# Electronic-structure calculations at macroscopic scales

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Mathematisches Forschungsinstitut
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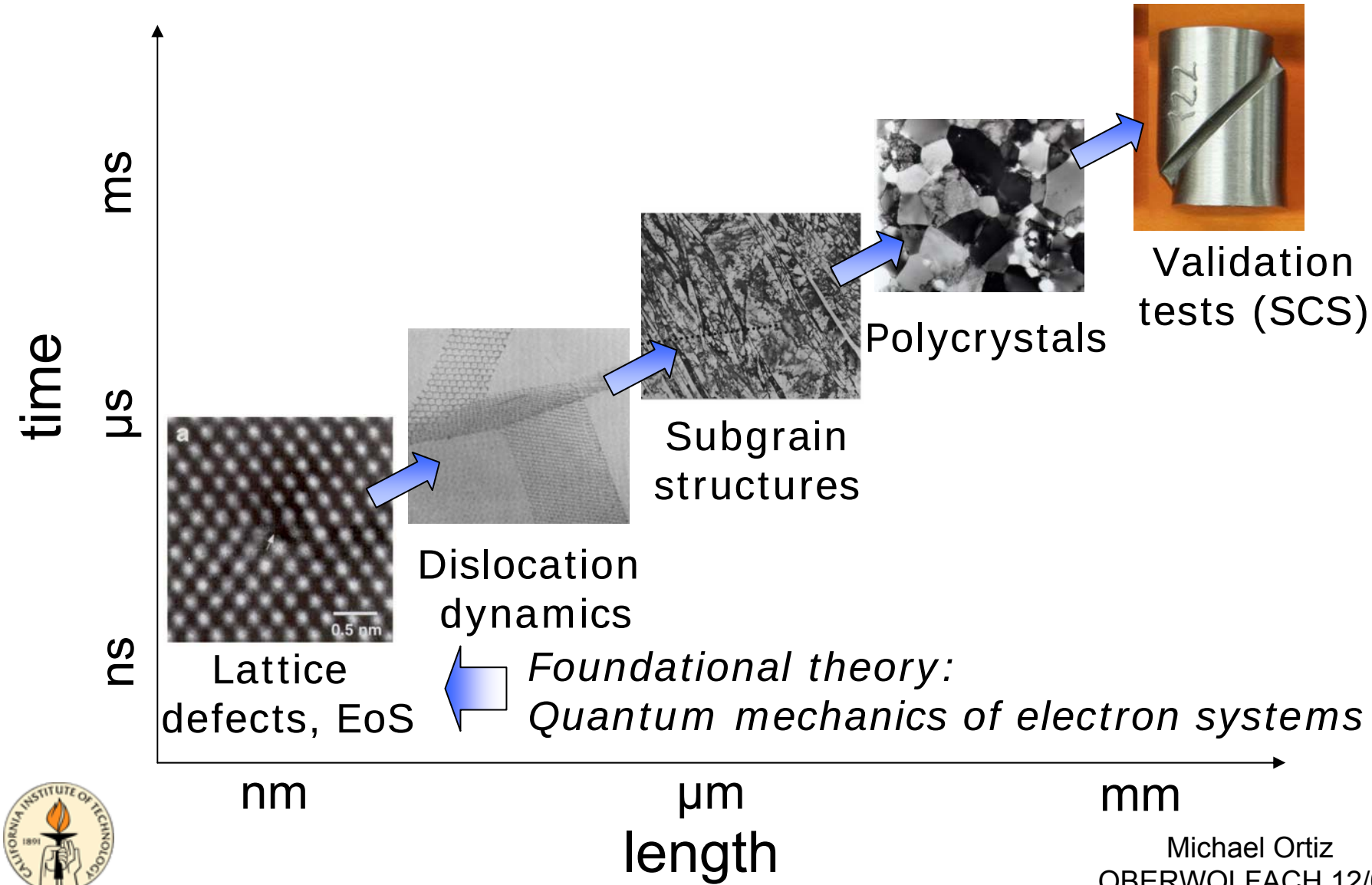
# Metal plasticity – Multiscale modeling



# Predicting Properties of Matter from Electronic Structure

- The quantum mechanics of electrons and ions lies at the foundation of a large part of low-energy physics, chemistry and biology
- The Born-Oppenheimer approximation: Decouples the electronic and nuclear motion, electrons respond instantaneously to any change in nuclear coordinates
- Time-independent Schrödinger equation for an isolated N-electron atomic or molecular system:

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = \sum_{i=1}^{N}(-\frac{1}{2}\nabla_i^2) + \sum_{i=1}^{N} v(\boldsymbol{r}_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

# Quantum mechanics and material properties

*Quantum Mechanics of Many-Electron Systems.*

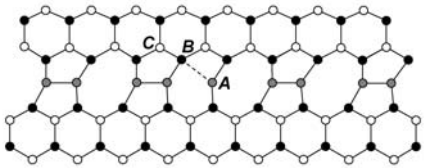
By P. A. M. DIRAC, St. John's College, Cambridge.

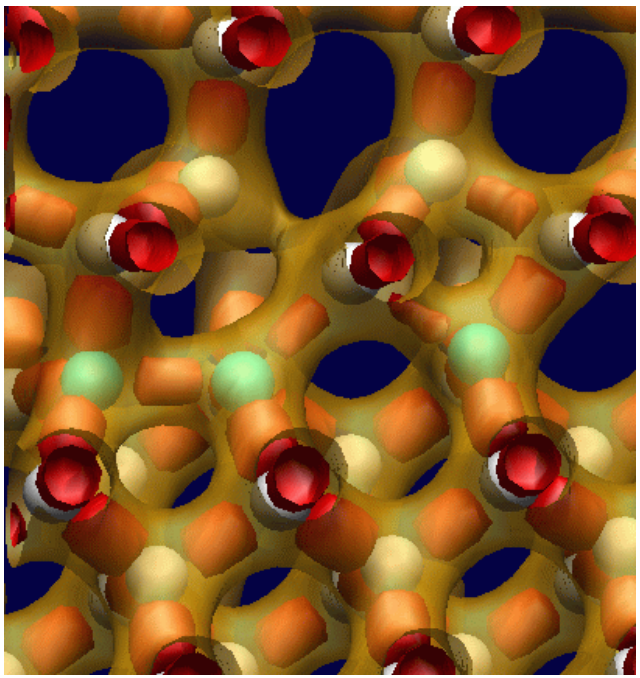
(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

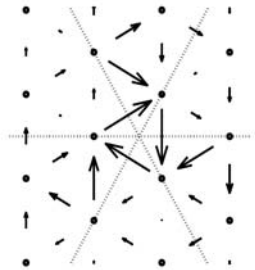
§ 1. *Introduction.*

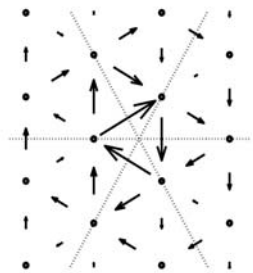
The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

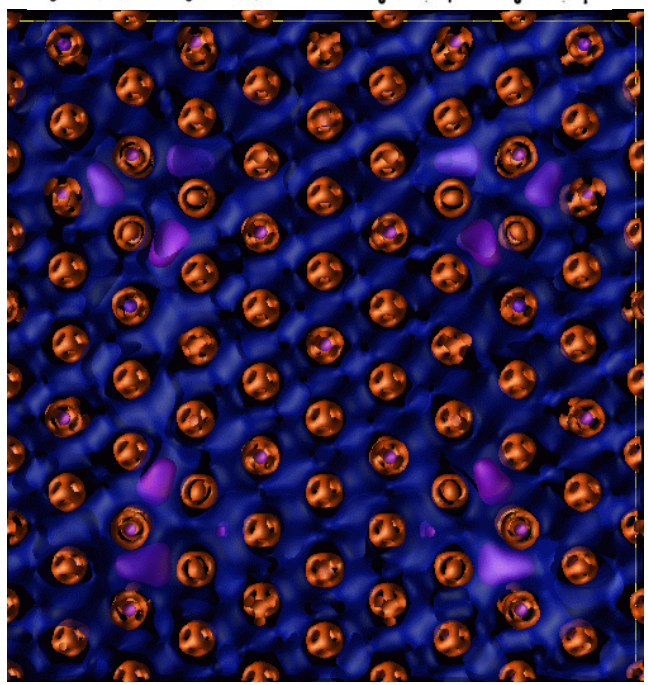
# Defective crystals – Supercells









Electronic structure of the 30° partial dislocation in silicon (Csányi, Ismail-Beigi and Arias, *Phys. Rev. Let*. **80** (1998) 3984).

*Ab initio* study of screw dislocations in Mo and Ta (Ismail-Beigi and Arias, *Phys. Rev. Let*. **84** (2000) 1499).

# Defective crystals – The chasm

- Because of computational cost, supercells limited to small sizes → Exceedingly large defect concentrations
- Often the objective is to predict *bulk properties* of defects:
  - *Vacancies: cell size* ~ 100 nm
  - *Dislocation cores: cell size* ~ 100 nm
  - *Domain walls: cell size* ~ 1 μm
  - *Grain boundaries: cell size* ~ 20 μm
- Small-cell calculations lead to discrepancies with experimental measurements!
- *How can bulk properties of defects (>> million atom computational cells) be predicted from electronic structure calculations?*

# Density Functional Theory

- Theorem [**Hohenberg-Kohn**, 1964] *The external potential* $v(\boldsymbol{r})$ *is determined by the ground state electron density*

$$\rho(\boldsymbol{r}) = N \int |\Psi|^2 ds_1 d\boldsymbol{x}_1 \dots \boldsymbol{x}_N$$

- Levy's constrained-search representation:

$$E[\rho] = \inf_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{ne} + \hat{V}_{ee} | \Psi \rangle$$

- Theorem [**Hohenberg-Kohn**, 1964] $\boxed{E_0 = \inf_\rho E[\rho]}$

- $E[\rho]$ not known explicitly! $\Rightarrow$ Model $E[\rho]$

# Orbital-Free Density Functional Theory

- Total energy functional: $E[\rho] = T_s[\rho] + E_{xc}[\rho]$

$$+\frac{1}{2}\int_\Omega\int_\Omega \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}\,d\boldsymbol{r}' + \int \rho(\boldsymbol{r})v(\boldsymbol{r})\,d\boldsymbol{r}$$

- Thomas-Fermi-Weizsacker (TF-$\lambda$W) KE:

$$T_s(\rho) = \frac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3}(\boldsymbol{r})d\boldsymbol{r} + \frac{\lambda}{8}\int \frac{|\nabla\rho(\boldsymbol{r})|^2}{\rho(\boldsymbol{r})}d\boldsymbol{r}$$

- Kernel-energies: Subsequent enhancements by Wang and Teter (1992), Smargiassi and Madden (1994), Wang, Govind and Carter (1998, 1999)...

# Orbital-Free Density Functional Theory

- Exchange-correlation energy (LDA + gradient expansion):

$$E_{xc}[\rho] \approx \int \epsilon_c(\rho)\rho(\boldsymbol{r})\,d\boldsymbol{r} - \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \rho^{4/3}(\boldsymbol{r})d\boldsymbol{r}$$

$$-\frac{7}{144}(81\pi^5)^{-1/3}\int \frac{|\nabla\rho(\boldsymbol{r})|^2}{\rho^{4/3}(\boldsymbol{r})}\,d\boldsymbol{r} + \dots$$

- OFDFT is a good model for systems with electronic structure close to that of a free-electron gas
- Still: Severe cell-size limitations, $\sim$ 100-1000 atoms!

# OFDFT Coarse-graining

- Defective lattices, well-separated defects:
  - *Away from defects: Cauchy-Born electron density + slowly varying modulation (Blanc, Le Bris and Lions, ARMA, 2002)*
  - *Only near defect cores the electron density and the electrostatic potential deviate significantly from those of a periodic lattice*
- Objective: Model reduction such that:
  - *The coarse graining is unstructured and adaptive*
  - *OFDFT is the sole input to the model (no spurious physics)*
  - *Convergence to all-atom OFDFT in fully-resolved limit*
- General approach (QC-OFDFT):
  - *Derive a real space, nonperiodic, formulation of OFDFT*
  - *Effect a quasi-continuum[1] (QC) model reduction*


[1]Tadmor, Ortiz and Phillips, *Phil. Mag*., **A73** (1996) 1529.

# OFDFT – Real space formulation

- Total energy functional:

$$E[\rho] = \underbrace{\int \epsilon_{loc}(\boldsymbol{r}, \rho, \nabla\rho)\, d\boldsymbol{r}}_{\text{finely oscillatory!}} + \underbrace{\frac{1}{2}\int_\Omega \int_\Omega \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d\boldsymbol{r}\, d\boldsymbol{r}'}_{\text{nonlocal!}}$$

- Local Lagrangian form:

$$E[\rho] = \sup_{\phi \in H^1(\mathbf{R}^3)} L[\rho, \phi]$$

$$L[\rho,\phi] = \int \epsilon_{loc}(\boldsymbol{r}, \rho, \nabla\rho)\, d\boldsymbol{r}$$

$$-\frac{1}{8\pi}\int_\Omega |\nabla\phi(\boldsymbol{r})|^2\, d\boldsymbol{r} + \int_\Omega (\rho(\boldsymbol{r}) + \underbrace{b(\boldsymbol{r})}_{\text{pseudopotentials}})\phi(\boldsymbol{r})\, d\boldsymbol{r}$$

# OFDFT – Real space formulation

- Enforce constraint $\rho > 0$ by setting $\rho = u^2$.
- Saddle-point problem:

$$\inf_{u \in H^1(\Omega)} \sup_{\phi \in H^1(\mathbb{R}^3)} L(u, \phi)$$

$$\text{subject to: } \int_\Omega u^2(\boldsymbol{r}) d\boldsymbol{r} = N$$

**Theorem** [BGKO] Let $E[u]$ be the TF-$\lambda$ W + LDA energy functional, $X = \{u \in H^1(\Omega), \|u\|_{L^2(\Omega)} = N\}$. Then $E[u]$ has a minimum in $X$.

# OFDFT – FE approximation

- Let $X_h \times Y_h$ be a sequence of finite-element subspaces of $H_0^1(\Omega) \times H^1(\mathbb{R}^3)$.
- Discrete problem: $F[u,\phi] \equiv$

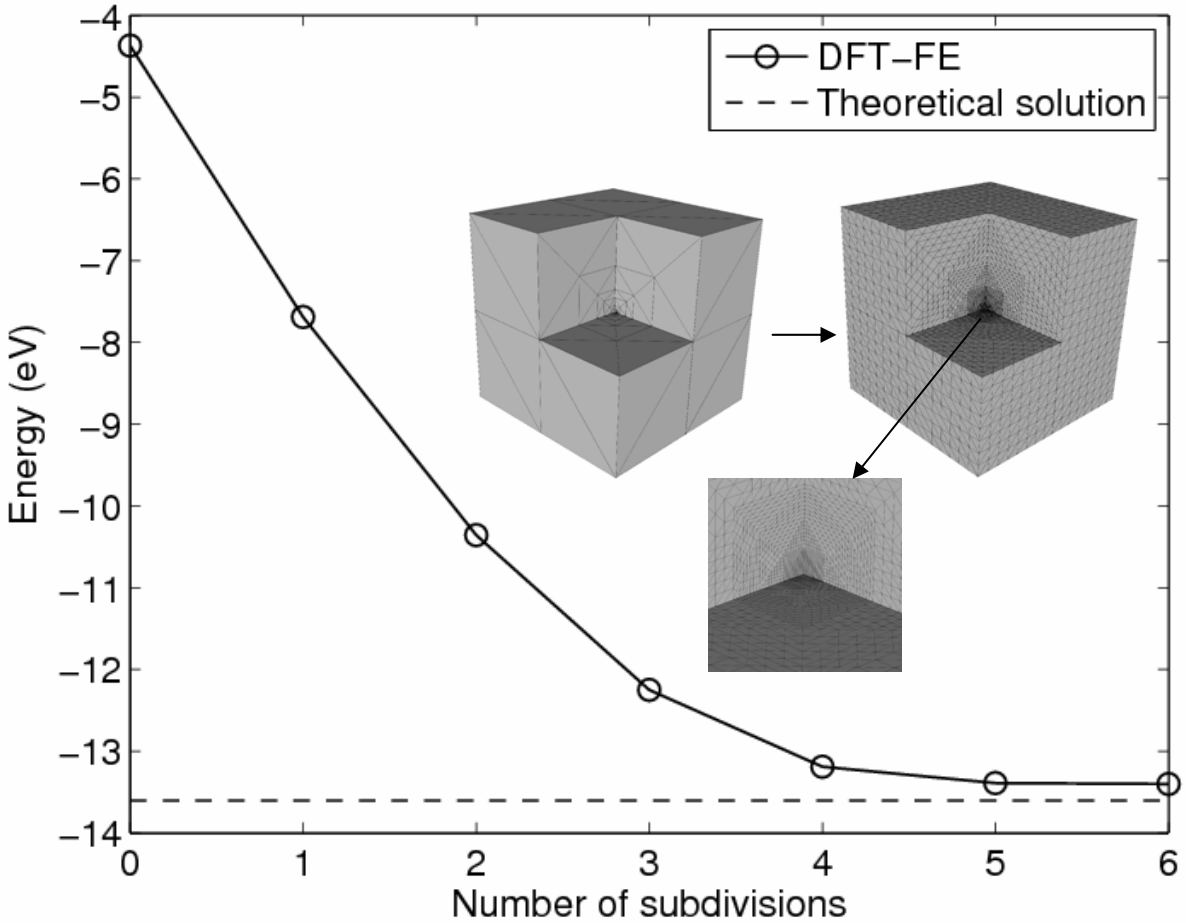
$$-\frac{1}{8\pi}\int_\Omega |\nabla\phi(\boldsymbol{r})|^2\,d\boldsymbol{r} + \int_\Omega (u^2(\boldsymbol{r}) + b(\boldsymbol{r}))\phi(\boldsymbol{r})\,d\boldsymbol{r}$$

$$F_h[u,\phi] = \begin{cases} F[u,\phi], & \text{if } \phi \in Y_h \\ -\infty, & \text{otherwise.} \end{cases}$$

$$E_h[u] = \begin{cases} E_{loc}[u] + \sup_\phi F_h[u,\phi], & \text{if } u \in X_h \\ +\infty, & \text{otherwise.} \end{cases}$$

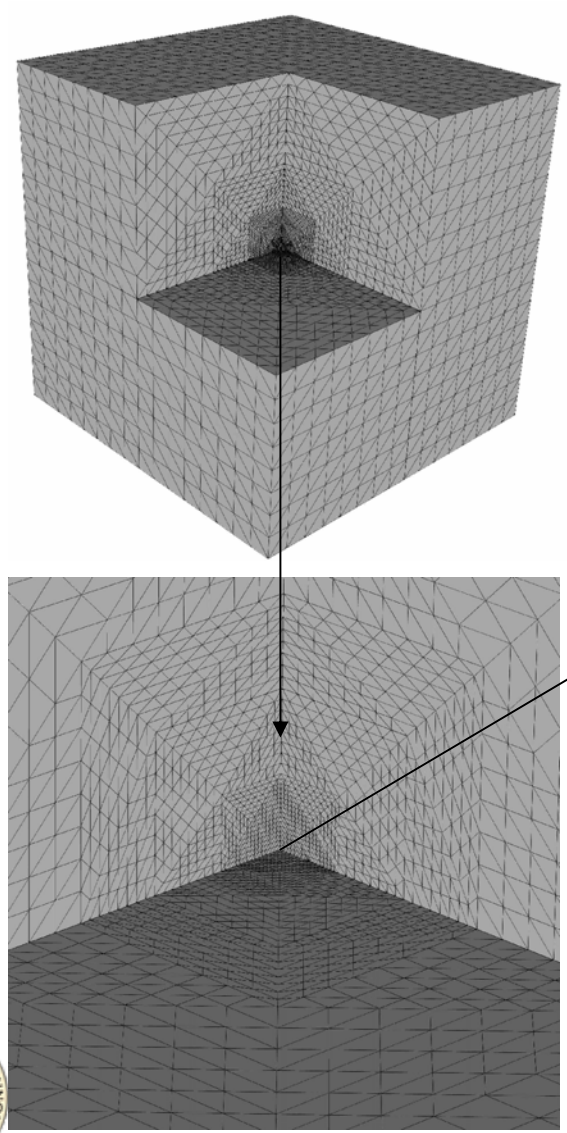
**Theorem** [BGKO] $\Gamma - \lim_{h\to 0} E_h = E$, $\inf E_h \to E_0$.

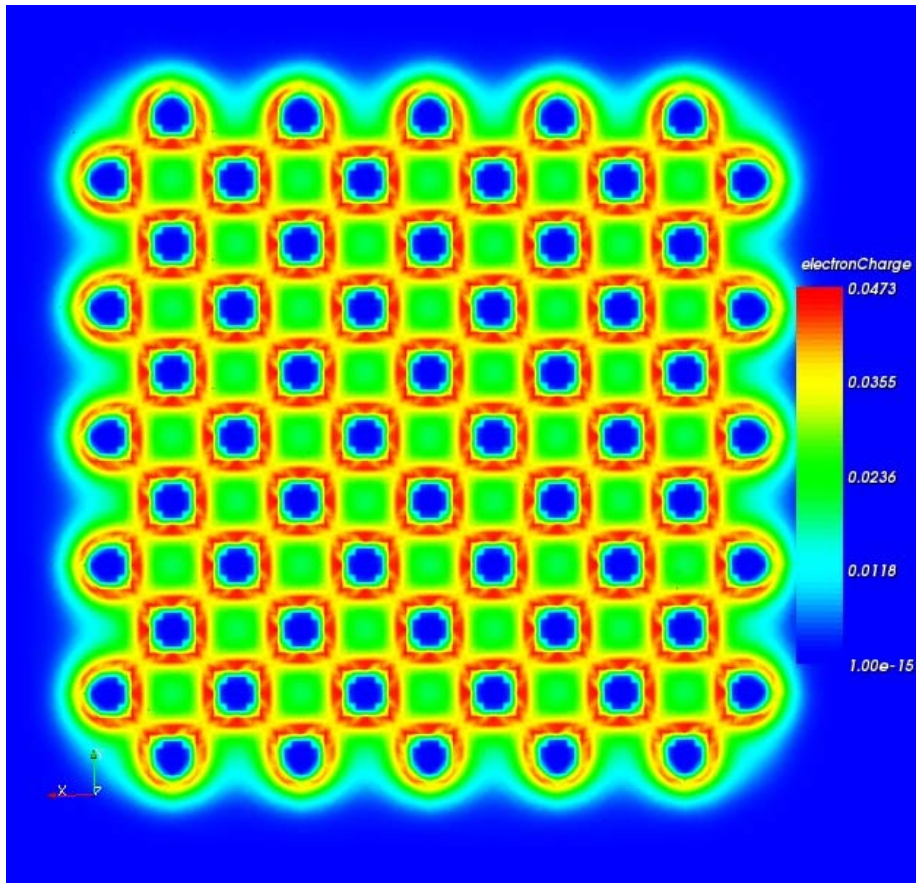
# Convergence test – Hydrogen atom




Energy of hydrogen atom as a function of number of subdivisions of initial mesh

# Example – Aluminum nanoclusters





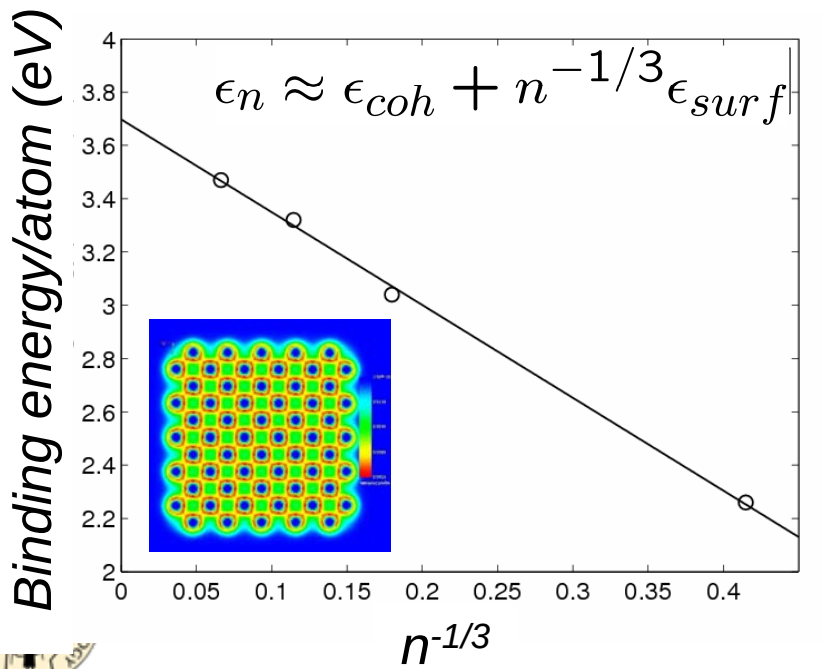

Contours of electron density in 5x5x5 aluminum cluster (mid plane)

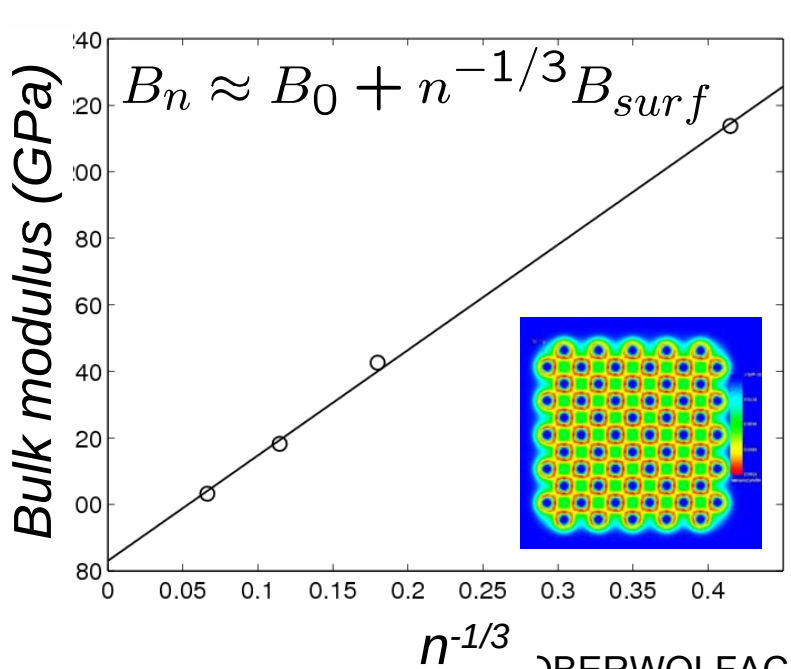
# Example – Aluminum nanoclusters

| Property | DFT-FE | KS-LDA[a] | Experiments[b] |
|---|---|---|---|
| Lattice parameter (a.u.) | 7.42 | 7.48 | 7.67 |
| Cohesive energy (eV) | 3.69 | 3.67 | 3.4 |
| Bulk modulus (Gpa) | 83.1 | 79.0 | 74.0 |

a/ Goodwin et al. (1990), Gaudion et al. (2002)

b/ Brewer (1997), Gschneider (1964)



# QC/OFDFT – Multigrid hierarchy

- Nuclear positions:

$$\boldsymbol{R} \in \mathbb{R}^{3M} \equiv Z$$

- Equilibrium problem:

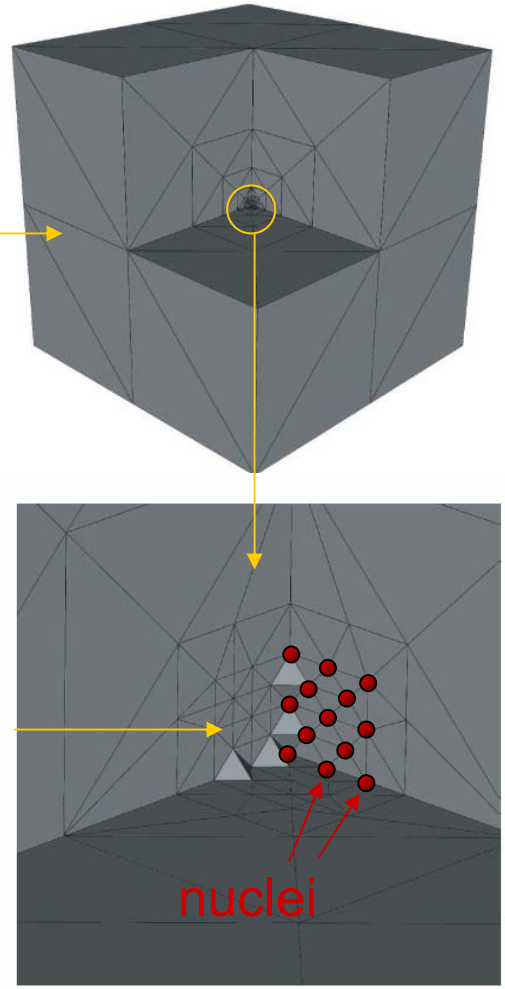
$$\inf_{\boldsymbol{R} \in Z} E_0[\boldsymbol{R}],$$

$$E_0[\boldsymbol{R}] = \inf_u \sup_\phi E[u, \phi]$$

- Reduced problem:

$$\begin{cases} \inf\limits_{\boldsymbol{R} \in Z_h} E_0[\boldsymbol{R}] \\ Z_h = \mathbb{R}^{3M_h},\ M_h \ll M \end{cases}$$

coarse resolution, nuclei in interpolated positions




atomic resolution, nuclei in arbitrary positions

Coarse grid

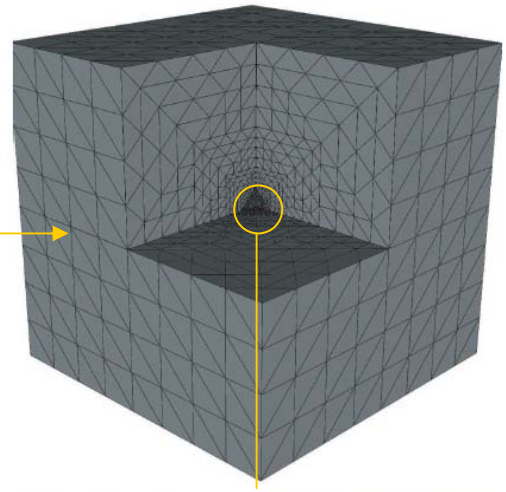
# QC/OFDFT – Multigrid hierarchy

- Predictor/corrector[1]:

$$\rho_h = \rho_h^0 + \rho_h^c$$
$$\phi_h = \phi_h^0 + \phi_h^c$$

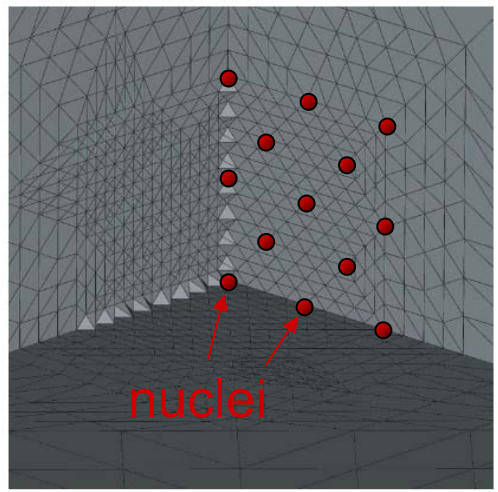
predictor corrector

coarse resolution, slowly-varying correction[1]



- Predictor: Local Cauchy-Born field (LQC/OFDFT)[2] defined everywhere
- Corrector: Interpolated on intermediate grid

subatomic resolution, rapidly-varying correction




Intermediate grid

[1]Blanc, LeBris, Lions, *ARMA*, **164** (2002) 341

[2]Fago el al., *Phys. Rev.*, **B70** (2004) 100102(R)

# QC/OFDFT – Multigrid hierarchy

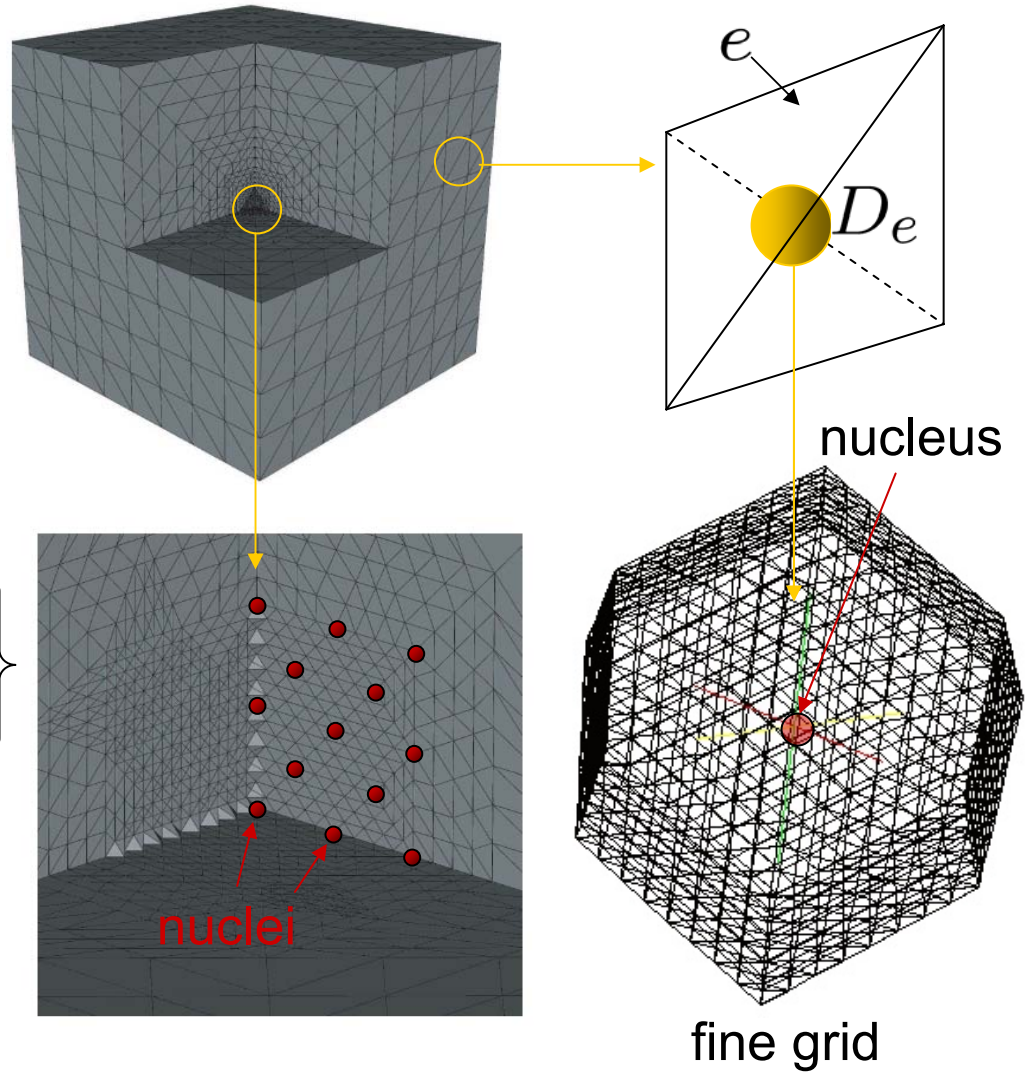
- Element quadrature:

$$\int_e f(\boldsymbol{r})\, d\boldsymbol{r} \approx |e| \langle f \rangle_{D_e}$$

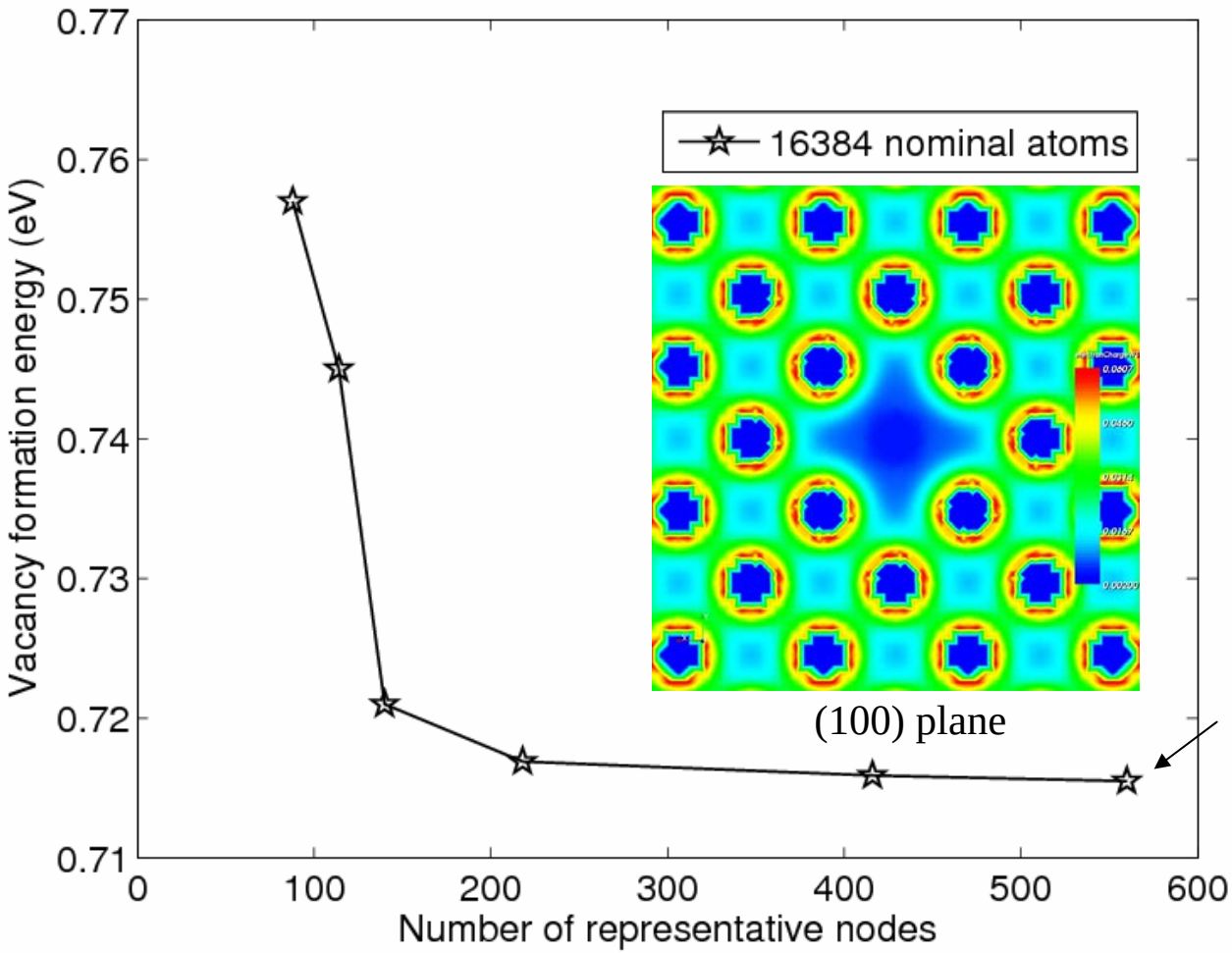
- Quadrature domain:

$$D_e = \min \left\{ \begin{array}{l} \text{atomic cell} \\ \text{element } e \end{array} \right\}$$

- $\langle f \rangle_{D_e}$ evaluated using a fine grid over $D_e$



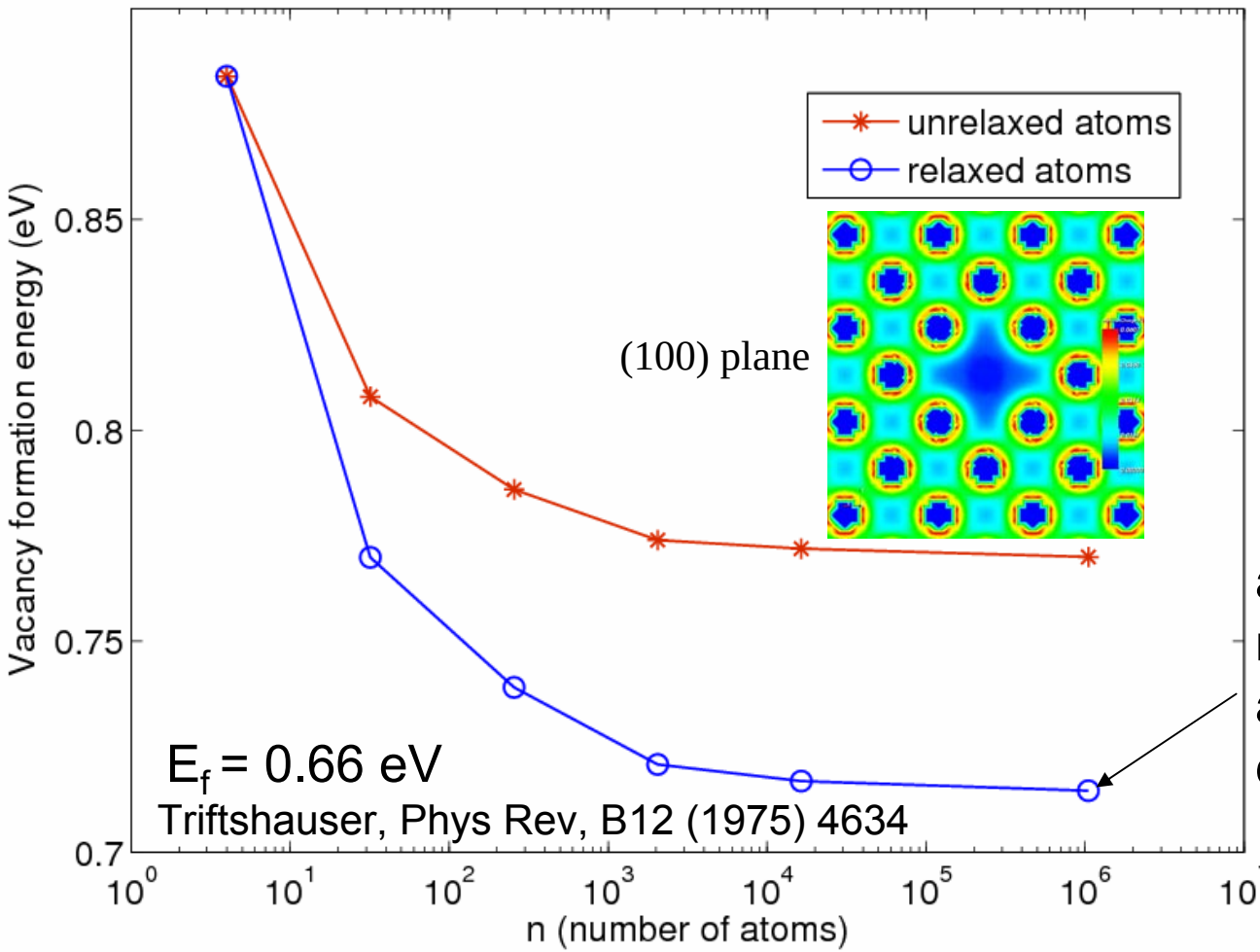
# Al vacancy – QC/OFDFT convergence




4% of nuclei accounted for in calculation at no loss of accuracy!

Convergence of QC reduction

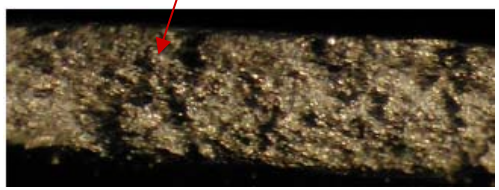
# Al vacancy – Cell-size dependence




1,000,000 atoms required to approach bulk conditions!

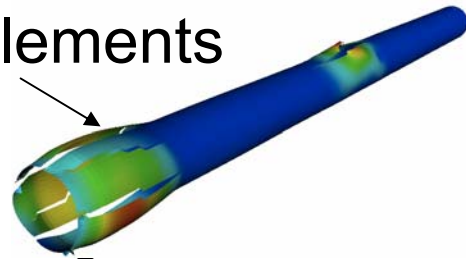
Convergence with material sample size

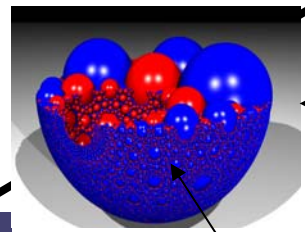
# Application: Nanovoid nucleation in Al



Chao and Shepherd (2004)

Localization elements

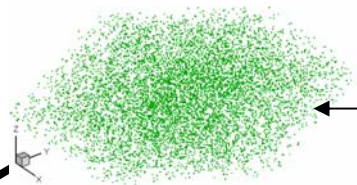




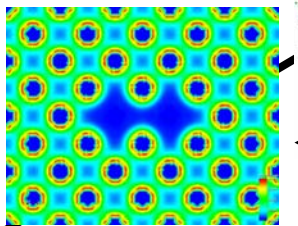
porous plasticity

Space-filling sphere packing (H.J. Hermann)

Quasicontinuum



Monte Carlo



QC/OFDFT

time

ms

μs

ns

nm

μm

mm

length

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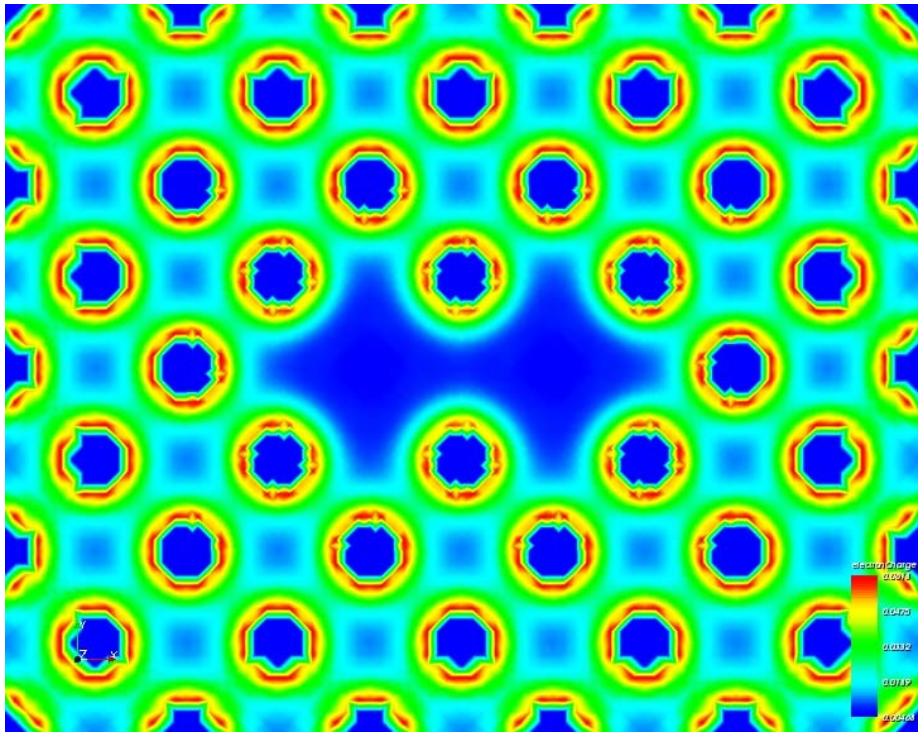
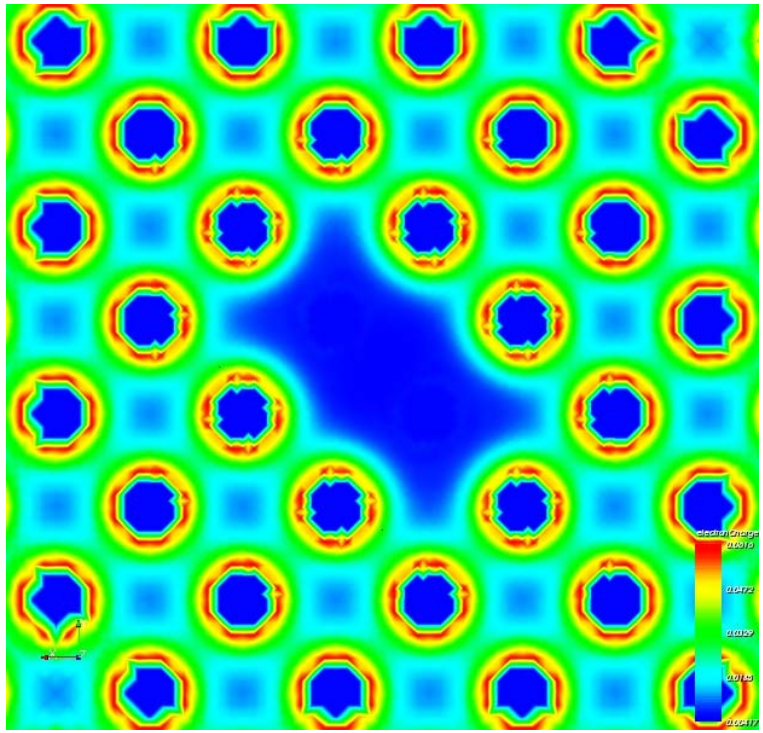
# Case study 1 – Di-vacancies in Al



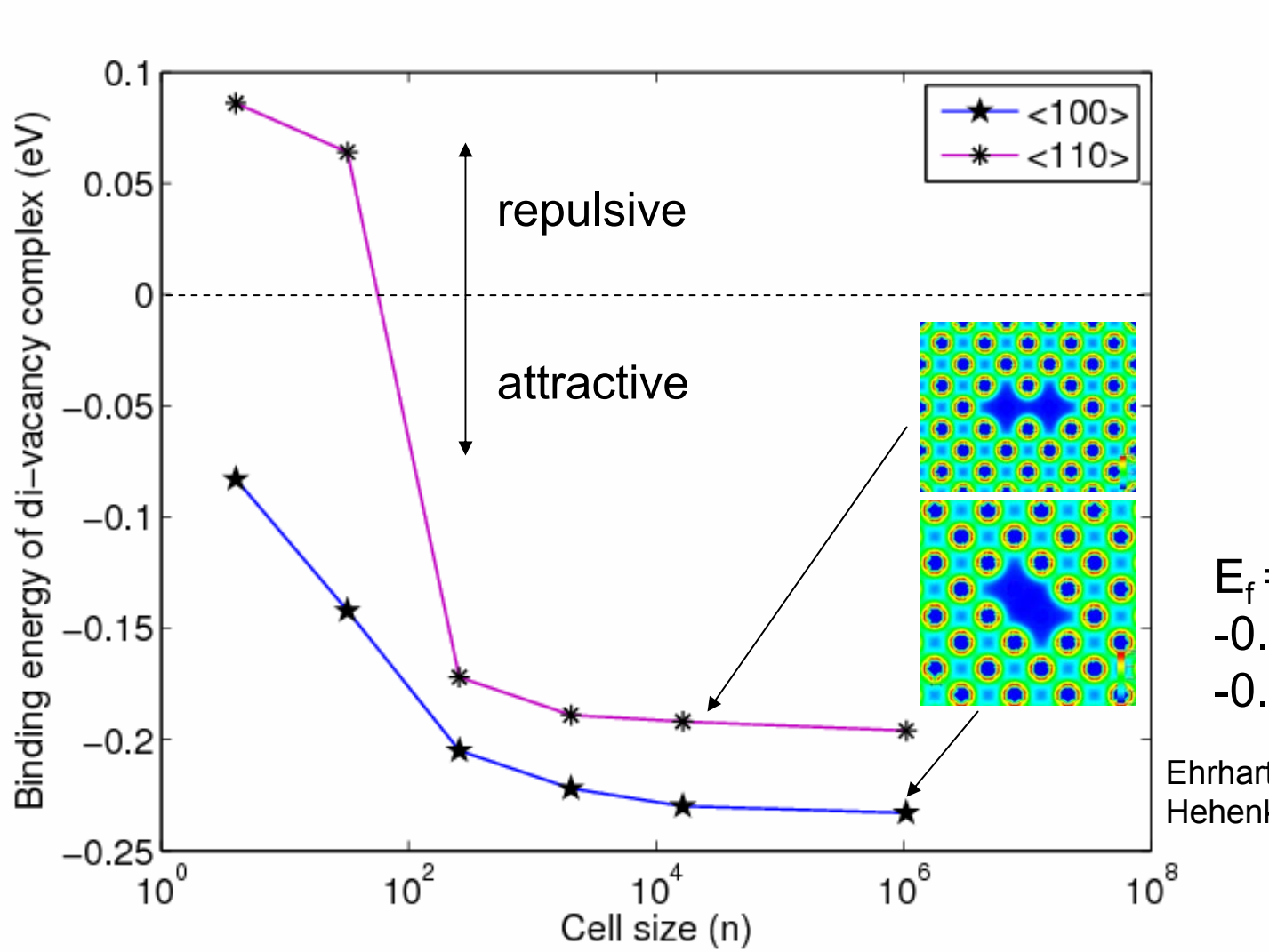
Di-vacancy along <100>



Di-vacancy along <110>

Core electronic structure

# Case study 1 – Di-vacancies in Al

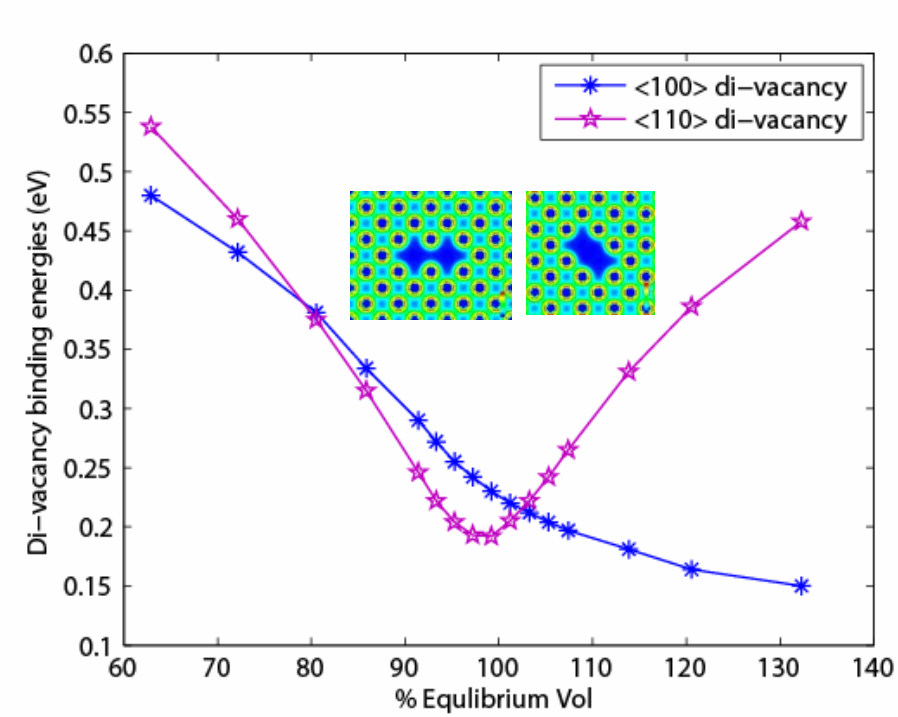


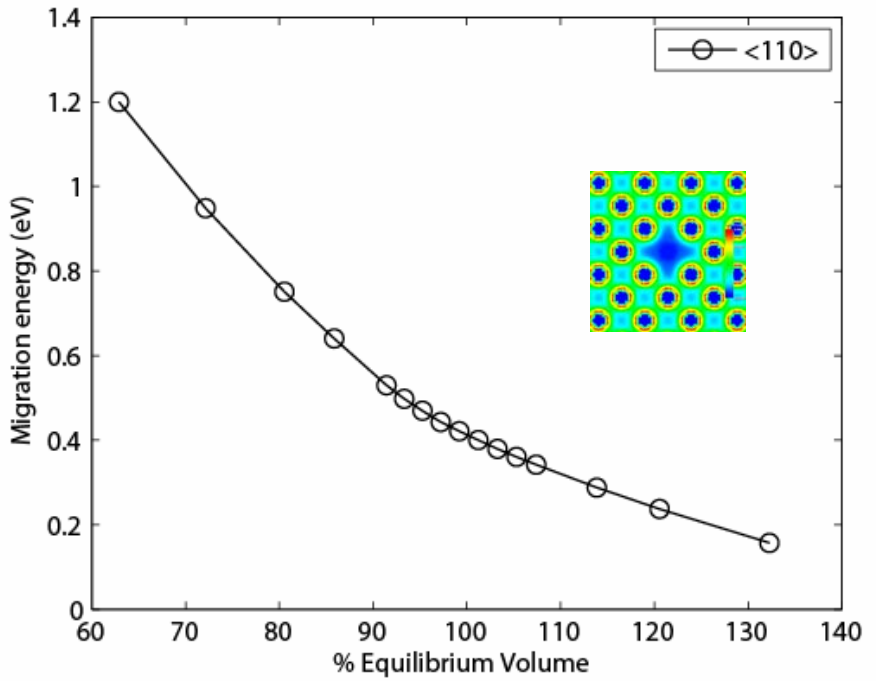

$E_f$ = -0.2 to -0.3 eV

Ehrhart et al., 1991
Hehenkamp, 1994

Binding energy *vs.* material sample size

# Case study 1 – Vacancies in Al




Binding energy *vs.* volume

Migration energy *vs.* volume

Vacancies in shocked aluminum

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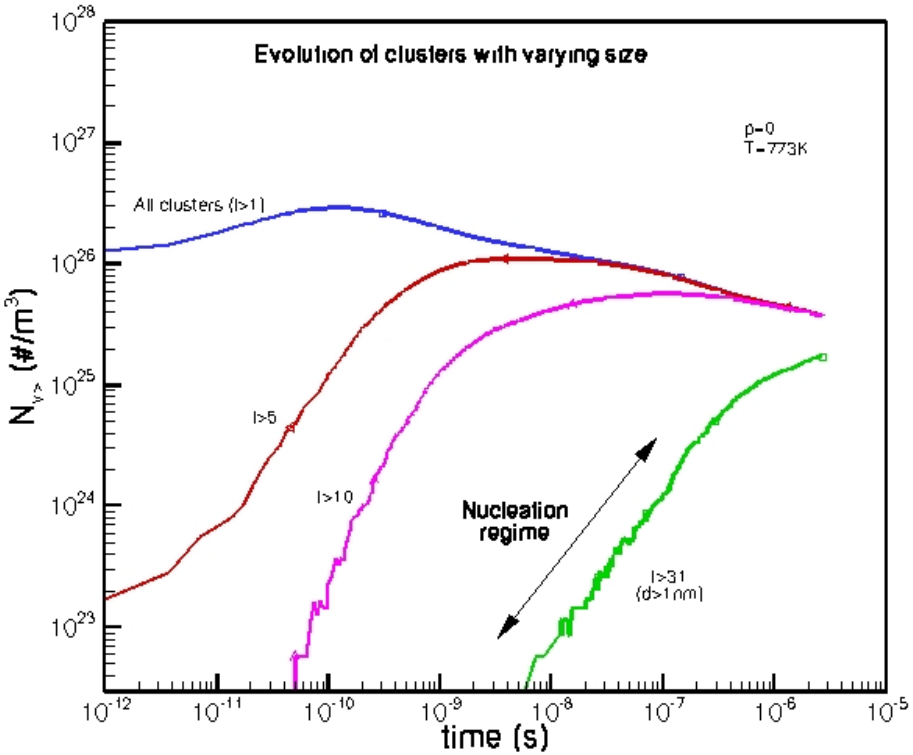
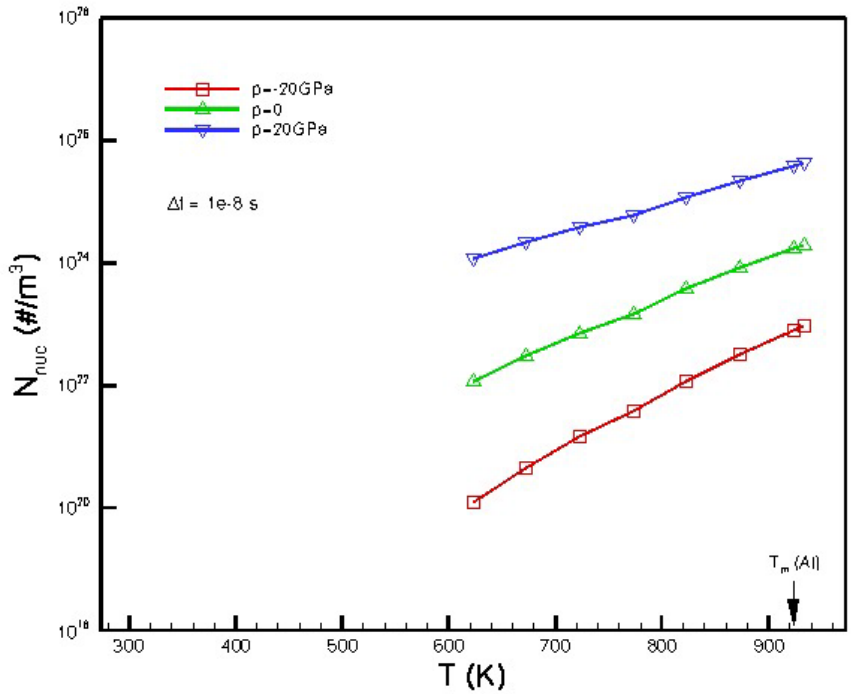
# Case study 1 – Vacancies in Al




Time evolution of number of voids of different sizes




Density of nanovoids (1nm) nucleated in $10^{-8}$ s

## Nanovoid nucleation in shocked aluminum

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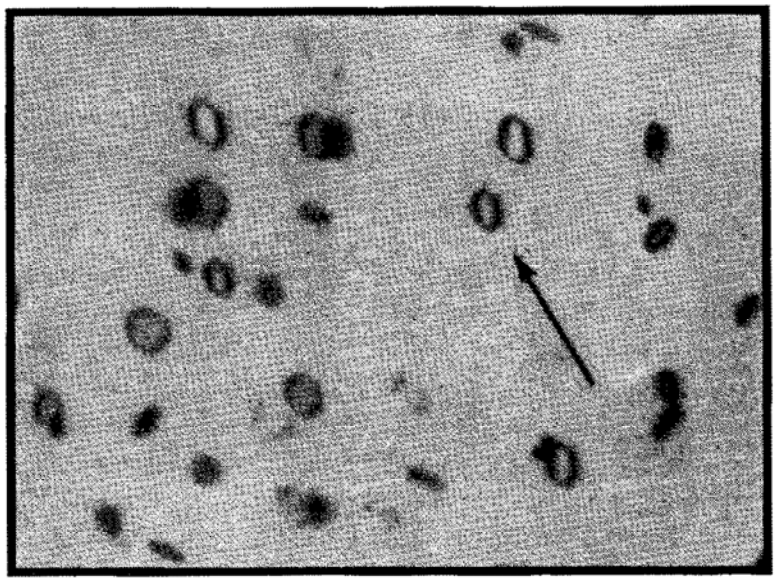
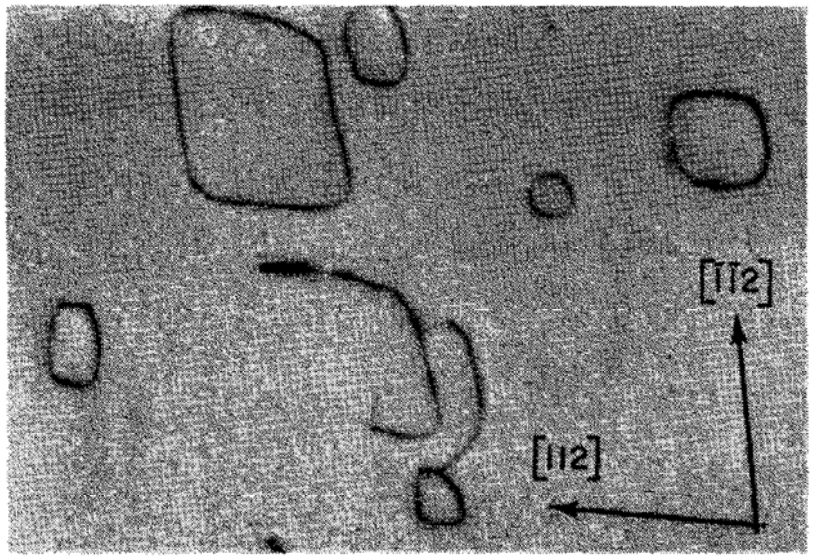
# Case study 2 – Prismatic loops in Al



Prismatic dislocation loops formed by condensation of vacancies in quenched aluminum

Kulhmann-Wilsdorff and Kuhlmann,
*J. Appl. Phys*., **31** (1960) 516.

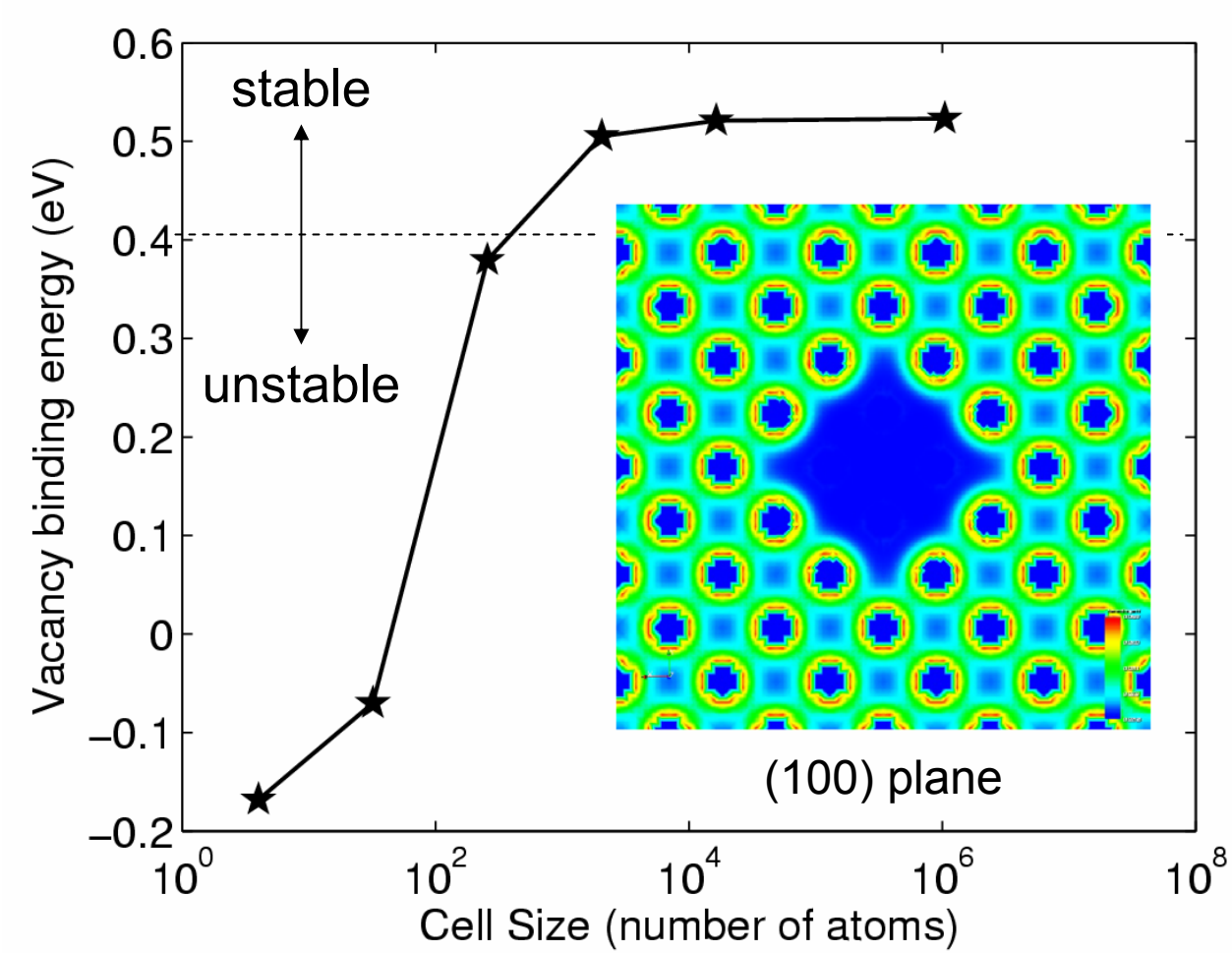



Prismatic dislocation loops formed by condensation of vacancies in quenched Al-05%Mg

Takamura and Greensfield,
*J. Appl. Phys*., **33** (1961) 247.

- Prismatic dislocation loops also in irradiated materials
- Loops smaller than 50 nm undetectable: Nucleation mechanism? Vacancy condensation?

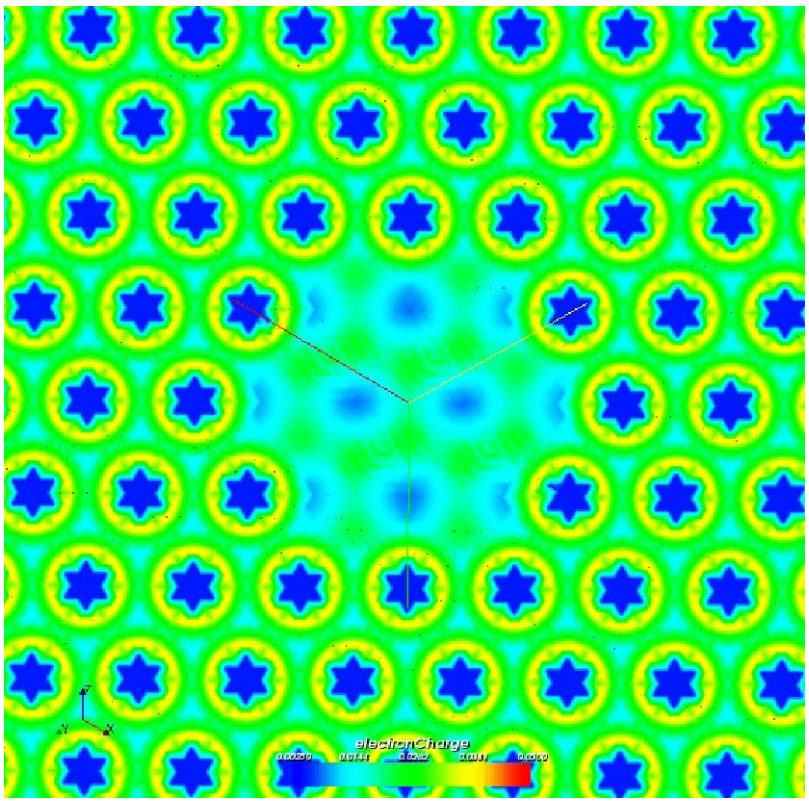
# Case study 2 – Prismatic loops in Al



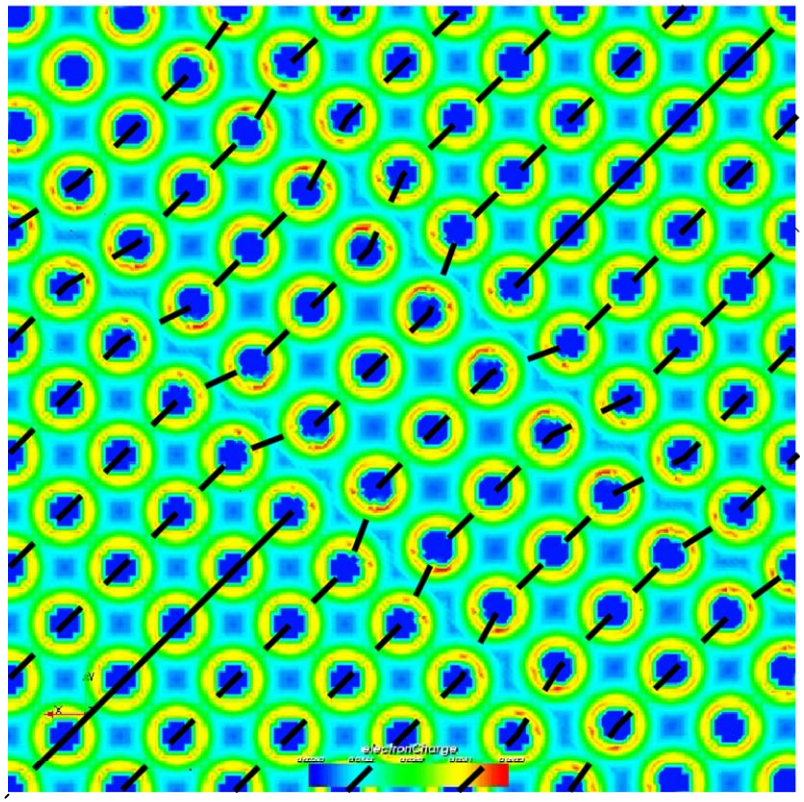

Quad-vacancy binding energy *vs.* material sample size

# Case study 2 – Prismatic loops in Al

(111)



(001)



(111)

Non-collapsed configuration

Binding energy = -0.88 eV

1/2<110> prismatic loop

Binding energy = -1.57 eV

Stability of hepta-vacancy

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OBERWOLFACH 12/07

# Concluding remarks

- Behavior of material samples may change radically with size (concentration): Small samples may not be representative of bulk behavior
- Need electronic structure calculations at macroscopic scales: Quasi-continuum OFDFT (QC/OFDFT)
- Outlook: Application to general materials requires extension to Kohn-Sham DFT…