

Mathematical Theory of Solids: from Atomic to Macroscopic Scales

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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:

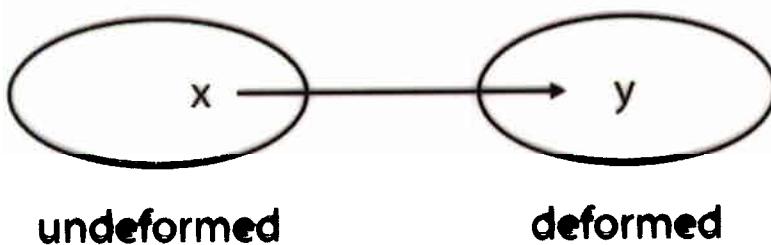
$$\rho \frac{\partial^2 u}{\partial t^2} = (\lambda + \mu) \nabla(\nabla \cdot u) + \mu \Delta u$$

Nonlinear elasticity:

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

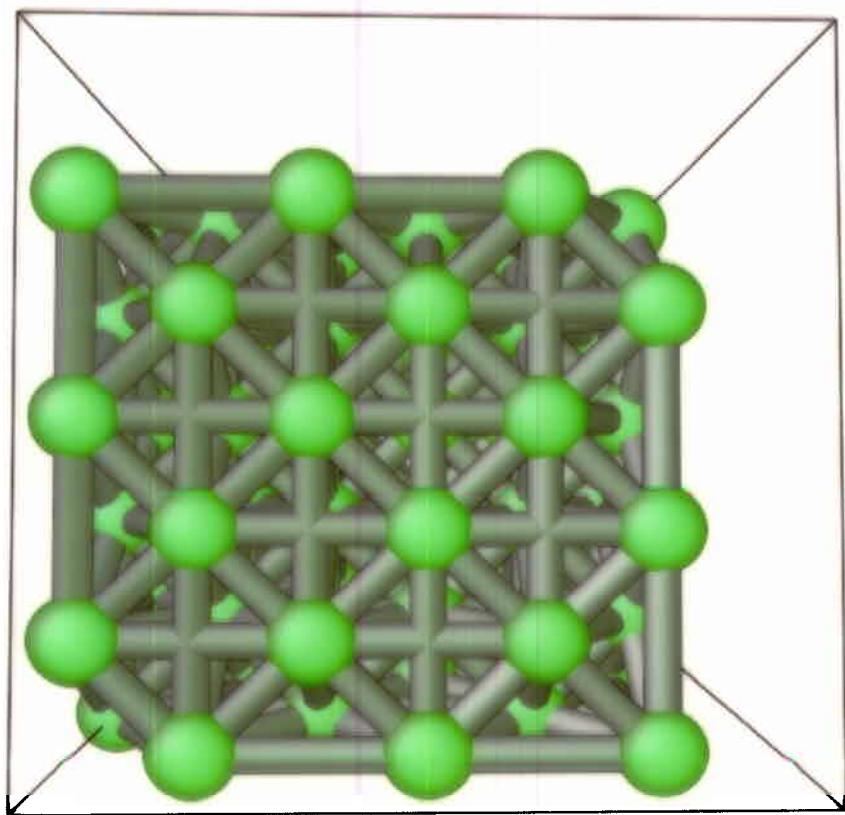
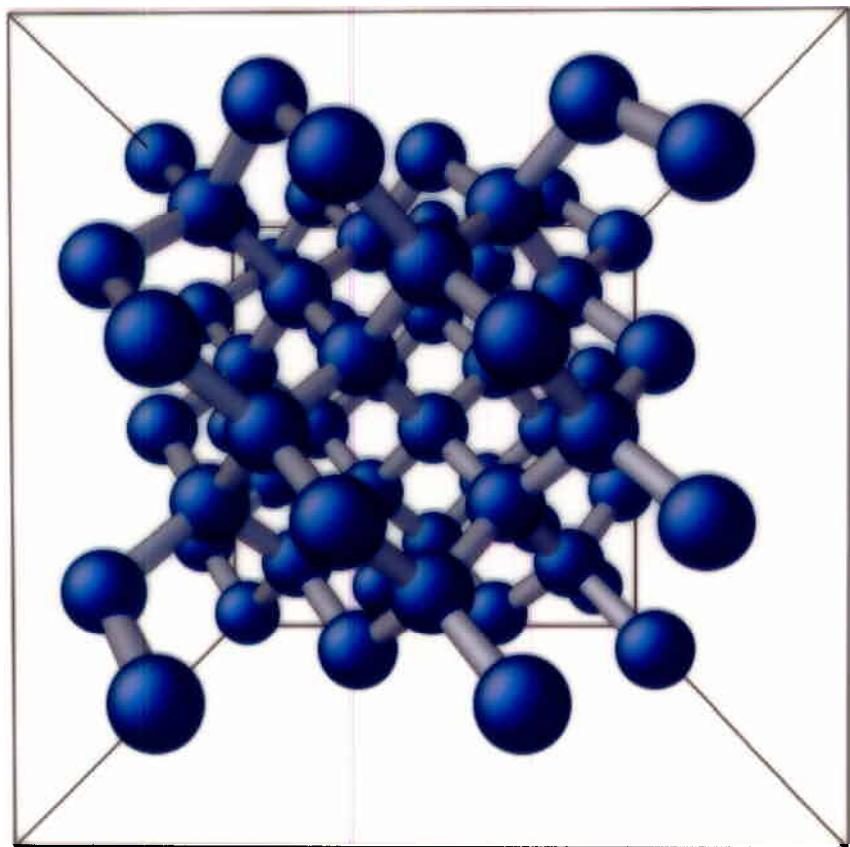
Plasticity

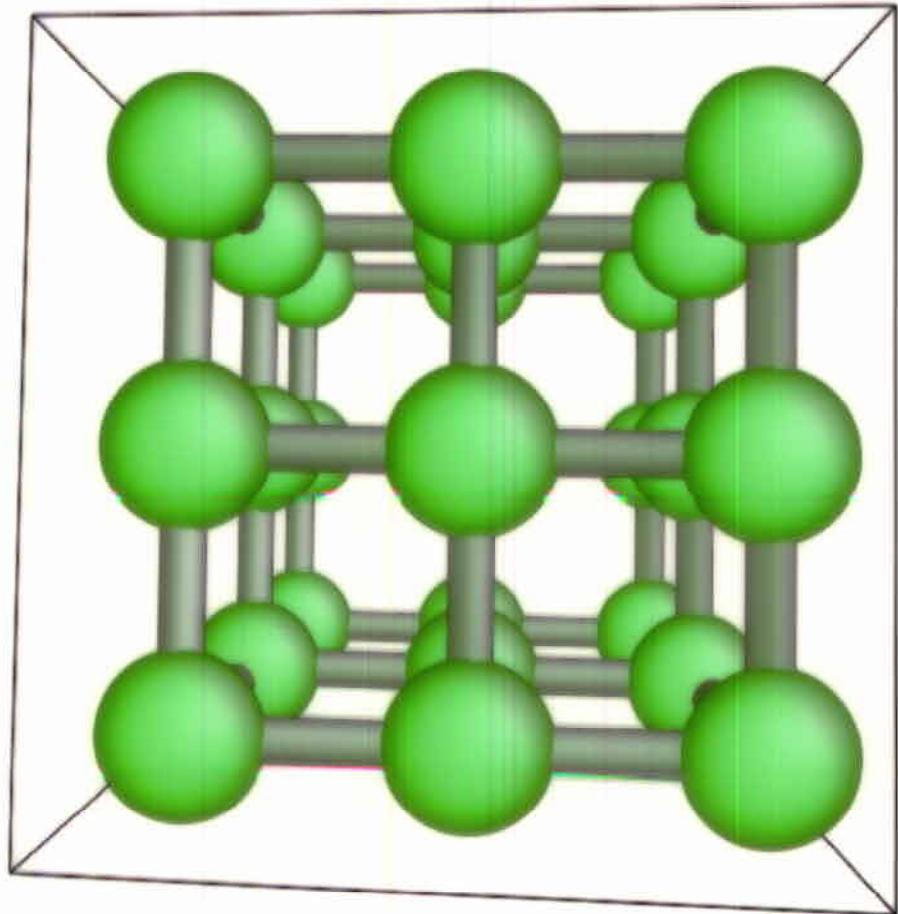
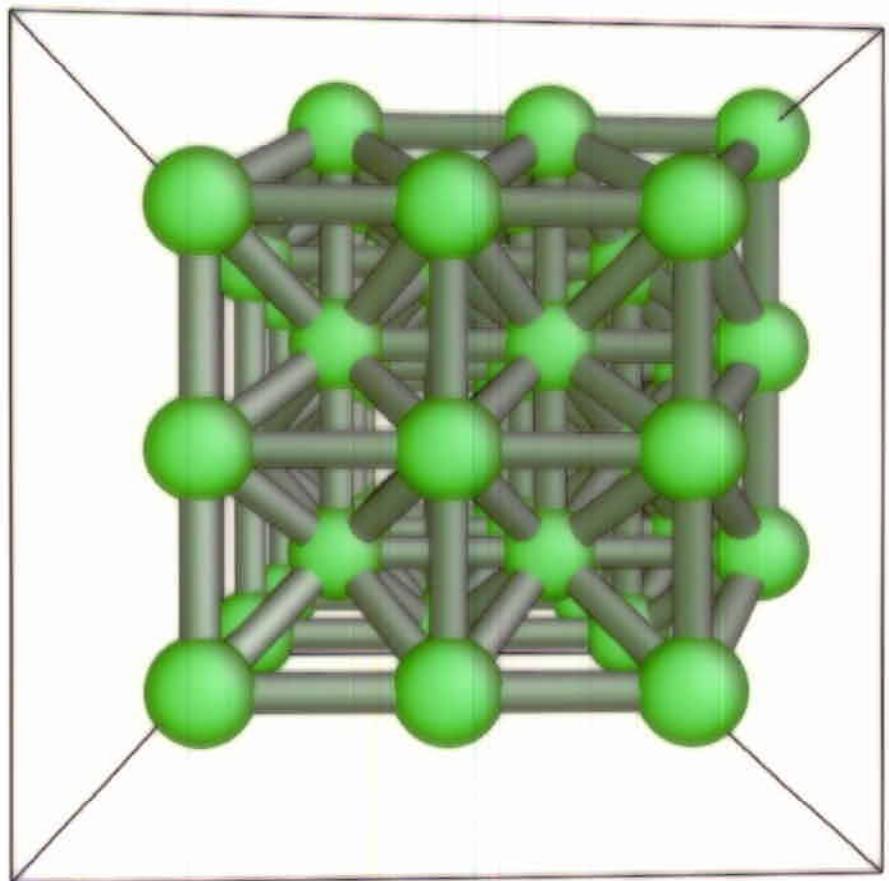
.....



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

$u(x)$ = displacement





Quantum many-body problem

$$V(R_1, R_2, \dots, R_N) =$$

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

R_I = position of the i -th nucleus

Z_I = charge of the i -th nucleus

E^* = ground state energy of the electrons

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

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

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

Dirac (1929)

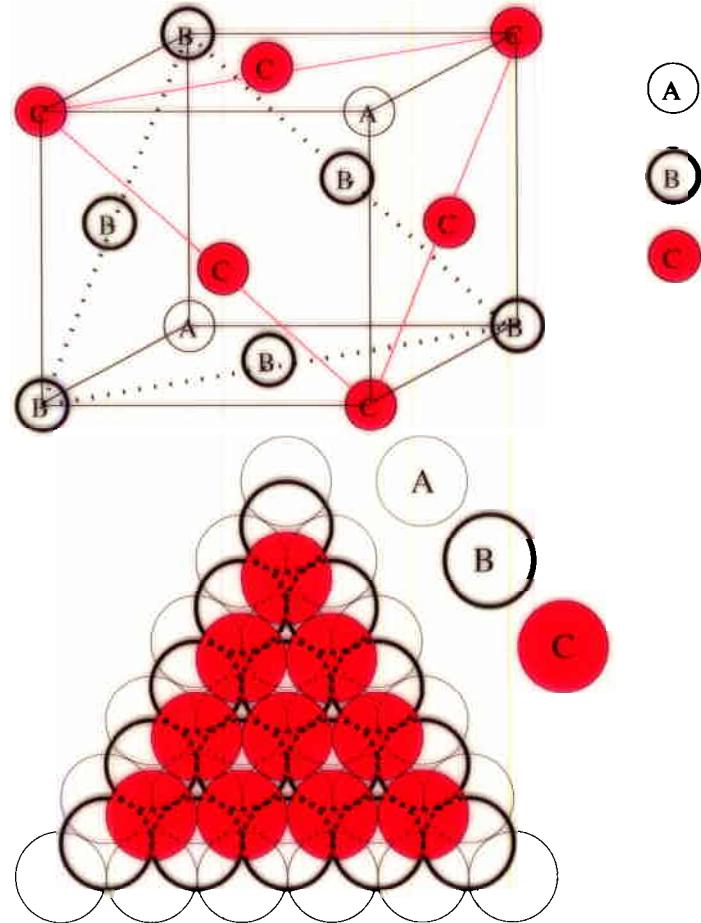
The underlying physical laws necessary for the mathematical theory of a *large part of physics* and *the whole chemistry* are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

What do we take as the starting point?

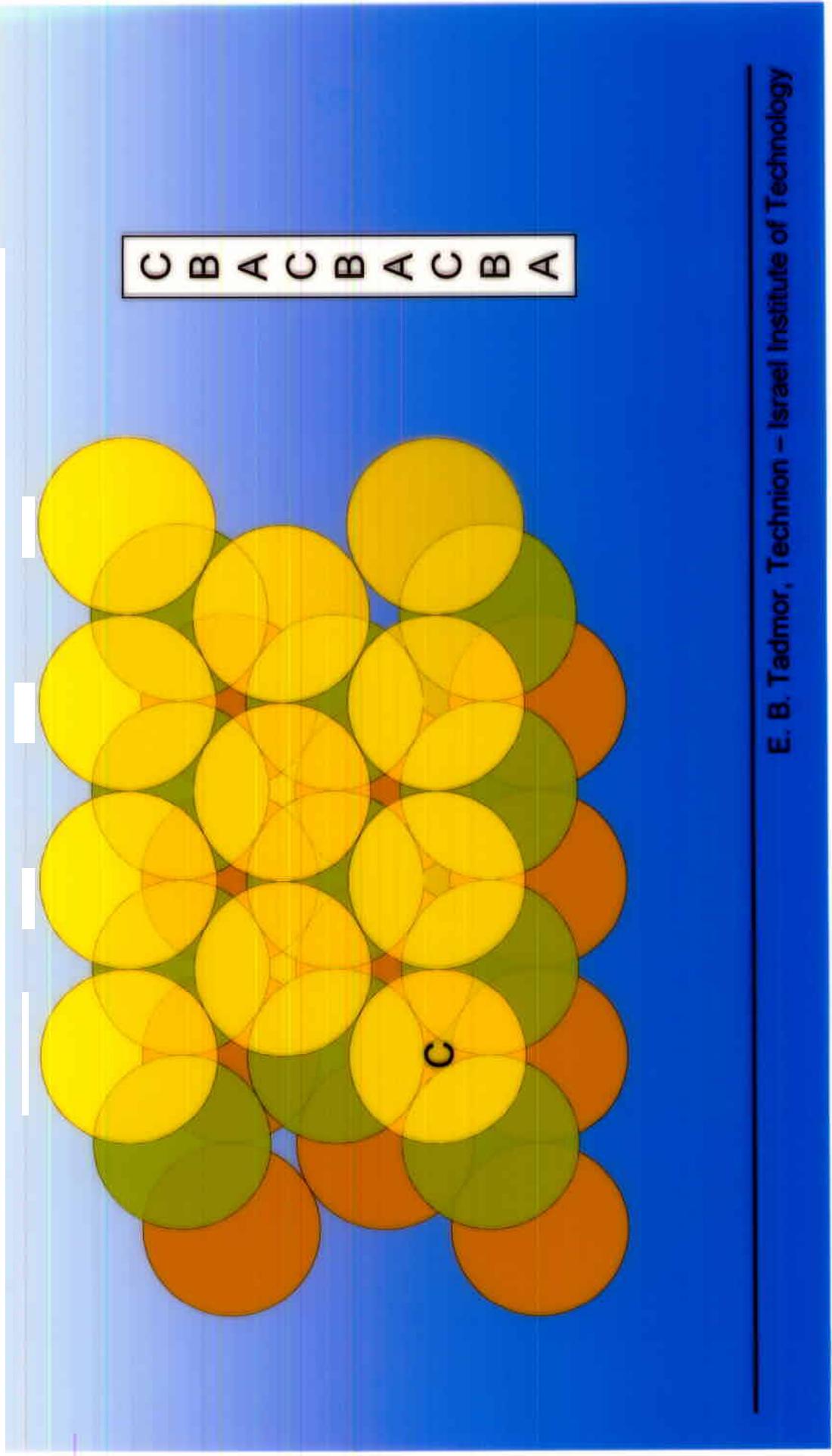
1. Quantum many-body
2. Simplified quantum models (density function theory, tight-binding, etc.)
3. Classical potential
 - Lennard-Jones
 - Embedded Atom Model (EAM)

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

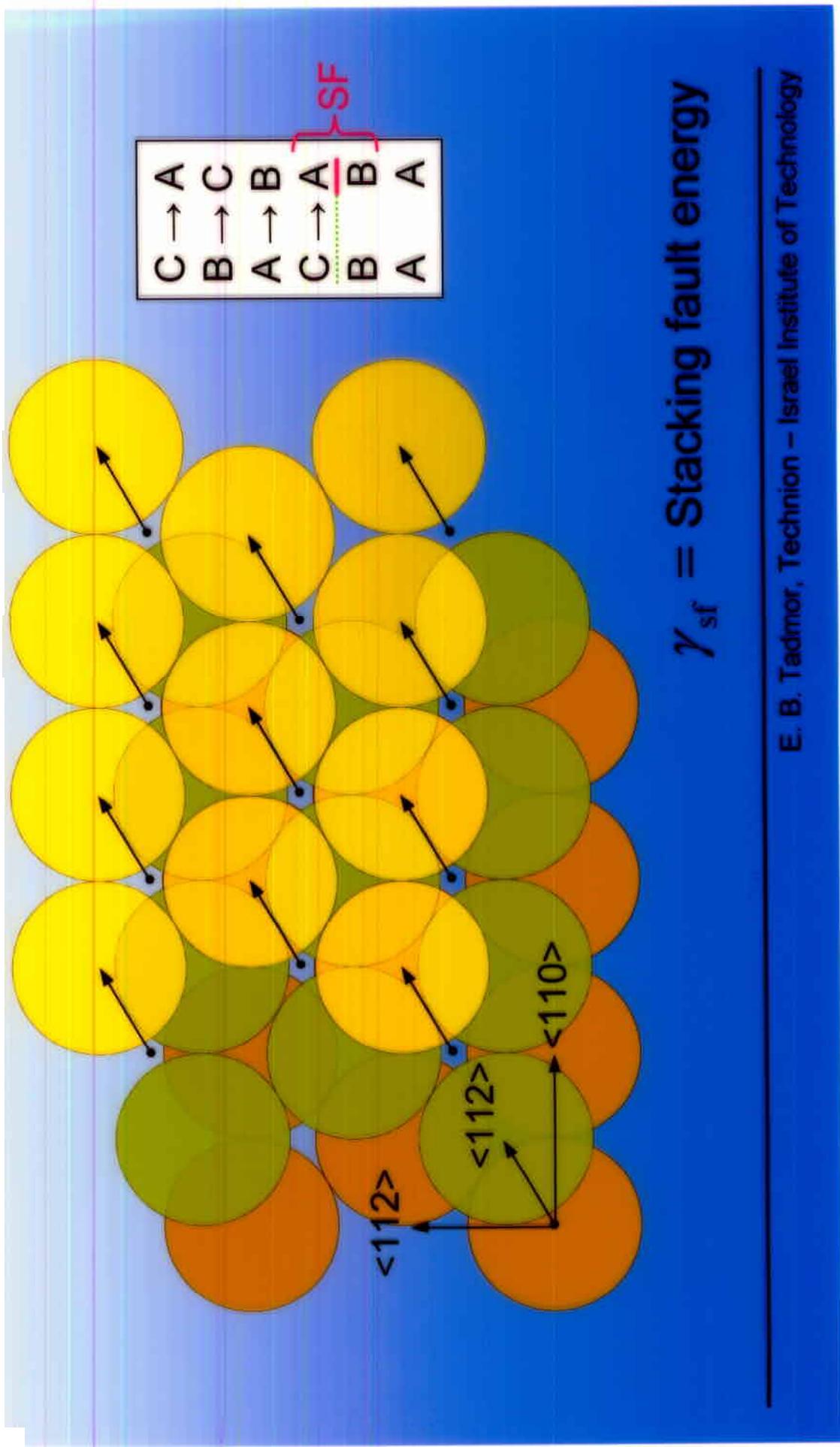
$$V_0(r) = 4\epsilon \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right)$$

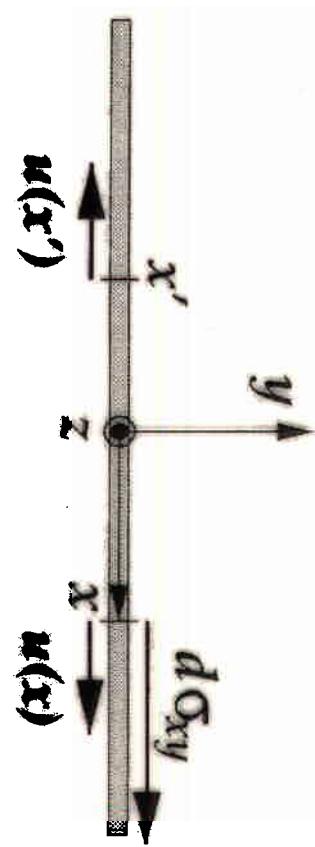
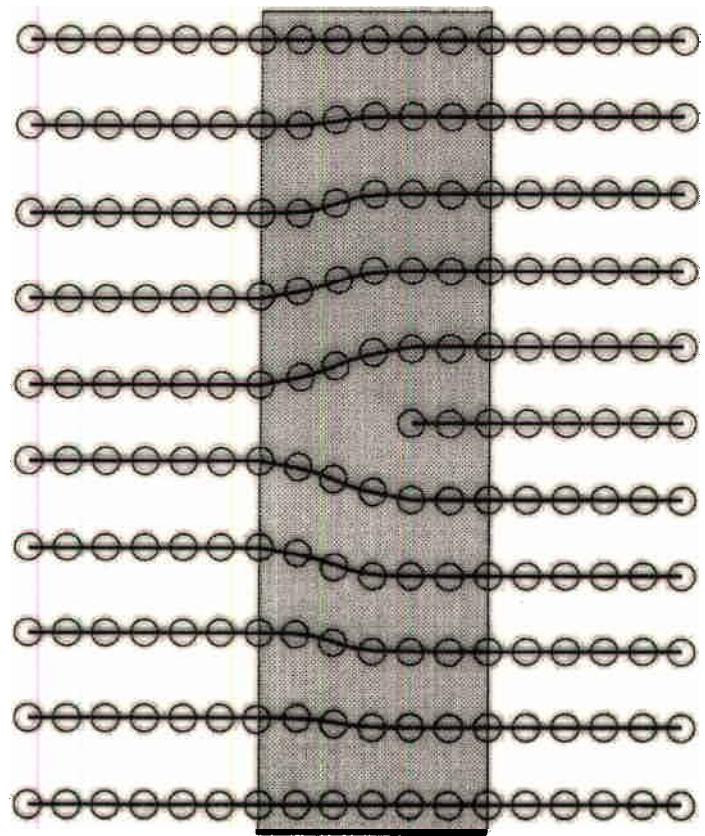


FCC Stacking

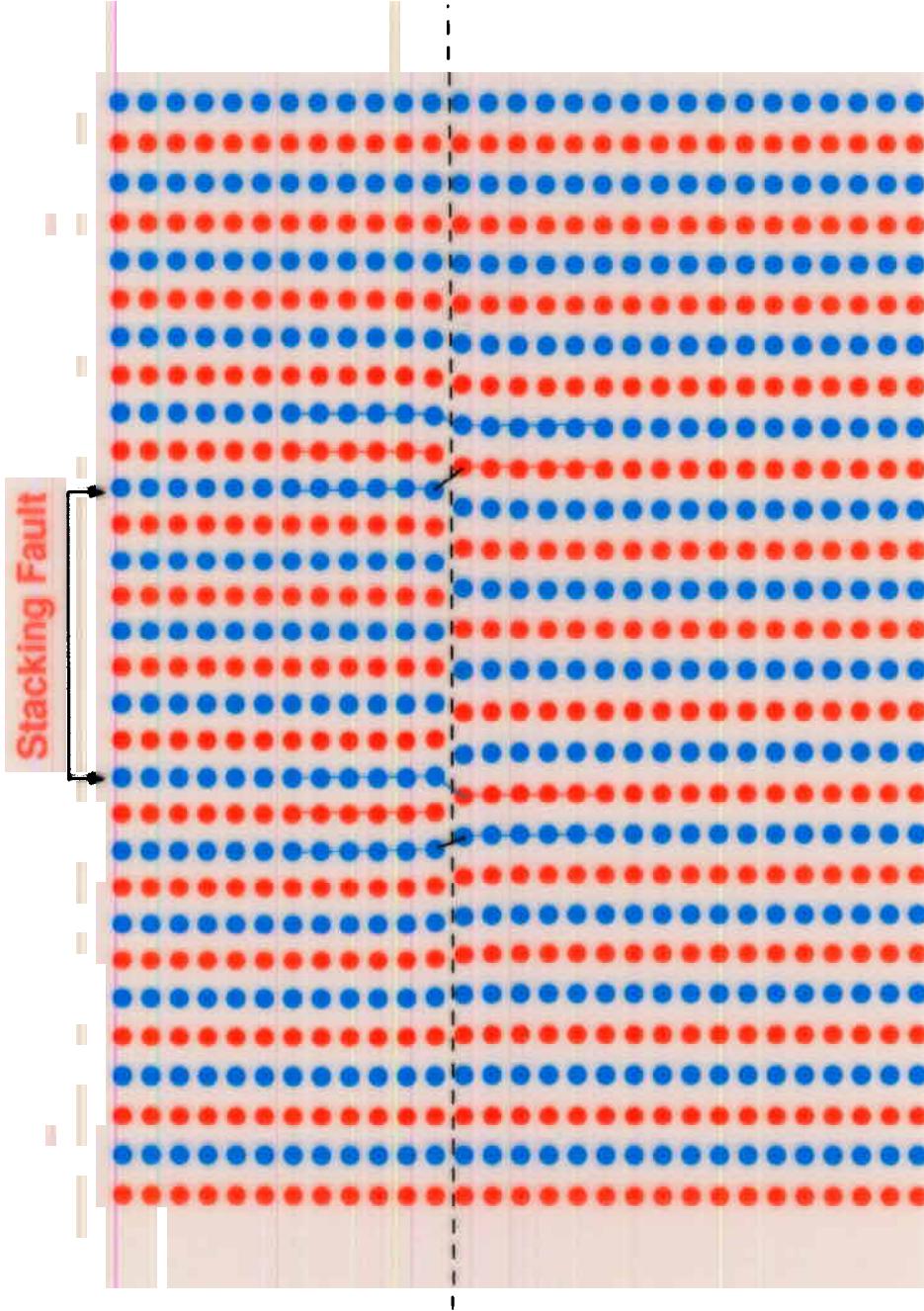


Intrinsic Stacking Fault (SF)

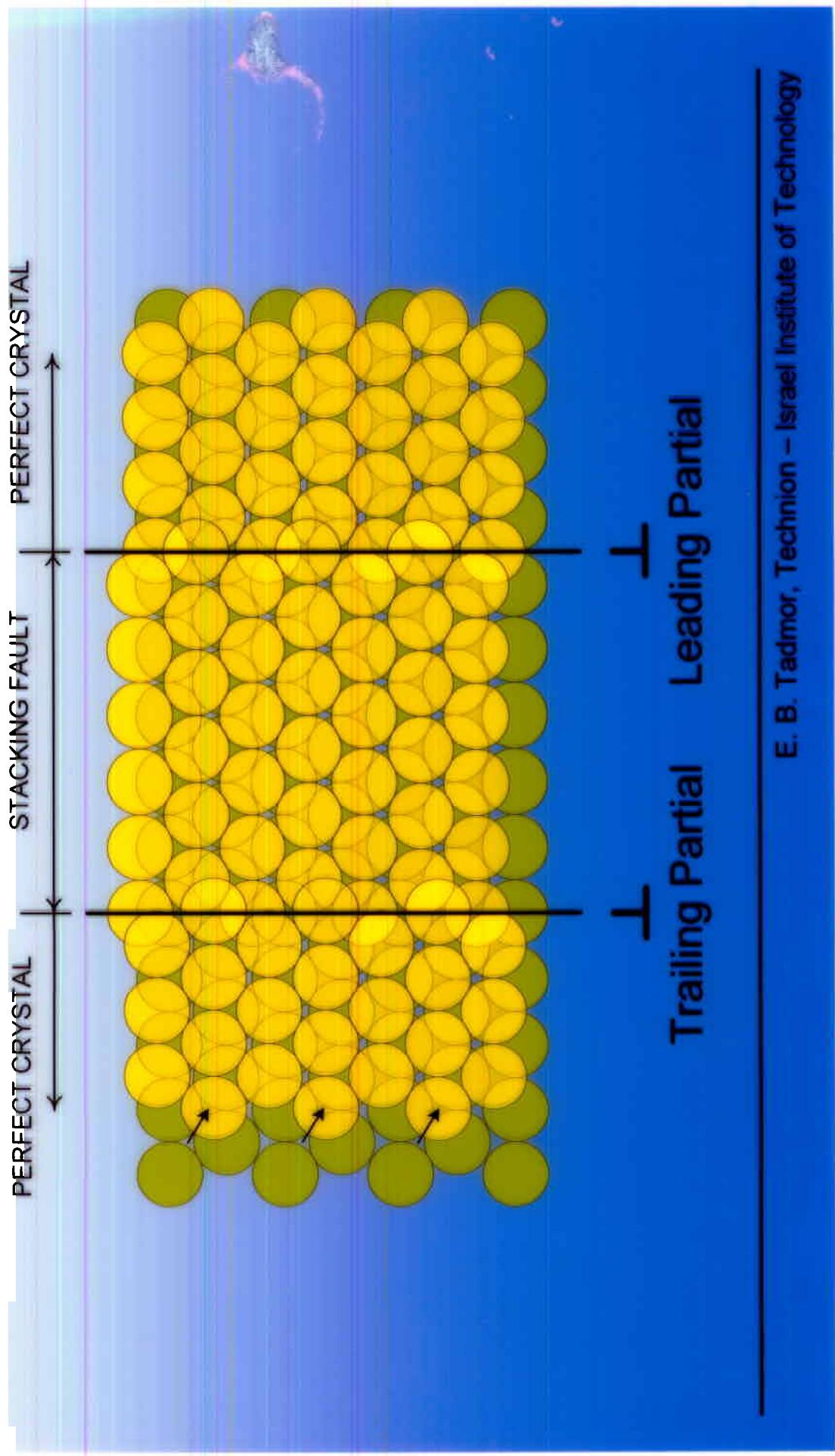




Partial dislocations & stacking fault



Formation of an Extended Dislocation



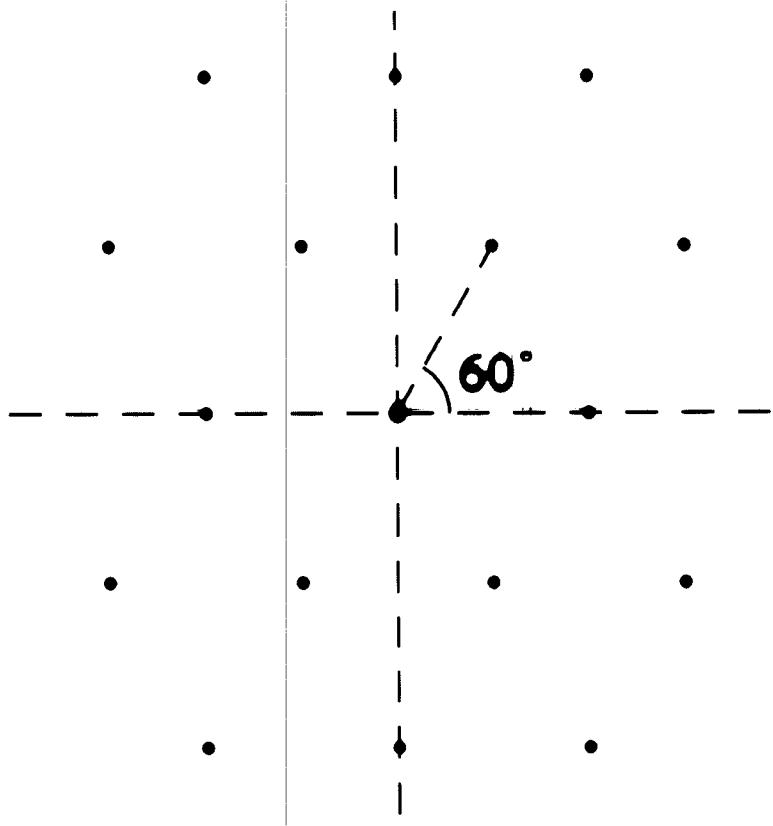
Two important themes

1. Geometry

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

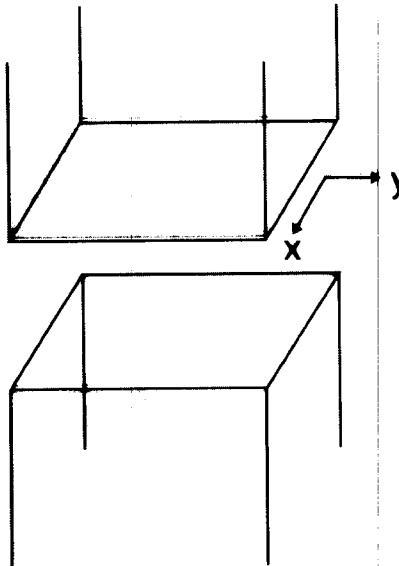
2. Physics

- (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

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

Observation: Γ has the symmetry of the lattice

$$\begin{aligned} G &= \text{point group of triangular lattice} \\ &= \{I, R_{60}, R_x, R_y, \dots\} \end{aligned}$$

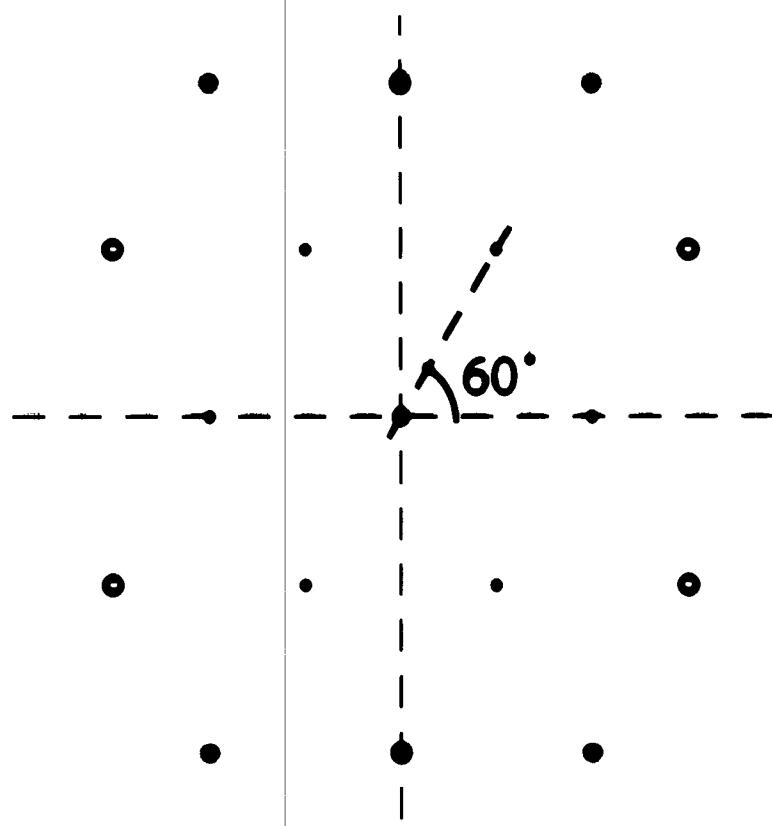
L^* = dual lattice (Fourier space)
= reciprocal lattice = triangular lattice

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

$\{O_K\}$ are invariant under G

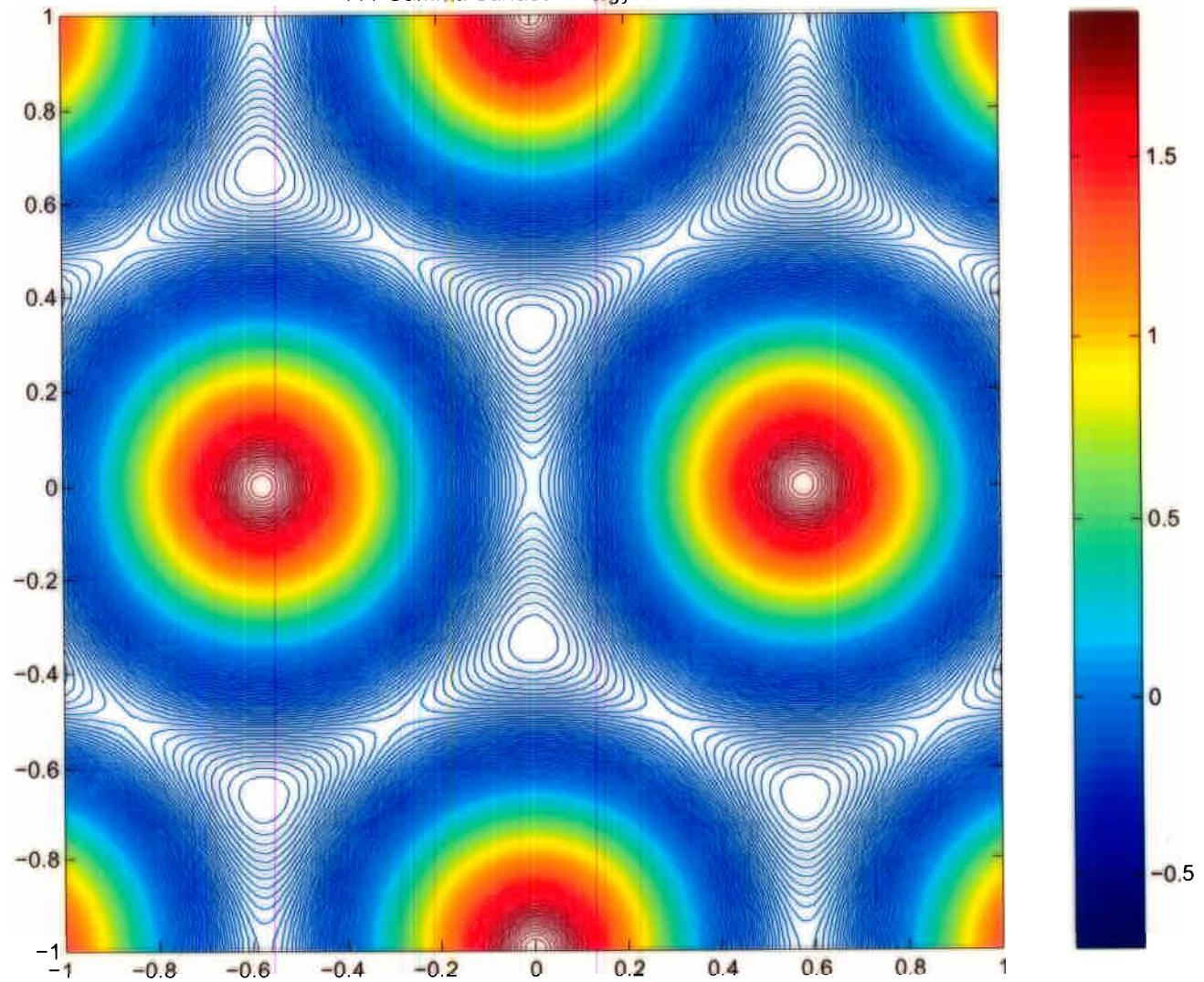
Leading order truncations give good approximation to Γ .

Conclusion: Geometry "determines" Γ .

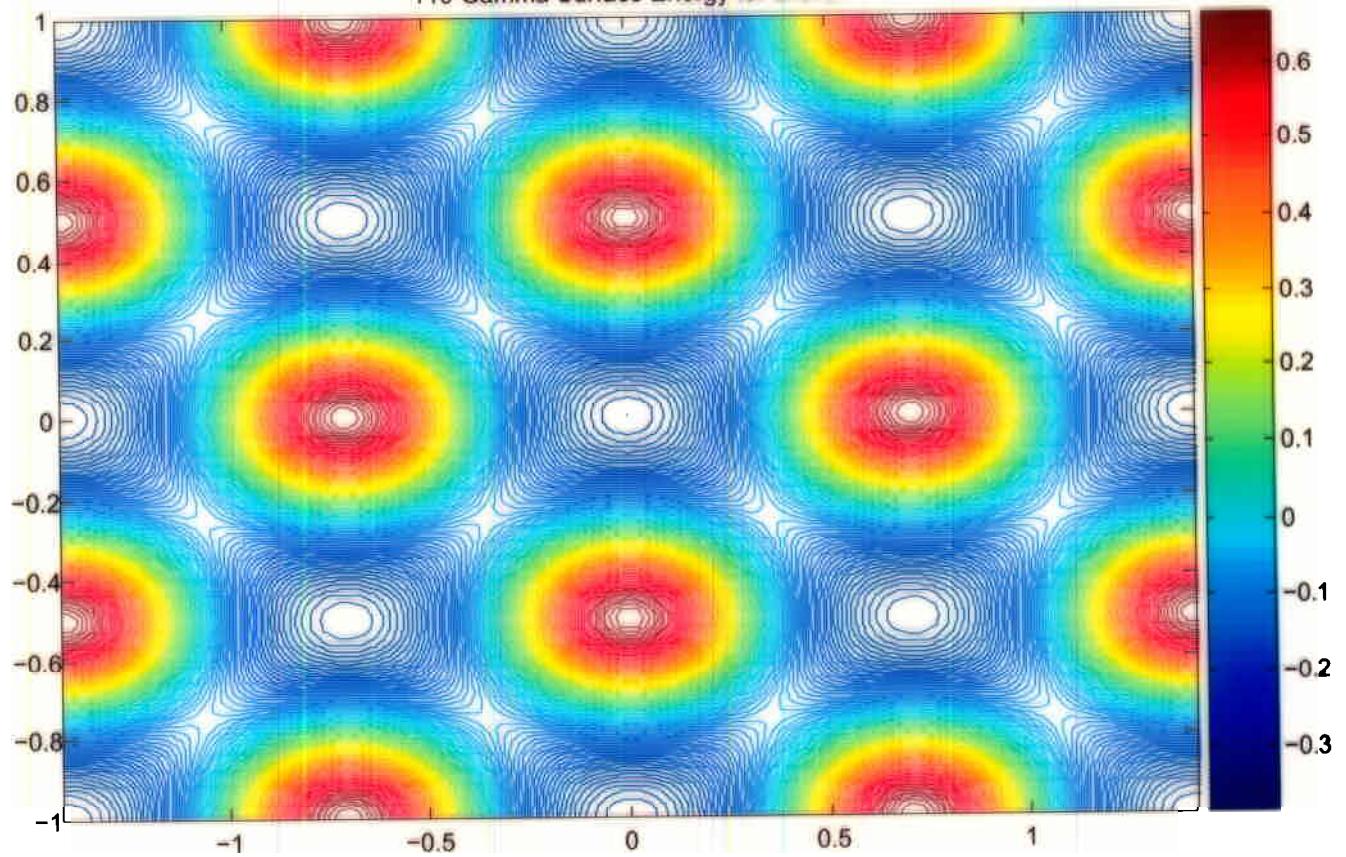


Lattice L

111 Gamma Surface Energy for F.C.C.

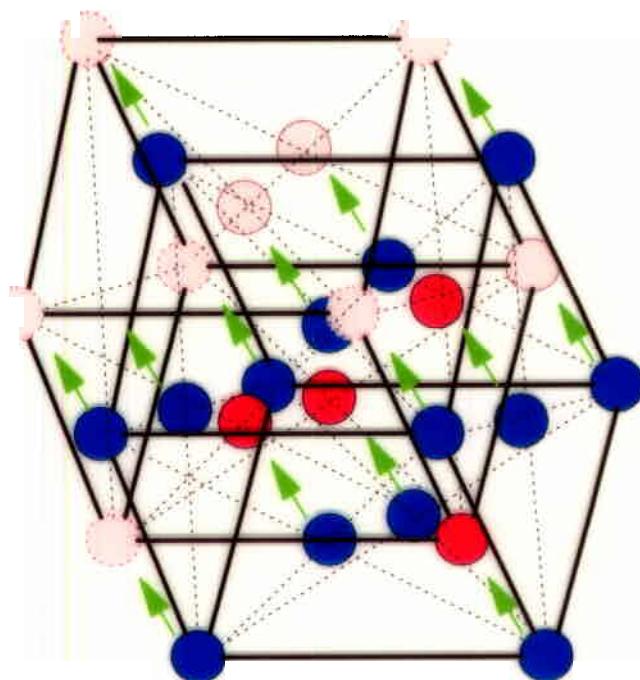
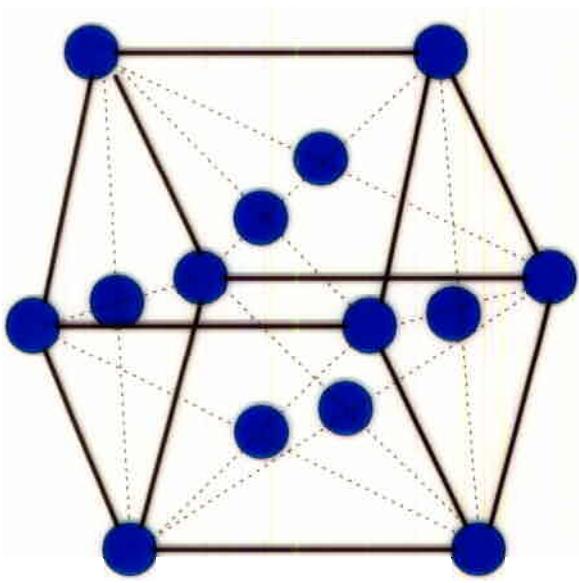
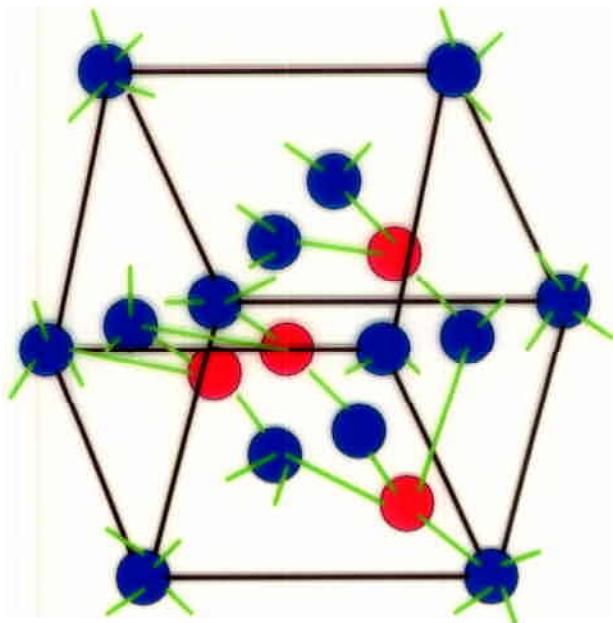
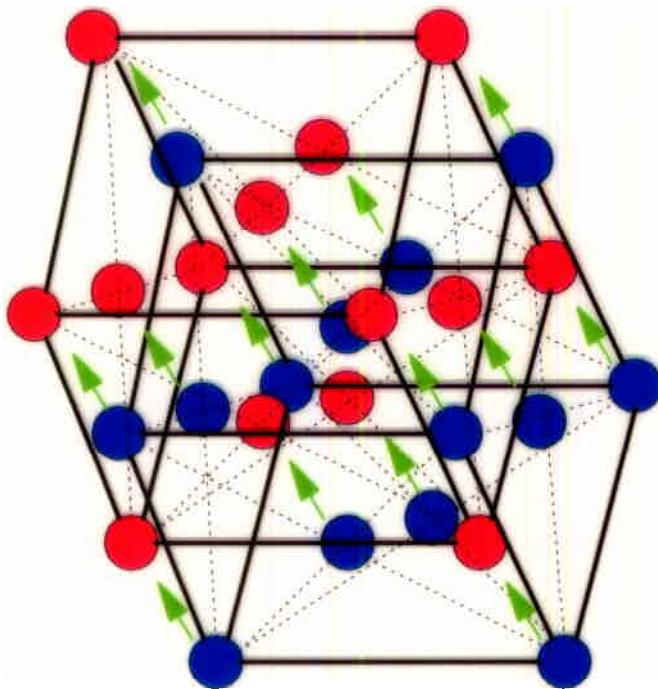


110 Gamma Surface Energy for B.C.C.



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**



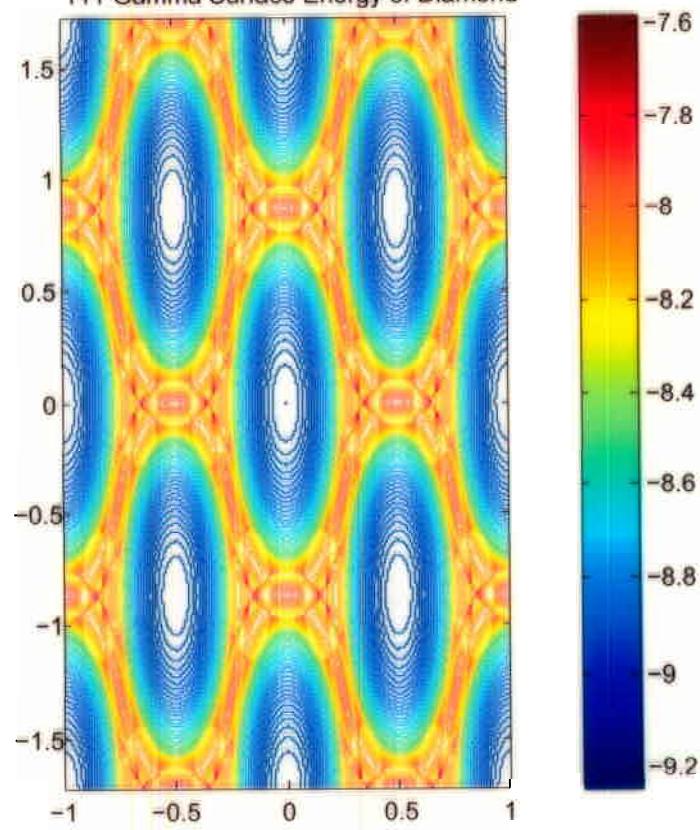
Diamond lattice

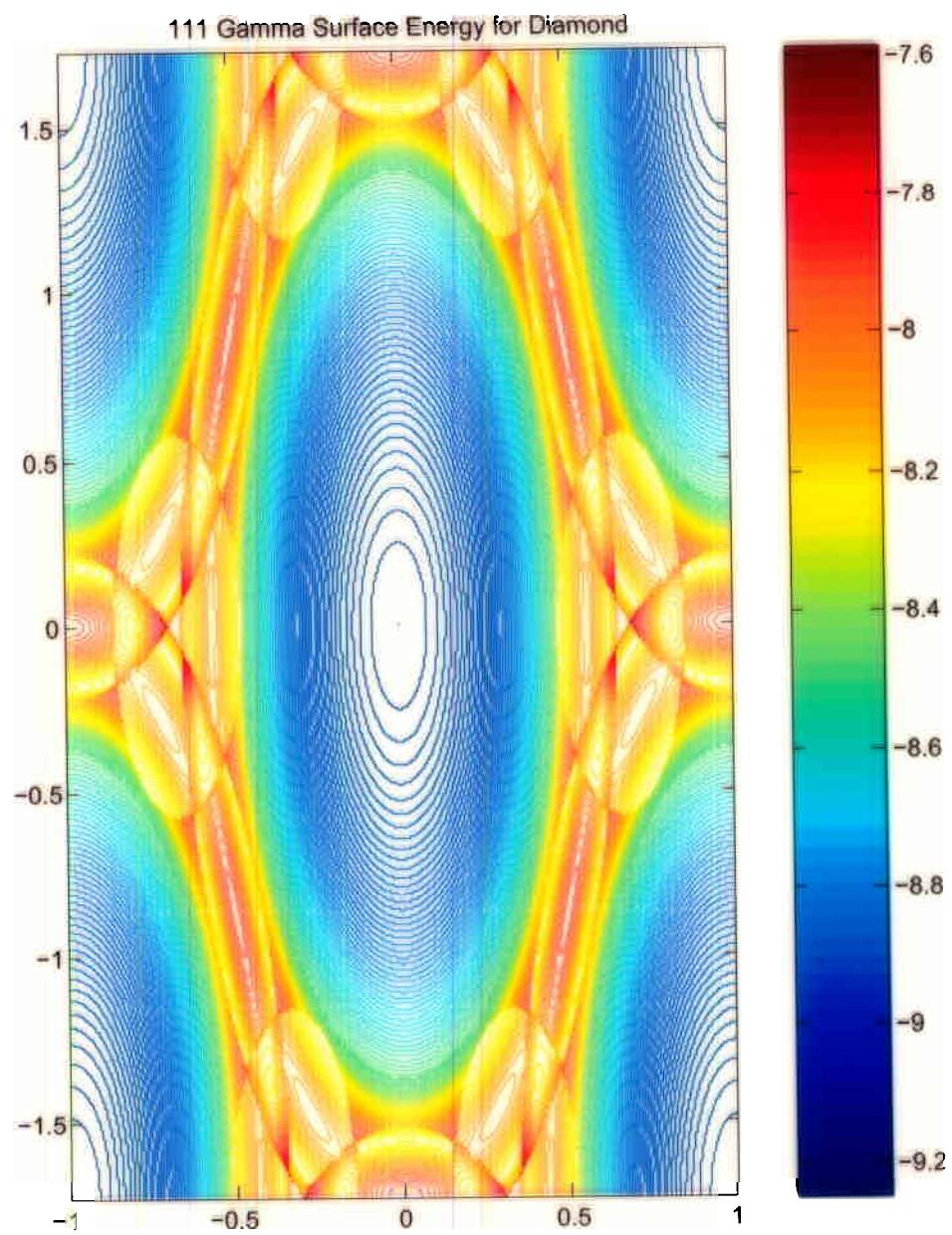
$\Gamma(x, y)$ nearly singular

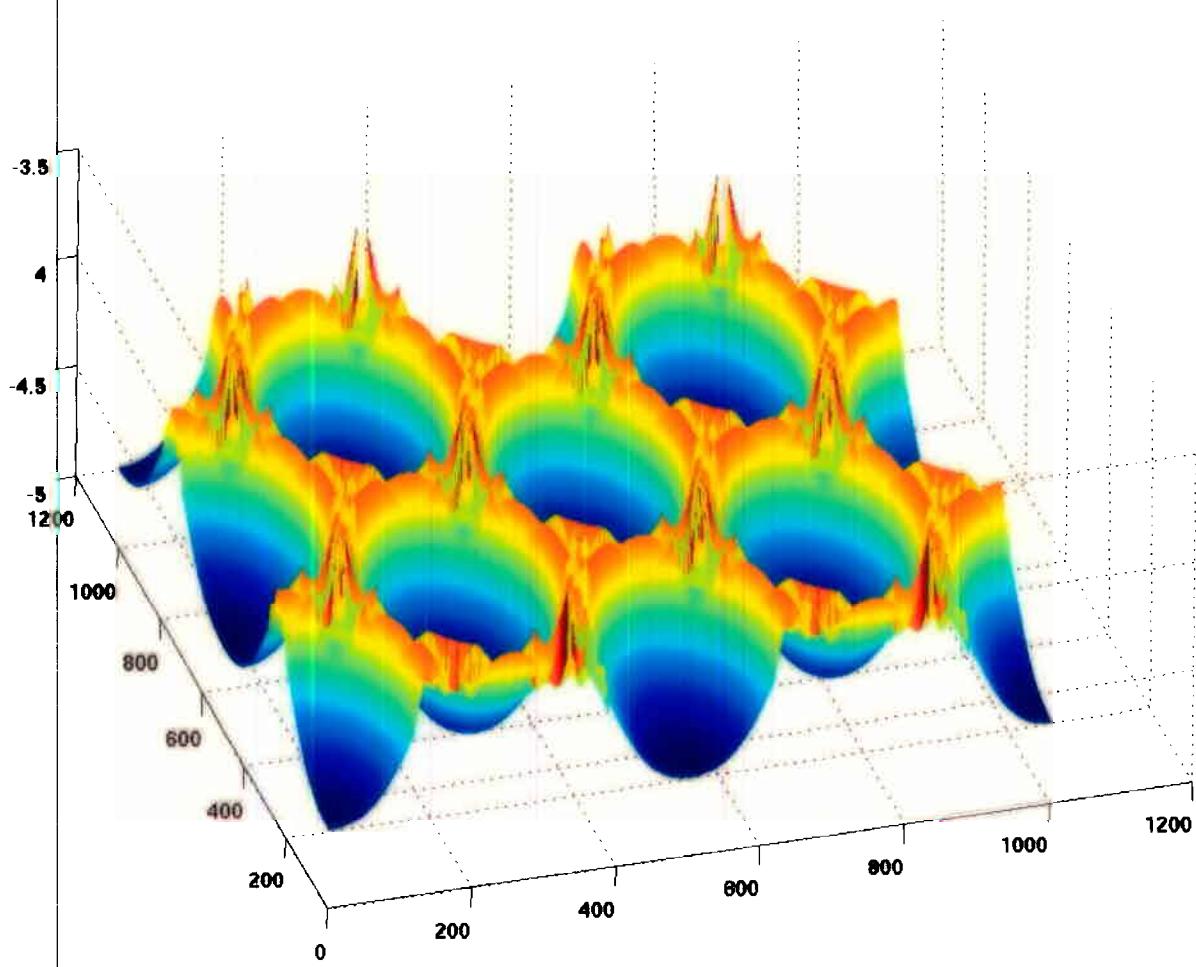
Geomtry tells little.

Physics (details of the atomic interaction) is important!

111 Gamma Surface Energy of Diamond

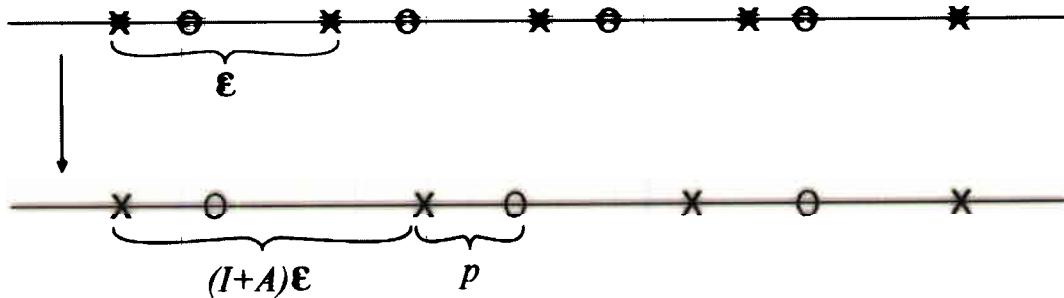






Nonlinear elastic regime (E and Ming)

Cauchy-Born rule



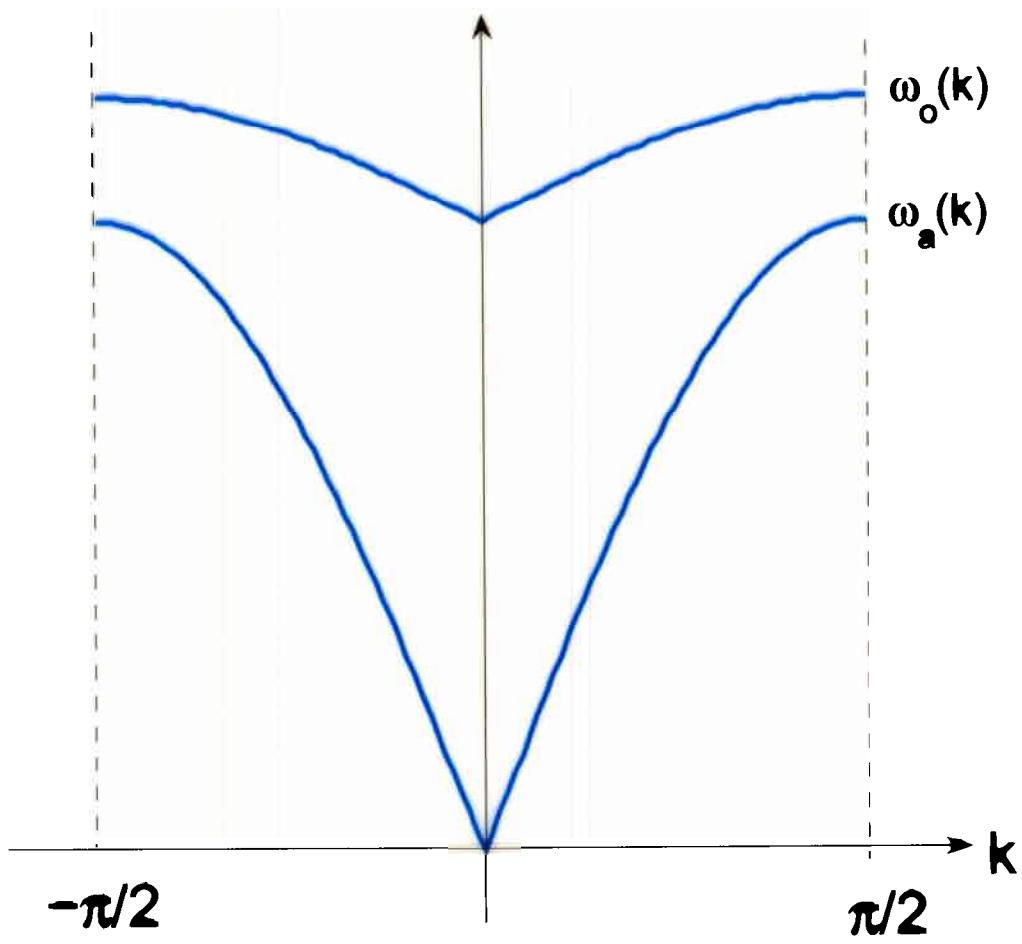
$W(A, p)$ = energy of unit cell in the deformed,
(by A), and displaced (by p)
configuration.

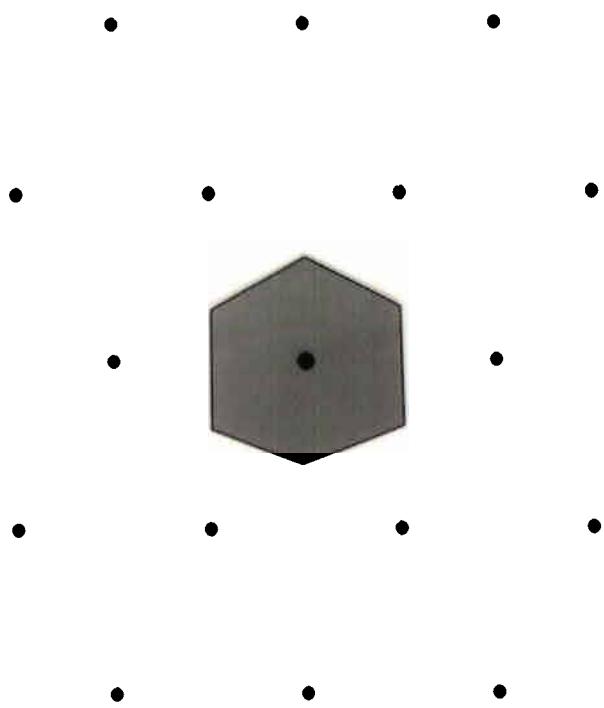
$$W_{CB}(A) = \min_p W(A, p)$$

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

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

$$y_j = x_j + v_j$$





Assumption A:

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

Assumption B: "phonons"

$$\begin{aligned} \omega_a(k) &\geq \Lambda_1 |k| \\ \omega_0(k) &\geq \frac{\Lambda_2}{\varepsilon} \end{aligned}$$

$k \in$ 1st Brillouin zone

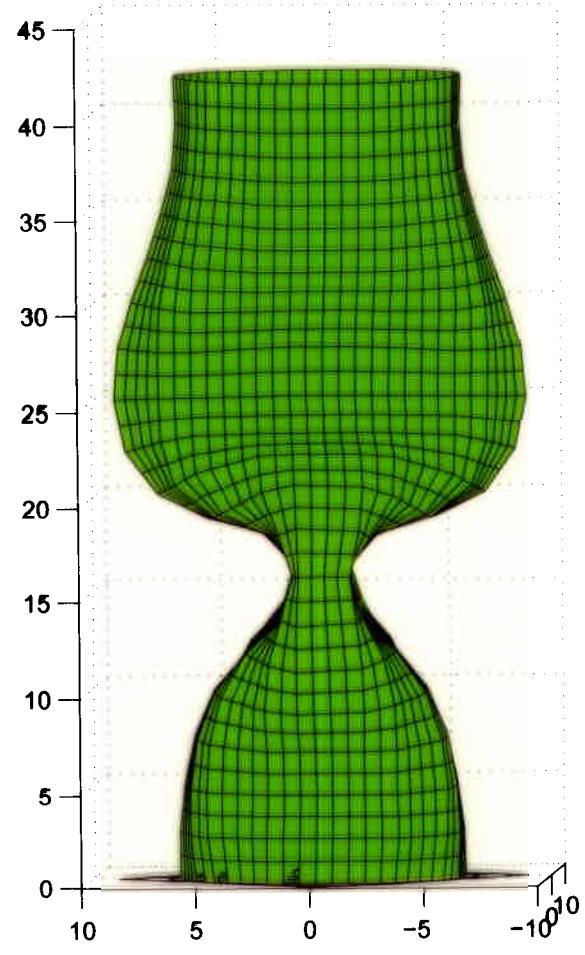
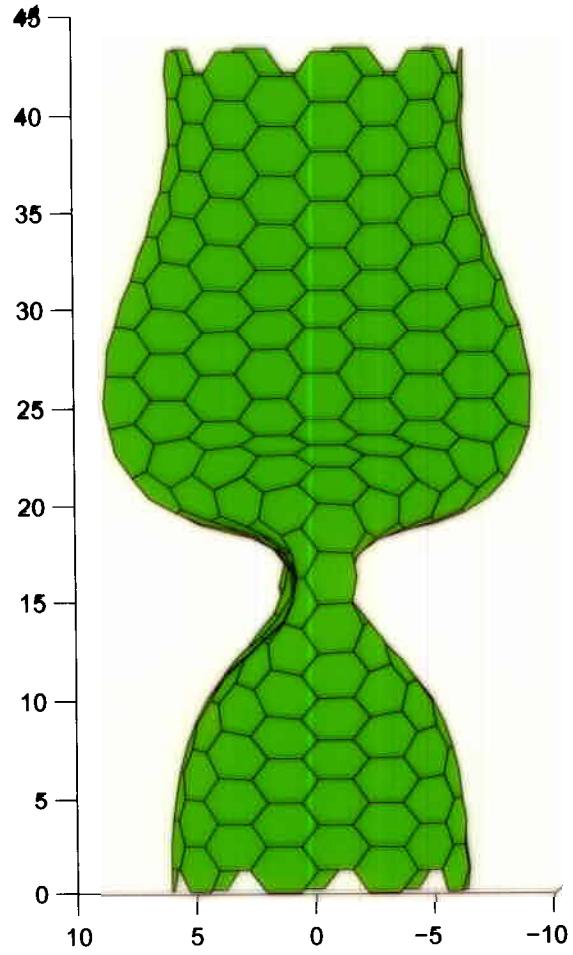
Theorem: ($p \geq d = \text{dimension}$) $\exists K, R$ such that if $\|f\|_{L^p} \leq K$, then \exists unique solution of $(*)$, $v = u_{CB}$, such that

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

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

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

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



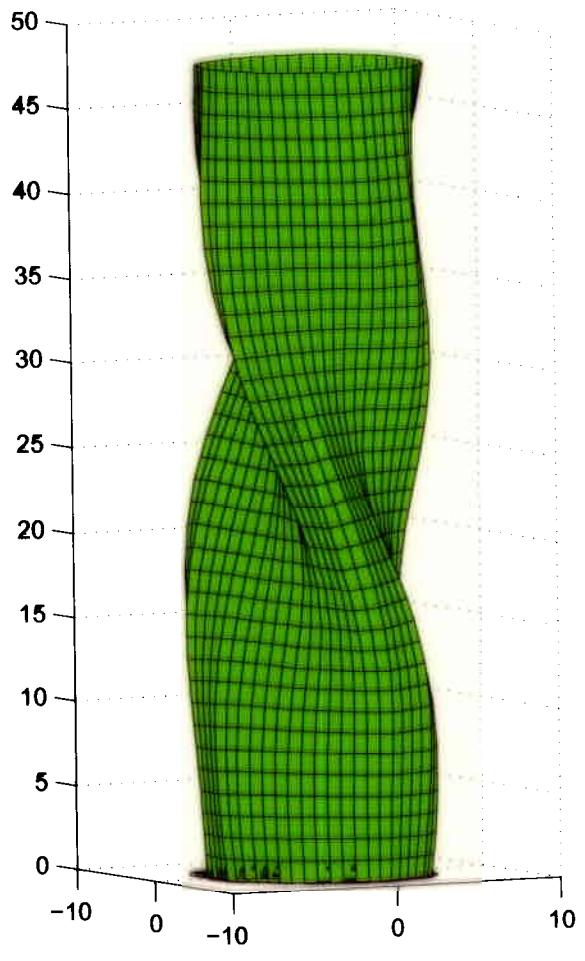
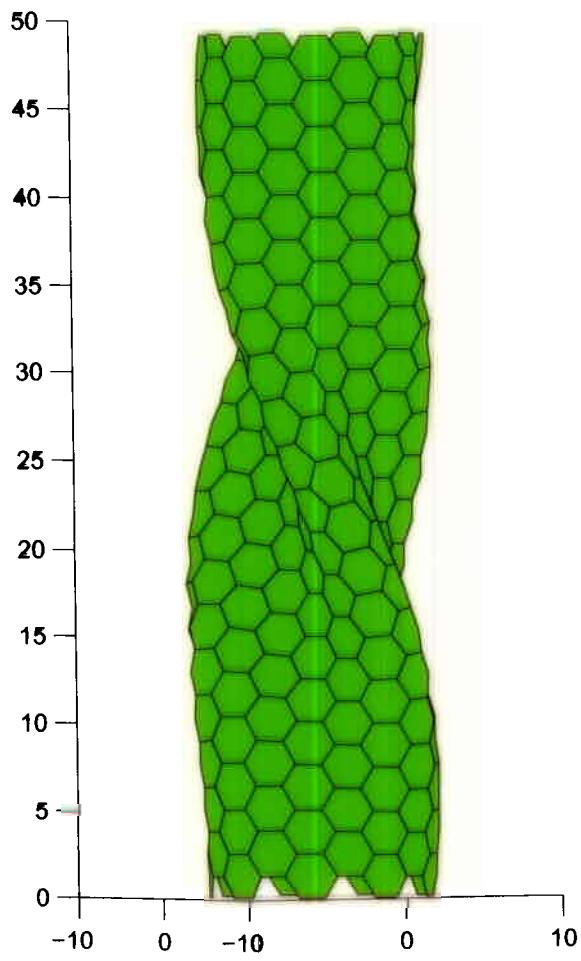
Remarks

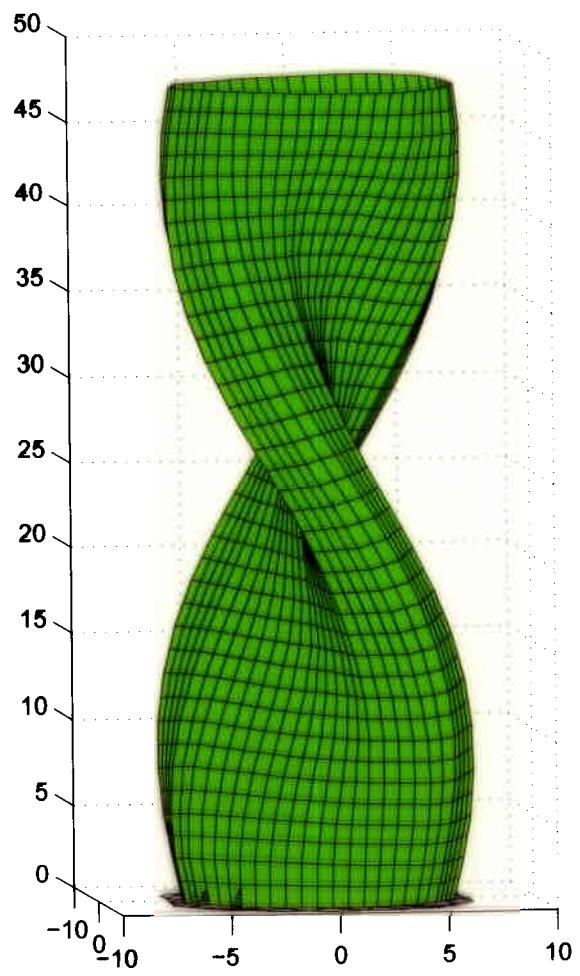
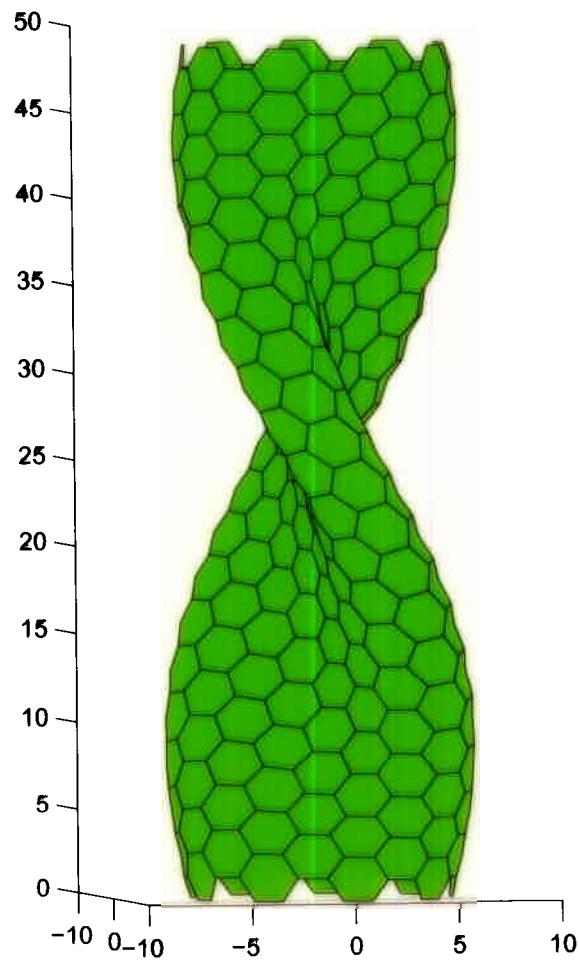
1. Result is sharp
Classification of instability, if $\|f\|_{L^P} > K$
Defect formation.
2. Result can be extended to dynamic problems.
3. Previous work of Blanc, LeBris and P.L. Lions. Assume $y_j = x_j + u(x_j)$, u is smooth, and study limit of V .

Example: Lennard-Jones potential, next nearest neighbor interaction

Case 1. Triangular lattice

Case 2. Square lattice





Summary

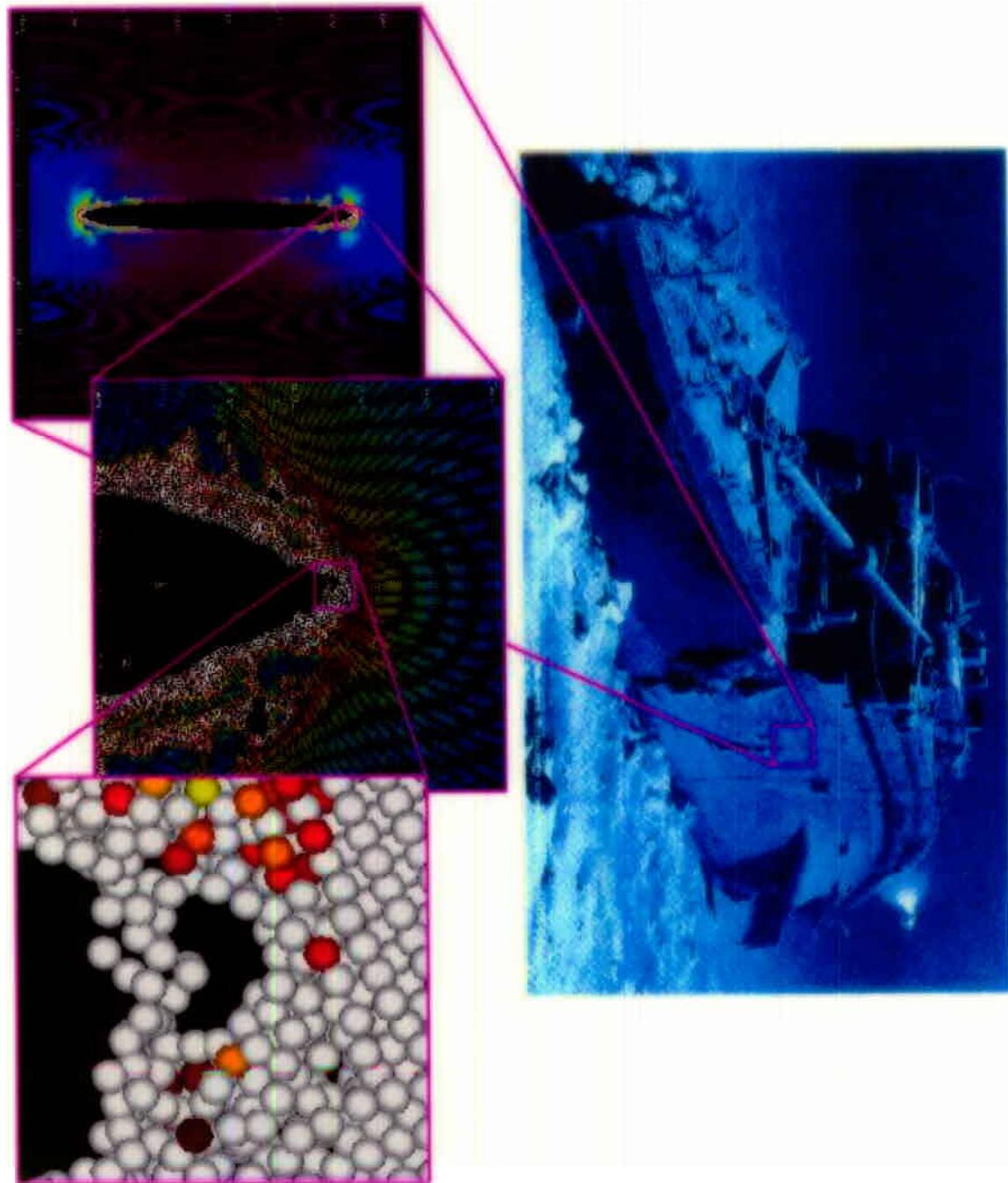
- 1. Atomistically-based mathematical theory of solids is both important and possible.**
- 2. Geometry and physics themes helpful.**

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

Atomic scale: Atoms, electrons
 → crystal lattice
 → lattice defects

Macroscopic: randomly packed grains

Hierarchy of structures



WebElements: the periodic table on the world-wide web

<http://www.webelements.com/>

1 hydrogen H 1.0079	2 helium He 4.0026	3 lithium Li 6.941	4 beryllium Be 9.0122	5 boron B 10.811	6 carbon C 12.011	7 nitrogen N 14.007	8 oxygen O 15.999	9 fluorine F 18.998	10 neon Ne 20.199
11 magnesium Mg 24.306	12 aluminum Al 26.982	13 silicon Si 28.086	14 phosphorus P 30.974	15 sulfur S 32.066	16 chlorine Cl 35.453	17 bromine Br 36.976	18 iodine I 79.904	19 bismuth Kr 83.80	20 polonium Xe 131.26
21 scandium Sc 44.956	22 titanium Ti 47.867	23 vanadium V 50.942	24 chromium Cr 51.986	25 manganese Mn 54.938	26 iron Fe 55.845	27 cobalt Co 58.933	28 nickel Ni 58.693	29 zinc Zn 65.39	30 copper Cu 63.546
31 tantalum Ta 101.961	32 niobium Nb 92.906	33 molybdenum Mo 95.94	34 technetium Tc 97.907	35 ruthenium Ru 98.907	36 rhodium Rh 101.07	37 osmium Os 102.91	38 iridium Ir 103.92	39 platinum Pt 103.42	40 gold Au 106.42
41 zirconium Zr 91.224	42 niobium Nb 92.906	43 manganese Mn 95.94	44 technetium Tc 97.907	45 ruthenium Ru 98.907	46 rhodium Rh 101.07	47 osmium Os 102.91	48 iridium Ir 103.92	49 platinum Pt 103.42	50 gold Au 106.42
51 ruthenium Ru 101.961	52 osmium Os 102.907	53 iridium Ir 103.907	54 technetium Tc 97.907	55 ruthenium Ru 98.907	56 osmium Os 102.907	57 iridium Ir 103.907	58 technetium Tc 97.907	59 ruthenium Ru 98.907	60 osmium Os 102.907
59 rhodium Rh 102.907	60 osmium Os 102.907	61 iridium Ir 103.907	62 technetium Tc 97.907	63 ruthenium Ru 98.907	64 osmium Os 102.907	65 iridium Ir 103.907	66 technetium Tc 97.907	67 osmium Os 102.907	68 iridium Ir 103.907
69 rhodium Rh 102.907	70 osmium Os 102.907	71 iridium Ir 103.907	72 technetium Tc 97.907	73 ruthenium Ru 98.907	74 osmium Os 102.907	75 iridium Ir 103.907	76 technetium Tc 97.907	77 ruthenium Ru 98.907	78 osmium Os 102.907
77 rhodium Rh 102.907	78 osmium Os 102.907	79 iridium Ir 103.907	80 technetium Tc 97.907	81 ruthenium Ru 98.907	82 osmium Os 102.907	83 iridium Ir 103.907	84 technetium Tc 97.907	85 ruthenium Ru 98.907	86 osmium Os 102.907
85 rhodium Rh 102.907	86 osmium Os 102.907	87 iridium Ir 103.907	88 technetium Tc 97.907	89 ruthenium Ru 98.907	90 osmium Os 102.907	91 iridium Ir 103.907	92 technetium Tc 97.907	93 ruthenium Ru 98.907	94 osmium Os 102.907
95 rhodium Rh 102.907	96 osmium Os 102.907	97 iridium Ir 103.907	98 technetium Tc 97.907	99 ruthenium Ru 98.907	100 osmium Os 102.907	101 iridium Ir 103.907	102 technetium Tc 97.907	103 ruthenium Ru 98.907	104 osmium Os 102.907
105 rhodium Rh 102.907	106 osmium Os 102.907	107 iridium Ir 103.907	108 technetium Tc 97.907	109 ruthenium Ru 98.907	110 osmium Os 102.907	111 iridium Ir 103.907	112 technetium Tc 97.907	113 ruthenium Ru 98.907	114 osmium Os 102.907
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355 rhodium Rh 102.907	356 osmium Os 102.907	357 iridium Ir 103.907	358 technetium Tc 97.907	359 ruthenium Ru 98.907	360 osmium Os 102.907	361 iridium Ir 103.907	362 technetium Tc 97.907	363 ruthenium <	