Quantum Mechanics Based Multiscale Modeling of Materials Defects

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Introduction - 1

- *"Materials are like people – it's defects that make them interesting"* (Sir F. C. Frank)

  Many interesting materials properties are determined by defects.

- To model defects (dislocations, cracks, voids, etc.), one often needs QM-based multiscale modeling:

  -Large systems required to describe realistic defect concentrations

  - QM required to capture bond breaking, chemical interactions, etc. at defect cores

Conflicting requirements addressed by QM-based multiscale modeling

Introduction -2

Goal: To develop multiscale approaches that retain QM accuracy where it is necessary and at the same time can treat very large systems

- Challenge: the approaches physically sound and mathematically rigorous; free of *ad hoc* procedures for coupling different scales.

Two types of concurrent multiscale approaches:

- QM/MM *(quantum mechanics/molecular mechanics)* methods
- QCDFT *(quasi-continuum density functional theory)* methods

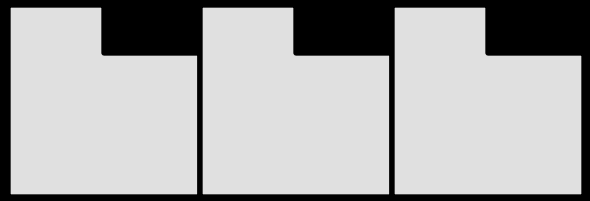
I focus on concurrent multiscale methods because they face some unique mathematical and algorithm challenges different from sequential multiscale modeling

Problems in Periodic DFT Modeling of Defects

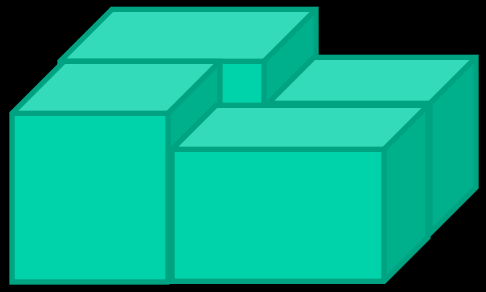
Real System (isolated defect)

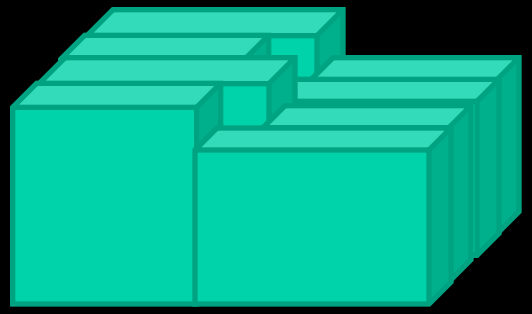
Periodic DFT (array of defects at exceedingly high density)

Step

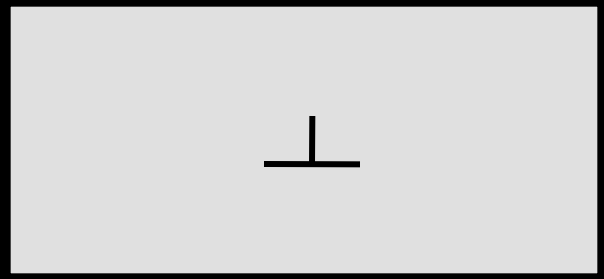


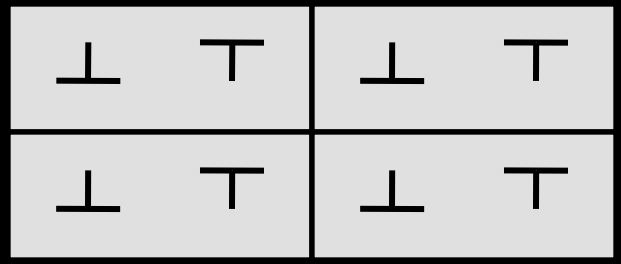
Kink

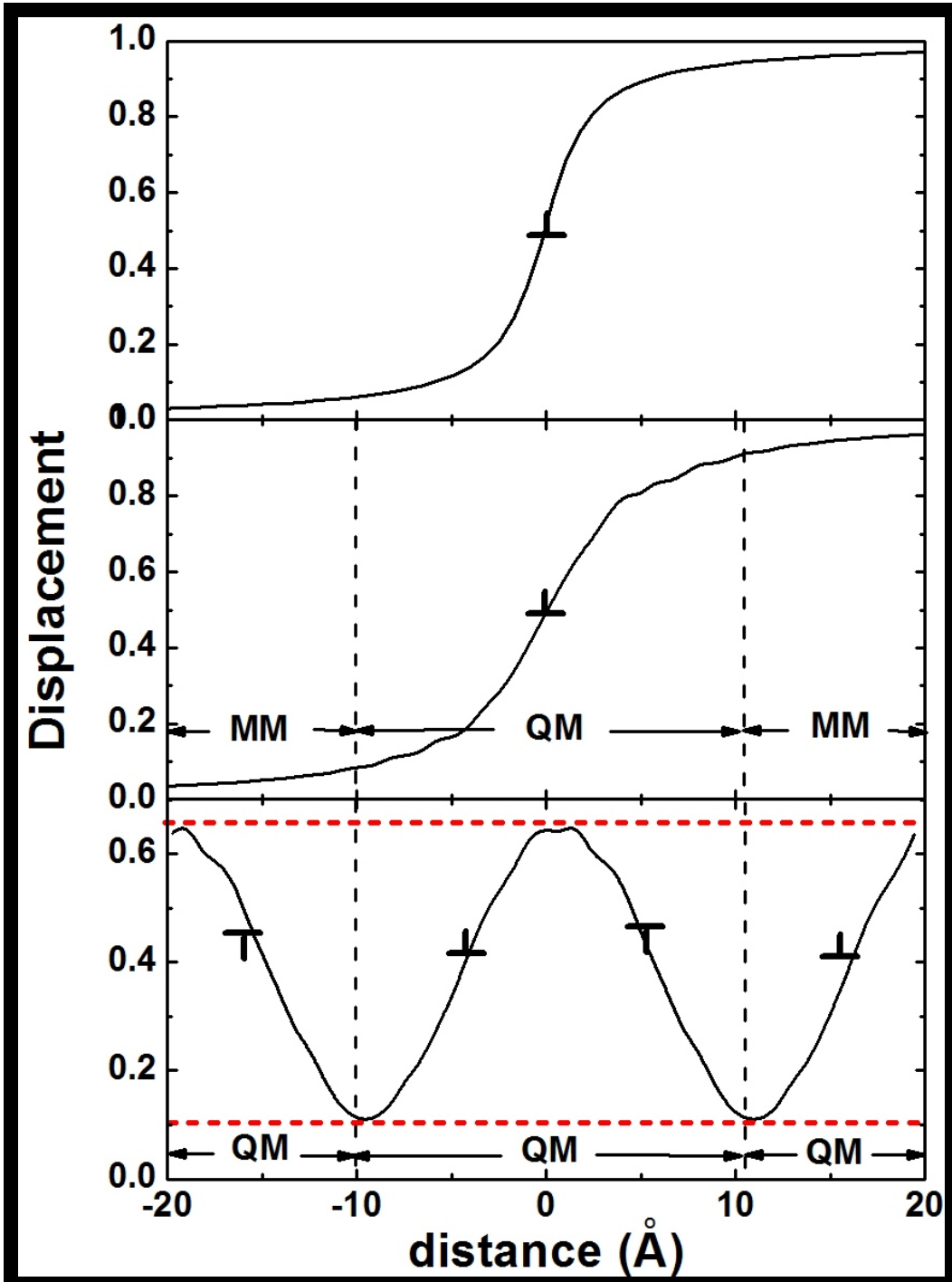




Dislocation







Edge dislocation in bcc-Fe

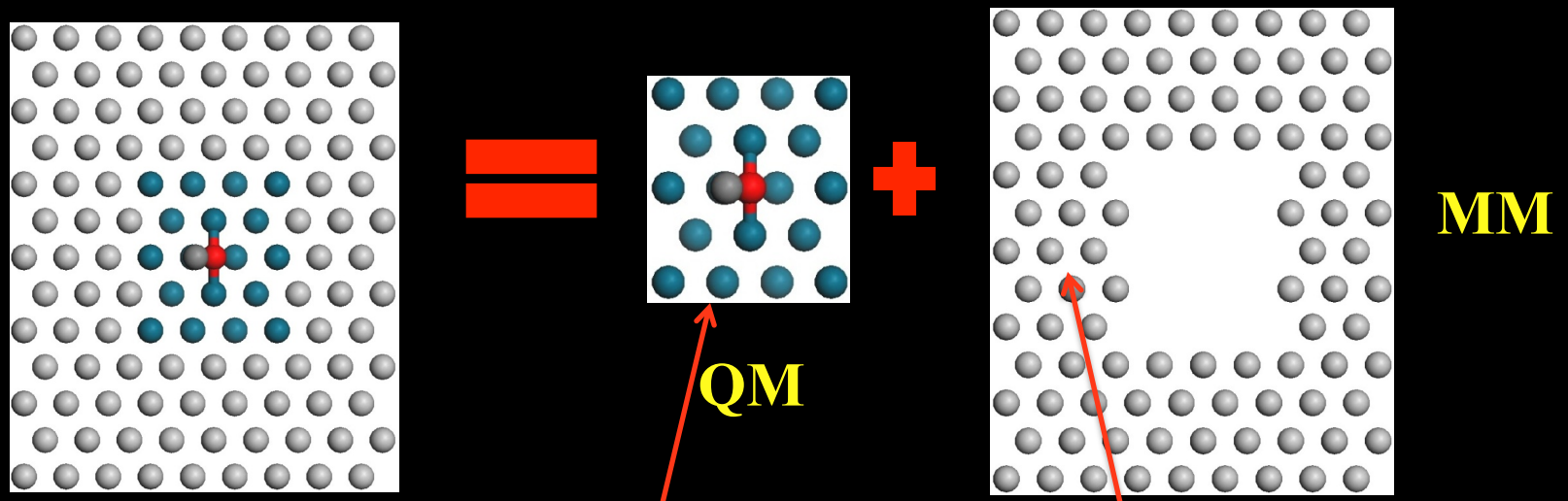
Typical displacement profile

QM/MM (QM for dislocation core; MM for long-range elastic tails) can reproduce the correct profile

Periodic DFT with the same size of QM box: displacement tails are incorrect (possibly affect the core structure)

Quantum Mechanics /Molecular Mechanics (QM/MM) Methods

- QM/MM: atomistic modeling method coupling QM simulation of a chemical "reactive" region **(region I)** with MM modeling of surrounding non-reactive region **(region II).**

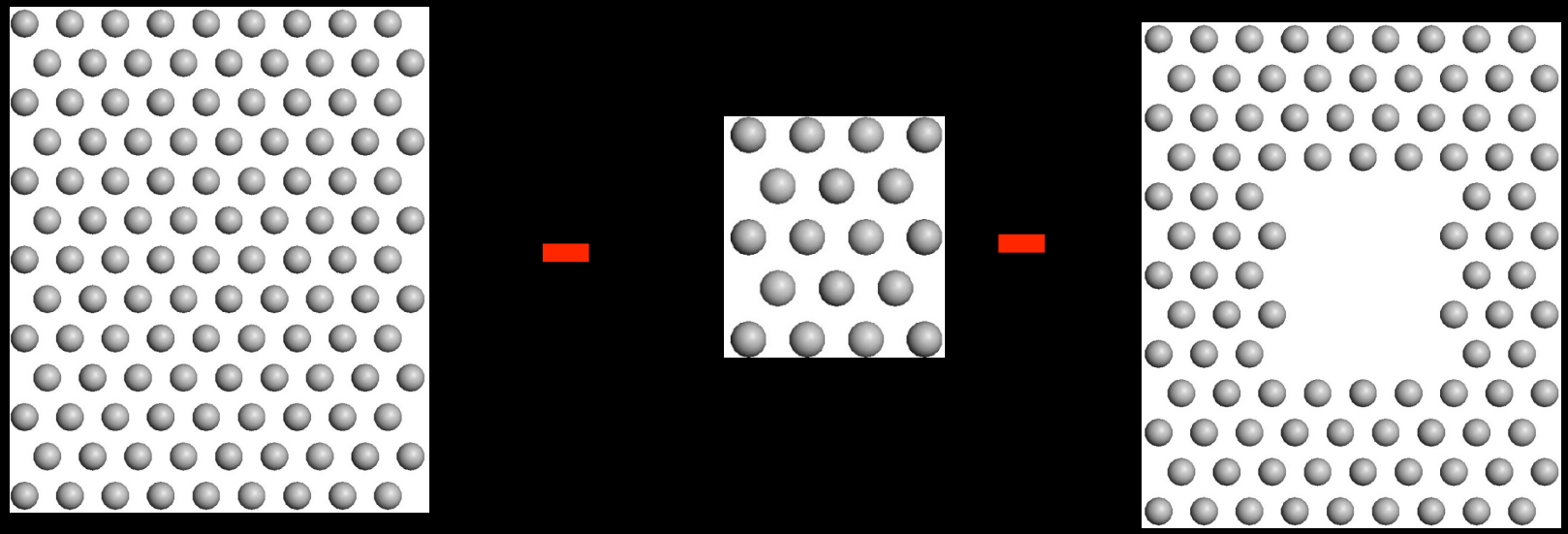


$$E^{tot}[I+II] = E_{QM}[I] + E_{MM}[II] + E^{int}[I,II]$$

Interaction between QM and MM regions

E^{int} [I,II] can be calculated at different levels depending on the problem at hand; For example, E^{int}[I,II] calculated at MM level (mechanical coupling):

$$E^{int}[\text{I+II}] = E_{MM}[\text{I+II}] - E_{MM}[\text{I}] - E_{MM}[\text{II}]$$



- Advantage: simplicity; If high quality interatomic potentials are available, this method could be a good choice
- Disadvantage: coupling errors are problematic for certain materials (such as Fe) due to cluster cal. for QM region
- Efficient methods have been developed to correct for possible coupling errors

Self-Consistent DFT Embedding Method

If satisfactory interatomic potentials are unavailable, calculate interaction energy quantum mechanically

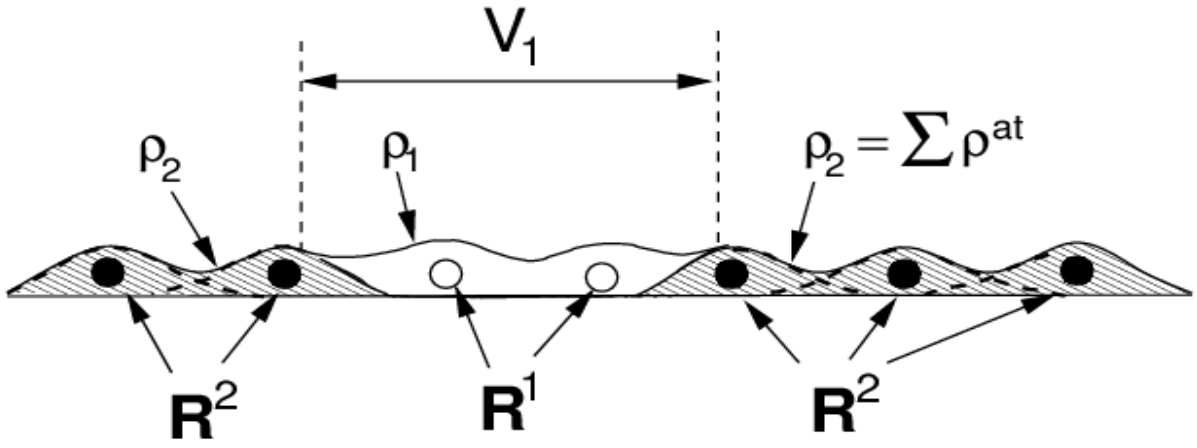


FIG. 1: An illustration of the partitioning of the system according to the second coupling method.

Open circle: DFT
Filled circle: MM

Assumption:
MM is elastically deformed defect-free lattice

Attach ρ^{at} and pseudopotential to each MM atom $\mathbf{R}_i^2$

Both constructed in advance; ρ_2 superposition of ρ^{at}, provides B.C.

Goal: self-consistently determine ρ_1 in the presence of ρ_2 and pseudopotential
- No longer a cluster cal for QM.

Self-Consistent Embedding Theory

The energy of entire QM/MM system:

$$E_{tot}[\vec{R}_1+\vec{R}_2]=E_{DFT}[\vec{R}_1]+E_{MM}[\vec{R}_2]+E^{\text{int}}_{OFDFT}[\vec{R}_1,\vec{R}_2]$$

OFDFT (approximates K.E. in terms of electron density as opposed to wave-functions) used to calculate the interaction energy

$$E^{\text{int}}_{OFDFT}[\vec{R}_1,\vec{R}_2]=E_{OFDFT}[\vec{R}_1+\vec{R}_2]-E_{OFDFT}[\vec{R}_1]-E_{OFDFT}[\vec{R}_2]$$

The G.S. energy is given by minimizing the energy functional w.r.t. ρ_1

$$E_{tot}=E_{MM}[\vec{R}_2]+\min_{\rho_1}[E_{OFDFT}[\rho^{tot}]-E_{OFDFT}[\rho_1]-E_{OFDFT}[\rho_2]+E_{DFT}[\rho_1]]$$

$$\rho_{tot}(\vec{r})=\rho_1(\vec{r})+\rho_2(\vec{r})$$
$$\rho_2(\vec{r})=\sum_{j\in II}\rho^{at}(\vec{r}-\vec{R}_2^{\,j})$$

$\rho_1(\vec{r})$ degree of freedom

Zhang & Lu, PRB 76, 24511 (2007) & Zhang, Wang & Lu, PRB, 78, 235119 (2008)

$$E_{tot} = E_{MM}[\vec{R}_2] + \min_{\rho_1}[E_{OFDFT}[\rho^{tot}] - E_{OFDFT}[\rho_1] - E_{OFDFT}[\rho_2] + E_{DFT}[\rho_1]]$$

The minimization of $E_{\mathrm{DFT}} + E^{\mathrm{int}}_{\mathrm{OFDFT}}$ with respect to ρ_1 results in an additional term (embedding potential) into the original Kohn-Sham Hamiltonian

$$H = T + V_{\mathrm{ion}}[\mathbf{R}_1] + V_{\mathrm{H}}[\rho_1] + V_{\mathrm{xc}}[\rho_1] + V_{\mathrm{emb}}[\rho_1, \rho_2; \mathbf{R}_1, \mathbf{R}_2]$$

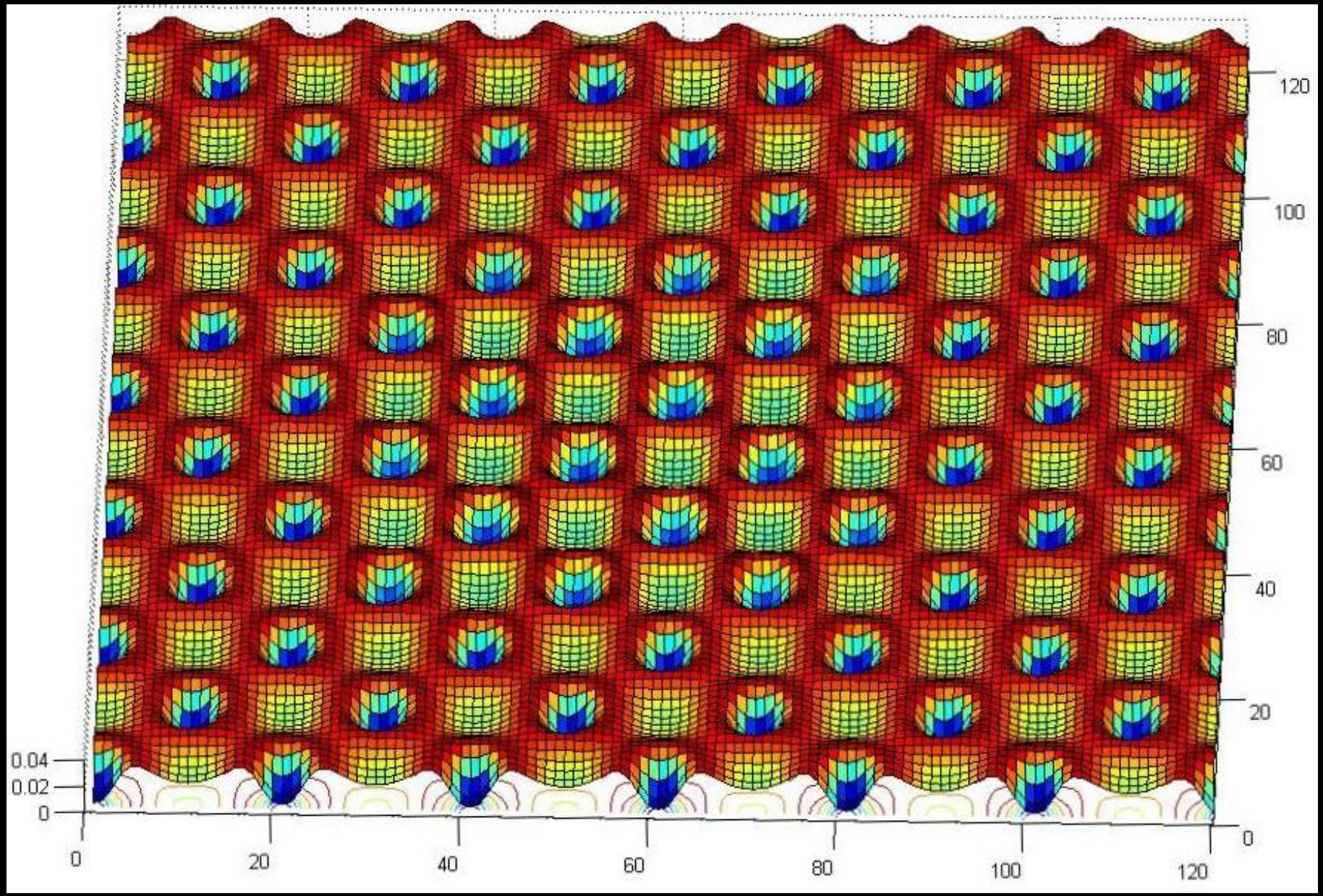
$$V_{\mathrm{emb}}[\rho_1, \rho_2; \mathbf{R}_1, \mathbf{R}_2] = \frac{\delta E^{\mathrm{int}}_{\mathrm{OFDFT}}[\rho_1, \rho_2; \mathbf{R}_1, \mathbf{R}_2]}{\delta \rho_1}$$

V_{emb} contains **all** the effects of the MM region upon DFT region

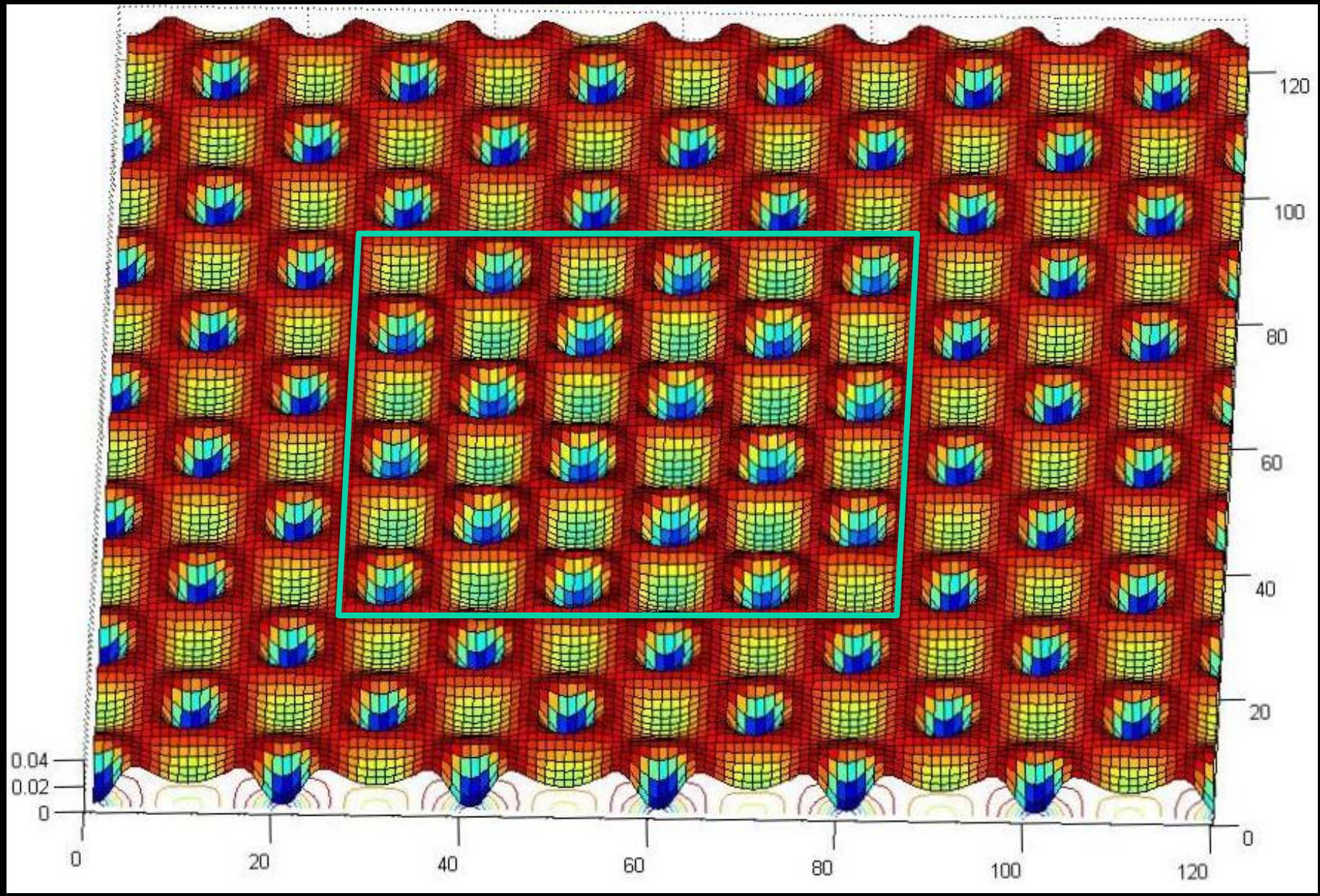
Modified KS-equation of ***H*** is solved for DFT region self-consistently

We have implemented this method in VASP taking advantage of its numerical machinery and parallelization scheme

Contour plot: total charge density of DFT/EAM system in bulk Al



EAM density provides B.C. for solving DFT density



Test **bulk** system of Al consisting of 14x14x1a0 (2x2x1 a0) unit cells

System initially in **perfect** fcc configuration (EAM rescaled)

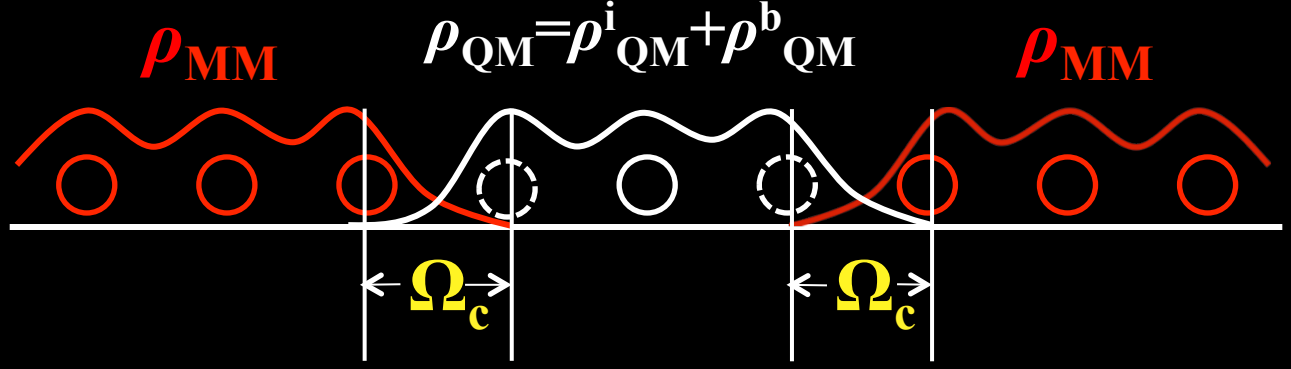
If QM/MM coupling were perfect, force on each atoms should vanish and no atom should move - an unambiguous way to identify coupling errors

	$F_{max}(1)$ (eV/A)	$F_{max}(2)$ (eV/A)	$d_{max}(1)$ (A)	$d_{max}(2)$ (A)
QM/MM method	0.02	0.00	0.002	0.00

Comparable to typical DFT force convergence criterion

QM/MM Method Based on Constrained DFT

(potentially more accurate/versatile; doesn't rely on interatomic potential or OFDFT)



MM: elastically deformed defect-free lattice;

ρ^{b}_{QM}: bulk-like charge density constructed a priori

ρ^{i}_{QM}: degree of freedom

MM (R_{MM})

QM boundary (R^{b}_{QM})

QM interior (R^{i}_{QM})

$$E_{tot}[\rho_{tot};\vec{R}_{tot}] = E_c^{DFT}[\rho_{QM};\vec{R}_{QM}] + E^{MM}[\vec{R}^{b}_{QM} \cup \vec{R}_{MM}] - E^{MM}[\vec{R}^{b}_{QM}]$$

ρ_{QM} is self-consistently determined based on the constrained DFT with the charge density constraint that $\rho_{QM} = \rho^{b}_{QM}$ within Ωc.

Bulk-like ρ^{b}_{QM} is constructed as a superposition of "atomic" charge densities:

$$\rho^{b}_{QM}(\vec{r}) = \sum_{i \in B} \rho_{\mathrm{at}}(\vec{r} - \vec{R}_i)$$

as target charge density which ρ_{QM} converges to.

Associated with the target density, a constraint potential in $\boldsymbol{\Omega_C}$

$$v_{\mathrm{c}}(\vec{r} \in \Omega_{\mathrm{c}}) = \lambda \int_{\Omega_{\mathrm{c}}} \frac{\rho_{\mathrm{QM}}(\vec{r}\,') - \rho^{b}_{QM}(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} dr'$$

λ is a penalty parameter

is added to original KS Hamiltonian of QM region:

$$H'_{\mathrm{KS}}[\rho_{\mathrm{QM}}; \vec{R}_{\mathrm{QM}}] = H_{\mathrm{KS}}[\rho_{\mathrm{QM}}; \vec{R}_{\mathrm{QM}}] + v_c(\vec{r})$$

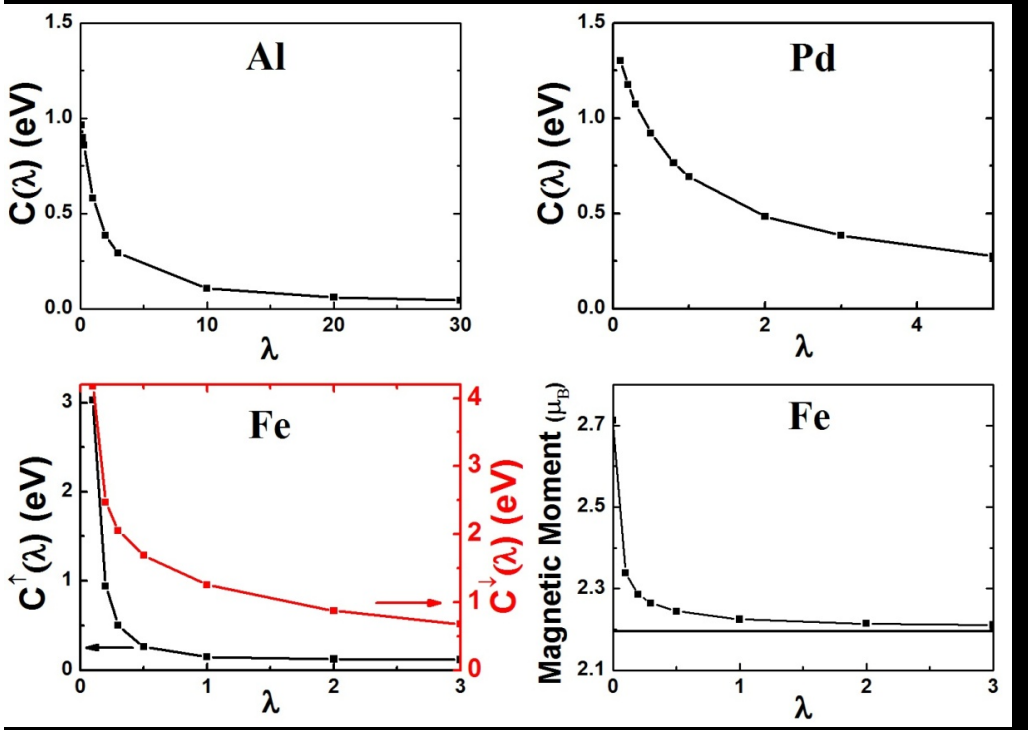
$$E^{\mathrm{DFT}}[\rho_{\mathrm{QM}}; \vec{R}_{\mathrm{QM}}] = E'_{\mathrm{KS}}[\rho_{\mathrm{QM}}; \vec{R}_{\mathrm{QM}}] - \int_{\Omega_{\mathrm{c}}} \rho_{\mathrm{QM}}(\vec{r}) v_{\mathrm{c}}(\vec{r}) d\vec{r}$$

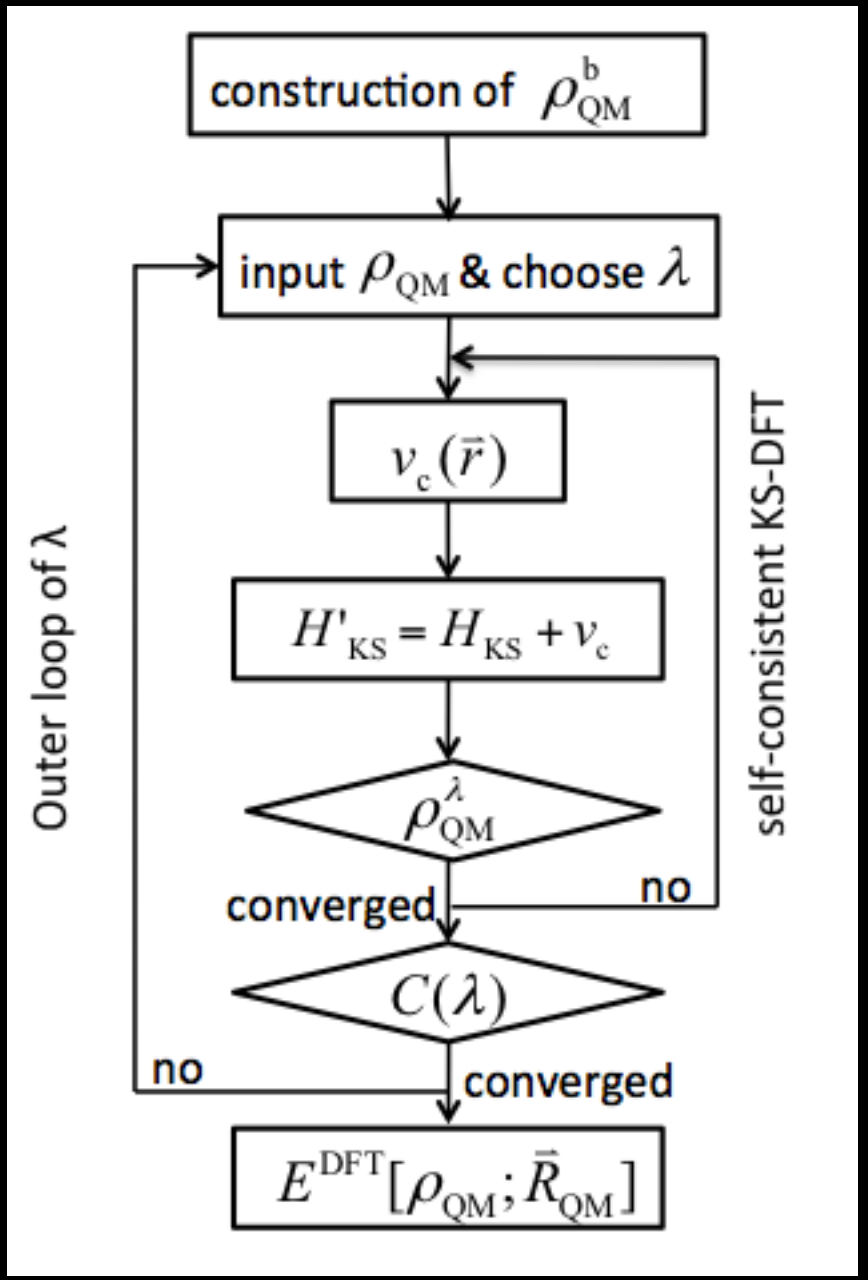
Energy of the QM region

Remove energy contribution of the constraint potential

$$C(\lambda) = \frac{1}{2\lambda}\int_{\Omega_c} [\rho^{\lambda}_{QM}(\vec{r}) - \rho^{b}_{QM}(\vec{r})] v^{\lambda}_{c}(\vec{r}) d\vec{r}$$

quantify the how close the converged charge density matches the target charge density at the QM boundary

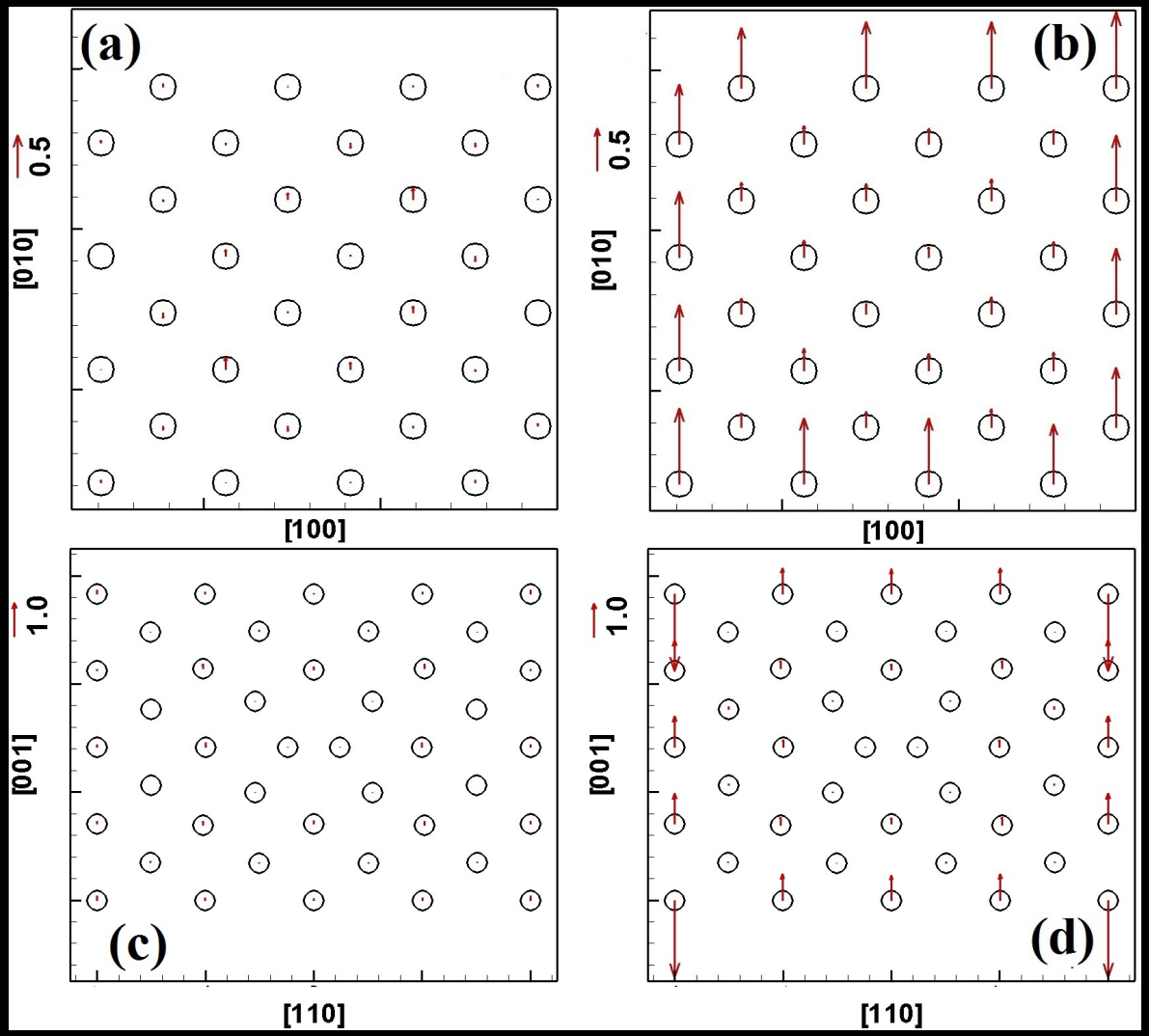




Validation of constrained DFT based QM/MM method

Magnetic moments in Fe relative to periodic DFT results: $\mu_{QM/MM}-\mu_{DFT}$

$\mu_{cluster}-\mu_{DFT}$



perfect lattice

self-interstitial defect

QM/MM method

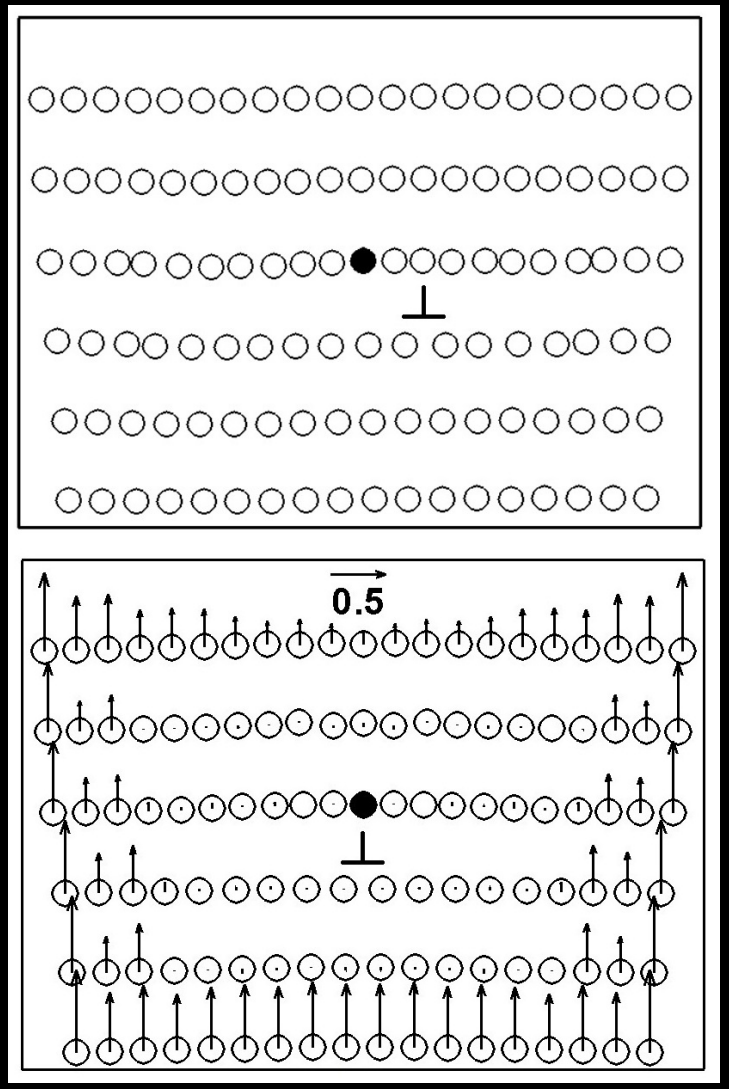
DFT cluster

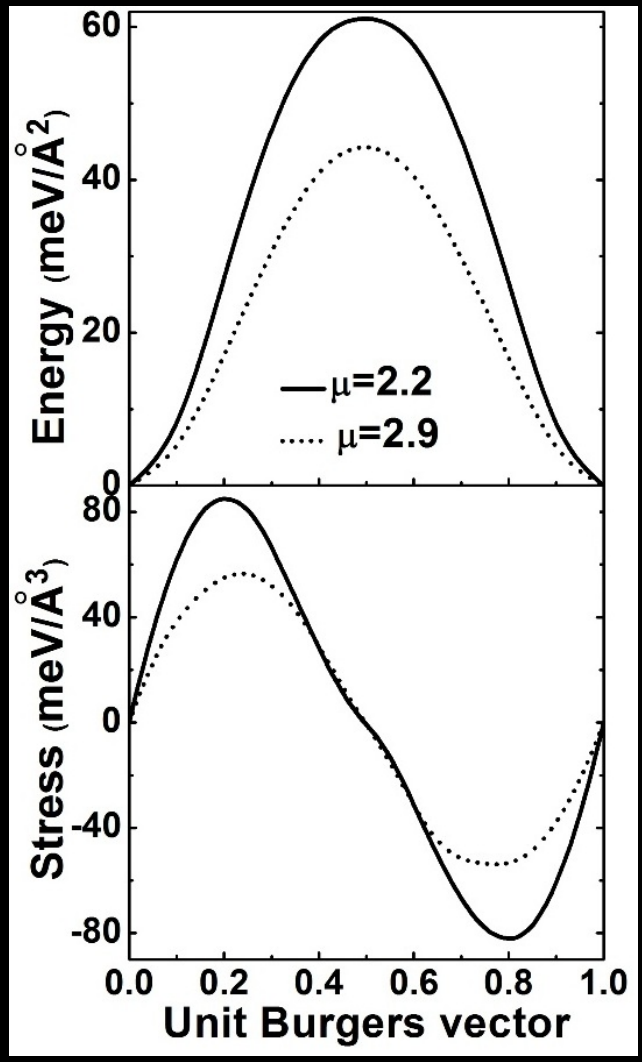
Lead to errors in mechanical QM/MM

Cr impurity introduced at dislocation core of Fe

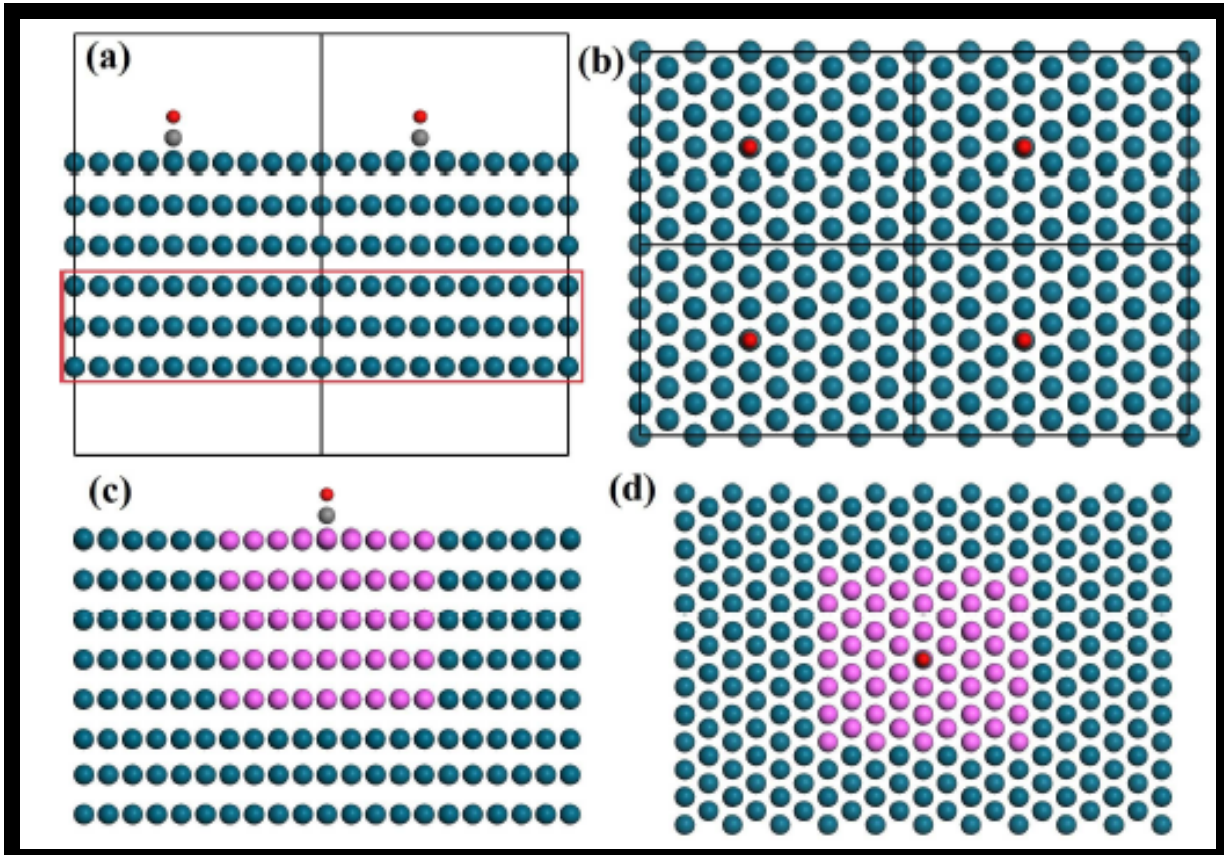
Constrained DFT QM/MM (dislocation glides spontaneously)

Mechanical coupling QM/ MM (No dislocation gliding)





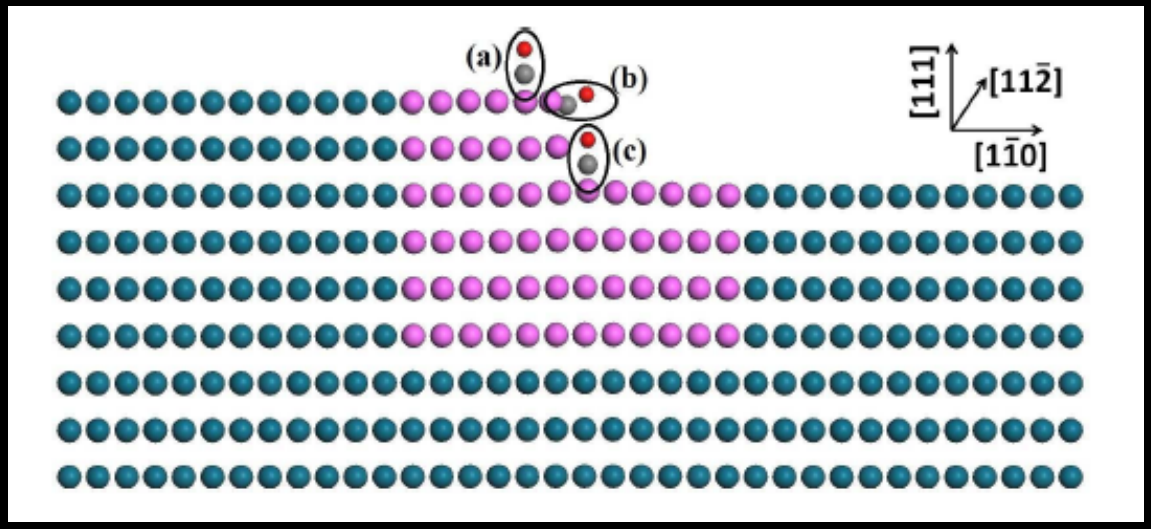
Magnetic moment influences stacking fault energy, hence dislocation core structure



Surface adsorption of CO on Pd surface: side (left) and top view (right)

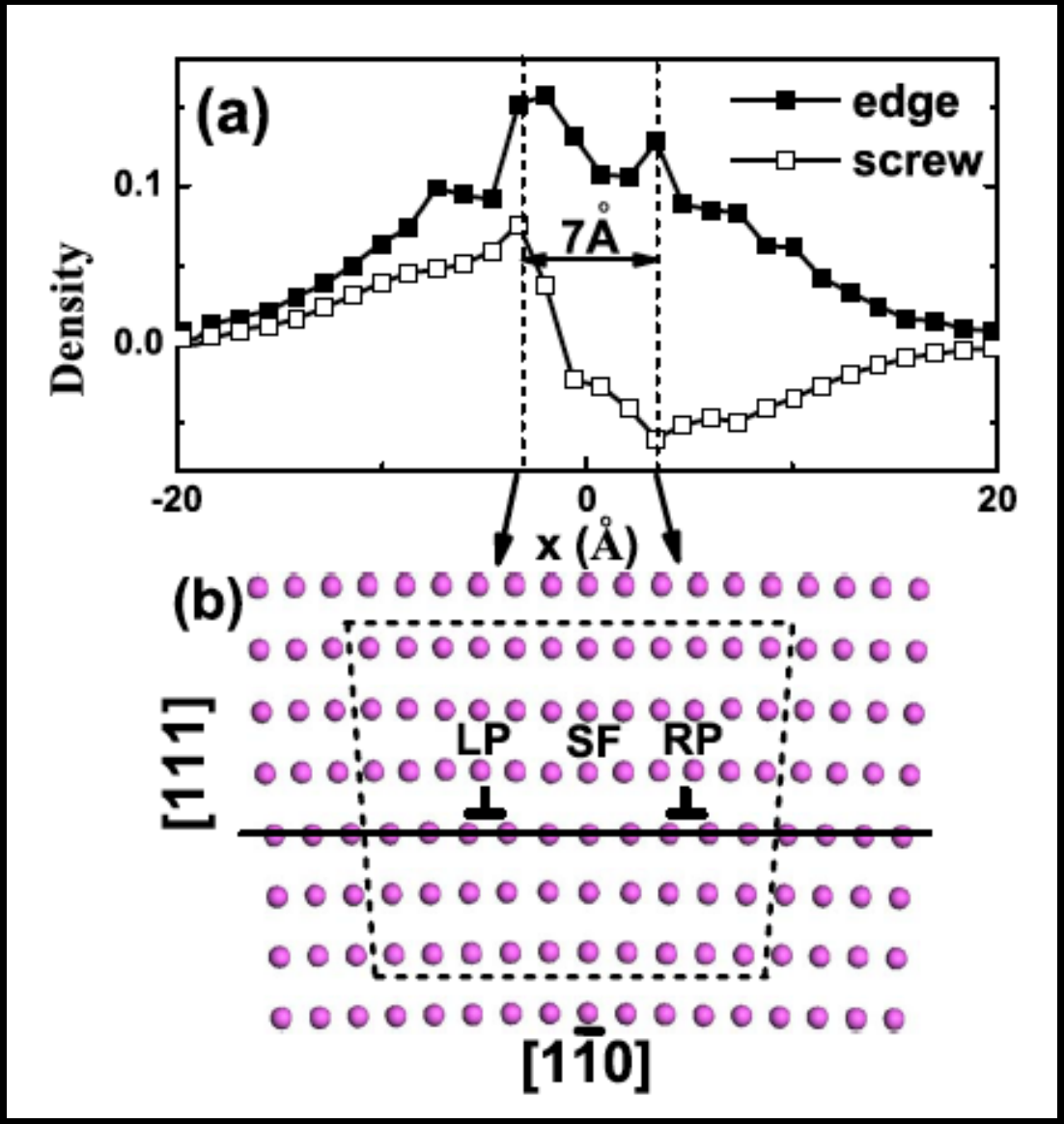
Periodic DFT (top) vs. QM/MM (bottom) for adsorption energy

Can treat low coverages using QM/MM with same DFT size



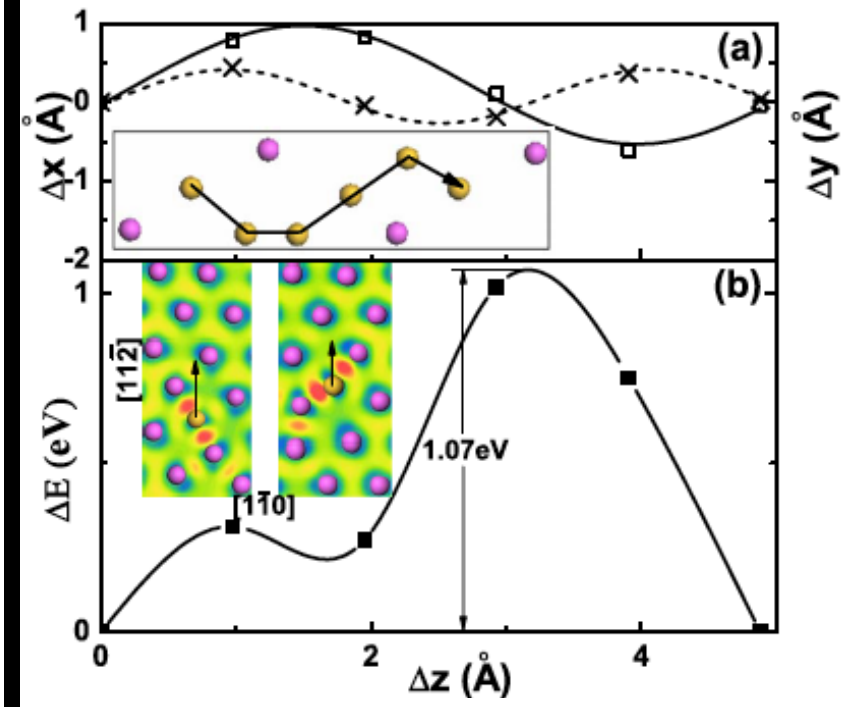
CO adsorption energy at surface step of Pd using QM/MM

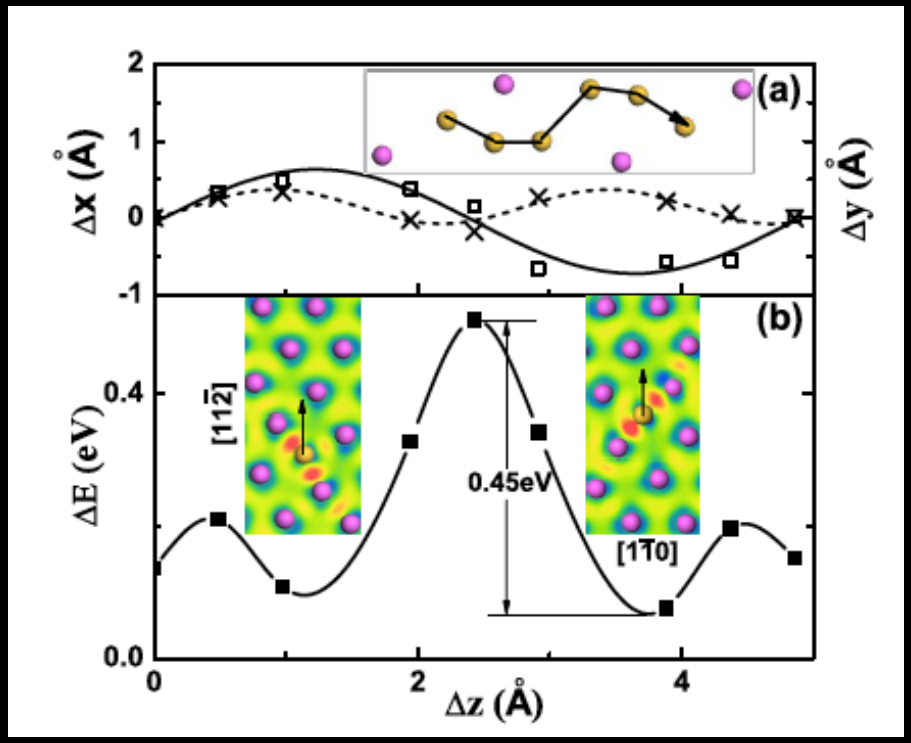
Pipe Diffusion of Si Interstitial Along Dislocation in Al

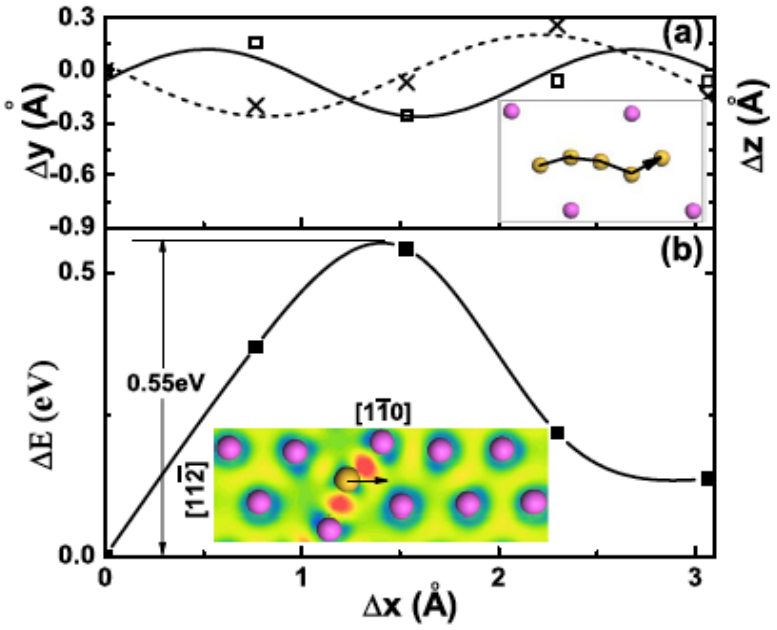


M. Legros, et al. "Observation of Giant Diffusivity Along Dislocation Cores", Science, (2008)

- Three orders of magnitude increase in pipe diffusivity along dislocation core comparing to bulk at 600-700 K.
- Pipe diffusion energy barrier at 700K is 1.12 eV.
- It is not clear whether Si diffuses along partial core or stacking fault (SF width is ~ 7 Å)





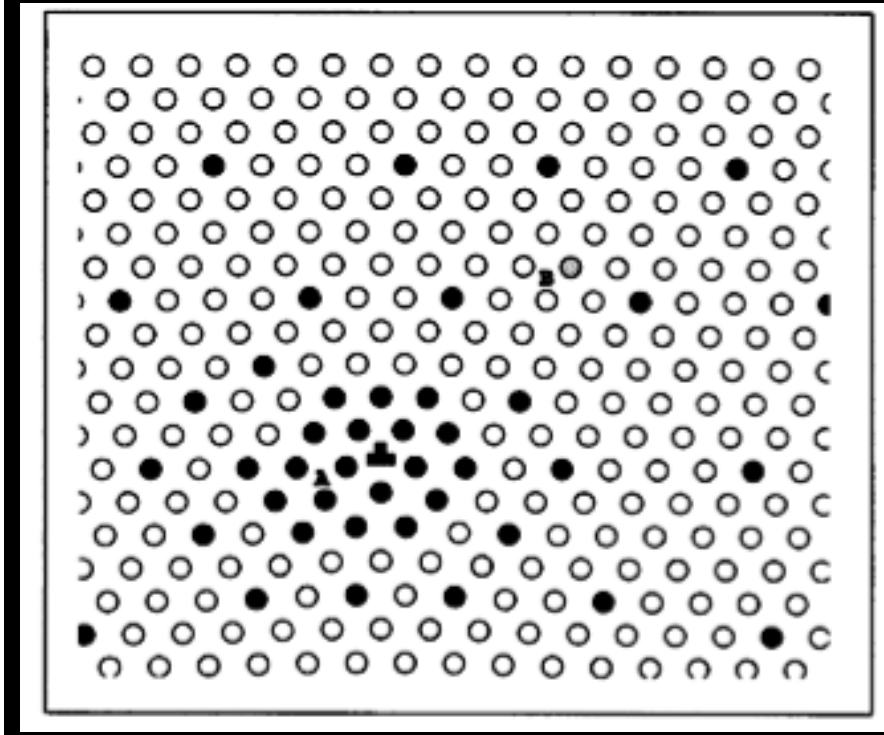


- Diffusion barrier along LP(RP): 1.07 eV; Experimental value: 1.12 eV.
- Diffusion barrier along SF: 0.45 eV - six to seven orders of magnitude increase in diffusivity comparing to bulk (**1.30 eV**).
- Si is more stable in LP relative to SF (one to four ratio of prob. at 700K); 0.55 eV barrier from LP to SF.

SF is an extremely fast channel for diffusion

Quasicontinuum (QC) Method: Basic Framework for QCDFT

(Tadmor, Ortiz, Phillips, 96)



Key ideas behind QC:

• A small subset of atoms with varying density is selected to represent the energetics of the system.

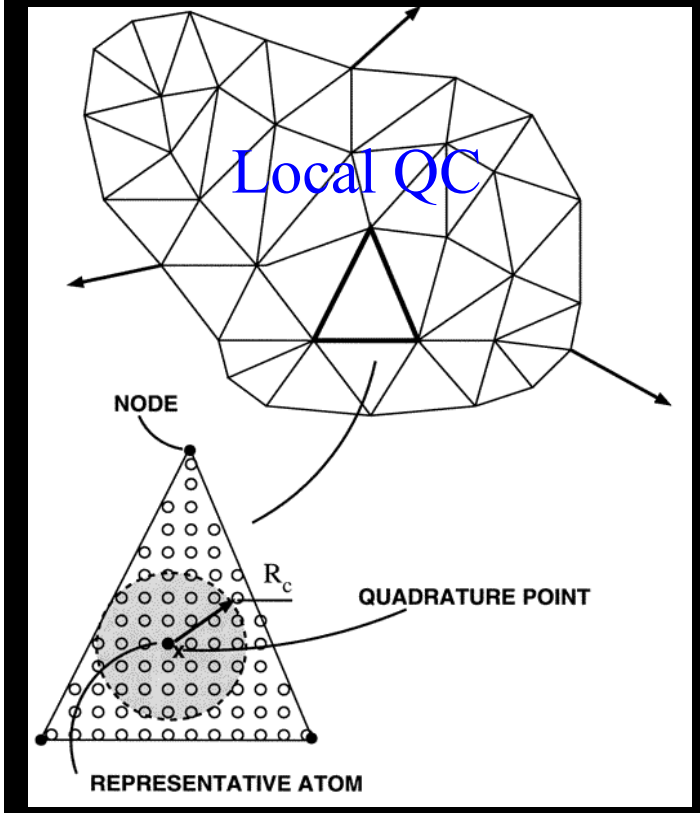
"**repatoms**" – d.o.f. (filled circles)

- near defect core where deformation changes more rapidly: more repatoms (**nonlocal QC**)

- less deformed region: fewer repatoms (**local QC**) – perfect lattice elastically deformed

• The representation is adaptively updated as deformation evolves.

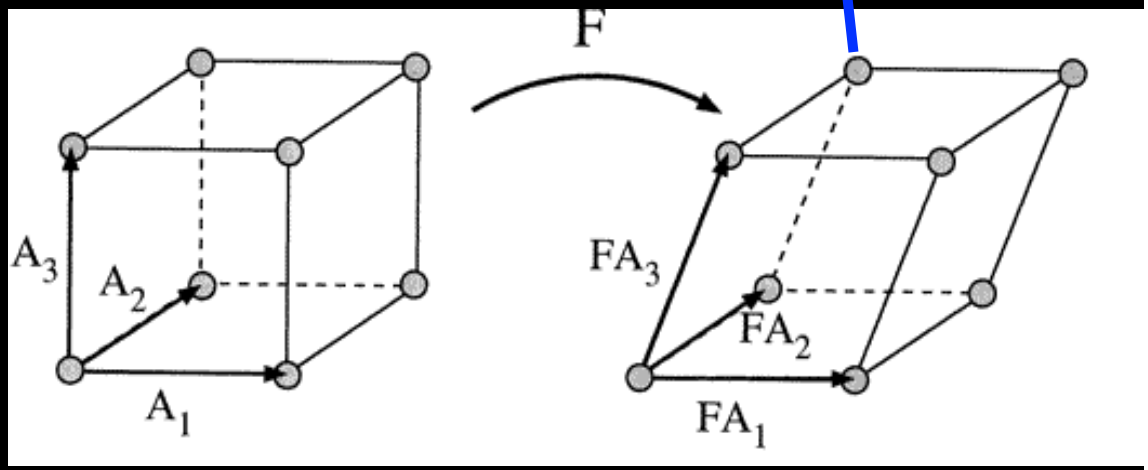
Local QC: atomistically-informed FEM



Strain energy density stored in deformed unit cell calculated by periodic DFT (1 atom/cell) or EAM;
Following Cauchy-Born Rule, the energy of the FE is

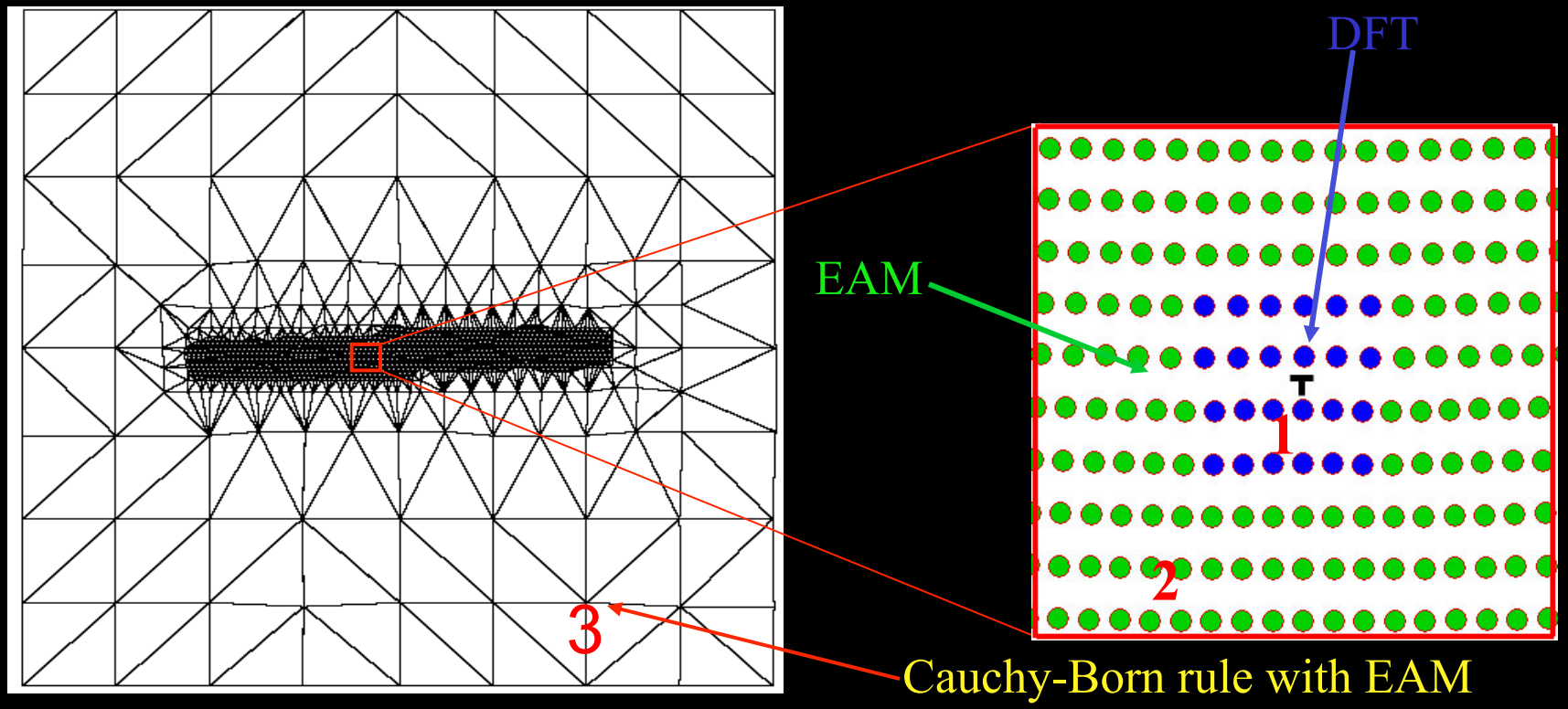
$$E_{tot} = \sum_{j=1}^{N_{atom}} E_j^{atom} \approx \sum_{i=1}^{N_{element}} n_i \overline{E}_i$$

$$N_{element} << N_{atom}$$



For a given FE, there is a deformation gradient (tensor) **F.**
Lattice vectors of unit cell undergo deformation
$\mathbf{A_i} \longrightarrow \mathbf{FA_i}$

Quasi-continuum DFT (QCDFT) method (06')
(QCDFT=QC + QM/MM)

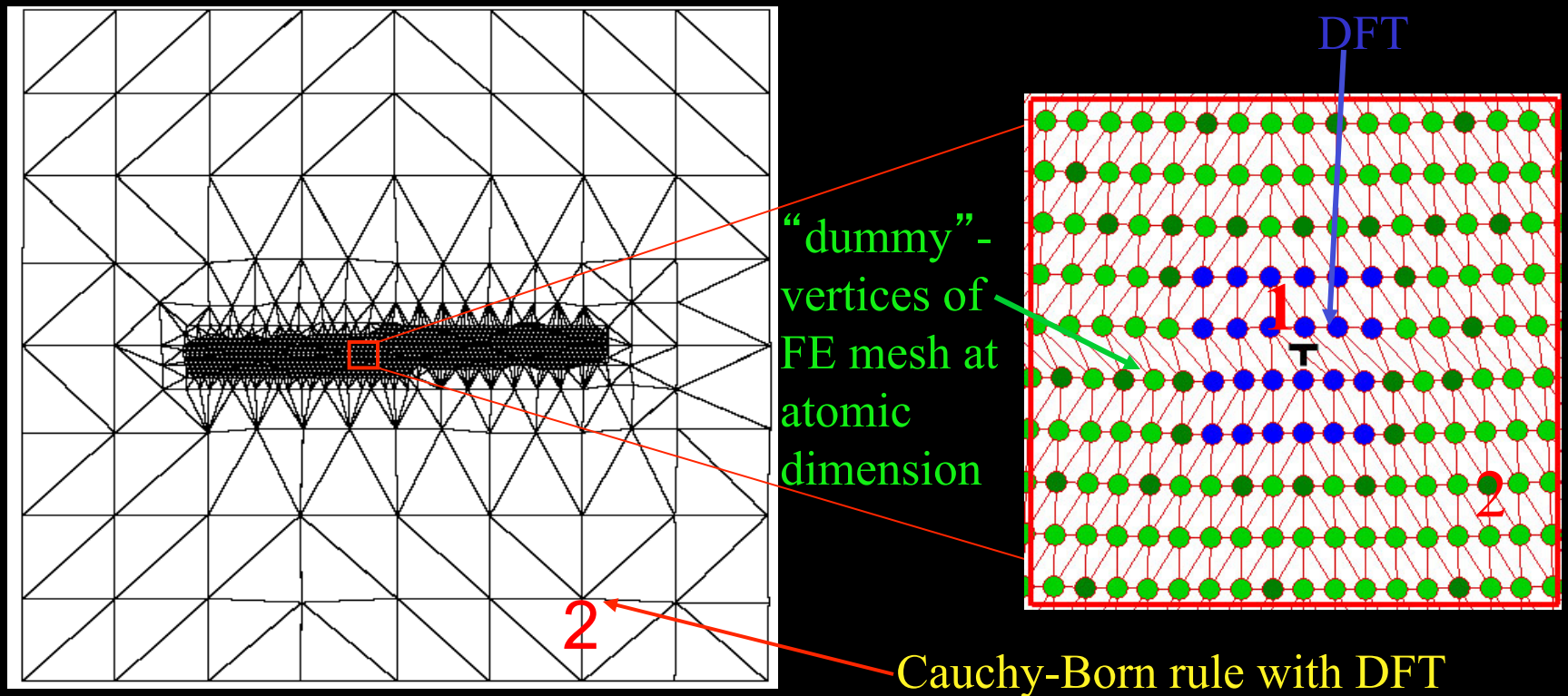


- All QM processes contained in region 1 treated with DFT
- The remaining nonlocal QC region 2 treated by EAM

QM/MM

- Energy in FE region (region 3) calculated by EAM with Cauchy-Born rule

New QCDFT method: KS-DFT for macroscale modeling

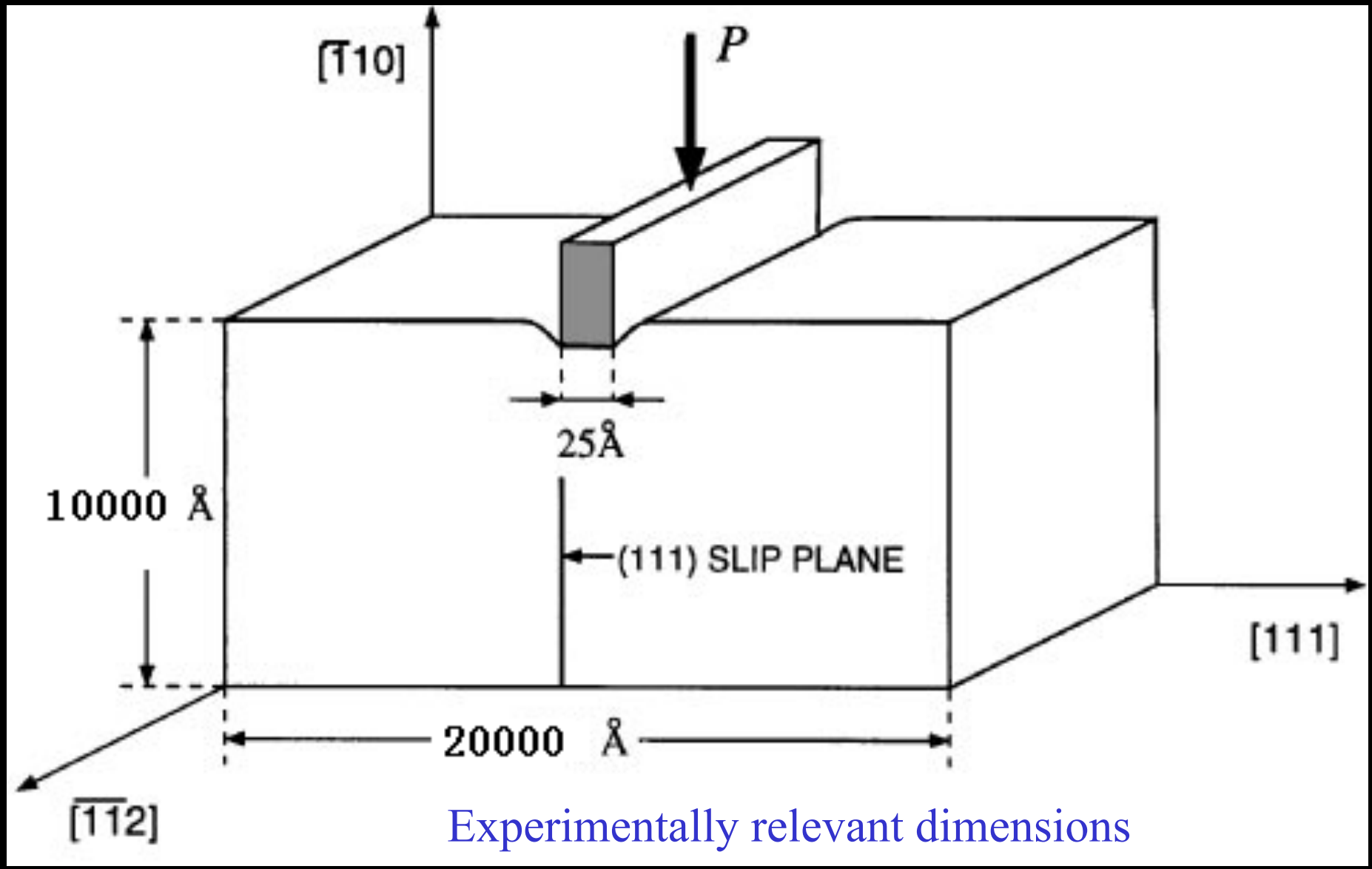


- All QM processes contained in region 1 treated with KS-DFT
- Region 1 connected to finite-element region (2) directly
- Energy in FE region (2) calculated by KS-DFT with Cauchy-Born rule

QM/MM Constrained DFT

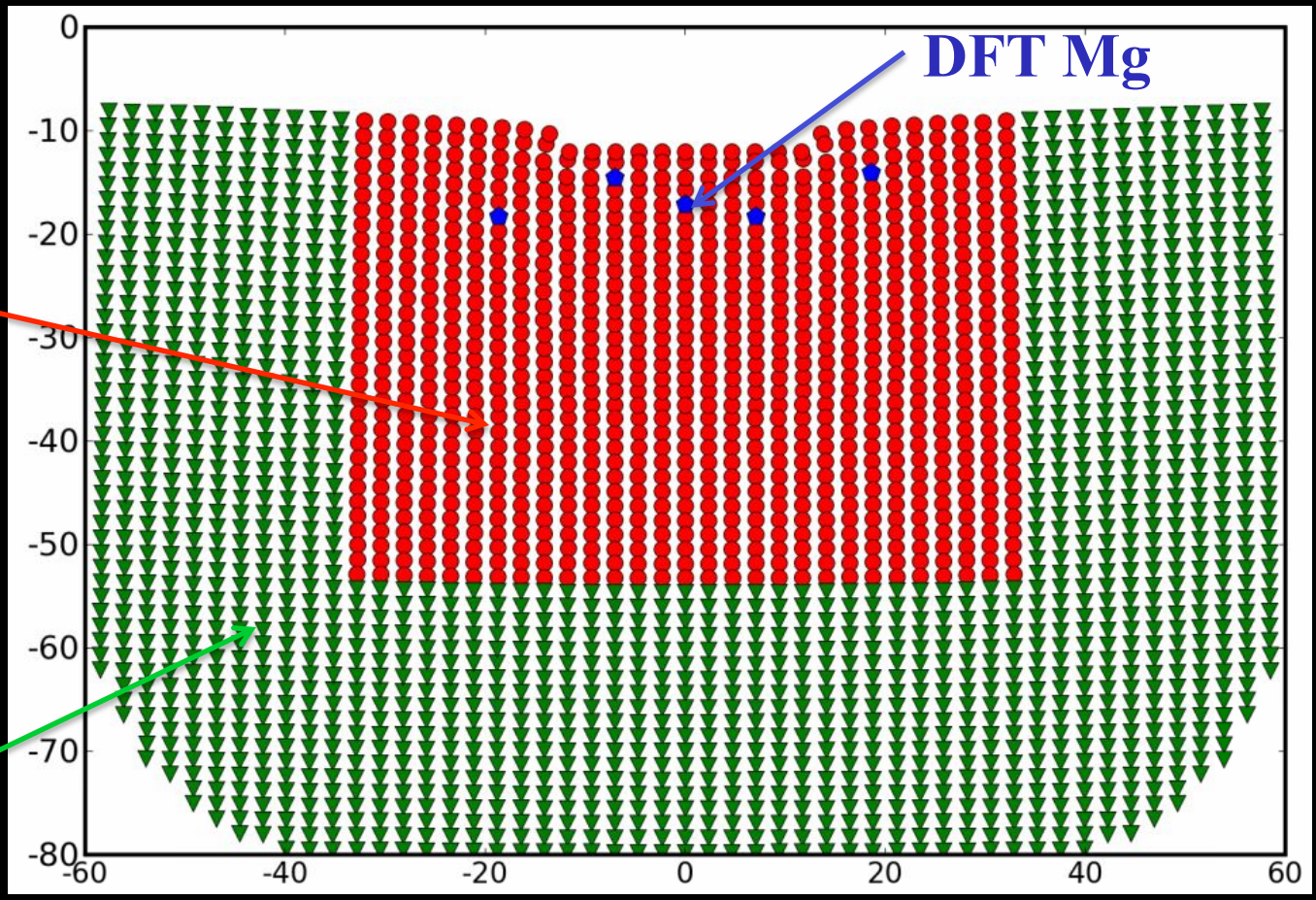
QCDFT Study of Nanoindentation of Al Thin Film

Peng, PRB 78, 054118 (2008); Peng, Model. Simul. Mater. Sci. Eng. (2010)

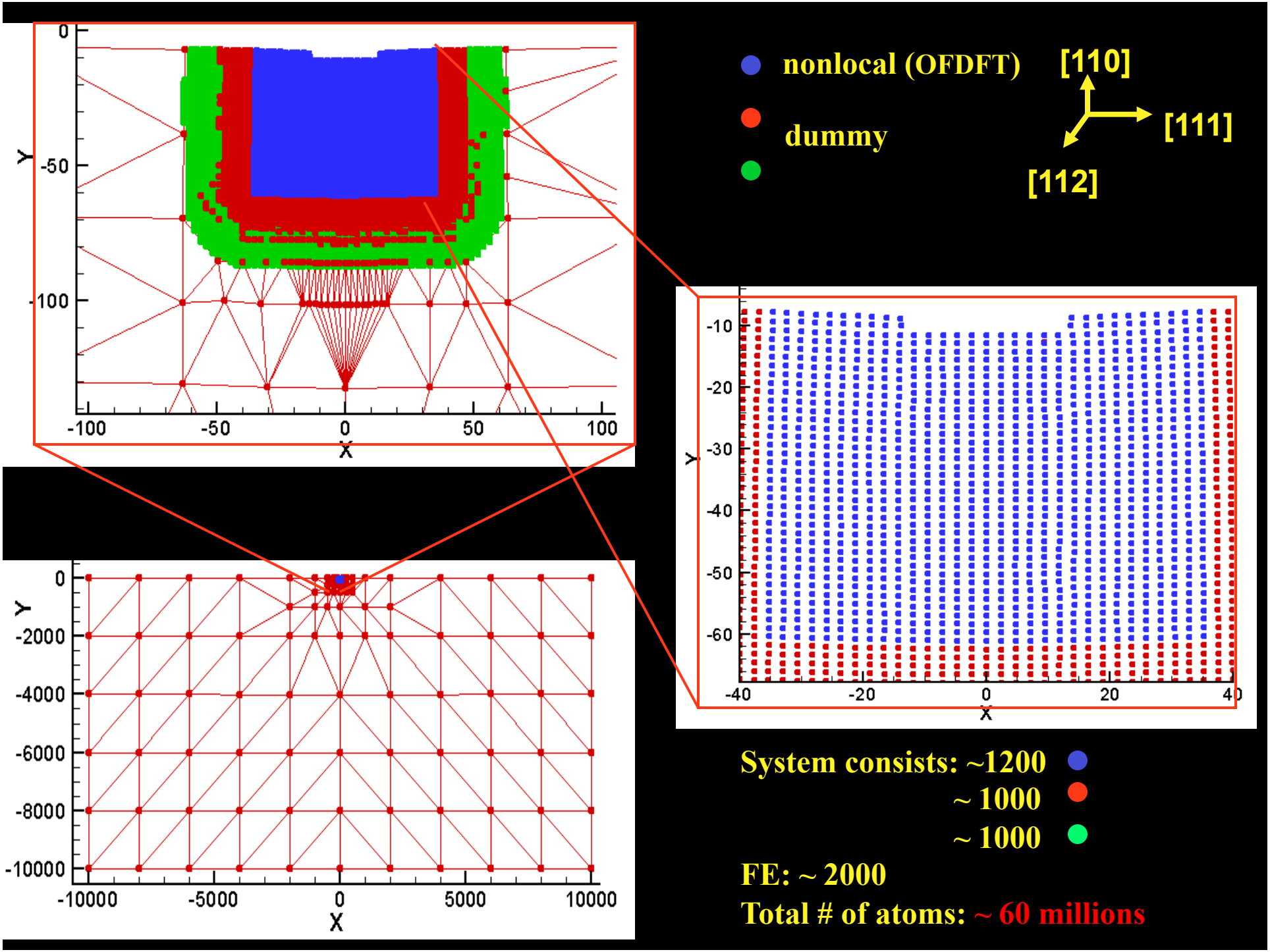


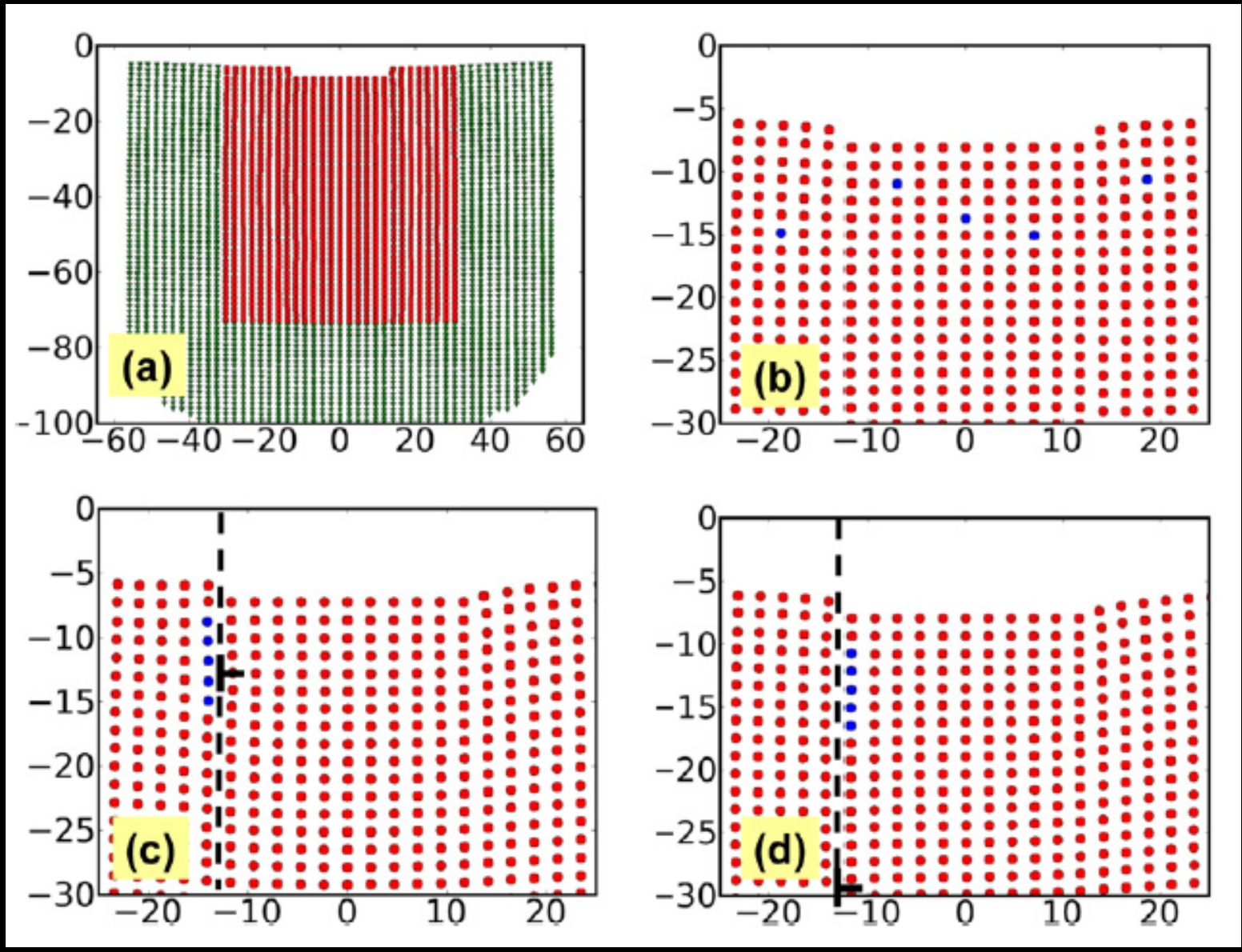
Experimentally relevant dimensions

Mg impurities introduced near surface of Al thin film



Goal: effect of Mg on the ideal strength of Al thin film - It's well-known that impurities can affect the motion of dislocations; but it is not clear whether impurities would affect the nucleation of dislocations in an otherwise perfect crystal.


nonlocal (OFDFT)
dummy
[110]
[111]
[112]
0
-50
-100
Y
-100
-50
0
50
100
X
-10
-20
-30
-40
-50
-60
Y
-40
-20
0
20
40
X
0
-2000
-4000
-6000
-8000
-10000
Y
-10000
-5000
0
5000
10000
X
System consists: ~1200
~ 1000
~ 1000
FE: ~ 2000
Total # of atoms: ~ 60 millions

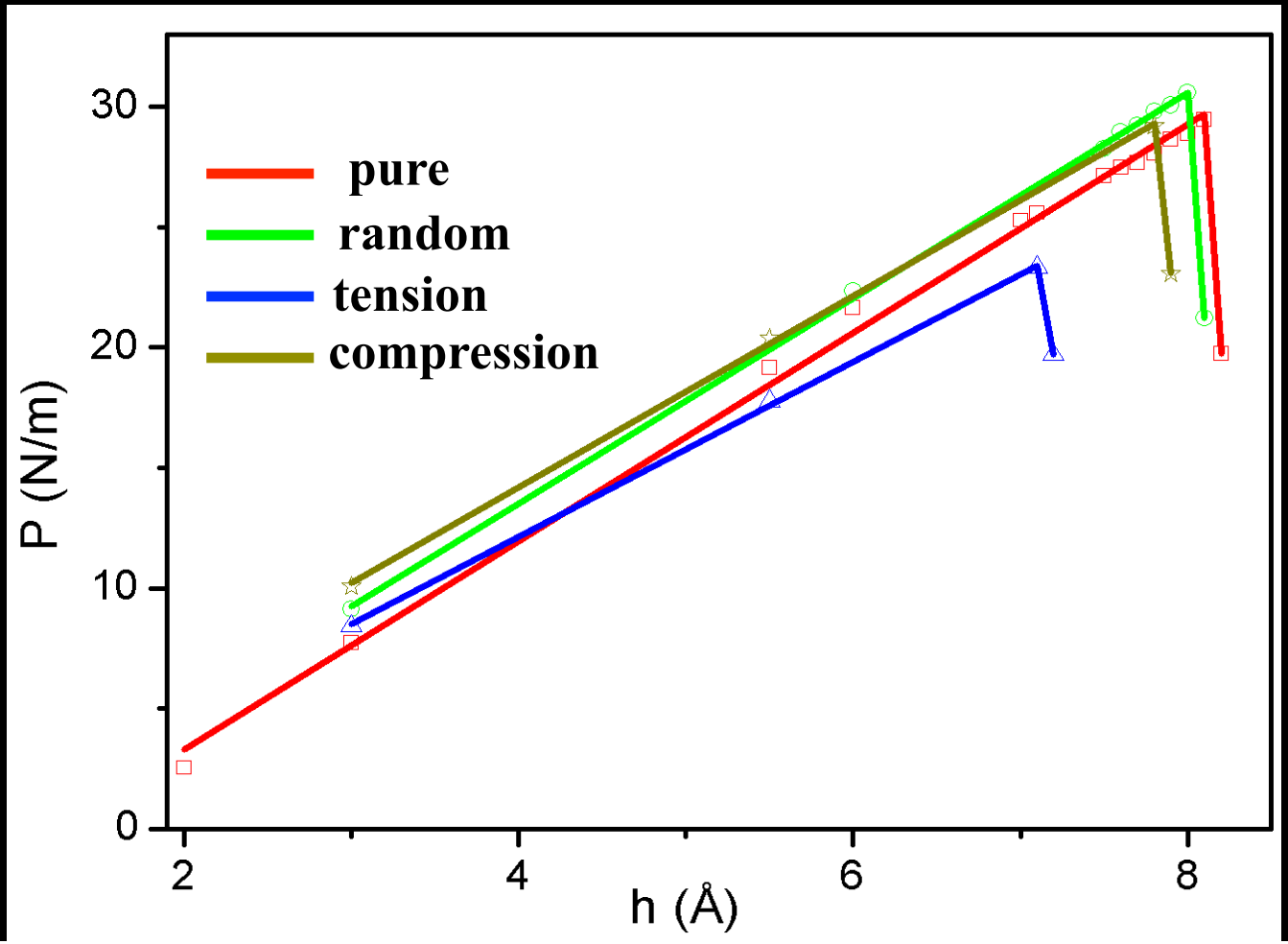


tension compression

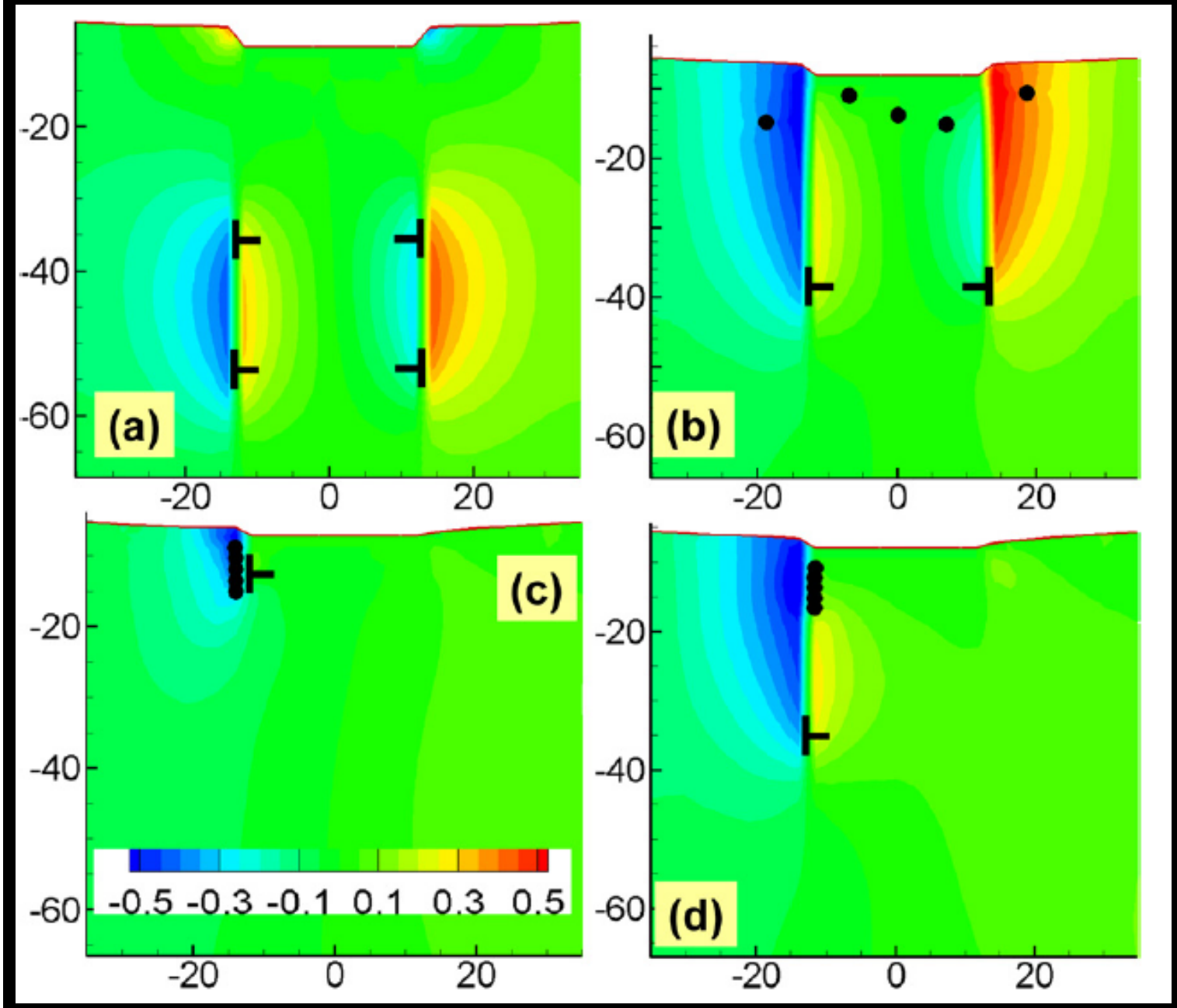
Applied pressure (P) – Indentor displacement (h): Onset of plasticity

- Initially elastic behavior;
- At critical point, thin film snaps - starts yielding and pressure drops; onset of plasticity;
- Critical P is ideal strength

Random distribution slightly increases ideal strength, but tension case significantly softens material

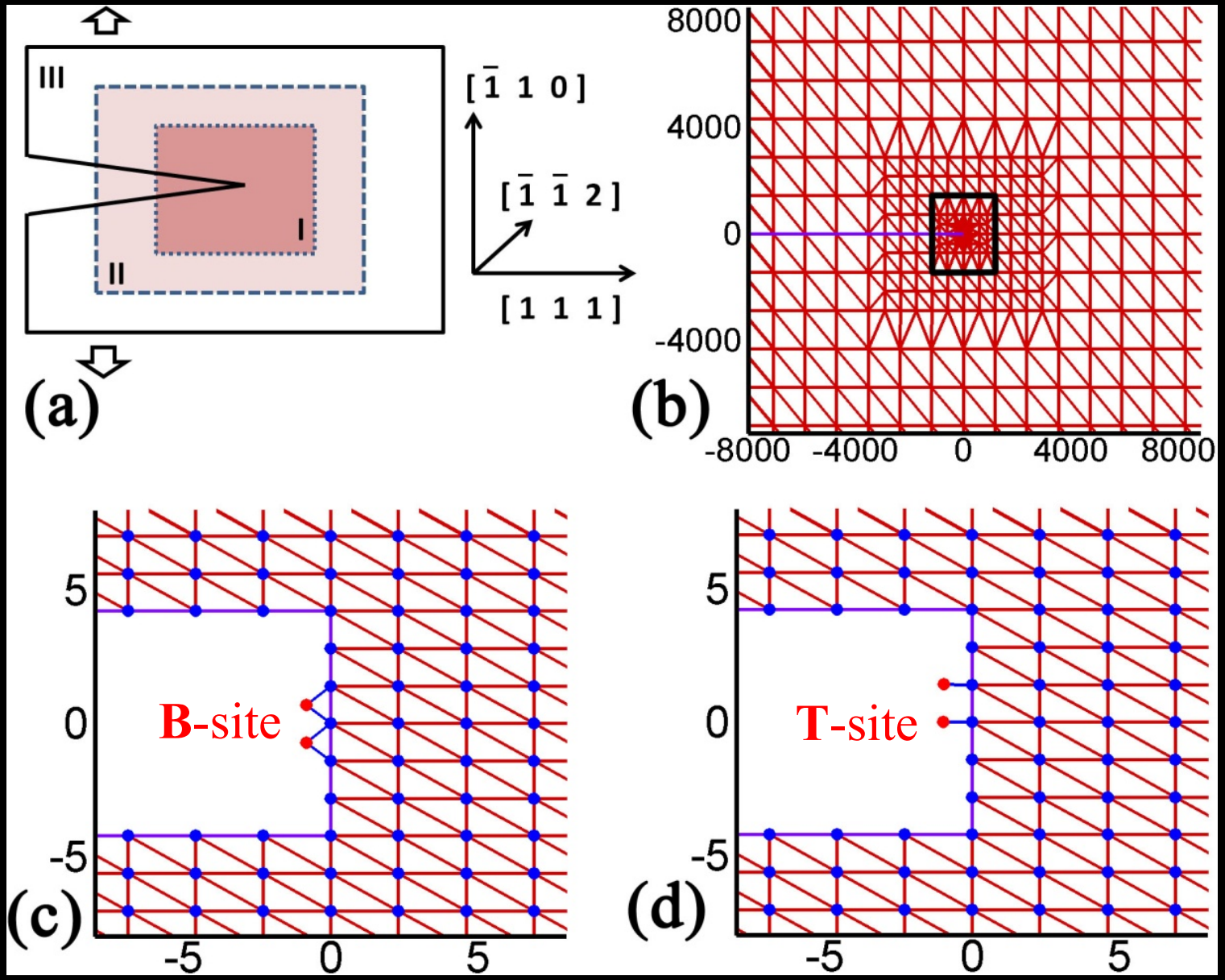


Displacement contours along dislocation line at yielding



Incipient plasticity depends sensitively on impurity distribution!

Hydrogen Assisted Cracking in Al with QCDFT



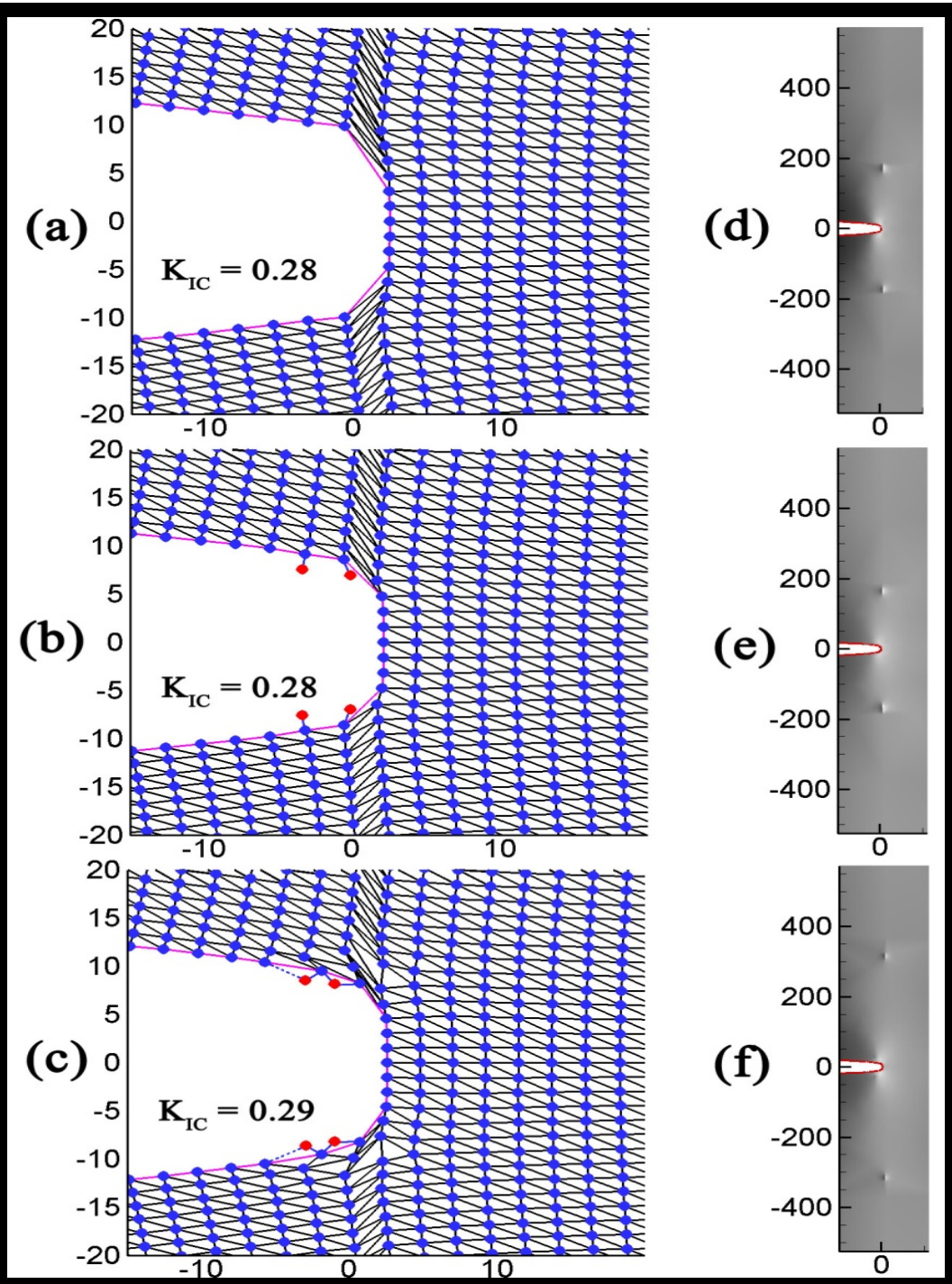
Dimensions: 1.6x1.6 um^2 80 million atoms

300 – 400 KS-DFT atoms (I);

16,000 EAM atoms (II)

6,000 finite elements (III)

Both Bridge (B) and Top (T) sites for H considered

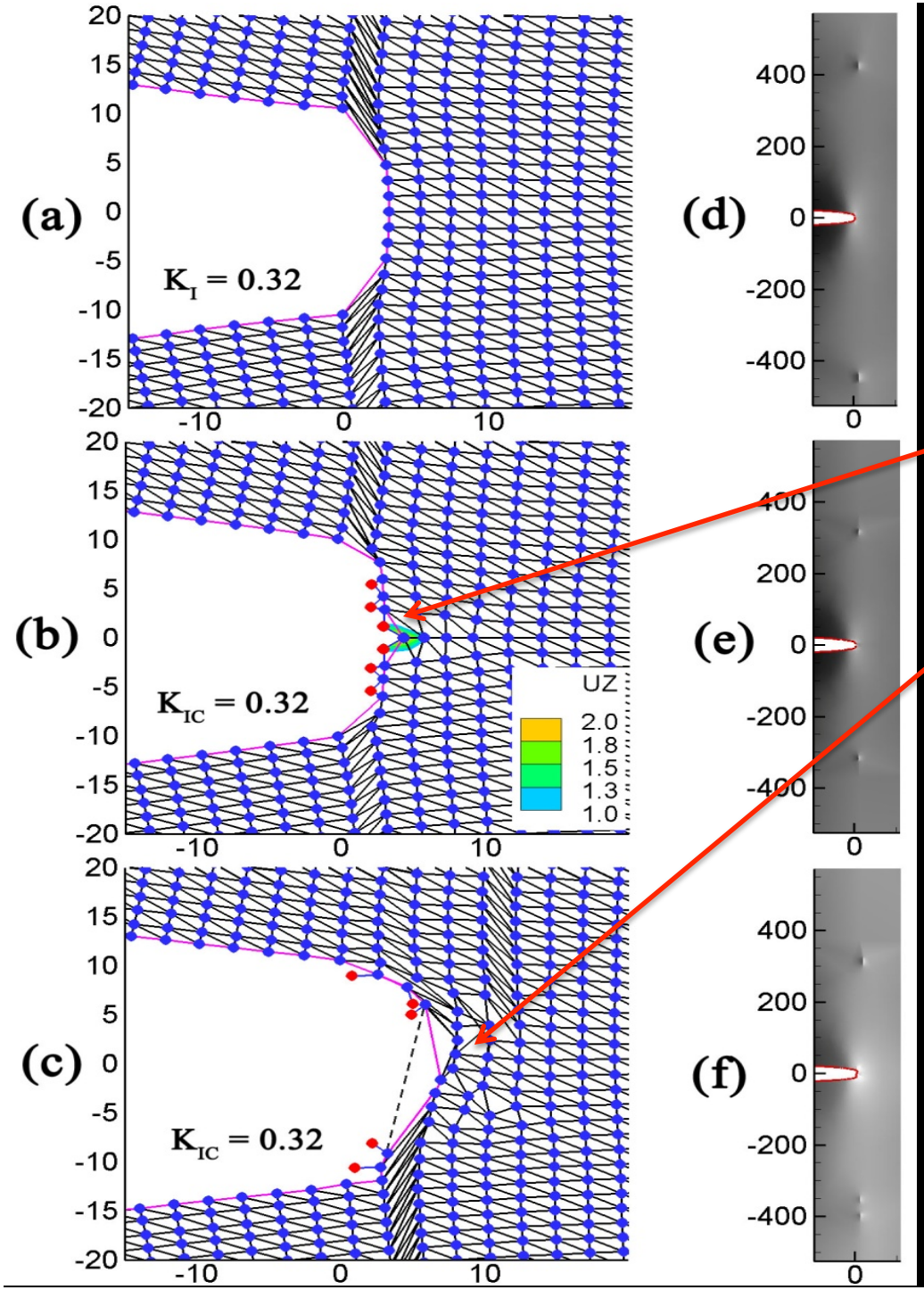


H on top/bottom crack surfaces:

K_{IC} (eV/Å$^{2.5}$): critical stress intensity for dislocation nucleation

- Partial dislocations (±200 Å) emitted from crack tip; crack tip is blunted, not propagating
- Cracks with both **T**-site and **B**-site H atoms exhibit the similar crack tip plasticity and critical stress intensity as in pure Al
- For 4 to 10 H, crack tip behavior all similar to pure Al

There is no H embrittlement on top/bottom surfaces incl. corners

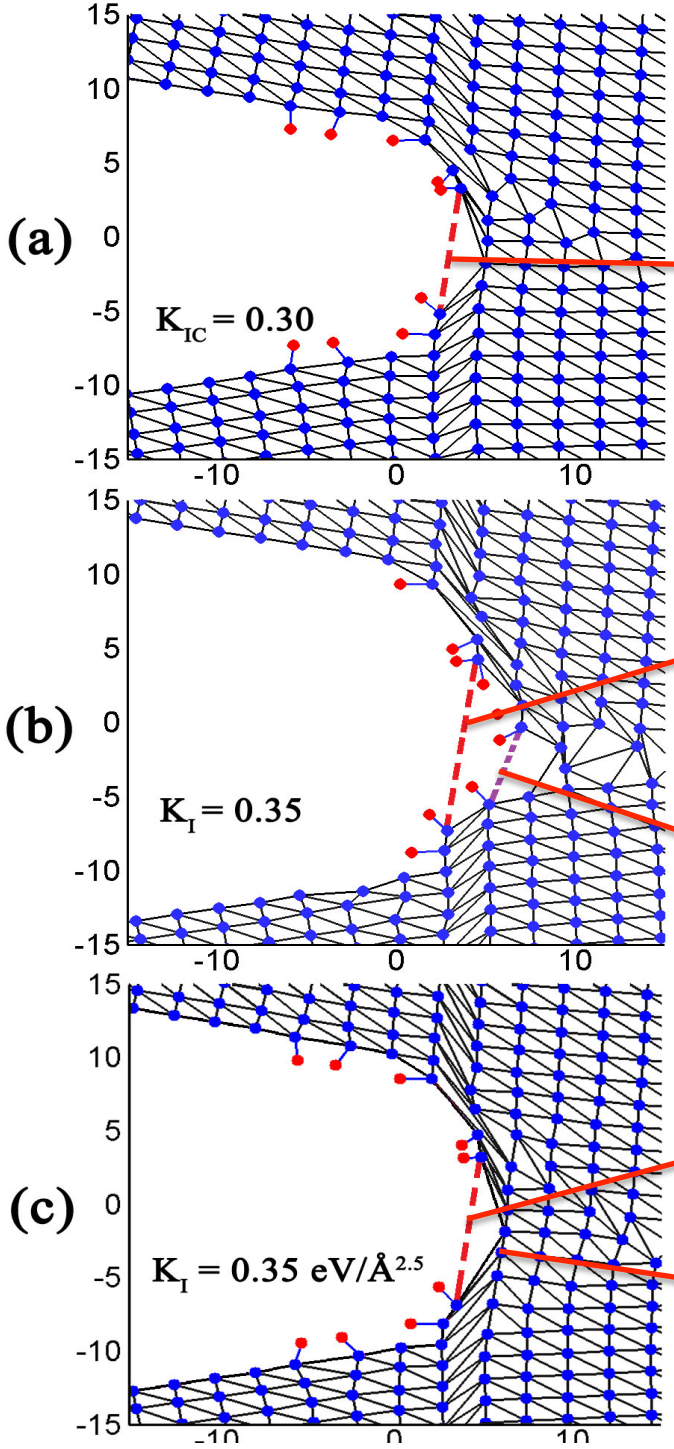


H on crack front surface: 2-10 H atoms

H embrittlement could occur depending on H sites:

For the same K_I:

- For **B**-sites, crack shows ductile behavior; no H-embrittlement
- For **T**-sites, crack shows brittle behavior (crack opens up and propagates) in addition to plasticity; several Al-Al bonds broken
- Critical stress intensity for dislocation nucleation is also greater with H at front surface compared to pure Al:
  H at front surface makes Al more brittle



Closer look of T-site H at crack front:

first cleavage

- Fracture of 1st layer occurs at K_{Ic} = 0.30 with T-site H atoms

first cleavage

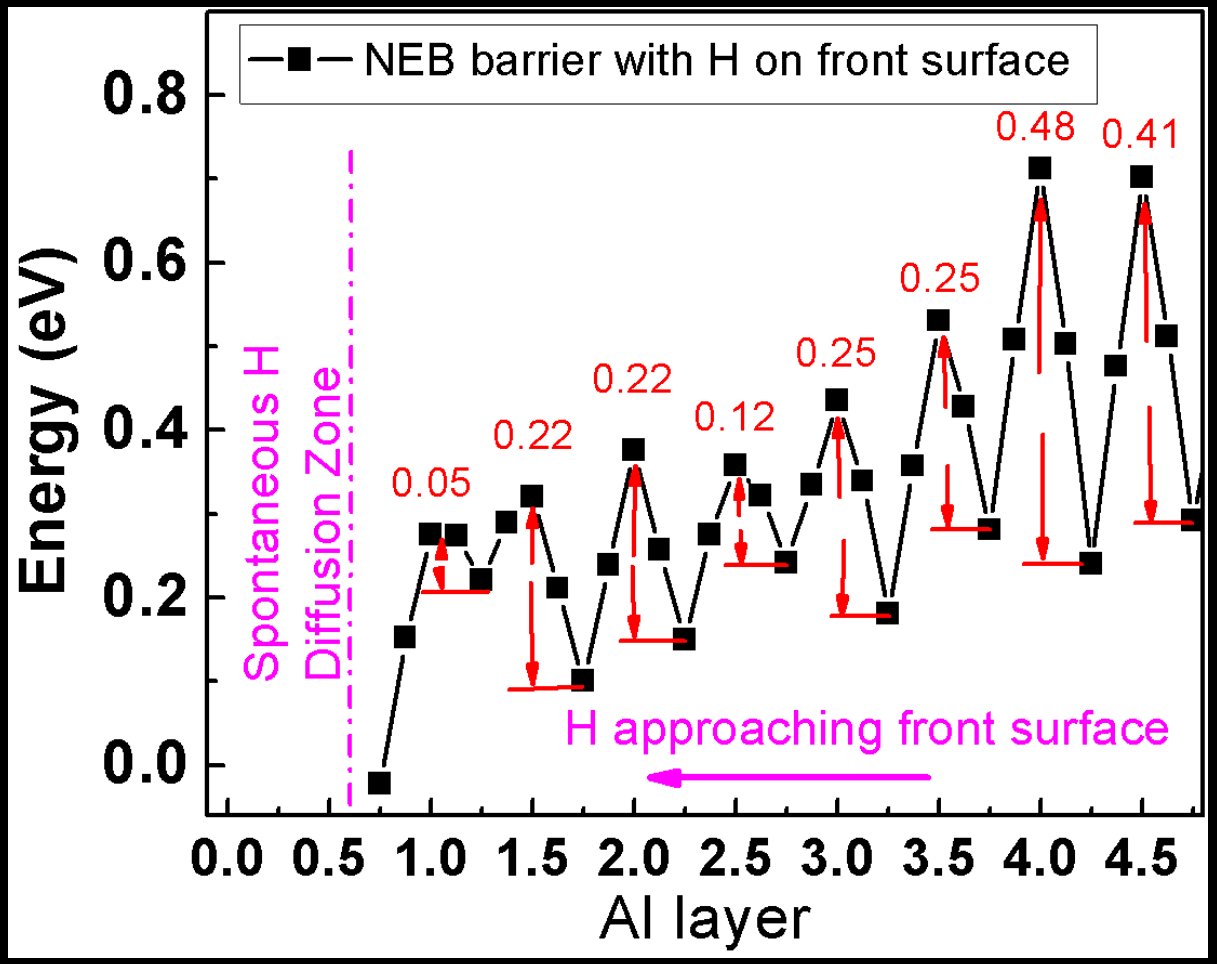
second cleavage with T-site H

- Increase K_I to 0.35, 2nd layer fractures if there are T-site H atoms at the 2nd layer

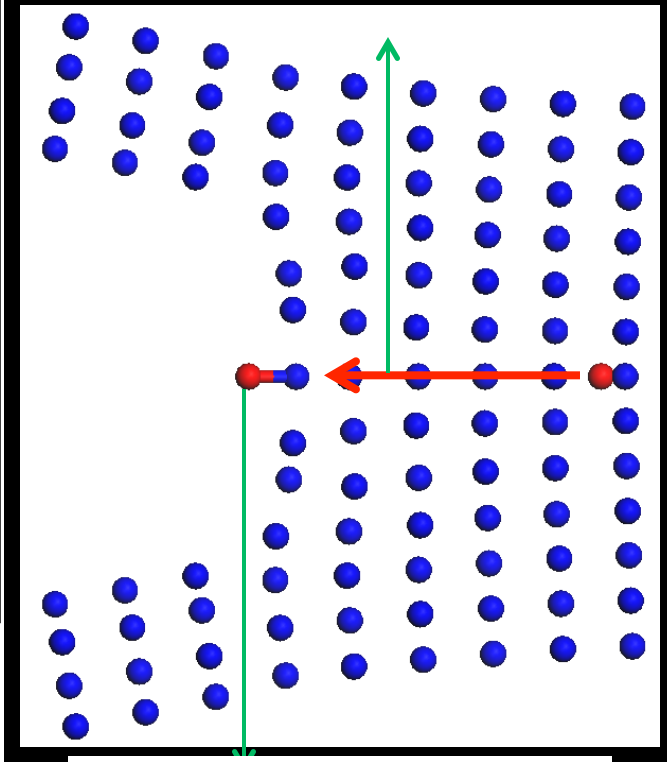
first cleavage

No cleavage without T-site H

- If there are no **T**-site H atoms on 2nd layer, fracture will not continue even at larger loading



Preliminary results of H diffusion



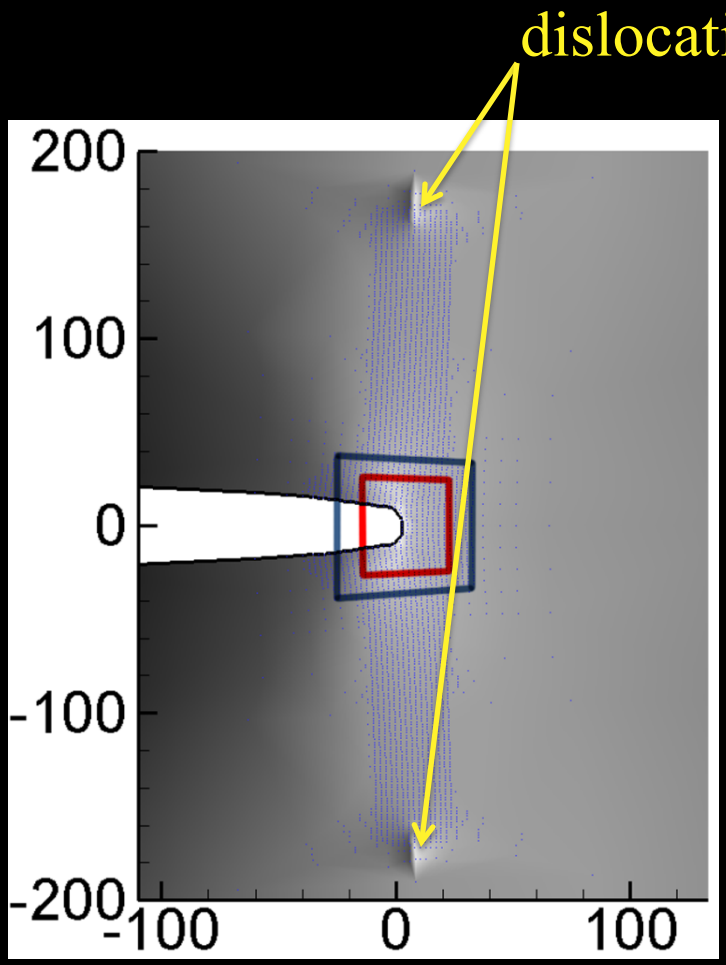
H on front surface

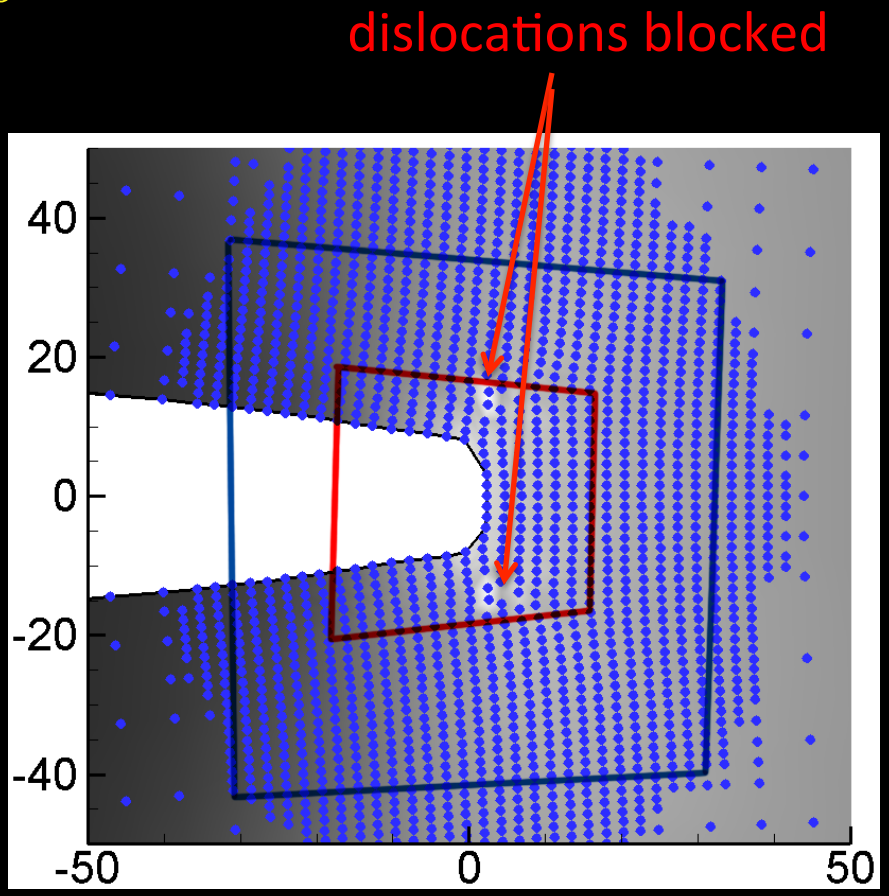
H on front surface has two effects:

(1) Assists the cracking with T-site H;

(2) Facilitates fast H diffusion from bulk interior to crack tip – "pulling H out to crack surface"

Comments on importance of multiscale coupling





Good coupling: dislocations can pass smoothly across through QM/MM and local/nonlocal boundaries

Bad coupling: dislocations are blocked at the QM/MM boundary

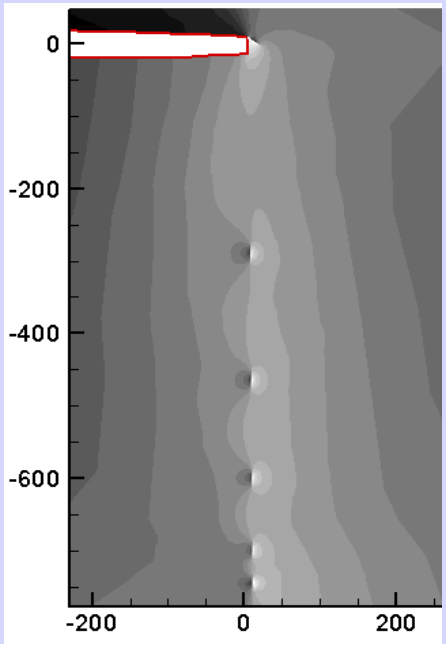
EAM-QC

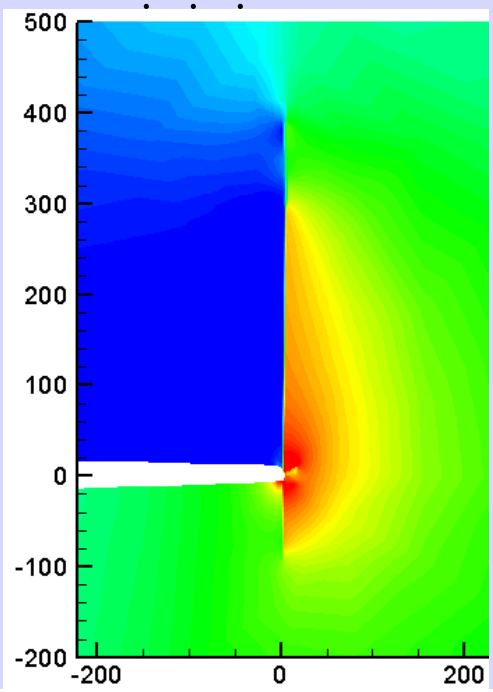
QCDFT

Importance of QM modeling at crack tip

single plane

three adjacent planes

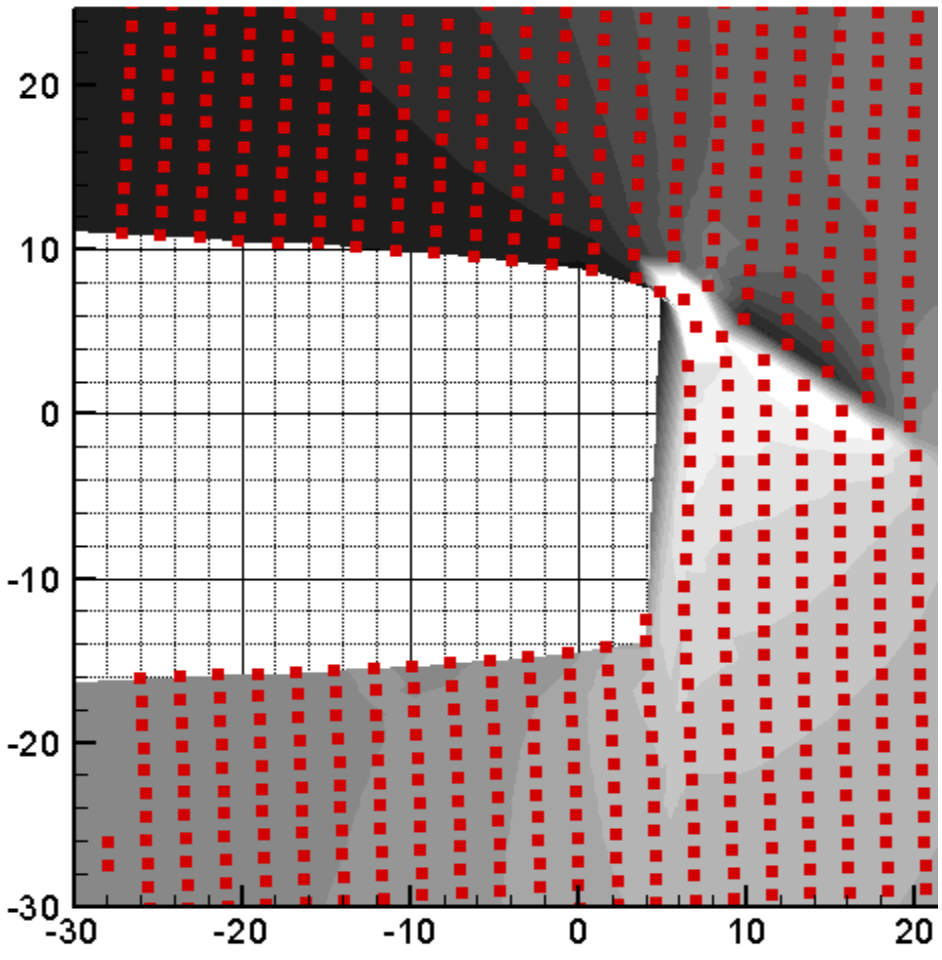


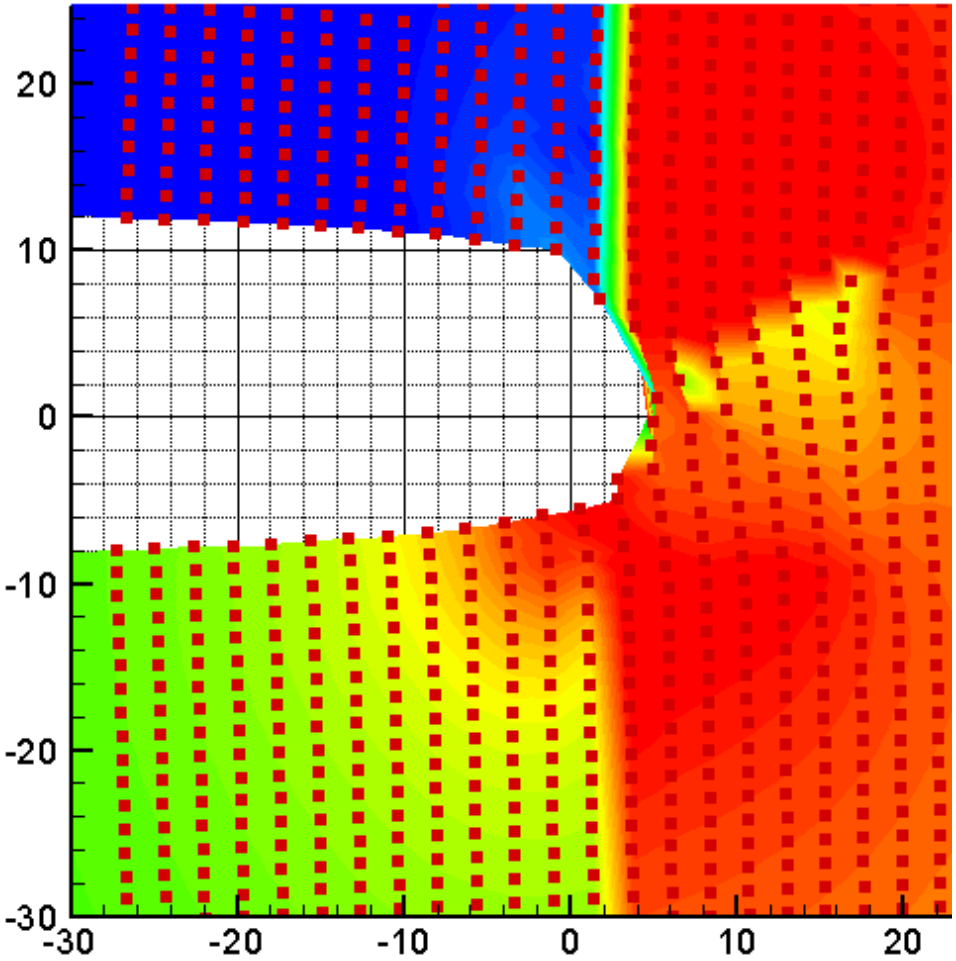


Crack profile comparison:

EAM: straight crack front
- one active slip plane
- sharp corners

DFT: “curved” crack front
- three active slip planes
- smooth corners
- minimize K.E.





Summary & Outlook

- Some examples of our effort to develop multiscale modeling approaches to address key materials problems involving extended defects; QCDFT method allows us to study mechanical properties of materials quantum mechanically at a length-scale that is relevant to experiments.

- Algorithm development and mathematical analysis of multiscale approaches are critical for the progress of the field.

- Ongoing/future work include electron excitations - TDDFT/ TDOFDFT (plasmonics); large-scale hybrid DFT for charge-transfer states (organic solar cells); electrocatalysis at solid-liquid interface (fuel cells).

Thank You for Your Attention!