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SMR.550 - 36

SPRING COLLEGE IN MATERIALS SCIENCE ON
"NUCLEATION, GROWTH AND SEGREGATION IN MATERIALS
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ATOMISTIC SIMULATION OF MATERIALS

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"Atomistic Simulation of Materials"

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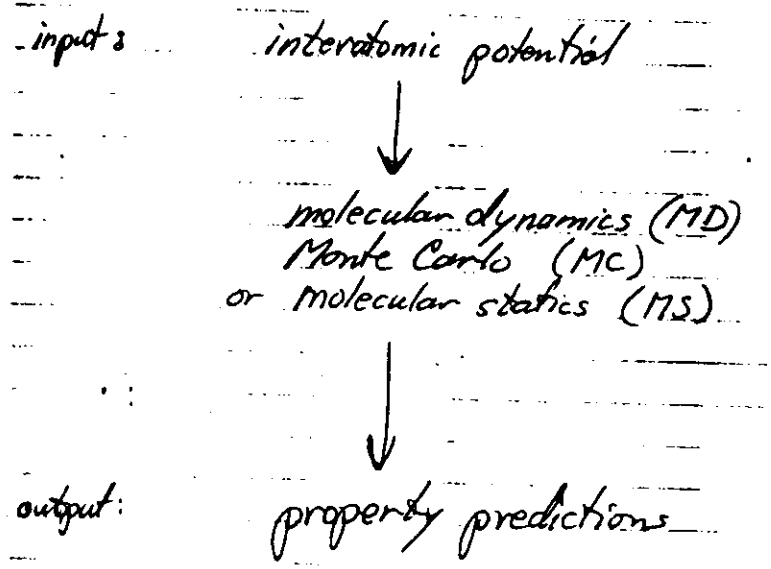
Outline

1) Interatomic Potentials
2) Simulation Methods
   Molecular Statics
   Monte Carlo
   Molecular Dynamics
3) Applications
   Surface Diffusion
   Fracture

Interatomic Potentials

Atomistic simulation flow chart:



→ for predictions on real materials, the output is only as good as the input (the potential)

for model calculations (eg. to test a method) simple potentials are adequate

general properties of a good potential

① form of potential allows fast evaluation

② has continuous derivatives (1st and maybe 2nd)

③ form of potential contains essential physics

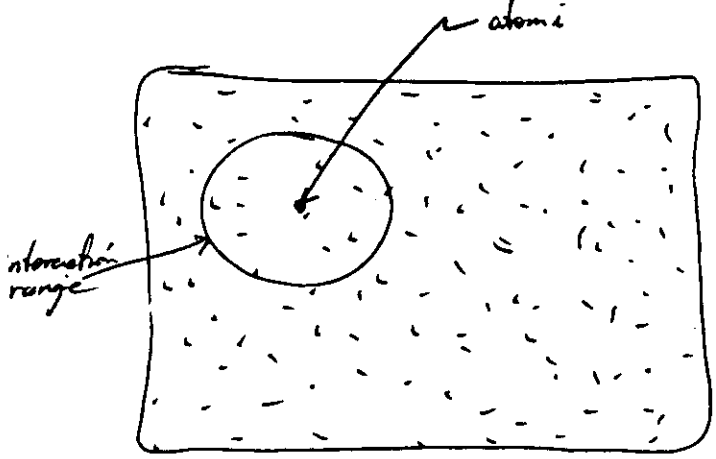
simplest potential: pair potential

for N atoms:

$$E_{TOT} = \sum_{i}^{N} E_i$$

$$E_i = \frac{1}{2} \sum_{j(\neq i)} \phi(r_{ij})$$

If $\phi(r)$ has finite range, computational work scales as N, rather than N^2, for large N



- each atom has relatively constant number of neighbors
- neighbor lists updated periodically

∴ limiting range of $\phi(r)$ is very desirable

N-scaling also holds for many other types of potential

Typical pair potentials

Lennard-Jones 6-12

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

ε = depth of well

$2^{\frac{1}{6}}\sigma$ = position of minimum

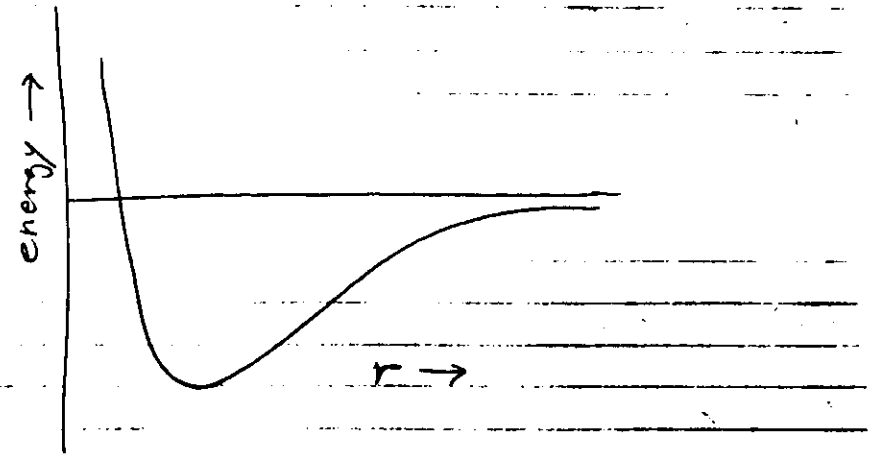
Morse

$$\phi(r) = D\left[e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)}\right]$$

D = depth of well

r_e = position of minimum

α = measure of curvature near minimum

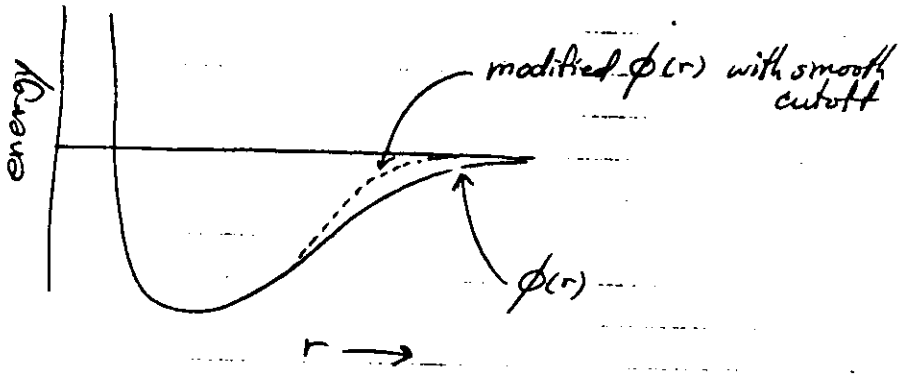


smooth cutoffs

a cutoff for $\phi(r)$ speeds computation

a <u>smooth</u> cutoff provides a continuous $\phi(r)$ and $\frac{d\phi(r)}{dr}$,

continuous $\phi'(r)$ is better for MD



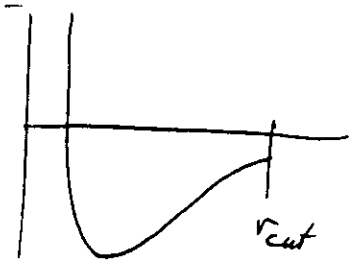
Using a good, smooth cutoff will save trouble later.

typically cut ~~off after~~ 2nd or 3rd neighbor shell

cutoff methods

<u>abrupt cut (bad)</u>

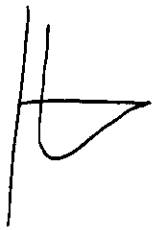
$$\phi(r) = \begin{cases} \phi(r) & r < r_{cut} \\ 0 & r \geq r_{cut} \end{cases}$$



ϕ discontinuous, ϕ' discontinuous

<u>simple shift (better)</u>

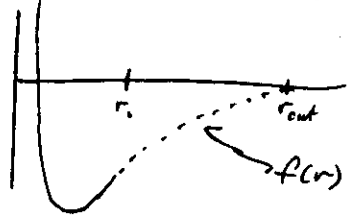
$$\phi(r) = \begin{cases} \phi(r) - \phi(r_{cut}) & r < r_{cut} \\ 0 & r \geq r_{cut} \end{cases}$$



ϕ continuous, ϕ' discontinuous

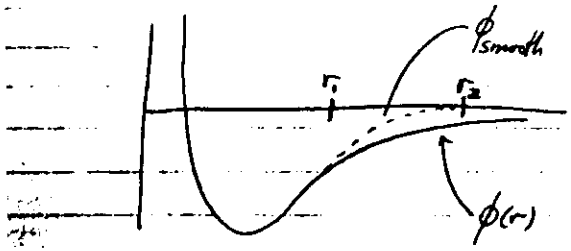
<u>smooth (best)</u>

$$\phi(r) = \begin{cases} \phi(r) & r < r_i \\ f(r) & r_i \leq r \leq r_{cut} \text{ or } \phi(r) \cdot P(r) \\ 0 & r > r_{cut} \end{cases}$$



$\phi(r)$, $\phi'(r)$ continuous

smooth cutoff (cont)



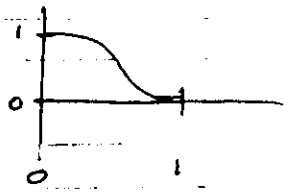
from r_1 to r_2, $\phi(r)$ is replaced by either

$f(r)$ - designed to match at endpoints

or

$\phi(r) \cdot P[(r - r_1)/(r_2 - r_1)]$

$P(r)$ = polynomial

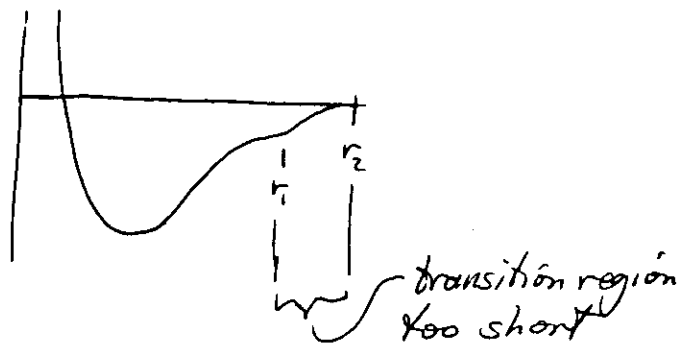


examples:

Tersoff (ref 13)
Baskes et al (ref 6)
Vater et al (refs 10, 11)

cutoffs (cont)

a commonly used approach:



<u>advantage</u> - original $\phi(r)$ shape retained as far out as possible

<u>disadvantage</u> - outermost neighbors can contribute more to derivative of ϕ than closer neighbors - this is unphysical

How good is a pair potential?

① fast evaluation? - yes

② continuous derivatives? - yes, with good cutoff

③ essential physics?

noble gas - yes

metals - no - need volume term

covalent solids - no - need directionality

ionic solids - pretty good

pair potential for fcc metal

Cohesive energy

- assume nearest neighbor cutoff, r_{nn} = distance to neighbor
- each atom sees 12 neighbors
- each of those 12 "bonds" is shared by 2 atoms

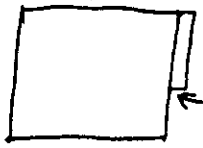
Thus, cohesive energy, E_{coh}, is

E_{coh} = energy $/$ atom to vaporize solid

$= \frac{12}{2}$ bonds per atom

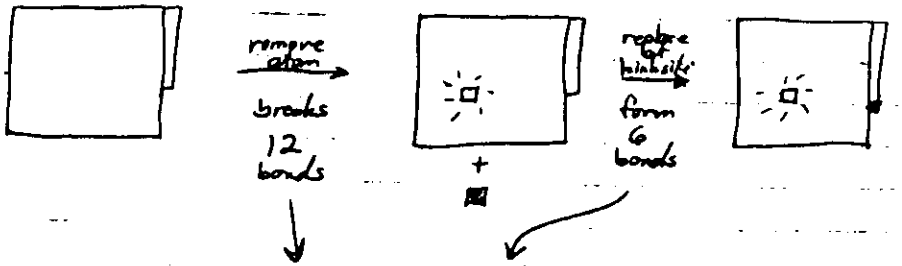
$= 6\,\phi(r_{nn})$

Vacancy formation energy



← block of atoms

kink site – successive atom additions at kink site builds crystal indefinitely



$$E_{vac} = 12\phi(r_m) - 6\phi(r_m) = 6\phi(r_m)$$

$\therefore$ $E_{vac} = E_{coh}$ for pair potential

However, in real metals, $E_{vac} < E_{coh}$,

because later bonds are weaker

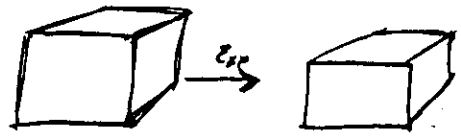
eg. for Ni $E_{coh} = 4.45\ eV$

$E_{vac} = 1.6\ eV$

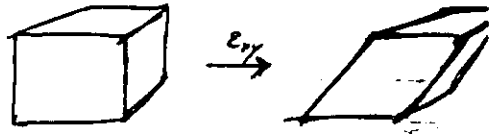
Pair potential has equal bond strengths.

Elastic Constants – fcc metal

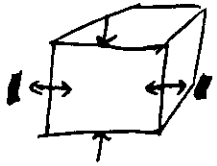
$$C_{11} = \frac{1}{V}\frac{\partial^2 E}{\partial \varepsilon_{xx}^2}$$ on



$$C_{44} = \frac{1}{V}\frac{\partial^2 E}{\partial \varepsilon_{xy}^2}$$



$$C_{12} = \frac{1}{V}\frac{\partial^2 E}{\partial \varepsilon_{xx}\partial \varepsilon_{yy}}$$



$C_{12} - C_{44}$ = "Cauchy Pressure"

real metals: $C_{44} < C_{12}$

pair potential: $C_{44} = C_{12}$ (any cubic crystal)

see Nye – Physical Properties

Volume dependent pair potential

motivation: metal viewed as ions immersed in electron gas - energy of e^- gas depends on density

$$E_{Tot} = \sum_i \frac{1}{2} \sum_{(j \neq i)} \phi(r_{ij}) + f(V)$$

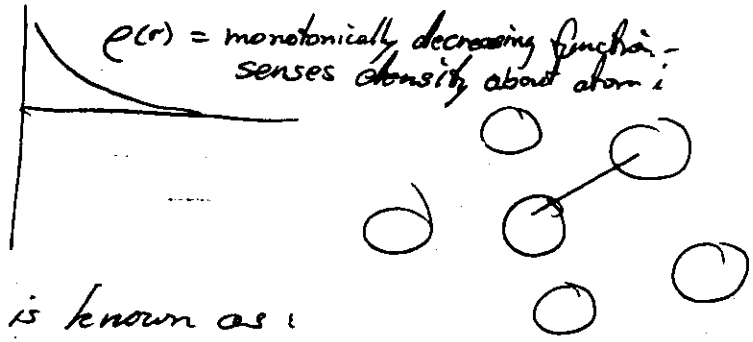
V = system volume

- $\phi(r)$ is fit, or derived, for a given system volume
- this form is valid for modeling defects that do not change the density very much
  eg. - grain boundary
- $E_{vac} \neq E_{coh}$, because $f(V)$ contains some of E_{coh}
- $C_{12} \neq C_{44}$, because E_{xy} conserves volume while E_{xx} does not
- major disadvantage - not valid when "volume" is ill-defined, such as at a free surface

Local Volume Pair potential

$$E_i = \sum_j \phi(r_{ij}) + F\left[\sum_j \rho(r_{ij})\right]$$

concept: $\bar{\rho} \equiv \sum_j \rho(r_{ij})$ provides a local density (or "volume") for each atom i



This is known as:

→ Embedded Atom Method (Daw & Baskes, ref 4, 1983)

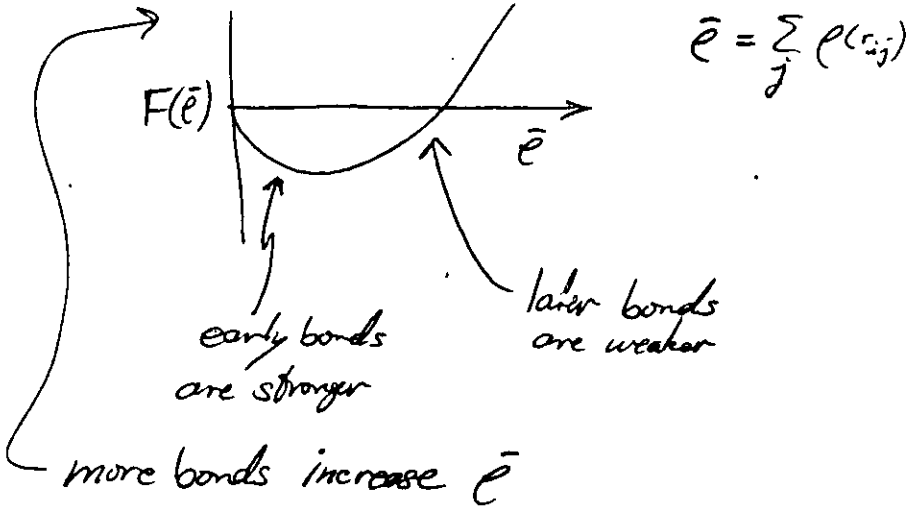
Second Moment Model (Finnis & Sinclair, ref 5)

Glue Model (Ercolessi, Tosatti, ref 12, ...)

→ this form of potential has revolutionized atomistic modeling of fcc metals - gives good results in a variety of situations

What does the embedding function (F) do?

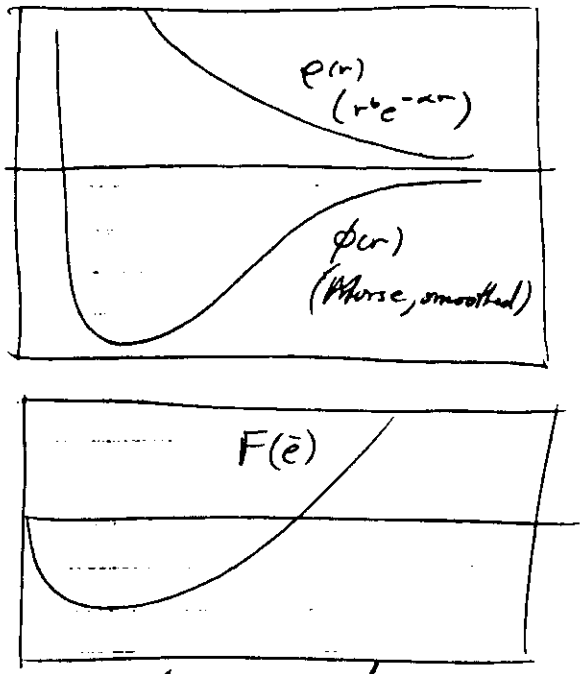
$$E_i = \sum_j \phi(r_{ij}) + F[\bar{\rho}]$$



- F gives a many-body contribution to energy
- if F is purely linear, then simply pairpot
- F does not provide directionality to bonds

example of EAM potential for Ni

Voter + Chen (refs 10 + 11)



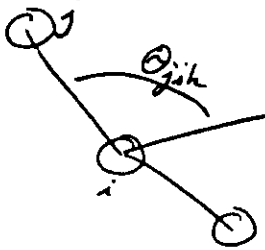
	expt	calc	
a_0	3.52 Å	3.52	fit exactly by numerically constructing $F(\bar{\rho})$
E_{coh}	4.45 eV	4.45	
B	1.81 Mb	1.81	
c_{11}	2.47 "	2.44	
c_{12}	1.47 "	1.49	
c_{44}	1.25 "	1.26	
ΔE_{vac}	1.60	1.60	
D_e	1.95	1.94	diatomic molecule - ensure earlier bonds are stronger
R_e	2.2	2.23	

$\frac{4.45}{4} = < 1$ eV

Covalent Materials

majority of work has been for silicon, due to importance in electronic devices

simplest approach – explicit angle function



$$E_i = \sum_j \phi(r_{ij}) + \sum_{j,k} f(\theta_{jik}) \qquad (1)$$

examples

- Keating (ref 15) (1966)
- Stillinger + Weber (16) (1985)
- Biswas + Hamann (17) (1985)

However, using form as simple as (1) can lead to problems.

Better to have some "volume" or "bond counting" terms also

Tersoff potential

J. Tersoff 1986 (ref 13)

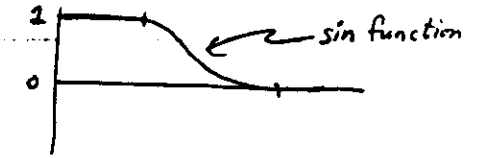
basic form:

$$E_i = \sum_j \left[\phi(r_{ij}) + b_{ij}\, e^{-\lambda r_{ij}} \right] f_c(r_{ij})$$

$$b_{ij} = f_c(r_{ij}) \left[1 + \sum_{k(\neq i,j)} \left(1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos\theta)^2} \right) \right]$$

(with a smoothing cutoff applied to all functions of r)

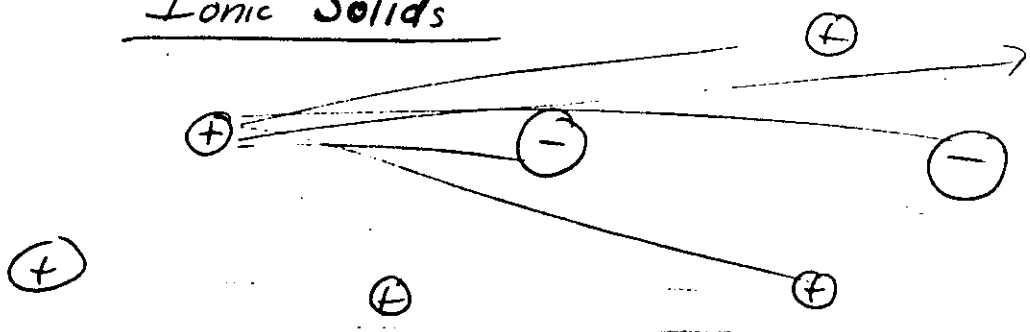
$f_c(r_{ij})$ = smooth cutoff function



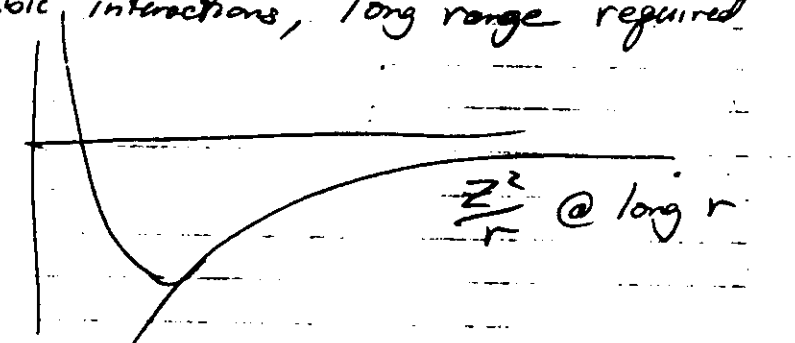
b_{ij} provides both bond counting and angular effects

Tersoff form has been quite successful for Si, and is probably the best existing form for covalent materials, though hard to fit due to many parameters existing: C, Si, Si–C Also has been fit to C, H, O (ref 14)

Ionic Solids



Coulombic interactions, long range required



@ short range: Pauli repulsions of core electrons

$Ae^{-r/R}$ ← Born Mayer form

intermediate range: Vander Waals attraction

$-Br^{-6}$

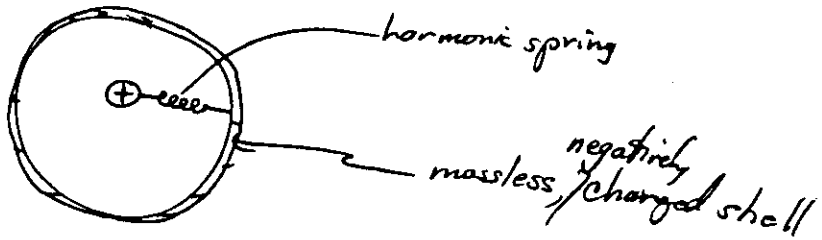
long R: $-\frac{Z^2}{R}$

see reviews by Catlow (18,19).

Ionic Solids (cont)

The Shell Model

[Dick + Overhauser (1958) (ref 20)



(note that this model requires iterative minimization of the shell positions)

The shell model allows coupling between polarizability and short range repulsion, giving much improved description of crystal properties.

Molecular Mechanics Potentials

- used for modeling proteins, polymers, etc.

for bonded atoms:

$$\phi(r) = \frac{1}{2}k(r-r_e)^2$$

- bonds can't dissociate
- interactions chosen according to type of bonding environment

→ not suitable for simulations of general materials, where bonds break and environments change.

fitting interatomic potentials

- if potential is not available for the system of interest, you may want to try to fit one.
  - choose a form with the appropriate physics
  - fit to either experimental properties or high-quality electronic structure results, or both
  - test potential against properties not in the fit
  - be careful that other crystal structures do not have a lower energy

fitting a good quality potential requires intuition, luck, and lots of patience.

troublesome forms of potential

1) forms that depend explicitly on "strain" or "volume," etc, unless they can be defined unambiguously for each atom

2) potentials that have different interactions for different environments
   e.g. - top surface layer atoms different from deeper layers
   - different potential for different oxydation states

these will cause trouble if simulation causes atoms to change "type"

3) forms requiring optimization of internal degrees of freedom - these will not scale as N because a minimization will be required for each geometry
   eg. - diagonalization of an NXN matrix

Other forms of potential worth knowing about
(new, or in development)

many of these are in proceedings R-1

2nd + 4th moment GEAM model — Si, Fe — Carlsson et al (ref 7)

Tight binding bond model — 3 metals, nonmetals — Pettifor et al (ref 9)

modified EAM (MEAM) — Si, Ge — Baskes et al (ref 6)

equivalent crystal method (ECM) — transition metals, Si — Smith et al (ref

3 and 4-body LDA potentials — transition metals — Moriarty (ref 22)

rotated second moment approx. (RSMA) — metallic, covalent — Krasko (ref 8)

interstitial electron model — metals, nonmetals — Li + Goddard (ref

elastic constant-corrected EAM — Posland, Farkas Savino (ref 24)

More advanced forms of "potential"

exact - solve $\mathcal{H}\Psi = E\Psi$ exactly for each geometry — unfeasible

tight binding-based potentials

1-electron $\mathcal{H}$ (see R/R-1)

requires NxN diagonalization, or can be converted to N-scaling problem using recursion method, but the overhead is quite large

local density electronic structure method

Car + Parrinello (ref 23) - combines LDF with dynamical evolution of atoms in a way that makes successive calculations of the energy much less expensive than for initial geometry

MD for 64 atoms feasible, very accurate with scales as N^3

Molecular Statics

The three principle atomistic simulation methods are:

Molecular Statics (MS)
- zero temperature properties
  - energies
  - structures
  - barrier heights

Monte Carlo (MC)
- finite temperature properties
  - equilibrium

Molecular Dynamics (MD)
- finite temperature properties
  - equilibrium
  - nonequilibrium
  - dynamical properties

Molecular Statics

concept: given an interatomic potential, and a system of N atoms, optimize the geometry to obtain the minimum energy.

more strictly:

define the gradient vector (3N long)

$$g_{i\alpha} = \frac{\partial E}{\partial x_{i\alpha}}$$

i = atom index
α = Cartesian index (x, y, or z)

we seek the stationary points (where $g = 0$) on the 3N-dimensional hypersurface.

- each $g = 0$ point may be a minimum or a saddle or a maximum

reasons for doing molecular statics

- to find a zero-temperature energy or structure for a defect

eg.
- grain boundary
- surface
- vacancy
- dislocation core
- interstitial

- to compare different crystal structures
- useful when temperature effects are expected to be of secondary importance
- useful when MD or MC molecular dynamics or Monte Carlo would be too expensive
- for computing (approximate) transition state theory rate constants

How to find a minimum

(see "Numerical Recipes", Press et al ___)

① - steepest descent method (simplest)

- simply take steps along $-g$

② conjugate gradient method (better)

- uses current g and previous g's
- converges faster than steepest descent

③ thermal annealing (also good)

- follow MD trajectory, thermostatted to lower and lower temperatures until $T=0$ reached

④ Newton-Raphson method (best - but expen

- form curvature matrix $\left(\underset{\approx}{B}\right)_{i_\alpha j_\beta} = \frac{\partial^2 E}{\partial x_{i\alpha} \partial x_{j\beta}}$

solve for correction vector $\underset{\approx}{\Delta}$:

$$\underset{\approx}{B}\,\underset{\approx}{\Delta} = -g$$

- quadratic convergence if close to solution
- can also find saddle point

Normal modes at the stationary point:

dynamical matrix $\underset{\approx}{D}$:

$$\left(\underset{\approx}{D}\right)_{i\alpha,j\beta} = \frac{\partial^2 E}{\partial x_{i\alpha}\partial x_{j\beta}} \frac{1}{\sqrt{m_i m_j}}$$

diagonalize $\underset{\approx}{D}$.

$$\underset{\approx}{C}^{+}\underset{\approx}{D}\underset{\approx}{C} = \underset{\approx}{\lambda}$$

eigenvectors $\left(\underset{\approx}{C}\right)$ = normal modes

eigenvalues $\left(\{\lambda_j\}\right)$ give frequencies: $\nu_j = \sqrt{\lambda_j}$

- any imaginary frequencies indicate (it is a) saddle point rather than a minimum

- Finding normal modes can be important because sometimes a solution that appears to be a minimum is actually a saddle point

  i.e. all $\frac{\partial^2 E}{\partial x_{i\alpha}^2} > 0$, but lowest $\lambda_j < 0$

example: Surface Diffusion

(demonstrates various concepts we have learned so far and some new ones)

diffusion constant for random walk of single hops:

$$D = \frac{1}{2\alpha} k_{hop} l_{hop}^2$$

α = dimensionality of diffusion space

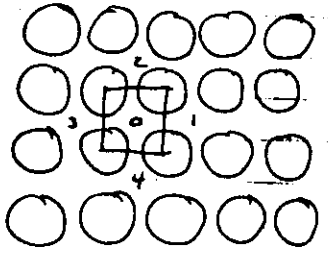
k_{hop} = rate constant for hops

l_{hop} = hop length

$$k_{hop} = 4 k_{01}$$ 4 hop directions

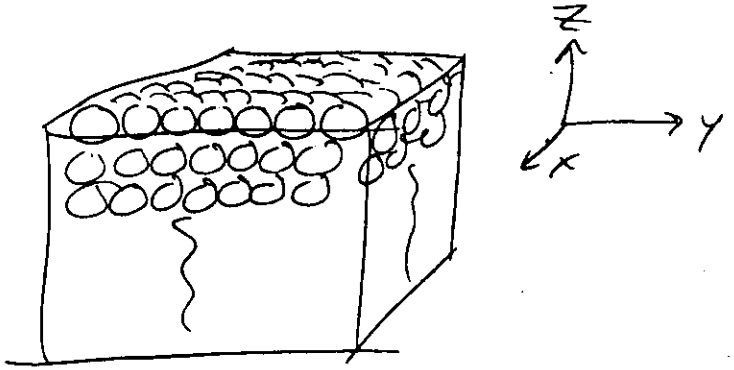
$$k_{01} = \nu_0 e^{-E_A/kT}$$

fcc(100) surface



calculating surface diffusion barrier

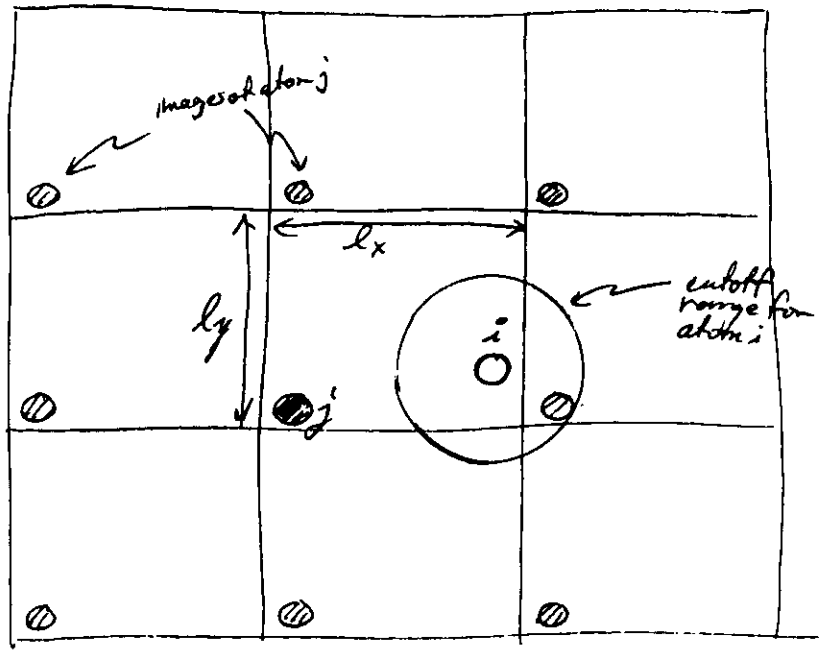
set up block of atoms to model substrate:



periodic boundary conditions in x and y, but not z

this way, every atom thinks it is part of an infinite surface.

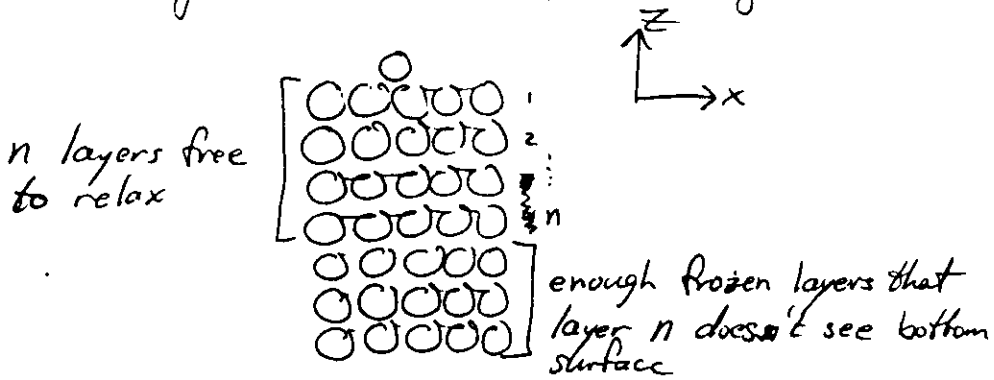
"minimum image" periodic boundary conditions



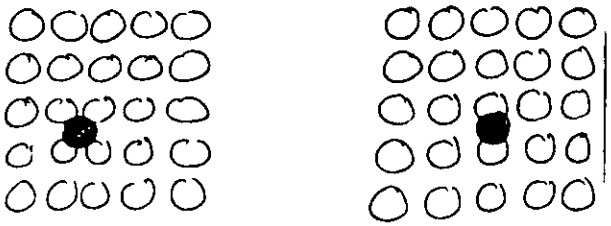
by making l_x, $l_y > 2 r_{cut}$, then at most one image of atom j will be within cutoff range of atom i.

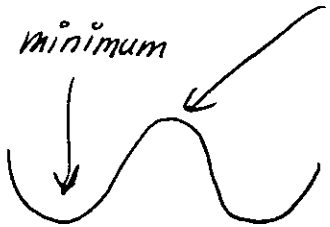
molecular statics description of surface diffusion (continued)

now put on extra atom on top of block



top view





rate constant $\propto e^{-E_A/kT}$

$E_A = E_{saddle} - E_{min}$

ensure that property is converged w.r.t. system si

layers free	$E_{saddle} - E_{min}$ (eV)	
0	0.738	
1	0.696	Pd/Pd(100)
2	0.687	
3	0.684	← converged w/ 3 layers free
4	0.684	
5	0.684	
6	0.684	

→ ___ layers are adequate

FIM - 0.63

verify that saddle point has 1 ≡ imaginary frequ.

the rate goes as

$$k = \nu_0 e^{-\Delta E/kT}$$

where ν_0 = attempt frequency $\approx \nu_{x\,adatom}$

Within the $T=0$ framework the most exact way to calculate ν_0 is from the full harmonic treatment using normal modes, $\{\nu_j\}$, $j = 1, \ldots 3N$

$$\nu_0 = \frac{\prod_{j}^{3N} \nu_j^{min}}{\prod_{j}^{3N-1} \nu_j^{saddle}}$$

← normal modes @ min

← 3N-1 real normal modes at saddle poi

(Vineyard ___)

Monte Carlo

Monte Carlo can be used to get equilibrium properties of a system at nonzero temperature

concept: A properly designed random walk in configuration space or phase space will leave a trail of points that are representative of the exact canonical (or other) ensemble.
An Equilibrium property of the system can then be evaluated by simply averaging the property over the trail of points.

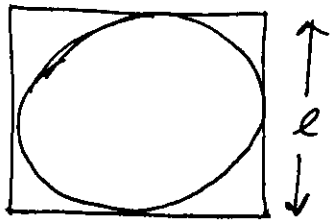
eg. for property $B(\underset{\sim}{R})$

$$\langle B(\underset{\sim}{R}) \rangle = \frac{\int e^{-H(\underset{\sim}{R})} B(\underset{\sim}{R})\, d^{3N}\underset{\sim}{R}}{\int e^{-H(\underset{\sim}{R})} d^{3N}\underset{\sim}{R}}$$

$$\cong \frac{1}{nstep} \sum_{i=1}^{nstep} B(\underset{\sim}{R}_i) \pm \frac{a}{\sqrt{nstep}}$$

very simple example: Monte Carlo evaluation of π

(1) construct a circle inside a square



(2) throw darts at square ← or generate random x,y positions

(3) count number of darts inside circle and fraction inside square

(4) estimate π

area of square $= \ell^2$

area of circle $= \pi\left(\frac{\ell}{2}\right)^2 = \frac{\pi}{4}\ell^2$

$$\pi = \frac{4(\text{area of circle})}{(\text{area of square})}$$

$$\approx \frac{4 \cdot N_{\text{in circle}}}{N_{\text{in square}}}$$

(5) the error will go as $\frac{1}{\sqrt{N_{\text{throws}}}}$

Metropolis Monte Carlo (ref 3)

random walk to establish canonical ensemble distribution of points

very simple algorithm:

1. given a point $\underset{\sim}{R}$ in configuration space (or phase space), with associated energy $E(\underset{\sim}{R})$
2. take a step to a new position $\underset{\sim}{R}'$ (eg. move one atom a little bit)

$$\underset{\sim}{R}' = \underset{\sim}{R} + \Delta\underset{\sim}{R}$$

$$\Delta E = E(\underset{\sim}{R}') - E(\underset{\sim}{R})$$

3. accept this step if $\Delta E < 0$
4. if $\Delta E > 0$, accept this step with probability

$$P_{accept} = e^{-\Delta E/kT}$$

(ie. draw a random number between 0 and 1 if this random number is less than P_{accept}, accept)

5. record the current position ($\underset{\sim}{R}'$ or $\underset{\sim}{R}$ if step was rejected)
6. go to 1

proof Metropolis MC works

canonical ensemble: $M(R \to R') = \min(1, e^{-\Delta E/kT})$

$$\Delta E \equiv E(R') - E(R)$$

At steady state, we know there should be an equal number of steps per "time" in each direction between two points:

steps from R to R' = steps from R' to R

$n(\underset{\sim}{R}) \equiv$ probability of being at $\underset{\sim}{R}$

$$n(\underset{\sim}{R})\, M(\underset{\sim}{R} \to \underset{\sim}{R}') = n(\underset{\sim}{R}')\, M(\underset{\sim}{R}' \to \underset{\sim}{R})$$

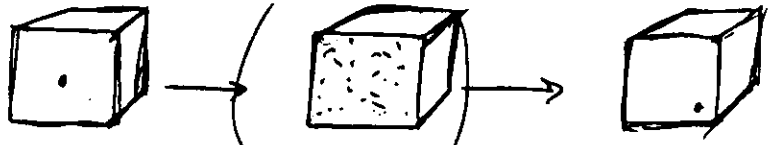
$$\frac{n(\underset{\sim}{R}')}{n(\underset{\sim}{R})} = \frac{M(R \to R')}{M(R' \to R)} = \frac{\min(1, e^{-\Delta E/kT})}{\min(1, e^{+\Delta E/kT})}$$

$$\frac{\min(1, e^{-\Delta E/kT})}{\min(1, e^{+\Delta E/kT})} = \begin{cases} \dfrac{1}{e^{+\Delta E/kT}} & \text{if } \Delta E < 0 \\ \dfrac{e^{-\Delta E/kT}}{1} & \text{if } \Delta E > 0 \end{cases}$$

$$\therefore \boxed{\frac{n(R')}{n(R)} = e^{-\Delta E/kT}} \text{ as desired} \checkmark$$

Metropolis Monte Carlo - general points

(1) usually, the best way to take a step $\Delta \underset{\sim}{R}$ is by moving one atom to a new position chosen randomly inside box around that atom



(2) choose the size of the box so that roughly half of the steps are rejected

(3) requirement for validity of method is simply that for any $\Delta \underset{\sim}{R}$ chosen (ignoring whether or not the step is accepted or rejected) $-\Delta \underset{\sim}{R}$ is just as likely to be chosen

i.e., "unbiased a priori sampling probability"

(4) rejected steps <u>do get counted</u> in distribution

(5) other ensembles are also easy to generate:

$$P_{accept}(\underset{\sim}{R} \to \underset{\sim}{R}') = \min\left[1, \frac{e(\underset{\sim}{R}')}{e(\underset{\sim}{R})}\right]$$

["Metropolis function" $M(\underset{\sim}{R} \to \underset{\sim}{R}')$]

(6) A thermal ensemble average of some property B, or anything that can be made to look like one,

$$\langle B(\underset{\sim}{R}) \rangle = \frac{\int e^{-H(\underset{\sim}{R})} B(\underset{\sim}{R}) d^{3N}\underset{\sim}{R}}{\int e^{-H(\underset{\sim}{R})} d^{3N}\underset{\sim}{R}}$$

is simply evaluated by averaging $B(\underset{\sim}{R})$ over the n steps!

$$\langle B(\underset{\sim}{R}) \rangle = \frac{1}{n} \sum_{i}^{n} B(\underset{\sim}{R}_i)$$

(7) In general, it is <u>very hard</u> to evaluate the partition function directly

$$Q = c \int e^{-H(\underset{\sim}{R})} d^{3N}\underset{\sim}{R}$$

while it is much easier to <u>evaluate</u> quantities expressed in form:

$$(w > 0) \qquad \frac{\int B(x)\, w(x)\, dx}{\int w(x)\, dx}$$

by generating a distribution of points with weight w.

(8) Metropolis MC does not require energy derivatives (unlike MD and MS). This is helpful if the derivatives are expensive or messy.

(9) Relative to a quadrature approach, MC is very powerful for evaluating many-dimensional integrals, because the work for a quadrature scales as

$$(\text{npoint})^{\text{ndimension}}$$

while MC scales much less severely - almost independent of ndimension.

example - 108 atom system

ndimension = 324

10 quad points per dimension $= 10^{324}$ points !!

while $\sim 10^5 - 10^8$ MC steps would probably suffice for most properties

(10) Cannot use Metropolis MC to get dynamical properties of system, because there is no time associated with the walk

- must use MD to get dynamical correlation functions

(11) There is always the danger that an MC walk has not been run long enough to sample all the important parts of configuration space. The only way to be sure is to run it longer (!)

Experience helps here.

MC example 1 - pressure at given N, V, T

compute ρ from virial expression

$$\rho = \frac{NkT}{V} - \frac{1}{6V}\left\langle \sum_{ij} r_{ij}\frac{\partial E}{\partial r_{ij}} \right\rangle$$

① put atoms in periodic box in correct crystal structure and desired V (volume)

② do Metropolis walk at temperature T for a few thousand steps

① move one atom

② accept or reject step

$p_{acc} = \min(1, e^{-\Delta E/kT})$

③ go to ①

③ when an average energy has stabilized, continue walk, and begin recording every 100th step for ~10^n steps.

④ compute ρ for each recorded step and average

$$\langle \rho \rangle = \frac{1}{n}\sum_{i}^{n} \rho_i$$

⑤ compute error bars

$$\text{standard dev. of mean} = \frac{1}{\sqrt{n}}\left[\frac{1}{n}\sum_i (\rho_i - \langle\rho\rangle)^2\right]^{\frac{1}{2}}$$

pair potential

pressure from Virial expression (Verlet, refR3, p68)

$$\rho = \underbrace{\frac{NkT}{V}}_{\text{(ideal gas) kinetic term}} - \underbrace{\frac{1}{6V}\left\langle \sum_{i\neq j}\sum r_{ij}\frac{\partial v_{ij}}{\partial r_{ij}} \right\rangle}_{\text{potential term}}$$

From Stress tensor: (@ T=0)

$$\rho = \frac{1}{3}\mathrm{Tr}\left(\underline{\underline{\sigma}}\right) = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$$

$$\sigma_{11} = \frac{1}{V}\frac{\partial E}{\partial \varepsilon_{11}}$$

for pair pot, 1 atom i:

$$\sigma_{11} = \frac{1}{\Omega_i}\frac{1}{2}\sum_j \frac{d\phi(r_{ij})}{dr_{ij}}\frac{\Delta x_{ij}^2}{r_{ij}}$$

$$\rho = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) = \frac{1}{6\Omega_i}\sum_j \frac{d\phi(r_{ij})}{dr_{ij}}\left[\frac{\Delta x_{ij}^2 + \Delta y_{ij}^2 + \Delta z_{ij}^2}{r_{ij}}\right]$$

$$= \frac{1}{6\Omega_i}\sum_j \frac{d\phi(r_{ij})}{dr_{ij}} r_{ij}$$

for non-pair potential

$$\text{pressure @ one atom} = \frac{1}{3\Omega_i}\sum_j \left(\frac{\partial E_i}{\partial \underline{\underline{r_{ij}}}}\varepsilon_{11} + \frac{\partial E_i}{\partial \varepsilon_{11}} + \frac{\partial E_i}{\partial \varepsilon_{33}}\right)$$

free energy difference between states 0 and 1

we seek $A_1 - A_0$, the Helmholtz free energy difference

recall

$$A = -kT \ln Q \quad \text{(partition function)}$$

and

$$Q \equiv c \int e^{-U/kT} d^{3N} \quad \text{(N degrees of freedom)}$$

$$A_1 - A_0 = -kT \ln \frac{Q_1}{Q_0}$$

$$= -kT \ln \left[\frac{\int e^{-U_1/kT} d^{3N}}{\int e^{-U_0/kT} d^{3N}} \right]$$

rewrite $\int e^{-U_1/kT} d^{3N}$ as $\int e^{-U_1/kT} e^{U_0/kT} e^{-U_0/kT} d^{3N}$

so

$$A_1 - A_0 = -kT \ln \left\{ \frac{\int e^{-U_0/kT} \left[e^{-(U_1 - U_0)/kT} \right] d^{3N}}{\int e^{-U_0/kT}} \right\}$$

$$\boxed{A_1 - A_0 = -kT \ln \left\langle \exp\left[-(U_1 - U_0)/kT \right] \right\rangle_0}$$

ensemble average over state zero only

(see Bennett's contribution in 123 in Ref 23)

Thus, to compute the free energy difference $A_1 - A_0$ we could do a Metropolis walk in state zero, and accumulate

$$\exp\left\{ \left[U_1(\underline{R}) - U_0(\underline{R}) \right] / kT \right\},$$

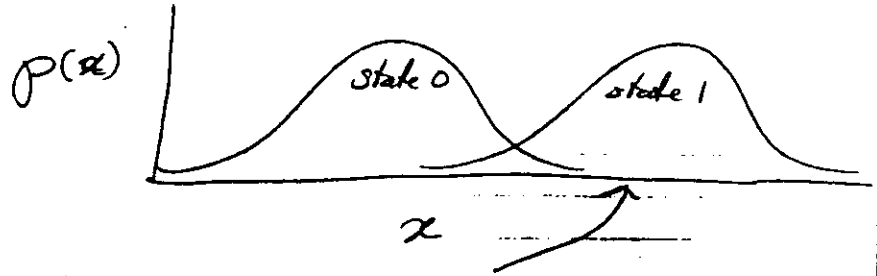
as long as there are no $\underline{R}$ values for which the probability for state zero is zero, while it is nonzero for state 1.

However, due to the exponential nature of the property being averaged, the convergence will be poor.

For various importance sampling techniques see.

Bennett, in Ref 23. (p 123)
Torrie + Valleau in Ref 23. (p 147)
Frenkel + Ladd in Ref 23. (p 107)

problem with using $\langle e^{-(U_1-U_0)/kT} \rangle_0$



Metropolis walk over state 0 will almost never reach this area, where state 1 is most probable.

importance sampling - thermodynamic integration: (ref R-7)

free energy A

define a parameter λ

$\lambda = 0$ gives reference system with known A

$\lambda = 1$ gives system of interest (unknown A)

if $\lambda = 0 \rightarrow \lambda = 1$ is a reversible path (even if it doesn't correspond to a physical reality), then

$$A(\lambda=1) = A(\lambda=0) + \int_0^1 \left(\frac{dA}{d\lambda}\right) d\lambda$$

notice we can write

$$\frac{dA}{d\lambda} = \left\langle \frac{\partial U}{\partial \lambda} \right\rangle$$ (see next page)

So we simply run the Metropolis walk for various values of λ computing $\langle \frac{\partial U}{\partial \lambda} \rangle$ at each point, and then integrate.

worksheet

$$\frac{dA}{d\lambda} = \frac{d}{d\lambda}\left[-kT\ln Q\right] = -kT\frac{\frac{\partial Q}{\partial \lambda}}{Q}$$

$$Q = c\int e^{-U(q)/kT}\,dq$$

$$\frac{\partial Q}{\partial \lambda} = c\int \frac{\partial}{\partial \lambda}\left(e^{-U(q)/kT}\right)dq$$

$$= c\int\left(-\frac{1}{kT}\frac{\partial U}{\partial \lambda}\right)e^{-U(q)/kT}\,dq$$

so

$$\frac{dA}{d\lambda} = -kT\left[\frac{c\int\left(-\frac{1}{kT}\frac{\partial U}{\partial \lambda}\right)e^{-U(q)/kT}\,dq}{c\int e^{-U(q)/kT}\,dq}\right]$$

$$= \left\langle\frac{\partial U}{\partial \lambda}\right\rangle \leftarrow$$

importance sampling – another standard approach

notice that we can rewrite a simple ensemble average as a ratio of averages, over some new weighting function w.

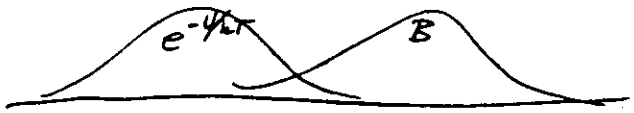
$$\langle B\rangle = \frac{\int B e^{-U/kT}\,dq}{\int e^{-U/kT}\,dq}$$

$$= \frac{\int w\left(\frac{B}{w}\right)e^{-U/kT}\,dq \Big/ \int w e^{-U/kT}\,dq}{\int w\left(\frac{1}{w}\right)e^{-U/kT} \Big/ \int w e^{-U/kT}\,dq}$$

$$= \frac{\left\langle\frac{B}{w}\right\rangle_w}{\left\langle\frac{1}{w}\right\rangle_w}$$

where $\langle X\rangle_w \equiv \dfrac{\int X w e^{-U/kT}\,dq}{\int w e^{-U/kT}\,dq}$

So, for example, if we have distributions in two regions of space, eg.



$\langle B \rangle$ will converge slowly, because B is large where $e^{-\psi/kT}$ is small,

but $\left\langle \frac{B}{w} \right\rangle_w$ and $\left\langle \frac{1}{w} \right\rangle_w$

may converge more quickly, if we choose w properly:

then $we^{-\psi/kT}$ will be large where B is large

Bennett's acceptance ratio method
(see refs 1, 2, R-3)

$\beta = \frac{1}{kT}$

Metropolis acceptance function

$$M(\Delta E) = \min(1, e^{-\beta \Delta E})$$

notice that for any two energies E_1 & E_2:

$$e^{-\beta E_1} M(E_2 - E_1) = e^{-\beta E_2} M(E_1 - E_2)$$

rearranging and integrating over all space:
(let $E_1 \equiv U(R_1)$; $E_2 \equiv U(R_2)$)

$$\frac{\int e^{-\beta E_1} M(E_2 - E_1)\, dq}{\int e^{-\beta E_2} M(E_1 - E_2)\, dq} = 1$$

dividing through by $Q_{1,2} = \int e^{-\beta E_{1,2}} dq$

$$\frac{\int e^{-\beta E_1} M(E_2 - E_1)\, dq \,/ \int e^{-\beta E_1} dq}{\int e^{-\beta E_2} M(E_1 - E_2)\, dq \,/ \int e^{-\beta E_2} dq} = \frac{Q_2}{Q_1}$$

$$\therefore \frac{Q_2}{Q_1} = \frac{\langle M(E_2 - E_1) \rangle_1}{\langle M(E_1 - E_2) \rangle_2}$$

Bennett's method (cont)

$$\frac{Q_2}{Q_1} = \frac{\langle M[U_2(R) - U_1(R)] \rangle_1}{\langle M[U_1(R) - U_2(R)] \rangle_2}$$

each ensemble average is simply the average probability that a Metropolis step into the other state would be accepted.

ie., walk around in state 1, sampling probability of accepting step into state 2, but never actually taking that step.

Molecular Dynamics

concept – obtain dynamical and/or equilibrium properties of system by evolving in time according to classical equations of motion.

given N atoms, there are 6N coords $\{\underline{x}, \underline{p}\}$

$$\frac{dx_i}{dt} = \frac{p_i}{m}$$

$$\frac{dp_i}{dt} = F_i = -\frac{\partial E}{\partial x_i}$$

integrate in time using ordinary differential equation solver

typical maximum run time ~ 1 nanosecond

Verlet algorithm – very popular for MD

power series:

$$x(t+\Delta t) = x(t) + \dot{x}\Delta t + \frac{1}{2}\ddot{x}\Delta t^2 + \cdots$$
$$+ \left[\, x(t-\Delta t) = x(t) - \dot{x}\Delta t + \frac{1}{2}\ddot{x}\Delta t^2 + \cdots \,\right]$$

$$x(t+\Delta t) = 2x(t) - x(t-\Delta t) + \ddot{x}\Delta t^2$$

current x value; previous x value

$$\ddot{x} = \frac{F}{m} = -\frac{\partial V}{\partial x}\left(\frac{1}{m}\right)$$

good to second order; works well

Higher-order algorithms – may be preferable if very smooth potentials are used, and high accuracy is needed.

eg. 4th order Runge Kutta

evaluating equilibrium properties

$$\langle A \rangle = \frac{1}{t_{run}} \int_0^{t_{run}} A(t)\,dt \quad \pm \frac{c}{\sqrt{t_{run}}}$$

$$\cong \frac{1}{n} \sum_i^n A(\underline{R}(t_i))$$

average over snapshots taken from trajectory

Note that this assumes that the system is ergodic — i.e., that the trajectory will visit all accessible parts of phase space.

This also assumes that the trajectory has been run long enough to properly sample phase space.

As with Monte Carlo, there is always the danger that something new will happen if the trajectory is run longer (!)

What ensemble is MD?

A carefully integrated trajectory will conserve total energy

$$E = \sum_i \tfrac{1}{2} P_i^2 + V(\underline{R}),$$

and thus represents the microcanonical ensemble.

(n, V, E)

However, for more than a few atoms the microcanonical ensemble is virtually the same as the canonical ensemble (n, V, T).

We can define the kinetic temperature:

$$T_k = \frac{1}{3Nk_B} \sum_i m_i v_i^2$$

which will fluctuate, and can be averaged over the trajectory.

Thus, a single, long trajectory is often used to represent a canonical ensemble with temperature $T = \langle T_k \rangle$.

To be more exact one can run many trajectories, with the proper distribution to represent a canonical ensemble.

canonical ensemble (n, V, T) with MD

To properly model a canonical ensemble:

(1) follow Metropolis walk with desired T

(2) select points from this walk

- these will be properly distributed in configuration space $\{\underline{x}\}$

(3) For each point, assign a momentum $\underline{p}$ to each of 3N directions by drawing random numbers from a Gaussian distribution:

$$\text{probability}(\underline{p}) \propto e^{-\frac{\underline{p}^2}{\sum m kT}}$$

These $\{\underline{x}, \underline{p}\}$ points will be the $t=0$ positions of trajectories representative of canonical ensemble.

(4) Integrate each of these trajectories and average properly over all of them

(Note that instead of step ③, one can also walk in p-space in step ②, but since $\underline{x}$ and $\underline{p}$ are uncorrelated, it is not necessary)

MD Thermostats

concept – slightly modify equations of motion to thermostat system to desired T

simplest thermostat: rescale velocities at each time step to get desired T_K

Nosé-Hoover Thermostat: add 1 new degree of freedom to equations of motion (EOM) (refs 25+26)

η = new variable
= 0 when $T_K = T_{desired}$

new EOMs:

3N eqns → $\frac{d\underline{p}_i}{dt} = \frac{\underline{F}_i}{m} \boxed{- \eta \underline{p}_i}$

1 eqn → $\dot{\eta} = f^2 (T_K - T_{desired}) / T_{desired}$

if $T_K > T_{desired}$, η goes positive, dragging the $\underline{p}_i$'s back down towards $T_{desired}$

η responds with time constant $(f)^{-1}$

$f \approx$ effective "collision rate" set by user

using thermostats

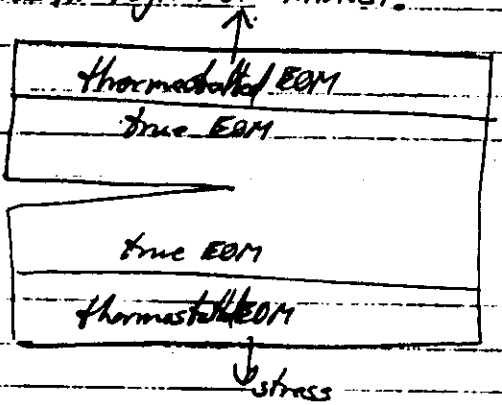
(1) EOM modified - not true dynamics, but sometimes good enough (be careful)

(2) just fine for equilibrium properties (n, V, T)

(3) very useful when a phase transition (or something else) is adding or removing heat to the system, and constant T is desired.

(4) Can thermostat just part of system for more realistic dynamics in region of interest.

eg. running crack



(5) thermostats very useful for bringing a system up to temperature to start a run.

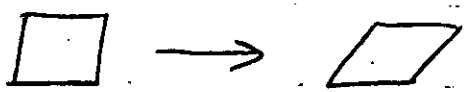
pressure-stats

concept - constant pressure ensembles can be modeled using a pressure-stat (barostat)

Anderson method (ref 27, 28) extra degree of freedom added to EOM

- system is driven towards desired pressure with a pre-chosen time constant, similar to the Nose-Hoover thermostat
- can also do constant P and constant T simultaneously

Parrinello + Rahman (ref 29) - allows shape changes of periodic box while maintaining constant pressure or stress
- very useful for studying phase transformations



MD vs MC vs MS

when to use MD

- for time correlation functions, eg. $\langle v(0)v(t)\rangle$
- for nonequilibrium properties eg. transport
- when MD samples space faster than MC (this is often the case, because the EOM's can follow concerted motions necessary to get to other parts of phase hard to reach by single moves.

when to use MC

- when derivatives are hard or impossible to compute $\left(\frac{\partial E}{\partial x_i}\right)$ e.g. for complicated new forms of potential
- when ensemble dictates unphysical moves such as changing an atom type in a simulation of grain boundary segregation
- when stiffness of EOM will make MD take too long eg. solidification or other phase change may go much faster w/ MC if barrier to transformation is high.

when to use MS (molecular statics)

- when $T=0$ property is good enough
- to find saddle points for rate constants

References - texts, collected reviews, proceedings

Atomistic Simulation of Materials - Beyond Pair Potentials, edited by V. Vitek and D.J. Srolovitz, Plenum Press, New York, 1989.

- conference proceedings, ASM, Chicago 1988
- good survey of advanced forms of interatomic potentials as of 1988

Computer Simulation of Liquids, M.P. Allen and D.J. Tildesley, Oxford Press, New York, 1987.

- textbook
- excellent introduction to simulation methods (MD and MC); includes lots of detail about tricks of the trade
- good list of literature references

Simulations of Liquids and Solids - Molecular Dynamics and Monte Carlo Methods in Statistical Mechanics, edited by G. Ciccotti, D. Frenkel, and I.R. McDonald, North-Holland, 1987.

- collection of reprints
- 49 of the most important papers in the field of MD + MC simulation, beginning with Metropolis et al (1953).

R-4. Molecular Dynamics Simulation of Statistical Mechanical Systems, Proceedings of the International School of Physics "Enrico Fermi," edited by G. Ciccotti and W.G. Hoover, North-Holland, 1986.

- conference proceedings
- many important papers

R-5. Simple Molecular Systems at Very High Density, edited by A. Polian, P. Loubeyre and N. Boccara, Plenum Press, New York, 1988.

- conference proceedings

eg, see papers by
Frenkel - introduction to simulation
Car + Parrinello - local density MD

R-6. Atomic Scale Calculations in Materials Science, Materials Research Society Symposium Proceedings #141, edited by J. Tersoff, D. Vanderbilt, and V. Vitek, MRS, Pittsburgh, PA. 1989.

- conference proceedings
- good survey of applications to materials

References (continued)

-7. Modern Theoretical Chemistry, Volume 5 Statistical Mechanics, edited by B.J. Berne, Plenum Press, New York, 1977.

- collection of review articles
- eg., see Valleau and Torrie, p 169 } Monte Carlo methods
and Valleau and Whittington, 137.

-8. Numerical Recipes,

References - papers (in no particular order)

1. C.H. Bennett, in Diffusion in Solids: Recent Developments, edited by J.J. Burton and A.S. Nowick (Academic Press, New York 1975), p 3.

2. A.F. Voter, J. Chem. Phys. 82, 1890 (1985).

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