Grand-Canonical Monte-Carlo

NSCCS ADF/ReaxFF Workshop

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Grand-Canonical Monte-Carlo
Intro

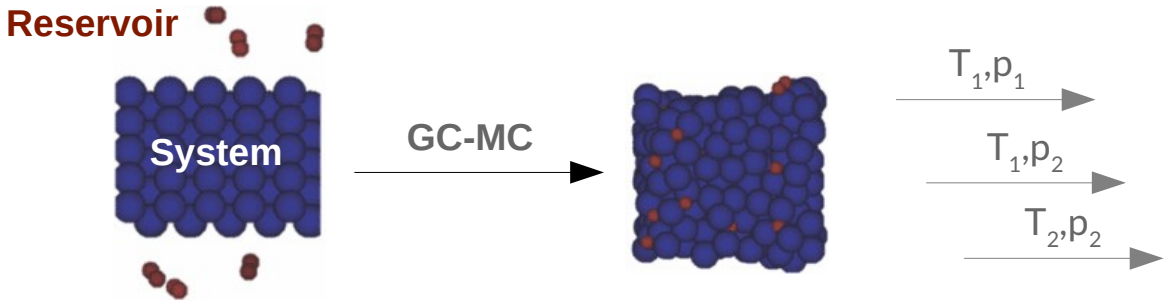
Task:

Model a system that is in
thermodynamic equilibrium
(e.g. sorption in multi-component systems)

MD (ambient P,T)
Limited by timescales,
Reactions are rare events

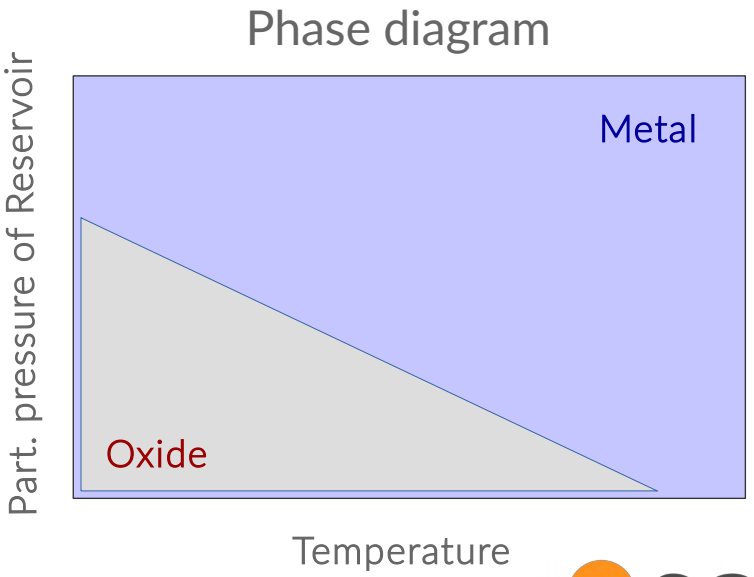
MD (high P,T)
High energy processes:
thermodynamically not feasible

Grand canonical MC: stochastical exchange of atoms (reservoir ↔ system) @ const. μ
-> create an $N_{System}VT\mu_{Reservoir}$ - Ensemble



Thermodynamic equilibrium:

$\mu_{Reservoir} = \mu_{System}$



Grand-Canonical Monte-Carlo

Under the hood

Monte Carlo moves & acceptance criteria:

1. Insert an atom into the system (random position)

$$P_{insert}^{accept} = min\left[1, \frac{V}{\Lambda^3 (N+1)} \exp[-\beta (E_2 - E_1 - \mu_{res})\right]$$

2. Remove an atom from the system (random atom)

$$P_{remove}^{accept} = min\left[1, \frac{N\Lambda^3}{V} \exp[-\beta (E_2 - E_1 + \mu_{res})\right]$$

3. Move an atom inside the system
   (random atom, random position)

$$P_{move}^{accept} = min\left[1, \exp[-\beta (E_2 - E_1)\right]$$

V: Volume of System
N: Num. exchangeable Particles
Λ: Thermal de Broglie wavelength
β: Boltzmann factor
E_2: Energy after MC-move
E_1: Energy before MC-move
μ_{res}: Chemical potential of reservoir

μ_{res}(p,T), T are the central parameters for this GCMC algorithm

Note:
Every MC-move is followed by a geomtry optimization (loose convergence criterium).
The three moves are generated with equal frequency.

Senftle et al.,J. Chem. Phys. **139**, 044109 (2013); http://dx.doi.org/10.1063/1.4815820

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Calculation of the chemical potential

The chemical potential of the reservoir, $\mu_{res}(p,T)$, sets the partial pressure of the simulation and depends on the Temperature. It needs to be re-calculated from thermodynamics data for the conditions that are about to simulated.

For diatomic molecules like O_2 the calculation is done as follows

$$\mu_{Res} = \mu_O(T,p) = \tfrac{1}{2}\,\mu_{O2}(T,p) = \tfrac{1}{2}\,[\mu_{O2}(T,p^0) + k_b T \cdot \ln(p^0/p) - E_d]$$

with $\mu_{O2}(T,p^0)$ calculated from published thermochemical data:

$$\mu_{O2}(T,p^0) = \Delta H_T - T \cdot S_T$$

$\mu_{O2}(T,p)$: chemical potential of O_2 at given Temperature (T) and partial Pressure (p)
$\mu_{O2}(T,p^0)$: chemical potential of O_2 at given Temperature (T) and standard Pressure (p^0)
E_d : ReaxFF dissociation energy of O_2
ΔH_T : Enthalpy at given Temperature, i.e. $H\text{-}H_{Tref\,=\,0K}$
S_T : Entropy at given Temperature

Senftle et al.,J. Chem. Phys. 139, 044109 (2013); http://dx.doi.org/10.1063/1.4815820

Hands on: Grand-Canonical Monte-Carlo

Inputfiles

GCMC does not have GUI-support (yet). The calculations will thus be run from the command line.
A listing of all input and output files can be found online, here only the central input options for this tutorial will be discussed.

The main input file is called **`control_MC`** it holds the GCMC settings. For now, the relevant ones being:

- **`niter`** – Number of GCMC Iterations
- **`mctemp`** – Temperature in K
- **`nmols`** – number of MC-molecule types
- **`cmpot`** – μ_{res} chemical potential of the reservoir in kcal/mol
- **`nmatom`** – Number of atoms in the molecule

Example:

Oxygen reservoir at p = 0.1 atm and T = 800K, 5000 GCMC steps @ $N_{sys}VT\mu_O$

```
niter  =  5000
mctemp = 800
nmols  = 1
cmpot  = -85.95
nmatom = 1
```

Note:

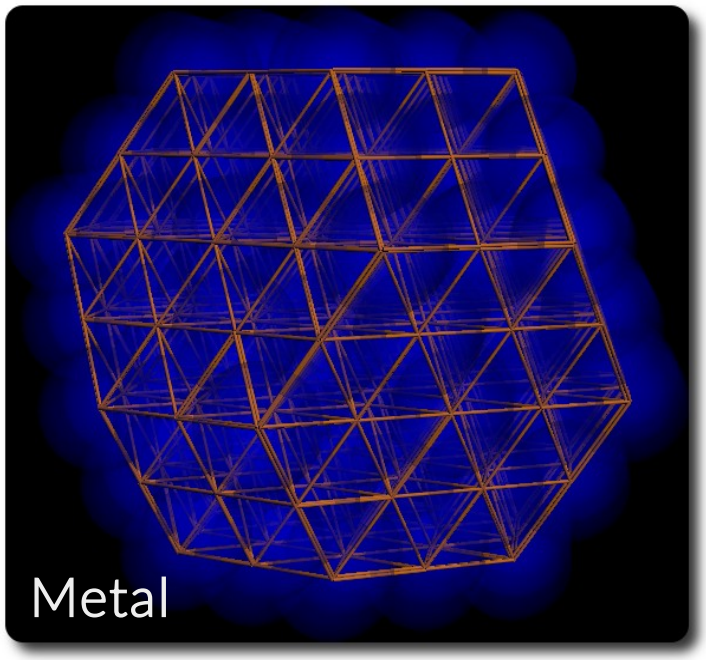
The partial pressure is set via **`cmpot`**, not via **`mcpress`**.
`cmpot` can be calculated as shown on slides 4-5 or in taken from these tables.

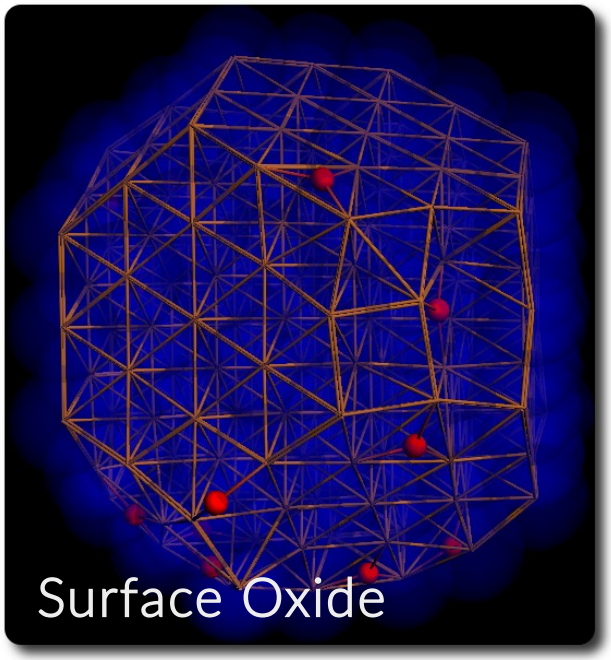
Hands on: Grand-Canonical Monte-Carlo

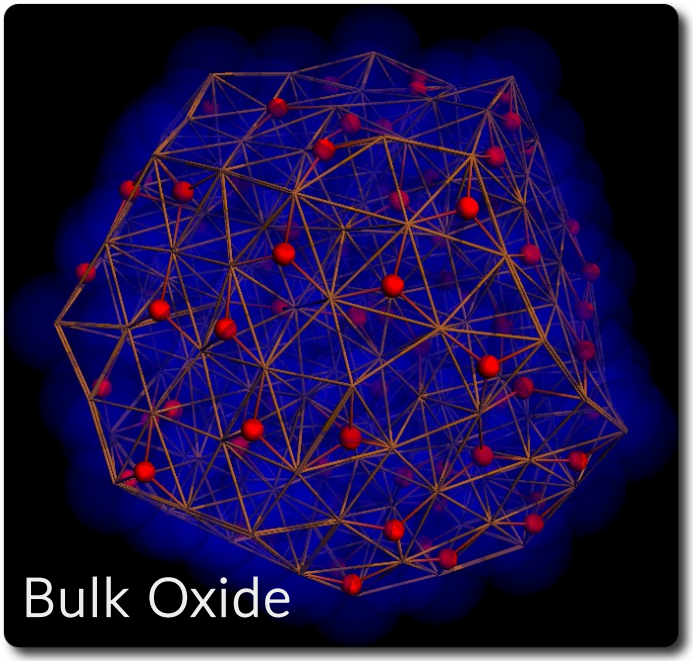
Simulate PdO formation

Learn how to:

- Setup and run GCMC calculations from the command line
- use Python for custom analysis of trajectories



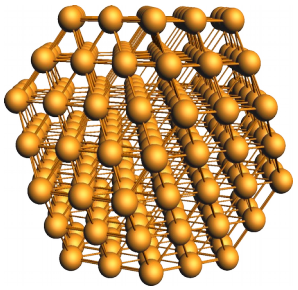




Which one is stable at given p,T???

Hands on: Grand-Canonical Monte-Carlo

Simulate PdO formation - Inputfiles



Task:

Simulate the oxidation of a small (201 atoms) Pd-Cluster* under different conditions p_O, T. The phase boundary between Bulk- and Surface-Oxide for this (test) system lies in between $p_0 > 10^{-10}$ and $p_0 < 10^{-14}$ atm @ 800K.

- Can you verify this?
- Can you narrow down the range?

Files:

Templates for the required ReaxFF input can be found in ./GCMC/PdO.

Preparation:

Prepare by creating a folder for each GCMC run and copy the input templates into this folder. Edit the input templates for the according GCMC-runs by using the chemical potentials from these tables.

---

* The structure of the cluster is given. However, how to cut clusters from Bulk is described in this GUI tutorial.

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Simulate PdO formation – Running the calculations

Run

The calculations are started by executing the run script **`GCMC.run`**

Make the script executable (only once):

```
chmod +x GCMC.run
```

run the script from inside it's folder:

```
./GCMC.run &
```

You can monitor the GCMC output using

```
tail -f MCstats
```

pressing **`CTRL + c`** will exit the tail command

Outputfiles

The central outpufiles are MCstats and reaxout.kf:

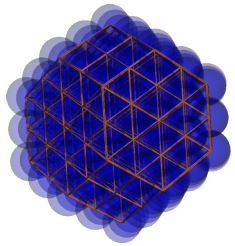
- MCstats contains information about the trials and acceptance of MC moves per each step
- reaxout.kf is an .rxkf results file that can be parsed with KF reading tools, as well as ADFmovie

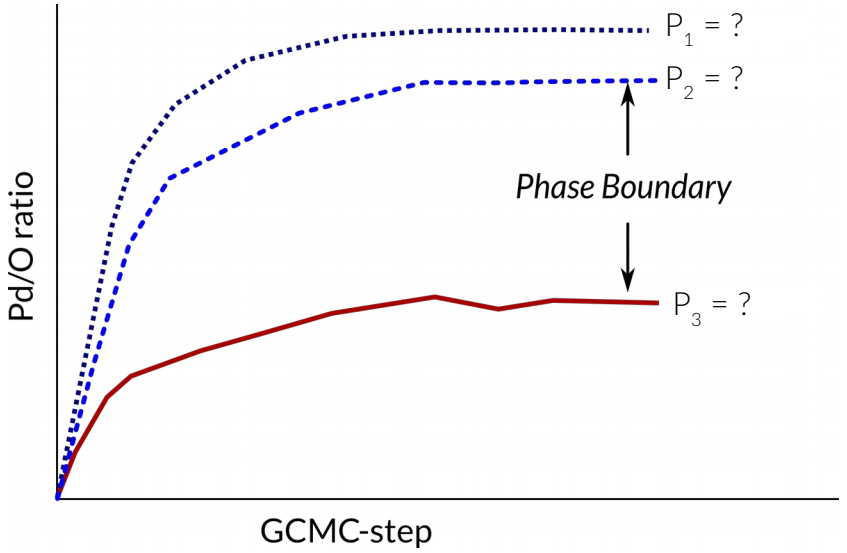
Hands on: Grand-Canonical Monte-Carlo

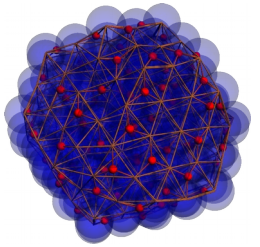
Simulate PdO formation – Convergence of the calculations

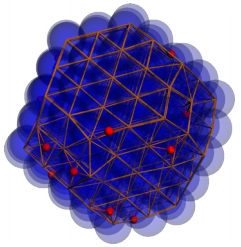
Check the convergence

The convergence of the GCMC procedure and the phase boundary can be estimated by looking at the Pd/O ratios per frame :









use the PYTHON script **`gcmc_converge.py`** to extract the Pd/O of every frame from the KF file:

```
startpython [path to script]/gcmc_convergence.py reaxout.kf
```

The resulting file, **`gcmc_convergence.out`**, contains the current GCMC-step as x- and the Pd/O-ratio as y-values.

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General information	**info@scm.com**
User support	**support@scm.com**

Visualize your GCMC-structure

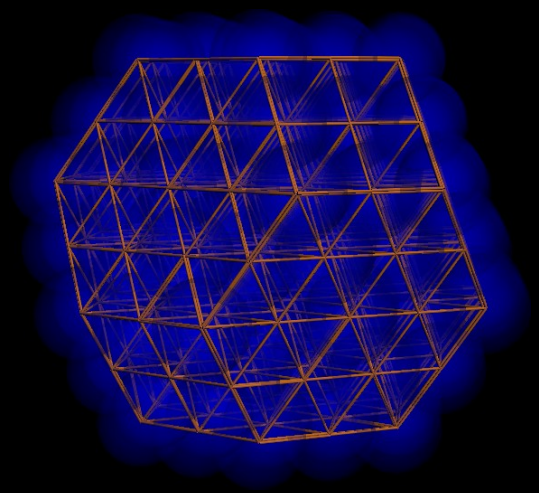
Even without direct GUI support…

Open **`reaxout.kf`** with ADFmovie

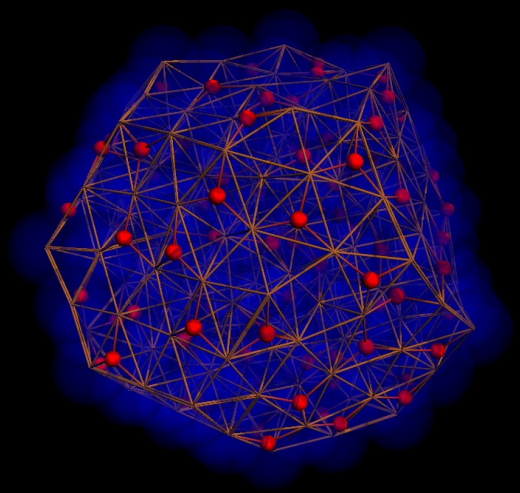
- Jump to the last frame
- File → Save Geometry

Open saved geometry with ADFinput

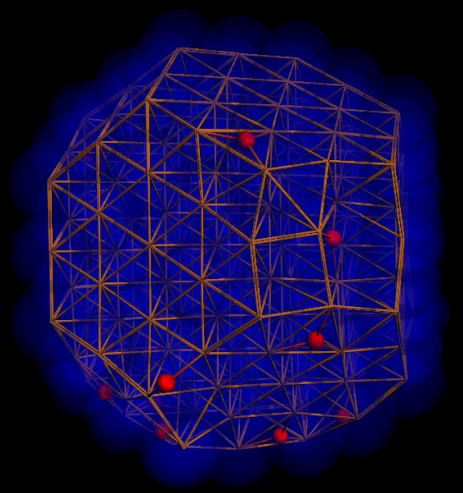
- Edit → Crystal → Map Atoms To Unit Cell



Metal



Bulk Oxide



Surface Oxide

Hint:
The glowing spheres can be set via assigning all O- atoms to one region and all Pd-atoms to another…

Grand-Canonical Monte-Carlo

Examples: Calculation of the chemical potential

Using the data from NIST and E_d = 129 kcal/mol*, we calculate the chemical potentials of an oxygen reservoir for the following conditions:

1. T = 500 K, p_{O2} = 1 atm:

$\mu_{O2}(500K, p^0) = \Delta H_T - T \cdot S_T = (6.084 + 8.683) - 500 \cdot 0.220693 = -95.5795$ kJ/mol

$\mu_O(500K, 1atm) = [\ (-95.58) + 0.008314 \cdot 500.0 \cdot \ln(1.0/0.9869) + (-129.0 \cdot 4.1839)\ ] / 8.3677$

$= -75.92$ kcal/mol

2. T = 500 K, p_{O2} = 10^{-6} atm:

$\mu_{O2}(500K, p^0) = \Delta H_T - T \cdot S_T = (6.084 + 8.683) - 500 \cdot 0.220693 = -95.5795$ kJ/mol // same!

$\mu_O(500K, 10^{-6}\ atm) = [\ (-95.58) + 0.008314 \cdot 500.0 \cdot \ln(10^{-6}/0.9869) + (-129.0 \cdot 4.1839)\ ]/8.3677$

$= -82.78$ kcal/mol

3. T = 1000 K, p_{O2} = 10^{-6} atm:

$\mu_{O2}(500K, p^0) = \Delta H_T - T \cdot S_T = (22.703 + 8.683) - 1000 \cdot 0.220693 = -212.192$ kJ/mol

$\mu_O(500K, 10^{-6}\ atm) = [\ (-212.192) + 0.008314 \cdot 1000 \cdot \ln(10^{-6}/0.9869) + (-129.0 \cdot 4.1839)\ ]/8.3677$

$= -103.57$ kcal/mol

* for consistency reasons the ReaxFF- rather than the DFT-energy is used

Grand-Canonical Monte-Carlo

μ_O(p,T) : oxygen chemical potentials (kcal/mol)

T(K)	1(atm)	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
298.15	-70.77	-71.45	-72.13	-72.81	-73.50	-74.18
300	*-70.81*	*-71.50*	*-72.19*	*-72.87*	*-73.56*	*-74.25*
350	-72.05	-72.85	-73.66	-74.46	-75.26	-76.06
400	-73.32	-74.23	-75.15	-76.06	-76.98	-77.90
450	-74.61	-75.64	-76.67	-77.70	-78.73	-79.76
500	-75.92	-77.06	-78.20	-79.35	-80.49	-81.64
600	-78.59	-79.96	-81.33	-82.71	-84.08	-85.45
700	-81.32	-82.92	-84.53	-86.13	-87.73	-89.33
800	-84.11	-85.95	-87.78	-89.61	-91.44	-93.27
900	-86.96	-89.02	-91.08	-93.13	-95.19	-97.25
1000	-89.85	-92.13	-94.42	-96.71	-99.00	-101.28
1100	-92.78	-95.29	-97.81	-100.33	-102.84	-105.36
1200	-95.74	-98.49	-101.23	-103.98	-106.73	-109.47
1300	-98.75	-101.72	-104.70	-107.67	-110.64	-113.62
1400	-101.78	-104.99	-108.19	-111.39	-114.60	-117.80
1500	-104.85	-108.28	-111.72	-115.15	-118.58	-122.01
1600	-107.95	-111.61	-115.27	-118.93	-122.59	-126.25
1700	-111.07	-114.96	-118.85	-122.74	-126.63	-130.52
1800	-114.22	-118.34	-122.46	-126.58	-130.70	-134.82
1900	-117.40	-121.75	-126.09	-130.44	-134.79	-139.13
2000	-120.60	-125.17	-129.75	-134.33	-138.90	-143.48

back to hands-on back to intro

Grand-Canonical Monte-Carlo

μ_O(p,T) : oxygen chemical potentials (kcal/mol) - continued

T(K)	10^{-6}(atm)	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
298.15	-74.86	-75.54	-76.23	-76.91	-77.59	-78.27	-78.95	-79.64	-80.32
300	-74.93	-75.62	-76.30	-76.99	-77.68	-78.36	-79.05	-79.74	-80.42
350	-76.86	-77.66	-78.46	-79.26	-80.06	-80.86	-81.66	-82.46	-83.26
400	-78.81	-79.73	-80.64	-81.56	-82.47	-83.39	-84.30	-85.22	-86.13
450	-80.78	-81.81	-82.84	-83.87	-84.90	-85.93	-86.96	-87.99	-89.02
500	-82.78	-83.92	-85.07	-86.21	-87.36	-88.50	-89.64	-90.79	-91.93
600	-86.82	-88.20	-89.57	-90.94	-92.31	-93.69	-95.06	-96.43	-97.81
700	-90.93	-92.53	-94.14	-95.74	-97.34	-98.94	-100.54	-102.14	-103.74
800	-95.10	-96.93	-98.76	-100.59	-102.42	-104.25	-106.08	-107.91	-109.74
900	-99.31	-101.37	-103.43	-105.49	-107.55	-109.61	-111.67	-113.73	-115.78
1000	-103.57	-105.86	-108.15	-110.44	-112.72	-115.01	-117.30	-119.59	-121.88
1100	-107.88	-110.39	-112.91	-115.43	-117.94	-120.46	-122.98	-125.49	-128.01
1200	-112.22	-114.96	-117.71	-120.45	-123.20	-125.94	-128.69	-131.44	-134.18
1300	-116.59	-119.57	-122.54	-125.52	-128.49	-131.46	-134.44	-137.41	-140.39
1400	-121.00	-124.21	-127.41	-130.61	-133.82	-137.02	-140.22	-143.42	-146.63
1500	-125.44	-128.88	-132.31	-135.74	-139.17	-142.60	-146.03	-149.47	-152.90
1600	-129.91	-133.57	-137.23	-140.90	-144.56	-148.22	-151.88	-155.54	-159.20
1700	-134.41	-138.30	-142.19	-146.08	-149.97	-153.86	-157.75	-161.64	-165.53
1800	-138.93	-143.05	-147.17	-151.29	-155.41	-159.53	-163.64	-167.76	-171.88
1900	-143.48	-147.83	-152.18	-156.52	-160.87	-165.22	-169.56	-173.91	-178.26
2000	-148.05	-152.63	-157.21	-161.78	-166.36	-170.93	-175.51	-180.08	-184.66

back to hands-on