Chair of Condensed Matter Physics
Institute of Theoretical Physics
Faculty of Physics, Universityof Warsaw

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Lecture

Modeling of Nanostructures and Materials

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Modeling of Nanostructures and Materials

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Lecture 9 – *April 25, 2013*

- **Basics of the alloy theory**
- **Continuum Methods in Materials Science**

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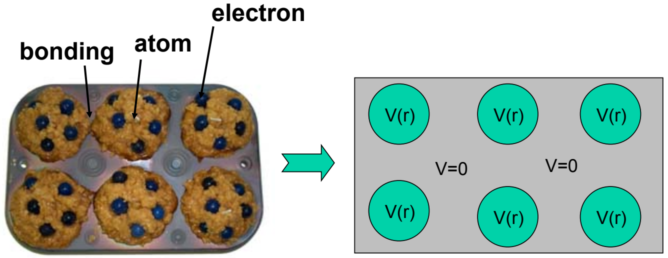
- ○ **Multiple Scattering Theory &**
- ○ **Basics of the alloy theory**

Muffin tin approaches (KKR & LMTO)

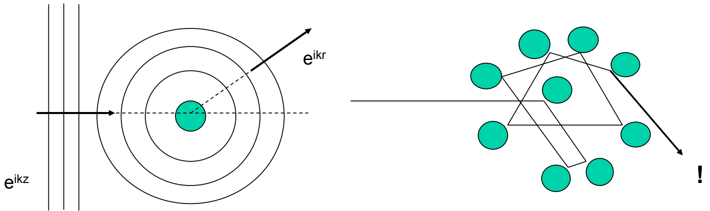


Every day life

Physical model

Multiple Scattering Theory (MST)

- ***Multiple scattering techniques*** determine electronic structure by accounting for the scattering events an electron wavefunction experiences within a solid.
- **This is tougher than it looks**
  - single scatterer, single scattering event – analytic solution
  - two or more scatterers, *infinite* number of possible scattering events, recursive solutions required for wavefunctions



Single site

Multiple sites

Short History of MST

Lord Rayleigh (1892) “*On the Influence of Obstacles in Rectangular Order upon the Properties of a Medium*” Phil Mag. – Laplace Equation

- N. Kasterin (1897) – extends MST to Helmholtz equation (*scattering of sound waves by collection of spheres*)
- Korringa (Physica, 1947) – first use to find electronic states in solids (computational facilities however not up to the task)

Kohn and Rostoker

– rediscover in 1950’s (Phys. Rev.)

- This leads to the Korringa Kohn Rostoker approach (KKR)
- 1960’s – **first serious calculations using the approach – computers begin to catch up with the theory!**

Archives (http://www.aip.org/history/esva)

Multiple Scattering Theory – Basic Equation

$$\boxed{\left[H_o + V\right]\psi(\vec{r}) = E\psi(\vec{r})}$$

-**H$_o$** is the free space Hamiltonian
-**V** is the perturbing potential
−Y is the electron wavefunction

$$\boxed{\psi(\vec{r}) = \chi(\vec{r}) + \int G_o(\vec{r},\vec{r}\,')V(\vec{r}\,')\psi(\vec{r}\,')d^3r'}$$

- We can express the wavefunction at some position as a sum of the free space wavefunction, χ, and contributions from the perturbing potential, ***V***, at different sites.
- In this case, G$_o$ is the free electron propagator and describes motion in regions where no scattering from the potential occurs.

Letting Green do the expansion

- In analogy to the previous wave function equation, we can do a similar expansion for the system ***Green function***.

$$\boxed{G = G_o + G_oVG}$$

- We can expand this equation out to infinity…

$$\boxed{G = G_o + G_oVG_o + G_oVG_oVG_o + G_oVG_oVG_oVG_o + \ldots}$$

- The total ***Green function*** acts as the system propagator.
- This expansion shows the infinite number of scattering events that can occur through potential interactions.
- Electron propagation in free space is described by G_o.

George Green's Mill
Nottingham, England

Introducing *T*-matrix

- We can rearrange the last equation to isolate the effects of the potential.

$$G = G_o + G_o\left(V + VG_oV + VG_oVG_oV + \ldots\right)G_o$$

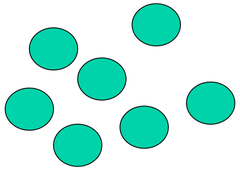
$$\boxed{G = G_o + G_oTG_o}$$

where

$$\boxed{T(V) = V + VG_oV + VG_oVG_oV + \ldots}$$

- The ***scattering matrix***, ***T***, completely describes scattering within the potential assembly.
  It contains all possible scattering paths.

Multiple Scattering Sites



- Assume the potential is made up of a sum of terms due to different cells or atoms. $V = \sum_i V^i$
- The ***T*** matrix in this case becomes:

$$T = T\left(\sum_i V^i\right) = \sum_i V^i + \sum_i V^i G_o \sum_j V^j + \ldots$$

- We can separate out the sequences where the scattering always involves the same cell or atom into the cell ***t*** matrix.

$$\boxed{t^i = V^i + V^iG_oV^i + V^iG_oV^iG_oV^i + \ldots}$$

Atomic *t*-matrix

- Solve the radial Schrodinger's equation for an isolated muffin tin potential and determine the regular and irregular solutions, Z and S.
- The atomic ***t*** matrix is diagonal in the angular momentum representation.

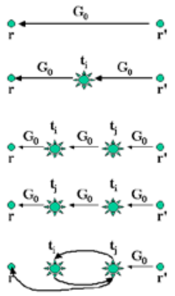
$$\boxed{t_l^{\alpha} = i\sin\delta_l e^{i\delta_l}}$$

- The phase shift, d, can be found from the atomic wavefunction.

All the possible paths …

- We can now write the T matrix in terms of the single site scattering matrices, t_i.

$$T\left(\sum_i V^i\right)=\sum_i t^i+\sum_i\sum_{j\neq i} t^i G_o t^j+\ldots$$



- This equation shows that the scattering matrix of an scattering assembly is made up of all possible scattering sequences.
- Each scattering sequence involves scattering at individual cells with free electron propagation in between.

$$T=\sum_{ij} T^{ij} \quad \text{where} \quad T^{ij}=t^i\delta_{ij}+t^i G_o\sum_{k\neq i} T^{kj}$$

Getting the Band Structure Together

- In the ***MT*** formalism, the $\boldsymbol{T}$ matrix becomes:

$$T^{ij}=t^i\delta_{ij}+t^i\sum_{k\neq i}\tilde{G}^{ik}T^{kj}$$

- There exists a matrix M such that $\boldsymbol{T^{ij}}$ are the elements of its inverse.
- The matrix $\boldsymbol{m}$ is just the inverse of the cell $\boldsymbol{t}$ matrix.

$$M^{ij}=m^i\delta_{ij}-\tilde{G}^{ij}\left(1-\delta_{ij}\right)$$

- *The inverse of the T matrix is cleanly separated into*
  - ***potential*** *scattering components, m^i, and*
  - ***structural*** *components, G^{ij}.*

Getting the Band Structure Together

- The poles of $\boldsymbol{M(E)}$ determine the ***eigenenergies*** for the system for a given $\boldsymbol{k}$ through the following equation:

$$\boldsymbol{det\left[m(E)-\tilde{G}\left(E,\vec{k}\right)\right]=0} \implies \boxed{\boldsymbol{\varepsilon(\vec{k})}}$$

- **This allows us to calculate the system band structure**.
- **Possibility to calculate non-periodic systems (clusters)**

Problem with the KKR method

- Linking interstitial region (V=0) with spherical regions with muffin tin potentials can be difficult
- Determinant used to find band structure is a non-linear function of energy (energy dependence carried in the site *t* matrices) – *this can not be reduced to a standard matrix eigenvalue problem*
- *The Solution* – ***Linearize the equation*** – LMTO approach (Andersen, PRB, 1975 – 1370 citations)

Present Applications the KKR method

- **Practically only first-principles method for very important class of materials, i.e., random alloys on the market**

  Other methods → supercells

- **Coherent Potential Approximation (CPA) relatively easily implemented**

- **Virtual Crystal Approximation (VCA)**
  - **Potential of a Random Binary Alloy A_xB_{1-x}**

    $$V(A_xB_{1-x}) = xV(A)+(1-x)V(B)$$

  ⇒ **Periodicity of the system restored**

Random Alloys

$$\langle G\rangle = G_0 + G_0\Sigma(G) = (G_0^{-1}-\Sigma)^{-1}$$

Self-energy

Configurationally averaged Green"s function

$$\langle G\rangle = G_0 + G_0\langle T\rangle G_0$$

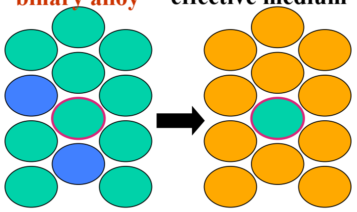
$$\boxed{\Sigma = \langle T\rangle(1+G_0\langle T\rangle)^{-1}}$$

Coherent Potential Approximation (CPA)

Best *single-site* solution for describing scattering in substitutional alloys

Atom in binary alloy

Atom in equivalent effective medium

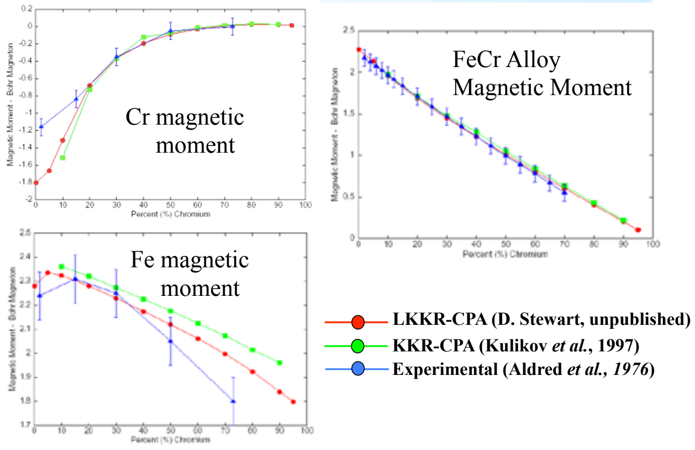


Scattering properties of alloy can be represented by an effective medium

How to determine effective medium ?

- Treat scattering by atom as an impurity in the effective medium.
- Introduction of atom should give no scattering in the correct effective medium (iterative solution).

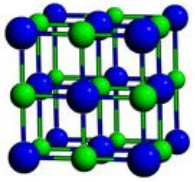
Application of KKR-CPA method- FeCr Alloys



Cluster expansion

Ortho-normal and complete set of basis functions are introduced.

s is the configuration variable (+/- 1 for binary systems)



Basis for M lattice sites is given as:

$$\Phi_{\alpha\nu}^{(M)}(\boldsymbol{\sigma}) = \Theta_{v_1}(\sigma_1)\Theta_{v_2}(\sigma_2)\cdots\Theta_{v_M}(\sigma_M).$$

Energy of the lattice (M sites) is given as:

$$E(\boldsymbol{\sigma}) = J_0 + \sum_{K=1}^{M}\sum_{\alpha_K}\sum_{\nu_K} J_{\alpha\nu}^{(K)}\Phi_{\alpha\nu}^{(K)}(\boldsymbol{\sigma}).$$

For all cluster sizes

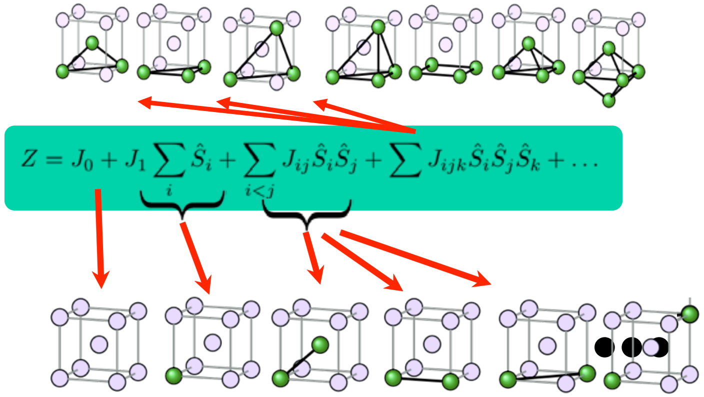
For all clusters with number of atoms =K

$$J_{\alpha\nu}^{(K)} = \langle E(\boldsymbol{\sigma}) | \Phi_{\alpha\nu}^{(K)}(\boldsymbol{\sigma}) \rangle$$

Average of energies of all configurations projected onto the basis function

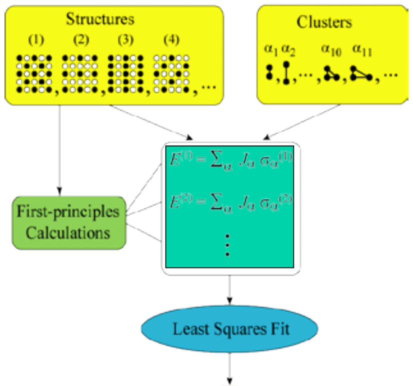
Cluster expansion

For binary system



$$Z = J_0 + J_1 \underbrace{\sum_i \hat{S}_i}_{} + \underbrace{\sum_{i<j} J_{ij}\hat{S}_i\hat{S}_j}_{} + \sum J_{ijk}\hat{S}_i\hat{S}_j\hat{S}_k + \ldots$$

Cluster expansion fit



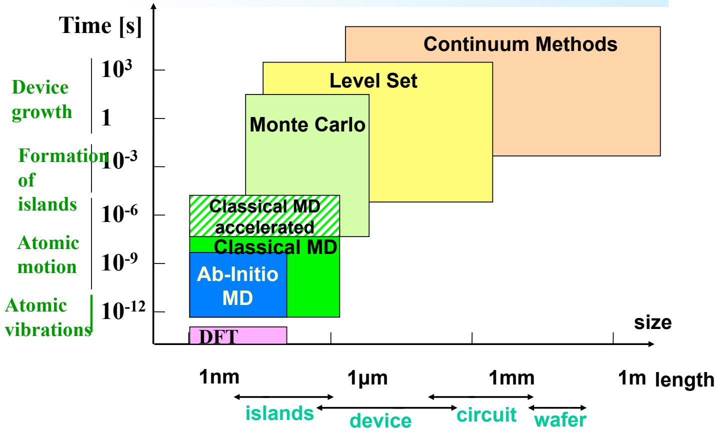
Connolly-Williams method, Phys Rev B, 1983

- **The cluster expansion is able to represent any function E(*s*) of configuration *s* by an appropriate selection of the values of J_a.**
- **Converges rapidly using relatively compact structures (e.g. short-range pairs or small triplets).**
- **Unknown parameters of the cluster expansion is determined by fitting first-principles energies as shown.**

Continuum Methods in Materials Science

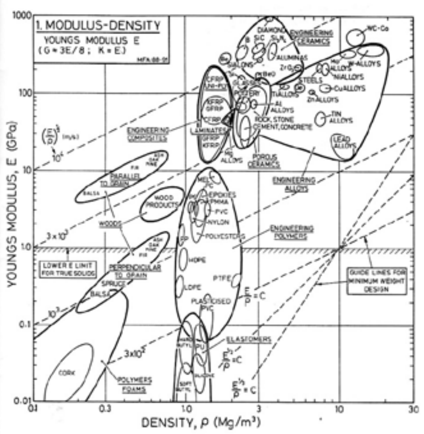
- ❖ Hierarchy of theoretical approaches
- ❖ Continuum models of carbon nanotubes composites
- ❖ Continuum Field Description of Crack Propagation
- ❖ Continuum models of crystal growth

Hierarchy of Theoretical Approaches



Elasticity of composite materials

The Young’s Moduli of Engineering Materials



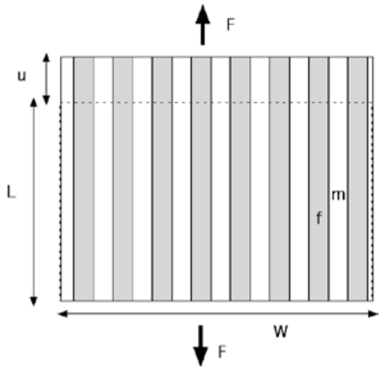
The different classes of material tend to cluster:

Metals have relatively high moduli and high densities.

Polymers have low moduli and densities.

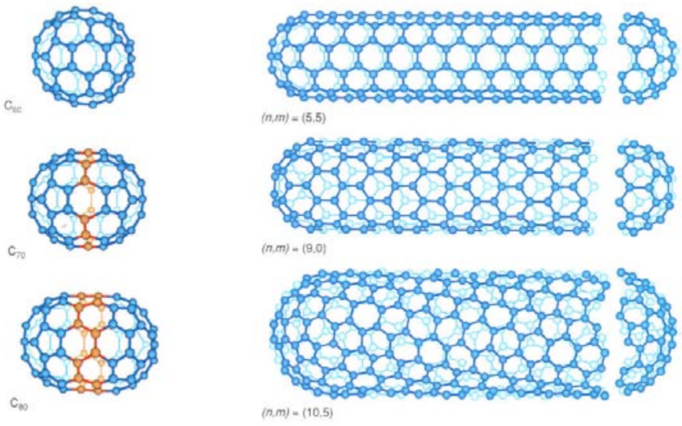
Elastic moduli of composites, anisotropic materials

CFRP – carbon fiber reinforced polymers



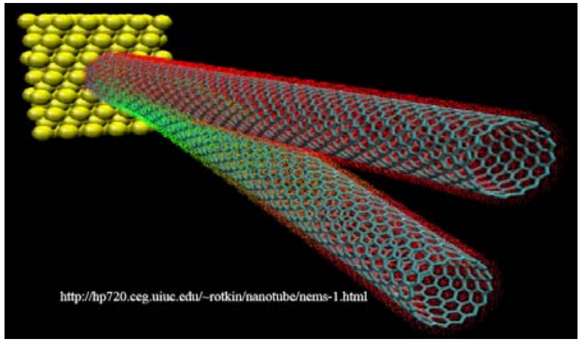
What happens if the composite is loaded by force F ?

Carbon nanotubes (CNTs)



S. Iijima, Nature ***354****, 56 (1991)*

CNTs – Mechanical Properties

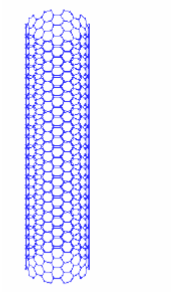


Mechanical strength – graphite-like strong bonds
-- no dangling bonds
-- no weakly bound sheets

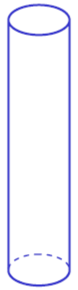
CNTs – Mechanical Applications

- **very high Young's modulus** ~ 10^{12} N/m^2 (5 times the value for steel)
  - deformations (bending, squeezing) are elastic, i.e., they disappear when the load is removed
- new composite materials with high strength and elasticity
- **futuristic applications???**
  - earthquake-resistant buildings;
  - cars which come to its undamaged form after a crash

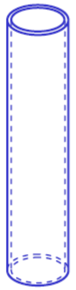
Continuum Models of Carbon Nanotube-Based Composites



Discrete (MD) model



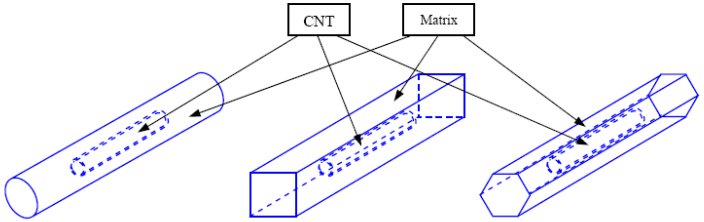
Continuum *shell* model



Continuum *solid* model

Continuum Models of Carbon Nanotube-Based Composites

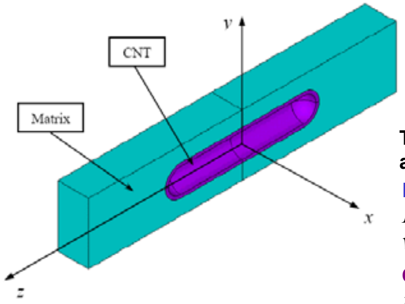
Three possible representative volume elements (RVE) for the analysis of *CNT-based nanocomposites*



Circular (Cylindrical) RVE **Square RVE** **Hexagonal RVE**

Continuum Models of Carbon Nanotube-Based Composites

A short single-walled carbon nanotube (CNT) embedded in a matrix material



Matrix:
height = width = 10 nm,
length = 100 nm;

CNT: outer radius = 5 nm,
inner radius = 4.6 nm,
length = 50 nm

The Young's moduli and Poisson's ratios:

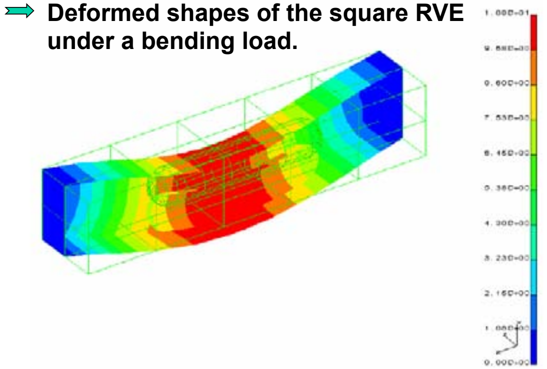
Matrix:
E_M = 100nN/nm^2 (=100GPa)
ν_M = 0. 3

CNT:
E_{CNT} = 1000nN/nm^2 (=1000GPa)
ν_{CNT} = 0. 3

Continuum Models of Carbon Nanotube-Based Composites

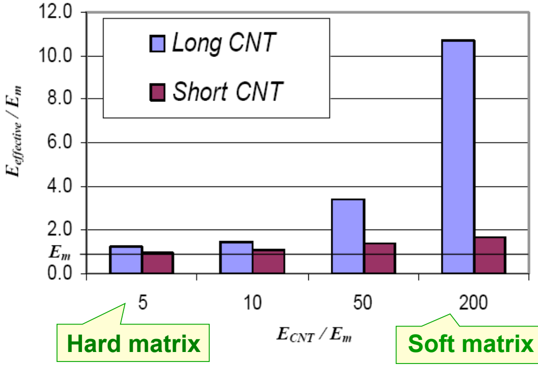
- **Simulations of CNT-based composites using the continuum mechanics approach**

⇒ **Deformed shapes of the square RVE under a bending load.**



Continuum Models of Carbon Nanotube-Based Composites

Effective Young's moduli in the CNT direction for CNT-based Composites with various matrices



CNT modulus 1000 GPa

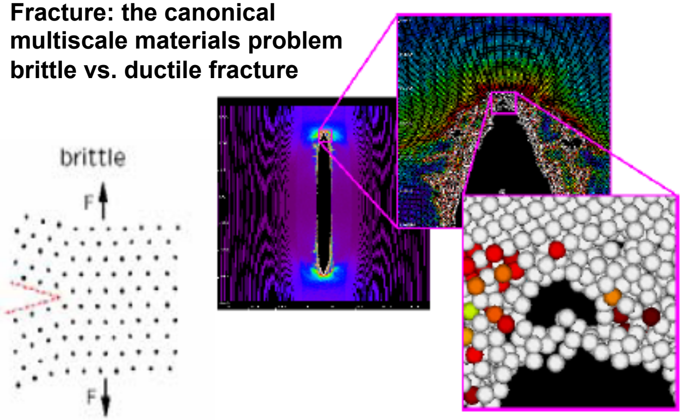
volume fraction = 0.05 **(long)**

volume fraction = 0.02 **(short)**

Crack spreading

Multiscale Simulations of Fracture

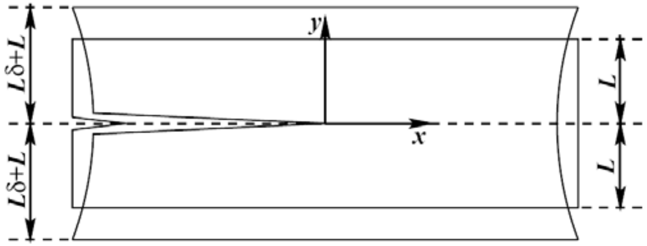
Fracture: the canonical multiscale materials problem brittle vs. ductile fracture



Continuum Field Description of Crack Propagation

I. S. Aranson et al., Phys. Rev. Lett. **85**, 118 (2000)

Schematic representation of fixed-grips loading



The two-dimensional geometry focusing on the so-called type-I crack mode

Continuum Field Description of Crack Propagation

- ***Model of the crack propagation*** - is a set of the elastodynamic equations coupled to the equation for the ***order parameter*** ρ

  ρ is related to the relative concentration of point defects in the amorphous material (e.g., microvoids) and characterizes ***local order***
- We define **ρ = 1 *outside*** the crack (no defects) and **ρ = 0 *inside*** the crack (all the atomic bonds are broken).
- At the crack surface ρ varies from 0 to1 on the scale much larger than the interatomic distance, justifying the continuum description of the crack.
- Material fails to support tensile stress and breaks when ρ becomes below critical value ρ_c.

Continuum Field Description of Crack Propagation

Equations of motion for an elastic medium

the density of material

accounts for viscous damping, η is the viscosity coefficient

$$\boxed{\rho_0\ddot{u}_i = \overbrace{\eta\Delta\dot{u}_i} + \frac{\partial\sigma_{ij}}{\partial x_j}, \qquad j = 1, 2.}$$

u_i - the components of displacements

σ_{ij} -- ***the stress tensor*** is related to deformations

$$\sigma_{ij} = \frac{E}{1+\sigma}\left(u_{ij} + \frac{\sigma}{1-\sigma}u_{ll}\delta_{ij}\right) + \nu\dot{\rho}\delta_{ij}$$

Continuum Field Description of Crack Propagation

The stress tensor

$$\sigma_{ij} = \frac{E}{1+\sigma}\left(u_{ij} + \frac{\sigma}{1-\sigma}u_{ll}\delta_{ij}\right) + \nu\dot{\rho}\delta_{ij}$$

trace of the elastic strain tensor

- u_{ij} -- the elastic strain tensor
- E -- the Young's modulus
- σ -- the Poisson's ratio
- To take into account the effect of weakening of material with the decrease of ρ one assumes dependence of E upon ρ, $E = E_0\rho$
- $\nu\dot{\rho}\delta_{ij}$ -- accounts for the hydrostatic pressure created due to generation of new defects; ν is a constant

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Continuum Field Description of Crack Propagation

Equations of motion for order parameter

- We assume that the order parameter ρ is governed by pure dissipative dynamics which can be derived from the "free-energy" type functional F
- Following Landau ideas on phase transitions, we adapt the simplest form for the free energy

$$F \propto \int dxdy\,[D|\nabla\rho|^2 + \varphi(\rho)]$$

"local potential energy" φ has minima at $\rho = 0$ and $\rho = 1$.

Polynomial form for *$\varphi(\rho)$*

Continuum Field Description of Crack Propagation

Equations of motion for order parameter

$$\dot{\rho} = D\Delta\rho - a\rho(1-\rho)F(\rho, u_{ll}) + f(\rho)\frac{\partial\rho}{\partial x_l}\dot{u}_l$$

Coupling of the order parameter to the displacement field enters through the position of the unstable fixed point defined by the function $F(\rho, u_{ll})$

Coupling of the order parameter to the velocity. It is responsible for the localized shrinkage of the crack due to material motion.

This term is crucial to maintain the sharp form of the crack tip.

Continuum Field Description of Crack Propagation

Constrains imposed on function F

- The constraint imposed on $F(\rho, u_{ll})$ is that it must have one zero in interval $1 > \rho > 0$
- $F(\rho_c, u_{ll}) = 0 \qquad 1 > \rho_c > 0$
- $\partial_\rho F(\rho, u_{ll})\big|_{\rho=\rho_c} < 0$
- The simplest form of F satisfying this constraint is

$$\boxed{F(\rho, u_{ll}) = 1 - (b - \mu u_{ll})\rho}$$

Material constants related to such properties as crack toughness and strain to failure

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Continuum Field Description of Crack Propagation

Constrains imposed on function f

- The specific form of this function is irrelevant
- One takes $\boxed{f(\rho) = c\rho(1-\rho)}$

a dimensionless material constant

to ensure that f vanishes at $\rho = 0$ and $\rho = 1$

Continuum Field Description of Crack Propagation

Static solutions

The static one-dimensional equations read $\dfrac{\partial \rho u_{yy}}{\partial y} = 0$

$$\frac{\partial^2 \rho}{\partial y^2} - \rho(1-\rho)[1 - (b - \mu u_{yy})\rho] = 0$$

With the fixed-grips boundary conditions (BC)

- $u_y(y = \pm L) = \pm L\delta$
- $\rho(y = \pm L) = 1$
- $\partial_y(\rho = 0) = 0$

Continuum Field Description of Crack Propagation

Static solution

- **The width of the crack** opening d defined as $\rho(d/2) = 1/2$

$$\boxed{d = \sqrt{\frac{8}{b} \ln\left[\frac{\sqrt{8b}}{\pi} L\left(\frac{2\mu\delta}{b-2} - 1\right)\right]}}$$

- The solution exists only if δ exceeds some critical value

The strain to failure $\delta_c \approx (b/2 - 1)/\mu$

- The logarithmic, instead of linear, dependence of crack opening on system size L is a shortcoming of the model resulting from an oversimplified dependence of the function F on u_{ll}

Continuum Field Description of Crack Propagation

- To study the ***dynamics of cracks***, one has to perform numerical simulations.
- Usually, one uses an explicit second order scheme.

Discretization methods :
finite difference
finite element method (FEM)

- The number of grid points used in simulation of the model discussed here -- up to **4000 x 800** grid points.

Continuum Field Description of Crack Propagation

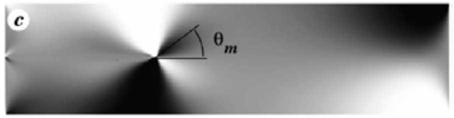
Results of the simulation

Quasistationary propagation

The crack produces the stress concentration near the tip, while the stress is relaxed behind the tip

Hydrostatic pressure
$p = -(\sigma_{xx} + \sigma_{yy})$

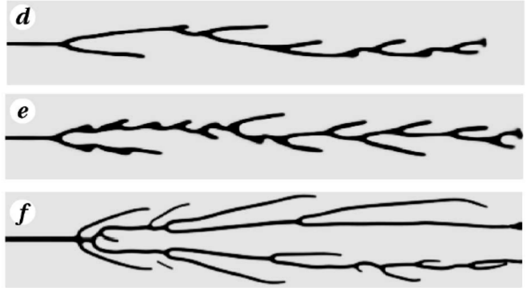
Shear σ_{xy}



Continuum Field Description of Crack Propagation

Results of the simulation -- *Instability of crack propagation*

Order parameter $\rho(x, y)$



propagation with fragmentation

Crystal Growth

Growth science

- In recent times, the evolution processes have ultimately become a central object of scientific study in many fields.
- A vast variety of phenomena are studied by ***growth science***, ranging from
    - **the spread of a forest fire to**
    - **the sedimentation of sand on the bottom of a water basin**.
- These growth phenomena have been recently reviewed in beautiful articles and books
    - T. Halpin-Healy & Y.-C. Zhang, *Phys. Rep.* **254,** 215 (1995)
    - Evans, *Rev. Mod. Phys.* **65,** 1281 (1993)
    - A.L. Barab´asi & H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge: Cambridge University Press, 1995)

Crystal growth and growth science

Crystal growth is special in that it was studied in detail,
because of its practical importance,
much before the present fashion

Hurle D T J (ed) *Handbook of Crystal Growth*
(Amsterdam: North-Holland, 1993)

- Atomistic description of crystal growth

➡ **Continuum models of crystal growth**

dependent on the physics of growth

Traditional concepts of crystal growth

Surface growth

- For stable growth the most widely considered geometry is that of a planar or quasi-planar surface, moving in the positive z-direction with (on average) constant velocity v.

The chemical potential of the vapor μ

of the crystal μ_{eq}

- **The driving force for crystal growth:** $\boxed{\Delta\mu = \mu - \mu_{eq}}$
- Two basic and related questions are:
    - what is the ***growth mode*** and
    - what is the ***growth kinetics***, i.e., how does the rate of growth G depends on the driving force

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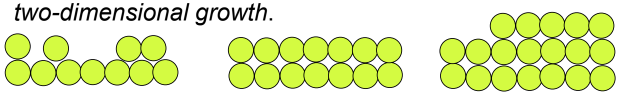
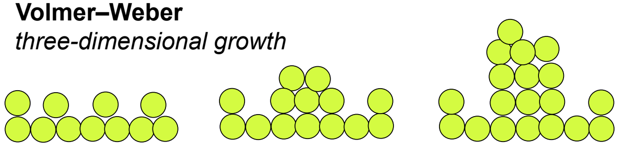
Growth modes

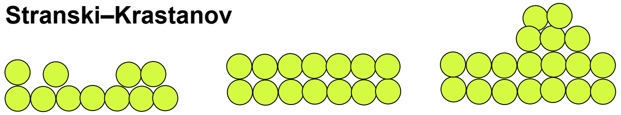
Frank–van der Merwe ***(layer-by-layer)***
two-dimensional growth.



Volmer–Weber
three-dimensional growth



Stranski–Krastanov



Growth of rough surfaces

- Quantitatively, the surface roughness is described by the surface width *w*.
- Let us consider a surface in a *d*-dimensional space given by a single-valued function *h*(**x**; *t)* of a *d*′-dimensional (*d* = *d*′+1) substrate coordinate **x**

$$\boxed{w^2 = \langle N^{-1} \textstyle\sum_i (h_i - \bar{h})^2 \rangle}$$

The average height $\bar{h} = N^{-1} \sum_i h_i$ $\quad N = L^{d'}$

$$h_i = h(\boldsymbol{x}_i)$$

is a linear size of the system,

Growth of rough surfaces – Stochastic differential equations

- The simplest time-dependent description of a stochastic surface is afforded by the ***Edwards–Wilkinson*** (EW) equation

Edwards S F and Wilkinson D R,
Proc. R. Soc. A **381,** 17 (1982)

$$\frac{\partial h}{\partial t} = \nu \, \nabla^2 h + \eta$$

has the dimensions of a diffusion coefficient

a noise term

- The solutions of the EW equation give rise to a ***mean square height difference*** $g(\boldsymbol{x}) = \langle [h(\boldsymbol{x}) - h(\boldsymbol{0})]^2 \rangle$ behaving asymptotically as ln *r*

Growth of rough surfaces – Stochastic differential equations

- A non-linear perturbation of the EW equation is the ***Kardar–Parisi–Zhang (KPZ) equation***

Kardar M, Parisi G and Zhang Y,
Phys. Rev. Lett. **56,** 889 (1986)

$$\boxed{\frac{\partial h}{\partial t} = \nu \, \nabla^2 h + \lambda (\nabla h)^2 + \eta}$$

- The KPZ equation generates surfaces whose roughness may be stronger than logarithmic, i.e. of *power-law* form.

Growth of rough surfaces – Stochastic differential equations

- If the EW equation is perturbed by a *periodic force* favoring the *integer levels* (i.e. if the crystal structure is taken into account) the ***Chui–Weeks*** (CW) equation is obtained

Chui S. and Weeks J.,
Phys. Rev. Lett. **40,** 733 (1978)

$$\frac{\partial h}{\partial t} = \nu \, \nabla^2 h + y_0 \sin 2\pi h + \eta$$

- and the surface tends to become *smoother.*
- Thus a surface obeying the CW equation either is smooth, or if it is rough cannot be more than logarithmically rough.

Growth of rough surfaces – Stochastic differential equations

An important class of equations are the *conserving* equations of the form

$$\frac{\partial h(\boldsymbol{x},t)}{\partial t} = -\boldsymbol{\nabla}\cdot\boldsymbol{J}[\boldsymbol{\nabla} h(\boldsymbol{x},t)] + \eta(\boldsymbol{x},t)$$

J is the surface current depending on the derivatives of *h* and possibly on *h* itself.

A linear diffusion equation is obtained for

$$\boldsymbol{J} = -K\,\boldsymbol{\nabla}\,\nabla^2 h(\boldsymbol{x},t)$$

With the particular choice

$$\boldsymbol{J} = -K\,\boldsymbol{\nabla}\nabla^2 h(\boldsymbol{x},t) + \lambda\,\boldsymbol{\nabla}(\boldsymbol{\nabla} h)^2$$

where *J* is the gradient of the right-hand side of the KPZ equation, we obtain the so-called ***conserved KPZ equation***.

Thank you !