Self-diffusion in Mo using the AM05 density functional

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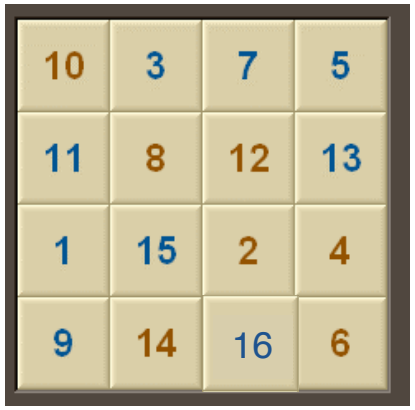
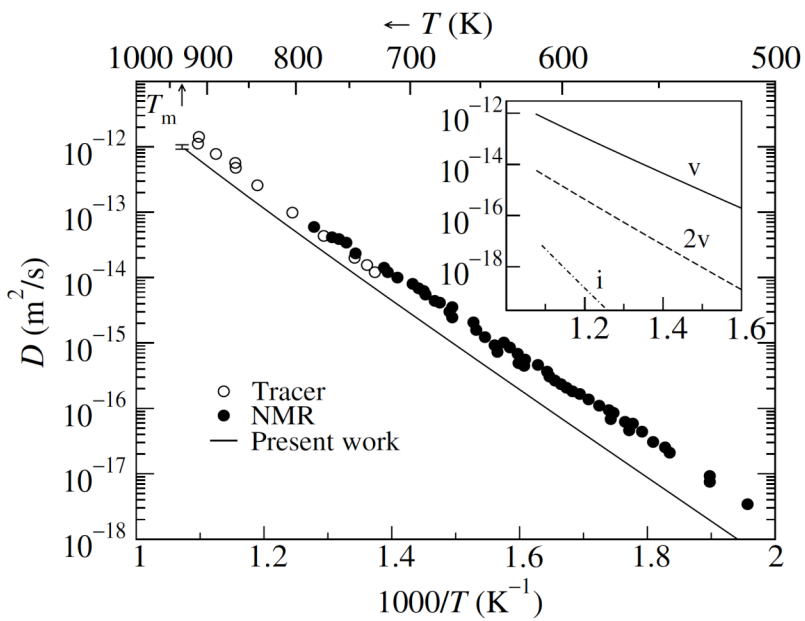
Vacancy mediated diffusion is the main mechanism for mass transport in solids



- Vacancies are important for
  - Self-diffusion
  - Defect migration
  - Radiation damage/ swelling
  - Aging of materials
  - Solid phase transformations.
  - Segregation of phase and alloy boundaries.
  - Process aware materials modeling

From first principles calculations to estimation of self diffusion coefficient



Self-diffusion in Aluminum

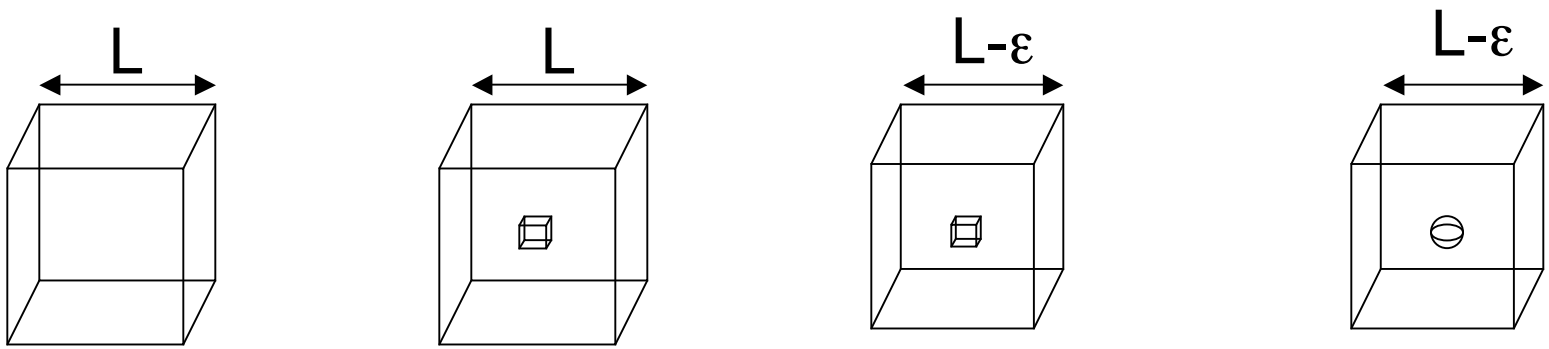
- Diffusion is: how many, how fast?
  - $D(T) = c(T)\ \Gamma(T)$
  - $c(T) = c_0 \exp(-E_f/k_B T)$
  - $\Gamma(T) = \Gamma_0 \exp(-E_D/k_B T)$
  - $D(T) = c_0\ \Gamma_0 \exp(-(E_D + E_f)/k_B T)$

What can we do?

Exponential dependence make accuracy in calculations of paramount importance

Calculating vacancy formation energies.

$$E_f = E_{(N-1)} - (N-1)/N\ E_N$$



N	N-1	volume	structural
bulk	static	relaxation.	relaxation.

In itself a rather basic DFT calculation.

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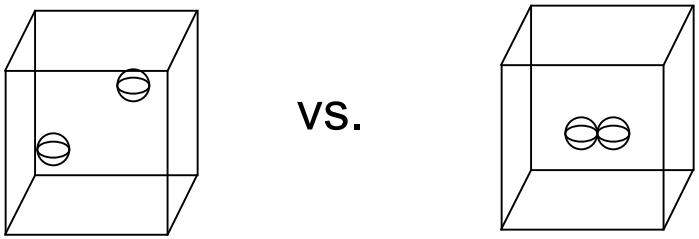
Making sure the system is converged.

$$E_f = E_{(N-1)} - (N-1)/N\ E_N$$

- Many k-points.
- High cutoff energies.
- Well converged forces.

Vacancy formation, eV.			
N	Al (GGA)	Pt (LDA)	Pt relaxed
27	-	1.28	
32	0.52	-	
64	-	1.25	0.99
80	0.54	-	
108	0.54	1.22	
125	0.54	1.21	0.95

The results were not basic: a di-vacancy in Al



$$E_{2V}^{B} = 2\,E_{V}^{F} - E_{2V}^{F}$$

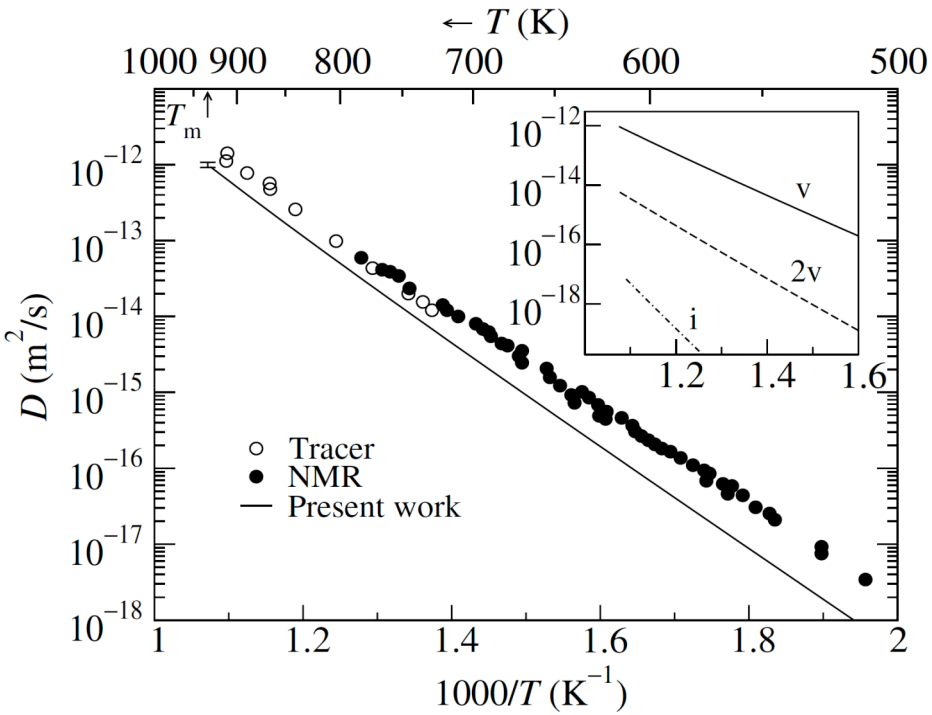
Method	E_V^F	E_{2V}^F	E_{2V}^B
LDA	0.70	1.48	-0.07
GGA	0.55	1.19	-0.08

Q: what makes LDA/GGA agree on E_{2V}^{B} but disagree on E_V^F and E_{2V}^F ?

A:
The intrinsic surface error made by the two functionals.

Karin Carling et al, Phys. Rev. Lett. **85**, 3862 (2000).

Self diffusion in fcc Al: DFT + surface correction + EAM an-harmonic at high T is quantitative



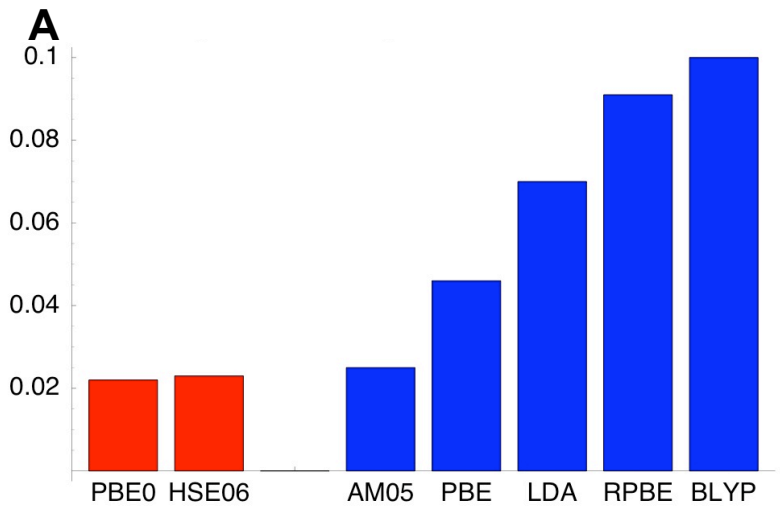
[$]N. Sandberg, B. Magyari-Kope, T.R. Mattsson, PRL **89**, 065901 (2002).

- Formation energy from DFT
- Vacancy migration from DFT
- Vacancy/interstitial competition in diffusion important for void swelling
- EAM (Ercolessi-Adams) simulations at elevated temperatures to calculate the anharmonicity
- Al (fcc) quantitative agreement with experimental data
- How about bcc metals?

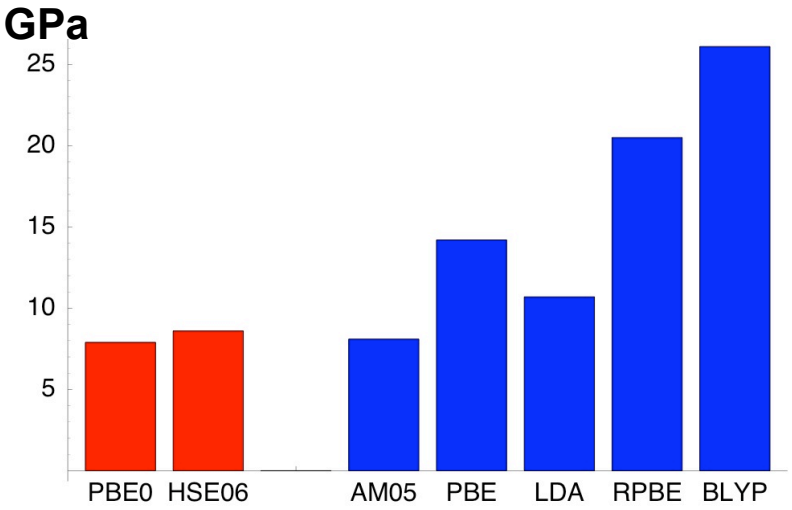
A new level of accuracy using the new surface-accurate XC functional AM05: benchmark for 20 solids[$]

Li, Na, Al,
BN, BP, C, Si, SiC,
β-GaN, GaP, GaAs,
LiF, LiCl, NaF, NaCl, MgO,
Cu, Rh, Pd, Ag.

AM05 performs as well for solids as the hybrids HSE and PBE0 do, while being 60-1000 times less expensive in computer time.
Accurate and fast is possible



Mean absolute error: lattice const.



Mean absolute error: bulk moduli.

[$]A.E. Mattsson, et al J. Chem. Phys. **128**, 084714 (2008).

Density functional theory (DFT) based MD is a well-established approach, but far from a black box

- VASP 5.1 code (Georg Kresse, Vienna, Austria)
- Plane-wave basis-set allowing controlled convergence and free electrons/ionization
- Finite-temperature DFT (Mermin)
- Projector augmented wave core functions (PAW)
- We employ the Sandia developed AM05 functional (Armiento and Mattsson, Phys Rev B 2005)

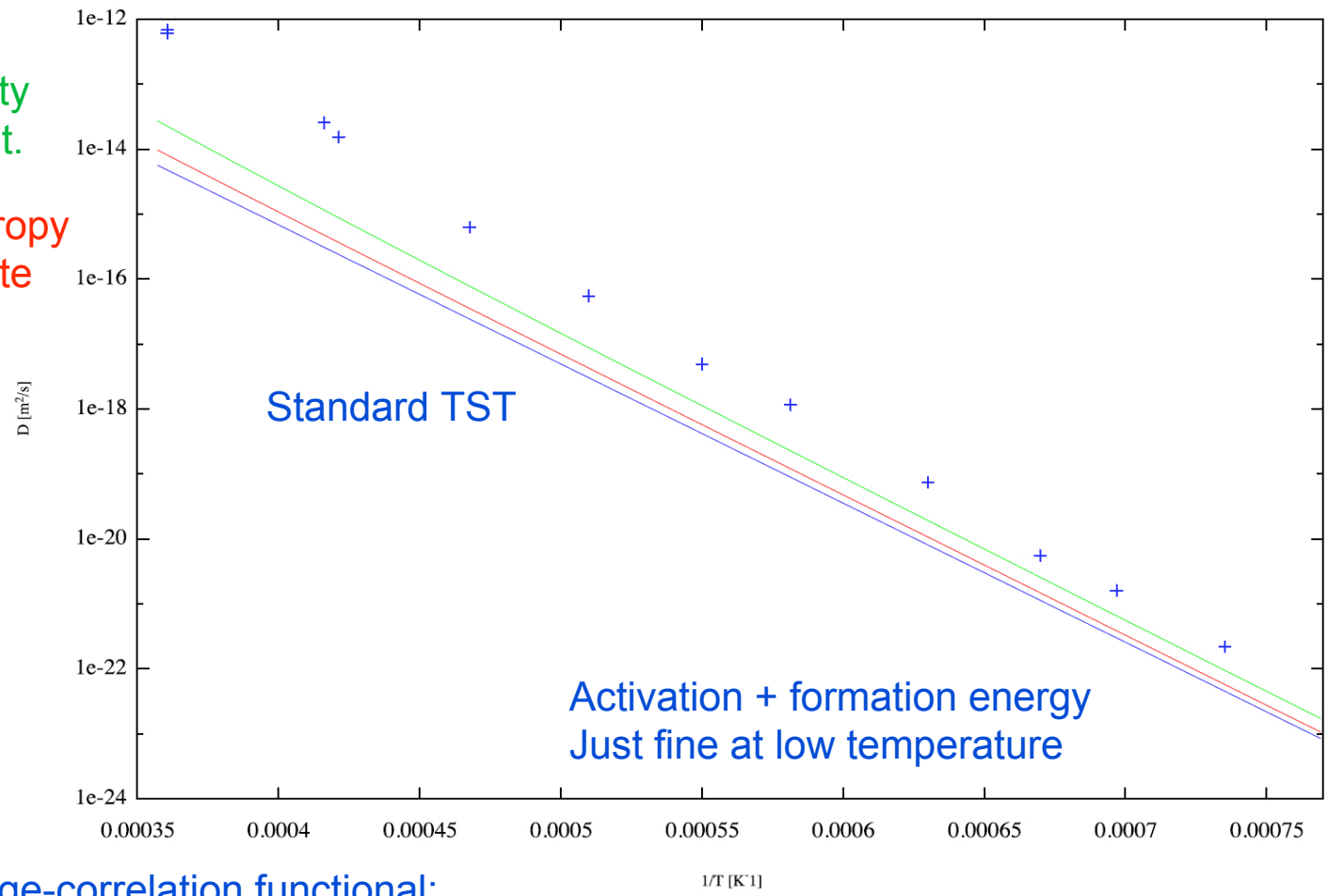
- Accuracy of DFT calculations determined by the exchange-correlation (xc) functional
- Understanding xc functionals/ many-body theory a foundation for high-fidelity simulations: *right answer for the right reason*
- Original research in DFT at Sandia: **dft.sandia.gov** : Rudy Magyar, Anatole von Lilienfeld, Ann Mattsson

- *These are demanding large scale DFT-MD simulations: between 128 and 432 Mo atoms*
- Utilizing Red Storm at Sandia HPC

Self diffusion in bcc Mo: DFT + Finnis-Sinclair model potential: not even close!

+ anharmonicity from model pot.

+electronic entropy from ground state



AM05 exchange-correlation functional:
Excellent lattice constant, bulk modulus, vacancy formation and diffusion barrier at low T.
There is no reason it should not work for Mo.

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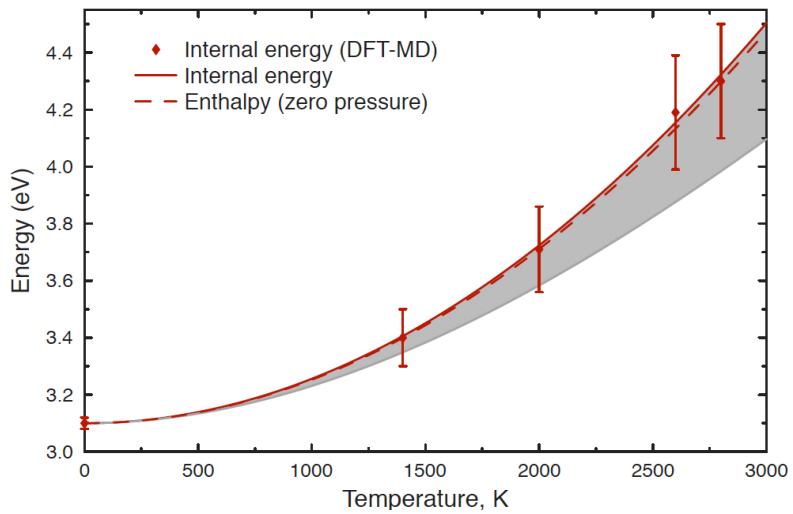
BCC metals display anomalous activation energy for self-diffusion

Vacancy formation energy Mo

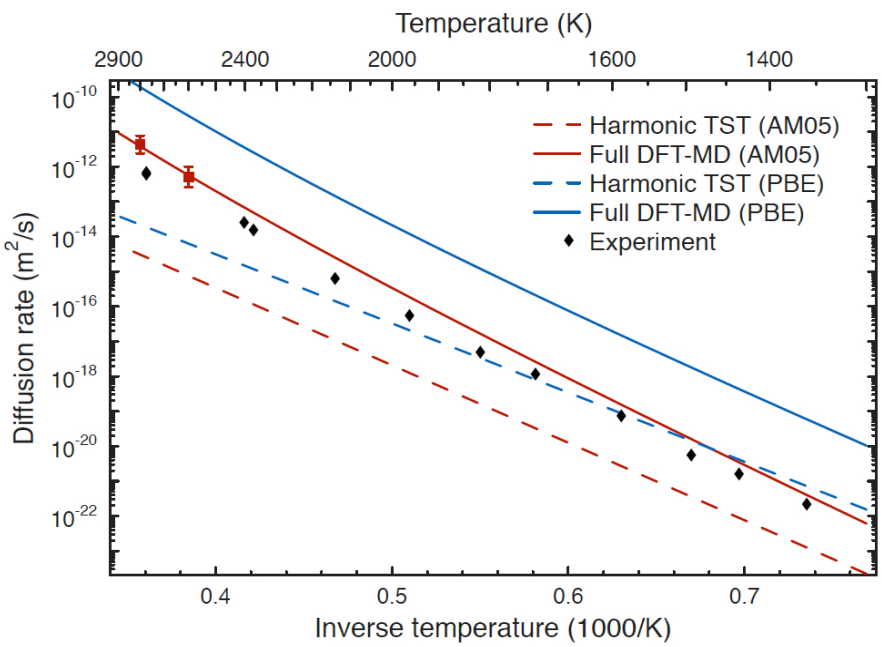


Significant shift in vacancy formation energy with increased temperature

- First-principles Density Functional Theory (DFT) simulations
  - VASP 5.1 code (Kresse/Hafner)
    - Allows multiple XC-functionals on PAW cores.
  - AM05 XC-functional.
  - Massively parallel on Red Storm
  - 128/127 Mo atoms for tens of ps
  - Shaded is contribution from electronic entropy
  - Majority is an-harmonic effects

Quantitative results for self diffusion in bcc molybdenum from DFT-AM05

Self diffusion coefficient Mo

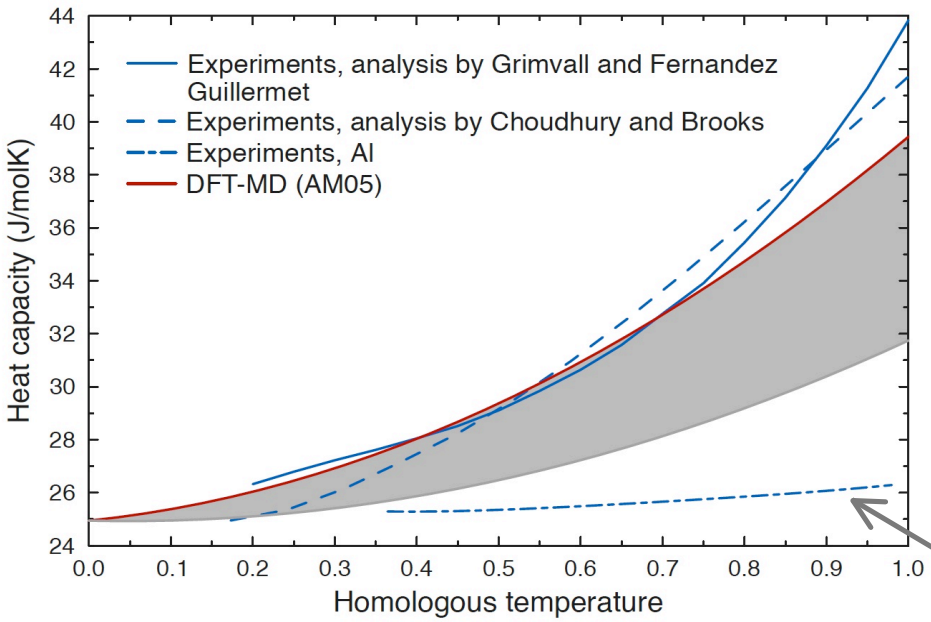


Quantifying the anomalous diffusion of molybdenum by first-principles simulations
TR Mattsson, N. Sandberg, R. Armiento, AE Mattsson

- Extensive DFT-MD simulations
  - AM05 and PBE XC-functionals.
  - 127 Mo atoms for 30 ps
    - Follow the hopping motion of the vacancy, calculate self-diffusion
    - Very demanding simulations, millions of CPU-hours.
  - AM05 quantitative results over 11 orders of magnitude.
  - AM05 considerably improved accuracy compared to PBE.

BCC metals display anomalous heat capacity

Heat capacity for Mo



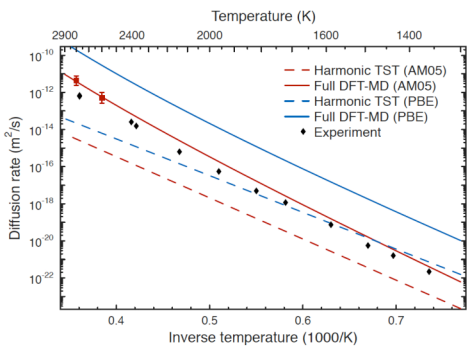
- First-principles Density Functional Theory (DFT) simulations
  - Finite-temperature DFT crucial
  - AM05 XC-functional
  - 128-250-432 Mo atoms
  - 90% of an-harmonicity captured
  - Experimental uncertainties
  - Working on vacancy contribution to heat capacity

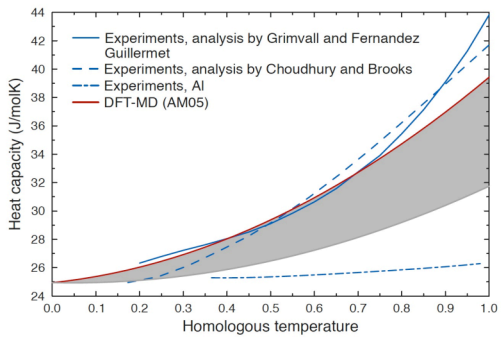
Al - small, but noticeable
An-harmonic contribution

First-principles thermodynamics

Consistent description of first-principles thermo-dynamics and defect dynamics for bcc Mo

Self diffusion and heat capacity for Mo





We have made significant progress on first-principles thermodynamics and defect dynamics for also complex metals like BCC Mo.

- We thank
  - Göran Grimvall for stimulating discussions
  - Georg Kresse for the early opportunity to use VASP 5.1
  - Paul Kent for porting VASP 5.1 to Cray XT.
  - Dennis Dinge at Sandia High Performance Computing for support on RED STORM

Backup slides to follow

DFT-XC AM05 solids benchmark

PBEsol yields virtually identical results to AM05 for transition metals, refractory metals, oxides, and semiconductors

Comparison of PBEsol and AM05, employing two different codes:
EMTO-KKR: M. Ropo, K. Kokko, and L. Vitos, PRB **77** 195445 (2008).
VASP 5.1: Joachim Paier (unpublished) or myself (unpublished).

Lattice const. A			**Bulk moduli GPa**		
Solid	PBEsol	AM05	Solid	PBEsol	AM05
BN	3.609	3.607	BN	384	383
BP	4.522	4.520	BP	168	167
C	3.556	3.553	C	447	449
Si	5.429	5.431	Si	93.3	92.3
GaN	4.494	4.492	GaN	187	185
GaP	5.438	5.442	GaP	84.1	82.1
GaAs	5.665	5.673	GaAs	68.6	66.5
α-Al2O3	5.139	5.141	α-Al2O3	244	241
MgO	4.222	4.228	MgO	157	154
Cr	2.82	2.82	Cr	274	273
Fe	2.79	2.79	Fe	220	223
Ta	3.29	3.29	Ta	188	188
Mo	3.139	3.134	Mo	283	284
Nb	3.27	3.27	Nb	160	162
V	2.96	2.96	V	188	187
W	3.16	3.16	W	305	307

The differences between AM05 and PBEsol are for these solids very difficult, if at all possible, to resolve.

PBEsol yields virtually identical results to AM05 for transition metals, refractory metals, oxides, and semiconductors

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Lattice const. A			**Bulk moduli GPa**		
Solid	PBEsol	AM05	Solid	PBEsol	AM05
Ru	2.95	2.94	Ru	336	339
Tc	3.00	3.00	Tc	310	312
Y	3.93	3.94	Y	38.2	37.5
Zr	3.50	3.51	Zr	93.0	93.1
Al	4.016	4.007	Al	81.7	85.7
Au	4.10	4.09	Au	170	168
Cu	3.569	3.567	Cu	163	162
Ir	3.85	3.85	Ir	376	382
Ni	3.47	3.47	Ni	223	222
Pb	4.93	4.93	Pb	50.1	53.0
Pd	3.877	3.871	Pd	202	200
Pt	3.94	3.93	Pt	281	283
Rh	3.780	3.773	Rh	294	295
Ag	4.052	4.054	Ag	118	113

The differences between AM05 and PBEsol are for these solids very difficult, if at all possible, to resolve.

Ongoing discussion on differences and similarities between PBEsol and AM05

AM05
R Armiento and AE Mattsson
PRB **72**, 085108 (Aug 2005).

AM05 benchmark 20 solids
AE Mattsson et al
JCP **128**, 084714 (Feb 2008).

PBEsol
JP Perdew et al
PRL **100**, 136406 (April 2008).

Benchmark for metals (bulk and surface)
M Ropo et al
PRB **77**, 195445 (May 2008).

Comment on PBEsol
AE Mattsson, R Armiento, and TR Mattsson
PRL **101**, 239701 (Dec 2008).
Reply to comment
JP Perdew et al
PRL **101**, 239702 (Dec 2008).

LAPW benchmark for 80 solids
P Haas, F Tran, and P Blaha
PRB **79**, 085104 (Feb 2009).