ALD application

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Syntax:
app_style ald

- *ald=style name of this application*

Examples:
app_style ald

Description:
This application simulates the chemical reaction of atomic layer deposition (ALD) on a crystalline hafnium oxide lattice. This application reads in all lattice sites via the read_sites command.
This application stores 2 integers per lattice site. The first integer (i1) is the element on the site:

- *element=1=O*
- *element=2=OH*
- *element=3=HfX4O (adsorbed precursor and X shows amide group)*
- *...*

The second integer (i2) is the 'coordination' of the site.
The 3_fold lattice should be created using the read_sites, which gives details of its geometry, initial value, and neighbor connectivity. The 3_fold lattice is initialized by low coordinated O and OH as substrate. The remainder are vacant.
The event command is used to define what kinds of diffusion, dissociation, and densification occur in the model. The relative probability of each event is computed as a function of the rate, coordination number, and time specified in the event command. The details explained in the event command. Temperature is specified by the temperature command.
This application includes the interaction between the remaining precursor (steric effect) and influence of remaining fragments on adsorption sties (blocking). This is implemented using the neighbor list (see read_sites).
This application can be evolved only by a kinetic Monte Carlo (KMC). You must thus define a KMC solver to be used with the application via the solve_style command.

Restrictions:

This application can only be run in serial simulations, not parallel.

event command:

event type old1 new1 old2 new2 A n E coord pressureOn expression

- *type=1,2,3*
- *old1,old2=chemical species before reaction occurring*
- *new1,new2=chemical species after reaction occurring*
- *A= pre-factor or rate of adsorption*
- *n=exponential factor in Arrhenius equation*
- *E=activation energy*
- *coord=c.n. of the first lattice site*
- *pressureOn=0,1,2*
- *expression=details of reaction*

Examples:

event 1 O HfX4O 44879.2084 0 0.00 1 1 HfX4(g)+O(s)→HfX4...O(s)
event 1 HfX4O O 1.042296E13 0 1.00 2 0 HfX4(g)+O(s)→HfX4...O(s)
event 1 HfH2X2 HfHX 1.042296E13 0 0.80 4 0 HfH2X2→HfHX
event 1 HfH2X2 HfHX 1.042296E13 0 0.30 5 0 HfH2X2→HfHX
event 2 O OH OH O 1.042296E13 0 0.46 1 0 O→OH
event 2 O OH OH O 1.042296E13 0 0.75 2 0 O→OH
event 2 HfX4O HfX4OH OH O 1.042296E13 0 0.75 2 0 HfX4...O+OH→HfX4...OH+O
event 2 HfX4OH HfX4O O OH 1.042296E13 0 0.75 2 0 same
event 3 HfX2O O VAC HfX2 1.042296E13 0 0.20 0 0 HfX2...O+VAC→O+HfX2
event 3 HfX2OH OH VAC HfX2 1.042296E13 0 0.20 0 0 HfX2...OH+VAC→HfX2+OH
event 3 OH2HfX HfX VAC OH2 1.042296E13 0 0.30 4 0 OH2HfX+VAC→HfX+OH
event 3 OH2HfX HfX VAC OH2 1.042296E13 0 0.30 5 0 OH2HfX+VAC→HfX+OH

Description:

This command defines an event for the "app_style ald" application. It can be an event involving one or two lattice sites, as specified by *type*. The *type* 1 only changes the species of a site. The *type* 2 and 3 change the species

of a site and its second and first neighbor site respectively. App_style ald operates on a 3-fold lattice which contains monoclinic hafnium oxide sites. The chemical species in a site and its neighboring site specify the event. If *type* = 1, then only *old1* and *new1* are specified. If *type* = 2 or 3, then *old1, new1, old2,* and *new2* are specified. The chemical specify what atoms or fragment must be on those sites in order for the event to potentially take place. The possible atoms and fragment are specified in in.ald file.

For the adsorption events, A shows the rate given by Maxwell-Boltzmann statistics, while For the other events A shows the pre-factor.

n corresponds to 0 the original Arrhenius equation below.

E shows activation energy and the rate setting determines the relative rate at which the event will occur.

coord shows c.n. of species in the first site. E.g. in the first example above, an adsorption of precursor must be on an oxygen species with c.n.=1 for the event to be possible.

In ALD simulation, the respective adsorption reactions are turned on and off as simulation time advances. Adsorption reactions of the two precursors occur alternately as time progresses. *pressureOn* = 0 shows that the reaction is possible all simulation time. Similarly, 1 and 2 show metal pulse and oxygen pulse respectively. This option also used to filter out wasteful events.

$rate = A(T/T_0)^n exp(-E/kT)$

Where T is the temperature you have specified. In this case the rate setting should be in the energy units defined by the application's Hamiltonian and should be consistent with the units used in the temperature command.

Pulse and purge time command:

Syntax:
pulse_time T1 T3
purge_time T2 T4

- *T1=time for the metal pulse*
- *T2=time for the first purge*

- *T3=time for the oxygen pulse*
- *T4=time for the second purge*

Example:
pulse_time 0.0001 0.0001
purge_time 0.0001 0.0001

Description:

These commands set time for pulse and purge of a cycle in ald application. In the ALD process, gaseous precursors are admitted to the reactor in alternate pulses separated by periods of purging. To implement this in KMC, the respective adsorption reactions are turned on and off as simulation time advances. Adsorption reactions of the two precursors occur alternately as time progresses. During the purge, no adsorption reaction is allowed.
Diag_style ald command:

Syntax:
diag_style ald keyword value keyword value ...

- *ald=style name of this diagnostic*
- *zero or more keyword/value pairs may be appended*
- *see the diag_style command for additional keyword/value pairs that can be appended to a diagnostic command and which must appear before these keywords*
- *keyword=list*
- *list values = events or O or OH or HfX4O or ... or s1 or d1 or v1 or ...*
  O, OH, HfX4O = counts of how many lattice sites of this type exist
  events = total # of events for all sites
  sN,dN,vN = cumulative # of events for this reaction that have occurred.

Examples:
diag_style ald keyword yes list events O OH Hf HfX4O HfHX4O HfH2X4O HfH3X4O HfH4X4O s78 v18
Description:

The ald diagnostic prints out statistics about the system being modeled by app_style ald. The values will be printed as part of stats output and it can be in any order.
The O, OH, HfX4O and ... values will print counts of the number of chemical species of sites. The events value will print the total # of possible events that can occur as defined by the event command, given the current state of the lattice, summed over all sites.
The sN, dN, and vN values refer to a specific events that have occurred, as defined by the event command. The letter 's' means reactions involving a single site, 'd' means reactions involving a site and its second neighbor, and 'v' means reactions involving a site and its first neighbor. The N refers to which reaction (from 1 to the number of the type of reaction). For instance, 'v18' means the 18^{th} of type III reaction defined in your input script.
Restrictions:

This command can only be used as part of the app_style ald application.