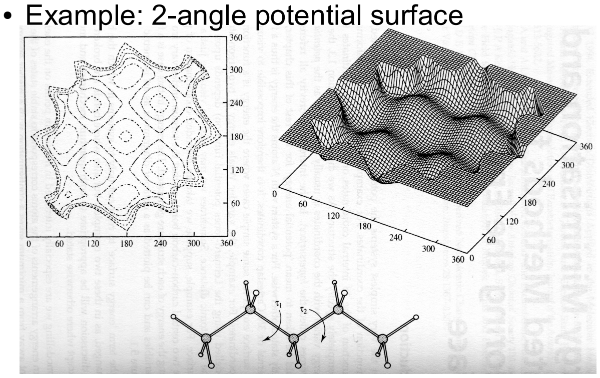
Energy Minimization

- Energy function is a multidimensional function of coordinates
- Can define a *potential energy surface*
- For N atoms, we get a 3N dimensional surface
  - e.g. 1D, 2-LJ particles with positions x_1 and x_2

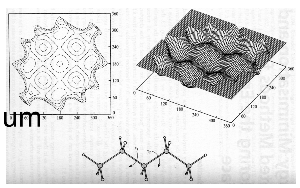
Energy Minimization

- Example: 2-angle potential surface



Example: 2-angle potential surface

Features:



- Numerous local minima
- Could have global minimum
- Saddle points
  (indicating transition points)
- Minima and saddle points are stationary, where function derivatives are zero

Energy Minimization

Statement of the problem:

- Upon starting a simulation, the initial conformation is usually not at a minimum
  - Overlaps
  - Non-uniform density
  - Non-relaxed interactions

Energy Minimization

Solution:

- Drive the system into a minimum before starting the simulation
- Mathematically, this is a minimization problem. Thus minimize the potential energy function.

Energy Minimization

Function *f* of coordinate variables $x_1, \ldots x_N$

- Find values of coordinates that minimize *f*
- At minimum points,

$$\frac{\partial f}{\partial x_i} = 0; \quad \frac{\partial^2 f}{\partial x_i^2} > 0$$

- Because of the complex form of *f*, the minimization has to be carried out numerically

Energy Minimization

Minimization will require derivatives.

- If analytical form is not possible, calculate numerical derivatives:
  - For $\partial E/\partial x_i$ (x_i one of the coordinates) can use one of two methods

Energy Minimization

1. For $\partial E/\partial x_i$ valid at $x_i+\Delta x_i/2$:
   - Have E at x_i, calculate it at $x_i+\Delta x_i$
   - Derivative is approximated by $\Delta E/\Delta x$
2. For $\partial E/\partial x_i$ valid at x_i:
   - Calculate E at $x_i-\Delta x_i$ and $x_i+\Delta x_i$
   - Derivative is approximated by $\Delta E/(2\Delta x)$

Energy Minimization

Two typical methods to find minima:

A) Steepest Descents

B) Conjugate Gradients

Both are first-order methods, i.e. only deal with first derivatives of the potential

Energy Minimization

- Second order methods (2nd derivative) are good for harmonic potentials
  - In our case, the potential is only approximately harmonic

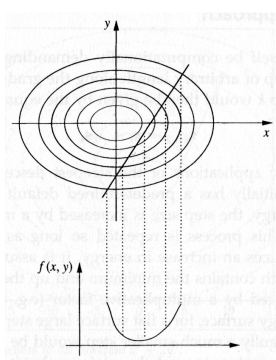
$$V(x)=V(x_k)+(x-x_k)V'(x_k)+(x-x_k)^T\cdot V''(x_k)\cdot(x-x_k)/2+\ldots$$

- Problems arise from the non-harmonic behavior of real potentials and far from minima
  - e.g. Newton-Raphson is acceptable only close to harmonic regime; but even then it involves matrix inversion at every point

A. Steepest Descents

- Moves parallel to force
- Equivalent to moving along gradient of potential
- Define a direction to move by

$$s_k = -\frac{\nabla f}{|\nabla f|}$$

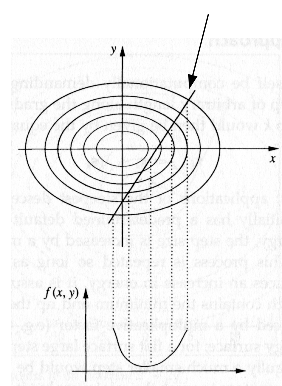


A. Steepest Descents

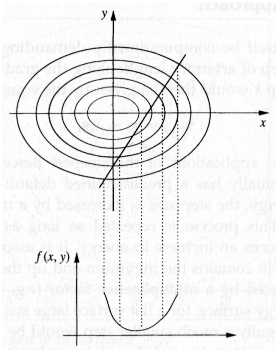
- Starting position at arrow
- Calculate direction

$$s_k = -\frac{\nabla f}{|\nabla f|}$$

- Define line along direction
- Line traces minima
- Decide on method to find local minima



A. Steepest Descents



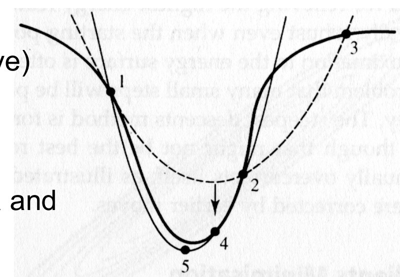
Two ways to find local (or global) minima:

- *Line search (bracket)*
- *Arbitrary size step*

A. Steepest Descents: <u>line search</u>

1. Find bracket with three points (1,2,3)

- Iteratively reduce distance and find minima (expensive)
- Or fit points to function (e.g. quadratic). Find analytical minima and repeat



A. Steepest Descents: <u>arbitrary step</u>

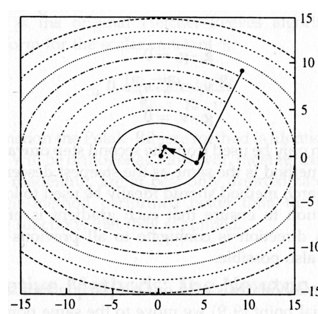
Less computationally demanding than *line search*

- Starting from an initial position in energy space, find next by

$$x_{k+1} = x_k + \lambda_k s_k$$

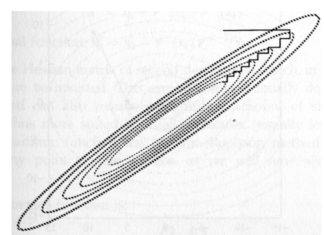
- λ_k is the size of the step
- Size of step may be adjusted depending on getting lower or higher energy
- Could take more steps than *line search*, but may require fewer function evaluations.

A. Steepest Descents



Next direction is perpendicular to previous direction

Not too effective in narrow potential surfaces



B. Conjugate Gradients

- Does not show the oscillatory behavior found in the *steepest descents*
- New directions are not orthogonal, but conjugate
- For non-zero u and v vectors to be conjugate:

$$u^T A v = 0$$

- In our case, for coordinate direction vectors

$$\mathbf{v}_i \cdot V''_{ij} \cdot \mathbf{v}_j = 0$$

wrt to second derivative of potential (*i,j* are successive points)

B. Conjugate Gradients

- Other properties

$$\mathbf{g}_i \cdot \mathbf{g}_j = 0$$
$$\mathbf{g}_i \cdot \mathbf{v}_j = 0$$

where $\boldsymbol{g}_k$ is the gradient at point k

- Every new direction (from point *k*) is along the gradient plus the previous direction

$$\mathbf{v}_k = -\mathbf{g}_k + \gamma_k \mathbf{v}_{k-1}$$

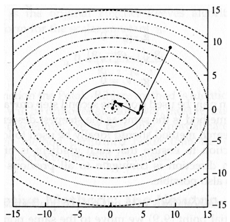
where

$$\gamma_k = \frac{\mathbf{g}_k \cdot \mathbf{g}_k}{\mathbf{g}_{k-1} \cdot \mathbf{g}_{k-1}}$$

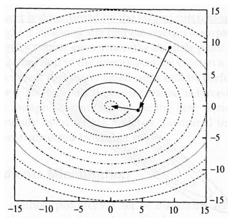
Needs a "first" direction, usually provided by the steepest descents

Line search is still used for moving when locating minima

Comparison



A) Steepest Descents



B) Conjugate Gradients