Mathematical Theory of Solids: from Atomic to Macroscopic Scales

Weinan E
Princeton University

Fluids and solids: A comparison

Fluids: Fundamental model:
Navier-Stokes equation

$$\begin{cases} v_t + (v \cdot \nabla)v + \nabla p = \frac{1}{Re}\Delta v \\ \nabla \cdot v = 0 \end{cases}$$

$v(\cdot, t) =$ velocity field at time t.

Solids: fundamental model?

Linear elasticity:

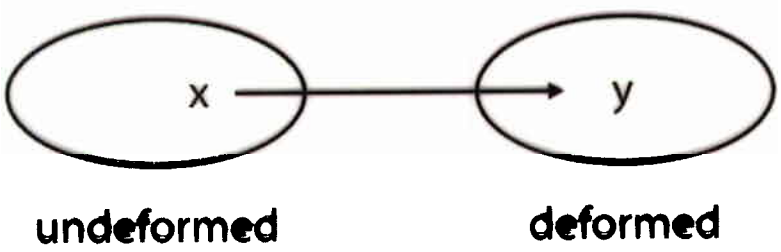
$$\rho \frac{\partial^2 u}{\partial t^2} = (\lambda + \mu)\nabla(\nabla \cdot u) + \mu \Delta u$$

Nonlinear elasticity:

$$\rho \frac{\partial^2 u}{\partial t^2} = \nabla \cdot \nabla_A W(\nabla u)$$

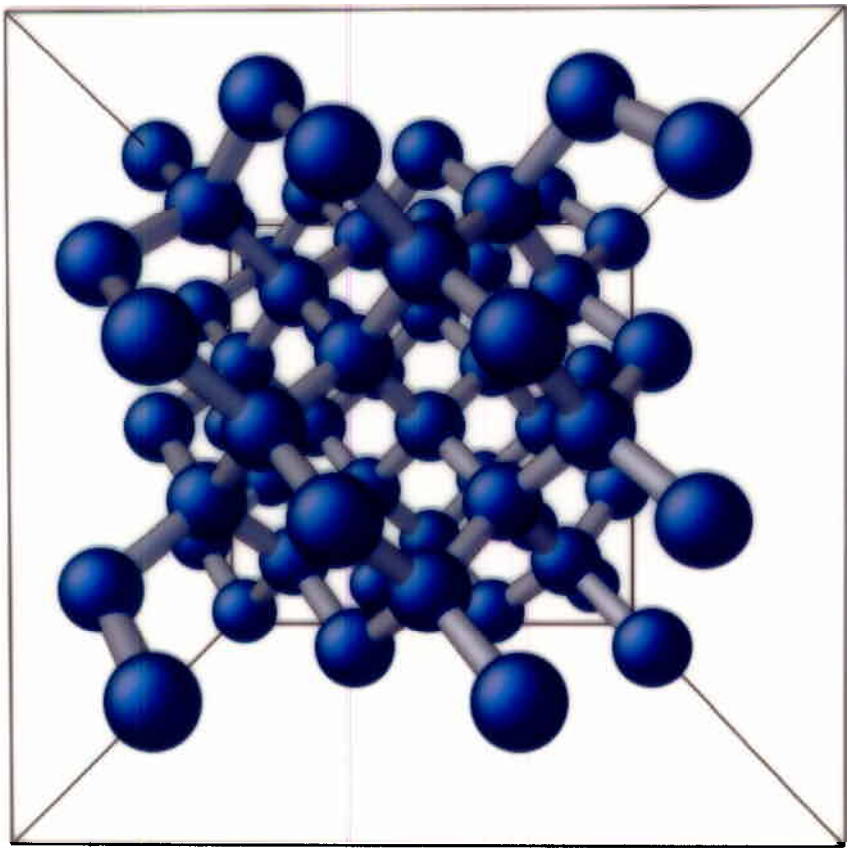
Plasticity

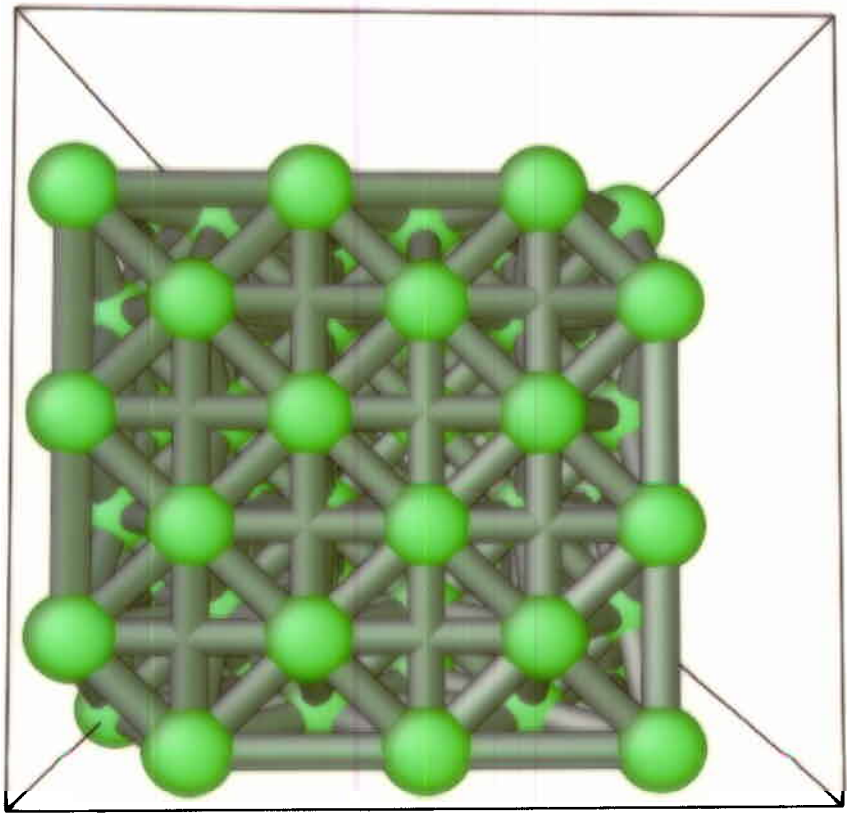
.....

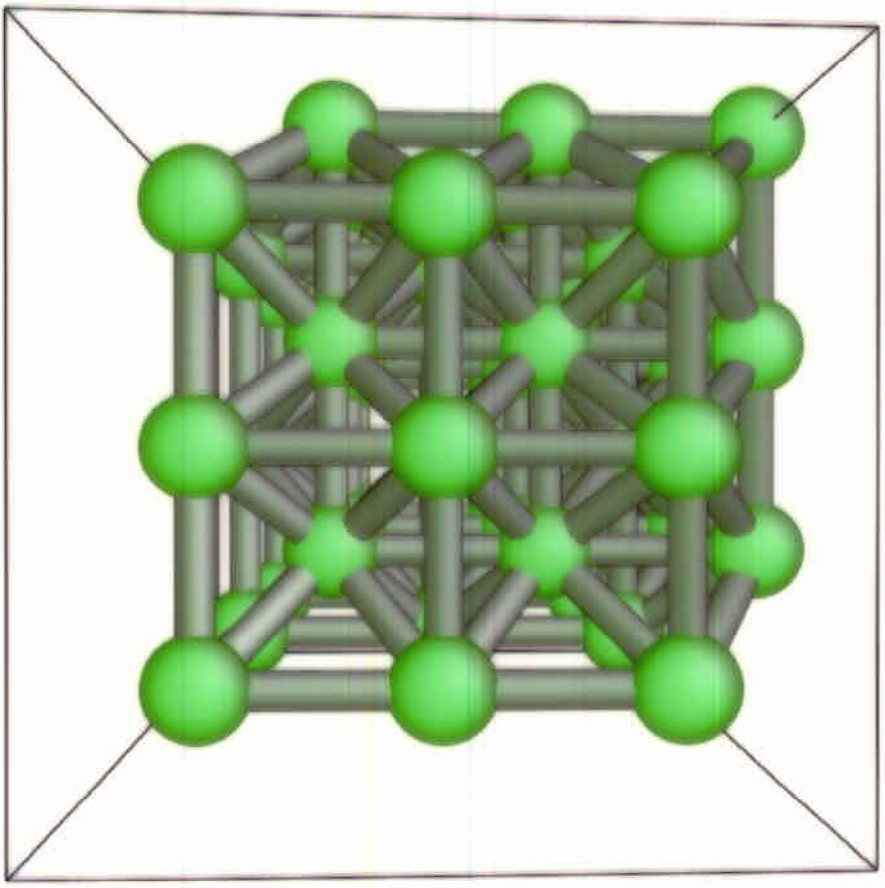


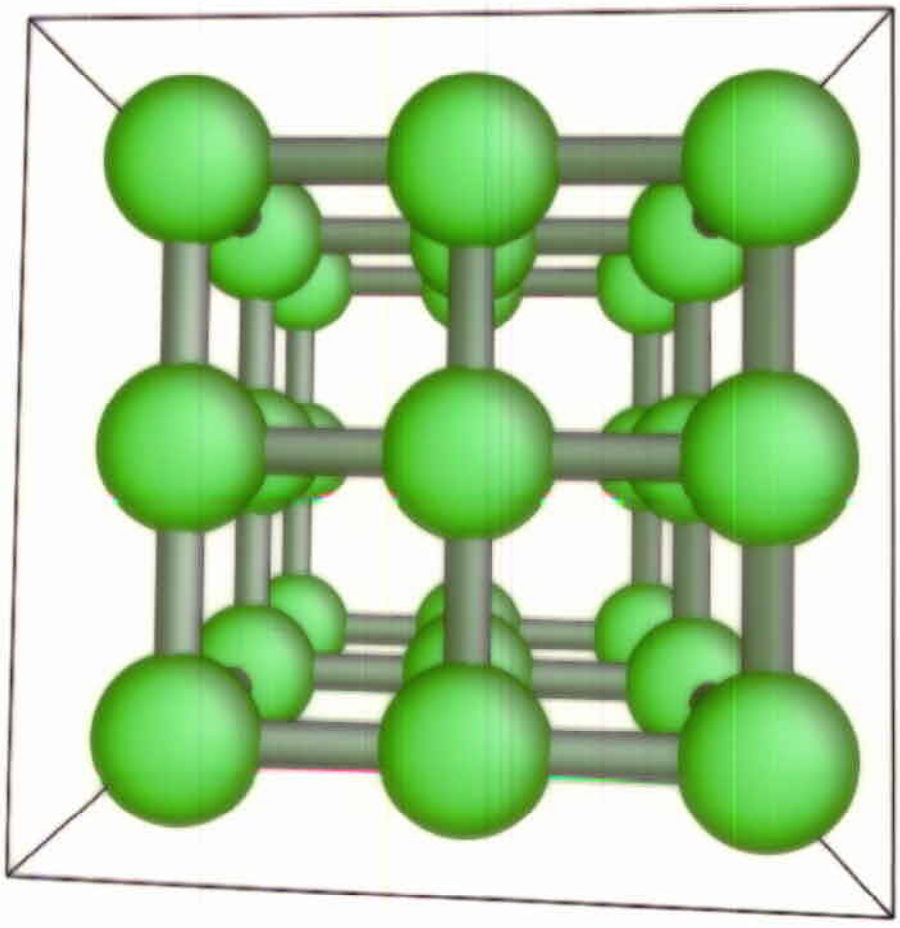
$$y = x + u(x)$$

$u(x)$ = displacement









Quantum many-body problem

$$V(R_1, R_2, \ldots, R_N) = E^*(R_1, R_2, \ldots, R_N) + \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|}$$

R_I = position of the i-th nucleus

Z_I = charge of the i-th nucleus

E^* = ground state energy of the electrons

$$\mathbf{H} = -\sum_i \frac{1}{2}\Delta_{r_i} + \sum_{i<j} \frac{1}{|r_i - r_j|} + \sum_i v(r_i)$$

$$v(r_i) = -\sum_I \frac{Z_I}{|r_i - R_I|}$$

$$\Psi = \Psi(r_1, r_2, \ldots, r_M)$$

Dirac (1929)

The underlying physical laws necessary for the mathematical theory of a *large part of physics* and *the whole 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.

What do we take as the starting point?

1. Quantum many-body

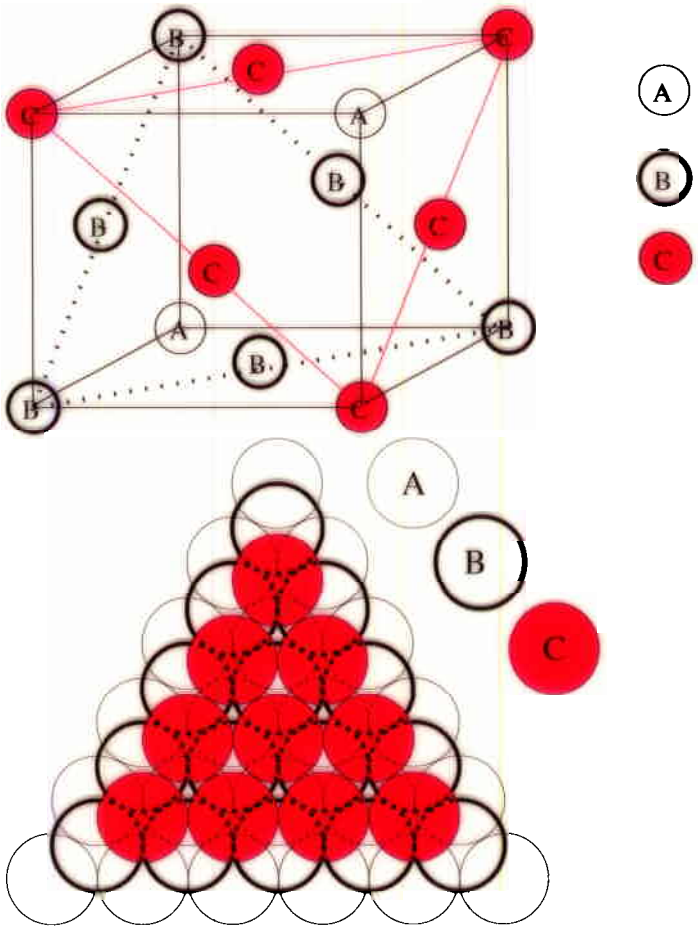
2. Simplified quantum models (density function theory, tight-binding, etc.)

3. Classical potential

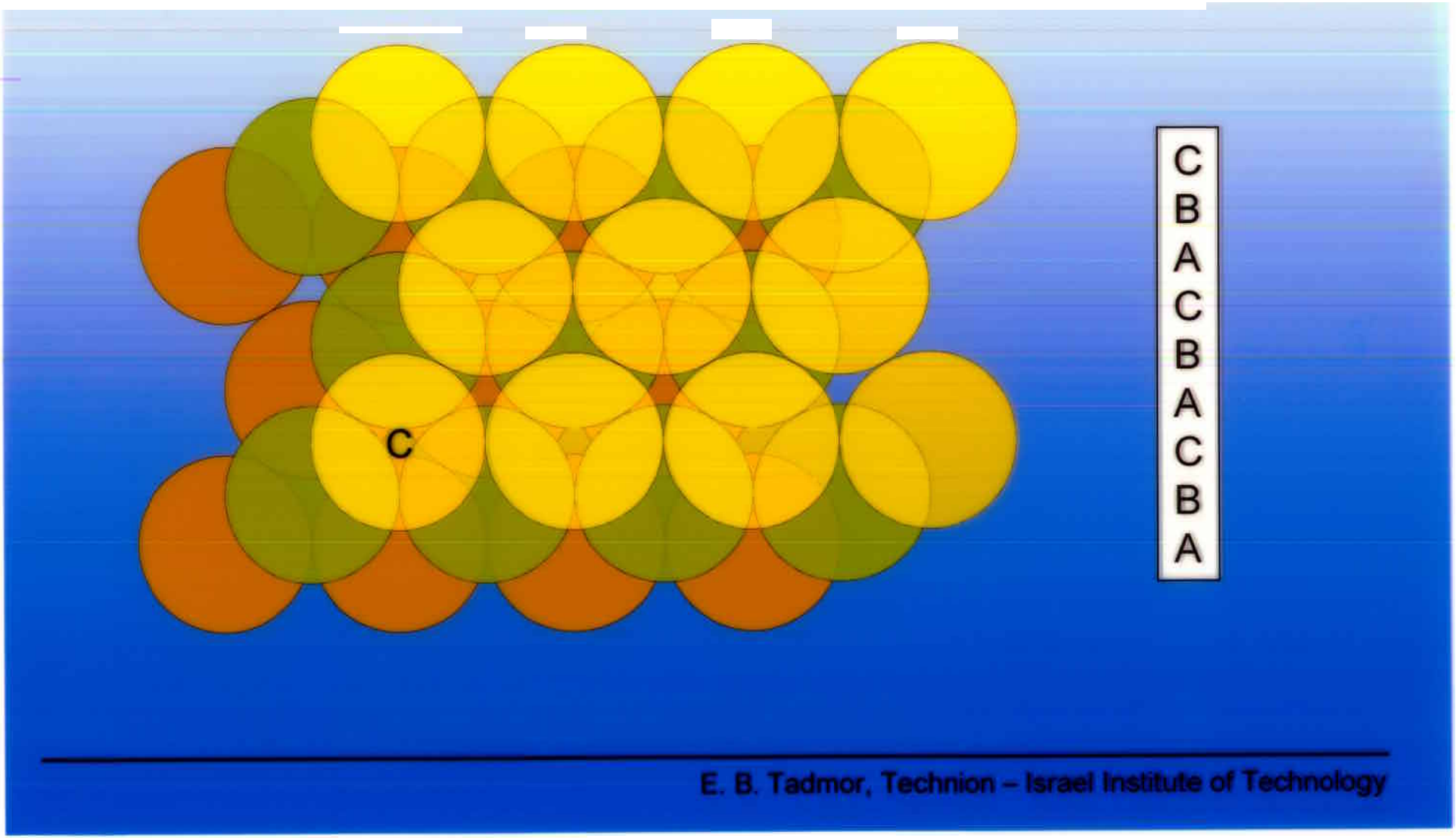
   - Lennard-Jones
   - Embedded Atom Model (EAM)

$$V(R_1, R_2, \ldots, R_N) = \sum_{I \neq J} V_0(|R_I - R_J|)$$

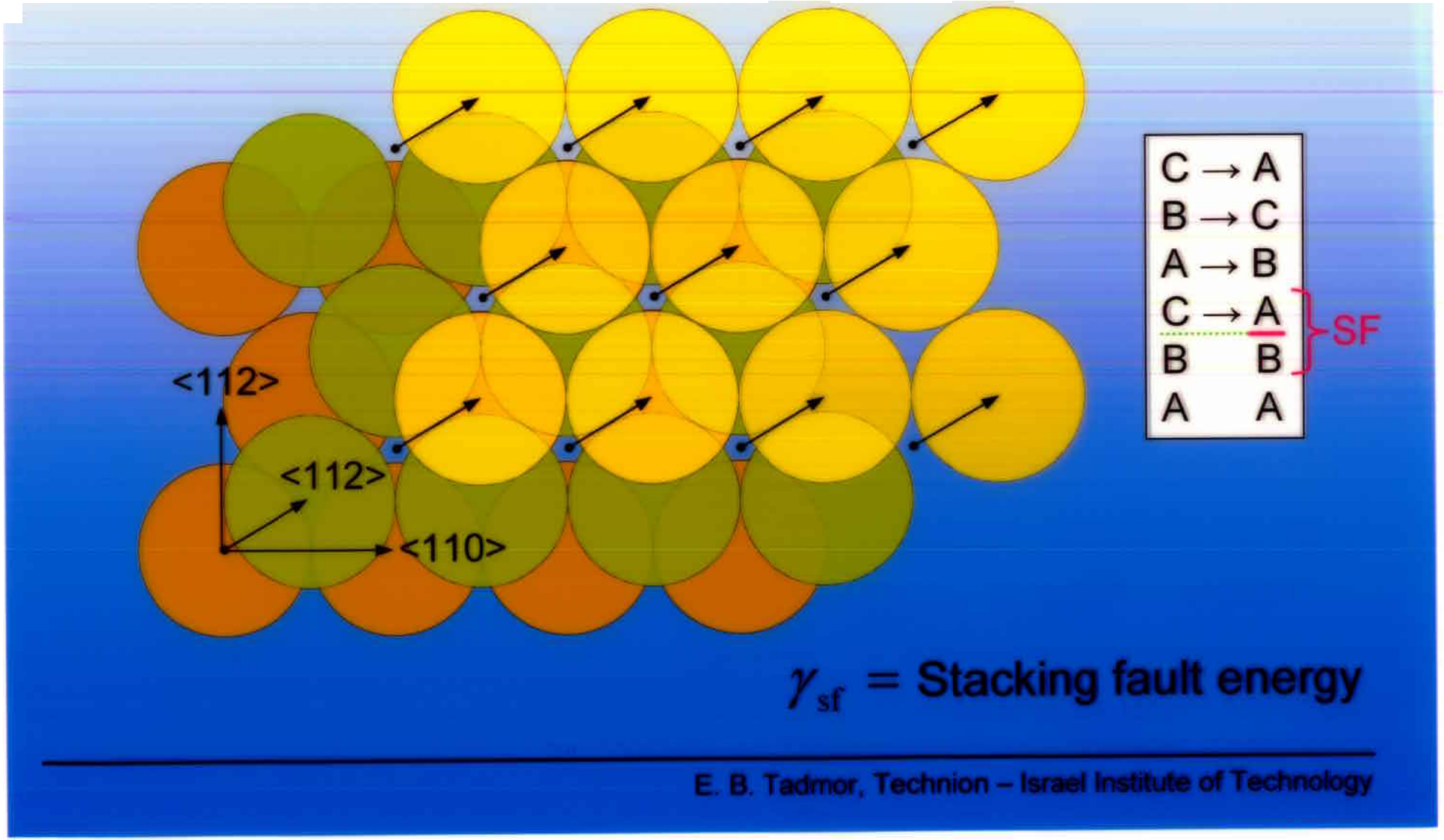
$$V_0(r) = 4\varepsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right)$$

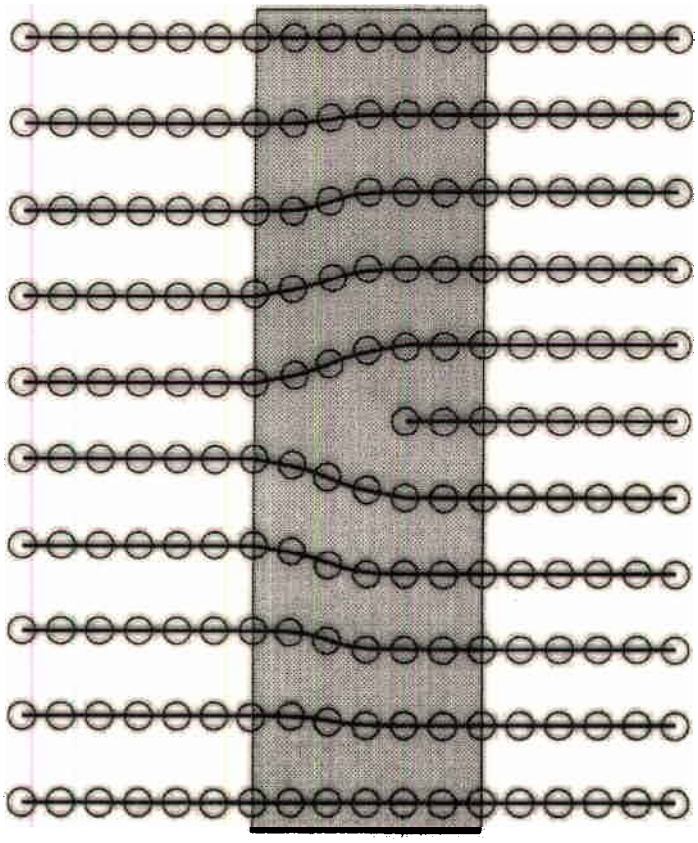

A
B
C
A
B
C

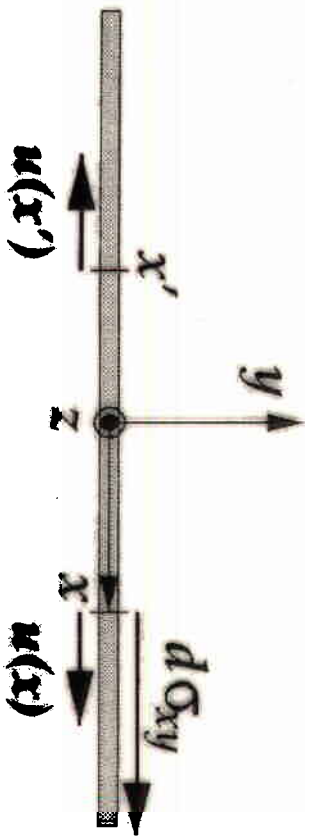
FCC Stacking



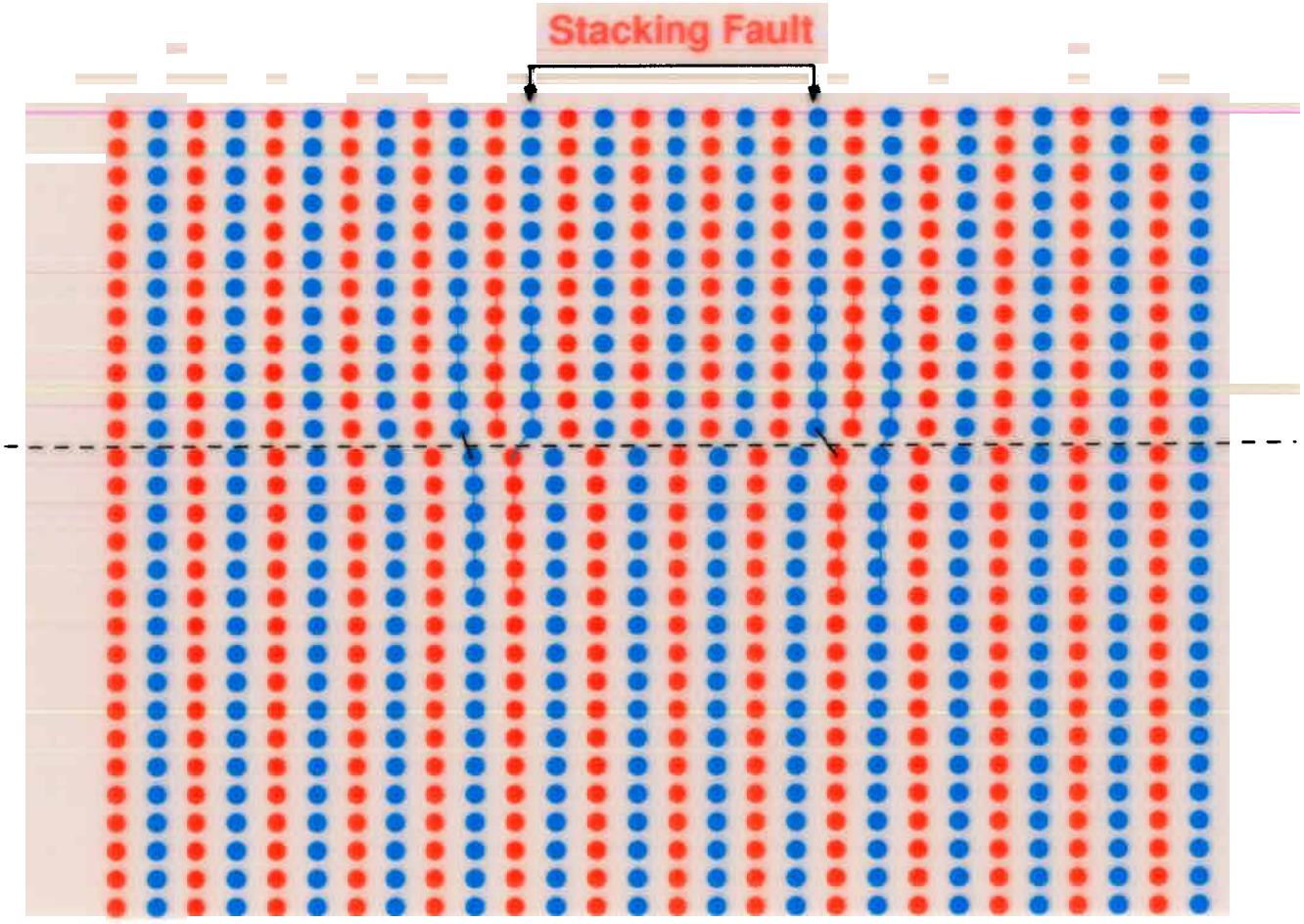
Intrinsic Stacking Fault (SF)



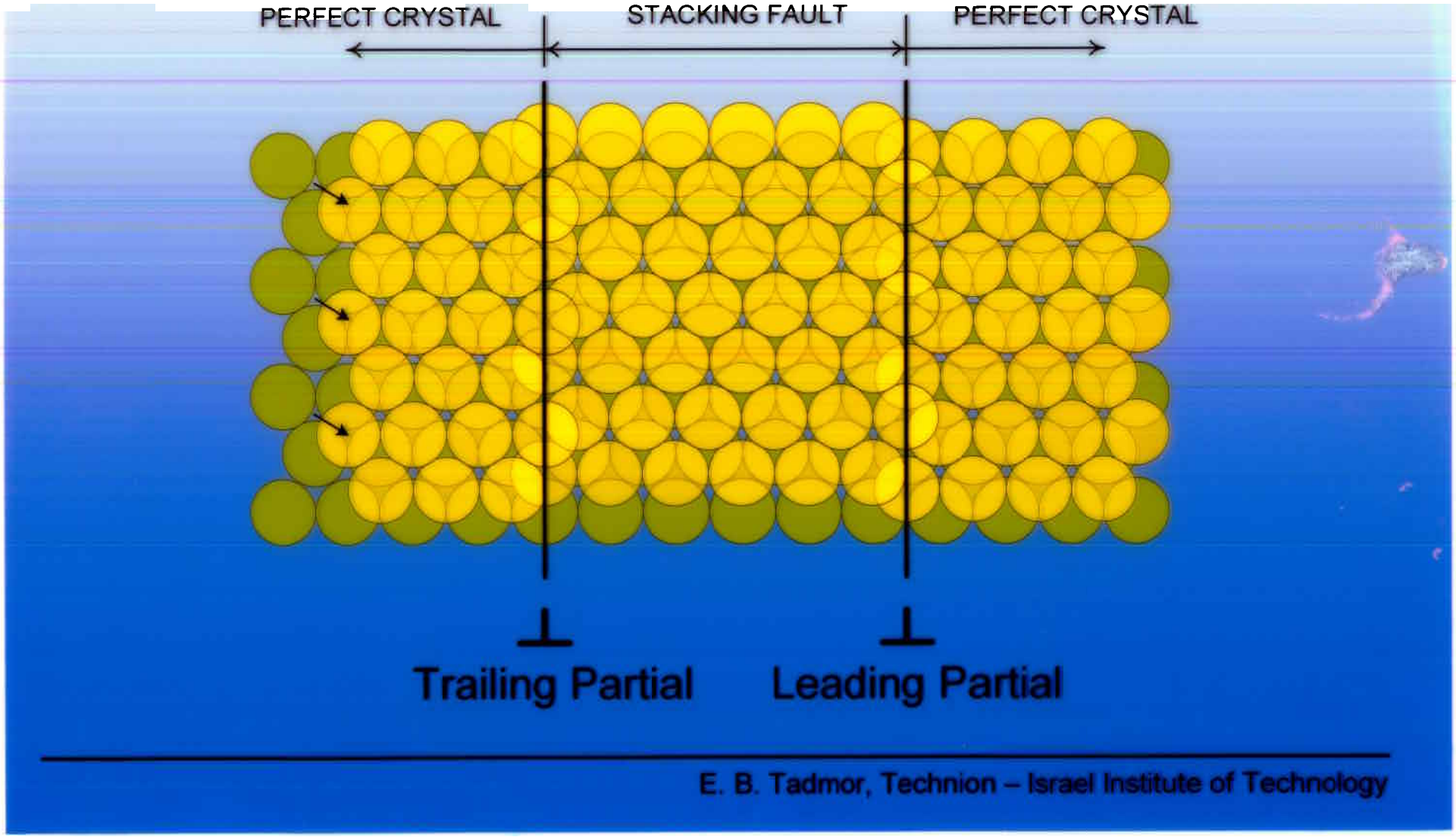



u(x')
x'
y
z
x
u(x)
dσxy

Partial dislocations & stacking fault



Formation of an Extended Dislocation



Two important themes

1. Geometry

   - Crystal lattice: Cubic, BCC, FCC, HCP, Diamond, . . .
   - Lattice defects: stacking fault, dislocations

2. Physics

   (a) Why selecting the particular lattice? (Quantum packing problem)

   (b) Origin of cohesion: Why do atoms stick together?

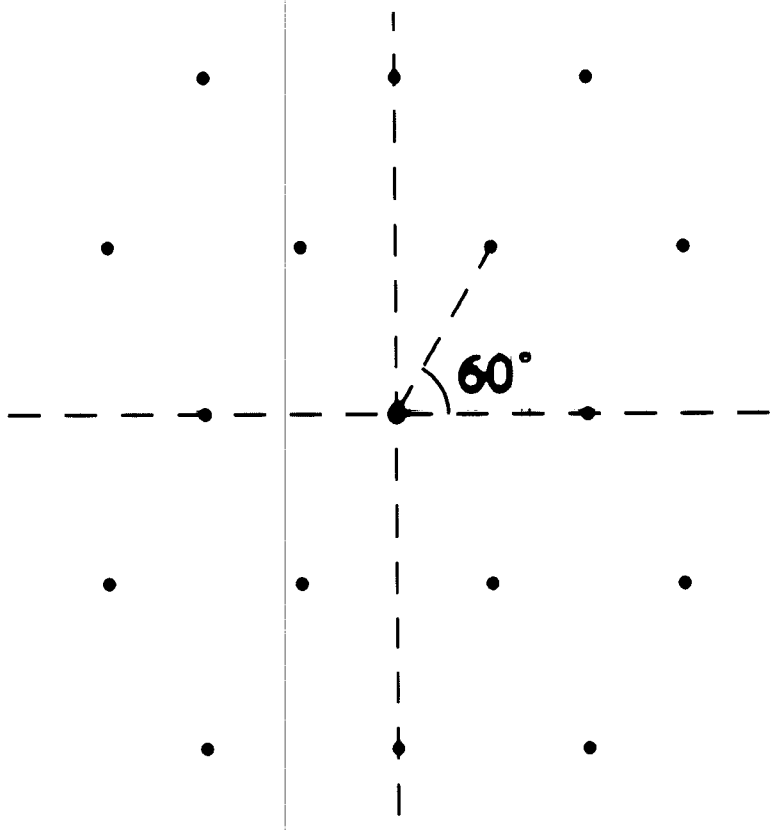
      i. Molecular (van der Waals force)

      ii. Covalently-bonded (e.g. Si)

      iii. Metallic

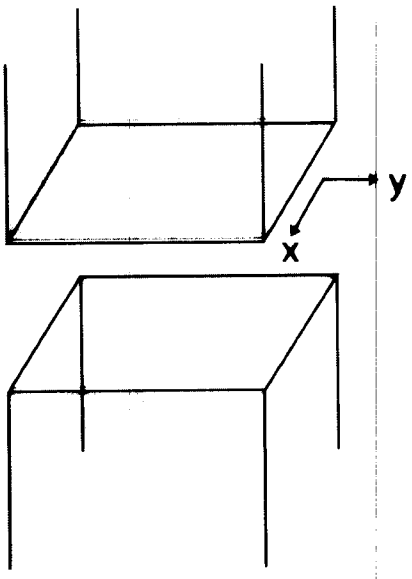
      iv. Ionic (e.g. NaCl)

      v. Hydrogen-bonded



Lattice L

Gamma surface energy



$\Gamma(x,y)$ = energy per unit cell at the surface when the two half crystals are displaced uniformly by (x,y)

Example: FCC lattice in (111) direction

Illustration: displacing two triangular lattices

$$\Gamma(x,y) = \sum_{i\in L_1, j\in L_2} V_0(r_i' - r_j),\ r_i' = r_i + (x,y)$$

Observation: Γ has the symmetry of the lattice

G = point group of triangular lattice

$= \{I, R_{60}, R_x, R_y, \ldots\}$

L^* = dual lattice (Fourier space)

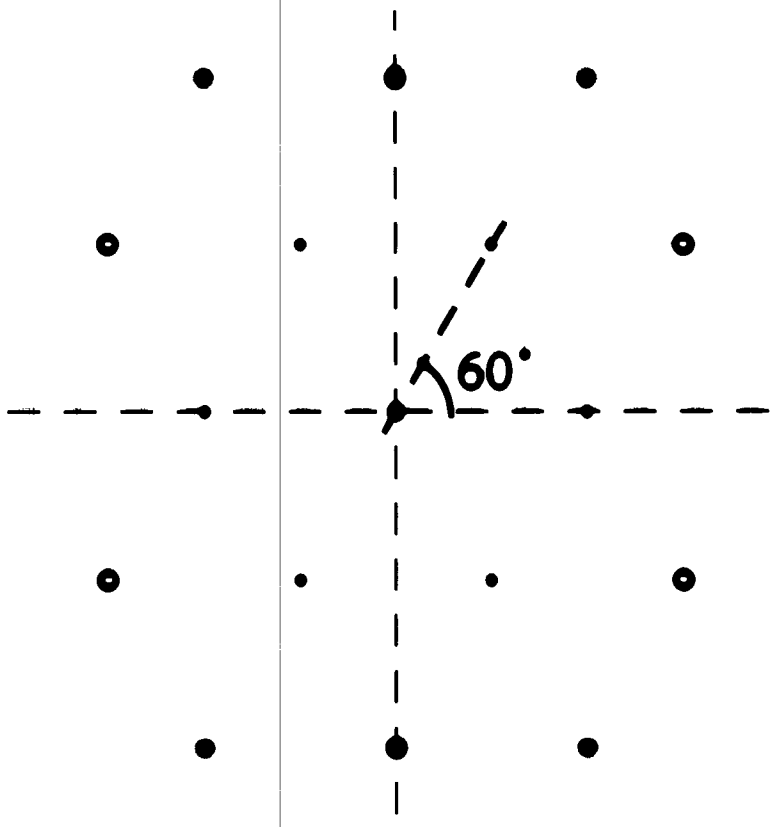
= reciprocal lattice = triangular lattice

$$\Gamma(x,y) = \sum_{\text{orbits}} c_K O_K(x,y)$$

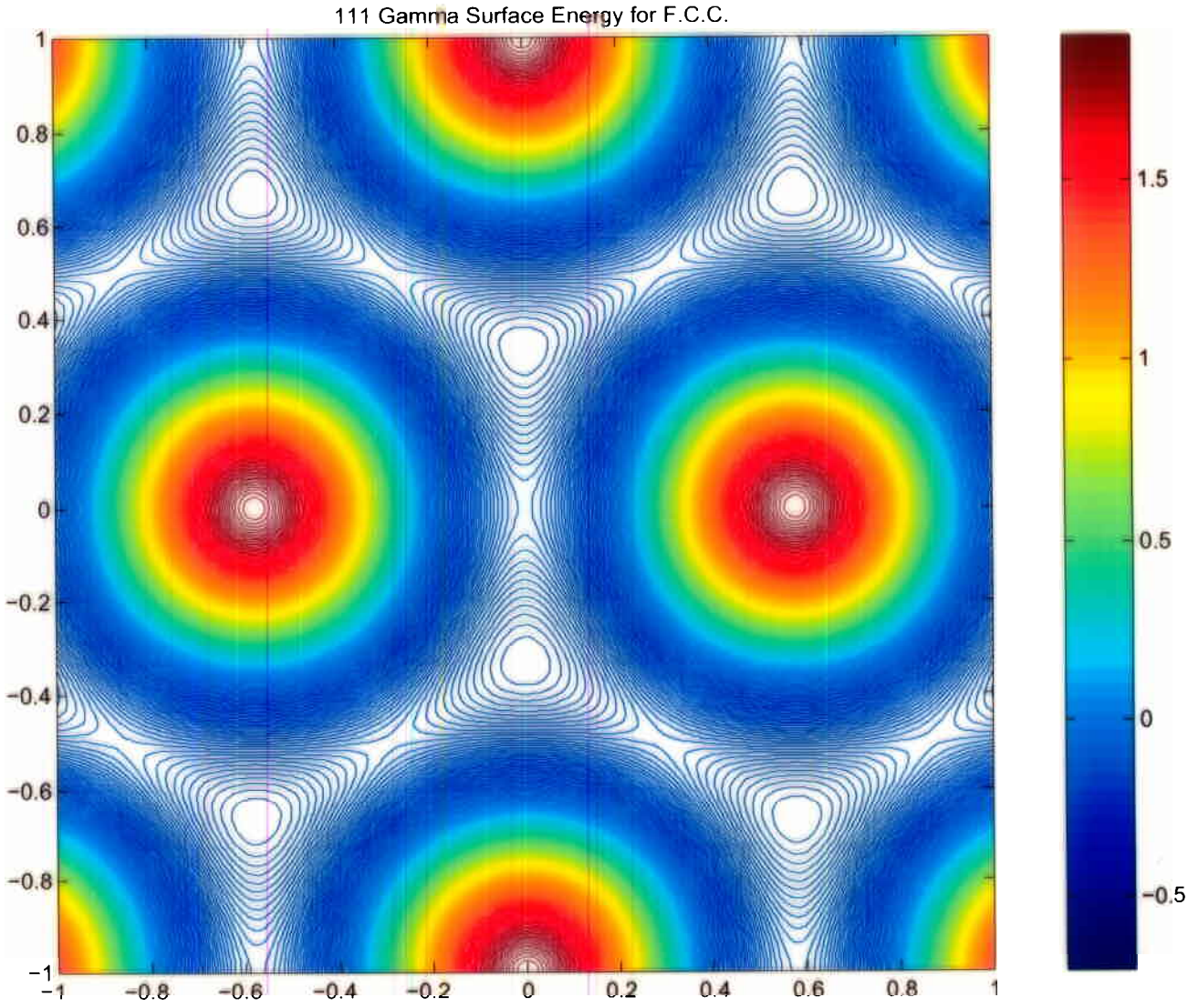
$\{O_K\}$ are invariant under G

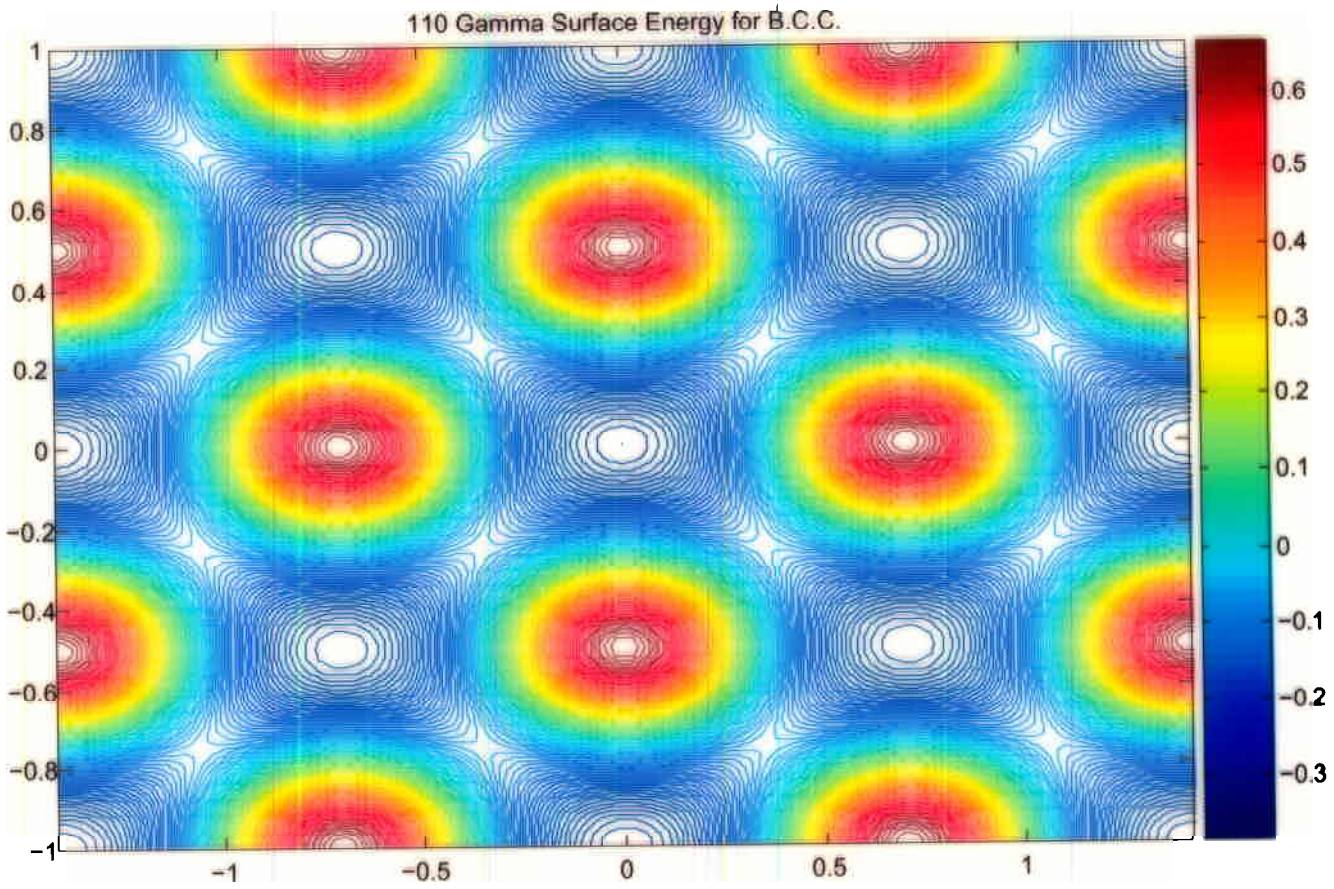
Leading order truncations give good approximation to Γ.

Conclusion: Geometry "determines" Γ.



Lattice L


111 Gamma Surface Energy for F.C.C.
1
0.8
0.6
0.4
0.2
0
−0.2
−0.4
−0.6
−0.8
−1
−1
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4
0.6
0.8
1
1.5
1
0.5
0
−0.5


110 Gamma Surface Energy for B.C.C.
1
0.8
0.6
0.4
0.2
0
−0.2
−0.4
−0.6
−0.8
−1
−1
−0.5
0
0.5
1
0.6
0.5
0.4
0.3
0.2
0.1
0
−0.1
−0.2
−0.3

What questions do we need to address?

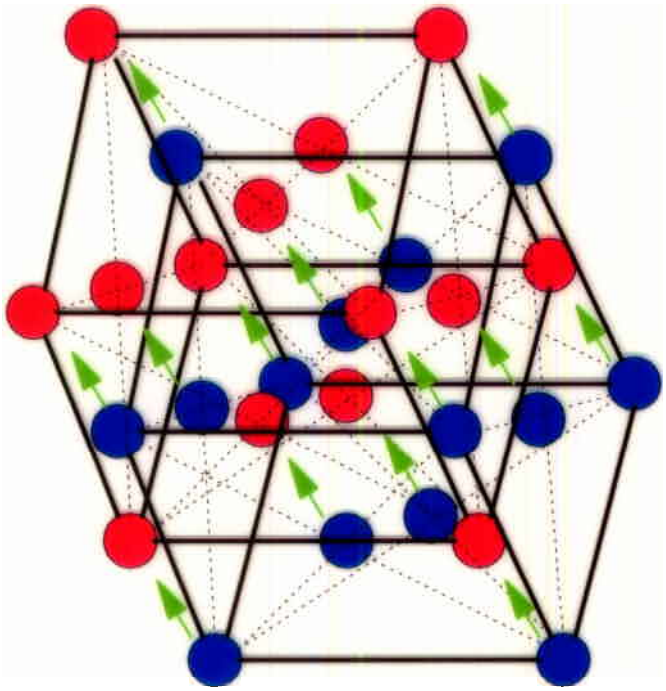
1. Quantum packing problem:
   Why selecting the specific crystal structure?

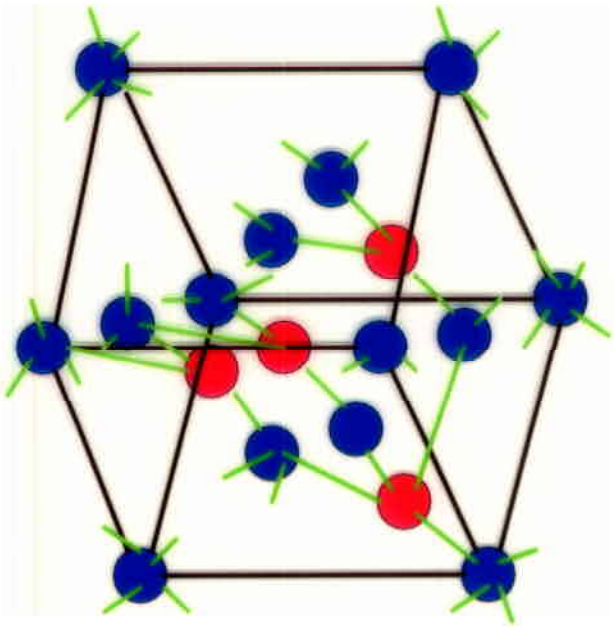
2. Stability of crystals (nonlinear elastic regime)

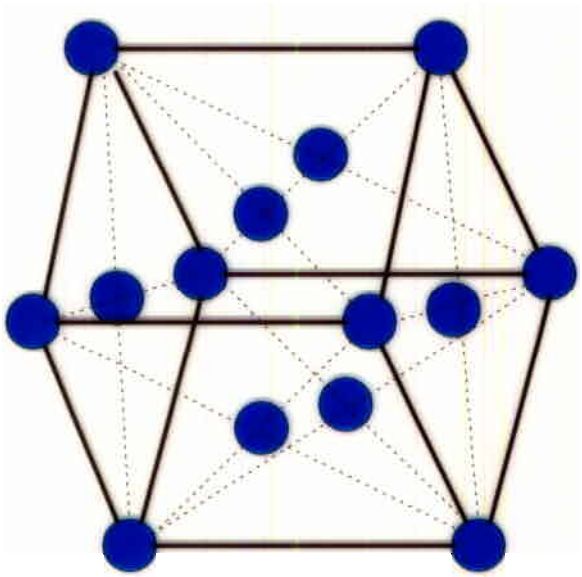
3. Instability of crystals, defect formation

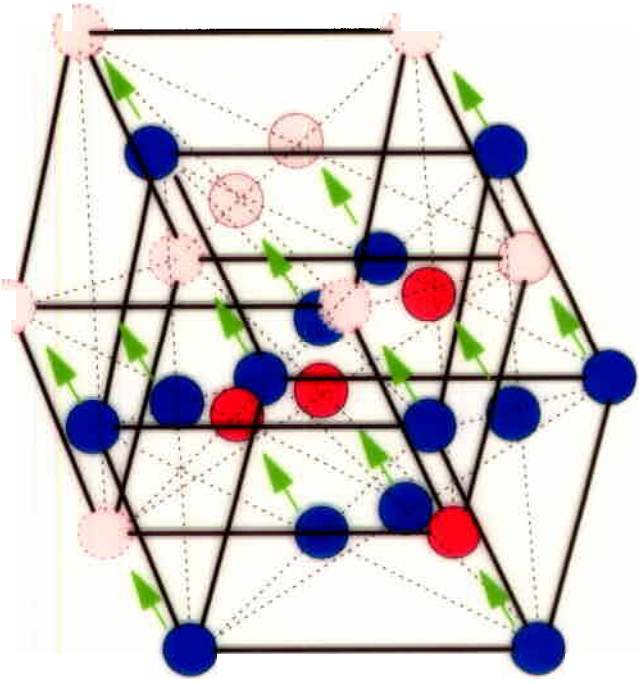
4. Defect structure and dynamics (isolated)

5. Defect-defect interactions, plasticity







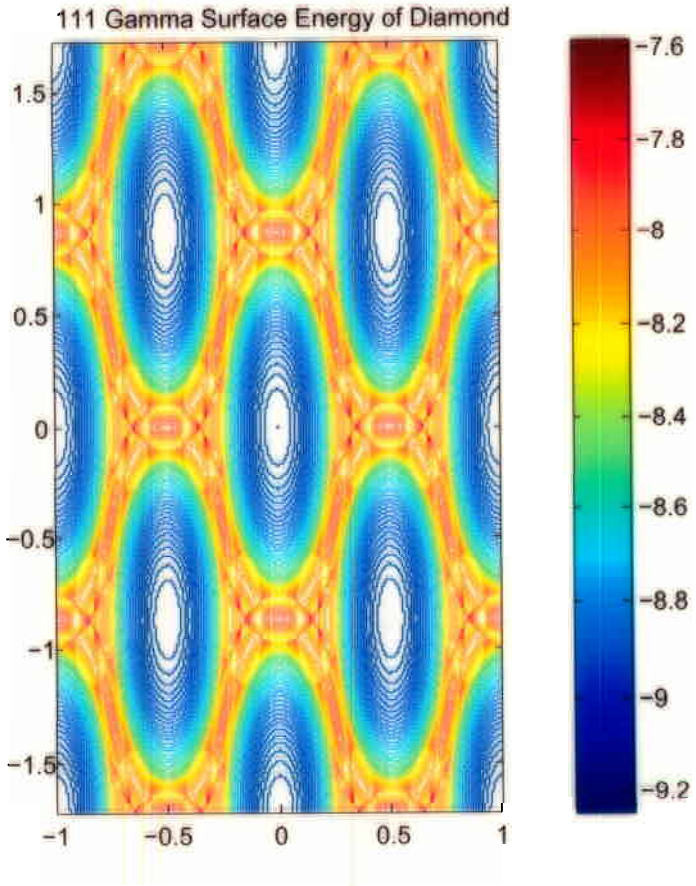


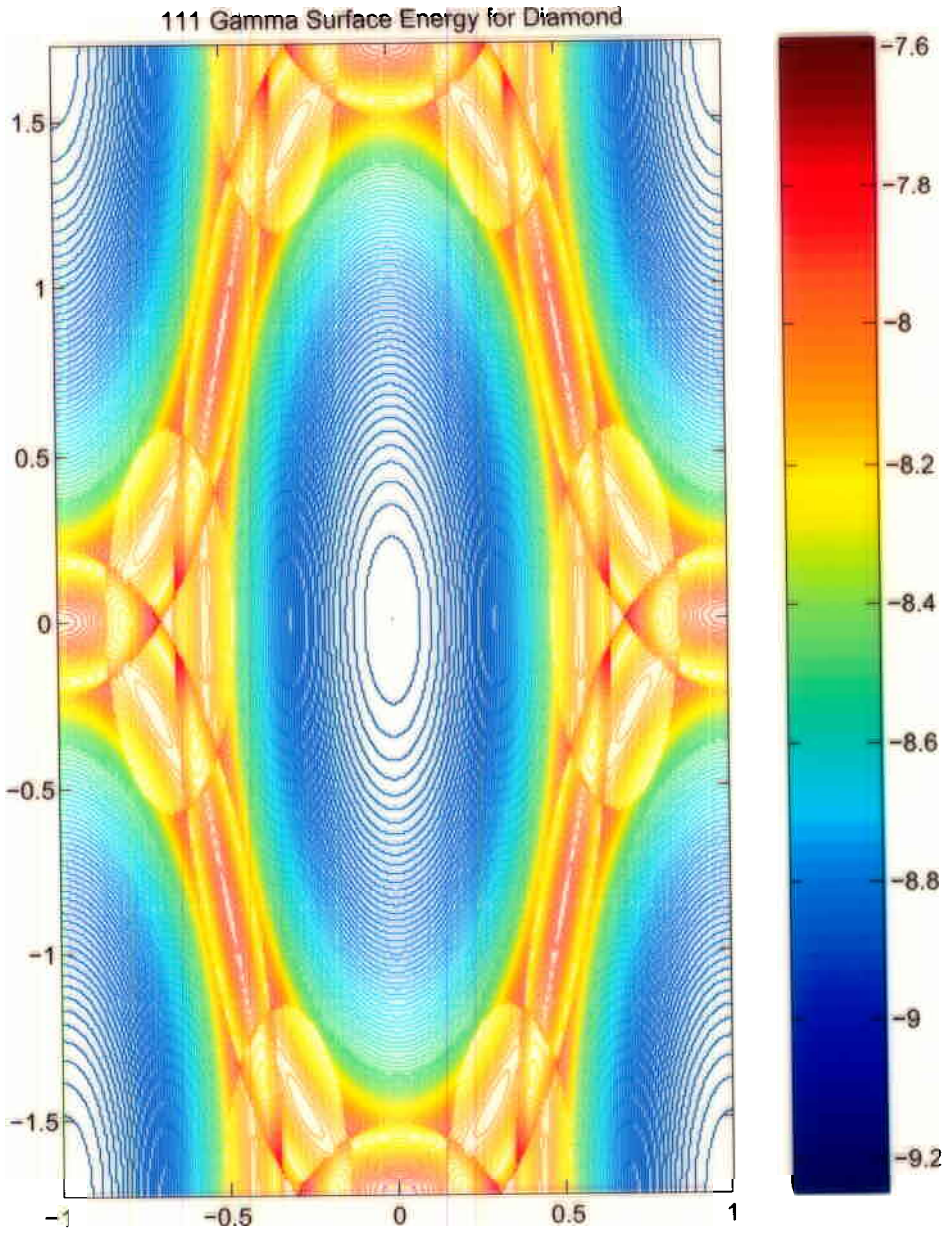
Diamond lattice

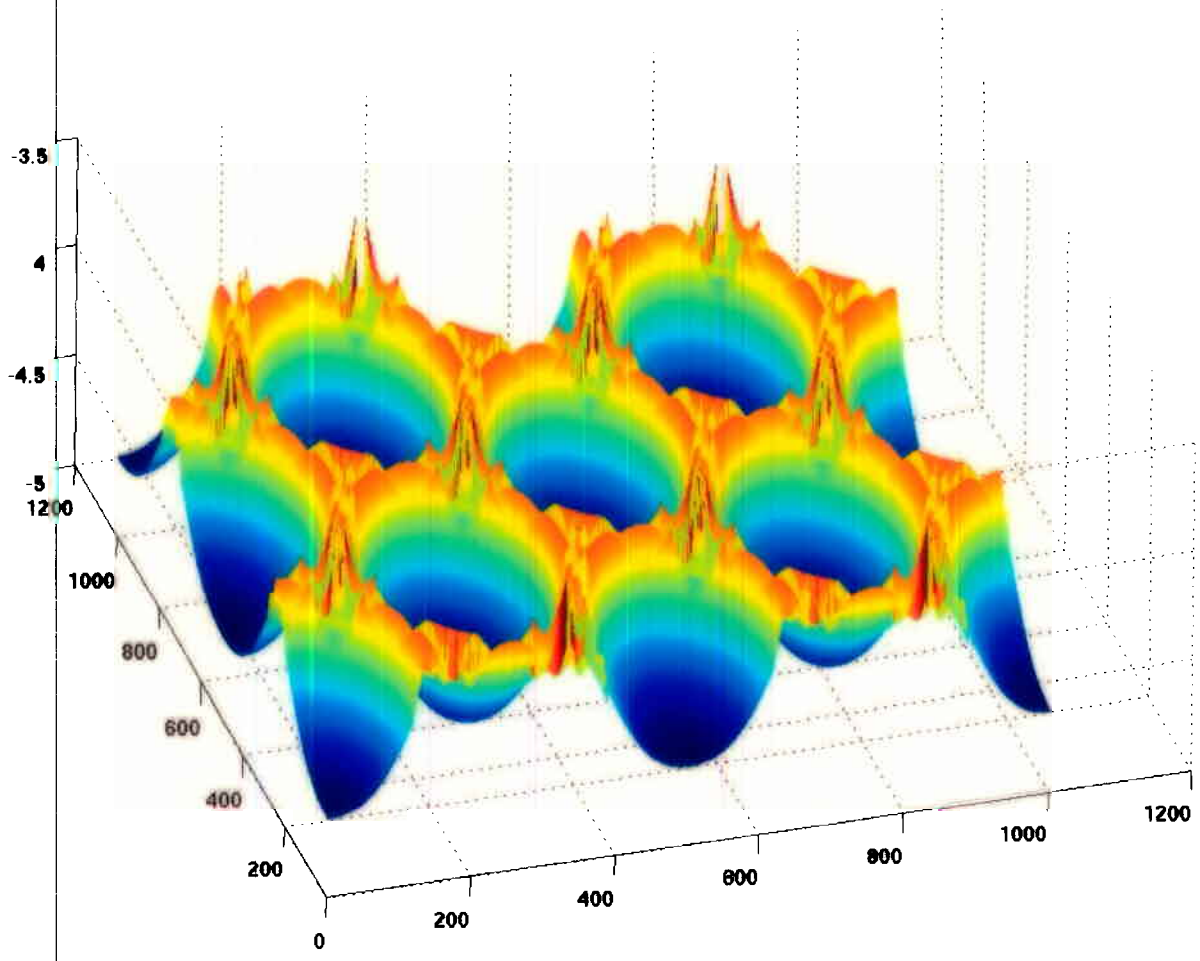
$\Gamma(x, y)$ nearly singular

Geomtry tells little.

Physics (details of the atomic interaction) is important!


111 Gamma Surface Energy of Diamond
1.5
1
0.5
0
−0.5
−1
−1.5
−1
−0.5
0
0.5
1
−7.6
−7.8
−8
−8.2
−8.4
−8.6
−8.8
−9
−9.2

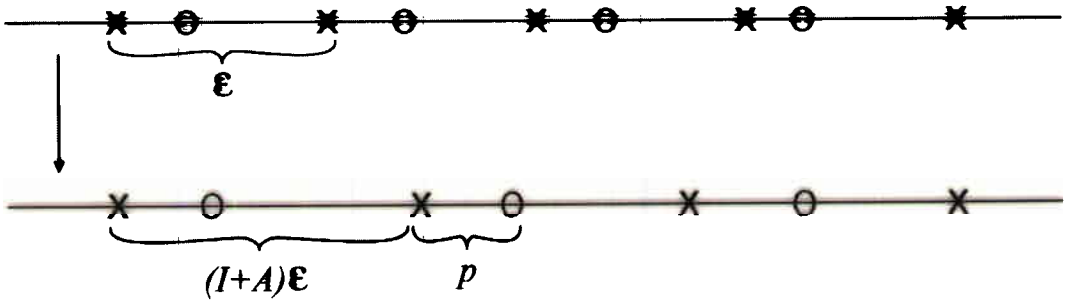

111 Gamma Surface Energy for Diamond
1.5
1
0.5
0
−0.5
−1
−1.5
−1
−0.5
0
0.5
1
−7.6
−7.8
−8
−8.2
−8.4
−8.6
−8.8
−9
−9.2


-3.5
4
-4.5
-5
1200
1000
800
600
400
200
0
200
400
600
800
1000
1200

Nonlinear elastic regime

(E and Ming)

Cauchy-Born rule



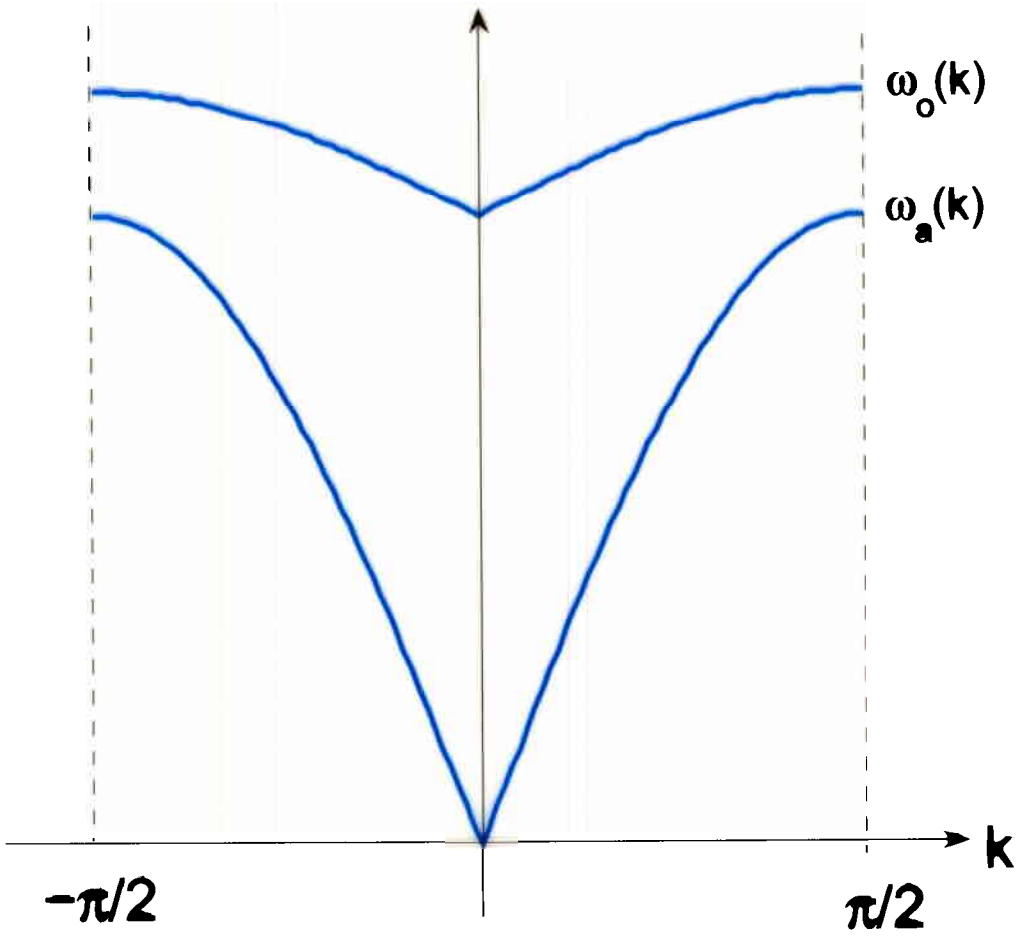
$W(A,p)$ = energy of unit cell in the deformed, (by A), and displaced (by p) configuration.

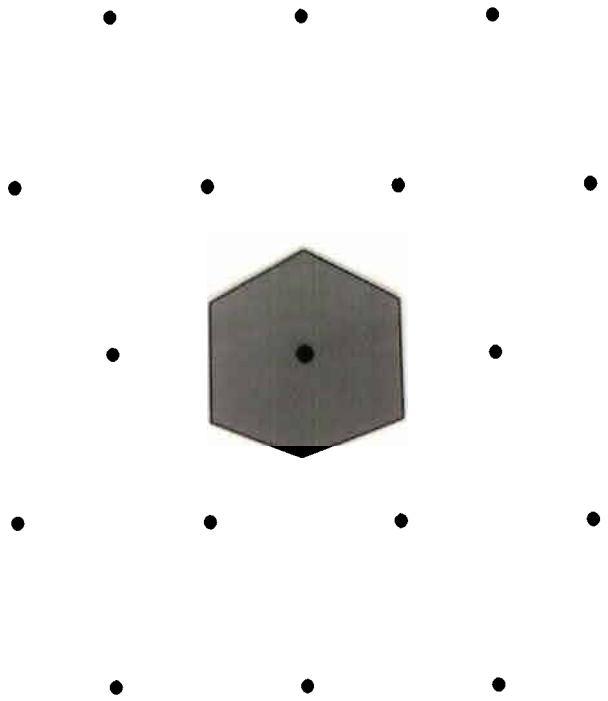
$$W_{CB}(A) = \min_p W(A,p)$$

$$I(v) = \int_\Omega \{W_{CB}(\nabla v) - f(x)v(x)\}dx \qquad (*)$$

$$I_h(\{v_j\}) = V(y_1,\ldots,y_N) - \sum f(x_j)v_j \qquad (**)$$

$$y_j = x_j + v_j$$


$\omega_o(k)$
$\omega_a(k)$
k
$-\pi/2$
$\pi/2$



Assumption A:

$$\begin{pmatrix} D_{AA}W(A,p), & D_{Ap}W(A,p) \\ D_{Ap}W(A,p), & D_{pp}W(A,p) \end{pmatrix} > 0 \qquad \begin{matrix} A = 0, \\ p = p_0 \end{matrix}$$

Assumption B: "phonons"

$$\omega_a(k) \geq \Lambda_1 |k|$$
$$\omega_0(k) \geq \frac{\Lambda_2}{\varepsilon}$$

$k \in$ 1st Brillouin zone

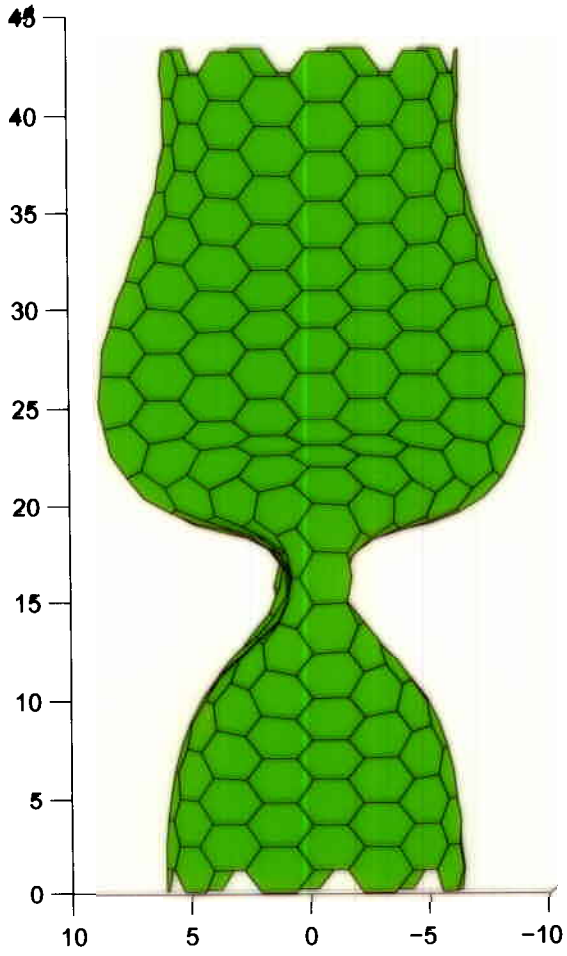
Theorem: ($p \geq d$ = dimension) $\exists K, R$ such that if $\|f\|_{L^p} \leq K$, then $\exists$ unique solution of $(*), v = u_{CB}$, such that

$$\|u_{CB}\|_{W^{2,p}} \leq R$$

Theorem: $\exists$ solution y of $(**)$, such that

$$\|y - y_{CB}\|_1 \leq C\varepsilon$$

$y_{CB}(x) = x + u_{CB}(x)$, $\|\cdot\|_1$ = discrete H^1 norm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15
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−5
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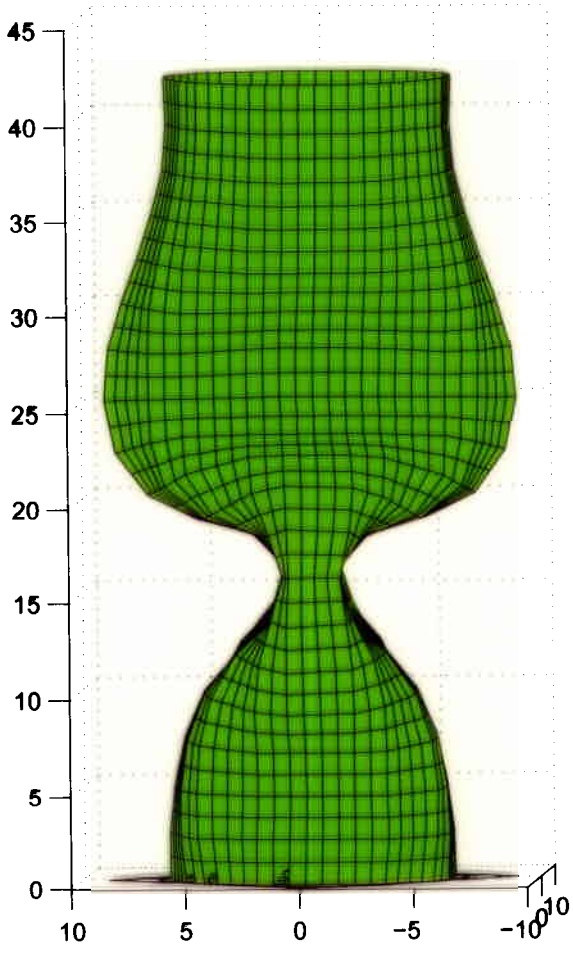
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Remarks

1. Result is sharp
   Classification of instability, if $\|f\|_{L^P} > K$
   Defect formation.

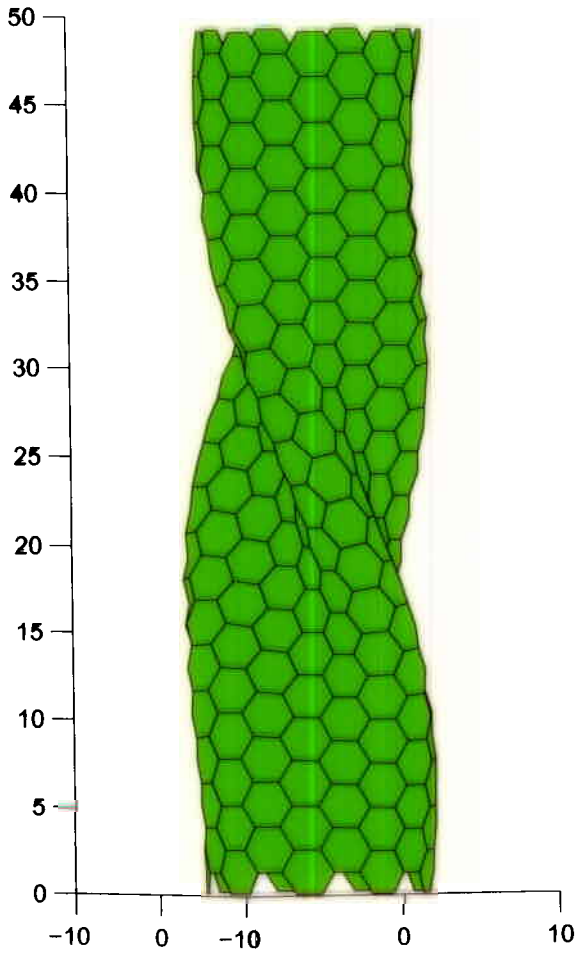
2. Result can be extended to dynamic problems.

3. Previous work of Blanc, LeBris and P.L. Lions. Assume $y_j = x_j + u(x_j)$, u is smooth, and study limit of V.

Example: Lennard-Jones potential, next nearest neighbor interaction

Case 1. Triangular lattice

Case 2. Square lattice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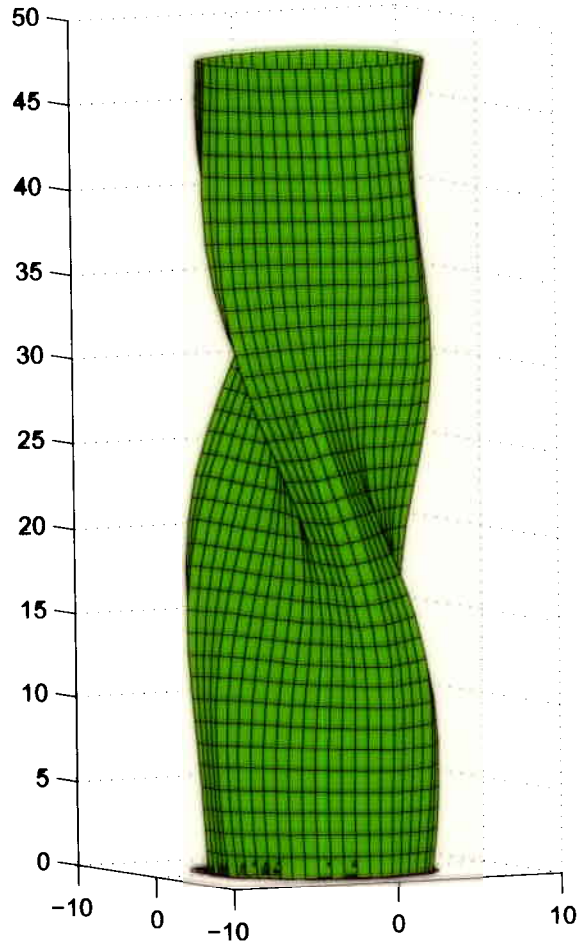
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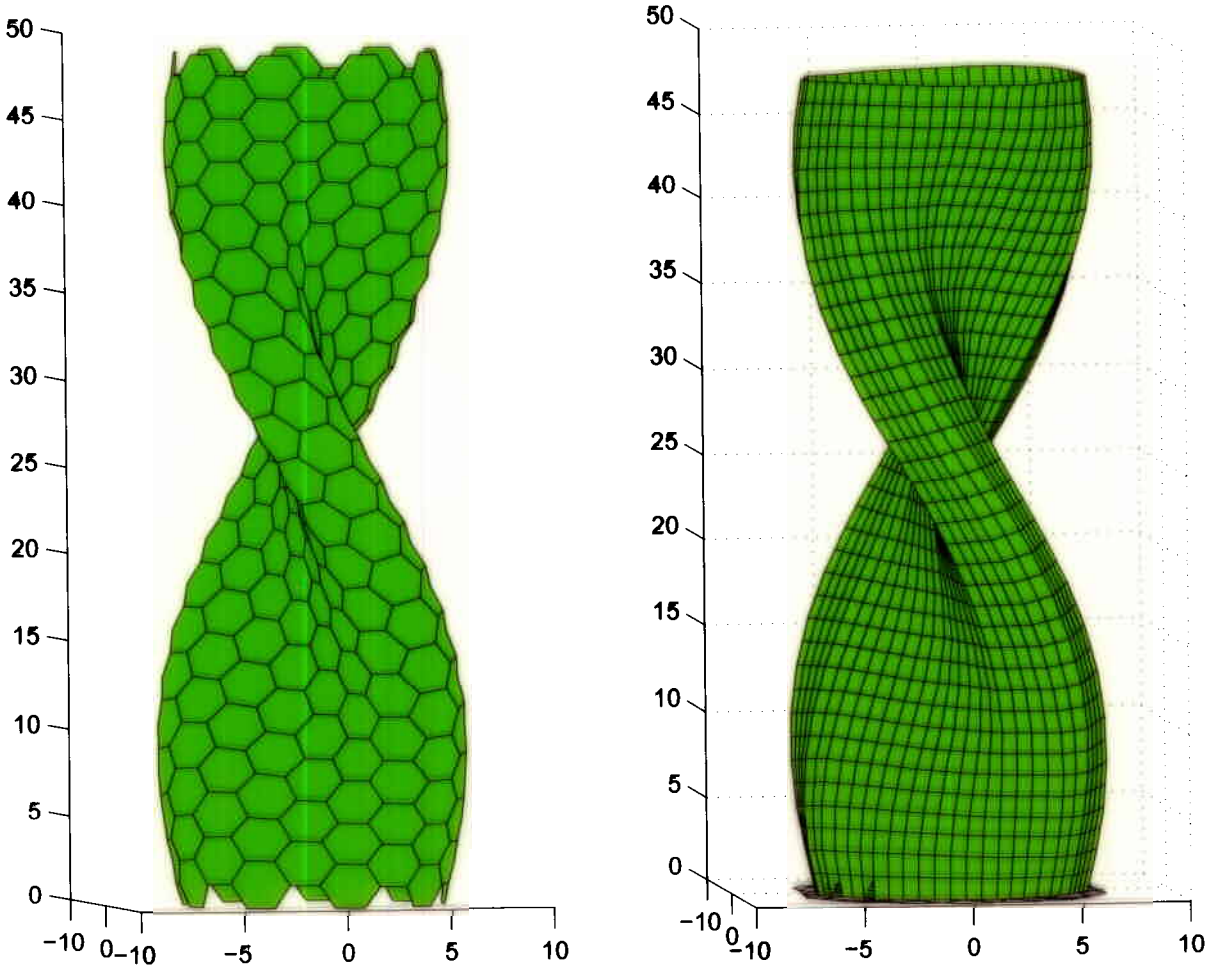
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Summary

1. Atomistically-based mathematical theory of solids is both important and possible.

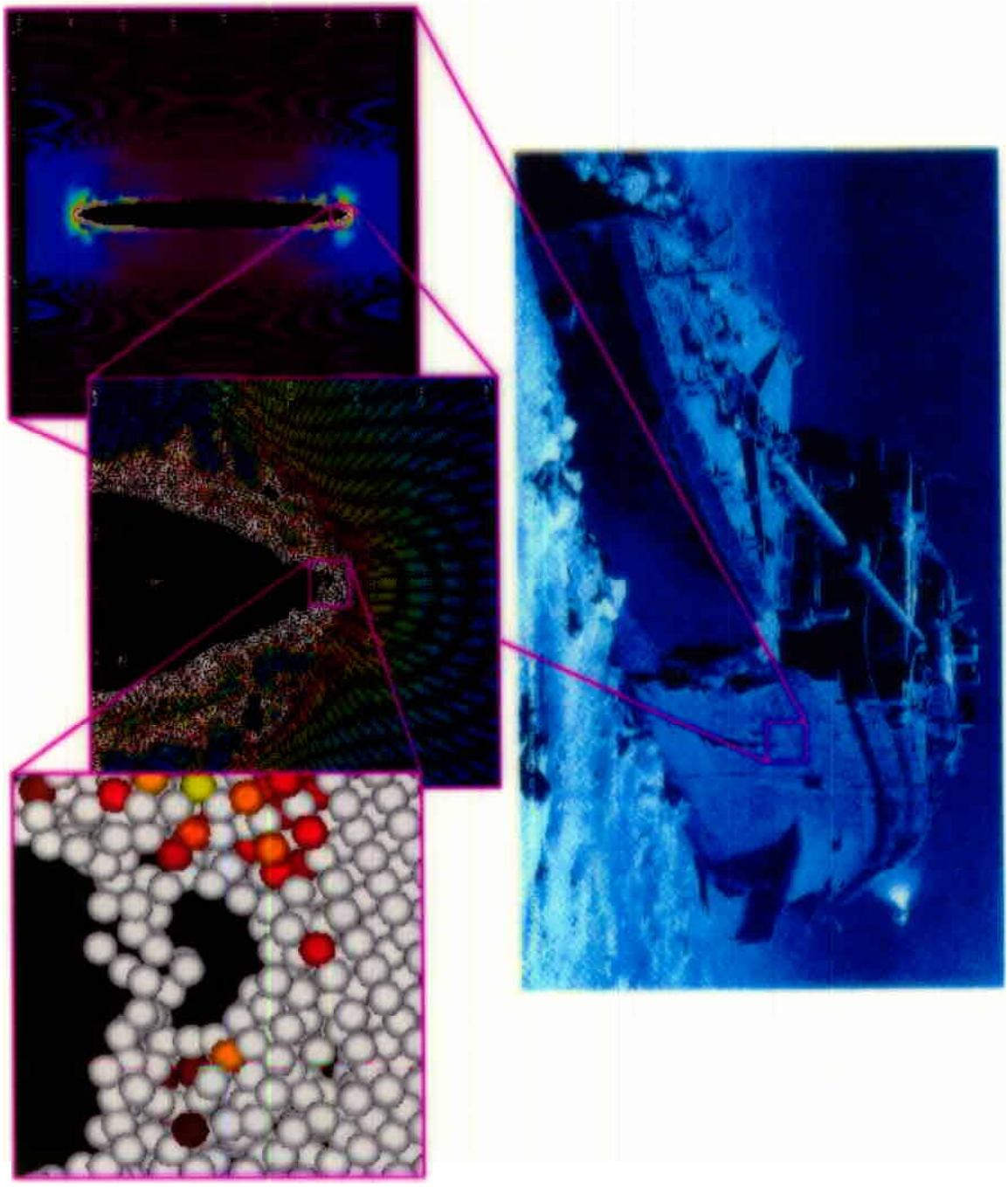
2. Geometry and physics themes helpful.

Reason: Solids are much more *multi-scaled* (and heterogeneous)

Atomic scale: Atoms, electrons
$\longrightarrow$ crystal lattice
$\longrightarrow$ lattice defects

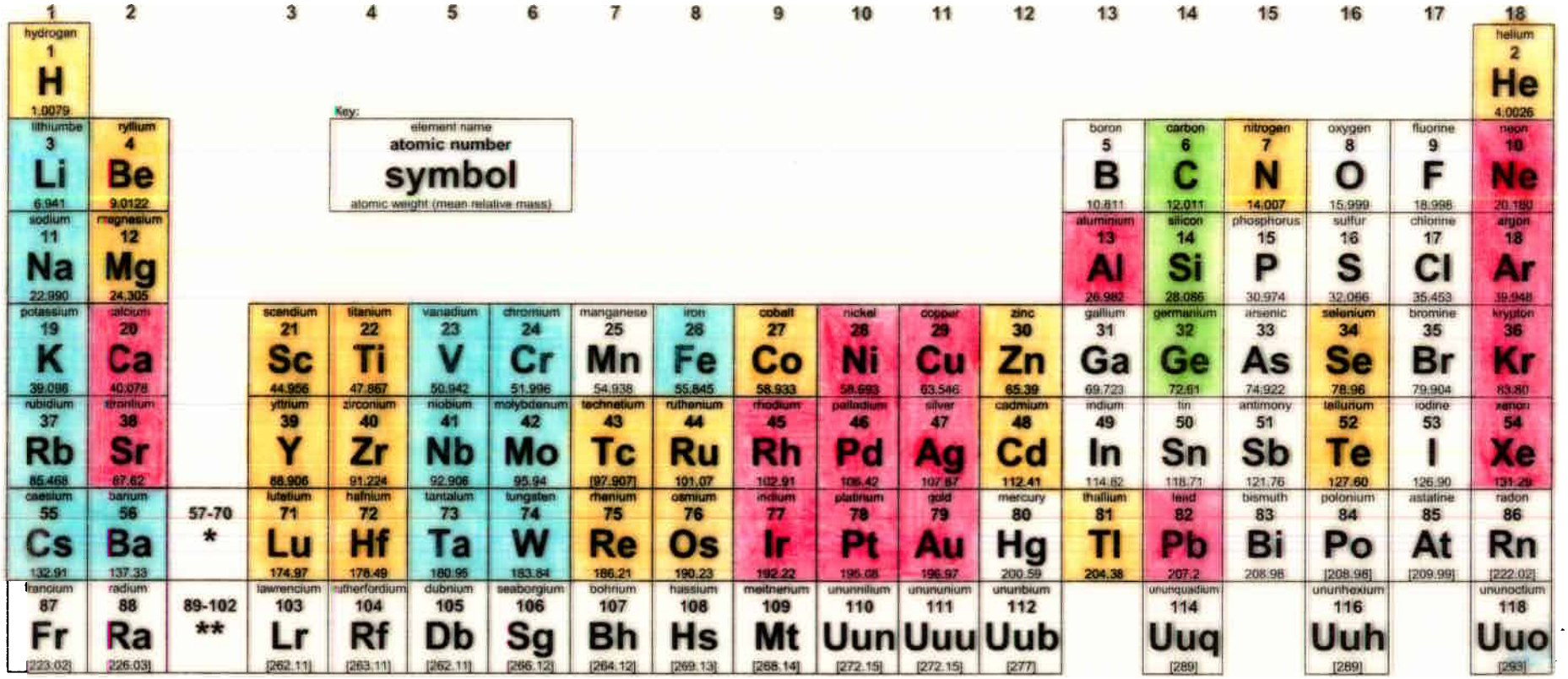
Macroscopic: randomly packed grains

Hierarchy of structures



WebElements: the periodic table on the world-wide web

http://www.webelements.com/



Symbols and names: the symbols and names of the elements, and their spellings are those recommended by the International Union of Pure and Applied Chemistry (IUPAC - http://www.iupac.org/). Names have yet to be proposed for the most recently discovered elements 110–112, 114, 116, and 118 so those used here are IUPAC's temporary systematic names. In the USA and some other countries, the spellings **aluminum** and **cesium** are normal while in the UK and elsewhere the common spelling is **sulphur**.
Group labels: the numeric system (1–18) used here is the current IUPAC convention.
Atomic weights (mean relative masses): Apart from the heaviest elements, these are the IUPAC 1997 values and given to 5 significant figures. Elements for which the atomic weight is given within square brackets have no stable nuclides and are represented by the element's longest lived isotope.

colored by Ilene E