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Computational Simulation of Materials
Notes for lectures given at UCSB
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Computational Simulation of Materials

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I. Introduction:

A. Content of course:

1. General purpose

- a. to introduce modern computer simulation techniques for materials properties and response
 - i. to be able to construct models and simulation codes
 - ii. to be able to better assess simulation results of others

b. NOT to create experts

- i. will cover basics so could become experts

c. NOT to become expert code writers/hackers

2. Subject organization (see "Physical modeling of materials problems," M.F. Ashby, Mat. Sci. and Tech. **8**, 102 (1992), Figure 15)

a. we will divide subject material into three main areas

- i. atomistics
- ii. mesoscale (i.e., microstructure)
- iii. macroscale (i.e., continuum)

b. we will work from atoms to the continuum

c. NB. we will not do electronic structure

3. Course organization

a. requirements

- i. problem sets (some as I think instructive)
- ii. project (will discuss later)
 - 1. will do projects as teams of 2-3
 - 2. the purpose is to do problems not to write code

b. grades

- i. mostly the project

c. languages

- i. FORTRAN 77 or 90 (all examples will be in some form of FORTRAN)
- ii. this is not a programming course. I assume you have some knowledge.

- d. my schedule
 - i. April 1-12, May 17-June 5
- e. exams
 - a. none
- 4. General definitions
 - a. theory:
 - fundamental description of behavior that as far as we know holds "exactly," e.g., Newton's laws
 - b. modeling
 - an idealization of real behavior - an approximate description based on empirical and/or physical reasoning
 - c. simulation
 - study of the dynamical response of a modeled system by subjecting models to inputs which simulate real events, e.g., finite-element simulation of the bending of an airframe in flight based on models of material behavior
- 5. This course
 - a. on computer simulations, but based on models
 - i. will discuss models
 - ii. will discuss simulation techniques
 - iii. will discuss theoretical underpinnings of both models and methods

B. Modeling (see "Physical modeling of materials problems," M.F. Ashby, Mat. Sci. and Tech. **8**, 102 (1992).)

- 1. What is a model?
 - a. an idealization of real behavior - an approximate description based on empirical and/or physical reasoning
- 2. Importance of modeling
 - a. foundation of all simulations
 - b. no matter how good a method or computer one uses, the results are no better than the models on which it is based.
- 3. How do we construct a model?
 - a. Ashby figure 1
 - i. discussion of stages of modeling
- 4. Example: creation of a model for interatomic interactions - the Lennard-Jones potential
 - a. problem
 - i. interatomic potential between closed-shell atoms (e.g., rare gas atoms)

- ii. What do we mean by interatomic potential?
 1. suppose the energy of an isolated atom a is $E(a)$ (from interactions of electrons with each other and the nucleus and the kinetic energy of the electrons)
 2. if we have two atoms a and b , the energy of the combined system does not equal the sum of the energies of the isolated atoms, $E(a + b) \neq E(a) + E(b)$, unless the atoms are infinitely far apart. Why? the presence of one atom changes the electronic properties of the other.
 3. the difference in energies is the interaction energy:

$$\phi(r) = E(a + b) - (E(a) + E(b))$$
, where r is the distance between the atoms.
 4. this energy goes by many names, including interaction potential
 5. why potential? because it is a potential energy. Later we will use results from classical mechanics that says the force between the two atoms is given by $\vec{F}(r) = -\vec{\nabla}\phi(r)$
- b. inputs and outputs
 - i. input: distance between atoms (r)
 - ii. output: interaction potential energy ($\phi(r)$)
- c. identify physical mechanisms
 - i. long-range: dispersion interactions (induced dipole-induced dipole) ($1/r^6$)
 - ii. short-range: "Pauli" repulsion - atoms cannot be in the same place
- d. target the precision
 - i. seeking generic form with parameters to fit specific materials
- e. construct the model
 - i. dispersion interactions: $-A/r^6$ (note: ignoring higher-order terms that go as $1/r^{2n}$, where $n > 3$) and A is some constant that depends on the materials
 - ii. short-range interactions - we don't know their form, except that they must be steeper than the attractive part and decay with r faster at long range so that we have net repulsion at short range and $1/r^6$ at long range
 1. for convenience take B/r^{12} where B is some material-specific constant
 - iii. net potential is of the form
$$\phi(r) = \frac{B}{r^{12}} - \frac{A}{r^6}$$
- f. dimensional analysis, group variables
 - i. we want the potential to be generic with few parameters, so express in a dimensionally more appealing form

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \text{ where } \sigma = (B/A)^{1/6} \text{ and } \epsilon = A^2/(4B)$$

- ii. note that $\phi(\sigma)=0$, the minimum is at $r_m = 2^{1/6}\sigma$ with $\phi(r_m)=-\epsilon$,
- ii. two parameters: σ has units of distance and ϵ of energy
 - 1. these 2 parameters define the properties of the potential and thus the material
 - 2. they vary with material (e.g., for Ne, $\sigma = 2.74 \text{ \AA}$ and $\epsilon = 0.0031 \text{ eV}$;

for Xe, $\sigma = 3.98 \text{ \AA}$ and $\epsilon = 0.0200 \text{ eV}$)

- iii. define *reduced units* as $x=\sigma/r$ (unitless) and $v=\phi/\epsilon$ (unitless)

$$v(r) = 4 \left[\left(\frac{1}{x} \right)^{12} - \left(\frac{1}{x} \right)^6 \right]$$

- iv. as we shall see later, with reduced units can describe any material with one simulation (within accuracy of LJ potential): to convert to real units, multiply energy by ϵ and distance by σ

- g. computer implementation and display
- h. interrogate the model
 - i. comparison of LJ potentials with experimentally-determined potentials shows that an LJ potential is too stiff (i.e., the repulsive wall is too steep) and not overly accurate - see Figure I-1 below.
- i. use the model (we'll do this later)
- j. iterate and improve - 12,6 $\Rightarrow$ m,n

$$\phi_{m,n}(R) = \frac{\epsilon}{m-n} \left(\frac{m}{n} \right)^{\frac{1}{m-n}} \left[\left(\frac{\sigma}{r} \right)^m - \left(\frac{\sigma}{r} \right)^n \right]$$

- i. this offers more flexibility - 4 parameters
 - ii. $m=10$ or so gives better repulsive walls
 - iii. not really much better, but can fit more materials
5. we'll see many examples throughout the course of constructing models and using them

Next Page:

Figure I-1. Comparison of experimental pair potential for Ar (solid curve) with best Lennard-Jones potential (dashed curve).

Fig. 1.3 Argon pair potentials. We illustrate the BBMS pair potential for argon (solid line) [Matland and Smith 1971]. The BFW potential [Barker *et al.* 1971] is numerically very similar. Also shown is the Lennard-Jones 12-6 effective pair potential (dashed line) used in computer simulations of liquid argon.

II. Atomistic simulations:

A. Cohesive energy of a system with many atoms. [see "Solid State Physics," N.W. Ashcroft and N. D. Mermin, Chapter 20 [AM] (on reserve) and "Computer Simulation of Liquids," M.P. Allen and D.J. Tildesley [AT] (on reserve).]

1. The cohesive energy of a system of N atoms is the the negative of energy needed to take all the atoms and move them infinitely far apart (i.e., the same idea as an

interaction potential between two atoms): $U = E(\text{all } N \text{ atoms}) - \sum_{i=1}^N E(i)$

2. We could calculate $E(\text{all } N \text{ atoms})$ and subtract the energies of the isolated atoms using electronic structure calculations - very expensive and restricted to small systems.
3. Instead, we approximate the total potential energy of a system with N atoms by expanding in terms that depend on the coordinates of the individual atoms, pairs, triplets, etc:

$$U = \sum_{i=1}^N v_1(\vec{r}_i) + \sum_{i=1}^N \sum_{j>i}^N v_2(\vec{r}_i, \vec{r}_j) + \sum_{i=1}^N \sum_{j>i}^N \sum_{k>j>i}^N v_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots$$

- a. the $\sum_{i=1}^N \sum_{j>i}^N$ notation indicates a summation over all distinct pairs i and j without

counting any pair twice. It gives the same result as would $\frac{1}{2} \sum_{i=1}^N \sum_{j \neq i=1}^N$, where the

1/2 accounts for including every interaction twice

- b. the first term (v_1) represents the effect of an external field (i.e., an electric field) and includes N terms
- c. the second term (v_2) is the pair potential that depends only on $r_{ij} = |\vec{r}_j - \vec{r}_i|$ and includes $N(N-1)/2$ terms (i.e., $O(N^2)$)
- d. the third term is due to *many-body* interactions, and is large for condensed-phase systems but is usually ignored because it involves sums over triplets of atoms and is very computationally costly ($O(N^3)$ terms)

4. if we have a pairwise additive and central-force potential, the cohesive

energy of a system of N atoms is $U = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i=1}^N \phi_{ij}(|\vec{r}_j - \vec{r}_i|)$

5. For a solid with an n -atom basis:

- a. we can write $u = \frac{1}{2} \sum_{\vec{R}} \sum_{i=1}^n \sum_{j \neq i=1}^n \phi(\vec{r}_j - \vec{r}_i + \vec{R})$, (Expression A), where $\vec{R}$ is a lattice

U

Make clear energy/atom

See Revision-II.A. (below)
AT END OF WORKSHEET THIS SECTION

vector, $\vec{r}_i$ is the vector for the position of the i th atom within the unit cell, and ϕ is the interatomic potential.

6. For simple crystal lattices (no basis), the expression simplifies to $u = \frac{1}{2} \sum_{\mathbf{R} \neq 0} \phi(\mathbf{R})$ [AM]

7. For simple crystal lattices (fcc, bcc, sc) and a $1/r^n$ potential (like Lennard-Jones), it is convenient to rewrite the lattice vector $\mathbf{R}$ as a dimensionless number $\alpha(\mathbf{R})$ times the nearest-neighbor separation r_{nn} and to subsume the detailed information on the lattice structure into a lattice sum. For the Lennard-Jones potential (stable structure is fcc)

Energy per atom $\left\{ u = 2\epsilon \left[A_{12} \left(\frac{\sigma}{r_{nn}} \right)^{12} - A_6 \left(\frac{\sigma}{r_{nn}} \right)^6 \right], \text{ where } A_n = \sum_{\mathbf{R} \neq 0} \frac{1}{\alpha(\mathbf{R})^n} \text{ is a lattice sum (like a Madelung constant). Values of } A_n \text{ have been tabulated for most common crystal structures for many values of } n. \text{ (See attached Table)}$

a. fcc: $A_{12} = 12.1318$, $A_6 = 14.4539$

b. bcc: $A_{12} = 9.1142$, $A_6 = 12.2533$

8. From this simple expression, can minimize the cohesive energy to find properties of solids at 0°K , (i.e., set $\frac{\partial u}{\partial r_{nn}} = 0$) [AM]

a. equilibrium nearest-neighbor distance: $r_0 = \left(\frac{2A_{12}}{A_6} \right)^{1/6} \sigma = 1.09\sigma$

b. 0°K cohesive energy: $u_0 = -\frac{\epsilon}{2} \left(\frac{A_6^2}{A_{12}} \right) = -8.6\epsilon$

c. 0°K bulk modulus: $B_0 = -V_0 \left(\frac{\partial P}{\partial V} \right)_{T=0} = V_0 \left(\frac{\partial^2 U}{\partial V^2} \right)_{T=0} = -8 \frac{u_0}{V_0} = 75 \frac{\epsilon}{\sigma^3}$

where V_0 is the volume per particle at 0°K

d. Note that for an LJ solid, have only two parameters. Can fit 2 of these experimental parameters (u_0 , r_0 , B_0) but not necessarily the third. Even then, the fit might not be very good because we ignore many-body effects and the LJ potential is inadequate. Also, ignores the zero-point motion (a quantum-mechanical effect).

see Revision II.A below

2.12 (9-)
per atom

e. For the rare gas solids (using theory from above):

		Ne	Ar	Kr	Xe
r_o (Å)	(Experiment)	3.13	3.75	3.99	4.33
	(Theory)	2.99	3.71	3.98	4.34
u_o (eV/atom)	(Experiment)	-0.02	-0.08	-0.11	-0.17
	(Theory)	-0.027	-0.089	-0.120	-0.172
B_o (10^{10} dyne/cm ²)	(Experiment)	1.1	2.7	3.5	3.6
	(Theory)	1.81	3.18	3.46	3.81

9. From the general expression (A), we can write a computer program to perform the lattice sums and thus to find the 0°K crystal structures and energies

- a. minimize u with respect to $a, b, c, \alpha, \beta, \gamma$ and r_i
 - i. Note: must find some way to simplify lattice sums because cannot sum to infinity.
- b. potential cutoff
 - i. for shorter-ranged ($1/r^n$ where $n > 3$) potentials (e.g., LJ): cut off potential at some distance (i.e., set $\phi=0$ for $r > r_c$)
 - ii. introduces errors because do not include all interactions between atoms
- c. long-range potentials (like for charged systems where $\phi \sim 1/r$) require a more complicated method which we'll discuss later
- d. note that LJ systems are boring - just fcc. Need more complicated potentials to make this interesting

Revisions to II.A. Atomistics

There is some confusion with the discussion of lattice sums and energies from II.A.4 to

II.A.8. Replace what is in your notes with the following:

4. if we have a pairwise additive and central-force potential, the cohesive

energy of a system of N atoms is
$$U = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i=1}^N \phi_{ij}(|\vec{r}_j - \vec{r}_i|)$$

Note that here and below we will use a capital U for the total energy. Below we will use a lower case u to indicate the energy per atom, U/N .

- 4'. We have given two ways to write the lattice sum. What are we really talking about?

Consider a system with 4 atoms:

We assume that the total potential energy is just the sum of the interactions between all the atoms without including any interaction twice and with no self-interactions. The two forms of writing the lattice sums are equivalent:

$$U = \sum_{i=1}^N \sum_{j>i}^N \phi_{ij}(|\vec{r}_j - \vec{r}_i|) = \phi(r_{12}) + \phi(r_{13}) + \phi(r_{14}) + \phi(r_{23}) + \phi(r_{24}) + \phi(r_{34})$$

$$U = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i=1}^N \phi_{ij}(|\vec{r}_j - \vec{r}_i|) = \frac{1}{2} \{ \phi(r_{12}) + \phi(r_{13}) + \phi(r_{14}) + \phi(r_{21}) + \phi(r_{23}) + \phi(r_{24}) \\ + \phi(r_{31}) + \phi(r_{32}) + \phi(r_{34}) + \phi(r_{41}) + \phi(r_{42}) + \phi(r_{43}) \}$$

The expressions are equivalent since $r_{12}=r_{21}$ and the $1/2$ corrects for overcounting.

5. For a solid with an n -atom basis:

a. we can write
$$U_{\text{cell}} = \frac{1}{2} \sum_{\vec{R}} \sum_{i=1}^n \sum_{j \neq i=1}^n \phi(\vec{r}_j - \vec{r}_i + \vec{R}),$$
 where $\vec{R}$ is a lattice

vector, $\vec{r}_i$ is the vector for the position of the i th atom within the unit cell, and ϕ is the interatomic potential. Note that this gives the total energy per unit cell, i.e., we find the interaction between all other atoms and those in the unit cell, as well as the interactions within the unit cell.

For example, the vector connecting 1 to 2' is just $\vec{r}_{12'} = \vec{R} + \vec{r}_2 - \vec{r}_1$

6. For simple crystal lattices (no basis), the expression simplifies to $u = \frac{1}{2} \sum_{\mathbf{R} \neq 0} \phi(\mathbf{R})$ [AM],
which is just the energy per atom, since there is 1 atom per cell.

7. For simple crystal lattices (fcc, bcc, sc) and a $1/r^n$ potential (like Lennard-Jones), it is convenient to rewrite the lattice vector $\mathbf{R}$ as a dimensionless number $\alpha(\mathbf{R})$ times the nearest-neighbor separation r_{nn} and to subsume the detailed information on the lattice structure into a lattice sum.

- 7'. Consider what we mean by this. Consider $S_n \equiv \sum_{\mathbf{R} \neq 0} \frac{1}{|\vec{R}|^n}$, where in the sum we visit

each lattice site, find its distance back to the origin, find its inverse n^{th} power and sum. In an fcc lattice, for example, we'd find 12 atoms at the nearest neighbor distance r_{nn} , 6 at the second-nearest neighbor distance of $\sqrt{2}r_{nn}$, 18 at the third-nearest neighbor distance $\sqrt{3}r_{nn}$, etc. So, all the lattice distances are some factor times the nearest neighbor distance. It is thus convenient to rewrite S by factoring out r_{nn} ,

$$S_n \equiv \frac{1}{r_{nn}^n} \sum_{\mathbf{R} \neq 0} \left(\frac{r_{nn}}{|\vec{R}|} \right)^n = \frac{1}{r_{nn}^n} \sum_{\mathbf{R} \neq 0} \frac{1}{\alpha(\vec{R})^n}, \text{ where } \alpha(\mathbf{R}) \text{ is a dimensionless number. For fcc}$$

we have $\alpha = 1$ for the nearest neighbors, $\sqrt{2}$ for the second-nearest, etc. We then

define the dimensionless lattice sum $A_n = \sum_{\mathbf{R} \neq 0} \frac{1}{\alpha(\mathbf{R})^n}$ (like a Madelung constant) and we

have for S , $S_n = \frac{1}{r_{nn}^n} A_n$. Consider A_n for an fcc lattice:

$$A_n(\text{fcc}) = 12 + 6\left(1/\sqrt{2}\right)^n + 24\left(1/\sqrt{3}\right)^n + \dots$$

Values of A_n have been tabulated for most common crystal structures for many values of n . (See attached Table)

8'. For a system described by a $1/r^n$ potential, we can then avoid doing lattice sums ourselves and use these results. For example, for a Lennard-Jones potential

$$u = \frac{1}{2} \sum_{R \neq 0} \phi(R) = \frac{1}{2} \sum_{R \neq 0} 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right] = 2\epsilon [\sigma^{12} S_{12} - \sigma^6 S_6]$$

$$\text{or } u = 2\epsilon \left[A_{12} \left(\frac{\sigma}{r_{nn}} \right)^{12} - A_n \left(\frac{\sigma}{r_{nn}} \right)^6 \right]$$

NOTE: equation in the original II.A.7 is incorrect - the power of the second sum should be 6 as it is here.

- B. Other potentials (see MRS Bulletin, February 1996, Volume 21, articles are listed by author)
1. Assessment of potentials
 - a. usually, people justify by comparing calculated with experimental quantities
 - b. often, however, we can see what or will not work by looking at the form of the potentials
 - c. NOTO BENE: remember that potentials are models; they are equivalent to constitutive laws
 2. Interatomic potentials for specific classes of potentials
 - a. four classes of materials
 - i. closed-shell atoms/molecules
 1. molecules require potentials that depend on shape
 2. potentials are reasonably short-ranged, except for molecules with dipole moment
 3. generic form like LJ
 - ii. ionic atoms/molecules
 1. potentials have long-range $1/r$ interactions
 2. generic form like LJ + $1/r$ potential
 - iii. metals
 1. delocalized electrons (electron gas) are very important
 2. generic form not like LJ plus something
 - iv. covalent materials
 1. directional bonding requires different approach
 3. Atomistic simulations for generic trends.
 - a. a legitimate use of atomistics, however, is to look for trends or generic physical phenomena.
 - i. not for a specific material
 - ii. the potentials must then just capture basic physics of the problem
 - iii. this is why Lennard-Jones is the most-studied material (Lennard-Jonesium)
 4. Pair potentials (central force) (see Vitek in MRS Bulletin)
 - a. most were designed originally for closed-shell atoms and ionics
 - b. materials have essentially no electrons within space between atoms
 - c. Lennard-Jones (see above)
 - i. besides having a very approximate short-range part, we know that the long-range part of the dispersion energy should have higher-order terms ($1/r^8$, $1/r^{10}$, etc.)

d. Morse potential

- i. $\phi(r) = D[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}]$
- ii. D , α , and r_0 are parameters that can be determined by fitting to cohesive energy, lattice spacing and bulk modulus
- iii. based on theory for diatomic molecules

e. Born-Mayer

- i. repulsive term $Ae^{-\alpha r}$
 1. why? $1/r^n$ too stiff
- ii. add attractive term
 1. $-C/r^6$: van der waals (may add higher-order terms)
 2. $-q_i q_j / r$: ionics

f. many-body corrections

- i. for example, we know that the dispersion energy has terms that involve all atoms at once. To first order, those terms can be described with the Axilrod-Teller triple-dipole term (for atoms ijk , $v_{AT} \propto \frac{1}{r_{ij}^3 r_{jk}^3 r_{ki}^3}$) Note that

for N atoms, this requires $O(N^3)$ operations so is very expensive

g. Vitek sp potentials (see Vitek in MRS Bulletin)

- i. These potentials are not designed for metals, where have delocalized electrons
 - i. often cannot match data (u , a , B)
 - ii. could add volume-dependent term to account for cohesive energy of electron

$$\text{gas } u = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i=1}^N \phi_{ij}(|\vec{r}_j - \vec{r}_i|) + U(V)$$

1. can match energy-volume and pressure-volume curves (bulk properties)
2. note that $U(V)$ is not structure dependent, so doesn't affect predictions at constant volume.
3. can affect predictions of phase stability if there are volume changes (i.e., could yield bcc with an LJ pair potential if large enough)
4. still fails to match many defect properties, where there can be large changes in local electronic structure

- iii. people introduced Embedded Atom Model potentials to account for different physics

j. These potentials are not designed for materials with directional bonds (Si, etc.)

- i. build models to incorporate these forms

- ii. tight-binding potentials
- 5. METALS: Embedded-atom model (EAM) potentials (see Foiles in MRS Bulletin)
 - a. The general class of potentials is referred to as *pair functional* potentials.
 - b. basic form is $E = \sum_i F_i \left(\sum_{j \neq i} f_{ij}(r_{ij}) \right) + \frac{1}{2} \sum_{ij} \phi_{ij}(r_{ij})$, where F is a *functional* of $\sum_{j \neq i} f_{ij}(r_{ij})$, f is a function of the interatomic distance and ϕ is a pair potential
 - c. What these functions are depends on whose version one uses. They arise from different derivations and have different functional forms depending on author. See Foiles's article for a reference for a review.
 - d. We'll use the Daw and Baskes Embedded-Atom Model (EAM) here. (The rest are similar, though the functional forms may be quite different.
 - i. the F functional is considered to represent the energy to embed an atom in a uniform electron gas
 - ii. the $\sum_{j \neq i} f_{ij}(r_{ij})$ represents the local electronic density at the site of atom i
 - iii. the pair potential ϕ is due to electrostatic interactions and is purely repulsive
 - iv. while "theory" is built in, most parameters are determined by fitting to data
 - e. EAM for noble metals (e.g., Cu, Ni, ...) (see Foiles et al, Phys. Rev. B, **33**, 7983 (1986), [FBD])
 - i. we assume that the electronic density can be described by the atomic electronic densities, which we will calculate from electronic structure calculations (Hartree-Fock) on the individual atoms. We ignore the inner (i.e., core) electrons and only consider the outer electrons. For Ni, Pd, and Pt, there are 10 outer electrons and for Cu, Ag, and Au, there are 11. In [FBD] they give the electronic configurations used.
 - ii. we define $\bar{\rho} = \sum_{j \neq i} \rho_j(r_{ij})$ (where $f \Rightarrow \rho$) as the local electronic density at point i .
 - iii. we approximate $\rho_i(R) = n_s \rho_s(R) + n_d \rho_d(R)$, where $\rho_{s(d)}$ is the electronic density of the $s(d)$ outer electrons (normalized to 1) as determined from Hartree-Fock calculations and $n_{s(d)}$ is the number of s and d outer electrons. Because there is some ambiguity as to the electronic structure, we use n_s as a parameter that we will determine by fitting to experiment. n_d is determined by requiring that $n_s + n_d =$ the total number of outer electrons. Note that in the calculations,

a cutoff is introduced beyond which all quantities are set to zero.

- iv. the pair potential is purely repulsive and represents the electrostatic interactions

$\phi_{ij}(R) = Z_i(R)Z_j(R)/R$, where $Z(R)$ is an effective charge for each atom and

has the form $Z(R) = Z_0(1 + \beta R^v)e^{-\alpha R}$. Z_0 is set to the total number of outer electrons, and β , v , and α are found by fitting predictions to data.

- v. The embedding function F is found by requiring that the overall cohesive energy curve (i.e., energy with volume) matches the so-called "universal binding curve" of Rose et al.: $E(a) = -E_{\text{sub}}(1 + a^*)e^{-a^*}$, where E_{sub} is the absolute value of the sublimation energy at 0 pressure and temperature, and a^* is a measure of the deviation from the equilibrium lattice constant a ,

$a^* = (a/a_0 - 1)/(E_{\text{sub}}/9B\Omega)^{1/2}$, where B is the bulk modulus and Ω the volume per atom. a is the fcc lattice constant and a_0 the equilibrium lattice constant. F is found numerically.

- vi. adjustable parameters are: Z_0 , α , β , v , n_s

- vii. For single component systems, they fit sublimation energy, lattice constant, elastic constants, vacancy formation energy, and internal energy of the bcc phase (not the stable structure).

viii. for parameters, see the handout from [FBD]

- f. inadequacies of pair functional potentials [see Foiles article in MRS Bulletin]

i. they are reasonably good for metals with completely full or completely empty d bands because the potentials are spherically symmetric.

ii. The pair functional methods are not very good for materials with any angular component to interactions: partially-filled bands, covalent materials, etc.

iii. they seem to be too anharmonic in their vibrational properties (will discuss later)

- g. how to improve? [See Foiles in MRS Bulletin for references]

i. include some angular dependence

ii. tight-binding methods [see Sutton in MRS Bulletin]

7. COVALENT MATERIALS

- a. problem

i. angular forces (Si forms tetrahedra with strong bonds)

- b. empirical potentials

i. material specific (only for a single material)

- c. Stillinger-Weber potential for Si (Phys. Rev. B 31, 5262 (1985))

i. designed to treat tetrahedral form of Si (others have later modified this to handle other structures - 18 parameters!)

ii. based on expression

$$U = \sum_{i=1}^N v_1(\vec{r}_i) + \sum_{i=1}^N \sum_{j>i}^N v_2(\vec{r}_i, \vec{r}_j) + \sum_{i=1}^N \sum_{j>i}^N \sum_{k>j>i}^N v_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots$$

iii. $v_1 = 0$

iv. $v_2(\vec{r}_{ij}) = \epsilon f_2(r_{ij}/\sigma)$, where $f_2(r) = A(Br^{-p} - r^{-q})\exp[(r-a)^{-1}]$ for $r < a$ and $f_2 = 0$ for $r \geq a$. A, B, p , and q are positive parameters. This form of f_2 is chosen so as to have continuous derivatives at the cutoff (will be important when discussing molecular dynamics)

v. $v_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) = \epsilon f_3(\vec{r}_i/\sigma, \vec{r}_j/\sigma, \vec{r}_k/\sigma)$, where

$$f_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj})$$

and θ_{jik} is the angle between $\vec{r}_j$ and $\vec{r}_k$ subtended at vertex i , etc.

$$h \text{ takes the form } h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda \exp\left[\gamma(r_{ij}-a)^{-1} + \gamma(r_{ik}-a)^{-1}\right] \left(\cos\theta_{jik} + \frac{1}{3}\right)^2$$

Note: h is zero unless both distances are less than a . Note also that this has a minimum at the ideal tetrahedral angle ($h=0$ there).

vi. works well, but does require 3-body interactions.

vii. for Si: $A=7.049556277$, $B=0.6022245584$, $p=4$, $q=0$, $a=1.80$, $\lambda=21.0$, $\gamma=1.20$

d. Tersoff potential for Si (Phys. Rev. Lett. **56**, 632 (1986).

i. designed to treat tetrahedral and non-tetrahedral forms of Si

ii. includes many-body nature more in flavor of EAM potentials

iii. pair potential is Morse-like $\phi_{ij}(r_{ij}) = f_c(r_{ij})[A \exp[-\lambda_1(r_{ij})] - B_{ij} \exp[-\lambda_2(r_{ij})]]$,

where f_c is a cutoff function and $A, B, \lambda_1, \lambda_2$ are positive parameters, and

$$B_{ij} = B_0 \exp[-z_{ij}/b], \quad z_{ij} = \sum_{k \neq i, j} \left[\frac{w(r_{ik})}{w(r_{ij})} \right]^n \left[c + \exp(-d \cos \theta_{ijk}) \right]^{-1}, \text{ and}$$

$w(r) = f_c(r) \exp(-\lambda_2 r)$. Note that still have sums over triplets.

iv. Tersoff gives parameters and cutoff function (needed to keep everything short ranged).

e. tight-binding methods

i. see Sutton in MRS Bulletin

6 7. IONIC MATERIALS

- a. problems
 - i. very long ranged (creates computational issues)
 - ii. strong polarizations
- b. see Stoneham in MRS Bulletin
 - i. shell model

discuss
shell model

8. Summary

- a. we still don't have good potentials for most materials
 - i. take all atomistic simulations with a grain of salt
- b. creating potentials is tedious, requiring curve fitting, etc.
- c. there are books and a multitude of articles for more information

Table I. Lattice sums (A_n) for cubic crystals (Jones and Ingham 1925).

n	simple cubic	body-centered cubic	face-centered cubic
4	16.5323	22.6387	25.3383
5	10.3775	14.7585	16.9675
6	8.4019	12.2533	14.4539
7	7.4670	11.0542	13.3593
8	6.9458	10.3552	12.8019
9	6.6288	9.8945	12.4925
10	6.2461	9.5645	12.3112
11	6.2923	9.3133	12.2009
12	6.2021	9.1142	12.1318
13	6.1406	8.9518	12.0877
14	6.0982	8.8167	12.0590
15	6.0688	8.7030	12.0400
16	6.0483	8.6063	12.0274
17	6.0339	8.5236	12.0198
18	6.0239	8.4525	12.0130
19	6.0168	8.3914	12.0094
$n \geq 20$	$6 + 12(1/\sqrt{2})^n + 8(1/\sqrt{3})^n$	$8 + 6(\sqrt{3/4})^n + 12(\sqrt{3/8})^n$	$12 + 6(1/\sqrt{2})^n + 24(1/\sqrt{3})^n$

C. Atomistic calculations at 0°K [All the codes are based on those in Allen and Tildesley for ease of comparison]

1. Calculating the potential

- a. suppose we have a system of N atoms interacting with a Lennard-Jones potential
- b. suppose the coordinates are stored in arrays: RX(I),RX(J),RY(I); the potential parameters are $\sigma = \text{SIG}$ and $\epsilon = \text{EPS}$.
- c. a code that would calculate all the interactions is (making sure to include interactions only once and delaying the multiplication of 4ϵ until the end to save time):

```

SIGSQ = SIG*SIG
V = 0.0
DO I = 1, N
  RXI = RX(I)
  RYI = RY(I)
  RZI = RZ(I)
  DO J = I+1, N
    RXIJ = RX(J)-RXI
    RYIJ = RY(J)-RYI
    RZIJ = RZ(J)-RZI
    RIJSQ = RXIJ**2 + RYIJ**2 + RZIJ**2
    RAT = SIGSQ/RIJSQ
    V6 = RAT**3
    POT = V6*(V6-1.0)
    V = V + POT
  END DO
END DO
V = 4.0*EPS*V

```

- i. NOTE: this code is a generic two-body sum - we'll use the same code for Monte Carlo spin models, dislocation dynamics, etc, just with different energetics.
- d. Suppose have an alloy with atom types A and B. Typically, there would different potential parameters for AA (i.e., between two atoms of type A), AB, and BB interactions. Typically, we can find the AA and BB interactions, but have problems finding the potential between atoms of different types (AB). One approximation often used with potentials defined by σ and ϵ are the Lorentz-Berthelot mixing rules, where $\sigma_{AB} = 1/2[\sigma_{AA} + \sigma_{BB}]$ and $\epsilon_{AB} = [\epsilon_{AA}\epsilon_{BB}]^{1/2}$. In a computer program, we would need to identify the type of atom and use the correct σ and ϵ . For example, we might have ITYPE(I) = 1 for A and 2 for B. We could then define: $\text{EPS}[1,1] = \epsilon_{AA}$, $\text{EPS}[1,2] = \text{EPS}[2,1] = \epsilon_{AB}$ and $\text{EPS}[2,2] = \epsilon_{BB}$ with the same kind of thing for SIG. We then would have:

```

SIG(1,1) = SIGAA
SIG(2,2) = SIGBB
SIG(1,2) = 0.5*(SIGAA + SIGBB)
SIG(2,1) = SIG(1,2)
...
V = 0.0
DO I = 1, N
  RXI = RX(I)
  RYI = RY(I)
  RZI = RZ(I)
  ITI = ITYPE[I]
  DO J = I+1, N
    RXIJ = RX(J)-RXI
    RYIJ = RY(J)-RYI
    RZIJ = RZ(J)-RZI
    RIJSQ = RXIJ**2 + RYIJ**2 + RZIJ**2
    ITJ = ITYPE[J]
    SIGIJ = SIG[ITI,ITJ]
    EPSIJ = EPS[ITI,ITJ]
    RAT = SIGIJ*SIGIJ/RIJSQ
    V6 = RAT**3
    POT = V6*(V6-1.0)
    V = V + EPSIJ*POT
  END DO
END DO
V = 4.0*V

```

3. Studying small systems

- we will typically include only a few 100 to a few 1000 atoms in a simulation
- if we put 1000 atoms in a box with typical metal densities, the box would be about 10 atoms, or 30 Å, on a side: the surfaces dominate - 488 of the atoms would be on a surface face
- clearly, this would not model a solid or a liquid very well

4. periodic boundary conditions

- to overcome problems of surface effects, we use *periodic boundary conditions*.
- we take our simulation cell and replicate it throughout space to form a periodic lattice (see Figure II-1)
- as an atom in the central (simulation) cell moves, its replicas move in the same way
- there are no walls and no surface atoms - the box just forms a convenient way to keep track of things and is an axis system for measuring the coordinates
- note that can use any shape box as long as can fill space - i.e., can use any crystal lattice system. Most use cubic, but could use triclinic. Depends on the problem one wants to solve.
- Problems:
 - introduces correlations between cells (i.e., move an atom and all its replicas

just make sure cell is commensurate
the structure you want

move too), which inhibits long wavelength fluctuations, which can mess up phase transitions and calculations of phonons, for example.

1. should check by increasing system size (i.e., a bigger central cell will cause less problems). Balance is computational cost versus accuracy.

5. Truncating the potential (for short-range potentials like LJ)

a. issue

- i. we want to include the interaction of an atom (call it 1) with all other atoms in the simulation cell - there are $N-1$ interactions. (See Figure II-2)
- ii. really should include all images, but clearly cannot because there are an infinite number
- iii. must truncate the potential somehow (except for ionics and other long-range interactions, which we'll discuss later)

b. minimum image convention (see picture II-2)

- i. draw a box the same size as the simulation cell centered at atom 1 (dashed box in II-2)
- ii. include only those atoms (and images) that fall within that new box - these are the *nearest images*. Historical note: method first used in 1953.
- iii. requires calculation of $1/2N(N-1)$ terms (same as including all atoms without using periodic boundary conditions.)
- iv. Note: this is OK for cubic boxes. It may cause problems with other shapes.

c. We can reduce the number of interactions by much more if we cut the potential off at some distance r_c (see II-2)

- i. in II-2, any atoms outside the dashed circle would not be included
- ii. for short ranged potentials, we can usually do this with little error. For example, at $r=2.5\sigma$ in a Lennard-Jones potential, the energy is just 1.6% of the well depth.
- iii. Note that if we do this, any calculated quantities would differ from those where we use no cutoff.
- iv. Note: for consistency, if use minimum image convention, must set the cutoff to less than half the box length

d. simple code for periodic boundaries/minimum image convention

- i. assume a box of size L and ranging from $-L/2$ to $L/2$
- ii. note that if an atom moves outside the box, we could simply change to its image that comes into the box but adding or subtracting L to the appropriate coordinate as needed (let $\text{BOXL} = L$ and $\text{BOXL2} = L/2$)

```
IF(RX(I).GT.BOXL2) RX(I) = RX(I) - BOXL
IF(RX(I).LT.-BOXL2) RX(I) = RX(I) + BOXL
```

and the same for the other coordinates

- iii. A cleaner way to do this is to use the ANINT function, where ANINT(X) returns the nearest integer as a real number: ANINT(-0.49) = ANINT(0.49) = 0.0, ANINT(0.51) = 1.0, and ANINT(-0.51) = -1.0. Then we have

```
RX(I) = RX(I) - BOXL*ANINT(RX(I)/BOXL)
```

- iv. an easy way to program the minimum image convention that is independent of whether one corrects the atoms positions or not is to, immediately after finding the pair separation vector, use

```
RXIJ = RXIJ - BOXL*ANINT(RXIJ/BOXL)
RYIJ = RYIJ - BOXL*ANINT(RYIJ/BOXL)
RZIJ = RZIJ - BOXL*ANINT(RZIJ/BOXL)
```

- v. Note. If we use as the unit of length the box length (i.e., rescale all distances) then the coding is very simple:

```
RXIJ = RXIJ - ANINT(RXIJ)
RYIJ = RYIJ - ANINT(RYIJ)
RZIJ = RZIJ - ANINT(RZIJ)
```

Most people (including me) do this.

- e. introducing a spherical cutoff

- i. If we want to cutoff the potential at a distance $r_c = \text{RCUT}$, we could define RCUTSQ outside the loop and include an IF statement in the inner loop

```
...
RIJSQ = RXIJ**2 + RYIJ**2 + RZIJ**2
IF(RIJSQ.LT.RCUTSQ) THEN
  RAT = SIGSQ/RIJSQ
  V6 = RAT**3
  POT = V6*(V6-1.0)
  V = V + POT
END IF
END DO
```

we still loop over everything and calculate distances, but avoid calculating the potential every time.

- ii. one can do separate tests in each direction (i.e., if $\text{RXIJ} > \text{RCUT}$ then don't include), which will save more time

6. Combined code

```
SIGSQ = SIG*SIG
RCUTSQ = RCUT*RCUT
V = 0.0
DO I = 1, N
  RXI = RX(I)
  RYI = RY(I)
```

```

RZI = RZ(I)
DO J = I+1, N
  RXIJ = RX(J)-RXI
  RYIJ = RY(J)-RYI
  RZIJ = RZ(J)-RZI
C  MINIMUM IMAGE CONVENTION
  RXIJ = RXIJ - BOXL*ANINT(RXIJ/BOXL)
  RYIJ = RYIJ - BOXL*ANINT(RYIJ/BOXL)
  RZIJ = RZIJ - BOXL*ANINT(RZIJ/BOXL)
  RIJSQ = RXIJ**2 + RYIJ**2 + RZIJ**2
C  SPHERICAL CUTOFF
  IF(RIJSQ.LT.RCUTSQ) THEN
    RAT = SIGSQ/RIJSQ
    V6 = RAT**3
    POT = V6*(V6-1.0)
    V = V + POT
  END IF
END DO
END DO
V = 4.0*EPS*V

```

7. Accuracy

- The overall accuracy depends on the quality of the lattice sums, which depends on cutoff and system size.
- If we assume minimum image convention and the cutoff set to half the box length, then the only variable is system size.
- How do we know if we have enough atoms? Run a series of calculations with a different size and check the results.

8. Initial conditions

- For lattice minimizations, we'd start at the lattice sites. We can easily write a code to generate these.
- For example, if we want fcc lattice sites (note: BOXL is the box length and the (XP,YP,ZP) are (0,0,0), (1/2,0,1/2), (0,1/2,1/2), (1/2,1/2,0). This generates M cells in each direction, so $N=4M^3$.

C LOOP OVER 4 ATOMS IN BASIC FCC CELL

```

IKNT = 0
BOXL2 = 0.5*BOXL
DO IP = 1, 4
  X1 = XP(IP)
  Y1 = YP(IP)
  Z1 = ZP(IP)

```

C MAKE M UNIT CELLS IN EACH DIRECTION

```

DO I = 1, M
  DO J = 1, M
    DO K = 1, M
      IKNT = IKNT + 1

```

C SCALE BY LATTICE SIZE (ALL COORDINATES BETWEEN 0 AND BOXL)

```

RX(IKNT) = BOXL*(X1 + DFLOAT(I-1))/DFLOAT(M)

```

← FLOAT

← FLOAT

```

RY(IKNT) = BOXL*(Y1 + DFLOAT(J-1))/DFLOAT(M)
RZ(IKNT) = BOXL*(Z1 + DFLOAT(K-1))/DFLOAT(M)
C  MOVE ATOMS TO BE BETWEEN -BOXL/2 AND BOXL/2
RX(IKNT) = RX(IKNT) - BOXL2
RY(IKNT) = RY(IKNT) - BOXL2
RZ(IKNT) = RZ(IKNT) - BOXL2
      END DO
    END DO
  END DO
END DO

```

9. To find the minimum cohesive energy at 0°K, we could use (for cubic systems) the box length L (BOXL) as a variational parameter and use a canned minimization routine as found in Numerical Recipes to find the minimum in V.

Figure
II-1

Fig. 1.9 A two-dimensional periodic system. Molecules can enter and leave each box across each of the four edges. In a three-dimensional example, molecules would be free to cross any of the six cube faces.

Figure
II-2

Fig. 1.12 The minimum image convention in a two-dimensional system. The central box contains five molecules. The 'box' constructed with molecule 1 at its centre also contains five molecules. The dashed circle represents a potential cutoff.

10. Revised program with scaled coordinates:

- a. As noted above, most people, including me, used scaled coordinates so that the positions are in the range $-1/2$ to $1/2$ (or 0 to 1) instead of $-L/2$ to $L/2$. When one does this, changing the length of box side scales the atomic coordinates uniformly, making it quite easy to find how the energy changes with volume.
- b. generation of scaled fcc coordinates (revision of earlier program). Note that we must either set M (the number of replicas of the fcc cell in each direction) in the program or read it in. Note that this generates atom positions between $-1/2$ and $1/2$.

```

DATA XP(1),XP(2),XP(3),XP(4)/0.0,0.5,0.0,0.5/
DATA YP(1),YP(2),YP(3),YP(4)/0.0,0.5,0.5,0.0/
DATA ZP(1),ZP(2),ZP(3),ZP(4)/0.0,0.0,0.5,0.5/
C LOOP OVER 4 ATOMS IN BASIC FCC CELL
  IKNT = 0
  DO IP = 1, 4
    X1 = XP(IP)
    Y1 = YP(IP)
    Z1 = ZP(IP)
  C MAKE M UNIT CELLS IN EACH DIRECTION
    DO I = 1, M
      DO J = 1, M
        DO K = 1, M
          IKNT = IKNT + 1
        C SCALE BY LATTICE SIZE (ALL COORDINATES BETWEEN 0 AND 1)
          RX(IKNT) = (X1 + FLOAT(I-1))/FLOAT(M)
          RY(IKNT) = (Y1 + FLOAT(J-1))/FLOAT(M)
          RZ(IKNT) = (Z1 + FLOAT(K-1))/FLOAT(M)
        C MOVE ATOMS TO BE BETWEEN -1/2 AND 1/2
          RX(IKNT) = RX(IKNT) - 0.5
          RY(IKNT) = RY(IKNT) - 0.5
          RZ(IKNT) = RZ(IKNT) - 0.5
        END DO
      END DO
    END DO
  END DO

```

- c. Lattice sum code code. Note that we need to rescale the distance by multiplying by the box length (since x,y,z are in fractions). Note that changing BOXL does not change the scaled coordinates, but does change the "real" coordinates.

```

BOXLSQ = BOXL*BOXL
SIGSQ = SIG*SIG
RCUT = BOXL/2.0
RCUTSQ = RCUT*RCUT
V = 0.0
DO I = 1, N
  RXI = RX(I)
  RYI = RY(I)
  RZI = RZ(I)
  DO J = I+1, N

```

```

      RXIJ = RX(J) - RXI
      RYIJ = RY(J) - RYI
      RZIJ = RZ(J) - RZI
C   MINIMUM IMAGE CONVENTION
      RXIJ = RXIJ - ANINT(RXIJ)
      RYIJ = RYIJ - ANINT(RYIJ)
      RZIJ = RZIJ - ANINT(RZIJ)
      RIJSQ = BOXLSQ*(RXIJ**2 + RYIJ**2 + RZIJ**2)
C   SPHERICAL CUTOFF
      IF(RIJSQ.LT.RCUTSQ) THEN
        RAT = SIGSQ/RIJSQ
        V6 = RAT**3
        POT = V6*(V6-1.0)
        V = V + POT
      END IF
    END DO
  END DO
V = 4.0*EPS*V

```

- d. In the above code, if you vary the box length BOXL, then everything scales uniformly. You could minimize the energy V by varying BOXL.

11. General minimization problems.

- a. One does not have to minimize just the lattice parameter. The potential V is a function of all the coordinates as well. For example, one could introduce a defect, like a grain boundary, and minimize the energy by varying the positions of the atoms near the boundary.
- b. If one had a cell with other than cubic symmetry, one could also minimize the energy with respect to the lattice parameters of that system. Note that the distance equations are more complicated than those shown. We'll discuss these later.
- c. There are standard minimization routines. See Numerical Recipes, for example.

```

c  a program to do simple LJ lattice sum (fcc)
c  with minimum image convention and a cutoff
c  set to half the box length
c  sig = eps = 1 (reduced units)

      program latticesum
      implicit none
c  m = number of repeats of fcc unit cell
c  boxl = box length
      integer m,i,n
      real boxl,energy,v,energyn,rnn
      real rx,ry,rz
      common/coordinates/rx(864),ry(864),rz(864),n

      write(6,*) 'input M, the number of fcc replicas'
      read(5,*) m

c  make simulation cell mxmxm fcc units
      call fccmake(m)

c  loop over box lengths.  we know the minimum
c  is with the nearest neighbor distance about
c  1.09, which means the fcc lattice parameter
c  is about 1.54, which means that at the minimum
c  the overall box length is about 1.54m.  so
c  we will loop from m to 2 m, with 21 steps
c  rnn = nearest neighbor distance, and energyn is the
c  energy per atom for comparison with what we discussed

      write(6,*) '  box length      rnn      energy',
1 '      energy per atom'
      do i = 1 , 21
        boxl = float(m)*(1.0 + float(i-1)*0.05)
        energy = v(boxl)
        energyn = energy/float(n)
        rnn = boxl/(float(m)*sqrt(2.0))
        write(6,*) boxl,rnn,energy,energyn
      end do

      stop
      end

      subroutine fccmake(m)
      implicit none
      integer m,ip,i,j,k,iknt,n
      real xp,yp,zp,xl,yl,zl
      real rx,ry,rz
      common/coordinates/rx(864),ry(864),rz(864),n
      dimension xp(4),yp(4),zp(4)
      data xp/0.0,0.5,0.0,0.5/
      data yp/0.0,0.5,0.5,0.0/
      data zp/0.0,0.0,0.5,0.5/

c  stop code if m>5 (see dimensions of rx,ry,rz)

```

```

    if(m.gt.5) then
        write(6,*) 'm is too big, m= ',m
        stop
    end if

c   loop over 4 atoms in basic fcc cell
    iknt = 0
    do ip = 1,4
        x1 = xp(ip)
        y1 = yp(ip)
        z1 = zp(ip)
c   make m unit cells in each direction
        do i = 1 , m
            do j = 1 , m
                do k = 1 , m
                    iknt = iknt + 1
                    rx(iknt) = (x1 + float(i-1))/float(m)
                    ry(iknt) = (y1 + float(j-1))/float(m)
                    rz(iknt) = (z1 + float(k-1))/float(m)
c   move atoms between -1/2 and 1/2
                    rx(iknt) = rx(iknt) - 0.5
                    ry(iknt) = ry(iknt) - 0.5
                    rz(iknt) = rz(iknt) - 0.5
                end do
            end do
        end do
    end do

    n = iknt
    return
end

function v(boxl)
    implicit none
    integer i,j,n
    real boxl,boxlsq,rcut,rcutsq
    real sig,sigsq,eps
    real v,rat,v6,pot
    real rx,ry,rz,rxl,ryl,rzl
    real rxij,ryij,rzij,rijsq
    common/coordinates/rx(864),ry(864),rz(864),n
    parameter (eps = 1.0, sig = 1.0)

    boxlsq = boxl*boxl
    rcut = boxl/2.0
    rcutsq = rcut*rcut
    sigsq = sig*sig
c   do energy sum
    v = 0.0
    do i = 1 , n
        rxl = rx(i)
        ryl = ry(i)
        rzl = rz(i)
        do j = i+1 , n

```

```

        rxij = rx(j) - rxi
        ryij = ry(j) - ryi
        rzij = rz(j) - rzi
c   minimum image convention
        rxij = rxij - anint(rxij)
        ryij = ryij - anint(ryij)
        rzij = rzij - anint(rzij)
        rijsq = boxlsq*(rxij*rxij + ryij*ryij + rzij*rzij)
c   spherical cutoff
        if(rijsq.lt.rcutsq) then
            rat = sigsq/rijsq
            v6 = rat*rat*rat
            pot = v6*(v6-1.0)
            v = v + pot
        end if
    end do
end do
v = 4.0*eps*v
return
end
c

```

D. Introduction to Statistical Mechanics (see "Introduction to Modern Statistical Mechanics," D. Chandler [C] or "Computer Simulation of Liquids," M.P. Allen and D.J. Tildesley, Chapter 2 [AT] (on reserve).]

1. Why Statistical Mechanics?

- a. Up to now, have only discussed the cohesive energy at 0°K and the potentials from which it is calculated.
- b. To study more interesting phenomena requires $T > 0$
- c. The field that enables us to get to finite temperature is Statistical Mechanics.

2. What is Statistical Mechanics?

- a. statistics of ergodic mechanics(?)
- b. provides a tie between 10^{23} mechanical degrees of freedom (i.e., positions and velocities) to bulk systems described by only a few parameters (thermodynamics)
- c. the study of *fluctuations* and their connection to phase stability, heat flow, etc.

3. What do we hope to accomplish in this course?

- a. not a complete study (a course in itself)
- b. we want to summarize results that are important to atomistic simulations
- c. we assume some knowledge of thermodynamics
- d. discussion based on that in [AT] and [C]

4. Time averages versus ensemble averages

- a. suppose have a system of N atoms
 - i. assume it is classical and thus follows Newton's laws (classical mechanics)
 - ii. the system is characterized by $6N$ quantities - $3N$ positions ($\mathbf{r}$) and $3N$ velocities ($\mathbf{v}$). We will use the momenta, $\mathbf{p} = m\mathbf{v}$, instead of velocity.
 - iii. these positions and momenta can be thought of as coordinates in a multidimensional space - *phase space*, which has $6N$ dimensions
 - iv. at any point in time, the system is characterized by a point in phase space (i.e., a specific set of positions and momenta)
 - v. over time, the system evolves and the point in phase space changes (i.e., the positions and momenta change)
 - vi. for convenience, call the point in phase space that characterizes our system $\Gamma(t)$ (remember that it is a $6N$ dimensional vector)
- b. time averages
 - i. any property of the system, $\mathcal{Z}$ (e.g., the potential energy), will depend on $\Gamma(t)$ so we write $\mathcal{Z}(\Gamma[t])$ and note that it will change with time.
 - ii. it is reasonable to assume that the macroscopic quantity that we observe in a

real system, $\mathcal{S}_{\text{obs}}$, is really the *time average* taken over a long time interval

$$\mathcal{S}_{\text{obs}} = \langle \mathcal{S} \rangle_{\text{time}} = \langle \mathcal{S}[\Gamma(t)] \rangle_{\text{time}} = \lim_{t_{\text{obs}} \rightarrow \infty} \frac{1}{t_{\text{obs}}} \int_0^{t_{\text{obs}}} \mathcal{S}[\Gamma(t)] dt$$

c. ensemble averages

- i. introduced by Gibbs
- ii. assume that over long periods of time, a system will have the opportunity to sample all parts of phase space (ergodic hypothesis)
- iii. if we had infinite time, we could sit on a point in phase space, Γ , and count how often the system reaches that point.
- iv. we then could calculate a *probability* that the system takes on the value Γ .
- v. we can then specify the system by the set of points Γ and the probability density $\rho(\Gamma)$ [the probability density is the probability divided by the integral of all the probabilities, so that if we integrate ρ over all states we get 1] - this set of points and probabilities is called an *ensemble*
- vi. this probability density will depend on the *constraints* set upon the system, i.e., ρ will differ if we have NVT fixed rather than NPT (some states will be more or less probable). [Notational note: N = number of particles, V = volume, P = pressure, and T = temperature. If we say NVT, we mean that each of those variables is fixed, i.e., would have N particles in a box of volume V being held at a temperature T]
- vii. Thus, we have many possible ensembles and we'll use the notation ρ_{ens} , where $\text{ens} = \text{NPT}, \text{NVT}, \text{etc.}$, to differentiate them
- viii. given the probability densities, we write the ensemble average as

$$\mathcal{S}_{\text{obs}} = \langle \mathcal{S} \rangle_{\text{ens}} = \sum_{\Gamma} \mathcal{S}(\Gamma) \rho_{\text{ens}}(\Gamma)$$

d. ergodicity

- i. the key assumption is that we have an *ergodic* system, i.e., if we wait long enough, we will eventually get to all points in phase space.
- ii. in computer simulations, we are more concerned with efficient sampling of phase space. the system may be ergodic, but we may not be able to wait long enough for all parts of phase space to be sampled. We'll discuss this in detail.

5. Ensembles

a. there are 4 main ensembles used in atomistic computer simulations

- i. NVE: this is the *microcanonical* ensemble, with N particles in a box of volume V with the total energy of the system E fixed. This is essentially the ensemble of molecular dynamics (MD) simulations.
- ii. NVT: this is the *canonical* ensemble, with N particles in a box of volume V with the temperature T fixed. This is the standard ensemble of Monte Carlo (MC) atomistic simulations.
- iii. NPT: the isobaric, isothermal ensemble. It is easy to perform MC simulations in this ensemble and, with some clever tricks, MD simulations.
- iv. μ VT: grand canonical ensemble, with the chemical potential μ fixed instead of the number of particles (which fluctuate). Variations of this ensemble have been implemented in MC for examining segregation of materials to boundaries.

b. Partition Functions

- i. the fundamental quantity is the probability density ρ_{ens} . We rewrite ρ_{ens} by introducing a weighting function w_{ens} which satisfies the following relations

$$\rho_{\text{ens}}(\Gamma) = \frac{w_{\text{ens}}(\Gamma)}{Q_{\text{ens}}}$$

$$Q_{\text{ens}} = \sum_{\Gamma} w_{\text{ens}}(\Gamma)$$

$$\langle \mathcal{Z} \rangle_{\text{ens}} = \frac{\sum_{\Gamma} w_{\text{ens}}(\Gamma) \mathcal{Z}(\Gamma)}{\sum_{\Gamma} w_{\text{ens}}(\Gamma)} = \frac{1}{Q_{\text{ens}}} \sum_{\Gamma} w_{\text{ens}}(\Gamma) \mathcal{Z}(\Gamma)$$

- ii. Q_{ens} is called the *partition function* and is the sum of all the weighting functions. Q is the fundamental quantity - connected to thermodynamics.
- iii. At thermodynamic equilibrium, we have the following connection between the partition function and macroscopic thermodynamic properties:
 1. $S = k_B \ln Q_{\text{NVE}}$
 2. $A = -k_B T \ln Q_{\text{NVT}}$
 3. $G = -k_B T \ln Q_{\text{NPT}}$
 4. $PV = k_B T \ln Q_{\mu\text{VT}}$
 5. where k_B is the Boltzmann constant, A is the Helmholtz free energy, and G is the Gibbs free energy.

- iv. NOTE: we have written everything in sums over points in phase space. For classical (i.e., not quantum) atomic systems, these are continuous functions and we write:

$\sum_{\Gamma} \Rightarrow \frac{1}{N!} \frac{1}{h^{3N}} \int dr^{3N} dp^{3N}$, where the $N!$ accounts for the fact that the particles are indistinguishable, the h^{3N} is required to yield the correct results for the entropy of an ideal gas, and the superscript $3N$ indicates that we are considering all $3N$ coordinates. (e.g., $dr^{3N} = dx_1 dy_1 dz_1 dx_2 dy_2 \dots$)

c. Microcanonical ensemble

i. $w_{NVE} = \delta(H(r^{3N}, p^{3N}) - E)$ so $Q_{NVE} = \frac{1}{N!} \frac{1}{h^{3N}} \int dr^{3N} dp^{3N} \delta(H(r^{3N}, p^{3N}) - E)$

1. H is the Hamiltonian of the system ($H=K+U$, where K is the kinetic

energy [$K = \frac{1}{2} \sum_{i=1}^N m_i v_i^2 = \frac{1}{2} \sum_{i=1}^N \frac{p_i^2}{m_i}$] and U the potential energy). Note

that the Hamiltonian has a value of E , which is constant in this ensemble.

2. δ is the Dirac delta function

- ii. This ensemble incorporates all positions and momenta such that $K+U$ is constant

- iii. As we shall see, in molecular dynamics, energy is conserved so this is the appropriate ensemble.

- iv. Note that in this ensemble, T and P are not fixed, but fluctuate around some average value. We'll define these quantities later.

d. Canonical ensemble (for atomic systems)

i. $w_{NVT} = e^{-H(r^{3N}, p^{3N})/k_B T}$ so $Q_{NVT} = \frac{1}{N!} \frac{1}{h^{3N}} \int dr^{3N} dp^{3N} e^{-H(r^{3N}, p^{3N})/k_B T}$

- ii. Since $H(r^{3N}, p^{3N}) = K(p^{3N}) + U(r^{3N})$ and we know the form of K , we can integrate over dp^{3N} (see below for how) and rewrite Q_{NVT} as

$$Q_{NVT} = Q_{NVT}^{id} Q_{NVT}^{ex}$$

1. $Q_{NVT}^{id} = \frac{V^N}{N! \Lambda^{3N}}$ is the partition function for an ideal gas ($U=0$),

$\Lambda = (h^2 / 2\pi m k_B T)^{1/2}$ is the thermal de Broglie wavelength

2. the excess part is $Q_{NVT}^{ex} = \frac{1}{V^N} \int dr^{3N} e^{-V(r^{3N})/k_B T}$

3. usually refer to the configurational integral $Z_{NVT} = \int dr^{3N} e^{-V(r^{3N})/k_B T}$

- iii. In this ensemble, the system has a probability $\exp(-H(\Gamma)/k_B T)$ of being at a given point Γ in phase space
- iv. Since we can easily derive everything we need for the ideal gas part, the interesting physics is in evaluating the excess part, which depends on the atomic *configurations*. MC methods are perfectly suited to sample the configurational part of phase space.
- v. T is fixed, but the total energy fluctuates as does the pressure.

e. Isothermal-Isobaric Ensemble (NPT) for atomic systems

- i. $w_{NPT} = e^{-(H(r^{3N}, p^{3N}) + PV) / k_B T}$ so

$$Q_{NPT} = \frac{1}{N!} \frac{1}{h^{3N}} \frac{1}{V_0} \int dV \int dr^{3N} dp^{3N} e^{-(H(r^{3N}, p^{3N}) + PV) / k_B T}$$
, where V_0 is some unimportant constant to that defines some basic unit of volume
- ii. We integrate over dp^{3N} as before and can define a configurational integral as

$$Z_{NPT} = \int dV e^{-PV / k_B T} \int dr^{3N} e^{-V(r^{3N}) / k_B T}$$
- iii. a variant of this ensemble that is useful for solids, is the isothermal-isostress ensemble, where the applied stress is fixed. We'll discuss this below.
- iv. The volume fluctuates as does the energy.

f. Grand Canonical Ensemble (μVT) for atomic systems

- i.
$$Q_{\mu VT} = \sum_{N=0}^{\infty} e^{(\mu N / k_B T)} Q_{NVT}$$

$$= \sum_{N=0}^{\infty} \frac{1}{N!} \frac{1}{h^{3N}} e^{(\mu N / k_B T)} Q_{NVT}^{id} \frac{1}{V^N} \int dr^{3N} e^{-(U(r^{3N}, p^{3N})) / k_B T}$$
- ii. A useful variant of this was used by Foiles to examine segregation to interfaces in a 2 component system.
- iii. Here, the pressure, energy, and number of particles fluctuates.

6.. A few comments on averages and fluctuations.

- a. In all of these ensembles, some quantities are fixed and some are not. Those that are not will fluctuate around some average value. The goal of most computer simulations is to calculate those average values. In a system of finite size (like we'll use in simulations), there will be a distribution around those average values. For example, in an NPT simulation, the volume will fluctuate around $\langle V \rangle$ with some width.
- b. In macroscopic systems, i.e., in the thermodynamic limit, the distribution of

Energy $\propto E/N$

values around the average become very sharply peaked - essentially a delta function.

7. Transforming between ensembles

- a. Suppose we have two ensembles, f and F , where f is the intensive variable and F the extensive.
 - i. intensive: independent of system size, like T
extensive: scale with system size (N), like E
 - ii. in the thermodynamic limit of infinite size $\langle \mathcal{Z} \rangle_f = \langle \mathcal{Z} \rangle_F$ if $F = \langle F \rangle_f$
 - iii. e.g., averages in a constant NVE ensemble will equal those in a constant NVT ensemble (in the thermodynamic limit) as long as T and E are chosen such that $E = \langle E \rangle_{NVT}$
- b. For finite-sized systems, we can show that
 - i. $\langle \mathcal{Z} \rangle_F = \langle \mathcal{Z} \rangle_f + C$, where C is a correction term that is of order $O(N^{-1})$
 - ii. thus, the corrections die off rapidly with system size
 - iii. BUT: for small systems in simulations, they can make a few percent difference

8. Simple thermodynamic averages.

- a. Consider the average energy in the canonical ensemble, with NVT held constant.

$$\begin{aligned} \langle E \rangle_{NVT} &= \frac{\frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{r}^{3N} d\mathbf{p}^{3N} H(\mathbf{r}^{3N}, \mathbf{p}^{3N}) e^{-H(\mathbf{r}^{3N}, \mathbf{p}^{3N}) / k_B T}}{Q_{NVT}} \\ &= \frac{\frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{r}^{3N} d\mathbf{p}^{3N} \{K + U\} e^{-H(\mathbf{r}^{3N}, \mathbf{p}^{3N}) / k_B T}}{Q_{NVT}} \\ &= \langle K \rangle + \langle U \rangle \end{aligned}$$

- b. The average kinetic energy is:

$$\begin{aligned} \langle K \rangle_{NVT} &= \frac{\frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{r}^{3N} d\mathbf{p}^{3N} \left\{ \frac{1}{2} \sum_{i=1}^N \frac{p_i^2}{m} \right\} e^{-H(\mathbf{r}^{3N}, \mathbf{p}^{3N}) / k_B T}}{Q_{NVT}} \\ &= \frac{\frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{p}^{3N} e^{-\left(\frac{1}{2} \sum_{i=1}^N \frac{p_i^2}{m}\right) / k_B T} \left\{ \frac{1}{2} \sum_{i=1}^N \frac{p_i^2}{m} \right\} \int d\mathbf{r}^{3N} e^{-U(\mathbf{r}^{3N}) / k_B T}}{Q_{NVT}^{id} Q_{NVT}^{ex}} \end{aligned}$$

$$\begin{aligned}
&= V^N \frac{1}{N!} \frac{1}{h^{3N}} \int dp^{3N} e^{-\left(\frac{1}{2} \sum_{i=1}^N \frac{p_i^2}{m}\right) / k_B T} \left\{ \frac{1}{2} \sum_{i=1}^N \frac{p_i^2}{m} \right\} \\
&\quad V^N / (N! \Lambda^{3N}) \\
&= \left(\frac{1}{2\pi m k_B T} \right)^{3N/2} \int dp^{3N} e^{-\left(\frac{1}{2} \sum_{i=1}^N \frac{p_i^2}{m}\right) / k_B T} \left\{ \frac{1}{2} \sum_{i=1}^N \frac{p_i^2}{m} \right\} \\
&= \left(\frac{1}{2\pi m k_B T} \right)^{3N/2} \frac{1}{2} \sum_{i=1}^N \frac{1}{m} \int dp^{3N} e^{-\left(\frac{1}{2} \sum_{i=1}^N \frac{(p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2)}{m}\right) / k_B T} (p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2)
\end{aligned}$$

- i. note that used definition of Q and that the r -dependent integral cancels.
- ii. note that we have $3N$ integrals to do: N atoms with 3 integrals each, i.e. over p_x , p_y , and p_z
- iii. Note that all integrals in the sum are equal and are given by:

$$\int dp^{3N} e^{-\left(\frac{1}{2} \sum_{i=1}^N \frac{(p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2)}{m}\right) / k_B T} (p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2) = 3 \left\{ \int_{-\infty}^{\infty} dp e^{-p^2 / (2 k_B T)} \right\}^{3N-1} \left\{ \int_{-\infty}^{\infty} dp e^{-p^2 / (2 k_B T)} p^2 \right\}$$

- iv. why? Since integrate from $-\infty$ to ∞ and since each integral is independent of the other. Note that when integrating over one component of p^2 , all the other integrals (all $3N-1$) are the same. Work it out.
- v. these are just integrals that are in all integral tables. We have:

$$\begin{aligned}
\int_{-\infty}^{\infty} dp e^{-p^2 / (2 m k_B T)} &= (2\pi m k_B T)^{1/2} \\
\int_{-\infty}^{\infty} dp e^{-p^2 / (2 m k_B T)} p^2 &= \frac{\pi^{1/2}}{2} (2 m k_B T)^{3/2}
\end{aligned}$$

- vi. putting it all together we have

$$\langle K \rangle = \frac{3}{2} N k_B T$$

- vii. This is the familiar *equipartition* principle: and average kinetic energy of $k_B T/2$ per degree of freedom.
- viii. We'll use this to *define* the instantaneous temperature, $\mathcal{T}$, whose average

is the temperature T ($T = \langle \mathcal{T} \rangle$):

$$\mathcal{T} = 2K / 3Nk_B = \frac{1}{3Nk_B} \sum_{i=1}^N \frac{p_i^2}{m_i}$$

- ix. Actually, it is a lot easier to derive this from the virial theorem (look it up)
- c. the potential energy
 - i. using the same procedure, you can easily show that

$$\langle U \rangle_{NVT} = \frac{\int d\mathbf{r}^{3N} U(\mathbf{r}^{3N}) e^{-U(\mathbf{r}^{3N})/k_B T}}{\int d\mathbf{r}^{3N} e^{-U(\mathbf{r}^{3N})/k_B T}}$$

- ii. Note that since this depends on the potential, we cannot derive this analytically - that's what computer simulations are for.
 - iii. This is the form for any system, whether atoms or molecules.
9. A truly cool result: Relation between fluctuations and thermodynamics.
- a. Consider the average energy $\langle E \rangle = \langle H(\mathbf{r}^{3N}, \mathbf{p}^{3N}) \rangle$

$$\langle E \rangle_{NVT} = \frac{\frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{r}^{3N} d\mathbf{p}^{3N} H(\mathbf{r}^{3N}, \mathbf{p}^{3N}) e^{-H(\mathbf{r}^{3N}, \mathbf{p}^{3N})/k_B T}}{Q_{NVT}}$$

- b. Now, take the derivative of E with respect to T

$$\left(\frac{\partial \langle E \rangle}{\partial T} \right)_{N,V} = \frac{\frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{r}^{3N} d\mathbf{p}^{3N} \left(\frac{H^2(\mathbf{r}^{3N}, \mathbf{p}^{3N})}{k_B T^2} \right) e^{-H(\mathbf{r}^{3N}, \mathbf{p}^{3N})/k_B T}}{Q_{NVT}} - \frac{1}{k_B T^2} \left[\frac{\int d\mathbf{r}^{3N} d\mathbf{p}^{3N} H(\mathbf{r}^{3N}, \mathbf{p}^{3N}) e^{-H(\mathbf{r}^{3N}, \mathbf{p}^{3N})/k_B T}}{Q_{NVT}} \right]^2$$

where we take the derivative inside the integral and use the chain rule. The second term arises from the derivative of $1/Q_{NVT}$ with respect to temperature.

- c. Recognizing that the first term is $\langle E^2 \rangle$ and the second term is $\langle E \rangle^2$, we have

$$\langle (\delta E)^2 \rangle_{NVT} \equiv \langle (E - \langle E \rangle)^2 \rangle_{NVT} = \langle E^2 \rangle_{NVT} - \langle E \rangle_{NVT}^2 = k_B T^2 \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{N,V} = k_B T^2 C_V$$

where we used the definition of C_V , the heat capacity at constant volume

- d. This is remarkable: $\langle (\delta E)^2 \rangle$ is just a measure of the fluctuations in E, i.e., it is the mean-square deviation of the instantaneous values of E from its mean, $\langle E \rangle$. This result says that the heat capacity is just proportional to the fluctuations. Note: this is true for any kind of system
- e. For atomic systems, we can again split off the kinetic energy contributions

$$i. \quad \langle (\delta H)^2 \rangle_{NVT} = \langle (\delta K)^2 \rangle_{NVT} + \langle (\delta U)^2 \rangle_{NVT}$$

- ii. where (doing the same kinds of integrals as before) we can show

$$\langle (\delta K)^2 \rangle_{NVT} = \frac{3N}{2} (k_B T)^2,$$

which indicates that the ideal part of C_V is $(3/2)Nk_B$

- iii. if we do an NVT simulation on N atoms we'll then have

$$\langle (\delta U)^2 \rangle_{NVT} = k_B T^2 \left(C_V - \frac{3}{2} N k_B \right)$$

10. Other fluctuations:

- a. There are many other relationships between fluctuations and thermodynamic quantities: see [AT] and [C]
- b. A useful notation is $\sigma^2(A) = \langle (\delta A)^2 \rangle = \langle (A - \langle A \rangle)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2$
 - i REMEMBER: these are ensemble dependent

11. A very useful result: A formula for pressure.

- a. From the virial theorem (in classical mechanics), we can define an expression for an instantaneous "pressure" function, $\mathbf{p}$, whose average is P ($P = \langle \mathbf{p} \rangle$):

- i.
$$\mathbf{p} = \frac{N}{V} k_B \mathcal{T} - \frac{1}{3V} \sum_{i=1}^N \vec{r}_i \cdot \nabla_{\vec{r}_i} U$$

- b. for central-force pair potentials, this takes a very simple form

- i.
$$\mathbf{p} = \frac{N}{V} k_B \mathcal{T} - \frac{1}{3V} \sum_{i=1}^N \sum_{j>i}^N \vec{r}_{ij} \frac{d\phi(r)}{dr}$$

- ii. so
$$P = \frac{N}{V} k_B \langle \mathcal{T} \rangle - \frac{1}{3V} \left\langle \sum_{i=1}^N \sum_{j>i}^N \vec{r}_{ij} \frac{d\phi(r)}{dr} \right\rangle$$

- c. this is just as easy to calculate as the potential energy, thus giving us a way to find P in a constant volume simulation.

12. Time-dependent properties.

- a. so far we've discussed equilibrium averages.
 - i. a lot of interest in time-dependent properties
 - ii. we define *time correlation functions*.
- b. Correlation Functions:
 - i. correlations between quantities A and B are measured in the usual statistical way (using the expression from II.D.10.b): $c_{AB} = \frac{\langle (A - \langle A \rangle)(B - \langle B \rangle) \rangle}{\sigma(A)\sigma(B)}$
 - ii. Note that if A and B are perfectly correlated (i.e., $A=B$), $c_{AB}=1$, if not at all correlated, $c_{AA} = 0$.

iii. Define an unnormalized time correlation function by taking A at one time (t) and B at another (t=0) $C_{AB}(t) = \langle (A(t) - \langle A \rangle)(B(0) - \langle B \rangle) \rangle_{\text{ens}}$

iv. we then can write $c_{AB}(t) = C_{AB}(t) / \sigma(A)\sigma(B)$

v. an important case is the autocorrelation function

$$c_{AA}(t) = C_{AA}(t) / \sigma^2(A) = C_{AA}(t) / C_{AA}(0)$$

vi. Example: the velocity autocorrelation function

$$c_{vv}(t) = \frac{\langle (\bar{v}_i(t) - \langle \bar{v}_i \rangle) \cdot (\bar{v}_i(0) - \langle \bar{v}_i \rangle) \rangle}{\langle v_i^2 \rangle - \langle \bar{v} \rangle^2} = \frac{\langle \bar{v}_i(t) \cdot \bar{v}_i(0) \rangle}{\langle v_i^2 \rangle}$$

where the average velocity is zero (can go in any direction)

vii. Useful to calculate, because the diffusion constant is given by

$$D = \frac{1}{3} \int_0^\infty dt \langle \bar{v}_i(t) \cdot \bar{v}_i(0) \rangle = \frac{\langle v^2 \rangle}{3} \int_0^\infty dt c_{vv}(t)$$

where $\langle v^2 \rangle$ is easy to calculate (see $\langle K \rangle$)

13. Recap of some useful thermodynamics

a. As we move to simulations, we will be calculating average thermodynamic quantities, which are related in the normal way.

b. For example, in the canonical ensemble we have

i. $A = -k_B T \ln Q_{NVT} = E - TS$

ii. $dA = -SdT - PdV + \sum_{i=1}^r \mu_i dn_i$

iii. so we have the usual relations: $\left(\frac{\partial A}{\partial T}\right)_{N,V} = -S$, $\left(\frac{\partial A}{\partial V}\right)_{N,V} = -P$, etc.

iv. Consider $\left(\frac{\partial A/T}{\partial 1/T}\right)_{N,V} = \left(\frac{\partial}{\partial 1/T} \left[\frac{E}{T} - S \right]\right)_{N,V} = E$

Of course, statistical mechanics gives the same result:

$$\begin{aligned} \left(\frac{\partial \beta A}{\partial \beta}\right)_{N,V} &= \left(\frac{\partial}{\partial \beta} - \ln Q_{NVT}\right)_{N,V} = -\frac{1}{Q_{NVT}} \left(\frac{\partial}{\partial \beta} \int dr^{3N} dp^{3N} e^{-\beta(K+U)}\right)_{N,V} \\ &= -\frac{1}{Q_{NVT}} \int dr^{3N} dp^{3N} - (K+U) e^{-\beta(K+U)} = \langle K+U \rangle = E \end{aligned}$$

where $\beta = 1/k_B T$.

v. Also, we have (show this) $\langle U \rangle = -\left(\frac{\partial \beta Z_{NVT}}{\partial \beta}\right)_{N,V}$, where Z_{NVT} is the

configurational integral defined in II.D.5.d.ii.3

c. microcanonical ensemble

i. $S = k_B \ln Q_{NVE}$

ii. $dS = \frac{1}{T} dE + \frac{P}{T} dV - \sum_{i=1}^r \mu_i dn_i$

d. isothermal-isobaric ensemble

i. $G = -k_B T \ln Q_{NPT} = A + PV = E - TS + PV$

ii. $dG = -SdT + VdP + \sum_{i=1}^r \mu_i dn_i$

iii. enthalpy $H = E + PV$

14. Phase stability

a. From free energy of two phases, can determine points where *phase transitions* can occur from one to another

i. Helmholtz free energy - the Maxwell construction

1. plot $A(N,T)/N$ versus V/N for each phase at the same T
2. find common tangent between curves
3. slope is $-P$, where P is the transition pressure.
4. can determine $\Delta(V/N)$ for the transition

ii. Gibbs free energy

1. plot $G(N,P,T)/N$ vs P for a given T
2. intersection of two curves is transition pressure

15. Further words on fluctuations (see II.D.9)

- a. suppose simulating in a canonical (NVT) ensemble, where E is not constant but fluctuates

- i. the distribution in E would look something like
- ii. the relative root mean square (rms) value of the fluctuations is

$$\frac{\sqrt{\langle (E - \langle E \rangle)^2 \rangle_{NVT}}}{\langle E \rangle} = \frac{\sqrt{k_B T^2 C_V}}{\langle E \rangle} \sim \mathcal{O}\left(\frac{1}{\sqrt{N}}\right)$$

- iii. for "real" systems, $N \sim 10^{23}$, so the relative rms fluctuations is $\sim 10^{-11}$ so the distributions are highly peaked.
- iv. Note that for computer simulations with $N \sim 10^4$, the relative fluctuations are reasonably large.

16. Radial distribution functions

a. gives correlation between particle positions

b. $g(r)$ is defined (formally) by $g(r) = \frac{V}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(\vec{r} - \vec{r}_{ij}) \right\rangle$

c. $g(r)$ gives the probability of finding atoms a distance r apart

i. it says nothing of the structure, just the distance (from which we infer structure)

d. The number of neighbors in a sphere of radius r around a central atom is given by

$$n = 4\pi\rho \int_0^r r^2 g(r) dr$$

e. Typical $g(r)$ for a liquid

f. For a solid like fcc, would have peaks centered at each neighbor distance, i.e.,

for fcc at r_{nn} , $\sqrt{2}r_{nn}$, $\sqrt{3}r_{nn}$, ... Integrating $4\pi r^2 g(r) dr$ over each peak will give the number of neighbors, i.e., for fcc 12, 6, 24, ...

g. Besides telling us structure, we can also show that the average potential energy and the average pressure can be calculated from $g(r)$. For a pair interaction:

$$\langle U \rangle = 2\pi \frac{N^2}{V} \int_0^\infty r^2 \phi(r) g(r) dr \quad \text{and} \quad PV = Nk_B T - (2/3)\pi \frac{N^2}{V} \int_0^\infty r^2 \left\{ r \frac{\partial \phi(r)}{\partial r} \right\} g(r) dr$$

E. Atomistic Simulations

1. Given a description of the potential energy, a *computer simulation* can give us the properties of a material at finite temperatures
 - a. thermodynamic quantities:
 - i. equation of state: PV, EV, etc.
 - ii. phase transitions: melting points, solid-solid transitions, etc.
 - b. structural properties
 - i. crystal structures, fluid structures
 - c. defect properties: grain-boundaries, dislocations, etc.
 - d. dynamical properties: fracture, time correlation functions, etc.
2. Depending on what you want, you can choose from three main methods
 - a. Quasiharmonic theory
 1. assume a harmonic lattice and do lattice dynamics
 2. yields the free energy
 3. no dynamics and restricted to solids where we know the structure
 - b. Molecular Dynamics (MD)
 1. solve Newton's equations and find time averages
 2. yields dynamic information
 - c. Monte Carlo (MC)
 1. numerically sample ensembles to find averages
 2. generally yields only average quantities - no dynamics
3. Depending on what you want, can also choose the ensemble to work in
4. The goal is to determine averages
5. We'll start our discussion with lattice dynamics.

F. Lattice Dynamics (See "Statistical Mechanics," by D. McQuarrie, Chapter 11).

1. In solids at equilibrium, the atoms vibrate around their equilibrium positions with the interatomic distance larger than the amplitude of the vibrations.
 - a. we approximate the potential energy of such a system as follows:
 - i. let $\bar{r}_i^0$ be the equilibrium position of particle i.
 - ii. Define $\bar{\xi}_i \equiv \bar{r}_i - \bar{r}_i^0$ as the deviation from the equilibrium positions ($|\bar{\xi}_i|$ is assumed to be small).
 - iii. Expand the total potential energy U around all $\bar{\xi}_i = 0$.

$$U(\bar{\xi}_1, \bar{\xi}_2, \dots, \bar{\xi}_N) = U(0, 0, \dots, 0) + \sum_{i=1}^N \sum_{\alpha=1}^3 \left(\frac{\partial U}{\partial \xi_{i\alpha}} \right)_0 \xi_{i\alpha} \\ + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \sum_{\alpha=1}^3 \sum_{\beta=1}^3 \left(\frac{\partial^2 U}{\partial \xi_{i\alpha} \partial \xi_{j\beta}} \right)_0 \xi_{i\alpha} \xi_{j\beta} + \dots$$

where we explicitly sum over the components of the positions, where here and below, Roman indices indicate atoms and Greek indices indicate components of the coordinates (i.e., x, y, or z).

1. Note that we take derivatives with respect to the components of

$\bar{\xi}_i \equiv \bar{r}_i - \bar{r}_i^0$ and that, since the $\bar{r}_i^0$ are fixed at the equilibrium positions, this is the same as taking derivatives with respect to the components of $\bar{r}_i$.

2. The derivatives are taken and then evaluated at $\{\bar{\xi}_i \equiv 0\}$.

iv. the first term is just the cohesive energy when all the atoms are in their equilibrium positions, U_0 , and the second term is, by definition of the minimum, zero when at equilibrium.

v. if we write the force constant matrix as $K_{ij\alpha\beta} = \left(\frac{\partial^2 U}{\partial \xi_{i\alpha} \partial \xi_{j\beta}} \right)_0$ and we

truncate at the second-order term, we have

$$U(\bar{\xi}_1, \bar{\xi}_2, \dots, \bar{\xi}_N) = U_0(N, V) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \sum_{\alpha=1}^3 \sum_{\beta=1}^3 K_{ij\alpha\beta} \xi_{i\alpha} \xi_{j\beta} + \dots$$

Remember that U_0 depends on the equilibrium positions as well as the density of the system, $\rho = N/V$.

vi. Consider $K_{ij\alpha\beta}$. Here, i and j are particles, α and β are components of the displacement vectors, i.e., x, y, or z. If U is a sum of pair potentials, $\phi(r_{ij})$, then we have

$$K_{ii\alpha\beta} = \sum_{j \neq i=1}^N \left\{ \left(\frac{\partial^2 \phi(r_{ij})}{\partial r_{ij}^2} \right)_0 \left[\frac{(r_{j\alpha}^0 - r_{i\alpha}^0)(r_{j\beta}^0 - r_{i\beta}^0)}{(r_{ij}^0)^2} \right] \right. \\ \left. + \left(\frac{\partial \phi(r_{ij})}{\partial r_{ij}} \right)_0 \left[\frac{\delta_{\alpha\beta}}{r_{ij}^0} - \frac{(r_{j\alpha}^0 - r_{i\alpha}^0)(r_{j\beta}^0 - r_{i\beta}^0)}{(r_{ij}^0)^3} \right] \right\}$$

$K \approx$ is block form

$ii \Rightarrow$ lattice sums
 $ij \Rightarrow$ no lattice sums

$$K_{ij \neq i\alpha\beta} = - \left\{ \left(\frac{\partial^2 \phi(r_{ij})}{\partial r_{ij}^2} \right)_0 \left[\frac{(r_{j\alpha}^0 - r_{i\alpha}^0)(r_{j\beta}^0 - r_{i\beta}^0)}{(r_{ij}^0)^2} \right] + \left(\frac{\partial \phi(r_{ij})}{\partial r_{ij}} \right)_0 \left[\frac{\delta_{\alpha\beta}}{r_{ij}^0} - \left(\frac{(r_{j\alpha}^0 - r_{i\alpha}^0)(r_{j\beta}^0 - r_{i\beta}^0)}{(r_{ij}^0)^3} \right) \right] \right\}$$

where $\delta_{ij}=1$ if $i=j$ and 0 otherwise, and the superscript 0 means that these are distances between atoms at their equilibrium sites.

- vii. It is straightforward to derive this for other potentials, like EAM.
 - b. We have approximated the system as a set of coupled harmonic oscillators. They are coupled because of the terms in $K_{ij\alpha\beta}$ that connect different atoms, i.e., $K_{ij \neq i\alpha\beta}$.
2. Vibrational frequencies.
- a. We need to solve for the vibrational frequencies, which are just the eigenvalues of the mass weighted force constant matrix (see McQuarrie).
 - i. If this is a one-component system, the mass weighted force constant matrix is just $K_{ij\alpha\beta}/m$, where m is the mass of the atom. If it is a multicomponent system, then we divide each component in $K_{ij\alpha\beta}$ by $\sqrt{m_i m_j}$.
 - b. If we have an N atom system with no periodic boundaries, then we just solve for eigenvalues of the mass-weighted $K_{ij\alpha\beta}$ (using some canned program).
 - i. The eigenvalues of the dynamical matrix are the *normal mode frequencies*, $\omega_i = 2\pi\nu_i = \sqrt{\frac{k_i}{\mu_i}}$, $i=1 \dots 3N-6 \sim 3N$.
 - 1. There are $3N-6$ of these *normal modes*, where the 6 arises from the 3 translations and 3 rotations of the system as a whole.
 - 2. k_i and μ_i are effective force constants and mass
 - c. If we have periodic boundaries, then we need to take into account of the symmetry that this introduces.
 - i. See Ashcroft and Mermin Chapter 22 for a description of generating the dynamical matrix, which incorporates this symmetry.
3. Free energy
- a. Given the vibrational frequencies, ω_i , we have for the total energy

$$E = U_o(N, V) + \sum_{i=1}^{3N} \left(n_i + \frac{1}{2} \right) \hbar \omega_i, \text{ where since the vibrational states are } \textit{quantized}$$

we need to sum over states.

- i.. The 1/2 accounts for the fact that there is energy associated with the lowest lying state - the zero-point energy - a strictly quantum phenomena
- ii. note that at high enough T, the average state $\langle n \rangle$ will be greater than 1
- b.. Because of the discrete form of E, we can over states and evaluate the canonical partition function, which is:

$$Q(p, T) = e^{-U_o(N, V) / k_B T} \prod_{i=1}^{3N} \left(2 \sinh(\hbar \omega_i / 2 k_B T) \right)^{-1}$$

- c. The Helmholtz free energy is then ($A = -k_B T \ln Q$)

$$A(N, V, T) = U_o(N, V) + k_B T \sum_{i=1}^{3N} \ln \left(2 \sinh(\hbar \omega_i / 2 k_B T) \right)$$

- d. The above expression is for a quantum system. The equivalent results for a strictly classical system (i.e., $\hbar$ is small) is

$$A(N, V, T) = U_o(N, V) + k_B T \sum_{i=1}^{3N} \ln(\hbar \omega_i / k_B T)$$

- e. If N is very large (like a periodic crystal) the 3N normal frequencies are essentially continuously distributed and we can introduce the function $g(\omega)d\omega$, which gives the number of frequencies between ω and $\omega+d\omega$, and we can write

$$A(N, V, T) = U_o(N, V) + k_B T \int \ln \left(2 \sinh(\hbar \omega_i / 2 k_B T) \right) g(\omega) d\omega$$

- f. From A, we can calculate all thermodynamics.

4. Quasiharmonic theory

- a. Suppose one wanted the free energy of a harmonic crystal. For each density, one could calculate the dynamical matrix and find the frequencies. Note that these frequencies are independent of T - they only depend on structure. Which vibrational levels are populated depends on T.
- b. NOTE: must first find equilibrium positions by doing a lattice minimization, otherwise the linear term in the equation in II.F.1.a.iii is not zero.
- c. In a simulation, N is finite and we typically find all the frequencies and evaluate the free energy with the sum over frequencies, like in II.F.3.c, and find $A(N, V, T)$. Note: determine frequencies once for each volume and configuration and just vary T. This gives $A(T)$ for a specific V.
- d. Construct a family of $A(T)$ curves for a series of volumes.

- e. From the $A(T)$ curves for each volume, construct an $A(V)$ curve for each temperature of interest.
 - f. From $A(V)$ at constant T , can find the pressure $(\partial A / \partial V)_{N,T} = -P$. From this can construct $V(T)$ and $A(T)$ at constant P , i.e., the thermal expansion and free energy, i.e., the Gibbs free energy.
 - g. This is quasiharmonic lattice theory and yields reasonable values for the volume and free energy until close to the melting point, when the vibrations become more anharmonic and defects become important.
 - h. Has been used (by Adams) to study thermal properties of defects.
5. Positives and negatives:
- a. the most useful aspect of quasiharmonic lattice theory is that it gives free energies, which are hard to obtain otherwise
 - i. can predict phase stability
 - b. for small systems, it is very useful
 - c. for large systems, since we need to diagonalize a $3N \times 3N$ matrix, which is very time consuming for large N , other ways (MD and MC) are often easier

so generate

$V(T)$
 $A(T)$

for $P=0$ (or whatever)

note $P=0 \Rightarrow$ same as 1 atm
for a solid

G. Molecular Dynamics (MD)

1. What is MD?

- a. in MD, we calculate the forces on each atom and solve Newton's equations of motion to find how the positions and velocities of each atom change with time, i.e., we calculate the trajectory through phase space.

2. Equations of motion

- a. In Classical Mechanics, there are a number of ways to write the equations of motion (see Goldstein). We use the Hamiltonian equations of motion in molecular dynamics.

- i. $H(\mathbf{r}^{3N}, \mathbf{p}^{3N}) = K(\mathbf{p}^{3N}) + U(\mathbf{r}^{3N})$

- ii. in cartesian coordinates, Hamilton's equations become:

1. $\dot{\mathbf{r}}_i = \frac{\bar{\mathbf{p}}_i}{m}$ and $\dot{\bar{\mathbf{p}}}_i = -\nabla_{\mathbf{r}_i} U(\mathbf{r}^{3N}) = \bar{\mathbf{f}}_i$ (just standard $\mathbf{f} = m\mathbf{a}$)

2. $\nabla_{\mathbf{r}_i} U(\mathbf{r}^{3N})$ is the gradient of U with respect to the coordinates of atom i and $\mathbf{f}$ is the force on atom i .

3. For a system described by pair potentials, the force becomes

$$\begin{aligned}\bar{\mathbf{f}}_i &= -\bar{\nabla}_i U = -\sum_{\alpha=1}^3 \left(\frac{\partial U}{\partial r_{i\alpha}} \right) \hat{\mathbf{r}}_\alpha = \sum_{j \neq i=1}^N \sum_{\alpha=1}^3 \left(-\frac{\partial \phi(r_{ij})}{\partial r_{i\alpha}} \right) \hat{\mathbf{r}}_\alpha \\ &= \sum_{j \neq i=1}^N \sum_{\alpha=1}^3 \left(-\frac{\partial \phi(r_{ij})}{\partial r_{ij}} \right) \left(\frac{\partial r_{ij}}{\partial r_{i\alpha}} \right) \hat{\mathbf{r}}_\alpha = \sum_{j \neq i=1}^N \sum_{\alpha=1}^3 \left(-\frac{1}{r_{ij}} \frac{\partial \phi(r_{ij})}{\partial r_{ij}} \right) (r_{j\alpha} - r_{i\alpha}) \hat{\mathbf{r}}_\alpha\end{aligned}$$

$$\text{or } \mathbf{f}_{i\alpha} = \sum_{j \neq i=1}^N \mathbf{f}_{ij\alpha}, \text{ where } \mathbf{f}_{ij\alpha} = \left(-\frac{1}{r_{ij}} \frac{\partial \phi(r_{ij})}{\partial r_{ij}} \right) (r_{j\alpha} - r_{i\alpha})$$

where $\hat{\mathbf{r}}_\alpha$ is the the unit vector for the α th coordinate.

4. Note that with pairwise, central-force potentials, the force depends only on the separation between atoms. We find what we expect: $\mathbf{f}_{ij\alpha} = -\mathbf{f}_{ji\alpha}$, i.e., the force of i on j is minus that of j on i (one of Newton's laws.) This can be used to save time computationally.
5. Straightforward to derive force for EAM-like potentials. (will give in an Appendix)

b. Conservation of energy.

- i. it is straightforward to show that the derivative of H with respect to time, $\partial H / \partial t$, is zero, i.e., the energy is conserved (constant) (as long as K doesn't

depend on r and U does not depend on p)

c. Conservation of momentum

- i. For the periodic boundary conditions used here, the total momentum,

$$\bar{P} = \sum_{i=1}^N \bar{p}_i, \text{ is also conserved (constant)}$$

1. for convenience, choose the initial velocities with $P=0$ so that there is no overall drift of atoms

- ii. The total angular momentum, $\bar{L} = \sum_{i=1}^N \bar{r}_i \times \bar{p}_i$, is not, however, conserved.

- i. in practice, can start with it small and it doesn't change much.

d. Ensemble

- i. If momenta were not conserved, then this would be strictly in the NVE (microcanonical) ensemble. Strictly speaking, MD calculations are not, in the microcanonical, because of the extra conserved quantity. However, the differences are small and we will ignore them

3. Solving the equations of motion

a. initial conditions:

- i. have some initial set of $\{\bar{r}_i\}$ and $\{\bar{p}_i\}$
ii. will discuss how to set up below

- b. need to integrate the equations of motion to find changes of $\{\bar{r}_i\}$ and $\{\bar{p}_i\}$ with time

- c. there are many many methods, we'll show just one in detail here

- d. note that all methods assume that we use a discrete time step, δt .

4. Finite-difference methods:

- a. suppose we have an initial value for the position and its first three derivatives, $\bar{r}_i$, $\bar{v}_i$, $\bar{a}_i$, and $\bar{b}_i$ at time t

- i. assume continuous trajectories and that we can use a Taylor series to predict the values at $t+\delta t$ from those at t :

$$\bar{r}_i^p(t + \delta t) = \bar{r}_i(t) + \bar{v}_i(t) \delta t + \frac{1}{2} \bar{a}_i(t) \delta t^2 + \frac{1}{6} \bar{b}_i(t) \delta t^3 + \dots$$

$$\bar{v}_i^p(t + \delta t) = \bar{v}_i(t) + \bar{a}_i(t) \delta t + \frac{1}{2} \bar{b}_i(t) \delta t^2 + \dots$$

$$\bar{a}_i^p(t + \delta t) = \bar{a}_i(t) + \bar{b}_i(t) \delta t + \dots$$

$$\bar{b}_i^p(t + \delta t) = \bar{b}_i(t) + \dots$$

- iii. the superscript p means that these are the predicted values.
 - b. We could truncate at these equations and integrate with time.
 - i. incorrect trajectories, because they do not include the equations of motion
 - c. the goal of all the methods used to find trajectories is to make best use of the equations of motion.
5. Verlet algorithm
- a. just one of many in use.
 - i. used in the MD code for this course
 - b. not the best, but will do for now
 - c. we advance the positions as $\vec{r}_i(t + \delta t) = 2\vec{r}_i(t) - \vec{r}_i(t - \delta t) + \vec{a}_i(t) \delta t^2$
 - i. Where did this come from? From adding Taylor expansions around $r(t)$:

$$\vec{r}_i(t + \delta t) = \vec{r}_i(t) + \vec{v}_i(t) \delta t + \frac{1}{2} \vec{a}_i(t) \delta t^2$$

$$\vec{r}_i(t - \delta t) = \vec{r}_i(t) - \vec{v}_i(t) \delta t + \frac{1}{2} \vec{a}_i(t) \delta t^2$$
 - ii. velocities never are used and are not calculated directly. Must estimate by

$$\vec{v}_i(t) = \frac{\vec{r}_i(t + \delta t) - \vec{r}_i(t - \delta t)}{2\delta t}$$
 - 1. this is not a very good estimate of v - there are improved ways (e.g., the velocity Verlet algorithm)
 - d. advantages
 - i. simple
 - ii. accurate (positions accurate to δt^4)
 - iii. low computer storage
 - iv. time reversible
 - e. variations
 - i. many. See [AT].
63. A typical MD run
- a. initialization
 - i. positions
 - 1. usually choose lattice structure (know it is low energy) or the output from some other run
 - ii. momenta (velocities)
 - 1. can start at some temperature T by choosing randomly from a Boltzmann distribution for each component of the velocities

2. set total momentum to zero. First find $P_\alpha = \sum_{i=1}^N p_{i\alpha}$, and then take

$$p_{i\alpha} = p_{i\alpha} - \frac{P_\alpha}{N}$$

3. rescale momenta to give desired initial temperature,

$$\gamma = 2K/3Nk_B = \frac{1}{3Nk_B} \sum_{i=1}^N p_i^2$$

$$p_{i\alpha} = \sqrt{\frac{T}{\gamma}} p_{i\alpha}, \text{ where } T \text{ is the temperature you want the system to be}$$

- b. integrate equations of motion

- i. advance system by δt by integrating equations of motion
- ii. at each time step calculate r , p , total momentum, U , K (and T), $E=U+K$, pressure, and correlation functions and anything else you want.
- iii. keep running averages of quantities
- iv. output (at given number of timesteps) instantaneous values and running averages
- v. go to i

- c. output the results

4. Is it working properly?

- a. Are energy and momentum conserved?

- i. check instantaneous values of E and total momentum
 1. if fluctuations are about 1 part in 10^4 then OK
 2. if there is drift, then not OK.
- ii. if not working
 1. decrease time step
 2. check program
 3. choose new algorithm

5. What do simulations look like?

- a. from a short run (10,000 time steps) I did with the class MD code
- b. LJ system in reduced units: $E^*=E/\epsilon$, $U^*=U/\epsilon$, $r^*=r/\sigma$, $T^*=kBT/\epsilon$,

$$P^*=P\sigma^3/\epsilon, t^*=t/t_0 \text{ (} t_0 = \sqrt{m\sigma^2/\epsilon} \text{), } f^*=f\sigma/\epsilon$$

- c. this run at $N=108$, $\rho^*=N/V^*=0.88$, and $T^*(\text{initial}) = 2$, time step $\delta t^* = 0.005$. I started it in a perfect fcc lattice with the goal of melting the solid. It worked!

- d. Note, except for initial transient, maximum fluctuations in E are about 0.0026 with the mean being about -4.56, i.e., relative fluctuations are about 6×10^{-4} , which is probably OK.

- e. ($T^* = 2/3 K^*/N$) Note started at $T^* = 2$, but dropped to about 1. Note that it doesn't settle down to the final value until after about the 2000th time step.

- f. Note that the fluctuations in U (and K) are about 0.1, about 50 times greater than those in E ($=K+U$).

9

5. Equilibration.

- i. general comments. Note that at the beginning of the calculation, there is a trade off between kinetic and potential energy while equilibrium is established - the potential energy goes up, and so the kinetic energy must go down, since $E=K+U$ is constant.
- ii. This is a general circumstance. After starting a simulation, must wait until it equilibrates before taking any average quantities. In other words, we must let all initial transients die off before we start interrogating the system.
- iii. For example, in the runs shown above. With the volume I set and the temperature, this is a state in the liquid. However, I started it with the atoms in a perfect fcc lattice. Clearly, the system must melt before we can start studying the properties of the liquid.
- iv. How long is enough for equilibration? It depends on the system. One should run until the instantaneous values show no drift, i.e., they are fluctuating around a mean value. There are statistical ways to tell this.
- v. However, thermodynamic quantities may not be sensitive enough to structure to tell us the state of the system. We can calculate order parameters to tell solid from liquid, for example, or from one solid structure and another. The translational

order parameter $\rho(\mathbf{k}) = \frac{1}{N} \sum_{i=1}^N \cos(\bar{\mathbf{k}} \cdot \bar{\mathbf{r}}_i)$ can be used to watch melting, where $\mathbf{k}$ is a reciprocal lattice vector. For fcc, for example, choosing $\mathbf{k} = (2\pi/a)(-1, 1, -1)$, where a is the unit cell length, the $\rho(\mathbf{k}) = 1$ for a perfect fcc lattice and it goes to near zero in the liquid.

$$\langle T^* \rangle \approx 1.0$$

$$\rho^* = .88$$

blow up of σ_b

- v. $\rho(k)$ for this simulation. Note that melting doesn't really start until about 1600 time steps.
- vi. What does it look like for something that doesn't melt? This is from a run with $\langle T^* \rangle = 0.55$ at the same density:

$$\langle T^* \rangle \approx .55$$

$$\rho^* = .88$$

Note that it settles around 0.85. It isn't 1 because not a perfect lattice.

106.

Structural analysis.

- there are many other order parameters and correlation functions one can calculate to describe the structure of the system.
- One that we've mentioned is the radial distribution function. One calculates this as described in [AT]. You can look at the MD code for this course as well.

$$\langle T^* \rangle \sim 1$$

$$\rho^* = .88$$

drop off
this is an
artifact of
the simulation -
it is where the
cutoff is.

- c. $g(r)$ for the case with $\langle T^* \rangle \sim 1$. Note that is clearly a liquid.

- d. $g(r)$ for the case with $\langle T^* \rangle = 0.55$, note that this is a solid! You can clearly see the neighbor peaks, though the T is high enough that there is a lot of vibration, so the peaks are very broad.

(17) Data analysis (see [AT] for a very complete discussion)

- a. We want to determine average values of quantities.
 - i. **MUST START AVERAGING AFTER EQUILIBRATION.**
 - ii. Simulations are like experiments - must have good statistical analysis of both averages and fluctuations.
- b. Suppose have equilibrated the system, how do we get good averages?
 - i. suppose make a file with all the values of, for example, the potential U for each time step. (Note that the averaging of all quantities is the same).
 - ii. As we've said before, the average of U is just the time average

$$\langle U \rangle_{\text{run}} = \frac{1}{\tau_{\text{run}}} \sum_{\tau=1}^{\tau_{\text{run}}} U(\tau), \text{ where } \tau_{\text{run}} \text{ is just the length of the simulation}$$

- iii. We've given expressions for the fluctuations before and these we can calculate.
- iv. But, suppose one asks a different question. What is the variance of the mean of a quantity, i.e., $\sigma^2(\langle U \rangle_{\text{run}})$. This is just statistics, not thermodynamics. We're trying to find out what quality of result do we have for $\langle U \rangle$.

1. if all the values of U (or whatever) were statistically independent, then we'd have $\sigma^2(\langle U \rangle_{\text{run}}) = \frac{1}{\tau_{\text{run}}} \sigma^2(U)$, i.e., the variance in $\langle U \rangle$ would be

$$\text{just the average of the fluctuations in } U, \sigma^2(U) = \frac{1}{\tau_{\text{run}}} \sum_{\tau=1}^{\tau_{\text{run}}} (U(\tau) - \langle U \rangle_{\text{run}})^2$$

2. The problem is that the values of U are NOT independent - we typically dump the data to a file sequentially, one time step after another. Thus, a position at one time step is close to that at the previous time step, and the energy doesn't change much. How do we get a good variance?
3. To avoid the correlations in data, we divide the run into n_b bins of some length τ_b . We then find the averages over the bins and find the variance of those bin averages. We only need to make sure that the bins include enough steps so that the data at the end of the bin is uncorrelated

$$\text{from that in the beginning: } \langle U \rangle_b = \frac{1}{\tau_b} \sum_{\tau=1}^{\tau_b} U(\tau) \text{ and}$$

$$\sigma^2(\langle U \rangle) = \frac{1}{n_b} \sum_{b=1}^{n_b} (\langle U \rangle_b - \langle U \rangle_{\text{run}})^2$$

4. NOTE: the program used in this course does not do this. One can write an analysis code to take the instantaneous values and calculate this variance.

note:
corrected
from
earlier
version

12. Reduced Units

- a. Consider the LJ system in the simulation. We used reduced units. Where do these come from? We discussed earlier how we scaled the energy by ϵ and the distance by σ , $E^* = E/\epsilon$, $U^* = U/\epsilon$, and $r^* = r/\sigma$ (I.B.4.f.iii). If we do a calculation with ϵ and σ set to one, then we can recover real units by multiplying the energy by ϵ and any distance by σ . Of course, the volume then needs to be multiplied by σ^3 . Note that $k_B T$ is an energy. We can thus define a dimensionless temperature $T^* = k_B T/\epsilon$. What about the kinetic energy? We want K to be in units of ϵ , but $K \sim mv^2$, whose units are mass*distance/time². But we want K in units of ϵ , so that means that time must be in units of $t^* = t/t_0$, where $t_0 = \sqrt{m\sigma^2/\epsilon}$. We can also define a reduced pressure and force as $P^* = P\sigma^3/\epsilon$ and $f^* = f\sigma/\epsilon$.

13. Time scale

- a. Note that we set the time step to be $\delta t = 0.005 t_0$. What is t_0 ? We need to know the potential parameters. So let's consider using an LJ potential to describe gold. Experimental data on Au shows the sublimation energy $E_{\text{sub}} = -45.66 \times 10^{-13}$ ergs, $r_{\text{nn}} = 2.893 \text{ \AA}$, and $B_0 = 99.9 \times 10^{10}$ dynes/cm². We can fit two of these with an LJ potential, using $E_{\text{sub}} \sim u = -8.6\epsilon$ and $r_{\text{nn}} = 1.09\sigma$ (see II.A.8), i.e., $\epsilon = 5.5309 \times 10^{-13}$ ergs and $\sigma = 2.654 \text{ \AA}$. Using the expression $B_0 = 75\epsilon/\sigma^3$, these potential parameters yield $B_0 = 213 \times 10^{10}$ dynes/cm², over a factor of 2 too high, showing that an LJ potential does not describe a metal very well.
- b. Using the atomic weight for Au, we see that the unit of time in this simulation is $t_0 = 6.4 \times 10^{-13}$ sec. Thus the time step is about 3.2×10^{-15} sec and the total time for the simulation (10 000 steps) is 0.032 nanosecond.
- c. Why is δt so small? To integrate the motion accurately, we find that we need about 40-50 time steps per the period of the fastest vibration, which in a solid is about 10^{-14} seconds.
- d. This small time step limits the utility of MD, as a nanosecond takes a million time steps.

14. Cutting off the potential

- a. Why?
 - i. For the same reasons we've discussed - save computing time.
- b. Choice of cutoff
 - i. balance between quality of results (i.e., the errors introduced by truncating the potential energy) and computer time.
- c. Computational burden:
 - i. suppose in an fcc system, we choose a cutoff a cutoff after the first nearest neighbors shell. There are just 12 neighbors, but the potential is not calculated accurately (problem set 1). If we cut off after the 4th shell of neighbors, there are 54 total neighbors; after 7 shells then 134 neighbors, and after 12 shells there are a total of 248 neighbors. Clearly, the potential energy is being calculated more and more accurately as the cutoff distance is increased (the point of problem set 1). However, the total computational burden goes roughly as the number of atoms in the cell, N , times the number of neighbors, M , i.e., computer time scales like MN . Clearly, the calculation with 248 neighbors is more accurate than that with 12, but it takes about 20 times

longer to do. NOTE: This assumes potentials that are reasonably short-ranged. Ionic solids have $1/r$ potentials and require different approach.

d. Correcting the results.

- i. we mentioned that the average potential energy and pressure for a system

described by pair potentials can be written as $\langle U \rangle = 2\pi \frac{N^2}{V} \int_0^\infty r^2 \phi(r) g(r) dr$

and $PV = Nk_B T - (2/3)\pi \frac{N^2}{V} \int_0^\infty r^2 \left\{ r \frac{\partial \phi(r)}{\partial r} \right\} g(r) dr$

1. for liquids, $g(r) \sim 1$ at large r , so we can find the errors due to cutting off

at r_c (long-range corrections) as $\Delta U_{lr} = 2\pi \frac{N^2}{V} \int_{r_c}^\infty r^2 \phi(r) dr$ and

$\Delta P_{lr} = (2/3)\pi \frac{N^2}{V^2} \int_{r_c}^\infty r^2 \left\{ r \frac{\partial \phi(r)}{\partial r} \right\} dr$, where for analytic potentials (like LJ)

these are easy to evaluate. We then have expressions like

$$\langle U \rangle = \left\langle \sum_{i=1}^N \sum_{j>i} \phi(r_{ij}) \right\rangle + \Delta U_{lr}$$

2. since we don't know what $g(r)$ is for solids, these equations are not really applicable there.

e. THE REAL PROBLEM WITH CUT OFFS.

- i. the force goes as the derivative of the potential
- ii. at a cutoff the potential is discontinuous, which means the derivative is infinite
- iii. infinities are always a problem
- iv. typically, we either construct a potential that goes smoothly to zero at the cutoff, or we shift the potential to make it zero at the cutoff. Note that if we shift the potential, the force is not infinite, but it is discontinuous. The class MD code uses a shifted potential, which we then correct for.

5. Getting the temperature we want

- a. The problem with MD is that it is NVE, where we want (usually) to compare with experiment at NPT. As we see above, the temperature will vary from the initial temperature in unpredictable ways. Also, to obtain the pressure we want will require varying the volume over a series of runs. This is very time consuming. There are, however, ways to handle these problems.
- b. fixing the temperature in NVE molecular dynamics
 - i. the easiest way is to rescale velocities as we discussed before. Suppose that

we want the system to be at T

- ii. if we start it at T , it will change over some time steps to

$$\overline{\epsilon} = 2K/3Nk_B = \frac{1}{3Nk_B} \sum_{i=1}^N \frac{p_i^2}{m_i}, \text{ as we see above.}$$

- iii. We can recover the T we want by rescaling the velocities as $p_{i\alpha} = \sqrt{\frac{T}{\overline{\epsilon}}} p_{i\alpha}$ after a number of time steps until the system stabilizes where we want it.
- iv. Consider the schematic runs shown. We could have, after a number of time steps, rescaled T . The system would then relax again from there, so we could rescale again after some more time steps. We could repeat that process until the system stays at the temperature we want. Note: must still wait for equilibration after the last time we rescale velocities before taking averages.

c. NVT molecular dynamics (see [AT])

- i. NOT CORRECT to just rescale velocities at each time step. This greatly biases the equations of motion and one can show that this is not really a canonical ensemble.
- ii. a number of methods have been suggested that have been shown to yield the correct canonical ensemble averages
- iii. one such method is the Nosé thermostat (Nosé, Mol. Phys. **52**, 255 (1984)).
1. introduce a new variable (i.e., degree of freedom) that represents (in some way) connecting the system to some reservoir of energy, so energy can flow to and from the reservoir so we can constrain the temperature at T .
 2. call that new variable s . Note that to have dynamical equations to solve in MD, we must also associate a momentum with s , p_s .
 3. the real particle velocities are related to the time derivative of position by

$$\vec{v} = s \dot{\vec{r}} = \frac{1}{m s} \vec{p}$$
 4. we need both a potential and kinetic energy to implement the dynamics
 5. Nosé showed that by choosing $U_s = (f+1)k_B T \ln s$ (where $f = 3N-3$) and T is the specified temperature) and $K_s = p_s^2 / 2Q$ (where Q is some coupling parameter), we recover the correct averages in the NVT ensemble
 6. the Hamiltonian is then $\mathcal{H} = K_s + K + U_s + U$, where K and U are determined in the usual ways

Don't worry about details here

7. From $\mathcal{H}$ (or the Lagrangian $\mathcal{L}$), we can easily derive the equations of motion: $\ddot{\vec{r}} = \vec{f}/m s^2 - 2\dot{s}\dot{\vec{r}}/s$ and $Q\dot{s} = \sum m \dot{r}_i^2 s - (f+1)k_B T/s$
8. so, instead of just solving the normal equations of motion, we need to solve an additional one for s , i.e., for the rate of energy flowing into an out of the reservoir. Very easy to implement.
9. Note that Q is a parameter that we set. Too high a Q results in slow energy flow and too low a Q leads to poor equilibration.
10. Note that while this truly yields a canonical ensemble distribution in r and p , it doesn't necessarily give the correct short-term dynamics - we've messed up the equations of motion.

16. Getting the pressure or stress we want

- a. We have the same problem with pressure as we do with temperature - we set the volume and don't really know what the pressure will be.
- b. we could vary the box size until we obtain what we want, but this is tedious.
- c. also, in solids, we may want to model solid-solid phase transitions that would require a change in symmetry of the box.
 - i. Example: suppose we wanted to model a transition in some material that is fcc to bcc. This is common as we raise the temperature towards the melting point. There are 4 atoms/unit cell in fcc and 2 atoms/unit cell in bcc. It is difficult to find a simulation cell that can hold multiples of the basic unit cells for both structures.
 - ii. For example, a simulation cell with $3 \times 3 \times 3$ fcc unit cells has 108 atoms, which would include $(54)^{1/3}$ bcc cells which is not an integer number.
 - iii. consider the following representation of a bcc structure:

top view of 2x2 set of bcc cells:

bcc as a face-centered tetragonal: where $a_{\text{fct}} = b_{\text{fct}} = \sqrt{2}a_{\text{bcc}}$ and

$$c_{\text{fct}} = a_{\text{bcc}}$$

- iv. so, one can describe an fcc to bcc transition by representing the bcc as a 4 atom/unit cell fct, if one can find a way to let the size of the simulation cell box lengths change, i.e., from fcc to fct.
- d. so, we want a method where we can set the pressure as well as one where we can let the simulation cell change.
- e. Constant pressure (stress) molecular dynamics: (Parrinello and Rahman, J. Appl. Phys. **52**, 7182 (1981)). NOTE: Have applied pressure (or stress) and the size and shape of simulation cell changes - the volume and lattice parameters fluctuate. So does the internal, calculated pressure (stress), though it should average to the applied pressure (stress). Note that for the constant pressure case, the enthalpy $H=E+PV=K+U+PV$ is constant, not the energy, i.e., this is the NPH ensemble.
 - i. to let box size change we want to work in scaled coordinates, as we did with the lattice sum program for an LJ solid (problem set 1).

ii. write the position of atom i as: $\vec{r}_i = \xi_i \mathbf{a} + \eta_i \mathbf{b} + \zeta_i \mathbf{c}$, where ξ, η, ζ are numbers between 0 and 1 and $\mathbf{a}, \mathbf{b}$, and $\mathbf{c}$ are vectors describing the simulation cell (like lattice vectors, but describing an N atom simulation cell not a unit cell).

iii. define a vector $\vec{s}_i = (\xi_i, \eta_i, \zeta_i)$ and a matrix $\mathbf{h}$ whose columns are, in order, the vectors $\mathbf{a}, \mathbf{b}$, and $\mathbf{c}$ (i.e., $\mathbf{h} = \{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$). Note the volume of the simulation cell is given by: $V = |\mathbf{h}| = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})$.

iv. then we can write $\vec{r}_i = \mathbf{h} \vec{s}_i$. Note that when describing atom positions in this way, the images of $\vec{s}_i$ in a periodic system are $\vec{s}_i + (\lambda, \mu, \nu)$, where λ, μ , and ν are integers that range from $-\infty$ to ∞ .

v. the distance between two atoms, r_{ij} , is given by (where superscript T means transpose)

$$r_{ij}^2 = (\vec{r}_j - \vec{r}_i) \cdot (\vec{r}_j - \vec{r}_i) = (\mathbf{h} \vec{s}_j - \mathbf{h} \vec{s}_i)^T (\mathbf{h} \vec{s}_j - \mathbf{h} \vec{s}_i) = (\vec{s}_j - \vec{s}_i)^T \mathbf{h}^T \mathbf{h} (\vec{s}_j - \vec{s}_i) = (\vec{s}_j - \vec{s}_i)^T \mathbf{G} (\vec{s}_j - \vec{s}_i)$$

vi. $\mathbf{G}$ is the metric tensor: $\mathbf{G} = \mathbf{h}^T \mathbf{h} = \begin{pmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{pmatrix}$

where the lattice vectors and angles are defined at left.

vii. As with the Nosé thermostat, we are going to connect our MD system to some external force. In this case, we are going to connect the system to an external piston that will put forces on the box sides, i.e., stresses.

viii. We need equations for the motion of the box as well as a potential energy of the simulation cell. We also need to express the equations of motion for the particles in terms of the changing simulation. For the latter, we use $\mathbf{G}$.

ix. Without going into details, we find the following expressions for the kinetic energy of the changing simulation cell: $\frac{1}{2} W \text{Tr}(\dot{\mathbf{h}}^T \dot{\mathbf{h}})$, where W is the "mass"

of the box (just some parameter) and Tr means trace. Note that W serves the same purpose as Q in the Nosé thermostat and its value is chosen to obtain stable results. Under hydrostatic pressure, the potential is just $P_{\text{ext}} V$, where V is the volume of the cell and P_{ext} is the external pressure that we apply.

x. The equations of motion under hydrostatic pressure are:

$$m_i \ddot{\vec{s}}_i = \mathbf{h}^{-1} \vec{f}_i - m_i \mathbf{G}^{-1} \dot{\mathbf{G}} \dot{\vec{s}}_i \text{ and } W \ddot{\mathbf{h}} = (\rho - P_{\text{ext}} \mathbf{I}) V (\mathbf{h}^T)^{-1}, \text{ where } \mathbf{I} \text{ is the identity matrix and the calculated pressure (stress) tensor is given below.}$$

xi. Note that the pressure isn't fixed within the system - it will fluctuate, but (one hopes) about the value of the applied pressure.

xi. stress tensor

1. in II.D.5.11 we gave an expression for the instantaneous pressure of a

system: $\rho = \frac{N}{V} k_B T - \frac{1}{3V} \sum_{i=1}^N \vec{r}_i \cdot \nabla_{\vec{r}_i} U$, where T is the instantaneous

temperature, which is proportional to the kinetic energy. Remembering the definition for the force (-gradient of U), we can rewrite this as

$$V\rho = \frac{1}{3} \sum_i m_i v_i^2 + \frac{1}{3} \sum_{i=1}^N \sum_{j>i} \vec{r}_{ij} \cdot \vec{f}_{ij}, \text{ where we wrote } T = 2K/3Nk_B, K = \text{the}$$

sum of $1/2 m v^2$, and wrote the force on i as a sum of the forces due to the other atoms in the system

2. The stress is really a tensor with 9 components given by

$$V\rho_{\alpha\beta} = \sum_i m_i v_{i\alpha} v_{i\beta} + \sum_i \sum_{j>i} r_{i\alpha} f_{ij\beta}, \text{ where (once again) the roman indices}$$

are particles and the greek indices are components of a vector. The

hydrostatic pressure is just $1/3 \text{Tr} \mathbf{P}$, where Tr is the trace ($\text{Tr} \mathbf{P} = \sum_{\alpha=1}^3 P_{\alpha\alpha}$).

We see that we recover our earlier expression for the pressure.

3. In the crazy coordinate system we have with the changing box MD, the

$$\text{stress tensor becomes } \rho_{\alpha\beta} = \frac{1}{V} \sum_i m_i (\mathbf{h}\vec{s}_i)_\alpha (\mathbf{h}\vec{s}_i)_\beta + \sum_i \sum_{j>i} (\mathbf{h}\vec{s}_{ij})_\alpha (\vec{f}_{ij})_\beta$$

xii. Equations of motion under external stress (not just a pressure).

1. Please see the paper by : Parrinello and Rahman, J. Appl. Phys. **52**, 7182 (1981) for details.

2. The main difference is that we replace the $P_{\text{ext}} V$ term for the energy associated with the constraint on the box by the term for the elastic strain energy $U_{\text{elastic}} = P_{\text{ext}} (V - V_0) + V_0 \text{Tr}(\sigma - P_{\text{ext}}) \epsilon$, where σ and ϵ are the applied stress and calculated strain tensors, respectively. Note that we measure everything with respect to some reference state (to get strains) and that this reference state has volume V_0 .

3. Other than some minor changes in the equations, everything is the same as for constant P .

xiii. How does it all work and what does it look like?

Will show
example
in class

1. For example, suppose that we started a system in an fcc structure, but that bcc was stable at this pressure (and temperature, which is calculated not set). The system could (and we hope would) spontaneously change its lattice parameters such that it became a face-centered tetragonal, with two lattice parameters $\sqrt{2}$ times the other.
 2. We could use this to study phase transitions. For example, could do a series of calculations at a given pressure, slowly increasing the energy (and thus temperature) until the system spontaneously changes into a new structure.
17. Getting pressure and temperature what we want.
- a. use some combination, for example, of the Nosé thermostat and the Parrinello-Rahman variable box boundary conditions.
18. General comments about the utility of MD.
- a. limitations
 - i. very short times - $\delta t \sim 10^{-15} - 10^{-14}$ seconds
 1. typical time of a long run is about 1 nanosecond
 - ii. system sizes are small
 1. number of calculations scales as the number of atoms N .
 2. the linear size of a system scales as the $1/3$ power of the number of atoms. For example, if we have N atoms in a cubic volume V , the volume per atom is V/N , which is L^3/N , where L is the size of the box. Suppose we wanted to double L (i.e., look at a system twice as big), keeping the density the same. How many atoms would we need? We want $L^3/N = (2L)^3/N_2$, where N_2 is the number of atoms in the bigger system, $N_2 = 8N$.
 3. For example, a cubic micron of Cu would require about 8×10^{11} atoms.
 - iii. the potentials aren't so great.
 - iv. does not yield free energies
 - b. advantages
 - i. get dynamical information as well as thermodynamics
 - ii. can study fundamental properties of defects as well as bulk thermodynamics
 - c. prospects for future
 - i. BIG computers mean bigger systems.
 - ii. for example, the CM-5 is a massively-parallel computer
 1. 1024 CRAY 1s
 2. 26 M dollars

H. Monte Carlo (MC)

1 History of the Monte Carlo method

- devised at Los Alamos in the 1940s to solve multidimensional integrals
- While the method is based on statistical sampling (e.g., gambling), it is not called Monte Carlo because of that. At least not directly. It seems that about once a year, Stan Ulam's uncle (?) had to go to Monte Carlo to gamble. He just had to go. There was nothing else for him but to go to Monte Carlo. Ulam called this method the Monte Carlo method because it can solve problems that cannot be solved any other way.

2. What is MC?

- Earlier, we said that averages, such as for the potential energy, are given by

$$\text{expressions like } \langle U \rangle_{\text{NVT}} = \frac{\int dr^{3N} U(r^{3N}) e^{-U(r^{3N})/k_B T}}{\int dr^{3N} e^{-U(r^{3N})/k_B T}} = \int dr^{3N} U(r^{3N}) \rho_{\text{NVT}}(r^{3N}),$$

where $\rho_{\text{NVT}}(r^{3N}) = e^{-\beta U(r^{3N})} / \int dr^{3N} e^{-\beta U(r^{3N})}$ is the probability density of being in a configuration defined by a specific set of coordinates.

- in MD, we evaluated $\langle U \rangle$ by averaging over time
- in MC, we calculate these averages by *sampling* the configurations in discrete

steps, i.e., we'll find $\langle U \rangle_{\text{NVT}} = \sum_{i=1}^N U(r_i^{3N}) \rho_{\text{NVT}}(r_i^{3N})$, where the r_i^{3N} is just a series of configurations.

3. Why not integrate $\langle U \rangle$ directly?

- too many integrals - $3N$
- Since each term in U depends on more than one coordinate, we cannot evaluate the integrals.

4. How do we sample phase space?

- Technically, we need to sample all possible configurations.
- Some of these will be very improbable. For example, a set of atom positions that has two atoms close to each other would have very high energy and so $\exp(-\beta U)$ would be vanishingly small. The system will never attain that configuration. It turns out that $\rho_{\text{NVT}}(r^{3N})$ is very sharply peaked - of all possible configurations, there are relatively few that are probable. Note I said relatively. There are still huge numbers of configurations that are probable, it is just a far fewer number than the total.

i. Example: In a harmonic solid, we know the atoms stay close to their equilibrium positions.

c. Sampling all configurations with no regard to their probability would not be efficient.

d. Example: Suppose we wanted to measure the average depth of the Nile river. We could go all over the world measuring its depth and would find that most places it is zero. Or we could restrict our measurements to the river itself. Obviously the latter is more efficient.

e. We need a way to sample only those configurations that have non-vanishing probability. This is called *importance sampling*.

5. The Metropolis algorithm

a. Classic paper by Metropolis, Rosenbluth, Rosenbluth, Teller and Teller, June 1953. (This clearly shows that if you are going to collaborate with a number of people, be first author!)

b. It is a method that samples configuration space with a probability $\rho_{\text{NVT}}(r^{3N})$, i.e., it restricts the sampling to configurations that have non-vanishing probability.

c. Basic Metropolis algorithm:

i. We are going to construct a series of configurations v with the energy of each configuration being E_v .

ii. Suppose we are in a specific configuration i with E_i .

iii. We make a *trial* by moving the system randomly to a new configuration $i+1$ and find E_{i+1} .

iv. Calculate $\Delta E_{i+1,i} = E_{i+1} - E_i$.

v. Accept or reject move according to:

1. $\Delta E_{i+1,i} \leq 0$ then accept (because the probability is $\exp(-\beta \Delta E_{i+1,i}) > 1$)

2. $\Delta E_{i+1,i} > 0$ then accept move with probability $\exp(-\beta \Delta E_{i+1,i})$

a. How do we do this?

let x be points
at random

better if we had

[Handwritten signature]

[Handwritten signature]

So, the series of energies might look like

configurations →

We find a random number R between $(0,1)$. If $R < \exp(-\beta\Delta E_{i+1,i})$ (like ζ_1 in the picture), then we accept the move. If $R \geq \exp(-\beta\Delta E_{i+1,i})$ (like ζ_2 in the picture), then we reject the trial move.

- d. Generate the next configuration in the series:
 - i. If the trial move is accepted, then the configuration $i+1$ is the next configuration in the series.
 - ii. If we reject the move, then we duplicate configuration i as the next step in the series
 - iii. Each trial generates a configuration in the sequence, it just may be the same as the one previous to it.
- f. Can show that this algorithm generates a series of configurations with the correct probability for the canonical ensemble (see below).
- g. The average of a quantity G is just the average of its value over all the configurations in the series:

$$\langle G \rangle = \frac{1}{\tau} \sum_{v=1}^{\tau} G_v, \text{ where } \tau \text{ is the total number of trial moves.}$$

1. We create a series of configurations with the correct probability, evaluate G at each configuration, and average G over that series.
 2. NOTE: when we reject a trial move, we then set the configuration of the system to what it was before the trial move, count that as a configuration, accumulate averages and go to the next step (trial).
6. Does the Metropolis algorithm yield the correct distribution?
 - a. How can we generate a canonical distribution?
 - i. ρ_i is the probability that the system is in state i ($\rho_i = e^{-\beta E_i} / Q$)

- ii. let w_{ij} be the probability with time that the system goes from state i to state j
- iii. the time-rate of change of ρ_i is then just $\frac{d\rho_i}{dt} = -\sum_j w_{ij}\rho_i + \sum_j w_{ji}\rho_j$, where the first term is the rate the system leaves state i and the second term is the rate it enters state i .

- iv. at equilibrium $\frac{d\rho_i}{dt} = 0 = \sum_j (-w_{ij}\rho_i + w_{ji}\rho_j)$, so

$$\frac{w_{ij}}{w_{ji}} = \frac{\rho_j}{\rho_i} = \frac{e^{-\beta E_j} / Q}{e^{-\beta E_i} / Q} = e^{-\beta(E_j - E_i)}$$

- v. Thus, if we have a method to sample the configurations that yields $w_{ij} / w_{ji} = e^{-\beta(E_j - E_i)}$, then that sampling creates a canonical distribution

b. Does the Metropolis algorithm yield a canonical distribution?

- i. clearly the rate of going from state i to state j is proportional to the probability of going from i to j : $w_{ij} = C \text{ prob}(i,j)$, where C is some constant.
- ii. in the Metropolis algorithm, we have: $\text{prob}(i,j) = 1$ if $\Delta E_{ij} \leq 0$

$$\text{prob}(i,j) = e^{-\beta \Delta E_{ij}} \text{ if } \Delta E_{ij} > 0$$

$$\text{we have } \frac{w_{ij}}{w_{ji}} = \frac{C}{C e^{-\beta(E_i - E_j)}} = e^{-\beta \Delta E_{ij}} \text{ if } \Delta E_{ij} \leq 0$$

$$\text{and } \frac{w_{ij}}{w_{ji}} = \frac{C e^{-\beta(E_j - E_i)}}{C} = e^{-\beta \Delta E_{ij}} \text{ if } \Delta E_{ij} > 0.$$

- iii. Thus, the Metropolis algorithm generates the canonical ensemble

7. Application to spin systems

a. Ising model

- i. suppose have a two-dimensional square lattice
- ii. on each lattice site there is a spin with two possible values, $S_i = +1$ or -1
- iii. suppose the energy of the system is defined by $E = -\frac{1}{2} J \sum_{i=1}^N \sum_{nn} S_i S_j$, where we sum over the nearest neighbors only.
- iv. This is the Ising model. It is often used to describe magnetism.
- v. lowest energy state is one with all spins at $+1$ or all at -1 , i.e., the minimum energy state is $E_{\min} = -2NJ$ (4 nearest neighbors).

b. Monte Carlo simulation

- i. We want to find $\langle E \rangle$, $\langle S_i S_j \rangle$, etc. at $T > 0$.
- ii. Pick N, V , and T
- iii. generate a series of configurations with Monte Carlo method
 1. pick a lattice site at random
 2. make a trial change of the spin value (i.e., if +1 then go to -1 or vice versa)
 3. calculate the change in energy ΔE
 4. accept or reject the move according to the Metropolis algorithm
 5. if accept, then move to the new configuration with the new energy
 6. if reject, then the next configuration is the old configuration at the old energy
- iii. accumulate average energy, etc.
- c. What does data look like? Just like MD with fluctuations and everything. See the MD section for data analysis.
- d. The Q-state Potts model for grain growth: Just have Q spin values possible per site with energy $E = -\frac{1}{2} \sum_i \sum_{nn} J_{ij} (1 - \delta_{s_i, s_j})$, i.e., if the spins on adjacent sites are the same, then the energy is zero, if different, then the energy is J . As we shall see, we will use the MC method in this case to generate dynamics.
8. Application to atomic systems
 - a. Sampling of positions
 - i. pick atom at random
 - ii. move to new position by random displacement along each of the coordinate directions
 1. if R is a random number on $(0,1)$, then we have

$$x_i(\text{new}) = x_i(\text{old}) + (2R - 1)\Delta r_{\text{max}}$$
 where Δr_{max} is a parameter that defines the maximum displacement possible.
 2. Do the same for the other two directions, using a different random number for each trial.
 3. This defines the new position.

4. In the figure, the shaded square centered around one of the atoms is $\Delta r_{\max}$ on a side. In a trial move, the atom is moved randomly somewhere within the shaded square.

b. Find change in energy due to displacement.

- i. since only moved one atom, only need to recalculate energy terms involving

$$\text{that atom, For pair potentials: } \Delta U_{mn} = \sum_{\substack{j \neq i=1 \\ r < r_c}}^N \phi(|\vec{r}_j - \vec{r}_i^n|) - \sum_{\substack{j \neq i=1 \\ r < r_c}}^N \phi(|\vec{r}_j - \vec{r}_i^m|),$$

where the superscript n indicates the new positions and m the old positions

c. accept or reject move with Metropolis algorithm

- i. if accept the trial, the the next configuration in the MC series has $r_i = r_i^n$
 ii. if reject the trial, the the next configuration in the MC series has r_i set back to old values.

d. accumulate averages (with U_n if we accept the move or U_m if it is rejected).

e. How choose $\Delta r_{\max}$?

- i. Usually varied until about 50% of the moves are accepted.
 ii. Why? it seems to work.
 1. a balance between accepting enough moves to sample configuration space and making the moves big enough to sample configuration space

9. Other ensembles

a. unlike MD, it is trivial to extend MC to new ensembles.

b. Isobaric-isothermal ensemble

i. $Z_{NPT} = \int dV e^{-PV/k_B T} \int d\mathbf{r}^{3N} e^{-U(\mathbf{r}^{3N})/k_B T}$

ii. $\langle \mathcal{A} \rangle = \frac{1}{Z_{NPT}} \int dV e^{-PV/k_B T} \int d\mathbf{r}^{3N} \mathcal{A}(\mathbf{r}^{3N}) e^{-U(\mathbf{r}^{3N})/k_B T}$

iii. introduce scaled coordinates $\vec{r}_i = h\vec{s}_i$, as we did for constant-pressure MD

1. note: $dr^{3N} = \det(\mathbf{h})^N ds^{3N} = V^N ds^{3N}$
2. $\langle A \rangle = \frac{1}{Z_{NPT}} \int dV e^{-PV/k_B T} V^N \int ds^{3N} A(s^{3N}) e^{-U(s^{3N})/k_B T}$
- iv. in Metropolis algorithm, sample according to probability $e^{\{-\beta[PV + U(s^{3N})] + N \ln V\}}$
- v. sample positions (in scaled space) in the same way as for NVT MC.
- vi. sample volume by adding steps that randomly try to change the simulation cell parameters: $a_n = a_m + \Delta a_{\max} (2\mathcal{R} - 1)$, where $\Delta a_{\max}$ is a parameter giving the maximum change in a . There would be similar equations for the other lattice parameters $b, c, \alpha, \beta, \gamma$, with a different random number each time.
- vii. during run, calculate the average pressure (we should find $\langle P \rangle = P$) volume, energy, and any structural parameters you want.
- viii. An example: transition in solid oxygen at $P=0$ (note: 1 atmosphere pressure is the same as $P=0$ as far as the structure of a solid is concerned)
 1. The interaction between oxygen molecules has two parts: a pair potential (that depends on the relative orientation of the molecules) and a magnetic interaction that we modeled with a Heisenberg model (spins on movable particles with any spin orientation). There is a phase transition at low temperature accompanied by a change in magnetism. Note that we need to use MC, at least for magnetic interactions, because cannot do with MD.
 2. results of a constant pressure, variable box MC simulation

3. In the simulations, we would set the temperature and see what the lattice parameters became. At some temperatures, they went to one structure and at others to the other structure. We'd find the averages after equilibrating

in whatever structure the system chose.

4. agreed almost exactly with experiment, both for values of the parameters and the location of the phase transition.

ix. NOTE: This predicts a transition, but is not the thermodynamic transition.

1. Nosé showed that transitions in NPT ensemble driven by mechanical instabilities, not thermodynamic
2. should be close, but not necessarily good.
3. need to calculate free energies of each phase to be sure.
4. CANNOT CALCULATE FREE ENERGIES DIRECTLY - WE ARE NOT INTEGRATING THE PARTITION FUNCTION, BUT ARE JUST FINDING AVERAGES. (see below)

b. "Baby Grand" canonical ensemble:

- i. Earlier, we said that the Grand Canonical partition function is:

$$Q_{\mu VT} = \sum_{N_A=0}^{\infty} e^{\mu N / k_B T} Q_{NVT}, \text{ where } \mu \text{ is the chemical potential. The average}$$

number of particles will be a function of μ , V , and T .

- ii. For a system with two components (A and B), this becomes

$$Q_{\mu_A \mu_B VT} = \sum_{N_A=0}^{\infty} \sum_{N_B=0}^{\infty} e^{\beta[\mu_A N_A + \mu_B N_B]} Q_{N_A N_B VT}$$

1. Note that in this ensemble, the total number of neither atom is fixed - the system responds to the chemical potentials of each type, μ_A and μ_B .

- iii. Suppose that we have a solid, with the atoms restricted to a lattice with a total of N sites.

1. If we have two components, then the sum is restricted such that $N_A + N_B = N$.

2. The partition function for this ensemble is just (writing out Q and noting that $N_B = N - N_A$)

$$Q_{\Delta \mu VT} = e^{N \mu_B} \sum_{N_A=0}^N e^{\beta N_A (\mu_A - \mu_B)} \frac{1}{N_A! \Lambda_A^{3N_A}} \frac{1}{N_B! \Lambda_B^{3N_B}} \int d\mathbf{r}_A^{3N_A} d\mathbf{r}_B^{3N_B} e^{-\beta U(\mathbf{r}_A^{3N_A}, \mathbf{r}_B^{3N_B})},$$

where Λ_A is the de Broglie wavelength for particle A (see II.D.5.d.ii.1 on page II-20)

3. Since we have a restriction on N , this is not really the Grand Canonical Ensemble. I like to call it the "Baby Grand" Canonical Ensemble

c. Application of the Baby Grand Canonical Ensemble to alloys

- i. Foiles used this ensemble to study metal alloys (with EAM potentials). He studied bulk properties and segregation to interfaces.
- ii. He used the Monte Carlo method, where he sampled with the probability

$$\exp\left[\beta\left\{N_A\Delta\mu_A - U\left(r_A^{3N_A}, r_B^{3(N-N_A)}\right)\right\} - \ln\left(N_A!(N-N_A)!\Lambda_A^{3N_A}\Lambda_B^{3(N-N_A)}\right)\right]$$
 1. note that we must include the last term as it has an N_A dependence.
- iii. In addition to normal trial moves of the positions, he would randomly try to change an atom on a site from one kind to the other, using a standard Metropolis algorithm
- iv. The procedure is:
 1. fix the composition of the alloy by setting the chemical potential difference

$$\Delta\mu = \mu_A - \mu_B.$$
 2. introduce an interface (e.g., grain boundary) and calculate the concentration of each component at the interface, the energy, structure, ...
- v. Very nice method, though quite time consuming, as the particle acceptance ratio can be very low.

10. Summary of MC applications to atomic systems

a. Advantages

- i. easy to implement
- ii. easy to do many ensembles
- iii. gives averaged quantities, structure, etc.
- iv. can handle any description of energy of system
 1. MD can only do systems for which we can easily derive a force

b. Disadvantages

- i. for continuous potentials, we get NO DYNAMICS.
 1. We have no time in the problem when have continuous potentials.
 2. Note. For some systems (e.g., Potts) we can define a "time" (see below).
- ii. same as for MD
 1. system size

I. Free Energy Methods (see Daan Frenkel,)

1. Why do we want free energies?

- a. To predict stability of phases we need the free energy.
- b. As noted above, MC or MD simulations can show phase transitions (melting, solid-solid, etc.), but these occur at points of mechanical instabilities not at the thermodynamic transition point (Nosé, J. Chem. Phys. (1988?))

2. Why do we need a special method for calculating them?

- a. Cannot calculate them directly from simulations.

- b. Consider the relation $A = -k_B T \ln Q_{NVT}$, where $Q_{NVT} = \frac{1}{N!} \frac{1}{\Lambda^{3N}} \int d\mathbf{r}^{3N} e^{-U(\mathbf{r}^{3N}) / k_B T}$

and we have integrated over the momenta.

- i. To evaluate A directly would require a 3N-dimensional integration.

- ii. since U has terms coupling the atoms (i.e., $\phi(r_{ij})$), the integrals cannot be separated as we did for the momenta.

- iii. Consider as an example a system with only 4 atoms in a box of size L. Direct integration of Q would involve $3(N-1) = 9$ independent integrals (note that eventually would have an integral over the last two of the atoms, which we could rewrite as the volume times an integral over the interparticle distance). Suppose we used a numerical integration scheme and could get by with only 10 points per integral in the interval $(-L, L)$. To do the complete 12-dimensional integral would require 10^9 integration points. Imagine the situation for 100 particles. Clearly it is impractical to directly integrate Q.

- iv. Consider using importance sampling. If you remember the Nile river analogy, when we do importance sampling, it keeps us in the river to do the measurements. We get an estimate for the average depth, but it doesn't tell us the area, i.e., we cannot measure Q from direct importance sampling.

- v. We could try to find a way to measure Q by calculating average quantities.

Salsburg et al. used the relation $\langle e^{\beta U} \rangle = \frac{\int d\mathbf{r}^{3N} e^{\beta U} e^{-\beta U}}{Q} = \frac{V^N}{Q}$, or $Q = \frac{V^N}{\langle e^{\beta U} \rangle}$,

where we have dropped all terms from the integrals over momenta (they

cancel). Thus, if we could evaluate $\langle e^{\beta U} \rangle$, we'd have Q. However, there are

large contributions to $e^{\beta U}$ in regions where $e^{-\beta U}$ is vanishingly small, so you

don't gain much in terms of numerical accuracy.

- c. Must seek some other way to find the free energies that avoid these difficulties.

d. There are a number of methods.

3. Thermodynamic integration

a. We showed that $\left(\frac{\partial A/T}{\partial 1/T}\right)_{N,V} = \left(\frac{\partial}{\partial 1/T} \left[\frac{E}{T} - S \right]\right)_{N,V} = E = K + U$

1. We then have

$$\frac{A(T_1)}{T_1} = \frac{A(T_0)}{T_0} + \int_{1/T_0}^{1/T_1} (K + U) d\left(\frac{1}{T}\right) = \frac{3}{2} Nk_B \ln\left(\frac{T_0}{T_1}\right) + \int_{1/T_0}^{1/T_1} U d\left(\frac{1}{T}\right)$$

where we have used that $\langle K \rangle = \frac{3}{2} Nk_B T$ and the volume is constant.

2. So if we knew A at some temperature T_0 , and we knew $\langle U \rangle$ as a function of T , we could find A at some new temperature.

i. use MC or MD to obtain $\langle U \rangle$

b. We can also use $\left(\frac{\partial A}{\partial V}\right)_{N,V} = -P$ to find a change in free energy.

1. $A(V_1) = A(V_0) - \int_{V_0}^{V_1} P dV$, where the temperature is held constant.

c. From these relations, we can often integrate over T and V to find A .

1. Particularly useful in fluids and gases.

d. Note: if there are phase transitions, then we have a problem as we cannot necessarily find the free energy change unless we can do both phases.

4. Frenkel-Ladd method for the free energy of solids

a. The goal is convert the determination of free energies to a calculation involving averaged quantities, where the statistics are better.

b. We introduce a reference state, for which we know the free energy, and find deviations from that reference state. The smaller the deviations the better the result, so we need a good reference state.

i. Define a new potential, $U_\lambda = U_0 + \lambda(U - U_0)$, where U is the potential of the system for which we want the free energy and U_0 is the potential of some reference system for which we know the free energy. Note that for $\lambda=0$, $U_\lambda = U_0$ and $\lambda=1$, $U_\lambda = U$.

ii. The free energy for a system described by this potential is $A_\lambda = -k_B T \ln Q_{NVT}(\lambda)$,

$$\text{where } Q_{NVT}(\lambda) = \frac{1}{N!} \frac{1}{\Lambda^{3N}} \int d\mathbf{r}^{3N} e^{-U_\lambda / k_B T}.$$

iii. We can take the derivative of A_λ with respect to λ and we get

$$\begin{aligned}\frac{dA_\lambda}{d\lambda} &= -k_B T \frac{1}{Q_{NVT}(\lambda)} \frac{dQ_{NVT}(\lambda)}{d\lambda} = -k_B T \frac{1}{Q_{NVT}(\lambda)} \frac{1}{N!} \frac{1}{\Lambda^{3N}} \int d\mathbf{r}^{3N} \left(-\frac{U - U_o}{k_B T} \right) e^{-U_\lambda / k_B T} \\ &= \langle U - U_o \rangle_\lambda\end{aligned}$$

where $\langle U - U_o \rangle_\lambda$ is an average evaluated in the system described by U_λ .

iv. We can integrate to find $A_{\lambda=1}$, which is the free energy for the system we want,

$A_1 = A_0 + \int_0^1 \langle U - U_o \rangle_\lambda d\lambda$. So if we have a reference state for which we know the free energy, we can then do a series of simulations with different values of λ , perform the integration over λ , then we'll have the free energy we need. Note that we only have to calculate average quantities.

c. Suppose we want the free energy of an atomic solid. We know that a solid is reasonably well described by a harmonic lattice (see section II.D).

i. Assume for the reference potential an Einstein solid, i.e., all atomic vibrational frequencies are the same.

ii. The reference potential then becomes:

$$U_o = U(\mathbf{r}_o^{3N}) + \frac{1}{2} k_o \sum_{i=1}^N (\tilde{\mathbf{r}}_i - \tilde{\mathbf{r}}_i^o)^2 = U(\mathbf{r}_o^{3N}) + \frac{1}{2} m \omega_o^2 \sum_{i=1}^N (\tilde{\mathbf{r}}_i - \tilde{\mathbf{r}}_i^o)^2$$

where the super(sub)script o on $\mathbf{r}$ indicates that we use the equilibrium lattice positions. The Einstein frequency is ω_o .

iii. The (classical) Helmholtz free energy of the reference potential is then

$$A_o = U(\mathbf{r}_o^{3N}) + 3Nk_B T \ln \left(\frac{\hbar \omega_o}{k_B T} \right)$$

d. We then perform a series of simulations for different values of λ , finding $\langle U - U_o \rangle_\lambda$ for each simulation. We then integrate this quantity over λ , as in II.I.3.b.iv.

Typically, we'll pick points for λ that are special points from a numerical quadrature scheme.

e. How do we pick the reference state?

i. we presume that we have found the volume and structure at the temperature and pressure of interest.

ii. evaluate the potential energy of the atoms in their equilibrium positions at the volume of interest

- iii. find the Einstein frequency at that volume
- iv. For example, the force constant would be (in the Einstein model)

$$k_{\alpha\beta} = \sum_{\mathbf{R} \neq 0} \left(\frac{\partial^2 \phi}{\partial x_\alpha \partial x_\beta} \right). \text{ For cubic systems } k_{\alpha\beta} = k \delta_{\alpha\beta}, \text{ where } \delta_{\alpha\beta} \text{ is the Kronecker delta.}$$

- v. For the Lennard-Jones (mn) potential (I.B.4.j), the summation over the lattice

$$\text{yields } k = \frac{\epsilon}{3(m-n)\sigma^2} \left(\frac{m^m}{n^n} \right)^{\frac{1}{m-n}} \left\{ m(m-1)A_{m+2} \left(\frac{\sigma}{r} \right)^{m+2} - n(n-1)A_{n+2} \left(\frac{\sigma}{r} \right)^{n+2} \right\}.$$

where r is the nearest neighbor distance for the volume of interest.

- v. As an example of the size of the Einstein frequency, ω_0 , for an oscillator with mass

$$m_0 \text{ at } 0^\circ \text{K we have } m_0 \omega_0^2 = k_0 = \frac{\epsilon mn}{3(m-n)r_0^2} A_{m+2} \left(\frac{A_n}{A_m} \right)^{\frac{m}{m-n}} \{ (m-1) - (n-1)\psi \},$$

where $\psi = (A_{n+2} / A_{m+2})(A_m / A_n)$. For an LJ (12,6) potential,

$$\omega_0 = 19.4176 \left(\frac{\epsilon}{m_0 \sigma^2} \right)^{\frac{1}{2}}$$

III. Mesoscopic (i.e., microstructural) simulations

A. Why do we need them?

1. Microstructures are $\sim \mu\text{m}$ in scale

a. a micrograph of slip bands of $\langle 100 \rangle$ dislocations in cast and extruded Ni-48Al-2Cr after 0.7% deformation at 300 K.

b. note the many scales:

Feature	Scale
dislocation dipoles	$100 \text{ \AA} = 10 \text{ nm} = 0.01 \mu\text{m}$ (note that we can't really see these in the micrograph)
slip bands	$500 \text{ nm} = 0.5 \mu\text{m}$
grains	$10\text{-}100 \mu\text{m}$

c. what we call microstructure ranges from ~ 0.1 to $1000 \mu\text{m}$

d. we'll see we need different modeling depending on scale

2. What about atomistics?

a. "Best" MD code is SPaSM (Scalable Parallel Short-Range Molecular Dynamics)

i. on 1024-node CM-5 at Los Alamos

ii. for LJ potential with cutoff at 2.5σ

1. 131 M particles takes 34 seconds/time step - 2.6×10^{-7} sec/particle-timestep

2. 30 Gflops "real" performance

3. needs about 100 bytes/particles of memory

iii. for a cubic micron need about 10^{11} atoms

1. on a 30 Gflop machine would take 26000 sec/timestep

- 2. for a 1 nsec simulation, would need about 10^5 timesteps
 - 3. total simulation time is about 2.6×10^9 sec or 30,000 days
 - 4. need about 10 Tbytes of memory
- iv. for 30 Tflop computer - 30 days
- b. Clearly, atomistics cannot be used to directly study microstructure
- c. Can be used to study individual defects and (maybe) small numbers of defects
- d. We'll see that atomistics can provide INPUT to mesoscopic simulations
 - i. like interaction potentials are INPUT to atomistics
- 3. Philosophy
 - a. Focus on development of models for specific phenomena
 - i. note that in the section on atomistics, we took a set of models (the interatomic potentials) and developed methods to look at a large class of problems. Note that here we will use some of the techniques from atomistics, but will focus on developing models that approximate the physical phenomena of interest. We will then interrogate those models with simulations.
 - ii. In retrospect, should have focused more on applications of atomistics.
- 4. Classes of methods
 - a. it is convenient to break mesoscopic simulations into classes of methods.
 - i. no unique way
 - b. for this course, we will consider the following
 - i. Monte Carlo methods
 - 1. develop a Hamiltonian (energy expression) to describe phenomena and then use MC to look at evolution of method.
 - 2. for example, MC Potts model of grain growth
 - ii. Cellular automata
 - 1. use simple rules to propagate system
 - 2. for example, solidification models
 - iii. rate equation methods
 - 1. use model equations for competing rates of dynamic processes
 - 2. for example, stochastic solidification models
 - iv. "dynamic" methods
 - 1. derive equations of motion for system
 - 2. for example, dislocation dynamics

B. Monte Carlo methods

1. Grain growth

- a. some known properties of grains (i.e., the basis of a model)
 - i. almost all metals and ceramics are composed of many crystallites (grains) that, in a fully dense material, fill space
 - ii. grain boundaries occur where two grains meet in a sheet; grain edges where 3 or more grains meet along a curve; grain vertices where 4 or more grains meet at a point.
 - iii. because atomic bonds are altered at grain boundaries, boundaries contribute a finite free energy per unit boundary area to the system energy.
 - iv. when you heat a material, the grains evolve to lower the total boundary area
- b. some experimental observations about grain growth
 - i. grain growth occurs via boundaries migrating toward their centers of curvature
 - ii. in general, grains with few sides shrink, and grains with many sides grow
 - iii. grain structure is often observed to be self similar - while average sizes increases, the shapes of the grain area and grain shape distributions do not change.
- c. any successful model of grain growth must reproduce these features.
- d. summary of theories for grain growth
 - i. Burke and Turnbull, using simple approximations and rate theory for movement of atoms across the boundaries, showed that a spherical boundary moves with a rate $v = M\kappa$, where M is the atomic mobility and κ is the mean curvature of the boundary.
 1. the activation energy for moving an atom across a boundary is ΔE_A
 1. $M \equiv (\gamma/k_B T)v\lambda e^{-\Delta E_A/k_B T}$, which has dimensions of a diffusion coefficient. γ is the grain boundary interfacial energy, the activation energy for moving an atom across a boundary is ΔE_A , λ is the jump distance.
 2. Assuming spherical grains of radius R and that the radius of curvature of each spherical face is proportional to R , they show that the mean grain size should go as $\langle A \rangle \propto t$, at long times.
 3. Note that this results comes after many approximations, but seems to match some experiments.

- ii. von Neumann's law for growth in 2 dimensions: $\frac{dA}{dt} = -M \frac{\pi}{3} (6 - n)$, where A is the area of the grain, M is the mobility, and n is the number of sides of the grain.
 1. this assumes that grains meet only at trijunctions with an equilibrium angle of $2\pi/3$. Note that this matches many experimental observations.
 2. this says that grains with $n < 6$ shrink, those with $n > 6$ will grow and $n = 6$ is stable.
- iii. a good model/simulation will match these results, at least where the approximations in the theories hold.

2. Simulation methods.

a. continuum models

- i. boundary models (see, for example, the work of Frost and coworkers)
 1. the grain boundaries are discretized and each boundary moves towards its center of curvature according to $v = M\kappa$
- ii. vertex models (see, for example, Kawasaki)
 1. map grain structure as an array of triconnected vertices
 2. equations of damped motion for a vertex pulled by surface tensions of boundaries are solved with time.
- iii. continuum models are fast, but not overly flexible in terms of new phenomena.

3. Monte Carlo Potts model for grain growth (in 2-d).

- a. a variant of the Ising model (as we shall see)
- b. map lattice onto 2-d lattice, in this case triangular:

- c. each lattice site represents a unit area of material; site indices indicate the grain (or particle) in which a site is located. Thus, areas with the same site number (e.g., 52) are all in one grain.

- d. we assume that we have a total of Q possible site index values. Note: because of its outgrowth from the Ising model, site indices are referred to as spins and changes of site index from one value to another are called spin flips. We usually use s_i as the spin value of site i .
- e. Note that just like in the Ising model, this system has a critical temperature T_c that depends on Q and the lattice type. For $T > T_c$, thermal fluctuations are large enough for the system to disorder.

- e. The Hamiltonian describing the energy of the system is usually written as

$$H = \frac{1}{2} \sum_{i=1}^N \left(\sum_{j=1}^{z_i} E(s_i, s_j) [1 - \delta(s_i, s_j)] + F(s_i) \right)$$

- i. E is the energy of a unit of grain boundary between sites with unlike spins s_i and s_j .
- ii. δ is the Kronecker delta ($= 1$ if $s_i = s_j$ and 0 otherwise)
- iii. F is the energy of site i itself (we'll discuss a use of this later)
- iv. z_i is the number of neighbors of site i (a constant that depends on lattice and topology)
- f. if we have pure, isotropic, single-phase growth, the Hamiltonian reduces to

$$H = \frac{E_0}{2} \sum_{i=1}^N \left(\sum_{j=1}^{z_i} [1 - \delta(s_i, s_j)] \right)$$

- i. E_0 is a positive constant - the "grain-boundary energy"
- ii. This Hamiltonian essentially counts the number of unlike neighbors of site i
 - 1. the energy of site i is just E_0 times the number of neighbors with a different spin value
- g. We use a Monte Carlo method to look at dynamics
 - i. I thought we said MC doesn't yield dynamics? more later.
 - ii. thermodynamically it isn't interesting
 - 1. at 0°K , all the grain boundaries go away
 - iii. use Metropolis algorithm, where ΔE is the change in energy in flipping a spin

$$1. \quad \begin{aligned} \text{prob}(s_i, s_j) &= 1 & \Delta E \leq 0 \\ &= e^{-\Delta E / k_B T} & \Delta E > 0 \end{aligned}$$

- 2. at 0°K it reduces to

$$\begin{aligned} \text{prob}(s_i, s_j) &= 1 & \Delta E \leq 0 \\ &= 0 & \Delta E > 0 \end{aligned}$$

3. The general approach is the usual MC procedure
 - a. initialize system with random spins at each site
 - b. pick a spin at random and try to flip it
 - c. use Metropolis algorithm
 - d. if the move is accepted, then keep the change and go on
 - e. if the move is rejected, put the spin back and go on
 - f. time increases by $1/N$ Monte Carlo Steps (MCS) after each trial move, where N is the number of lattice sites
- h. What do we mean dynamics? We said MC was only good for equilibrium properties.
 - i. In the Potts model for $T < T_c$, only flips at certain "active" sites (i.e., along the boundaries) can contribute to the movement of boundaries. If there are any flips at other sites, then these will just be fluctuations about some mean value.
 - ii. using normal rate theory, Holm shows that the velocity of boundary motion is given in the Potts model by $v_p = M_p \kappa_x$
 1. the Potts model mobility is $M \equiv \frac{C\gamma}{k_B T} v_p \lambda_p e^{-\alpha E_A / k_B T}$, where C and α are constants, and E_A is some activation energy
 2. the curvature, κ_x , is averaged over the discrete lattice (i.e., a circle on a triangular lattice is a hexagon)
 - iii. Thus, by analogy with the Burke-Turnbull analysis, because we obtain the same rate law, it indicates that measuring time in MCS is correct.
 - iv. Why does it work? Because we have discrete events.
- i. What can we do with the Potts model:
 - i. almost anything - a very flexible model
 - ii. can include misorientation-dependent grain boundary energy through E
 - iii. can include stored energy (i.e., for recrystallization) by having positing dependent F
 - iv. can do 3d
 - v. can do anisotropic growth, as we'll see later
- j. A first study: map the microstructure with 40,000 sites on a triangular lattice with nearest neighbor interactions and the isotropic Hamiltonian

- i. the lattice is:
- ii. set $Q = 100$ and use the Metropolis algorithm
- ii. start with a random microstructure and let it evolve with time (in MCS)
(from E.A. Holm, Thesis).

$t=10,000$

$t=40,000$

$t=100,000$

- iv. the mean area with time is: (from E.A. Holm, Thesis).

v. the grains are self-similar

k. Square lattice

i. turns out that a square lattice with first nearest neighbors, sq(1), is too anisotropic and yields odd microstructures (case a), while a square lattice with the first and second neighbor shells, sq(1,2) (case b), works well

case a

case b

(a)

(b)

(c)

ii. For example, 100,000 sites with $sq(1,2)$. (from E.A. Holm, Thesis). (a) 3000 MCS, (b) 10,000 MCS, (c) 30,000 MCS

iii. results are self-similar and $\langle A \rangle \sim t$ at long times.

I. summary for many lattices (from E.A. Holm, Thesis).

m. 3D simulations

- i. one of the strengths of the Potts model is that 3D is easy to implement
- ii. However, slow relative to 2D
- iii. very strong lattice effects
 1. certain lattices inhibit grain growth
 2. sc(1), sc(1,2), fcc(1), fcc(1,2), hcp(1) all are lattices that inhibit growth, where (1) indicates first shell of neighbors, etc.
 3. sc(1,2,3) and sc(2*) show normal growth
 - a. sc(2*) means that interactions are with all neighbors within a cube with corners [222] from the central site.
 4. when have normal growth, find that cross-sectional area $\langle A \rangle \sim t$ at long times. Mean grain radius $\langle R \rangle \sim t^{1/2}$ and mean grain volume $\langle V \rangle \sim t^{3/2}$

n. Algorithms (for ease of discussion, we'll assume $T = 0^\circ\text{K}$ here. The same arguments hold for $0 \leq T \leq T_c$, though flips that increase the energy will be accepted with probability $\exp(-\Delta E/k_B T)$).

o. Consider the usual MC algorithm. At 0°K , only moves that lower the energy will be accepted. Thus, only those sites that are on a boundary are "active," i.e., they can flip. At long times we know that the mean area goes as $\langle A \rangle \sim t$. The number of sites within a grain goes as $\langle A \rangle$, i.e., as $\sim t$ at long times. The surface of the grain (i.e., the boundary) goes as the radius of the grain $\langle R \rangle \sim t^{1/2}$. Thus, the fraction of sites that are active goes as $n_{\text{active}} \sim 1/t^{1/2}$. Thus, just choosing sites at random

throughout the whole system becomes less and less efficient as the simulation proceeds.

- i. There are $Q-1$ possible values for the new spin value when you flip a spin.
If a spin is on a boundary with one other type of spin, then there is only a $1/Q-1$ chance of flipping to a spin that will actually lower the energy (i.e., the other type already on the boundary)
- ii. Conclusion: regular MC is very inefficient.
- p. It doesn't matter if the model is elegant, if we cannot compute with it!!!!!!
- q. The N-Fold way. Note that we will derive this for $T = 0^\circ\text{K}$ here. $T > 0$ has certain complications, but is straightforward.

i. general properties

1. originated for Ising model
2. every trial is accepted, so very efficient
3. the "timestep" changes as the simulation progresses

ii. define the "activity" of site i as $\pi_i = \sum_{s_i^* \neq s_i} P(\Delta E[s_i \rightarrow s_i^*])$

1. This is a sum of the probabilities of changing the spin value on site i from s_i to s_i^* . There are $Q-1$ terms in the sum.

2. At $T=0^\circ\text{K}$, $P(\Delta E[s_i \rightarrow s_i^*]) = 1 \quad \Delta E \leq 0$
 $= 0 \quad \Delta E > 0$

3. At $T=0^\circ\text{K}$, if a spin is not on a boundary, $\pi_i = 0$.

4. Let q be the number of different types of spins in the z neighbors of site i ($q=0$ in the example above).

5. if $1 \leq q \leq z$, then π_i is calculated by summing over i taking on those q possible spin values (sums of 1 or 0 depending on whether the energy decreases or increases, respectively).
6. So, at $T=0$, we can flip the value of the spin at site i from 1 to 2 in case 1,

from 1 to 2,3, or 4 in case 2, and to 2,3,4,5,6,7 with in case 3.

iii. We start the calculation by determining the activity of each site.

1. visit each site at random with probability π_i .
2. flip s_i to one of the energetically possible values (all are equally probable)
3. recalculate activites of site i and its neighbors
4. choose new site at random with probability π_i .

iv. Since we accept every trial move, we need to be able to convert from these steps to the conventional Monte Carlo step (MCS).

1. we want to find the average time between successful moves in conventional MC and use that to find the time in the N-fold way

2. define the total activity for the system to be $A = \sum_{i=1}^N \pi_i$

this is the overall chance that some site can change - since most sites at late time are in a grain, A decreases with time.

3. the total rate of successful moves is just the activity divided by the

time step ($\tau = 1$ MCS), i.e. $\dot{f} = \frac{A}{(Q-1)\tau}$, where $(Q-1)$ accounts for the

fact that at worst, only 1 out of $Q-1$ possible spin flips are accepted. (You will see below that whether it is $Q-1$ or $Q-2$, etc, doesn't matter). The probaility of a succesful flip in dt is just $\dot{f} dt$.

4. since we want average time between succesful moves, let us take $g(\Delta t)$ as the probability of no flips in a time interval Δt .

5. Consider then g at a longer time, $\Delta t + dt$. A Taylor expansion yields

$$g(\Delta t + dt) \approx g(\Delta t) + \frac{dg(\Delta t)}{dt} dt.$$

6. But, g is a probability, so

$$g(\Delta t + dt) = g(\Delta t)g(dt) = g(\Delta t)(1 - \dot{f} dt) = g(\Delta t)\left(1 - \frac{A}{(Q-1)\tau} dt\right)$$

7. comparing the expressions in 5. and 6., we can derive a differential

$$\text{equation for } g \text{ and solve it to find } \Delta t = -\frac{(Q-1)\tau}{A} \ln[g(\Delta t)]$$

8. But, Δt is a stochastic variable, i.e., it will vary with time depending on the

instantaneous values of the spin configuration. It will vary between 0 and some maximum in a stochastic way, i.e., with uniform probability over long times.. Thus, g will take on all of its possible values with equal probability. We replace g with a random number Γ in the interval (0,1) and

$$\text{we have } \Delta t = -\frac{(Q-1)\tau}{A} \ln[\Gamma]$$

9. So, after each flip in the N-fold way, we find A and a random number and increase time by Δt

v. How well does it work? (CPM = conventional method, NFW = N-Fold Way), given as cpu seconds per MCS. (from E.A. Holm, Thesis).

r. Other applications: recrystallization.

- i. Going back to the Hamiltonian $H = \frac{1}{2} \sum_{i=1}^N \left(\sum_{j=1}^{z_i} E(s_i, s_j) [1 - \delta(s_i, s_j)] + F(s_i) \right)$
- ii. Assume that F is a stored energy term that represents the strain energy from working the material (i.e., in processing).
- iii. In recrystallization, a grain with lower strain energy is nucleated and then grows in favor of more highly-strained (and thus higher energy) grains.
- iv. In the Potts model, we model that by assigning a value of 0 to F for sites that

are in an unstrained grain, and some higher value for those in strained grains.

v. For the examples here, we assume some nucleation density along the surface of the material (could do this better). We then see that the unstrained regions grow to take over the material:

vi. For example, assume $F=H=0$ in an unstrained region and H in a strained region. Assume that the grain boundary energy is E .

1. case 1: total energy = $8*0 + 8*H + 4*E = 8H + 4E$

case 2: total energy = $9*0 + 7*H + 6*E = 7H + 6E$

case 3: total energy = $10*0 + 6*H + 6*E = 6H + 6E$

2. the grains will grow (at 0K) only if $\Delta E \leq 0$. We have

1->2: $\Delta E = -H + 2E$

2->3: $\Delta E = -H$

3. as long as $H \geq 2E$, then case 2 can occur, and once in 2, then the transition to case 3 is favored.

4. so we will get *nucleation*, if $H \geq 2E$. We will have *recrystallization* as long as $H \neq 0$.

vii. An example. $H/E = 1$, small number of initial nuclei placed on inner and outer surface (from E. A. Holm)

$t = 1000 \text{ MCS}$

$t = 10,000 \text{ MCS}$

$t = 100,000 \text{ MCS}$

4. Diffusion calculations using MC:

- a. diffusion in solids (see "Nontraditional Methods in Diffusion," edited by G. E. March, H. K. Birnbaum, and J.R. Cost, pp 281-)
 - i. a number of simulation types depending on problem of interest
 - ii. the common thread is that diffusion is a an activated random-walk process
- b. simplest cast: tracer diffusion in a pure system - note: defect-assisted diffusion
 - i. experimentally one measures self-diffusion be examining how isotopic tracers diffusion
 - ii. diffusion constant D^* defined by Fick's law relating flux J^* to the concentration gradient ∇C^* : $J^* = -D^* \nabla C^*$
 - iii. D^* can be defined by the Einstein equation: $D^* = \frac{\langle R^2 \rangle}{6t}$, where $\langle R^2 \rangle$ is the mean-square displacement of the traceable particles
 - iv. if we assume that we have discrete hopping between one site and another in the lattice, we can write $D^* = \frac{n\lambda^2 f}{6t}$, where n is the number of jumps, λ is the jump distance and f , which is called the tracer correlation function, arises from correlation between successive jump directions of the tracer atom, which in turn arises from the type and location of the defect (often a vacancy) by which the tracer atom jumps. Note if $f = 1$ then a random walk. Typically $f \leq 1$. Note: n/t is the jump frequency Γ .

v. we can solve for f and then calculate it with MC: $f = \frac{\langle R^2 \rangle}{n\lambda^2}$

vi. MC procedure:

1. set up lattice with M sites, for example fcc, with periodic boundary conditions
2. put "atoms" at each site
3. introduce a defect, for example a vacancy (just take out one atom), so $M-1$ atoms left
4. while we could randomly choose atoms and try to move them, it is equivalent to move the vacancy (since only atoms adjacent to the vacancy can move)
5. pick randomly one of 12 directions the vacancy can move ($j = \text{int}(12 \cdot R)$, where R is a random number $(0,1)$)
6. switch vacancy and atom j , keeping track of the change in position of the atom
7. do lots of moves, say N of them
8. at end, calculate $\langle R^2 \rangle = \sum_{i=1}^{M-1} (\bar{r}_i(\text{final}) - \bar{r}_i(\text{initial}))^2$, where we take the final positions of each atom and find how far they've moved in the simulation.
9. in an fcc lattice, λ^2 is the square of the nearest-neighbor distance, and $n = N$, the number of jumps.
10. there is a truly horrible fortran program to do this in the reference

- c. at times we need to take account of more than one exchange frequency
 - i. more than one possible crystallographic site (i.e., interstitial)
 - ii. more than one species that can diffuse (i.e., alloys)
 - iii. if an ordered alloy, then the ordering energy can contribute
 - iv. need to include these probabilities in the jump step, i.e., instead of chosing a direction at random, choose with a probability that accounts for these effects
- d. MC solution of diffusion equation

correct
NOT correct

- i. Suppose we want to calculate the diffusion profile of material diffusing into another material.
- ii. The diffusion equation is $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$, with boundary conditions $C(x,0) = M\delta(x)$ and $\partial C/\partial x(0,t) = 0$, i.e., there is a concentration of M at the surface at time 0 with no gradient at the surface. Note that x is the distance into the material.
- iii. the analytic solution is $C(x,t) = \frac{M}{\sqrt{\pi Dt}} e^{-x^2/4Dt}$
- iv. we can solve this with a Monte Carlo method
 1. create lattice that represents diffusion sites in the infinite material (interstitials, for example)
 2. place a particle at the surface.
 3. do a random walk along the lattice
 4. after time t , measure the x position of the tracer
 5. do this many many times
 6. you get agreement with the analytical result
- v. why do it if we already have an analytical solution?
 1. can use a microstructure (like from Potts model) with different diffusion along boundaries. No analytical solution, so MC is needed.
- e. Other possible uses of MC
 - i. sintering (diffuse the porosity)
 - ii. aggregation
 - iii. surface growth
 - iv. etc., etc. etc

C. Cellular Automata (see, for example, "Theory and Applications of Cellular Automata," Wolfram, editor, World Scientific, 1986, especially the outline and Chapter 1.1).

0. Dates back to ideas of von Neumann and Ulam in the 1940s (at Los Alamos).

1. General defining characteristics:

- a. discrete in space: they consist of a discrete grid of spatial cells or sites
- b. discrete in time: the value in each cell is updated in a series of discrete time steps.
- c. discrete states: each cell has a finite number of discrete values
- d. homogeneous: each cell is identical and are in a regular array
- e. synchronous updating: all cell values updated at the same time, depending on previous values of neighboring cells
- f. deterministic rule: each cell value is updated according to a fixed, deterministic rule.
- g. spatially-local rule: the rule at each site depends only on the values of a local neighborhood around the site.
- h. temporally local rule: the rule for the new value depends only the values for a fixed number of preceding steps (usually one). NOTE: we'll only discuss rules that include one preceding step.

2. General one-dimensional CAs

- i. assume that each site can take values from 0 to $k-1$
- ii. in general, rules take the form:

$$a_i(t) = F[a_{i-r}(t-1), a_{i-r+1}(t-1), \dots, a_i(t-1), \dots, a_{i+r}(t-1)], \text{ where } F \text{ is some function}$$

3. Consider the simplest possibility: $k=2, r=1$

- i. Sites can be 0 or 1
- ii. The new value of site i depends on the value of site i and its neighbors at the previous time step:

0 1 0 1 1

- iii. there are 8 possible configurations of the previous time step that determine the new value of site i :

111 110 101 100 011 010 001 000

Note that these are ordered in decreasing value to the right, where we consider each trio of numbers as a binary number. In decimal numbers, they are

7 6 5 4 3 2 1 0. This is the standard way to order these.

- iv. we need a rule that shows how each of these configurations leads to a new value:

v. Example: $[a_i(t) = a_{i-1}(t-1) + a_{i+1}(t-1) \text{ modulo two}]$

1. i.e., if at time (t-1), site i and its neighbors have the values 1 0 1, the value of site i at time (t) would be $[1 + 1 \text{ mod}(2)] = 0$.

vi. The complete rule goes as:

<u>111</u>	<u>110</u>	<u>101</u>	<u>100</u>	<u>011</u>	<u>010</u>	<u>001</u>	<u>000</u>	(t-1)
0	1	0	1	1	0	1	0	(t)

vi. Note that the rule can be written (given the standard way of representing the possible configurations) as 01011010. If you consider this a binary number, then in decimal numbers it is Rule 90.

vii. Since any 8 digit binary number can specify a rule, there are $2^8 = 256$ possible rules.

viii. But, we insist that 000 always go to 0 and that 001 and 100 (and 110 and 011) yield the same value (by symmetry), so there are only 32 possibilities.

4. Rule 01011010 (90).

i. Suppose start with 1 site as 1 and the rest as 0, where dots are 1 and blanks are 0.

RULE : 01011010 (90)

ii. Suppose start with random initial state:

RULE : 01011010 (90)

- iii. Note pattern formation even with random initial state. Note that if had different initial state, would develop different patterns.
- iv. For small systems, boundary conditions matter
- 5. Why do we care about cellular automata in materials science?
 - i. we can obtain complex behavior from very simple rules and very simple computations.
 - ii. many CAs yield behavior very similar behavior to known complex phenomena.
- 6. Conway's "The Game of Life"
 - i. a two-dimensional rule. Cells can be either 0 [dead] or 1 [alive].
 - ii. Take a square lattice with nearest and next-nearest neighbor cells (sq(1,2))

- iii. Rule: let $S_i = \sum_{j \neq i}^8 s_j$. (note, since spins are 0 or 1, S just counts how many cells have a value of 1, i.e., that are alive). As usual, S is calculated for each cell at a time step and the value of S in that cell determines what happens to the site value of that cell in the next time step.

1. If $S_i=2$, leave s_i unchanged.
2. If $S_i=3$, change (or leave) s_i to 1
3. If $S_i=1$ or $S_i>3$, change (or leave) s_i to 0
- iv. at each "time step", use rule to change all cells at once.
- v. This simple rule gives rise to very interesting behavior:
 1. characteristic patterns arise that "move" with time (i.e., they appear in a slightly displaced position after some number of steps)
 2. patterns that are stable with time
 3. patterns that oscillate with time (i.e., pass through a cycle of configurations).
 4. many very complex interactions and behaviors
 5. very hard to anticipate behavior of system from initial condition.

- vi. Two views of the Game of Life, on the left showing the organization arising after several hundred steps beginning with a 50% random configuration. On the right, we see two "glider guns" producing streams of gliders. (From Toffoli, "Cellular Automata," Farmer et al. eds., North-Holland, 1984).
- vii. remarkably complex behavior from very simple rules
7. The "0 °K Ising Model" as a CA (Not very interesting, but instructive)
 - i. use same topology as the Game of Life
 - ii. assume cells have a value of 0 or 1
 - ii. define: $q_i = \sum_{j \neq i}^8 [1 - \delta(s_i, s_j)]$
 - iii. Rule:
 1. $q_i \geq 4$, then s_i changes, otherwise s_i remains the same.

2. Based on the energetics of the Ising model at 0°K, is this right?
 - iv. do all cells synchronously
 - v. how does it differ: instead of random flips, we flip all possible spins at the same time. But there is nothing in MC that demands that we flip one at a time or randomly, so it seems equivalent.
 - vi. Does it work? Who knows, I haven't tried it.
 - vii. Note, however, that with the same topology as the Game of Life, a simple change in the rules leads to completely different behavior.
8. Solidification (for example, see N. Packard in "Theory and Applications of Cellular Automata," Wolfram, editor, World Scientific, 1986).
- i. take 2-d lattice of hexagonal cells with nearest neighbor interactions only (6 neighbors)
 - ii. take 0 for liquid and 1 for solid
 - iii. take $a_i(t) = f(\sigma_i[t])$, where $\sigma_i(t) = \sum_{j=1}^{z_i} a_j(t)$, i.e., the new site value is just some function f (which can be either 0 or 1) of the *sum* of the site values of the neighbors at the previous time step.
 - iv. 4 types of growth from a small seed depending on what f is: (if you don't believe me, get out some graph paper and try it. I do this for case 3 below)
 1. no growth. For example, if $f(\sigma) = 0$.
 2. plate-like growth: This would occur if $f(\sigma) = 1$ for $\sigma > 0$ (and 0 otherwise).
 3. dendritic growth: For example, if you inhibit growth in certain directions by taking $f(\sigma) = 1$ for $\sigma = 1$ (and 0 otherwise).
 4. amorphous, asymptotically circular form if $f(\sigma) = 1$ for $\sigma = 2$ (and 0 otherwise).
 - v. Case 3:
 1. I've drawn out the first few steps

*Note: wrong symmetry
cells in growing*

t=3

t=4

2. Note that at $t=1$ and $t=3$, the growing crystal "closes in" on itself - it grows a "plate."
3. it turns out that every 2^n time steps, the growing seed forms a plate. Then arms grow from the corners of the plate, sidebranches grow, and eventually the sidebranches grow into a new plate. The long-term growth looks like:

a

b

(a) Growth from a single site initial condition under the action of a solidification cellular automaton rule on a hexagonal lattice. The gray level reflects the density of solid and liquid sites and changes with position, and repeats a cycle of light to dark every 2^n time steps that displays the self-

similarity of the growth process, as the growing seed oscillates between dendrite and plate forms. (b) A picture of a snowflake, showing internal structure reminiscent of the dendrite-plate alternation.

- vi. Does not include the fact that latent heat is released in the solidification process.
 - 1. a number of models have been proposed to couple with heat and temperature (see Packard's article).
 - 2. while some are not true CAs (e.g., Rappaz's work) because are stochastic not deterministic, they are a powerful tool for modeling solidification microstructures (see, for example, Rappaz and Gandin, *Acta metall mater.* **41**, 345 (1993)).

9. Lattice-gas methods (see Rothman and Zaleski, *Rev. Mod. Phys.* **66**, 1417 (1994).)

a. Background

- i. the continuum, macroscopic, hydrodynamic, flow of a liquid is described by the Navier-Stokes equation.
- ii. much progress has been made in understanding the connections between the microscopic (i.e., atomistic) properties of fluids and macroscopic hydrodynamics. For example, from MD we can calculate viscosities, etc. that are important parameters governing hydrodynamic flow. There have even been large-scale MD simulations (very expensive) that show that hydrodynamic flow can be obtained atomistically.
- iii. in 1986, Frisch, Hasslacher, and Pomeau (FHP) showed that one can derive the Navier-Stokes equation from a microdynamics based on an artificial set of rules for the collision and propagation of identical particles constrained to move on a regular lattice with discrete time steps and with only a few allowed velocities. Their approach, called the *lattice-gas* method, is a simple cellular automaton.
- iv. This is a remarkable result. The number of degrees of freedom in their system is small, yet on a scale much bigger than the lattice on which the particles move and at a time much longer than the time step of the simulation, these simple rules asymptotically simulate the incompressible Navier-Stokes equation.

b. FHP rules:

- i. have particles on a triangular lattice

- ii. each particle moves with unit speed, with directions given by the directions to the neighboring sites: $\mathbf{c}_i = \left(\cos\left(\frac{i\pi}{3}\right), \sin\left(\frac{i\pi}{3}\right) \right)$ $i = 1, 2, \dots, 6$
- iii. no more than one particle with the same velocity can occupy a lattice site at any time.
- iv. each time step of the lattice gas consists of two steps:
 1. each particle hops to a neighboring site in the direction given by its velocity
 2. if particles collide, their velocities change according to some rules.
- v. for example:

1. One time step of the FHP lattice gas. In (a) we show the initial condition, with each arrow indicating the velocity of a particle. In (b), the particles have jumped to the neighboring sites in the direction of their velocities. In (c), the velocities have been changed by collisions, using the rules we'll discuss next.
- vi. there are specific rules governing collisions. these rules are chosen to conserve both mass and momentum during each collision (i.e., no particles are destroyed and the sum of velocities before the collision equals the sum of velocities after the collision).

- vii. The FHP collision rules are (from Shuling Huo, Ph.D. Thesis, Kansas State University, 1995):

Input State	Output State

Figure 2.3: Collision rules for FHP model

viii. We interpret the rules as follows.

1. Suppose we take the top case in the rule list. In the previous step the system looked like:

2. When we move the particles during the movement phase of a time step, they *collide*, i.e., they move to the same site. We indicate that with

where we remember that we haven't invoked collisions yet.

3. Following the top rule, after collisions we have

which indicates that the particles come together on the x axis but leave, after collisions, along one of the diagonals.

4. Note that the particles could leave towards (5,2) or (3,6). Most people choose between those choices randomly, though some use deterministic

rules.

5. The other rules are interpreted the same way.

ix. There are mathematical representation of these rules given in the Rev. Mod. Phys. article. You can show that mass and momentum are preserved.

x. In the Rev. Mod. Phys. article, they show that these simple rules and geometries yield, asymptotically, the Navier-Stokes equation.

c. An example.

Two-dimensional flow past a flat plat simulated using the FHP lattice gas. Particles were injected from the left and removed from the right, creating a pressure gradient. The arrows indicate the overall velocity of the flow at a point, which are found by averaging over many particles. The underlying lattice is smaller than the flow patterns. See the vortex flow. These results qualitatively match numerical simulations of the Navier-Stokes equations.

d. Another example:

Lattice-gas simulation of flow in a porous medium. Flow is forced from left.

- e. There are some problems with the lattice-gas model:
 - i. a density-dependent coefficient in the convection term of the Navier-Stokes equation; an unphysical velocity-dependent pressure; inherent statistical noise that requires averaging to obtain smooth macroscopic properties
- f. These issues have been addressed in a variant of the lattice-gas model, called the lattice-Boltzman method.
 - i. replace the single particles that move around the lattice with single particle distribution functions, $f_i = \langle n_i \rangle$, where $\langle \rangle$ indicates a local ensemble average and n_i is the occupation number of each site (i.e., a set of 6 numbers indicating

whether there is a particle with velocity in the 6 possible directions)

- g. The lattice-Boltzmann method is widely used to model flows through porous media, where traditional computational fluid dynamics cannot be used (too complicated boundary conditions).

Errata: Section III (a).

Page III-15. 4.b.vi.5: To pick a random number between 1 and 12, find a random number between 0 and 1, multiply by 12 and take the next highest integer, i.e., $0.1 \rightarrow 1$, $4.7 \rightarrow 5$, etc. The fortran statement would use the function `int(12*ranf())`, if you used the random number generator in the MC code.

Page III-22. The figures at the top of the page are not really correct, though they show what I want. This is supposed to be a triangular lattice. A better set of pictures would be, where I draw dots at the sites that are now solid,

D. Dynamical Systems

1. What do we mean?

- a. Consider what we've done already.
 - i. in MC, we wrote a description of the energy and used Metropolis algorithm to sample the configurations
 - ii. in cellular automata, we wrote rules to describe local behavior and used those rules to generate the system's evolution
- b. here, we will derive equations of motion for the variables of interest and will follow their time evolution
- c. Our examples will be:
 - i. grain growth by boundary evolution
 - ii. grain growth by vertex motion
 - iii. dislocation dynamics

2. general procedure

- a. identify the important entities of the problem
- b. derive the forces acting on those entities
- c. solve the equations of motion over time

3. it's like molecular dynamics, it's just that our "particles" are not atoms

4. equations of motion that we'll encounter

a. Newton's equations

- i. $m \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_{\text{total}}(\vec{r}_i)$, where F arises from interparticle interactions (- the gradient of the potential, external forces, etc.)
- ii. as in MD, we will solve these equations with a discrete timestep to find $\vec{r}_i(t)$ and $\vec{v}_i(t) = \frac{d\vec{r}_i}{dt}$. From these quantities we get all system information.

b. equation of motion with dissipation

- i. $\vec{F}_{\text{total}}(\vec{r}) = \vec{F}(\vec{r}) + \vec{F}_{\text{diss}}(\vec{r})$, where $\vec{F}_{\text{diss}}(\vec{r})$ is a dissipative force, the form of which depends on the type of system that one is studying.
- ii. Here, we commonly discuss systems where we can use the form for "viscous drag," i.e., $\vec{F}_{\text{diss}}(\vec{r}) = -\gamma \vec{v}_i$, where v is the velocity and γ is a "friction coefficient." Note that the physical origins and size of γ will depend on the system being studied.

- iii. The net equation of motion would then become: $m \frac{d\bar{v}_i}{dt} = \bar{F}_{\text{total}}(\bar{r}_i) - \gamma \bar{v}_i$
 - iv. Note that as velocity increases, we tend to steady-state motion (given no large changes in the force), where the frictional drag balances the force and the acceleration goes to zero. Of course, the velocity doesn't go to zero necessarily, just its derivative.
- c. Mobility equation
- i. $\bar{v}_i = M_i \bar{F}(\bar{r}_i)$, where M is the mobility. This is a useful expression when we have either discrete jumping motion or damped motion. Note that M could depend on direction, as on a lattice, for example. Note also that the velocities at each time step depend only on the force at that time step and not on the previous velocities.
 - ii. Consider the case where we have steady-state motion, i.e., $dv/dt = 0$. Then the velocity is the force/ γ . The assumption when using this equation of is that any impulsive motions (accelerations) are quickly damped out and steady-state motion takes over.
 - iii. Over a discrete timestep, the motion of a particle would be $\Delta \bar{r}_i = \bar{v}_i \Delta t = M \bar{F}_i \Delta t$. We might use a dynamic time step, where we set the maximum motion allowed in any time step to Δ_{max} . Then for each time step, we will find the maximum value of $|M \bar{F}|$ in the system and then set the timestep by Δ_{max} divided by the maximum of $|M \bar{F}|$.
5. Example 1: grain growth via boundary motion
- a. a repeat of and addition to pages III-3 and III-4
 - b. some experimental observations about grain growth
 - i. grain growth occurs via boundaries migrating toward their centers of curvature
 - ii. in general, grains with few sides shrink, and grains with many sides grow
 - iii. grain structure is often observed to be self similar - while average sizes increases, the shapes of the grain area and grain shape distributions do not change.
 - c. Burke and Turnbull, using simple approximations and rate theory for movement of atoms across the boundaries, showed that a spherical boundary moves with a rate $v = M \kappa$, where M is the atomic mobility and κ is the mean curvature of the boundary. Note the boundary moves in the direction of the center of curvature:

- i. the activation energy for moving an atom across a boundary is ΔE_A
- ii. $M \equiv (\gamma / k_B T) v \lambda e^{-\Delta E_A / k_B T}$, which has dimensions of a diffusion coefficient. γ is the grain boundary interfacial energy, the activation energy for moving an atom across a boundary is ΔE_A , λ is the jump distance.
- iii. For isotropic grain growth (all grain have the same boundary energy), can only have vertices with 3 grain boundaries meeting and the angles must all be 120° .
- iv. The Potts model shows this, for example,

- d. Model of Frost and Thompson (J. Elect. Materials, **17**, 447 (1988)).
 - i. unlike Potts model, which focuses on energy differences between volumes of material, the Frost-Thompson model focuses on the movement of

boundaries.

- ii. They discretize the boundaries as

- iii. they allow only trijunctions to form
 iii. each segment of a boundary moves according to $v = M\kappa$.
 iv. the mobility M and the time step are input parameters
 v. the curvature is calculated at each segment point. Note that curvature is defined as $\kappa = d\alpha/ds$, the derivative of angle (relative to some reference state) with respect to arc length. For curves divided into segments, we can approximate the curvature as shown here:

We approximate the curvature at point i as $\kappa_i = \Delta\alpha_i / \Delta s_i$, where

$\Delta s_i = (\Delta S_{i-1,i} + \Delta S_{i,i+1})/2$. It's easy to show that

$\Delta\alpha_i = \cos^{-1}((\Delta x_{i-1,i} \Delta x_{i,i+1} + \Delta y_{i-1,i} \Delta y_{i,i+1}) / \Delta S_{i-1,i} \Delta S_{i,i+1})$, while

$\Delta S_{i-1,i} = (\Delta x_{i-1,i}^2 + \Delta y_{i-1,i}^2)^{1/2}$. The normal at i in the direction of the center of

curvature is n_i , which is approximated by $\hat{n}_i = \left(\frac{m}{\sqrt{m^2 + 1}}, \frac{-1}{\sqrt{m^2 + 1}} \right)$, where

m is the slope connecting point $i-1$ to $i+1$, i.e., $m = \frac{y_{i+1} - y_{i-1}}{x_{i+1} - x_{i-1}}$.

- vi. Given the curvature at each segment, they move the boundaries by $M\kappa_i \Delta t$

viii. They constrain the location of the trijunctions such that a 120° angle between the boundaries is maintained. (see figure in III.D.5.d above). After each time step they

1. fit all three boundary curves at a trijunction to a second-order polynomial with the position of the trijunction as a variable in the fits, i.e.,

$$y = y_t + \alpha(x - x_t) + 1/2\beta(x - x_t)^2$$
, where the trijunction is at (x_t, y_t) .
2. They use the two points on the boundary nearest the trijunction to determine α and β for each boundary.
3. the tangent at the trijunction is given by the value for α for each boundary.
4. vary the position of the trijunction to minimize the deviation of the angles from 120° .

ix. they introduce rules for recombination and annihilation trijunctions

1. in (a), junctions that are moving together, they recombine and move off in a new direction when they are closer than Δ apart. In (b), small grains are annihilated when they are smaller than Δ .

- ix. numerical errors arise from the finite number of points on each boundary, the definition of curvature, the finite time step, and the algorithm for moving the trijunctions. Note that at early times and after discrete recombination and annihilation events, the trijunction movement algorithm is less accurate.
- x. despite these errors, results are quite good and rather fast:

von Neumann's rule, $\frac{dA}{dt} = -M \frac{\pi}{3} (6 - n)$, is obeyed to better than 3%, they

find that the average grain area increases as t at long times.

xi. for example, starting from about 2500 random grains, they find:

$\tau = 0.0$

$\tau = 0.25$

$\tau = 0.5$

$\tau = 1.0$

$\tau = 3.0$

$\tau = 10.0$

xii. Strengths:

1. reproduce normal grain growth kinetics well, as well as matching experimental grain size and shape distributions.

xiii. weaknesses:

1. depends on an input model for the dynamics $v = M\kappa$ and for junction angles.

- 2. difficult to implement in 3d
- 3. no finite temperature effects
- 5. Example 1: grain growth via vertex motion
 - a. We've noted that for normal grain growth, there are only trijunctions with 120° angles.
 - b. If we examine the microstructures closely, we see that, at least at long times, the grain boundaries connecting the trijunctions are approximately linear:

- i. (b) Straight lines overlaid on Potts model grain boundaries.
- c. If they are indeed taken as straight lines, then we could imagine developing equations of motion for the *junctions*, or vertices, and later on connect them with straight lines.
- d. The advantage would be a great simplification, as we have far fewer vertices than grain boundary sites.
- 6. Kawasaki's vertex model for grain growth (see Kawasaki et al., Phil Mag B **60**, 399 (1989)).
 - a. derived damped equations of motion for the vertices
 - i. simulate motion of vertices
 - ii. fill in grain boundaries as straight lines
 - iii. characterize grain growth as usual
 - b. here we give results for isotropic growth, though they have done the derivation for variable grain boundary energies
 - c. Derivation of equations of motion
 - i. the goal is to derive the equations of motion of the vertices.
 - 1. it is sort of complicated and, if you want, you can skip to the final result

below.

- ii. the total energy of boundaries: $H = \sigma A$, where A is the total area of the grain boundaries in the system (total length in 2D) and σ is the grain boundary free energy per area.

- 1. $A = \int da$, where da is an infinitesimal segment along a boundary and we integrate over all boundaries.

- iii. we assume that each point on a boundary moves with velocity $v(a) = LK(a)$, where L is the mobility and K is the curvature at point a along the boundary. Note that $v(a)$ is in the direction of the radius of curvature.

- iv. Boundary motion is dissipative, i.e., energy is released as the boundaries move. Kawasaki shows that the dissipation functional is given by

$$R = \frac{\sigma}{2L} \int v^2(a) da. R \text{ is an average over all the boundaries (we integrate over } da).$$

- iv. From general dynamical systems theory, the system is governed by the equations

$$\frac{\delta R}{\delta v(a)} = -\frac{\delta H}{\delta q(a)}, \text{ where } \delta q(a) \text{ is an infinitesimal displacement of the boundary.}$$

- 1. These are functional derivatives. Without going into detail

$$\frac{\delta R}{\delta v(a)} = \frac{\sigma}{L} v(a) \text{ and } \frac{\delta H}{\delta q(a)} = \frac{\delta H}{\delta A} \frac{\delta A}{\delta q(a)} = \sigma \frac{\delta A}{\delta q(a)} = -\sigma K(a)$$

- 2. Combining terms, we find $\frac{\sigma}{L} v(a) = \sigma K(a)$, or $v(a) = LK(a)$.

- 3. The form of R was chosen to recover the known velocity equation.

- 4. We used the relation $\frac{\delta A}{\delta q(a)} = -K(a)$, which says that the change in area (length in 2D) of a boundary with an infinitesimal displacement of the boundary is minus the curvature. I cannot prove that here - just take my word for it.

- v. now, we need to evaluate R and H , from which we will derive the equations of motion.

- vi. Let us assume that we have a system as shown above, with trijunctions connected by straight lines. Let us locate the position of the vertices

(trijunctions) at $\vec{r}_i$. Note that we have only 3 boundaries connected to each vertex.

- vii. Then the energy of the system is just given by $H = \sigma A = \sigma \int da = \sigma \sum_{ij} r_{ij}$,

where the sum is over all vertices and the three boundaries connected to them.

Note that we arrange the sum to void overcounting. $r_{ij} = |\vec{r}_j - \vec{r}_i|$ is the length of the boundary connecting vertex i and vertex j .

- viii. We assume that the velocity on the boundary connecting i and j is just the weighted average of the velocity of the vertices, $\vec{v}_i$ and $\vec{v}_j$,

$$v(a) = \frac{1}{r_{ij}} (r_{aj} \vec{v}_i + r_{ai} \vec{v}_j) \cdot \hat{n}_{ij}, \text{ i.e., where } r_{aj} \text{ and } r_{ai} \text{ are the distances from point } a$$

to the vertices and $\hat{n}_{ij}$ is the unit normal to the boundary line. So, the velocity is just a linear combination of the velocities at the vertices and, since we assume that the boundary moves towards the center of curvature, we take the projection along the normal.

- ix. To evaluate R we need to integrate along the boundaries. We can envision this, however, as a sum of integrals over the lines connecting the vertices. Doing that, and integrating $v(a)^2$ over each segment, we get

$$R = \frac{1}{6} \frac{\sigma}{L} \sum_{ij} r_{ij} \left\{ (\hat{n}_{ij} \cdot \vec{v}_i)^2 + (\hat{n}_{ij} \cdot \vec{v}_i)(\hat{n}_{ij} \cdot \vec{v}_j) \right\}$$

- x. Finally, we use $\frac{\delta R}{\delta \vec{v}_i} = -\frac{\delta H}{\delta \vec{r}_i}$ to obtain the equations of motion:

$$\sum_j^{(i)} D_{ij} \cdot \left(\vec{v}_i + \frac{1}{2} \vec{v}_j \right) = -\sigma \sum_j^{(i)} \vec{r}_{ij} / r_{ij}, \text{ where we are summing over the three}$$

lines connected to site i and D_{ij} is a "friction tensor" given by:

$$D_{ij} = \frac{\sigma r_{ij}}{3L} \hat{n}_{ij} \hat{n}_{ij}$$

- xi. What is this? What Kawasaki did was to derive an equation of motion for a vertex that depends only on the distances and angles to the three vertices connected to it. It is a damped dynamics - there is drag on the vertex because it has to pull the boundaries with it as well as other dissipative terms.

- xii. It's still difficult to use (velocities on different sites are coupled, etc.).

- xiii. Simplify it:

1. drop the coupling between velocities: i.e., the $1/2 \vec{v}_j$ term on the left hand

side.

2. assume the normals $\hat{n}_{ij}$ are isotropically distributed
3. the resultant model (Kawasaki's model II) is

$$D_i^{\text{II}} \bar{v}_i = -\sigma \sum_j^{(i)} \bar{r}_{ij} / r_{ij}, \text{ where } D_i^{\text{II}} = \frac{\sigma}{6L} \sum_j^{(i)} r_{ij}$$

4. This then, is a very simple dynamics. It just says that at each time step, we sum over the lengths to the three connected vertices to get D and then v.

5. Even simpler is Kawasaki's model 1, where we use $D_i^{\text{I}} = \frac{\sigma}{2L} r_B(t)$,

where r_B is just the average boundary segment length.

- xiv. Note: they use recombination and annihilation processes as shown above for the Frost/Thompson method
- xv. How well does it work?

1. The edge number distribution: ● is the complete model, ○ is Model II, ▲ is Model I, and the solid line is the Potts model. The dashed line is from another method.

2. Normalized grain size distribution: thick solid line is the complete model, thin solid line is model II, dot-dash is the Potts model (the other lines is from a different method).
3. All in all, the results compare favorably to both experiment and the Potts model.

xvi. Strengths:

1. The point is that we've converted the problem to one where we track a relatively few number of variables with a relatively simple equation of motion.
2. And we know that since we have fewer grains at long time, the method gets better and better.
3. It's relatively easy to do 3D

xvii. Weaknesses:

1. is based on a lots of assumptions about growth
2. not as flexible as the Potts model.
3. No finite temperature effects.
4. can get vertices that deviate from 120° angles

7. Some general comments about modeling grain growth.

- a. In this course, we have discussed 5 ways to model grain growth
 - i. atomistically
 - ii. Monte Carlo Potts Model
 - iii. Cellular Automata
 - iv. boundary dynamics
 - v. vertex dynamics
- b. For atomistics:
 - i. Strengths and characteristics

1. only input are potentials
2. no assumptions about grain boundary structure or energy
3. no assumptions about dynamics
4. finite temperature
5. must track all atoms
- ii. Weaknesses
 1. too small a system for too short a time
- c. Potts model:
 - i. Strengths and characteristics
 1. input is the energy of the boundaries and mobilities
 2. very flexible
 3. no assumptions about dynamics
 4. finite temperature
 5. boundaries can take structure they want (given the lattice)
 6. must track all lattice sites
 - ii. weaknesses
 1. lattice effects
 2. dynamics are somewhat odd (not driven by forces)
- d. Cellular automata
 - i. Strengths and characteristics
 1. dynamics from local rules
 2. very flexible
 3. must track all lattice sites
 - ii. weaknesses
 1. deterministic (no finite temperature)
 2. lattice effects
 3. a true model - we have no clue a priori what the dynamics will be.
- e. boundary dynamics
 - i. Strengths and characteristics
 1. dynamics from local velocity relation
 2. fast and reasonably flexible
 3. dynamics are sound, given the assumptions
 4. boundaries are curved
 5. no lattice effects
 6. must track all boundary sites
 - ii. Weaknesses.

1. assumed dynamics
 2. no finite T
 3. not as flexible as Potts
- f. vertex dynamics
- i. Strengths and characteristics
 1. dynamics from local velocity relation of vertices
 2. fast
 3. dynamics are sound, given the assumptions
 4. no lattice effects
 5. must track all vertex sites
 - ii. Weaknesses.
 1. assumed dynamics
 2. straight boundaries
 3. no finite T
 4. not as flexible as Potts
- g. Note, however, what we've done
- i. as go from atomistics to Potts, to CAs, to boundary dynamics, to vertex dynamics, we have steadily reduced the dimensionality of the problem
 - ii. clearly we give up details as we go
 - iii. we gain computational speed, which means we can do more complicated problems
- h. Grain growth is a "paradigm" for materials modeling: to go to more macroscopic systems, we must give up detail.

8. Dislocation Dynamics

- a. As we've discussed, atomistics are too limited in size and time to model dislocation microstructure development.
 - i. typical slip bands are μm in size
 - ii. we need a new way to do such simulations
 - iii. we will ignore the atoms and simulate dislocations directly
- b. review of some dislocation properties (see "Introduction to Dislocations," by Hull and Bacon or, for an advanced discussion, "Theory of Dislocations," Hirth and Lothe)
 - i. types of dislocations

pure edge: note that the Burgers vector is $\perp$ to the line direction, which is into the paper

pure screw: note that the Burgers vector is $\parallel$ to the line direction

dislocation loop: note that character changes from pure edge to pure screw with a region of mixed character

ii. dislocation motion

edge movement along its glide plane

motion of a screw dislocation along its glide plane from AA' to BB'.

1. edge dislocation climb (i.e., movement perpendicular to the plane of the Burgers vector, is a diffusive process, requiring movement of material

into or out of the dislocation core.

iii. relation of dislocation motion to macroscopic strain

1. Suppose a stress is applied so that dislocations move and slip occurs.
2. The macroscopic displacement can be written in terms of the dislocation

movement as
$$D = \frac{b}{d} \sum_{i=1}^N x_i$$

3. From this, the macroscopic shear strain is $\epsilon = \frac{D}{h} = \frac{b}{dh} \sum_{i=1}^N x_i$
4. We then have $\epsilon = b\rho_m \langle x \rangle$, where ρ_m is the density of mobile dislocations.
5. The strain rate is thus $\dot{\epsilon} = b\rho_m \langle v \rangle$
6. These expressions hold for screw and mixed dislocations as well.
7. Thus, if we can calculate the dislocations that move and their average movement, we can determine macroscopic strain from a simulation of dislocations.

c. Forces on dislocations

- i. the force per unit length on a dislocation is determined using the Peach-

Koehler relation: $\frac{\vec{F}}{L} = (\vec{b} \cdot \vec{\sigma}_T) \times \vec{\xi}$, where $\vec{b}$ is the Burgers vector, $\vec{\xi}$ is the line direction of the dislocation and $\vec{\sigma}_T$ is the total stress tensor at the dislocation.

- ii. the total stress is a sum of contributions from various sources

$\sigma_T = \sigma_{\text{applied}} + \sigma_{\text{dislocations}} + \sigma_{\text{defects}}$: i.e., the applied (external) stress, the stress field of other dislocations, and the stress field of other defects in the material.

d. Stress due to a dislocation embedded in an isotropic elastic continuum

- i. For an infinite straight screw dislocation with line direction and Burgers vector along the $\hat{z}$ direction, the linear elastic stress field is:

$$\sigma_{xz} = \frac{-\mu b}{2\pi} \frac{y}{x^2 + y^2}, \quad \sigma_{yz} = \frac{\mu b}{2\pi} \frac{x}{x^2 + y^2}, \quad \sigma_{xy} = \sigma_{xx} = \sigma_{yy} = \sigma_{zz} = 0$$

- ii. For an infinite straight edge dislocation with line direction along the $\hat{z}$ direction and Burgers vector in the x direction, the linear elastic stress field is:

$$\sigma_{xx} = -\frac{\mu b}{2\pi(1-\nu)} \frac{y(3x^2 + y^2)}{(x^2 + y^2)^2}, \quad \sigma_{yy} = \frac{\mu b}{2\pi(1-\nu)} \frac{y(x^2 - y^2)}{(x^2 + y^2)^2},$$

$$\sigma_{xy} = \frac{\mu b}{2\pi(1-\nu)} \frac{x(x^2 - y^2)}{(x^2 + y^2)^2}, \quad \sigma_{zz} = -\frac{\mu b \nu}{\pi(1-\nu)} \frac{y}{(x^2 + y^2)}, \quad \sigma_{xz} = \sigma_{yz} = 0$$

- iii. μ is the shear modulus, $\mu = c_{44} = \frac{1}{2}(c_{11} - c_{12})$, where c_{ij} are elastic constants.

Typical values for μ are: Al: 2.65; Cu: 8.6, W: 16.0 (in units of 10^{10} Pa).

ν is Poisson's ratio and is about 0.3 for most metals.

- iv. Expressions are available for dislocation loops, finite straight segments, mixed dislocations etc. Please see Hirth and Lothe.
- v. Note: these expressions are valid when isotropic linear elasticity holds. When one is closer than some distance from the dislocation, these expressions are no longer valid. How close that is is under investigation. We shall refer to the region near a dislocation core where linear elasticity does not hold as short range.

e. Force on a dislocation from another dislocation

- i. assume we have two parallel edge dislocations (i and j) with line directions along the z direction and Burgers vectors along the x direction. Assume they are far enough apart so linear elasticity holds.
- ii. the force on one dislocation from the other along the glide direction (x) is (using the Peach-Koehler force)

$$\frac{F_x(\vec{r}_i)}{L} = \frac{\mu b_i b_j}{2\pi(1-\nu)} \frac{x_{ij}(x_{ij}^2 - y_{ij}^2)}{(x_{ij}^2 + y_{ij}^2)^2}, \text{ where the Burgers vectors can be positive or}$$

negative depending on whether they are in the $+$ or $-x$ direction.

f. Force on a dislocation from many dislocations

- i. assume (for the long-range forces) pairwise additivity
- ii. for a number of parallel edge dislocations (i and j) with line directions along the z direction and Burgers vectors along the x direction the force

$$\text{would be } \frac{F_x(\vec{r}_i)}{L} = \sum_j \frac{\mu b_i b_j}{2\pi(1-\nu)} \frac{x_{ij}(x_{ij}^2 - y_{ij}^2)}{(x_{ij}^2 + y_{ij}^2)^2}$$

- iii. Note that the force decreases as the inverse of the interdislocation separations

g. Net force on a dislocation

- i. The net force on a dislocation is $\bar{F}_{\text{net}} = \bar{F}_T - \gamma \bar{v}$
- ii. γ is a damping term that arises from emission of phonons, etc.
- iii. for example, the phonon drag coefficient varies with temperature as

$$\gamma_{\text{phonon}} = C \frac{\mu b}{C_s} g\left(\frac{T}{\Theta}\right), \text{ where } C \text{ is a constant, } C_s \text{ is the sound speed, } \Theta \text{ is the}$$

Debye temperature, and g is a function that (ignoring electron scattering) varies from 0 to 1 at $T = \Theta$, with a T^{-3} dependence at low T .

- iv. if we assume that climb of an edge dislocation is a diffusive process governed by vacancy diffusion, then we can show (H&L) that we can model climb by assuming a drag coefficient for climb given by $\gamma_{\text{climb}} = \frac{b_e^2 k_B T}{D_s v_a}$, where D_s is the self-diffusion coefficient, and v_a is the volume of a vacancy. Note that this is valid only at high temperatures.

h. Peierls stress

- i. Because of the atomic nature of the lattice, there is an inherent barrier to dislocation movement, called the Peierls barrier or Peierls stress.
- ii. the simplest way to look at this is to say that a dislocation cannot move until the stress on it overcomes the Peierls stress, but can then move freely, i.e., the Peierls stress acts as an activation barrier to dislocation movement.

i. short-range interactions

- i. we do not know what form the interactions take when the dislocations are close to each other (i.e., core-core interactions).
 1. using large-scale MD to find out
- ii. however, can assume annihilation events

1. top: dislocations of different sign on same plane can annihilate
2. bottom: dislocations of different sign on planes within Δ of each other can annihilate. Δ is a parameter that we'd have to set. Note that even at low T , this can happen, even though it involves climb. The diffusion

would be stress driven.

j. long-range interactions

- i. we showed that we find the force on each dislocation by summing over the contributions from all other dislocations
- ii. we showed that the force goes as the inverse of the separation distance
- iii. we need a way to do that

9. An aside: the calculation of long-range forces

a. Suppose we have a system of particles (these could be atoms or dislocations or whatever) that has pairwise additive interactions (i.e., potentials) that are long range, i.e., the interactions fall off as $1/r^n$, where $n \leq D$, the dimensionality of the system

b. How do we evaluate the total force on particle (or total energy)?

i. case 1: add up all interactions

1. for a finite system with N particles, there would be $N-1$ terms in the sum to find the force on each particle and N particles $\rightarrow$ would take $O(N^2)$ sums. This is prohibitively expensive for even reasonably large N .
2. for an infinite system (e.g., when using periodic boundary conditions), this approach is impossible

ii. case 2: use a cutoff

1. WRONG.
2. we can show that introducing a cutoff in systems with long-range interactions leads to incorrect results
3. example. suppose had charged particles with a $+$ charge at the center. if we cutoff interactions at some distance r , then $+$ particles would tend to arrange themselves just outside the cutoff and $-$ charges just inside:

4. long experience has shown that doing this leads to very unphysical behavior.
5. Presumably, one could eventually make the cutoff big enough so that it

wouldn't change the results significantly. However, the time per calculation would go as N times the number of neighbors within the cutoff, M . M would be huge, so NM interactions would be too large to deal with.

- iii. We need a better way.
- c. Ewald sums (complete derivations are given elsewhere)
 - i. must have periodic system (e.g., periodic boundary conditions)
 - ii. the most-used method for ionic systems
 - iii. Suppose we have a system of N point charges in a periodically repeated cell. The total electrostatic potential energy is:

$$U_{\text{electrostatic}} = \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ \text{if } i \neq j}}^N \sum_{\substack{\mathbf{R} \neq 0}} \frac{q_i q_j}{|\mathbf{R} + \mathbf{r}_{ij}|}, \text{ where } \mathbf{R} \text{ is a lattice vector and the } q\text{'s are}$$

charges.

- iv. This sum is conditionally convergent - the answer depends on the order the sum is carried out.
- v. In the Ewald method, we subtract from each lattice point a charge distribution with the same sign and magnitude of charge as that on the lattice site. Often

we use a Gaussian distribution of the form $\rho_i = q_i \left(\frac{\alpha}{\sqrt{\pi}} \right)^3 e^{-\alpha^2 r^2}$, where α

governs the width of the distribution. We can show that subtracting this charge distribution changes the long-range sum in iii. above to a sum of short-ranged potentials. Specifically, the interaction between two charge distributions ρ located at $\mathbf{r}_i$ and $\mathbf{r}_j$ is given by

$$\phi(r_{ij}) = \iint \frac{\rho_i(\bar{\mathbf{r}} - \bar{\mathbf{r}}_i) \rho_j(\bar{\mathbf{y}} - \bar{\mathbf{r}}_j)}{|\bar{\mathbf{r}} - \bar{\mathbf{y}}|}. \text{ Substituting } \rho_i(\bar{\mathbf{r}}) = q_i \left\{ \delta(\bar{\mathbf{r}}) - \left(\frac{\alpha}{\sqrt{\pi}} \right)^3 e^{-\alpha^2 r^2} \right\}$$

and integrating results in a potential that goes as the complementary error function, erfc , which is short ranged.

$$\text{erfc}(x) = 1 - \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-u^2} du. \quad \text{erfc}(0) = 1, \text{erfc}(\infty) = 0. \quad \text{Note that}$$

$$\text{erfc}(3) = 2.2 \times 10^{-5}.$$

- vi. However, since we subtracted the Gaussian distributions from the system we wanted, we need to add them again and find the correct energy. We evaluate the energy of just the added distributions by taking their Fourier transform and summing the energy in reciprocal space.
- vii. It turns out we include a self-energy that shouldn't be there, so we have to subtract it off.
- viii. The final result is :

$$U_{\text{electrostatic}} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left\{ \sum_{\substack{\vec{R} \neq 0 \\ \text{if } i=j}} \frac{q_i q_j \text{erfc}(\alpha |\vec{R} + \vec{r}_{ij}|)}{|\vec{R} + \vec{r}_{ij}|} + \frac{1}{\pi V} \sum_{\vec{k} \neq 0} \frac{4\pi^2 q_i q_j}{k^2} e^{-k^2/4\alpha} \cos(\vec{k} \cdot \vec{r}_{ij}) \right\} - \left(\frac{\alpha}{\sqrt{\pi}} \right) \sum_{i=1}^N q_i^2 + \left(\frac{2\pi}{3V} \right) \left| \sum_{i=1}^N q_i \vec{r}_i^2 \right|$$

- ix. Each term in the direct lattice sum goes as $\text{erfc}(\alpha r_{ij})$, so a small value of α leads to a longer-ranged sum. The terms in the reciprocal lattice go as $\exp(-k^2/4\alpha)$, so that the smaller α is, the faster the reciprocal lattice terms drop off.

Thus, there is a balance between efficiency of the sums and we choose α to optimize the overall calculation.

- xi. Carlsson has developed an Ewald sum approach for dislocations in 2d.
- d. Heierarchical methods.
 - i. there are a number of different forms of heierarchical approaches, each leading to an algorithm of $O(N \ln N)$ or $O(N)$ (Note: $\ln N$ is small ($\ln(10^6) = 13.8$)).

- ii. all the algorithms are similar in that they build up a hierarchy of levels to minimize the computational burden.
- iii. we'll show one approach here, the fast-multipole method (FMM) of Greengard, L. and V. Rokhlin, J. Comp. Phys., **73**, 325 (1987). They used it first for galaxy interactions in 2D and later for charged systems in 2D and even later for charged systems in 3D.
- iv. we'll present the method for interacting dislocations in 2D.
- e. Fast Multipole Method (FMM) for interacting dislocations in 2D. For complete details, see Wang and LeSar, Phil Mag **71**, 151 (1995).
 - i. the basic idea is that is two sets of interacting dislocations (or charges or whatever) are separated from each other, then we can calculate the interactions between them by finding the interactions between the multipole moments of their distributions. If they are well-separated, as shown here, then we can give an a priori estimate of the error introduced by using the multipole expansions.

- ii. Suppose we had a system on interacting dislocations. Separate out a single dislocation interacting with a group of dislocations, with the separation of the dislocation and the center of the group being R .

We could describe the interactions in this system with a multipole expansion. For charged particles (ions), we'd have the charge of the single particle interacting with the net charge, dipole, octopole, hexadecapole, etc. of the group of dislocations. Now, if we moved that group farther away, then we'd

need fewer terms in the multipole expansion to obtain the same accuracy. (the charge-charge term goes as $1/r$, the charge-dipole terms goes as $1/r^2$, etc.). We could, on the other hand, keep the same number of multipoles in our expansion and just consider a larger number (i.e., volume) of dislocations to interact with:

If we arranged the problem correctly, we could keep the same accuracy, but as the separation between dislocations increased, we use a multipole expansion for bigger and bigger areas. This is much more efficient and is the basis of the FMM

ii. we divide our simulation cell into smaller cells:

note that each level is the parent of the next level (i.e., the level with only one cell (0) is the parent of that with 4 cells (1). So we say that the level-1 cells are the children of a level-0 cell.

iii. the interactions will be calculated as follows.

3	3	3	3
3	3	3	3
2	2	2	2
1	1	1	2
1	0	1	2
1	1	1	2

We consider dislocations at the highest level we have created in our hierarchy of levels (i.e., the smallest cells), where we want the force on all dislocations (just to remind you where we are going with this). Consider a dislocation in the cell marked (0). We want the interaction of all other dislocations in the system with it. In the FMM, it will interact with dislocations in cells that are not well separated by a direct summation of the pair interactions. By well-separated, we mean that cells that are at least next-nearest neighbors away at the same level. Thus, a dislocation in cell (0) will interact via a direct summation with all other dislocations in cell (0) and with all dislocations in the nearest neighbor cells, marked (1). The cells marked (2) are at the same level as (0), but are next-nearest neighbors and so the dislocations in cell (0) will interact not via direct summation with the dislocations in cells (2), but with their multipole moments. Now, consider the parent cell of cell (0), which is made up of cell (0) and the three cells marked (1) to the left and below cell (0). Note that the cells marked (3) are well-separated from the parent of (0). In the FMM, we will then use the multipole moments of those cells that are at the same level as and are well-separated from the parent of (0). These are marked (3). Note that if we had a more finely-divided system, the next level of interactions would be with cells that are well-separated from the parent of the parent of (0) and we'd use those multipoles to interact with the dislocations in (0).

- iv. The FMM obtains $O(N)$ efficiency by being very clever about how to calculate the multipole moments. The point is that we first calculate the multipole expansions for all the smallest cells in the system. These are analytic expressions and involve summing over the particles. We then rewrite each of those expansions with the center of the expansion shifted from the center of the child cell to the center of the child's parent cell. These are just algebraic expressions. The multipole moments of the children's parents are then just sums of the children's multipoles, with some geometric factors. We then use

these multipoles to find those of the parents of the parents, and so on. This is a very efficient way to find all the multipoles at all levels, as we need to.

1. Let's make this concrete by considering a familiar problem from electrostatics, the 3-dimensional Coulomb system (i.e., charged particles in 3 dimensions).
2. Suppose we have a set of charges in a region interacting with one charged particle outside that region, as we saw in e.ii on page III.50.

3. The total electrostatic potential would be given by $\Phi(\vec{r}) = \sum_{i=1}^M \frac{q_i}{|\vec{r} - \vec{r}_i|}$, where

there are M particles in the region of interest and r is outside that region.

From any electromagnetism book (like Jackson), we see we can rewrite that

sum in the form $\Phi(\vec{r}) = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{M_{\ell m} Y_{\ell m}(\theta, \phi)}{(2\ell+1)r^{\ell+1}}$, where the multipole

moments $M_{\ell m}$ are given by $M_{\ell m} = \sum_{j=1}^m q_j r_j^{\ell} Y_{\ell m}^*(\theta_j, \phi_j)$, and the $Y_{\ell m}$ are spherical harmonics.

4. Note, however, that we the multipole moments are defined relative to a specific coordinate system, in this case centered at the centers of the smallest cells. We can shift that origin to the center of the cell's parent cell very easily. Then the multipole moments of the parents cell would be the sum of the 8 shifted multipoles of its children. Shifting from a child to its parent yields

$$M'_{\lambda\mu} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \left(4\pi \frac{(-r_c)^{\lambda-\ell} Y_{\lambda-\ell, \mu-m}^*(\theta_c, \phi_c) a_{\lambda-\ell, \mu-m} a_{\ell m} (2\lambda-1)}{(2\ell+1)[2(\lambda-\ell)+1] a_{\lambda\mu}} \right) M_{\ell m}, \text{ where}$$

$$a_{\ell m} = (-1)^{\ell+m} \frac{(2\ell+1)^{1/2}}{[4\pi(\ell+m)!(\ell-m)!]^{1/2}}. \text{ Note that these are just geometric}$$

factors and determining the multipole of the parent would not involve summing over the particles again.

- v. We can also be very efficient when calculating interactions.

The interactions of the level-3 particles (i.e., in a) with the multipoles of a level-2 cell (B) are calculated by shifting the center of the multipole expansion of the potential of the level-2 cell to the well-separated parent (level-2) of the cell in which the particle sits, creating what is usually referred to as a *local* expansion centered at the parent cell (A). In the 3-D Coulomb case this

becomes $\Phi(\vec{r}) = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} L_{\ell m} r^{\ell} Y_{\ell m}(\theta, \phi)$, where

$$L_{\lambda\mu} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \left(4\pi \frac{(-1)^{\ell+m} Y_{\lambda+\ell, \mu-m}^*(\theta_{AB}, \phi_{AB}) a_{\lambda\mu} a_{\ell m}}{r_{AB}^{\lambda+\ell+1} (2\ell+1) [2(\lambda+\ell)+1] a_{\lambda+\ell, \mu-m}} \right) M_{\ell m}. \text{ This local}$$

expansion is then shifted to be centered at the level-3 cell (a) and the net interaction determined by adding the terms for each particle. For the 3D Coulomb case, this last shift becomes

$$L_{\lambda\mu} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \left(4\pi \frac{r_c^{\ell-\lambda} Y_{\ell-\lambda, m-\mu}(\theta_c, \phi_c) a_{\lambda\mu} a_{\ell-\lambda, m-\mu}}{(2\lambda+1) [2(\ell-\lambda)+1] a_{\ell m}} \right) L_{\ell m}.$$

- vi. The point is that the FMM is efficient because we only sum over the particles a few times: once when finding the multipoles, once when finding the potential in the multipole expansion, and then for the direct summation.
- vii. Can we apply this to dislocations? Consider a set of screws with the Burgers vector and line direction in the z direction. Then we have for the stress due to one of these dislocations:

$$\sigma_{xz} = \frac{-\mu b}{2\pi} \frac{y}{x^2 + y^2}, \quad \sigma_{yz} = \frac{\mu b}{2\pi} \frac{x}{x^2 + y^2}, \quad \sigma_{xy} = \sigma_{xx} = \sigma_{yy} = \sigma_{zz} = 0$$

Our goal is to add up all the stresses from the dislocations at the site of each of the dislocations and then to use the Peach-Koehler force law. For

dislocations that are close by (i.e., in cells (0) and (1) above), we'll just add up the contribution from each dislocation to the total stress. For dislocations that are farther off, we'll use the FMM.

1. We want to be efficient, so consider the potential $\phi(z) = b \ln(z)$, where $z = x+iy$.

2. Note that $\phi'(z) = \frac{d\phi}{dz} = \frac{b}{z} = \frac{b}{x+iy} = b \frac{x-iy}{x^2+y^2}$, so $\sigma_{xz} = \frac{\mu}{2\pi} \text{Im}(\phi')$ and

$$\sigma_{xz} = \frac{\mu}{2\pi} \text{Re}(\phi')$$

3. So do all the multipole expansions for $\ln(z)$, take the derivative at the end, then find the real and imaginary parts.

4. For details, see Wang and LeSar. We also do edges there.

viii. I know this is probably not understandable, but it should give you a clue as to what is involved.

ix. It works.

O(N) Algorithm for Screw Dislocations

(a)

O(N) Algorithm for Edge Dislocations

(b)

the curve right along the y axis is what a direct $O(N^2)$ calculation takes.

x. Can also do in 3d and for other potentials

10. Back to dislocation dynamics

- a. So, we can now evaluate the total stress, what can we do with it?
- b. there have been studies of pattern formation, fracture, etc. as we discussed in class,
- c. we can also go to 3d as discussed in class.
- d. the point is: we derived equations of motion: the model
- e. we implement into a code and use it: simulation

11. One can imagine many other dynamical approaches, which we will not discuss

E. Other mesoscopic methods

1. there are other methods, including such things as percolation theory, rate theory, etc.,

which we just don't have time to discuss. We saw one such method in class: micromechanical fracture modeling.

2. The point is that mesoscale modeling is hard to talk about - each problem requires its own model and, often, its own simulation scheme.
3. For this course, just know that these models are important and possible and that they require an intimate knowledge of the problem to be solved.

IV. Macroscopic simulations

A. Introduction to the finite-element method (FEM) (I urge you to see "Finite Element Primer," by Irons and Shrive [IS]. I take a lot of examples from that book.)

1. Goal:

- a. goal is to simulate the response of a macroscopic system
- b. different types of response
 - i. elastic bodies - "old-style" engineering
 - 1. material responds elastically (linearly) for all displacements
 - ii. elastic-plastic response
 - 1. material responds linearly to some fixed stress and then has a non-linear response that is independent of loading rate.
 - 2. depends only on total load, i.e., loading history but not duration
 - 3. time independent but can depend on T
 - iii. elastic-viscoplastic response
 - 1. material responds linearly to its yield point, which may depend on loading rate.
 - 2. response depends on loading rate, temperature, etc.
 - 3. note that this is the most general case and is what we're most interested in.
- c. different types of applications
 - i. structural engineering
 - 1. static structures (i.e., elastic or elastic-plastic)
 - 2. dynamic structures (like crash scenarios)
 - ii. manufacturing
 - 1. forming, forging, machining, etc.
- d. the type of response to include will depend on material and application

2. General description

- a. no general analytical solution for macroscopic response
- b. we develop differential equations and discretize them to create algebraic equations that we can solve using matrix manipulations
 - i. represent body or structure by an assemblage of subdivisions call *finite elements* (see 1.1 below)
 - ii. elements are interconnected at joints that are called *nodes*
 - iii. simple functions are chosen to approximate the actual displacements in an element in terms of (usually) the node displacements (*displacement functions*) (see 1.2 below)
 - iv. variational principles (such as the Principle of the Minimum of the Potential)

are used to generate the differential equations

v. materials models connect displacements to load

c. examples of finite elements

Figure 1-1 Two-dimensional region represented as an assemblage of triangular elements.

- i. 1.1: two-dimensional region represented as an assembly of triangular elements
- ii. 1.2: isometric view of triangular elements with linear displacement mode plotted in the third dimension

d. A trivial example of a variational principle.

- i. Consider a simple spring with spring constant k under a load P as shown:

- ii. let u be the amount of displacement under the load.
- iii. the internal strain energy of the spring is $1/2$ (force in spring) (displacement):

$$U = 1/2 k u^2.$$

- iv. the potential energy due to the load is just (load) (displacement) $W = -Pu$
- v. total energy is $E = U + W$.
- vi. we find the minimum energy, i.e., where $\partial E / \partial u = 0$, or $ku = P$, i.e., the forces balance.
- e. input/output
 - i. input are material properties (models)
 - ii. output is materials response, including stress, strain, failure, etc.
- 3. The 6 steps in an FEM simulation
 - a. Step #1: discretize the body.
 - i. the process of dividing the body into discrete elements
 - ii. in 2d, can use triangles (see 1.1 above), quadrilaterals, etc.
 - iii. in 3d, can use tetrahedra, rectangular prisms, hexahedra, etc.
 - iv. generating the elements is sort of an art form. There are codes that automate this, but people can spend a month meshing a really hard problem.
 - v. there is a nationally funded project, the National Grid Project devoted entirely to developing grid generating methods
 - b. Step #2: select a displacement model
 - i. we need a form that approximates the real displacements throughout an element based on some calculatable displacements, like the nodal displacements.
 - ii. three factors
 - 1. type and degree of model. usually choose some polynomial, but we need to decide order, etc.
 - 2. need to decide which displacement magnitudes that describe the model to use. Usually use nodal displacements, but could use derivatives, etc.
 - 3. the model must satisfy certain continuity requirements.
 - c. Step #3: derive the element stiffness matrix.
 - i. usually based on a variational procedure
 - ii. stiffness relates the displacement of nodal points to the applied forces at the nodal points: $\mathbf{K} \mathbf{d} = \mathbf{F}$, where $\mathbf{K}$ is the (rectangular) stiffness matrix, $\mathbf{d}$ is the vector of nodal displacements, and $\mathbf{F}$ is the vector of nodal applied forces.
 - iii. determined by geometry of elements and materials models.
 - iv. a simple example: consider a plate with three springs along edges

1. the force put on system at A, B, and C is F_A, F_B, F_C .
2. the displacements at A, B, and C, are w_A, w_B, w_C .
3. assume that the total stiffness of the plate is k and that that is apportioned equally among the three springs, i.e., each has a spring constant of $1/3 k$. Note that they are located at the midpoints of the element boundaries.
4. assume a linear displacement field, so the displacement at the spring between A and C is just $1/2(w_A + w_C)$ and the total force on that spring is spring constant times displacement, i.e., $1/6 k (w_A + w_C)$. This load is assumed to be equally divided between nodes A and C, i.e., it contributes a load of $1/12 k (w_A + w_C)$ to each. Similarly, we have a contribution to the load at B and A of $1/12 k (w_A + w_B)$ and of $1/12 k (w_B + w_C)$ at B and C.
5. adding up all the contributions at each node, we obtain the total force at A, B, and C from the displacement of the springs, i.e., we have $1/12 k (2w_A + w_B + w_C)$ at A. These forces must be balanced by the applied forces, so we have:

$$\frac{1}{12} k \begin{bmatrix} 2 & 1 & 1 \\ 1 & 2 & 1 \\ 1 & 1 & 2 \end{bmatrix} \begin{bmatrix} w_A \\ w_B \\ w_C \end{bmatrix} = \begin{bmatrix} F_A \\ F_B \\ F_C \end{bmatrix}$$

6. the stiffness matrix is $\mathbf{K} = \frac{1}{12} k \begin{bmatrix} 2 & 1 & 1 \\ 1 & 2 & 1 \\ 1 & 1 & 2 \end{bmatrix}$
7. note that $\mathbf{K}$ depends on the geometry of the system and the material properties, in this case the model of springs of $1/3 k$ at the boundary midpoints.
8. the total energy is given by

$$U = \frac{1}{2} [w_A \quad w_B \quad w_C] \mathbf{K} \begin{bmatrix} w_A \\ w_B \\ w_C \end{bmatrix} = \frac{1}{2} \{w\}^T \mathbf{K} \{w\},$$

where $\{w\}$ is the vector of displacements

- v. NOTE: all the materials science is in this step.
- d. Step #4: put together equations for the overall system
 - i. assemble the overall stiffness matrix
 - ii. an example

1. suppose we want to model the displacement due to gravity of a membrane hooked securely on the left and supported by an elastic medium.
2. suppose we use a set of triangular elements as shown, with displacements being up or down for each node.
3. suppose we use the same model for the elastic properties as we did in 3c above. Note that we only assume that the forces are uniformly distributed across the element and that the springs are at the midpoints. Then it doesn't matter what shape or size the elements are. As long as we evenly distribute the forces, whether we use the equilateral triangle as in 3c or a right triangle as we do here doesn't matter.
4. we have the stiffness matrix for each element as given in 3c above
5. to assemble them we note that we must rename the nodes of I as: $A \rightarrow 1$, $B \rightarrow 2$, $C \rightarrow 4$.
6. create a new stiffness matrix for the system: 12×12
7. load in stiffness matrix from element I:

$$\frac{1}{12}k \begin{bmatrix} 2 & 1 & 0 & 1 & 0 & \dots & 0 \\ 1 & 2 & 0 & 1 & 0 & \dots & 0 \\ 0 & 0 & 0 & 0 & 0 & \dots & 0 \\ 1 & 1 & 0 & 2 & 0 & \dots & 0 \\ 0 & 0 & 0 & 0 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} w_1 \\ w_2 \\ w_3 \\ w_4 \\ w_5 \\ \vdots \\ w_{12} \end{bmatrix} = \frac{1}{3}L \begin{bmatrix} 1 \\ 1 \\ 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix}$$

where the load arises from gravity. The weight of each element is taken as L and we apportion it evenly to each node.

8. add the stiffness matrix from element II, keeping track of the numbering system. we get

$$\frac{1}{12}k \begin{bmatrix} 4 & 1 & 1 & 2 & 0 & \dots & 0 \\ 1 & 2 & 0 & 1 & 0 & \dots & 0 \\ 1 & 0 & 2 & 1 & 0 & \dots & 0 \\ 2 & 1 & 1 & 4 & 0 & \dots & 0 \\ 0 & 0 & 0 & 0 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} w_1 \\ w_2 \\ w_3 \\ w_4 \\ w_5 \\ \vdots \\ w_{12} \end{bmatrix} = \frac{1}{3}L \begin{bmatrix} 2 \\ 1 \\ 1 \\ 2 \\ 0 \\ \vdots \\ 0 \end{bmatrix}$$

9. keep doing this until have included all 12 elements

10. note that the overall stiffness matrix will be banded - it will have a band of non-zero elements down the diagonal with zeroes in the upper right and lower left corners. This is a consequence of how we ordered the elements. It is good, as there are many very efficient numerical schemes for dealing with banded matrices. The width of the band arises from the amount of connectivity, i.e., each node (other than the ends) is part of 3 elements and is connected to 4 other nodes.

- iii. include boundary conditions

1. in the above problem, we have $w_1 = w_2 = 0$ (fixed to wall), so we drop the top two rows and left two columns from $\mathbf{K}$, leaving a 10×10 matrix.

- e. Step #5: solve for displacements

- i. solve large sets of simultaneous equations

1. in the above example, we solve for 10 unknown displacements from the 10 equations. There are many ways to do this efficiently, especially when we've ordered the elements well.
2. we find the following results (from [IS]) (in order of w_3 to w_{12}): 1.03,

1.51,1.03,0.9,1.00,1.01,1.00,1.00,1.00,1.00).

3. It turns out that we could do this problem analytically, where we find that all displacements should be 1. So, except for a couple of nodes near the boundary, we do well. What is wrong at 4 and 6? Problem is due to the mesh and how we apportioned our forces (the displacement function).
 - ii. may be time-dependent
 - f. Step #6: compute stress, strains, etc from displacements
4. The point is that only in step c do we do materials science. The rest is algebra, geometry, numerical methods, etc.

B. Grids and Displacement Functions

1. we'll not discuss how to develop optimal grids for a specific problem - there are books describing how to go about it.

a. some possible shapes in 2D:

(a) Triangular element

(b) Rectangular element

(c) Quadrilateral element

(d) Quadrilateral formed by two triangles

(e) Quadrilateral formed by four triangles

(f) Axisymmetric triangular ring element

b. some possible shapes in 3D:

(a) Tetrahedron

(b) Rectangular prism

(c) Arbitrary hexahedron

2. suppose we have a grid in place

a. we assume we can write

$$u(x, y, z) = \sum_{i=1}^n N_i(x, y, z) u_i$$
, where u is the displacement field at any point in an element and u_i are the nodal displacements. The N_i are the shape functions, and serve as an interpolation scheme between the nodes and all other points. The shape functions can be chosen to given different levels of accuracy.

3. some general examples of shape functions

a. suppose we have a square grid as shown

i. the shape function is linear in x and y , i.e., we can only assume a linear variation because we don't have enough equations for the variables otherwise

ii. we know that $N_i = 1$ at node i and 0 at all other nodes.

iii. the answer in this case is that: $N_A = \frac{1}{4}(1-x)(1-y)$, $N_B = \frac{1}{4}(1+x)(1-y)$,

$$N_C = \frac{1}{4}(1+x)(1+y), N_D = \frac{1}{4}(1-x)(1+y)$$

iv. So, the displacement at a point is just given by

$$u(x, y, z) = N_A(x, y, z) u_A + N_B(x, y, z) u_B + N_C(x, y, z) u_C + N_D(x, y, z) u_D$$

b. suppose we didn't have a square grid, but a general quadrilateral that looked like

- i. we introduce scaled coordinates ξ and ψ that span from -1 to 1, i.e., they look like x and y in the square grid.
 - ii. for the linear grid shown here, the shape functions are the same, replacing x by ξ and y by ψ , i.e., the displacements are still linear functions of the variation between the node points, i.e., $N_A = \frac{1}{4}(1 - \xi)(1 - \psi)$, etc.
 - iii. for the system shown here, it is possible to show that the position at a point can be given by the same shape functions, i.e.,
 $x = N_A x_A + N_B x_B + N_C x_C + N_D x_D$, etc., where x_i is the x coordinate of the i^{th} node. We'd have similar equations for y and z .
 - iv. for this system, we have $\bar{r} = \sum_{i=1}^n N_i \bar{r}_i$ for coordinate of any point in an element.
 - v. what this means is that we can describe the system in the reduced grid space (ξ, ψ) , and, using the same shape functions, transform the grid back to real space as well as calculating the displacements at any point.
 - vi. elements that have this property are called *isoparametric*. We'll only talk about these type of elements.
- c. Suppose introduce nodes along edges
- i. We could have a system (the quadratic quadrilateral) that looks like

- ii. The shape functions would be generalized quadratic functions. Note that while the equations are more complicated, including nodes along the boundary greatly increases the flexibility of the elements, allowing parabolic behavior. see below
- iii. as an example, consider the modeling of a high curvature region with triangular elements

introducing extra grid points clearly leads to a better description of the shape of the curved region.

1. on the left we are using *linear* triangles; on the right *quadratic*, because the shape functions are linear if we have nodes at the vertices only and quadratic if we have nodes along the boundaries.

4. some comments on grids and shape functions

a. choice of grid shapes

- i. the linear triangle and linear rectangle have edges that are straight. Modeling curved boundaries with these elements is difficult and requires a large number of elements. Including nodes along the edges allows for "curvature."

b. choice of shape functions

- i. the strain, as we shall see, is a function of gradients of the shape function. linear triangles produce a constant strain in each element. Using linear triangles thus produces a patch-wise discontinuous strain field. If strain gradients are large, many elements might be needed to obtain an accurate solution. The linear quadrilateral does not have as severe a problem.

Looking at N_A , for example, from above, we see that it has terms like αxy , allowing for a linear strain-field variation.

- ii. choosing between linear and quadratic elements is usually based on the degree of strain in the problem. For relatively uniform strain, the extra degrees of freedom introduced by the quadratic elements is usually not worth the extra computational time. When there are large strain gradients, then it is worth it to use the more accurate elements.

5. an issue with shapes and shape functions

- a. suppose we use the quadratic quadrilateral shown above on Page IV-10.
- b. the shape functions for the midboundary nodes are all similar in form. For

$$\text{example, } N_F = \frac{1}{2}(1-x^2)(1+y) \text{ and } N_D = \frac{1}{2}(1-y^2)(1+x).$$

- c. the corners are also of similar form, e.g., $N_E = \frac{1}{4}(1+x)(1+y) - \frac{1}{2}N_D - \frac{1}{2}N_F$.

i.e., take what it would have been with no midboundary nodes and subtract off contributions from the neighbors

- d. suppose we look at the membrane problem again. There is one displacement per node and so we have an 8x8 stiffness matrix for this element.
- e. instead of assuming some set of equivalent springs, let's assume that there is a uniform "spring constant density," k , so the strain energy density is $1/2kw^2$ at each point in the element. This is as if we spread the elasticity uniformly over the body.

The total strain energy per element is $\int_{-1}^1 \int_{-1}^1 \frac{1}{2}kw^2 dx dy$. But, $w = \sum_{i=1}^8 N_i w_i$ and

$$w^2 = \left(\sum_{i=1}^8 N_i w_i \right) \left(\sum_{j=1}^8 N_j w_j \right) = \sum_{i=1}^8 \sum_{j=1}^8 N_i N_j w_i w_j. \text{ So the total strain energy per}$$

element is $\frac{1}{2} \sum_{i=1}^8 \sum_{j=1}^8 w_i w_j \int_{-1}^1 \int_{-1}^1 k N_i N_j dx dy = \frac{1}{2} \{w_n\}^T \mathbf{K} \{w_n\}$, where the components

of the stiffness matrix have the form $K_{ij} = \int_{-1}^1 \int_{-1}^1 k N_i N_j dx dy$. Since we have the N s

in terms of x and y , we can do all 64 integrals analytically.

- f. assume we have the following geometry, where we take the load as $4L$ per element, so that the total load is $12L$ as it was when we did the same problem with a triangular grid. Note that the load per area is just L . We spread the load evenly across all nodes, i.e., each element contributes $L/2$ to each node.

- g. construct the overall stiffness matrix as before, and introduce some symmetry to make the problem easier, i.e., as indicated by the element numbers.
- h. find the displacements by solving the matrix equations. We find we obtain terrible results and that the displacements go as: (from node 1 to 9)

2.03, 7.40, 1.43, 2.97, 6.89, 2.56, 2.52, 7.34, 2.45. Remember that the analytical solution has a uniform displacement of 1.

- i. if you take these nodal displacements and find the displacement throughout the elements, you'll see huge variations. For example, the displacements at the middle of the elements are -0.97, -2.2, and -2.08, from left to right. They go the wrong way!
- j. if we define the average displacements as $\langle w \rangle = \frac{1}{4} \int_{-1}^1 \int_{-1}^1 w \, dx dy$, and use the expression for w in terms of the N_s , we have for the three elements (from left to right), $\langle w \rangle = 0.600, .928, .978$.
- k. So, the average properties are OK, but something is weird about the displacements at specific points.
- l. the problem is that we spread the load evenly across all nodes, and yet all nodes are not equivalent. The ones at the corners are connected to 3 other nodes and the ones at the midpoints only to 2.
 - i. we can see that this might be the issue by finding the load needed to obtain the correct displacements (i.e., all $w=1$). We do this by multiplying the calculated stiffness matrix into the vector of the correct nodal displacements. We find that the load needed to make it all come out right is: $-1/3 L$ at the corners (a load in the wrong direction!) and $4/3 L$ at the edges.
- m. What's up? The point is that nodes do a lot for us. (1) They connect the system to springs via the displacement functions; (2) They connect the elements together; and (3) They connect loads to the elements and thus to the springs. So, if the nodes are not the same, then applying equal loads to all of them may not be correct.
- n. How do we fix it? Well, we use the principle of virtual work to find what the equivalent load should be to obtain the correct values.
 - i. suppose we consider the work done if we displace just one corner node from w_A to $w_A + dw_A$. The change in displacement at any point is $w = (N_A(w_A + dw_A) + \dots) - (N_A w_A + \dots) = N_A dw_A$. Since the load per area is L , the infinitesimal force on an area is just $L dx dy$. Thus the work due to this displacement is just $dw_A \int_{-1}^1 \int_{-1}^1 N_A L dx dy = -\frac{1}{3} L dw_A$. So, to have the equivalent load to gravity at a corner nodes would require a load of $-1/3 L$. We can do a similar analysis for the edge nodes.

- o. using these load leads to very good predictions of the right response, i.e., all displacements are, more or less, equal to 1 (within 15%).
- p. the point of all this is that we have to recognize that all nodes are not the same and that we must be careful when applying our loads and boundary conditions.

C. Stiffness matrix for a linear elastic body.

1. Case 1: linear strains

a. strains are defined as

$$\epsilon_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_{\alpha}}{\partial x_{\beta}} + \frac{\partial u_{\beta}}{\partial x_{\alpha}} \right)$$

i. note that we will use engineering strains most of the time, which are defined as $\epsilon_{\alpha} = \epsilon_{\alpha\alpha}$ and $\gamma_{\alpha\beta} = 2\epsilon_{\alpha\beta}$, for $\alpha \neq \beta$.

b. often will write strains a vector, with the form (using engineering strains)

$$\{\epsilon\} = \begin{bmatrix} \epsilon_x \\ \epsilon_y \\ \epsilon_z \\ \gamma_{yz} \\ \gamma_{xz} \\ \gamma_{xy} \end{bmatrix} = \begin{bmatrix} \partial/\partial x & 0 & 0 \\ 0 & \partial/\partial y & 0 \\ 0 & 0 & \partial/\partial z \\ 0 & \partial/\partial z & \partial/\partial y \\ \partial/\partial z & 0 & \partial/\partial x \\ \partial/\partial y & \partial/\partial x & 0 \end{bmatrix} \begin{bmatrix} u_x \\ u_y \\ u_z \end{bmatrix}$$

b. From before we had $\mathbf{u}(x,y,z) = \sum_{i=1}^n N_i(x,y,z) \mathbf{u}_i = \mathbf{N}\{\mathbf{u}_n\}$, where $\mathbf{N}$ is the shape matrix and $\{\mathbf{u}_n\}$ is the vector of nodal positions (in 2d, for example, it is a vector $2n$ long). Writing it out in matrix form we have

$$\{\mathbf{u}\} \equiv \begin{bmatrix} u_x \\ u_y \\ u_z \end{bmatrix} = \begin{bmatrix} N_1 & 0 & 0 & N_2 & \dots & 0 \\ 0 & N_1 & 0 & 0 & \dots & 0 \\ 0 & 0 & N_1 & 0 & \dots & N_n \end{bmatrix} \begin{bmatrix} u_{1x} \\ u_{1y} \\ u_{1z} \\ u_{2x} \\ \vdots \\ u_{nz} \end{bmatrix} = \mathbf{N}\{\mathbf{u}_n\}$$

c. Only $\mathbf{N}$ depends on x,y,z , so we can use the definition of strain and find

$$\{\epsilon\} = \begin{bmatrix} \partial/\partial x & 0 & 0 \\ 0 & \partial/\partial y & 0 \\ 0 & 0 & \partial/\partial z \\ 0 & \partial/\partial z & \partial/\partial y \\ \partial/\partial z & 0 & \partial/\partial x \\ \partial/\partial y & \partial/\partial x & 0 \end{bmatrix} \begin{bmatrix} N_1 & 0 & 0 & N_2 & \dots & 0 \\ 0 & N_1 & 0 & 0 & \dots & 0 \\ 0 & 0 & N_1 & 0 & \dots & N_n \end{bmatrix} \{\mathbf{u}_n\} \equiv \mathbf{B}\{\mathbf{u}_n\}$$

d. The $\mathbf{B}$ matrix thus connects the strain to the nodal displacements. All geometric information is contained in $\mathbf{B}$.

e. Note. If we are using isoparametric shape functions, then the N_s will be in terms of reduced coordinates (ξ, ψ in our earlier example). The derivatives with respect to x, y , and z will need to be found using the relationship between x, y, z and the nodal positions - just a coordinate transformation, but it can be messy.

f. Let us take a concrete example, the linear quadrilateral that we did before. In

reduced coordinates, we have $N_A = \frac{1}{4}(1-\xi)(1-\psi)$, $N_B = \frac{1}{4}(1+\xi)(1-\psi)$,

$N_C = \frac{1}{4}(1+\xi)(1+\psi)$, $N_D = \frac{1}{4}(1-\xi)(1+\psi)$. We also have

$x = N_A x_A + N_B x_B + N_C x_C + N_D x_D$, with a similar equation for y . To calculate

strains, we need $\partial/\partial x$ and $\partial/\partial y$. But the shape functions are functions of ξ and ψ .

We can convert $\partial/\partial x$ and $\partial/\partial y$ to the needed derivatives by noting that

$$\begin{pmatrix} \partial/\partial \xi \\ \partial/\partial \psi \end{pmatrix} = \begin{pmatrix} \partial x/\partial \xi & \partial y/\partial \xi \\ \partial x/\partial \psi & \partial y/\partial \psi \end{pmatrix} \begin{pmatrix} \partial/\partial x \\ \partial/\partial y \end{pmatrix} = \mathbf{J} \begin{pmatrix} \partial/\partial x \\ \partial/\partial y \end{pmatrix}, \text{ where } \mathbf{J} \text{ is the Jacobian of the}$$

transformation. If we find the inverse of $\mathbf{J}$, we have $\begin{pmatrix} \partial/\partial x \\ \partial/\partial y \end{pmatrix} = \mathbf{J}^{-1} \begin{pmatrix} \partial/\partial \xi \\ \partial/\partial \psi \end{pmatrix}$. It's

easy to show that

$$\mathbf{J}^{-1} = \frac{1}{(\partial x/\partial \xi)(\partial y/\partial \psi) - (\partial x/\partial \psi)(\partial y/\partial \xi)} \begin{pmatrix} \partial y/\partial \psi & -\partial y/\partial \xi \\ -\partial x/\partial \psi & \partial x/\partial \xi \end{pmatrix}. \text{ Of course, the}$$

derivatives $\partial x/\partial \xi$, etc. are easy to evaluate, e.g.,

$$\partial x/\partial \xi = -\frac{1}{4}(1-\psi)x_A + \frac{1}{4}(1-\psi)x_B + \frac{1}{4}(1+\psi)x_C - \frac{1}{4}(1+\psi)x_D$$

While it may be messy, computers are good at this. Thus we can put it all together to find the needed derivatives of the shape function matrix. This gives us an algebraic expression for $\mathbf{B}$ in terms of the actual nodal positions (x_A , etc.).

g. Note that this is a simple element! One can imagine that as get more complicated, it is difficult to generate the correct derivatives.

2. suppose have a solid that obeys linear elasticity

a. stress is given by

$$\begin{bmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \\ \tau_{xy} \\ \tau_{yz} \\ \tau_{zx} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & \dots & C_{16} \\ C_{21} & C_{22} & \dots & C_{26} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ C_{61} & C_{62} & \dots & C_{66} \end{bmatrix} \begin{bmatrix} \epsilon_x \\ \epsilon_y \\ \epsilon_z \\ \gamma_{xy} \\ \gamma_{yz} \\ \gamma_{zx} \end{bmatrix}, \text{ or } \{\sigma\} = C\{\epsilon\}, \text{ where the}$$

Cs are the elastic constants. Of course, as we know, everything becomes simpler when we add symmetry. For example, for an isotropic solid, C becomes

$$C = \begin{bmatrix} \lambda + 2\mu & \lambda & \lambda & 0 & 0 & 0 \\ \lambda & \lambda + 2\mu & \lambda & 0 & 0 & 0 \\ \lambda & \lambda & \lambda + 2\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{bmatrix}, \text{ where } \lambda \text{ is the Lamé constant and } \mu \text{ is the}$$

shear modulus. Note that we are using engineering strain.

- b. We can always write $\{\epsilon\}$ in terms of $\{\sigma\}$ by inverting C. For the isotropic case we have $\{\epsilon\} = C^{-1}\{\sigma\} = D\{\sigma\}$, where

$$D = \begin{bmatrix} 1/E & -\nu/E & -\nu/E & 0 & 0 & 0 \\ -\nu/E & 1/E & -\nu/E & 0 & 0 & 0 \\ -\nu/E & -\nu/E & 1/E & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/\mu & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/\mu & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/\mu \end{bmatrix}, \text{ and } \nu \text{ is Poisson's ratio and } E \text{ is}$$

Young's modulus.

- c. For problems with plane strain, we have no dependence on one of the directions,

say z. There, the strain matrix reduces to $\{\epsilon\} = \begin{bmatrix} \epsilon_x \\ \epsilon_y \\ \gamma_{xy} \end{bmatrix} = \begin{bmatrix} \partial/\partial x & 0 \\ 0 & \partial/\partial y \\ \partial/\partial y & \partial/\partial x \end{bmatrix} \begin{bmatrix} u_x \\ u_y \end{bmatrix}$, and

we use the appropriate elastic constants from above to relate stress and strain.

- d. The strain energy density is given by $w = \frac{1}{2}\{\epsilon\}^T\{\sigma\} = \frac{1}{2}\{\epsilon\}^T C\{\epsilon\} = \frac{1}{2}C_{ijkl}\epsilon_{ij}\epsilon_{kl}$, where the last form would arise using the non-engineering definitions of stress and strain
- e. the total strain energy of a system would be the integral of w over the volume.

3. Consider, now, the expression we had before for the strain in terms of the nodal displacements, $\{\epsilon\} = \mathbf{B} \{u_n\}$. Substituting that in the expression for the strain energy,

$$\text{we have } U = \int w \, dV = \frac{1}{2} \int \{\epsilon\}^T \mathbf{C} \{\epsilon\} \, dV = \frac{1}{2} \{u_n\}^T \left[\int \mathbf{B}^T \mathbf{C} \mathbf{B} \, dV \right] \{u_n\}$$

a. we thus can identify the stiffness matrix as $\mathbf{K} = \int \mathbf{B}^T \mathbf{C} \mathbf{B} \, dV$

b. Let's consider $\mathbf{K}$.

- i. It is an $Dn \times Dn$ matrix, where D is the dimension and n the number of nodes.
- ii. it involves an integration over volume (area in 2D) for each element. We will then construct the total $\mathbf{K}$ by adding all the elements one by one as we did before.
- iii. it contains all the materials properties in $\mathbf{C}$.
- iv. it contains all connections to geometry in $\mathbf{B}$.

c. How do we evaluate $\mathbf{K}$?

- i. we use a numerical integration

4. Numerical integration

a. we use a Gauss-Legendre quadrature, where we approximate

$$\int_{-1}^1 f(x) dx \approx \sum_{k=1}^n w_k f(x_k) \text{ where the weights } w_k \text{ and positions } x_k \text{ are specified and}$$

depend on the number of points. There is a whole theory of this, where the different quadratures are designed to integrate well different types of functions.

The points and weights are set by the number of points in the scheme and the type of quadrature.

- i. for example, $n=2$, we would approximate an integral by

$$\int_{-1}^1 f(x) dx \approx f(a) + f(-a), \text{ where } a = \frac{1}{\sqrt{3}} \text{ and the weights}=1.$$

- ii. How well could a 2-point integration work? Suppose we have

$f(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4 + \dots$. The integral of $f(x)$ over -1 to 1 is

$$\int_{-1}^1 f(x) dx = 2a_0 + \frac{2}{3}a_2 + \frac{2}{5}a_4 + \frac{2}{7}a_6 + \frac{2}{9}a_8 + \dots, \text{ where the integrals over the}$$

odd powers of x vanish because of symmetry. Using the 2-point quadrature scheme yields

$$\int_{-1}^1 f(x) dx \approx f(1/\sqrt{3}) + f(-1/\sqrt{3}) = 2a_0 + \frac{2}{3}a_2 + \frac{2}{9}a_4 + \frac{2}{27}a_6 + \frac{2}{81}a_8 + \dots \text{ So,}$$

the odd terms vanish, as expected, and the answer is correct to second order

in the polynomial expansion. The fractional errors in the 4th order term is about 0.3. This wouldn't be too bad for a smoothly varying function.

b. For a 2-D function and integration, we'd have

$$\int_{-1}^1 \int_{-1}^1 f(x,y) dx dy \approx f(a,a) + f(a,-a) + f(-a,a) + f(-a,-a), \text{ once again with } a = \frac{1}{\sqrt{3}}.$$

There would be 9 terms in an integral over a function in 3D, all of the same form with the same a values.

c. We could choose more points and get a more accurate result. However, the number of points in 3D goes as m^3 , where m is the number of points in the quadrature scheme. Obviously, we cannot afford too many. Often a 2-point scheme is used.

5. Now consider the expression $\mathbf{K} = \int \mathbf{B}^T \mathbf{C} \mathbf{B} dV$. Remember that $\mathbf{K}$ is a $Dn \times Dn$ matrix, where n is the number of nodes. Thus, we need to do this integral for all $(Dn)^2$ elements. But, as we said, the matrices are easy to multiply out so it isn't difficult, especially when using a low order integration scheme.

6. Think about $\mathbf{K}$ in a 2D element. If we use a 2-point integration, then we have

$\mathbf{K} = \mathbf{K}(a,a) + \mathbf{K}(a,-a) + \mathbf{K}(-a,a) + \mathbf{K}(-a,-a)$, where $\mathbf{K}(x,y) = (\mathbf{B}^T \mathbf{C} \mathbf{B})(x,y)$, i.e., what we have done is replaced $\mathbf{K}$ essentially by four effective springs located in the element. It is not very different than what we had in the first triangle we looked at, where we had effective springs at the midpoints of the edges.

D. Putting it all together.

1. just as we did for the simple case above, after we have $\mathbf{K}$ for all elements, we assemble the total $\mathbf{K}$ matrix by renumbering the nodal points and adding each contribution.

a. it is VERY important to do this in a way that yields a banded matrix. We have Dn linear equations to solve (as we'll see) and we must be efficient.

2. distribute the loads to the nodes

D. What do we now have?

1. we now have an expression for the total strain energy in the system

$$U = \frac{1}{2} \{u_n\}^T \mathbf{K} \{u_n\}, \text{ where we assume no already existing stresses or strains.}$$

2. The energy associated with loads on the system can be given by

$$W = \mathbf{F} u_n - \int \mathbf{b} u dV + \int \mathbf{T} u dA, \text{ where the first term is the force on the nodes, the second term is from body forces } \mathbf{b} \text{ (like gravity) that act on all points of the sample, and}$$

the third term is from surface tractions $\mathbf{T}$.

3. The total energy is $\pi = U - W$.
4. The requirement for equilibrium is $\delta[\pi] = 0$. Invoking this leads to a system of linear equations (for linear elastic systems), which take on the simple form, in the absence of body and traction terms, $\mathbf{K}\{\mathbf{u}_n\} = \mathbf{F}$.
5. We solve these equations for $\{\mathbf{u}_n\}$ using some standard method and then we have it.

E. Analysis

1. From displacements, we can calculate:
 - a. strains (from $\{\boldsymbol{\varepsilon}\} = \mathbf{B}\{\mathbf{u}_n\}$) and then stresses (from $\{\boldsymbol{\sigma}\} = \mathbf{C}\{\boldsymbol{\varepsilon}\}$).
 - b. It turns out that strains evaluated on (or near) element boundaries are far less accurate than those predicted in the interior of the element.
 - c. Strains calculated at the integration points tend to be the most accurate. Most codes calculate the strains at these points.
 - d. Note that the variation of strains throughout an element depends on the shape functions. In a linear triangle, there are only linear terms - the strains are constant throughout an element. Thus, as we said before, we obtain a patchwise discontinuous solution.

F. How do we know if it's correct?

1. we assume the mesh, the shape function, the integration scheme, and then the linear equation solver. We can estimate numerical errors from the integration and the linear equation solver, but the mesh itself and the shape functions are models.
2. One choice: pick a problem that is similar to what you are studying and for which you know the answer. Compare and then adjust your system until it gets it right.
3. Another choice. Go back to the original equations and carry through the operations and check the accuracy of your choices. Most people do the former.

G. How can we do more interesting materials science?

1. so far all we've done is small linear strains in materials - boring
 - a. we need to reformulate some things to obtain FEM for nonlinear materials.