Coverage dependent Surface Interactions

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1 Introduction

In this document, the theoretical underpinnings of various additions made to the Cantera software targeting heterogeneous catalysis are explained in detail.

2 Coverage Dependent Lateral Interactions of Surface Species

2.1 Theory

In a typical coverage independent model, the surface species are assumed to be non interacting with each other and as such the short range interactions are ignored. However, when the coverage of any surface species is very high and if there is a finite short range interaction, the previous assumption is broken. The coverage dependent lateral interactions of the surface species are accounted for with many different analytical formulations. At University of Delaware, the lateral interactions are accounted for by their contribution to the formation enthalpy of a surface species. In this model, the contribution of lateral interactions to formation enthalpy of a surface species i is given as

$$\Delta H_i = \sum_j LI_{i,j}\theta_j, \tag{1}$$

where $LI_{i,j}$ represents the lateral interaction parameter between species i and j, and θ_j represent the coverage of species j. $LI_{i,j}$ need not be symmetric w.r.t. i and j. Further, the interaction strength parameters are given as piece wise linear functions of surface coverage. A two piece linear function, $L_{i,j}$, given as

$$LI_{i,j} = \alpha_{i,j} \quad \forall\, \theta_j < \theta_0 \tag{2}$$

$$= \beta_{i,j} \quad \forall\, \theta_j > \theta_0, \tag{3}$$

is defined by three parameters α, β, and θ_0. This model is also called 3 parameter model. Similarly, one can define a one-parameter model which is essentially a linear function in between the coverages 0 and 1, and 5-parameter model with 3 piece linear functions in between 0 and 1 coverages.

2.2 Code

Our implementation of the piecewise lateral interactions is general enough to account for arbitrary number of linear functions in the model definition. The defintion of lateral interactions is in the files `LateralInteraction(.h,.cpp)`. Further on, when extensions are omitted, it implies both .h and .cpp files. The implementation extends to `MultiSpeciesInterThermo`, `SurfLatIntPhase` and `InterfaceInteraction.h` as well. A sample input in XML and CTI formats is given below.

Program 1 Sample XML input file showing parts relevant to define interactions.

```
...

  <phase id="terrace" dim="2">
    <elementArray datasrc="elements.xml">H N Ru He</elementArray>
    <speciesArray datasrc="#species_data">
      N2(S1)   N(S1)    H(S1)    NH3(S1)  NH2(S1)  NH(S1)
      RU(S1)</speciesArray>
    <reactionArray datasrc="#reaction_data"/>
    <state>
      <temperature units="K">300.0</temperature>
      <pressure units="Pa">101325.0</pressure>
    </state>
    <thermo model="SurfaceCoverage">
      <site_density units="mol/cm2">2.1671e-09</site_density>
    </thermo>
    <interactionArray datasrc="#interaction_data"/>
    <kinetics model="Interface"/>
    <transport model="None"/>
    <phaseArray>gas bulk</phaseArray>
  </phase>

...

  <interactionData id="interaction_data">
    <interaction id="0001">
      <speciesArray datasrc="#species_data">N(S1) N(S1)</speciesArray>
      <floatArray name="strength" units="kcal/mol">-4.70179E+01, </floatArray>
      <floatArray name="coverage_threshold">0.00E+00, 1.00E+00, </floatArray>
    </interaction>

    <interaction id="0002">
      <speciesArray datasrc="#species_data">N(S1) H(S1)</speciesArray>
      <floatArray name="strength" units="kcal/mol">-1.77545E+01, </floatArray>
      <floatArray name="coverage_threshold">0.00E+00, 1.00E+00, </floatArray>
    </interaction>

    <interaction id="0003">
      <speciesArray datasrc="#species_data">N(S1) NH3(S1)</speciesArray>
      <floatArray name="strength" units="kcal/mol">-2.51631E+01, </floatArray>
      <floatArray name="coverage_threshold">0.00E+00, 1.00E+00, </floatArray>
    </interaction>

    ...

  </interactionData>

...
```

Program 2 Sample CTI input file showing parts relevant to define interactions.

```
...
interacting_interface(name='TERRACE',
                  elements="H N Ru He",
                  species="""N2(S1)   N(S1)    H(S1)    NH3(S1)  NH2(S1)  NH(S1)
                           RU(S1)""",
                  site_density=2.1671e-09,
                  interactions="all",
                  phases="gas BULK",
                  reactions='all',
                  initial_state=state(temperature=300.0, pressure=OneAtm))

...

lateral_interaction(['N(S1) N(S1)'],     [0, -47.0179], [0])
lateral_interaction(['N(S1) H(S1)'],     [0, -17.7545], [0])
lateral_interaction(['N(S1) NH3(S1)'],   [0, -25.1631], [0])
lateral_interaction(['N(S1) NH2(S1)'],   [0, -20.762],  [0])
lateral_interaction(['N(S1) NH(S1)'],    [0, -48.7823], [0])

...
```