

Kharagpur Lectures

Classical Molecular Dynamics and Computational Statistical Mechanics

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Outline

1. Formulations of Mechanics

Newton's 2nd Law, Lagrange's formulation of mechanics, Hamilton's formulation of mechanics, Hamilton's least action principal

2. Numerical Integration

Example problems for students, programming algorithms, software

3. Equations of State

Temperature, phase diagrams, Virial Theorem, Heat Theorem

4. Monte-Carlo Methods

Random number generators, Maxwell-Boltzmann distribution, Equilibrium Monte-Carlo averages, Mayer Cluster integrals, pair distributions, collision rates

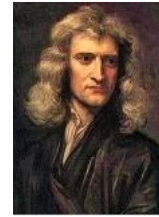
5. Molecular Dynamics

Potential models, initial conditions, boundary conditions, one-dimensional chains, time reversibility

1. Formulation of Mechanics

Newton's Second Law of Motion

$$\mathbf{F} = m\mathbf{a}$$



1643-1747

Particle in a gravitational field

$$F = m\ddot{y} = -mg \rightarrow y = -\frac{1}{2}mgt^2 + v_0t + x_0.$$

Harmonic Oscillator

$$m\ddot{x} = -\kappa x \rightarrow \ddot{x} = -x \rightarrow \{ \dot{x} = -\sin(t); x = \cos(t) \}.$$

Force on a particle in a one dimensional chain

$$\{ m\ddot{x}_I = -\kappa(x_{I+1} - 2x_I + x_{I-1}) \}$$

Lagrange's Formulation of Mechanics Least-Action Principle

An energy formulation useful when there are symmetry conditions in polar or spherical coordinates or other non-cartesian coordinates:

$$\mathcal{L}(y, \dot{y}) = K - \phi$$

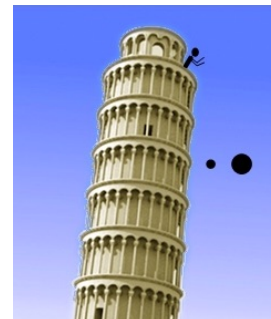
$$\delta \int_{t_1}^{t_2} \mathcal{L} dt = 0 \rightarrow \frac{d}{dt}(\partial \mathcal{L} / \partial \dot{y}) = (\partial \mathcal{L} / \partial y)$$

$$\mathcal{L}(y, \dot{y}) = m(\dot{y}^2/2) - mgy$$

$$(d/dt)m\dot{y} = m\ddot{y} = -mg \rightarrow \ddot{y} = -g \rightarrow$$



1736-1813



Galileo's
experiment?

Hamiltonian Formulation of Mechanics

An energy formulation that must be used in quantum mechanics!

$$\dot{q} = +(\partial\mathcal{H}/\partial p) ; \dot{p} = -(\partial\mathcal{H}/\partial q)$$

Particle in a gravitational field

$$\mathcal{H}(y, p_y) = K + \Phi = p_y^2/2m + mgy$$

$$\dot{y} = +(\partial\mathcal{H}/\partial p) = +p/m$$

$$\dot{p}_y = -(\partial\mathcal{H}/\partial y) = -mg$$

$$\{ \dot{y} = p/m ; \dot{p}_y = -mg \} \rightarrow \ddot{y} = -g$$

One dimensional chain with $m = \kappa = 1$

$$\{ \mathcal{H}(x, p_x) = \frac{1}{2}(x_I - x_{I-1})^2 + \frac{1}{2}(x_I - x_{I+1})^2 + \frac{1}{2}p_x^2 + \dots \}$$

(Similar terms for other particles in the chain)

$$\{ \dot{x}_I = p_I ; \dot{p}_I = (q_{I+1} - q_I + q_{I-1}) \}$$

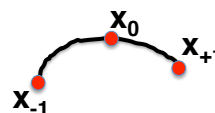


William Rowan Hamilton
1805-1865

Hamilton's Least Action Principle

Consider **discrete paths** in Hamilton's Least Action Principle :

$$\delta \int \mathcal{L} dt = 0 \text{ for } \mathcal{L} = K - \phi$$



$$\int_{-dt}^{+dt} \delta \left[\frac{1}{2} m \left(\frac{x_0 - x_{-1}}{dt} \right)^2 + \frac{1}{2} m \left(\frac{x_0 - x_{+1}}{dt} \right)^2 - \phi \right] dt' = 0$$

Exchange the variation and the integration and evaluate the variation of the integrand :

$$\delta = \delta x_0 \frac{\partial}{\partial x_0} \rightarrow \delta x_0 \left[m \left(\frac{x_0 - x_{-1}}{dt} \right) + m \left(\frac{x_0 - x_{+1}}{dt} \right) - \frac{\partial \phi}{\partial x_0} \right]$$

Since δx_0 is arbitrary, its coefficient must vanish in the interval $(-dt, +dt)$:

$$x_{+1} - 2x_0 + x_{-1} = \frac{F_0}{m} dt^2$$

This is the Störmer integration algorithm derived from the Least Action Principle!

R.E. Gillilan and K.R. Wilson, J. Chem. Phys. **97** (1992).

2. Numerical Integration

Numerically Integrating the Equations of Motion for the Harmonic Oscillator

- **The Harmonic Oscillator as a Standard Test Problem**

The harmonic oscillator equation(s) are a good standard test case for comparing numerical integration methods. The solution is known and can be used for calculating the error in the numerical solution. Amplitude, phase, and energy errors can be calculated. The known oscillator solution can be used to fill in points needed in algorithms that are not self starting.

- **Programming Assignments**

We recommend that students program the harmonic oscillator problem (using the Runge-Kutta fourth-order algorithm) and other problems as time permits. By doing this class members will have sufficient experience to program problems described in the next several lectures.

- **Compiler and Graphics Software**

The gfortran Fortran compiler and gnuplot graphics software is available and we will provide advice for using it between this lecture and the next lecture. Students need to write their own programs rather than using packaged software such as Mathematica or MatLab. Students who program in C rather than Fortran can use the standard C compiler.

gfortran : Free Fortran Compiler

gnuplot : Free Computer Graphics Software

gfortran is a Fortran standard compiler. Downloads for the binaries are available for most systems.

Well documented and conforms to standards up to the year 2000.

Trivial to install on Mac systems and Linux. Harder to install on Windows systems. Use Google search for *gfortran downloads* .

gnuplot is free graphics software used quite often for scientific research .

Well documented with a large collection of demonstration problems .

Google search *gnuplot* will take you to the Home page.

Our uses : Publications and books, research projects

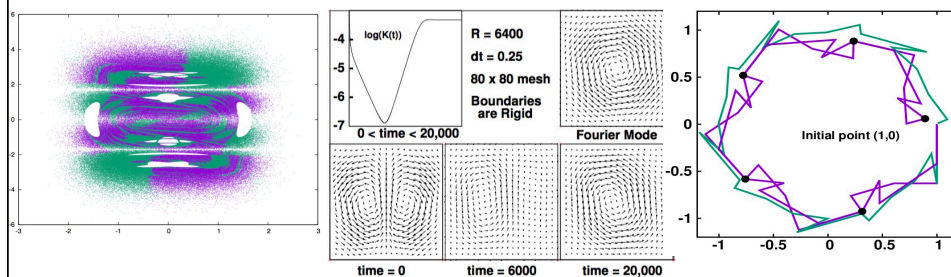
Graphics capability :

Line plots, point plots, contour plots, color labeling, multiple plots per page. Many advanced capabilities include 3d hidden surfaces, transparency, and coloring of surfaces.

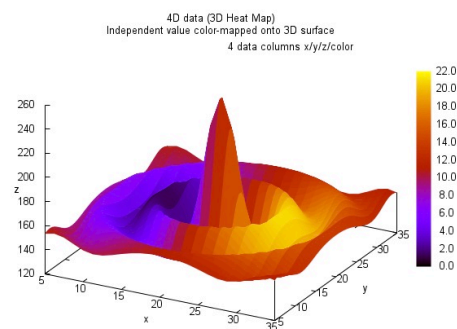
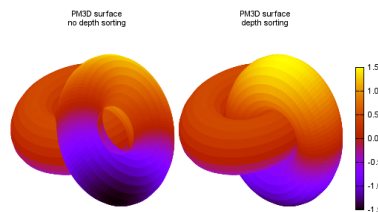
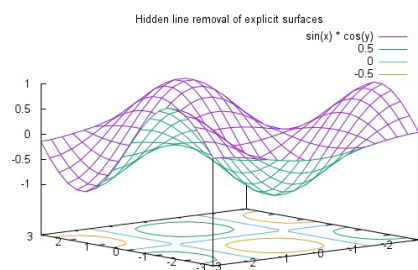
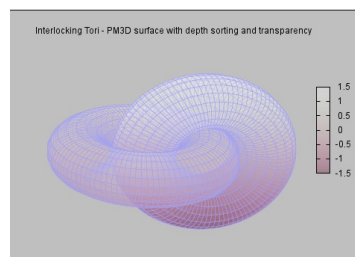
Gnuplot Examples

Example script file

```
set title "Plot the data in the files fort.10 and fort.11"
set xrange [0,1]
set yrange [0,10]
plot "fort.10" u 1:2 with lines lt 2 lw 2
replot "fort.11" u 1:2 with points pt 6 ps 2
set terminal postscript landscape color
set out "line-Pointplot.ps"
replot
set term x11
set out
```



Gnuplot Demo Plots in Three dimensions



Fourth-Order Runge-Kutta Algorithm

Compute r, v by averaging 4 values of derivatives $t = \{0, dt/2, dt\}$:

$$r(dt) = r(0) + \frac{dt}{6} (v_1 + 2v_2 + 2v_3 + v_4)$$

$$v(dt) = v(0) + \frac{dt}{6} (a_1 + 2a_2 + 2a_3 + a_4)$$

$$r_1 = r(0); \dot{r}_1 = v_1 = v(0); \dot{v}_1 = a_1(r_1);$$

$$r_2\left(\frac{dt}{2}\right) = r_1 + \frac{dt}{2} v_1; v_2\left(\frac{dt}{2}\right) = v_1 + \frac{dt}{2} a_1; a_2 = \dot{v}_2;$$

$$r_3\left(\frac{dt}{2}\right) = r_1 + \frac{dt}{2} v_2; v_3\left(\frac{dt}{2}\right) = v_1 + \frac{dt}{2} a_2; a_3 = \dot{v}_3;$$

$$r_4(dt) = r_1 + v_3 dt; v_4(dt) = v_1 + \frac{dt}{2} a_3.$$

The Program Structure for the Harmonic Oscillator Dynamics

$$\begin{array}{l} \dot{q} = +p \\ \dot{p} = -q \end{array} \longrightarrow \begin{array}{ll} yy(1) = q & yyp(1) = p \\ yy(2) = p & yyp(2) = -q \end{array}$$

```

c Main program for the oscillator
parameter (neq = 2)
implicit double precision(a-h,o-z)
dimension yy(neq),yyp(neq)
real*8 ke

dt = 2.0d00*3.141592653589793d00/30.0d00
time = 0.0d00
itmax = 30

c initial condition
q = 1.0d00
p = 0.0d00

c Runge-Kutta storage
yy(1) = q
yy(2) = p

do i = 1,itmax
call rk4(yy,yyp,dt)
time = i*dt
q = yy(1)
p = yy(2)
write (64,64)time,q,p
64 format(2f15.8," q,p")
pot = .5d00*q*q
ke = .5d00*p*p
etot = ke + pot
write(74,*)time,ke,pot,etot,i
end do
stop
end

subroutine rk4(yy,yyp,dt)
parameter (neq = 2)
implicit double precision(a-h,o-z)
dimension yy(neq),yyp(neq)
dimension yak1(neq),yak2(neq),yak3(neq),
& yak4(neq),ynew(neq)
.
.
.
return
end

subroutine fcn(yy,yyp)
parameter (neq = 2)
implicit double precision(a-h,o-z)
dimension yy(neq),yyp(neq)

q = yy(1)
p = yy(2)
f = -q

yyp(1) = p
yyp(2) = -q
return
end

```

Two Fourth Order Runge-Kutta Integrators for the Harmonic Oscillator

4 force evaluations

Compute solution vector and derivatives at time steps 0, dt/2, dt/2, dt
 Compute yy in subroutine rk4 ; Compute yyp in fcn

We use 2 subroutines to evaluate derivatives and the righthand sides

$$\begin{array}{lcl} \dot{q} = p & \longrightarrow & yy(1) = q \quad yyp(1) = p \\ \dot{p} = -q & & yy(2) = p \quad yyp(2) = -q \end{array}$$

<code>call fcn(yy,yyp) ! Right handside evaluation</code>	<code>call fcn(yy,yyp)</code>
<code>yak1 = yyp</code>	<code>yak1 = yyp</code>
<code>ynew = yy + (dt/2)*yak1 ! Solution update</code>	<code>ynew = yy + (dt/3)*yak1</code>
<code>call fcn(ynew,yyp)</code>	<code>call fcn(ynew,yyp)</code>
<code>yak2 = yyp</code>	<code>yak2 = yyp</code>
<code>ynew = yy + (dt/2)*yak2</code>	<code>ynew = yy - (dt/3)*yak1 + dt*yak2</code>
<code>call fcn(ynew,yyp)</code>	<code>call fcn(ynew,yyp)</code>
<code>yak3 = yyp</code>	<code>yak3 = yyp</code>
<code>ynew = yy + dt*yak3</code>	<code>ynew = yy + dt*(yak1 - yak2 + yak3)</code>
<code>call fcn(ynew,yyp)</code>	<code>call fcn(ynew,yyp)</code>
<code>yak4 = yyp</code>	<code>yak4 = yyp</code>
<code>! Average of 4 approximate solutions</code>	
<code>yyp = (yak1 + 2*yak2 + 2*yak3 + yak4)/6</code>	<code>yyp = (yak1 + 3*yak2 + 3*yak3 + yak4)/8</code>
<code>yy = yy + dt*yyp</code>	<code>yy = yy + dt*yyp</code>

Fifth Order Runge-Kutta Integrator

6 force evaluations

```

call fcn(yy,yyp)
yak1 = yyp
ynew = yy + (dt/2)*yak1

call fcn(ynew,yyp)
yak2 = yyp
ynew = yy + (3*yak1 + yak2)*dt/16

call fcn(ynew,yyp)
yak3 = yyp(i)
ynew = yy + yak3*dt/2

call fcn(ynew,yyp)
yak4 = yyp
ynew = yy + (-3*yak2 + 6*yak3 + 9*yak4)*dt/16

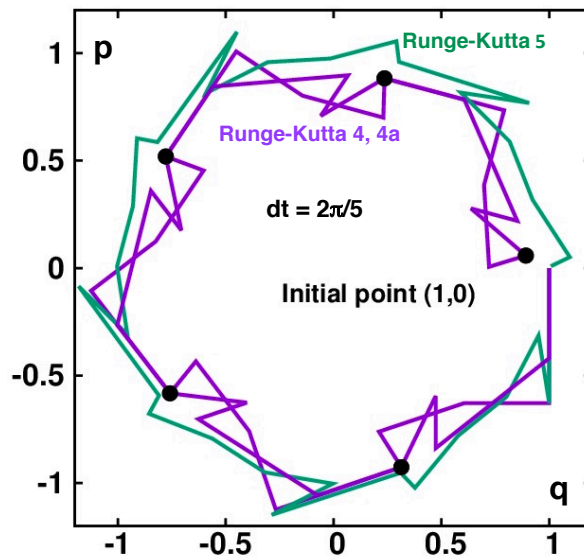
call fcn(ynew,yyp)
yak5 = yyp
ynew = yy + (yak1 + 4*yak2 + 6*yak3 - 12*yak4 + 8*yak5)*dt/7

call fcn(ynew,yyp)
yak6 = yyp

yyp = (7*yak1 + 32*yak3 + 12*yak4 + 32*yak5 + 7*yak6)*dt/90
yy = yy + dt*yyp(i)

```

Two Fourth Order and One Fifth Order Runge-Kutta Integrator One Harmonic Oscillator Period



Three Integrators Compared

Milne's method for the second order differential equation for the oscillator

$$y_{+1} = 2y_0 - y_{-1} + \frac{(dt^2)}{12}(y''_{+1} + 10y''_0 + y''_{-1})$$

To approximate the second order equation for q , substitute

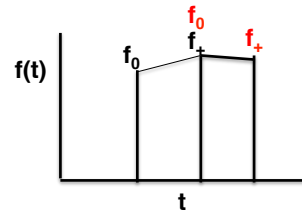
$$y = q, \quad y'' = -q$$

Similarly for p .

Rahman's method (trapezoidal rule) : Fast convergence for periodic functions

$$q_+ = q_0 + \frac{dt}{2}(\dot{q}_0 + \dot{q}_+)$$

$$p_+ = p_0 + \frac{dt}{2}(\dot{p}_0 + \dot{p}_+)$$

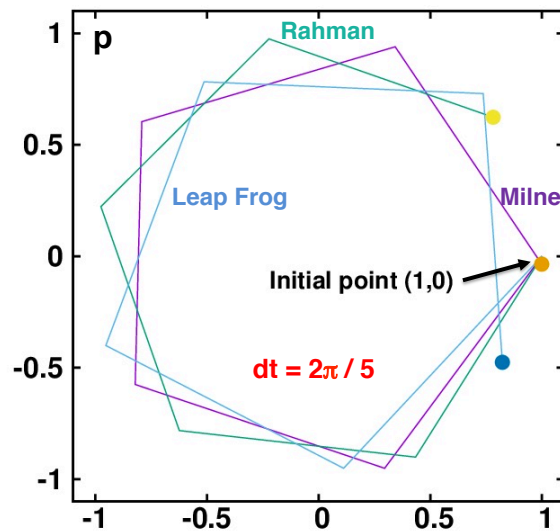


Leap frog : Add two Taylor's series together $\rightarrow f(t_0 + dt) + f(t_0 - dt)$

$$q_+ = 2q_0 - q_- + \frac{dt^2}{2}\ddot{q}_0$$

$$p_+ = 2p_0 - p_- + \frac{dt^2}{2}\ddot{p}_0$$

Three Integrators: Milne, Rahman, Leap Frog
One Harmonic Oscillator Period



Student Problem
Simpson's method is better than Rahman's method. Test it with the oscillator.

3. Equations of State

The Connection Between Atomistic Dynamics and Thermodynamics

- A **thermodynamic state** with energy E can be specified with three variables, temperature, pressure, and volume. The functional relationship between the three variables is the equation of state. Any of the three can be expressed as a function of the other two.
- The **ideal gas law**, $PV = NkT$, is measured experimentally and the ideal gas thermometer is the accepted standard for measuring **temperature**.
- The **Virial Theorem** links the atomistic coordinates, velocities, and forces to pressure and volume.
- A temperature gradient causes heat to flow from hot to cold. The **Heat Theorem** links the time-averaged convective flux of heat to the interparticle forces which contribute to both heat flow and work.

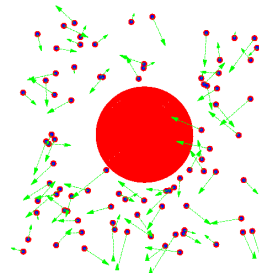
How is temperature defined ?

The ideal gas law, $PV=NkT$, is an experimentally measured equation of state and is the standard set for thermometers. The energy of an ideal gas which is sufficiently dilute has negligible potential energy. The energy is all kinetic.



We construct a thermometer as a heat reservoir with an infinite number of degrees of freedom described by the motion of ideal gas particles. Placed in contact with an isolated system the thermometer exchanges heat energy with the system to impose the constant temperature of the ideal gas.

Ideal Gas Thermometer

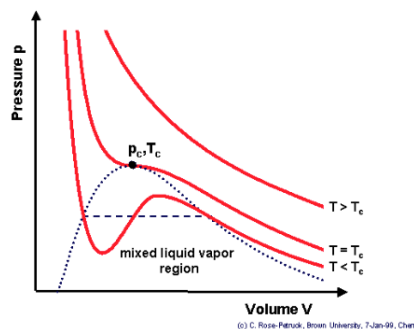
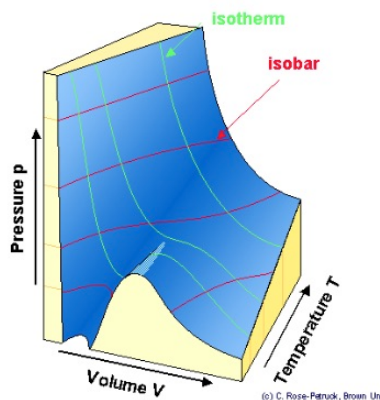


Analysis from statistical mechanics and kinetic theory shows that temperature is the comoving kinetic energy :

$$(kT/m) \equiv \langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle.$$

Van Der Waals Equation of State: Surface and Isotherms

$$(V - b) \left(P + \frac{a}{V} \right) = RT \quad \text{Van der Waals Equation of State}$$



Equations of state are represented with **phase diagrams** in two or three dimensions. Equilibrium Phase diagrams can be calculated with Monte-Carlo methods or Molecular dynamics and compared to experimental data.

Thermodynamics & Hydrodynamics from Dynamics

Equilibrium state variables: E, V ;

$$\{ F = ma \} \rightarrow T \text{ and } P .$$

Dynamics: Compute P and T from :

$$(x, y, z), (v_x, v_y, v_z), (F_x, F_y, F_z)$$

Define **kinetic temperature** as the mean squared values of the velocity components :

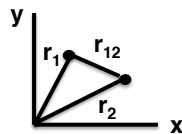
$$(kT/m) \equiv \langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle .$$

Use the Virial Theorem for the **Pressure Tensor P**

Away from equilibrium :

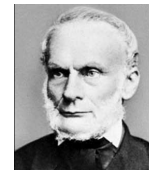
Use the Heat Theorem for the **Heat-Flux vector Q**

The Virial Theorem for the Pressure Tensor P



$$\phi_i = \phi_j = \frac{1}{2} \phi$$

$$f_i = -f_j$$



Rudolf Clausius
1822-1888

Multiply x-component the pairwise force components by the coordinate :

$$\sum x_i \cdot F_{ij} = \sum x_{ij}^2 f_{ij} / r_{ij}$$

Notice also : $m(d/dt)\langle x_i \dot{x}_i \rangle = m\langle \dot{x}_i^2 \rangle + m\langle x_i \ddot{x}_i \rangle$

Consider the x-component and time average over all particles and add wall forces.

$$\sum_i m\langle x_i \ddot{x}_i \rangle = \sum_{ij} \langle x \cdot F_{ij} \rangle - P_{xx}V = \sum_i m\langle d/dt \rangle \langle x_i \dot{x}_i \rangle - \sum_i m\langle \dot{x}_i^2 \rangle$$

where $x_i \dot{x}_i$ is a bounded quantity and $NkT_{xx} = \sum_i m\langle \dot{x}_i^2 \rangle$ in two dimensions .

The long-time derivative of a bounded quantity is zero, giving the Virial Theorem .

$$P_{xx}V = \sum_{ij} \langle f x^2 / r \rangle_{ij} + NkT_{xx}$$



Jean-Baptiste
Fourier
1768-1830

The Heat Theorem for the Heat-Flux Vector Q

In a temperature gradient heat flows from hot to cold.

$$Q = -\kappa \nabla T$$

The convective part of the heat flux is associated with the velocity and the energy in the volume .

$$\sum \dot{E}_i = \frac{1}{m} \sum \mathbf{p}_i \cdot \mathbf{F}_{ij} + \frac{1}{2m} \sum (-\mathbf{F}_{ij} \cdot \dot{\mathbf{r}}_i - \mathbf{F}_{ji} \cdot \dot{\mathbf{r}}_j) = \frac{1}{2m} \sum \mathbf{F}_{ij} \cdot (\dot{\mathbf{p}}_i + \dot{\mathbf{p}}_j)$$

Notice that :

$$\frac{d}{dt} \sum \langle \mathbf{r}_i \dot{\mathbf{E}}_i \rangle = \frac{d}{dt} \sum \langle \mathbf{r}_i \mathbf{E}_i \rangle - \frac{d}{dt} \sum \langle \dot{\mathbf{r}}_i \mathbf{E} \rangle$$

$$\sum \langle \mathbf{r}_i \dot{\mathbf{E}}_i \rangle = \frac{1}{2m} \sum \langle \mathbf{r}_i \mathbf{F}_{ij} \cdot (\mathbf{p}_i + \mathbf{p}_j) \rangle + \frac{1}{m} \sum \langle \mathbf{p}_i \mathbf{E} \rangle = \sum \langle \mathbf{r}_i \dot{\mathbf{E}}_i^{wall} \rangle$$

$$Q_i \delta V = \sum_i (\mathbf{v} \mathbf{E})_i + \sum_{ij} x_{ij} [\mathbf{F}_{ij} \cdot (\mathbf{v}_i + \mathbf{v}_j)] / 2$$

4. Monte-Carlo Methods

- Two random number generators
- Monte-Carlo generation of the Maxwell Boltzmann distribution and moments
- Equilibrium Monte-Carlo Averages, Mayer cluster integrals, pair distribution and collision rate

Time Reversible Two-Seed Random Number Generator Frederico Ricci-Tersenghi

```
function rund(intx,inty)
i = 1029*intx + 1731
j = i + 1029*inty + 507*intx - 1731
intx = mod(i,2048)
j = j + (i - intx)/2048
inty = mod(j,2048)
rund = (intx + 2048*inty)/4194304.0
return
end
```

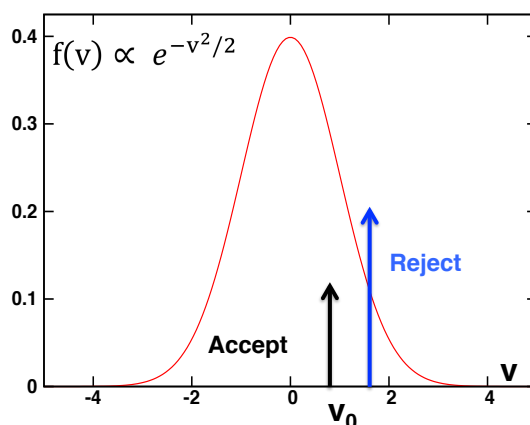
Use the program “federico” in [arxiv:1305.0961v2](https://arxiv.org/abs/1305.0961v2) ending the loops with 7 and write the seeds for 7 random numbers. Write another program to read the file of seeds and write out both forward and reverse numbers. Notice that the random number seeds are reversed when rund is called with the seeds
Intx = 1862 and inty = 1347. The random numbers generated are :

```
1 0.67508363723754883 0.74579644203186035
2 0.16147541999816895 0.65815877914428711
3 0.90861988067626953 0.97026991844177246
4 0.97026991844177246 0.90861988067626953
5 0.65815877914428711 0.16147541999816895
6 0.74579644203186035 0.67508363723754883
```

How do you decide if this is a good random number generator?

Moments of the Maxwell-Boltzmann Velocity Distribution using the Monte-Carlo Method

Sample 1, 000, 000 velocity values from the Maxwell-Boltzmann distribution



Pick : $-\frac{1}{2} \leq \mathcal{R}_1 \leq \frac{1}{2}$

Set : $v_0 = 10\mathcal{R}_1$

Calculate : $MB = e^{-v_0^2/2}$

Pick : $0 \leq \mathcal{R}_2 \leq 1$

If $MB \leq \mathcal{R}_2$ then accept,
Otherwise, try again .

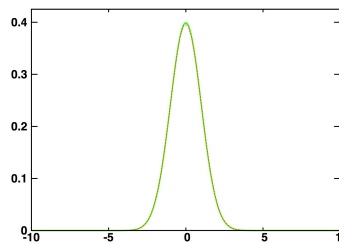
Moment Calculations Using Maxwell-Boltzmann Monte-Carlo Results

- Construct a Maxwell-Boltzmann density function

Set up a grid of velocity values and count the velocities in each bin. Plot the probability for each bin :

$$p = (\# \text{ in bin}) / (\text{total } \#)$$

Plot the analytical curve.



- Use Monte-Carlo to calculate the moments of the Maxwell-Boltzmann distribution. With 4 batches of 100,000 trials the first, second, and 4th moments were converging. The 6th moment was too high. The random number generator, rund, was incapable of producing the 6th moment correctly ! The
- Box-Muller algorithm is one good way in which to solve this problem.

Using the Fortran intrinsic random number generator, rand, with the same procedure and averaging the results of the four batches, the results are :

$$\langle v \rangle = 0.0005 ; \langle v^2 \rangle = .9996 ; \langle v^4 \rangle = 2.9985 ; \langle v^6 \rangle = 15.0195$$

Student problems :

- Calculate the moments analytically. Make sure you normalize your results.
- Calculate the moments using Monte-Carlo and determine the number of trials needed for convergence within .01.
- Notice the odd moments vanish. Why?

Equation of State Averages from Statistical Mechanics Hard-Disk Monte Carlo

The virial expansion is a representation of the pressure in powers of the density :

$$(PV/NkT) - 1 = B_1 \left(\frac{A_0}{A} \right) + B_2 \left(\frac{A_0}{A} \right)^2 + B_3 \left(\frac{A_0}{A} \right)^3 + \dots \text{Hard disks}$$

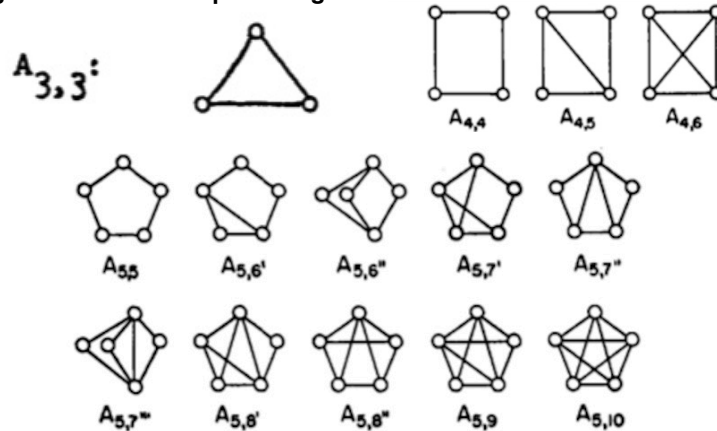
$$B_2 = \pi/3^{1/2} ; B_3 = 4\pi^2 A_{3,3}/9 ; B_4 = \pi^3 (6A_{4,5} - 3A_{4,4} - A_{4,6})/3^{3/2}$$

The $A_{i,j}$ are cluster integrals and represent the volume in configuration space in which i particles form j bonds. The Mayer f functions describing the clusters are integrated over the volume and are proportional to the constants in the density expansion¹. In Reference [2] below a Modified Monte Carlo technique is described which uses interacting hard spheres to numerically compare with the expansion using cluster integrals developed by the Mayers .

- J. E. Mayer M. G. Mayer, *Statistical Mechanics*, (John Wiley and Sons, Inc., New York, 1940) pp. 277-2911.
- Nicholas Metropolis, Ariana W. Rosenbluth, Marshall N. Rosenbluth, Augusta Teller, and Edward Teller, "Equation of State Calculations by Fast Computing Machines,

Mayer Cluster integrals

The virial coefficients are proportional to the “star” cluster integrals developed by the Mayers. The Mayer derivation involves expanding the partition function in terms of the product of single particle distributions to form two, three, ... , n-particle distributions. These **doubly-connected** products represent *clusters* formed by bonds between the n-particles. Below are examples of the *star clusters* formed for 3, 4, and 5 particles. The subscripts (i, j) denote the number of particles and the number of Mayer f-bonds in the configuration. Each figure denotes a unique configuration.



Mayer Cluster integral for three particles

$$f_{ij} = e^{(-\phi(r_i - r_j)/kT)} - 1 ;$$

$f_{ij} = -1$ for overlapping hard spheres

$f_{ij} = 0$ for nonoverlapping hard spheres

Calculate the Multidimensional cluster Integral for hard spheres :

$$I = \int \dots \int dx_{12} dx_{13} dy_{12} dy_{13} (f_{12} f_{23} f_{31})$$

$$f_{ij} = -1 \text{ if } r_{ij} < \sigma ; \quad f_{ij} = 0 \text{ if } r_{ij} > \sigma$$

$$\begin{aligned} B_3 &= -(1/3)I = 0.625(B_2)^2 \text{ in 3D} \\ &= 0.782(B_2)^2 \text{ in 2D} \\ &= 1.000(B_2)^2 \text{ in 1D} \end{aligned}$$

$$\begin{aligned} B_2 &= 2/3(\pi\sigma^3) \text{ in 3 dimensions} \\ B_2 &= 1/2(\pi\sigma^2) \text{ in 2 dimensions} \\ B_2 &= \sigma \text{ in one dimension} \end{aligned}$$

Student Problem

Calculate the third virial coefficient in one, two, and three-dimensions for $\sigma = 1$ using Monte-Carlo integration.

Calculation of B_3 in Three Dimensions

```

implicit double precision (a-h,o-z)
top = 0
bot = 0
intx = 0
inty = 0
itmax = 10 000 000
iout = itmax/10
do it = 1,itmax
  x3 = rund(intx,inty)*2 - 1
  y3 = rund(intx,inty)*2 - 1
  z3 = rund(intx,inty)*2 - 1
  x2 = rund(intx,inty)*2 - 1
  y2 = rund(intx,inty)*2 - 1
  z2 = rund(intx,inty)*2 - 1
  r12 = dsqrt( x2*x2 + y2*y2 + z2*z2 )
  r13 = dsqrt( x3*x3 + y3*y3 + z3*z3 )
  r23 = dsqrt( (x2-x3)**2 + (y2-y3)**2 + (z2-z3)**2 )
  if((r12.lt.1).and.(r13.lt.1).and.(r23.lt.1)) top = top + 1
  if((r12.lt.1).and.(r13.lt.1)) bot = bot + 1
  if(iout*(it/iout).eq.it) write(6,*) top,bot,top/bot,15/32.0d00
enddo
stop
end

```

Equilibrium Monte-Carlo Method for Canonical Averages

It follows from statistical mechanics that phase-space averages calculated by weighting microstates with the Boltzmann factor will converge to the canonical-ensemble averages for a physical variable $X(q,p)$:

$$\langle X \rangle = \sum X_i e^{-E_i/kT} / \sum e^{-E_i/kT}$$

For more than a few degrees of freedom random sampling of phase space will generate very few, if any at all, accepted microstates. This follows because the ratio of the occupied and the unoccupied part of phase space is close to zero. The **Modified Monte Carlo Method** of Metropolis, the Rosenbluths', and Tellers' corrects this deficiency for hard disks by examining microstates with relatively small energy changes, **$\Delta\phi = kT$, in configuration space only**. Then the microstate weights are not needed! The microstates are weighted evenly.

$$\langle X \rangle = \sum X_i / \sum 1$$

The detailed steps in the algorithm are listed on the next vugraph.

The Modified Equilibrium Monte Carlo Method

1. Generate a microstate with N particles.
2. Select a particle randomly: $i = (N-1)RN + 1$; Make a trial move less than a maximum step size.
3. Compute the energy. If it goes down, accept the move and update averages.
4. If the energy increased, select another random number. If this latter random number is less than the Boltzmann factor, accept the move.
5. Update the averages using the "new" configuration if the move was accepted.
6. Update the averages using the "old" configuration if the move was rejected.
7. If the number of steps is less than the total desired number of steps go to 2.
8. Stop when the total number of steps is reached.

Accuracy: A useful idea is to divide all the data into two, five, ten, or seventeen batches so that you can relate the standard deviation to the uncertainty of the average value.

Results for the Monte-Carlo Equation of State by Metropolis, Rosenbluths, Tellers

TABLE I. Results of this calculation for $(PA/NkT) - 1 = X_1$ compared to the free volume theory (X_2) and the four-term virial expansion (X_3). Also (PA_0/NkT) from our calculations.

ρ	(A/A_0)	X_1	X_2	X_3	(PA_0/NkT)	
2	1.04269	49.17	47.35	9.77	48.11	
4	1.14957	13.95	13.85	7.55	13.01	Solid phase
5	1.31966	6.43	6.72	5.35	5.63	
5.5	1.4909	4.41	4.53	4.02	3.63	
6	1.7962	2.929	2.939	2.680	2.187	
6.25	2.04616	2.186	2.323	2.065	1.557	
6.5	2.41751	1.486	1.802	1.514	1.028	
7	4.04145	0.6766	0.990	0.667	0.4149	

X_1 is the Monte-Carlo calculation.

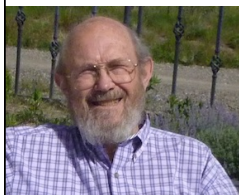
X_2 is the free volume estimate.

X_3 is the four term virial series. Ten virial terms are known now.

The virial expansion only describes the fluid state.

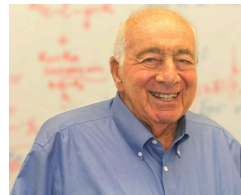
Today these numbers are accurate to five figures.

Generate Configurations Using the Unit Cells and Periodic Boundary Conditions

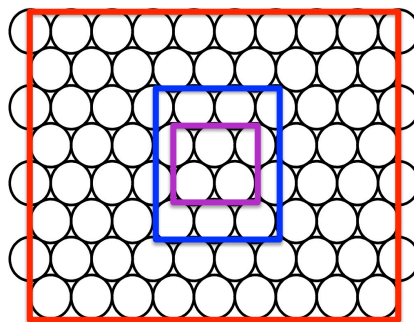


Bill Hoover

Consider the effects of the calculated collision rate along on the Monte-Carlo averages.



Berni Alder



Unit cells for 4, 12, 72 particles

William G. Hoover, and Berni Alder, "Studies in Molecular Dynamics. IV. The Pressure, Collision Rate, and their Number Dependence for Hard disks", *Journal of Chemical Physics*, 46 No. 2, pp. 686-691 (1966).

Pair Distribution Function

The pair distribution function was used in the early days of molecular dynamics to compare potential models with neutron and xray diffraction results.

Consider the ratio of pairs of particles with separation distance in a range dr . The pair distribution is constructed with bins of length dr containing the ratio of the number of pairs for a potential ϕ to the number of pairs for an ideal gas. We consider two potentials, an 8-4 potential and a repulsive potential.

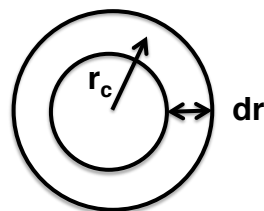
$$\phi_{84} = (2 - r^2)^8 - 2(2 - r^2)^4; r_{cutoff} = \sqrt{2}$$

$$\phi_{repulsive} = 100(1 - r^2)^4; r_{cutoff} = 1.0$$

$$N_k^\phi = \#pairs(r_k \leq r_c < r_{k+1})$$

$$N_k^{ideal\ gas} = 2\pi r_c dr N(N-1)/2V = \pi r_c dr (N-1)\rho$$

$$N_k = \frac{N_k^\phi}{N_k^{ideal\ gas}} \longrightarrow g(r_k) = \frac{\sum N_k}{itmax}$$

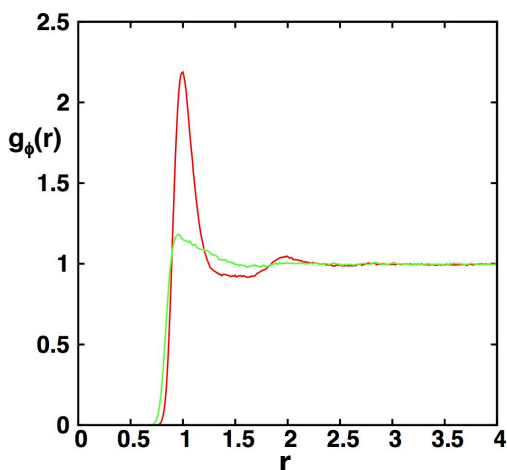
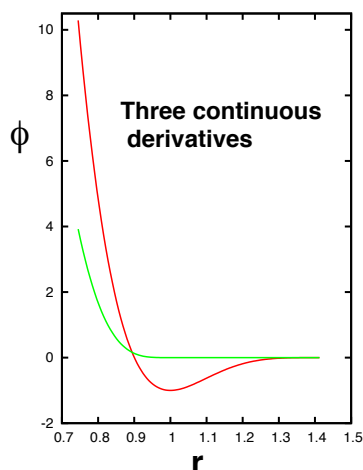


We use 400 bins of size 0.01 and $\max(r_c) = 4$ to construct $g(r)$ shown next.

The 8-4 and $(1 - r^2)^4$ Pair Potentials : Pair Distributions

$$\Phi_{84} = (2 - r^2)^8 - 2(2 - r^2)^4 ; r_{cutoff} = \sqrt{2}$$

$$\Phi_{repulsive} = 100(1 - r^2)^4 ; r_{cutoff} = \sqrt{2}$$



A Calculation of Equilibrium Averages with the Center of Mass set to Zero

The center of mass motion should always be set to zero when periodic boundary conditions are used. The effect of this is to increase the collision rate and therefore the pressure. The **Virial Theorem** for hard disks (rearranged terms) is

$$\frac{PA}{NkT} - 1 = \left\langle \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle / m \sum_{i=1}^N v_i^2 = (Nu^2\tau)^{-1} \sum_{collisions}^{ln \tau} \mathbf{r}_c \cdot \mathbf{v}_c$$

where the last term on the right is a collision term coming from the average over the internal pair forces and u^2 and τ are the mean squared velocity and the last sum measures the number of collisions occurring in a time τ .

Taking the ratio of the above equation with its low density form gives

$$g(\sigma) = \frac{PA/NKT - 1}{B_2(N/A)} = \frac{\Gamma}{\Gamma_0}$$

Here B_2 is the second Virial coefficient and the righthand side is the ratio of the high density to the low density collision rate. Both B_2 and Γ_0 are increased by the center of mass correction. The collision rates are calculated from molecular dynamics and agree with the calculation from the virial theorem as shown on the next vugraph.

Monte-Carlo Corrected Results for N = 12

A/A_0	PA/NkT^*	1000 collisions	Monte Carlo	Adjusted Monte Carlo	A/A_0	Correct factor
1.100	21.9	2	20.62 ± 0.09	22.40	1.100	1.090
1.250	9.99	2	9.18 ± 0.06	9.93	1.250	1.091
1.350	8.10	20	7.42 ± 0.08	8.01	1.350	1.091
1.400	7.42	10	6.86 ± 0.08	7.39	1.400	1.090
1.450	6.93	10	6.27 ± 0.09	6.75	1.450	1.091
1.475	6.61	20	6.21 ± 0.08	6.69	1.475	1.091
1.500	6.33	20	5.91 ± 0.05	6.36	1.475	1.092
1.525	6.17	20	5.79 ± 0.06	6.22	1.500	1.091
1.550	5.94	10	5.52 ± 0.06	5.94	1.525	1.089
1.600	5.56	10	5.23 ± 0.07	5.61	1.550	1.092
1.650	5.20	10	1.600	1.089
1.700	4.80	7	4.66 ± 0.07	4.99	1.700	1.090
1.800	4.26	4	4.07 ± 0.06	4.34	1.800	1.087
1.900	3.93	4	2.000	1.092
2.000	3.54	4	3.37 ± 0.06	3.59	3.000	1.087
2.100	3.30	2		
3.000	2.10	2	2.03 ± 0.03	2.12		

* These data are accurate within about 1%.

A/A_0 is the ratio of the area to the close-packed area.
The adjusted Monte-Carlo results show very good agreement over the full range of densities!

Kinetic theory predicts a correction of 1.091;
 12 particles give a correction 12/11.

5. Molecular Dynamics

- **Potential Models**
 Atomistic potential models, pair potentials, cutoff radius, three-body potential
 Reduced Units and the Principle of Corresponding States
- **Initial Conditions**
 Positions, velocities, energy
- **Boundary Conditions**
 Fixed and Periodic Boundary Conditions for the One-Dimensional Chain
 Mirror Boundary Conditions, Moving Boundaries, Shear Boundaries
- **Normal Mode Solutions for the One Dimensional Chain**
 6-particle periodic chain
 5-particle fixed boundary chain
- **Time Reversibility**
 Levesque-Verlet Bit-Reversible Algorithm
- **Computational Efficiency**
 Neighbor Lists and Cell Model

The Development of Potential Models for Molecular Dynamics

The interactions which determine bulk properties are primarily electrostatic in nature. A quantum mechanical treatment is the most fundamental treatment of these interactions. Fortunately there are several approximations which provide very good potential models for classical dynamics.

1. Born-Oppenheimer approximation : The ion coordinates can be used as the basis for the wave function calculations because of the electron to proton mass ratio, 1/1836. Experiments with He-He interactions confirm this approximation.
2. Forces between molecules are much weaker than intramolecular forces (vibrations) so that some molecules can be treated as rigid molecules with the location specified with the center of mass coordinate of the molecule. **This is not the case for polymers.**
3. Because of the mass ratio we can use classical dynamics and statistical mechanics and add quantum corrections.
4. Another simplification arises because to a first approximation the intermolecular potential is additive in the number of interacting particles within the range of the potential.

$$\phi = \sum_{\text{pairs}} \phi(r_{ij}) + \sum_{\text{triples}} \phi(r_{ij}, r_{ik}, r_{jk}) + \dots$$

J. A. Barker and . Henderson: "What is "Liquid"?", Rev. Mod. Phys. **48**, (October 1976).

Lennard-Jones Potential Calculated Phase Diagram for Argon

$$\phi_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad 1925$$

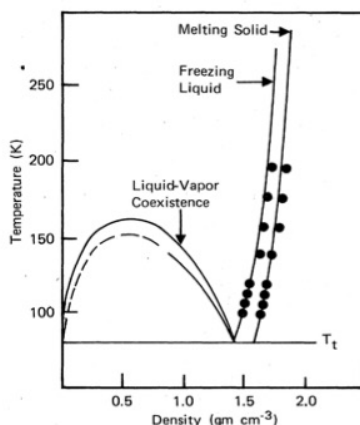


FIG. 1. Phase diagram for the 6-12 fluid, as calculated by Hansen and Verlet (1969) (solid lines), and for argon (dashed line and circles). The comparison assumes $\epsilon/k = 119.8$ K, $\sigma = 3.405$ Å.

Sir John Lennard-Jones



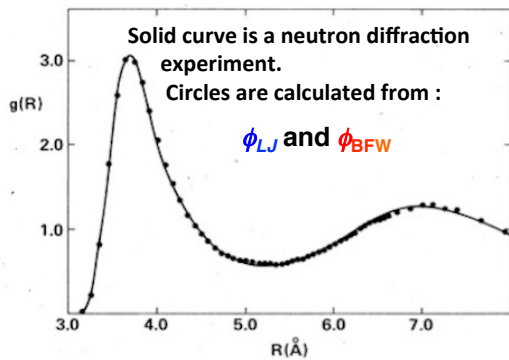
1894-1954

John Edward Jones received his Doctor of Science degree in 1924 at Cambridge and proposed the semi-empirical force law. In 1925 he married **Kathleen Lennard** adding his wife's name to his to become **Lennard-Jones**. He was knighted in 1946, becoming **Sir John Lennard-Jones**.

Lennard-Jones Potential

Calculated Pair-Distribution function **with quantum corrections**

The pair distribution compared to experimental diffraction data.



John Barker
1925-1995

$$\phi_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

ϕ_{BFW} is a pair potential with three-body angle-dependent and quantum corrections.

$$\phi_{BFW} = \epsilon \left(e^{\alpha(1-\bar{r})} \left(A_0 + A_1(\bar{r}-1) + A_2(\bar{r}-1)^2 + A_3(\bar{r}-1)^3 + A_4(\bar{r}-1)^4 + A_5(\bar{r}-1)^5 \right) - \left(\frac{C_6}{\delta + \bar{r}^6} + \frac{C_8}{\delta + \bar{r}^8} + \frac{C_{10}}{\delta + \bar{r}^{10}} \right) \right)$$

Barker, J. A., D. Henderson, and R. O. Watts, 1970, Phys. Lett. **31A**, 48.

Lennard-Jones Potential Parameters for Atoms

$$\phi_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

Atom	Source	$\epsilon/k_B(\text{K})$	$\sigma(\text{nm})$
H	[Murad and Gubbins 1978]	8.6	0.281
He	[Maitland <i>et al.</i> 1981]	10.2	0.228
C	[Tildesley and Madden 1981]	51.2	0.335
N	[Cheung and Powles 1975]	37.3	0.331
O	[English and Venables 1974]	61.6	0.295
F	[Singer <i>et al.</i> 1977]	52.8	0.283
Ne	[Maitland <i>et al.</i> 1981]	47.0	0.272
S	[Tildesley and Madden, 1981]	183.0	0.352
Cl	[Singer <i>et al.</i> 1977]	173.5	0.335
Ar	[Maitland <i>et al.</i> 1981]	119.8	0.341
Br	[Singer <i>et al.</i> 1977]	257.2	0.354
Kr	[Maitland <i>et al.</i> 1981]	164.0	0.383

Model Potentials Characterizing Material Behavior

Embedded-Atom Potentials for Metals :

Experimental data provide parameters for potentials for specific materials. Models for material behavior can be approximated from these data. Electrons in a metal form a charge-neutralizing background for the motion of the ions. The potentials for our two-dimensional copper simulations were a Lennard-Jones 6-12 potential and a density-dependent attractive potential, $\phi_{EA} \approx (\rho - 1)^2 / 2$, modeling the electronic distribution.

Long-Range Electrostatic Potentials

The method of Ewald sums is a reliable technique for calculating the long range interactions without resorting to the N^2 computational effort in the sum over all of the particles. The method is based on Fourier series and applies to periodic boundaries only. Ewald sums and related methods are described in detail in Frenkel and Smit's book.

Potentials Fit to Experimental Data

Curve-fitted experimental data has resulted in libraries of equation of state data for large collections of materials used at the National Laboratories in the United States.

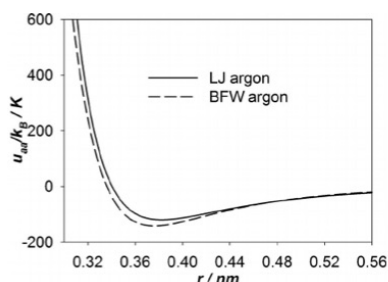
Daan Frenkel and Berend Smit, *Understanding Molecular Simulation : From Algorithms to Applications*, Academic Press, New York (2002).

Cutoff Radius for Pair Potentials

- To prevent large numerical errors the attractive part of the potential must vary smoothly from the minimum in the potential to the cutoff radius.
- The radius at the minimum energy in the Lennard-Jones is $2^{1/6}$. For $\sigma = 1$ and $\epsilon = 1$ this corresponds to a minimum energy of -1. The radius, $1/r^6 = 0.01$, corresponds to a cutoff radius between 2.0 and 3.0. Typically for argon the value used is $r = 2.6$.

$$\phi_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

- Spline fits are a good choice to smoothly extend the potential from the minimum to the cutoff radius. \longrightarrow



$$\begin{aligned}\phi &= C(1 - r^2)^4 \\ \phi &= C(1 - r)^3 \\ \phi &= C(1 - r)^4 \\ \phi &= C(1 - 6r^2 + 8r^3 - 3r^4)\end{aligned}$$

Dense fluid potentials

Yun Long, et. al., "On the molecular origin of high-pressure effects in nanoconfinement : The role of surface chemistry and roughness", J. Chem. Phys. **139**, 144701 (2013).

Beyond Two Body Pair Potentials → Three Body Potentials

Three-body potentials are needed when three atoms are close enough to interact with each other.

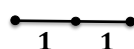
Quantum mechanical perturbation theory is used to compute three-body interactions between the electrons of the three atoms which have induced multipole interactions. The Axilrod-Teller potential, V_{ijk} , is an example of dipole-dipole interactions.



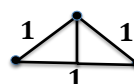
Edward Teller
1908-2003

$$V_{ijk} = E_0 \left[\frac{1 + 3\cos(\gamma_i)\cos(\gamma_j)\cos(\gamma_k)}{(r_{ij}r_{jk}r_{ik})^3} \right]$$

1943



$$V_{ijk} = -E_0/4$$

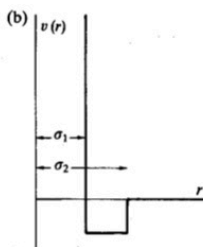
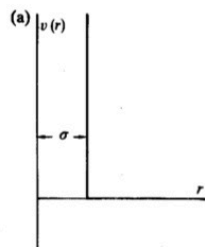


$$V_{ijk} = -3E_0/8$$

Where r_{ij} is the distance between the atoms i and j , and γ_i is the angle between the two vectors. The coefficient E_0 is positive and of the order $V\alpha^3$ where V is the ionization energy and α is the mean atomic polarizability. The exact value of E_0 depends on the magnitude of the dipole matrix elements and the energies of the p orbitals.

Axilrod, B. M.; Teller, E. (1943). "Interaction of the van der Waals Type Between Three Atoms", *Journal of Chemical Physics*, **11** (6): 299.

Atomistic Pair-Potential Models

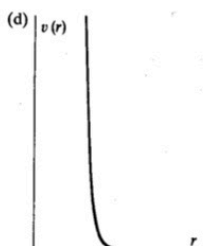
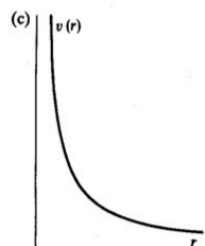


a) Hard-sphere potential

$$\phi_{HS} = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma \end{cases}$$

b) Square-well potential

$$\phi_{SW} = \begin{cases} \infty & r < \sigma_1 \\ -\epsilon & \sigma_1 \leq r \leq \sigma_2 \\ 0 & \sigma_2 \leq r \end{cases}$$



c) Coulomb and Gravitational potentials

$$\begin{aligned} \phi_{Coulomb} &= \pm(q_1q_2/r) \\ \phi_{Gravitational} &= (GM_1M_2/r) \end{aligned}$$

d) Soft-sphere potential

$$\phi_{SS} = \epsilon(\sigma/r)^v \text{ for } v = 12$$

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

Reduced Units for Short-Range Pair Potentials in Mechanical Systems with a Single Type of Particle

For systems with just one type of particle set $m = 1$ and a pair potential with well depth ϵ and particle diameter σ , the other variables can be expressed in terms of reduced units :

Density	$\rho^* = \rho\sigma^3$	$\phi_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$
Energy	$E^* = E/\epsilon$	
Temperature	$T^* = k_B T/\epsilon$	
Pressure	$P^* = P\sigma^3/\epsilon$	
Time	$t^* = (\epsilon/m\sigma^3)^{1/2} t$	
Force	$f^* = f\sigma/\epsilon$	
Torque	$\tau^* = \tau/\epsilon$	
Surface Tension	$\gamma^* = \gamma\sigma^2/\epsilon$	

Boltzmann's constant needs to be included to express the equivalence between the energy units of heat and work . When the parameters such as ϵ , σ , and $k_B T$ are set to one, they need not be carried along in the computer program.

Reduced properties are used to define corresponding states.

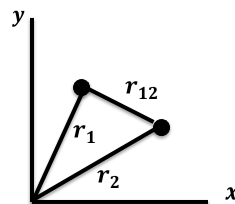
Pair Potentials with Periodic Boundaries

```
subroutine rhs(yy, yyp)
implicit double precision(a-h,o-z)
parameter (N = 1024, neq = 4*N)
dimension yy(neq), yyp(neq)
dimension x(N), y(N), px(N), py(N), fx(N), fy(N)
common elx, ely
```

```
do i = 1, N
  x(i) = yy(i)
  y(i) = yy(i + N)
  px(i) = yy(i + N + N)
  py(i) = yy(i + N + N + N)
  fx(i) = 0.0d00
  fy(i) = 0.0d00
end do
```

```
do i = 1, N-1
  do j = i+1, N
    xij = x(i) - x(j)
    yij = y(i) - y(j)
    if(xij.gt.+elx/2) xij = xij - elx
    if(xij.lt.-elx/2) xij = xij + elx
    if(yij.gt.+ely/2) yij = yij - ely
    if(yij.lt.-ely/2) yij = yij + ely
    rr = xij*xij + yij*yij
    if(rr.lt.2.0d00) then
      fx(i) = fx(i) + xij*16*((2-rr)**7 - (2-rr)**3)
      fy(i) = fy(i) + yij*16*((2-rr)**7 - (2-rr)**3)
      fx(j) = fx(j) - xij*16*((2-rr)**7 - (2-rr)**3)
      fy(j) = fy(j) - yij*16*((2-rr)**7 - (2-rr)**3)
    endif
  end do
end do
```

```
do i = 1, N
  yyp(i) = px(i)
  yyp(N+i) = py(i)
  yyp(N+N+i) = fx(i)
  yyp(N+N+N+i) = fy(i)
enddo
return
end
```



$$f_i = -f_j$$

$$\phi_i = \phi_j = \frac{1}{2} \phi$$

Reduced Units for Long-Range Pair Potentials in Electrical Systems with a Single Type of Particle

Electrostatic Potential

$$\phi_{ij} = q_1 q_2 / 4\pi\epsilon_0 r_{ij}$$

Fundamental Constants in Electrical Systems

Permittivity $\epsilon_0 = 8.9542 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$

Charge $1 \text{ C} = 2.9979 \times 10^9 \text{ e.s.u.}$

Dipole $1 \text{ C m} = 2.9979 \times 10^{11} \text{ e.s.u. cm}$

Quadrupole $1 \text{ C m}^2 = 2.9979 \times 10^{11} \text{ e.s.u. cm}^2$

Charge

$$q^* = q / (4\pi\epsilon_0 \sigma^3 \epsilon)^{1/2}$$

Dipole

$$\mu^* = \mu / (4\pi\epsilon_0 \sigma^3 \epsilon)^{1/2}$$

Quadrupole

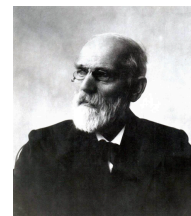
$$Q^* = Q / (4\pi\epsilon_0 \sigma^5 \epsilon)^{1/2}$$

Principle of Corresponding States

Van Der Waals first stated the **Principle of Corresponding States** :

"Substance at corresponding states behave alike"

In the case of the Van der Waals equation of state the parameters used to define the reduced quantity are the critical point values of pressure, temperature, and volume. In reduced variables measure the deviation



Van Der Waals

$$(V - b) \left(P + \frac{a}{V} \right) = RT \quad \text{Van der Waals Equation of State}$$

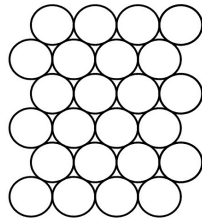
$$R = 8.3144598 \text{ JK}^{-1} \text{ kmol}^{-1}$$

Here **a** measures the strength of the attractive forces and **b** represents the available free volume.

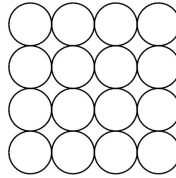
$$P_R = \frac{P}{P_c}, V_R = \frac{V}{V_c}, T_R = \frac{T}{T_c}; \quad V_c = 3b; \quad P_c = \frac{1}{27} \frac{a}{b^2}; \quad T_c = \frac{8}{27} \frac{a}{bR}$$

$$\left(P_R + \frac{3}{V_R^2} \right) \left(V_R - \frac{1}{3} \right) = \frac{8}{3} T_R \quad \text{Van der Waals Reduced Equation of State}$$

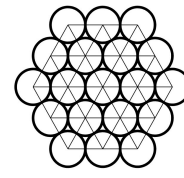
Initial Conditions – Many Body Systems



Triangular lattice
 $d_x = 1.0$, $d_y = (3/4)^{1/2}$



Square lattice
 $d_x = d_y = 1.0$



Hexagon with
interaction lines

c remove the center of mass motion

```
sumvx = 0.0d00
sumvy = 0.0d00
sumxx = 0.0d00
sumyy = 0.0d00
do i = 1,N
  sumx = sumx + vx(i)
  sumy = sumy + vy(i)
end do
do i = 1,N
  vx(i) = vx(i) - (sumvx/N)
  vy(i) = vy(i) - (sumvy/N)
  sumxx = sumxx + vx(i)*vx(i)
  sumyy = sumyy + vy(i)*vy(i)
end do
```

**c scale the initial kinetic energy
c to a value of N**

```
do I = 1,N
  vx(i) = dsqrt(N/sumxx)*vx(i)
  vy(i) = dsqrt(N/sumyy)*vy(i)
end do
```

Boundary Conditions – One Dimensional Chain

Displacements :

$$\delta_- = x_j - x_{j-1}$$

$$\delta_+ = x_j - x_{j+1}$$

$$\delta_j = \delta_+ - \delta_- = x_{j+1} - 2x_j + x_{j-1}$$

Fixed boundary condition



Periodic boundary condition



First and last particle forces :

$$\delta_- = x_j$$

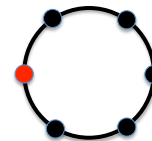
$$\delta_+ = x_j - x_{j+1}$$

Left boundary

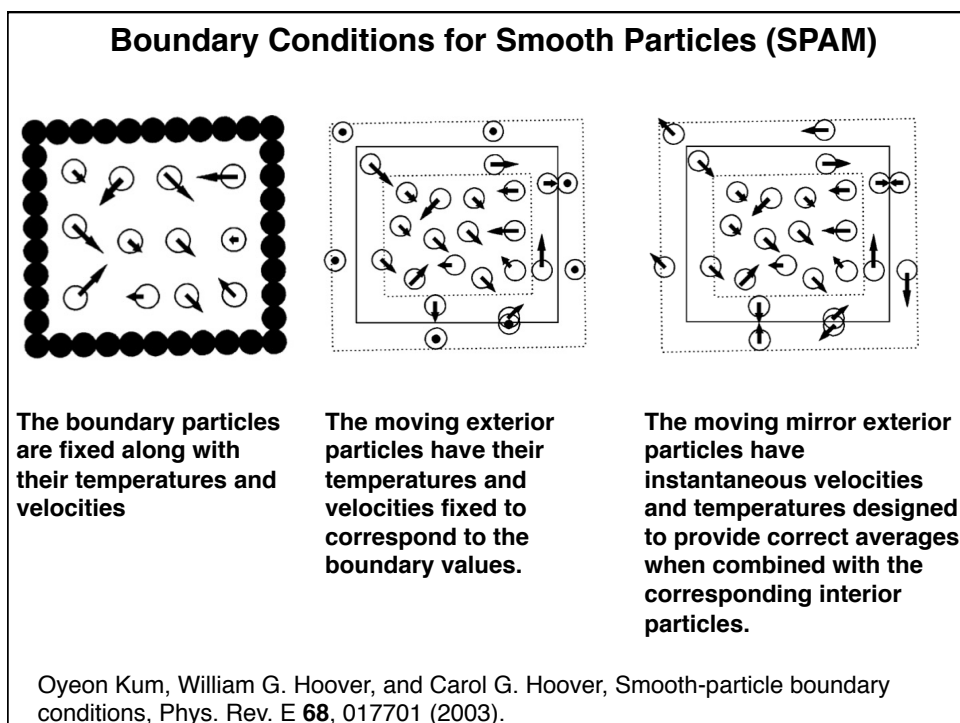
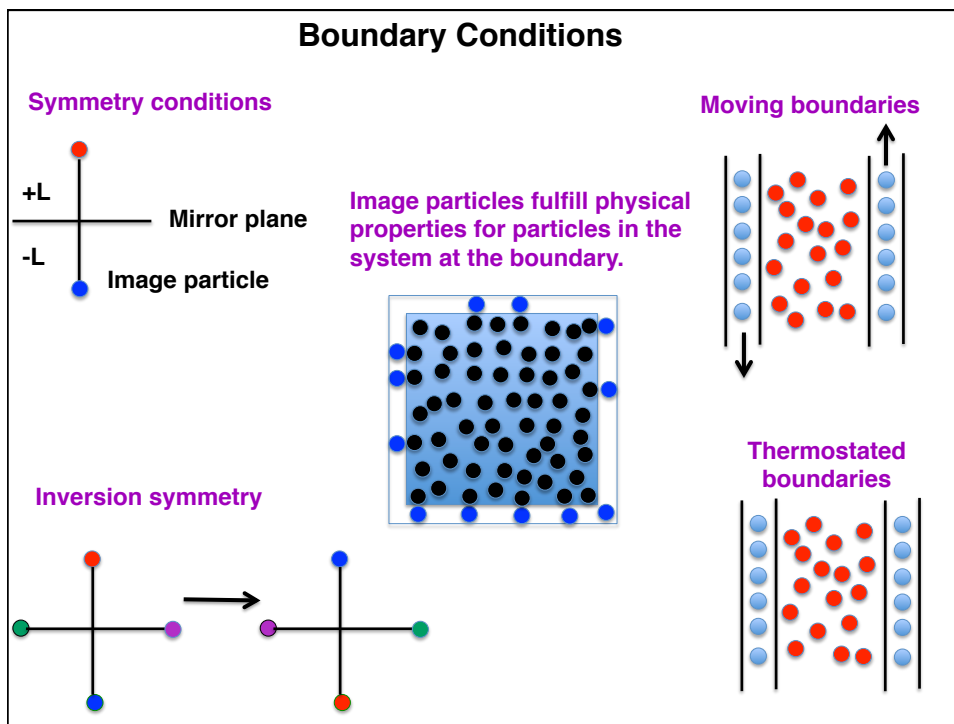
$$\delta_- = x_j - x_{j+1}$$

$$\delta_+ = x_j$$

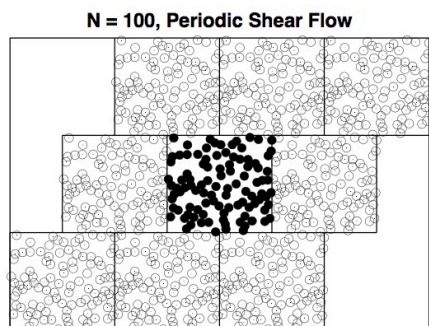
Right boundary



Apply the boundary conditions to δ !

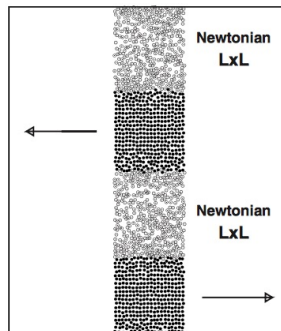


More Complex Boundary Conditions – Shear Flow



Eight moving particle cell images with the motion in the central cell being driven by the periodic image cells. The fixed speed of the moving images is $\pm L\dot{\epsilon}$. (Developed simultaneously by Lees-Edwards and Ashurst)

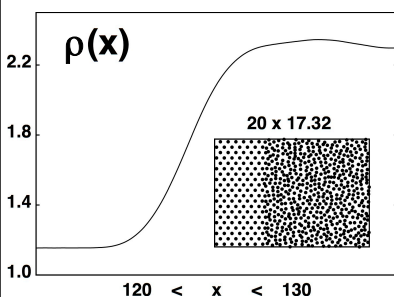
Boundary-Driven Shear Flows



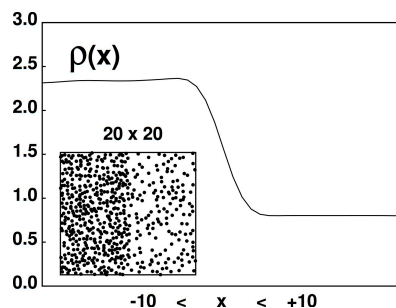
Four chambers : The moving chambers are thermostatted at a temperature T and lattice sites move at a speed $\pm L\dot{\epsilon}$ with particles tethered to their lattice sites with a quartic potential in their displacement.

William G. Hoover, Carol G. Hoover and Janka Petavic, Simulation of two- and three dimensional dense-fluid flows via nonequilibrium molecular dynamics: Comparison of time-and-space-averaged stresses from homogeneous Doll's and Slod shear algorithms with those from boundary driven shear, Phys. Rev. E, **78**, 046701 (2008).

Particle Injection and Removal at a Boundary



Shock-wave Compression
Cold fluid in a triangular lattice entering from the right experiences a 2-fold shockwave compression. Particles are removed from the right.



Joule-Thompson Expansion
Particles are input on the left in columns of an unstable square lattice. A repulsive **quartic plug potential** enforces the density gradient. Particles are removed on the right.

William G. Hoover, Carol G. Hoover, and Karl P. Travis, Phys. Rev. Lett. **112**, 144504 (2014).

Calculate Normal Modes and Frequencies
5-Particle Rigid Boundaries and 6-particle Periodic Boundaries

Hooke's Law

$$F_x = \kappa \delta \rightarrow \ddot{x}_j = x_{j+1} - 2x_j + x_{j-1} ; m, \kappa = 1 .$$

Dispersion relation for the modes

Solutions of the form $X(x, t) = e^{i(\omega t - kx)}$

$$\omega_n^2 = 2 - 2 \cos k_n d = 4 \sin^2(k_n d / 2)$$

Periodic Boundaries – 6 particles

$$\omega_n^2 = (1, 3, 4, 3, 1, 0) ; k_n = n(2\pi/6), n = 1, \dots, 6 .$$

$$\tau_n = (2\pi, 2\pi/\sqrt{3}, 2\pi/2, 2\pi/\sqrt{3}, 2\pi)$$

Rigid Boundaries – 5 particles

$$\omega_n^2 = (2 - \sqrt{3}, 1, 2, 3, 2 + \sqrt{3}) ; k_n = n(2\pi/12), n = 1, \dots, 5 .$$

$$\tau_n = \left\{ 2\pi/(2 - \sqrt{3})^{1/2}, 2\pi, 2\pi/\sqrt{2}, 2\pi/\sqrt{3}, 2\pi/(2 + \sqrt{3})^{1/2} \right\}$$

One-Dimensional Chain Displacements and Forces in Matrix Form

6 particle chain with periodic boundary conditions

$$\begin{pmatrix} -2 & 1 & 0 & 0 & 0 & 1 \\ 1 & -2 & 1 & 0 & 0 & 0 \\ 0 & 1 & -2 & 1 & 0 & 0 \\ 0 & 0 & 1 & -2 & 1 & 0 \\ 0 & 0 & 0 & 1 & -2 & 1 \\ 1 & 0 & 0 & 0 & 1 & -2 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \end{pmatrix} = \begin{pmatrix} F_1 \\ F_2 \\ F_3 \\ F_4 \\ F_5 \\ F_6 \end{pmatrix}$$

$F_1 = -2q_1 + q_6 + q_2$
 $F_2 = -2q_2 + q_1 + q_3$
 $F_3 = -2q_3 + q_2 + q_4$
 $F_4 = -2q_4 + q_3 + q_5$
 $F_5 = -2q_5 + q_4 + q_6$
 $F_6 = -2q_6 + q_5 + q_1$

5 particle chain with fixed boundary conditions

$$\begin{pmatrix} -2 & 1 & 0 & 0 & 0 \\ 1 & -2 & 1 & 0 & 0 \\ 0 & 1 & -2 & 1 & 0 \\ 0 & 0 & 1 & -2 & 1 \\ 0 & 0 & 0 & 1 & -2 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \end{pmatrix} = \begin{pmatrix} F_1 \\ F_2 \\ F_3 \\ F_4 \\ F_5 \end{pmatrix}$$

$F_1 = +x_2 - 2.0d00x_1$
 $F_2 = x_3 + x_1 - 2.0d00x_2$
 $F_3 = x_4 + x_2 - 2.0d00x_3$
 $F_4 = x_5 + x_3 - 2.0d00x_4$
 $F_5 = +x_4 - 2.0d00x_5$

6 Particle Periodic Chain Normal Mode Displacements

		Particle Displacements					
Mode #	k	1	2	3	4	5	6
1	$1\pi/3$	$+1/2$	$-1/2$	-1	$-1/2$	$+1/2$	$+1$
2	$2\pi/3$	$-1/2$	$-1/2$	$+1$	$-1/2$	$-1/2$	$+1$
3	$3\pi/3$	-1	$+1$	-1	$+1$	-1	$+1$
4	$4\pi/3$	$-1/2$	$-1/2$	$+1$	$-1/2$	$-1/2$	$+1$
5	$5\pi/3$	$+1/2$	$-1/2$	-1	$-1/2$	$+1/2$	$+1$
6	$6\pi/3$	$+1$	$+1$	$+1$	$+1$	$+1$	$+1$

Normal mode periods : $\tau_n = (2\pi, 2\pi/\sqrt{3}, 2\pi/2, 2\pi/\sqrt{3}, 2\pi)$

Calculated values for dt = 0.0001 and 63000 cycles

$$\tau_n = (6.2832, 3.6276, 3.1416, 3.6276, 6.2832)$$

5 Particle Chain with fixed boundaries Normal Mode Displacements

Mode #	k	λ
1	$1(2\pi/12)$	12
2	$2(2\pi/12)$	6
3	$3(2\pi/12)$	4
4	$4(2\pi/12)$	3
5	$5(2\pi/12)$	5/12

Normal Mode Periods (12.138, 6.2832, 4.442, 3.6276, 3.2524)

$$\tau_n = \left\{ 2\pi/(2 - \sqrt{3})^{1/2}, 2\pi, 2\pi/\sqrt{2}, 2\pi/\sqrt{3}, 2\pi/((2 + \sqrt{3})^{1/2}) \right\}$$

Calculated values for dt = 0.0001 and 63000 cycles

$$\tau_n = (12.139, 6.283, 4.45, 3.6276, 3.26)$$

Time Reversibility

Reversibility : Are the equations the same for $t' = -t$?

Reversibility is a movie played backwards with the same equations.

Microscopic equations are reversible ; Numerical results are not!

Round off error and Lyapunov instability ;
The cumulative growth of single-time step errors .

Time reversible Levesque-Verlet Algorithm is a bit reversible numerical algorithm .

$$\underline{x_+ - 2x_0 + x_-} = \{dt^2 F_0 / m\}_{\text{Integer}}$$

Reversible

Use integer coordinates with 15 digit precision in standard Fortran :

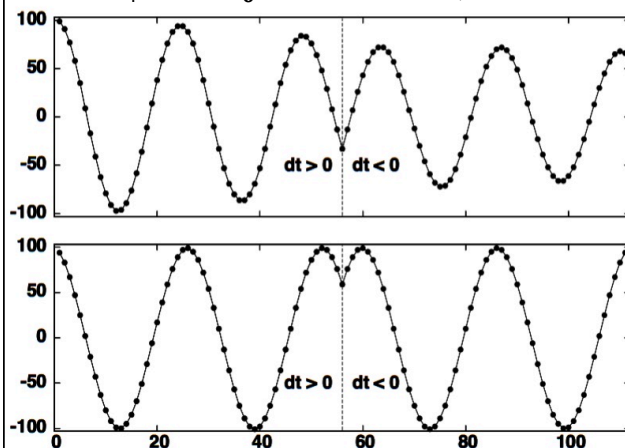
```
integer*16 ix
```

Integer = digits in pi → print *,integer

```
ix = x*(10**15)
```

Levesque-Verlet Bit Reversible Algorithm for the Oscillator

$$ix_+ = 2ix_0 + ix_- + dt^2 F; F = -x$$



56 steps Forward
56 steps Reversed
dt = 0.25

$$iforce = integer(dt^2 F)$$

$$ix_+ = 2ix_0 + ix_- + iforce$$

Outline for the next Lecture

1. **Integration Methods and Accuracy**
 - Accuracy checks with the harmonic oscillator or a benchmark problems
 - Symplectic Integrators for Hamiltonian Systems
 - Runge-Kutta Integrators for NonHamiltonian Systems
2. **Cell Model evaluation of integration techniques**
3. **Predictor-Corrector Methods**
 - Milne method
 - Gear predictor-Corrector
4. **Stiff Differential Equations :**
 - The Nosé Oscillator
 - Adaptive Integration
5. **The pendulum**
 - Regular and Chaotic Orbits