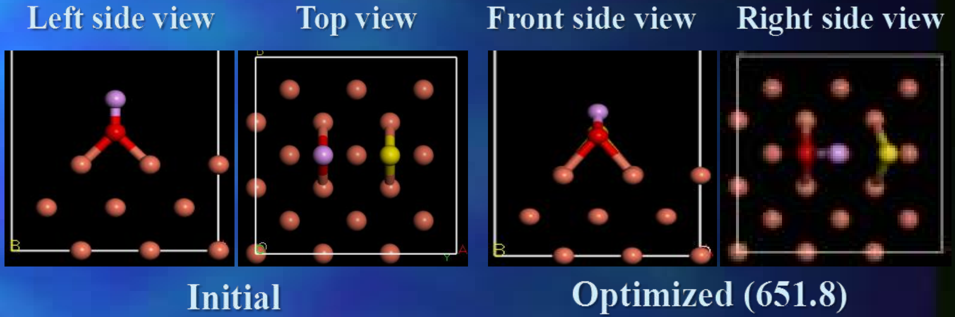

Optimized (478.2)

结果2 - 气相环境中S原子和PO分子在Fe(100), Al(100)和Cu(100)面的吸附构型和吸附能。黄色-S，红色 - O， Cu棕褐色 - Fe，橘黄色 - Cu，粉红色 - Al，括号内值是吸附能（单位：kJ·mol^{-1}）

Results 2 - Optimized adsorption configurations and energies (unit: kJ·mol^{-1}) of S atom and PO molecule on Fe(100) , Al(100) and Cu(100) surface in gas phase. Brown - Fe, red - O, cmyk - P, orange - Cu, pink - Al.



Fe-O-P and Fe-S

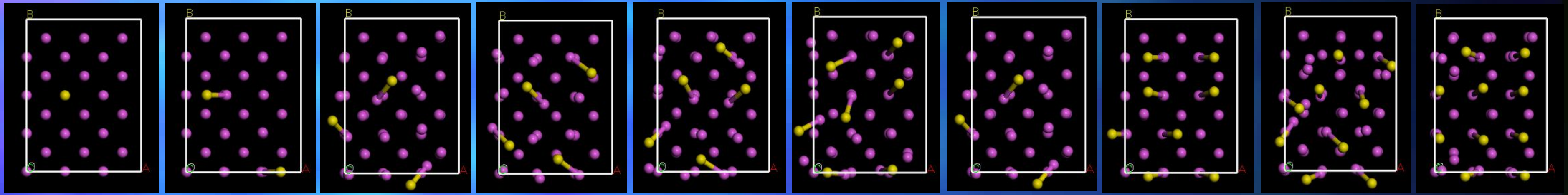


Cu-O-P and Cu-S

Al-P-O and Al-S

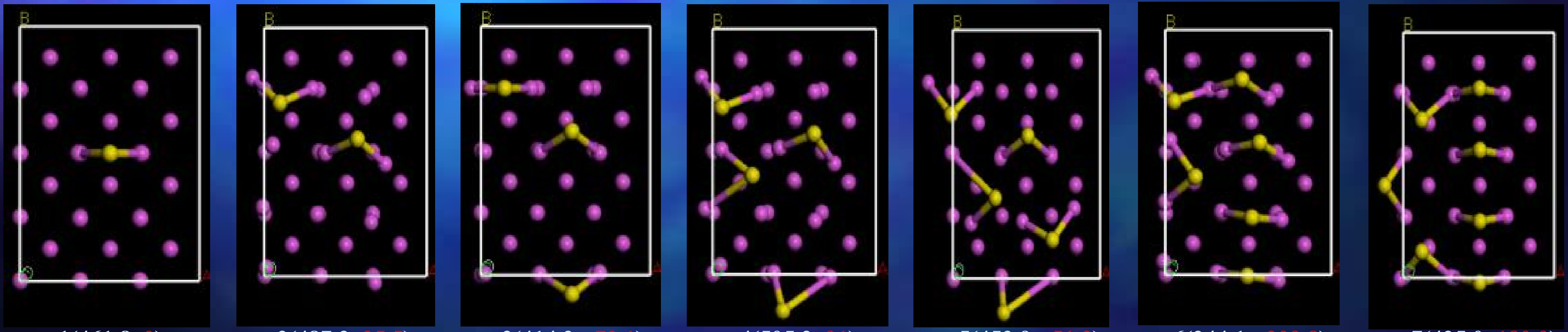
结果3 - 气相环境中不同覆盖度下S原子在Al(100)表面顶位(a)和桥位(b)上最稳定的吸附结构、对应的吸附自由能和排斥能。括号前的值是吸附的S原子数，括号内淡兰色值是吸附能、红色是排斥能。

Results 3 - The most stable configurations, adsorption and lateral repulsive energies (unit: kJ·mol-1) of the stepwise S atom adsorption at the top (a) and bridge (b) sites on Al(100) surface in gas phase (in parenthess, black value: adsorption energies; red value: lateral repulsive energies)



1(383.4, 0) 2(502.0, 118.6) 3(485.6, -16.4) 4(470.9, -14.7) 5(482.4, -99) 6(242.2, 141.2) 7(468.8, -85.4) 8(168.6, 214.8) 9(615.2,-232) 10(-105.7,489)

(a) 在顶位 at the top sites



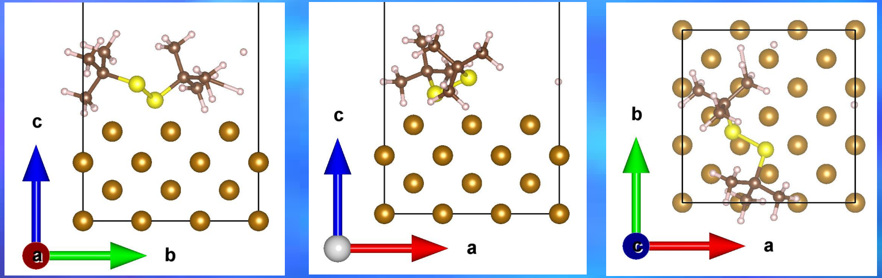
1(461.8, 0) 2(487.3, 25.5) 3(414.2, -73.1) 4(505.2, 91) 5(453.9, -51.3) 6(244.1, -209.8) 7(425.0, 180.9)

(b) 在桥位 at the bridge sites

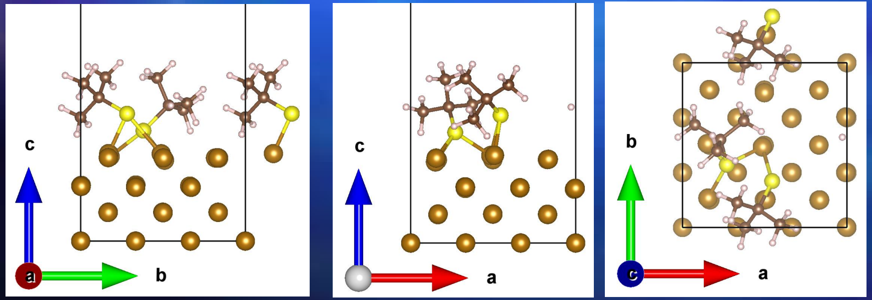
结果4 - 用 ReaxFF Fe/Cr/O/S 化学反应力场的LAMMPS计算di-tert-butyl disulfide分子在Fe(100)表面上最稳定的水平吸附结构。球体颜色表示棕色 - Fe，黄色-S，灰色 - C，白色 - H。

Results 4 - Adsorption geometry calculated by LAMMPS with ReaxFF force field for Fe/Cr/O/S for horizontal adsorption configuration on an Fe(100) surface. Atoms of Fe are brown, Sphere colors represent yellow - S, gray - C, white - H, and brown - Fe

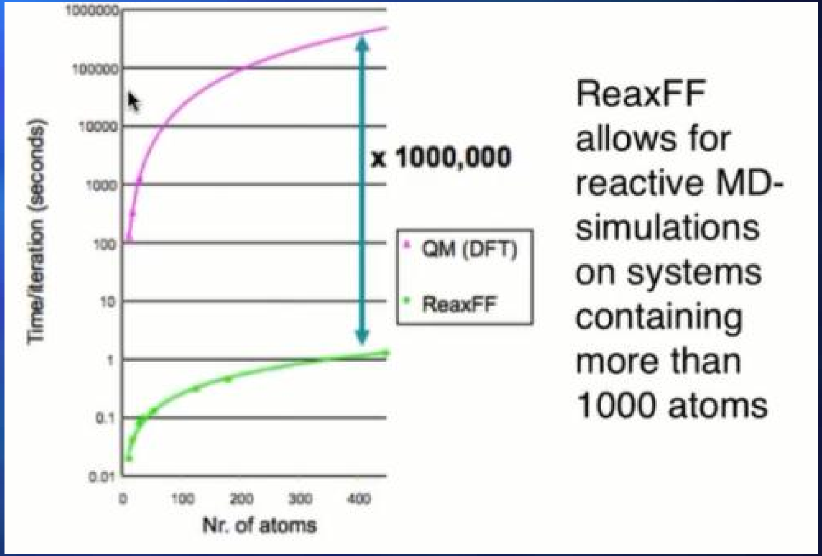
Front side view　Right side view　Top view



Initial



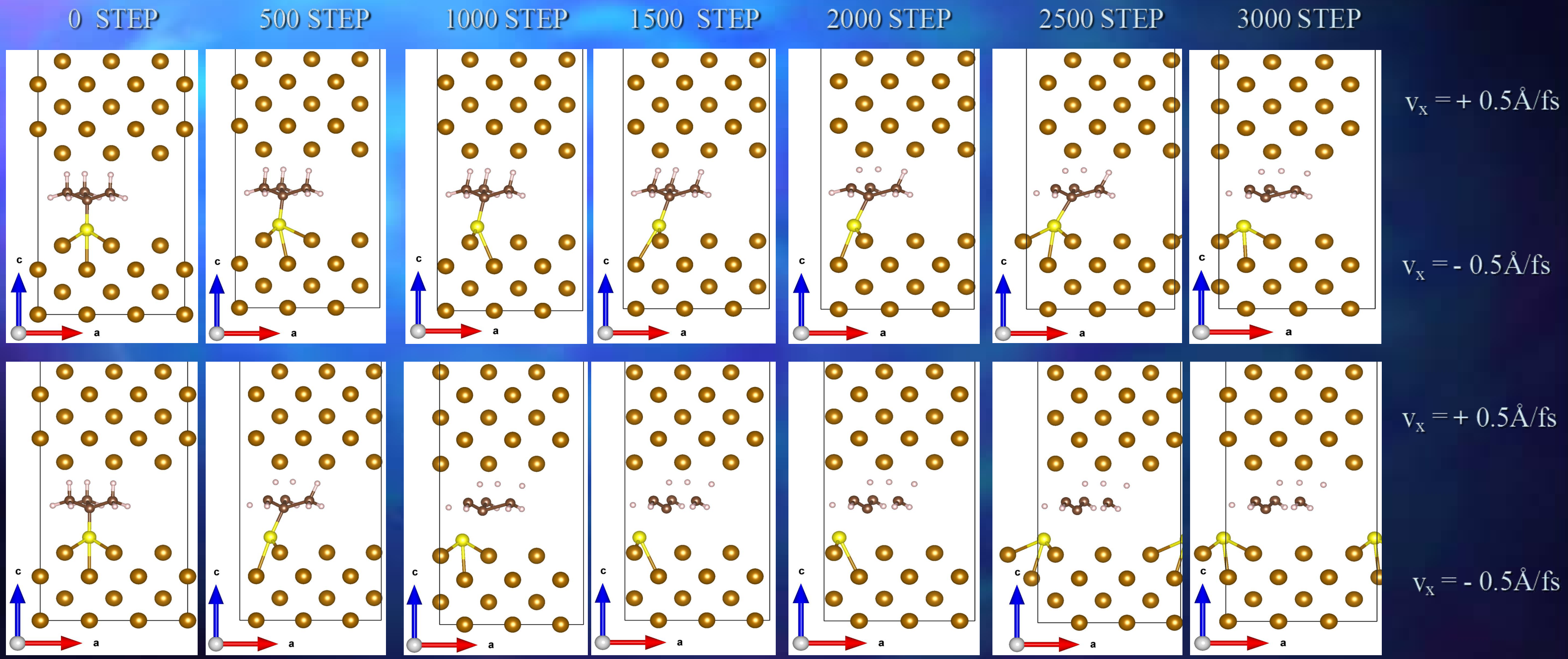
Minimized



ReaxFF allows for reactive MD-simulations on systems containing more than 1000 atoms

结果5 - 用 ReaxFF Fe/Cr/O/S 化学反应力场的LAMMPS分析剪切速度对tert-butyl sulfide与铁表面间化学反应的影响。剪切方向沿X（a）轴，温度300 K。球体颜色表示棕色 - Fe，黄色-S，灰色 - C，白色 - H。

Results 5 - Effects of shear speeds on reaction among tert-butyl sulfide and iron surfaces at temperature 300 K by LAMMPS with ReaxFF force field for Fe/Cr/O/S，shear in the x (a) direction. Sphere colors represent yellow - S, gray - C, white - H, and brown - Fe



讨论　Discussion

- S原子能在Fe(100), Al(100)和Cu(100)面上化学吸附　Chemisorption of S atom could occur on Fe(100), Al(100), and Cu(100) surfaces
- PO分子能在Fe(100)面上无条件化学吸附，而在Al(100)和Cu(100)面上有条件化学吸附

  Chemisorption of PO molecule could occur on Fe(100) surface unconditionally, and on Al(100) and Cu(100) surfaces conditionally
- S原子在Fe(100), Al(100)和Cu(100)面上最稳定的吸附位置顺序是：四重穴位、桥位、顶位

  The most stable adsorption site order of adsorbed S atom on Fe(100), Al(100), and Cu(100) was 4F hollow, bridge, top
- PO分子在Fe(100)面上最稳定的吸附位置顺序是：四重穴位、桥位、顶位

  The most stable adsorption site order of adsorbed PO molecule on Fe(100) was 4F hollow, bridge, top
- 分子键角影响吸附结构和吸附能，在Fe(100), Al(100)和Cu(100)表面上原子和分子间的横向排斥影响吸附的构型和吸附能

  Molecule bond angle influenced adsorption configurations and energies. Lateral repulsion among atoms and molecules on Fe(100), Al(100), and Cu(100) surfaces influenced adsorption configurations and energies
- 表面上吸附物的覆盖度取决于吸附表面和位置

  The coverage of the species adsorption on surfaces depended on adsorption surface and site
- 剪切加速化学吸附（铁-硫键形成）和tert-butyl离子的释放（硫-碳键解离）

  Both chemisorption (Fe−S bond formation) and tert-butyl release (S−C bond breaking) were accelerated by shear
- 本研究结果有助于深入了解目前各种使用的理论机理相对重要性、结合机器学习技术合理建立化学反应规则和反应控制体容积空间和时间的分区。本文提出的方法能用于摩擦副、系统的运行动力学、润滑剂和添加剂的设计

  The results of this study should provide insight on the relative significance of the various theoretical mechanisms that are believed to be at work, rational rules of tribochemical reaction and spatial and temporal sub-partition of the reactor volume by using machine learning technique. This approach could be a useful tool to design tribopairs, lubricants and additives

结论　Conclusion

- 本文提出了基于结构导向集总、量子化学和分子动力学的生成抗磨损膜的摩擦化学动力学模型，它是基于机理 和原子分子尺度的算法，涉及到参与物分子组成的特征、摩擦化学反应机理和规则、摩擦化学反应的反应网络和微分方程。因此，完全理解给定的边界润滑系统中摩擦化学反应机理的所有信息和建立反应规则时忽略次要的反应和保持关键的反应是重要的。

This study proposed the lubricant-chemistry kinetic model of antiwear film formation by oil additives based on structure-oriented lumping (SOL) approach. It is the mechanism-base and atom **molecular level approach and involves characterization of participating molecular compositions, mechanisms and rules, reaction network and kinetic differential equation of tribochemical reactions. Therefore for the given tribochamical systems, it is important to understand thoroughly all the information on mechanisms of tribochemical reactions, and then to ignore minor reactions and retain key reactions based on the antiwear film formation and removal processes in formulation of the reaction rules.**

- 同时实现计算的效率、精度和稳定性能可根据其在分子集总矩阵中的分子含量确定参与物材料的特殊分配，用改进传统的**4-5**阶**Runge-Kutta**法求解分子集总的运动微分方程，用混合量子化学分子动力学和机器学习方法确定反应速度常数、反应控制体容积及其空间和时间分区和间歇接触区域，优化反应网络的周期数和调节分子集总的总数。

Accuracy, computational efficiency, and stability can be simultanerously achieved with applications of the specific distribution of the particitating materials for its molecular content in the molecular lump matrix, modified classical fourth-and fifth-order Runge-Kutta method for the kinetic differential equations of the molecular lumps, hybrid quantum chemical molecular dynamic and machine learning approach for the reaction rate constants, the conceptions of reactor volume, its spatial and temporal sub-partitions, and area of intermittent contact for descriptions of the products, reactants, and states of interest within a tribological contact, the motion equations for dynamic loading conditions, optimization of cycle times of reaction network, and regulation of total number of the molecular lumps.

- 本文提出的方法能用于摩擦副、系统的运行动力学、润滑剂和添加剂的设计。

  This approach could be a useful tool to design tribopairs, lubricants and additives.

感谢聆听　　Thank You for Attention

欢迎提问　　Questions