Syllabus:

PH442: Theory and Simulation of Nanostructures 3 0 0 6

Interatomic Potentials: Potential energy Surface, pair potential approximation; advantages and limitations, Phenomenological potentials; Buckingham, Morse, Lennard-Jones and Berker, Pseudo potentials, Many-Body potentials.

Molecular Dynamics(MD): Models for MD calculations; initial value, Isothermal equilibrium, boundaries, Nano-design and Nano-construction, solution of the equation of motion; Verlet, Gear-Predictor, and other methods, Efficient Force Field Computation; Forcederivation, List method, Cell algorithm, Scalable parallel procedure.

Characterization: Thermal stability, Material properties, wear at the Nanometer level, Mean Values and correlation functions.

Nano-Engineering: Functional Nanostructures, Nano-Machines, Nano-clusters; influence of initial conditions, temperature, crystalline structure, etc. Simulated Nano-structure transformations.

Text Books:

1. Nano-Engineering in Science and Technology, M. Reith.
2. Computer Simulation of Liquids, M. P. Allen and D. J. Tildesley.
3. Understanding Molecular Simulation, D. Frenkel and B. Smith. 4. Molecular Dynamics Simulation, J. M. Haile.

Molecular Dynamics

Preliminaries

A Brief History of MD

✓1957, 59 **Alder-Wainwright,** introduction of basic MD

- Of hard sphere particles.

✓1964 **Rahman**, study of liquid Ar (NVE-MD)

- First quantitative study reported.

✓1980, 81 **Andersen, Parrinello-Rahman**

- Constant Pressure (NPT) MD.

✓1984, 86 **Nose, Hoover**

- Constant Temperature (NVT) MD.

✓1985 **Car-Parrinello**, *ab initio* MD

- Based on Density Functional Theory (1960s)
  - **Hohenbrg-Sham**
  - **Kohn-Sham**

A movie

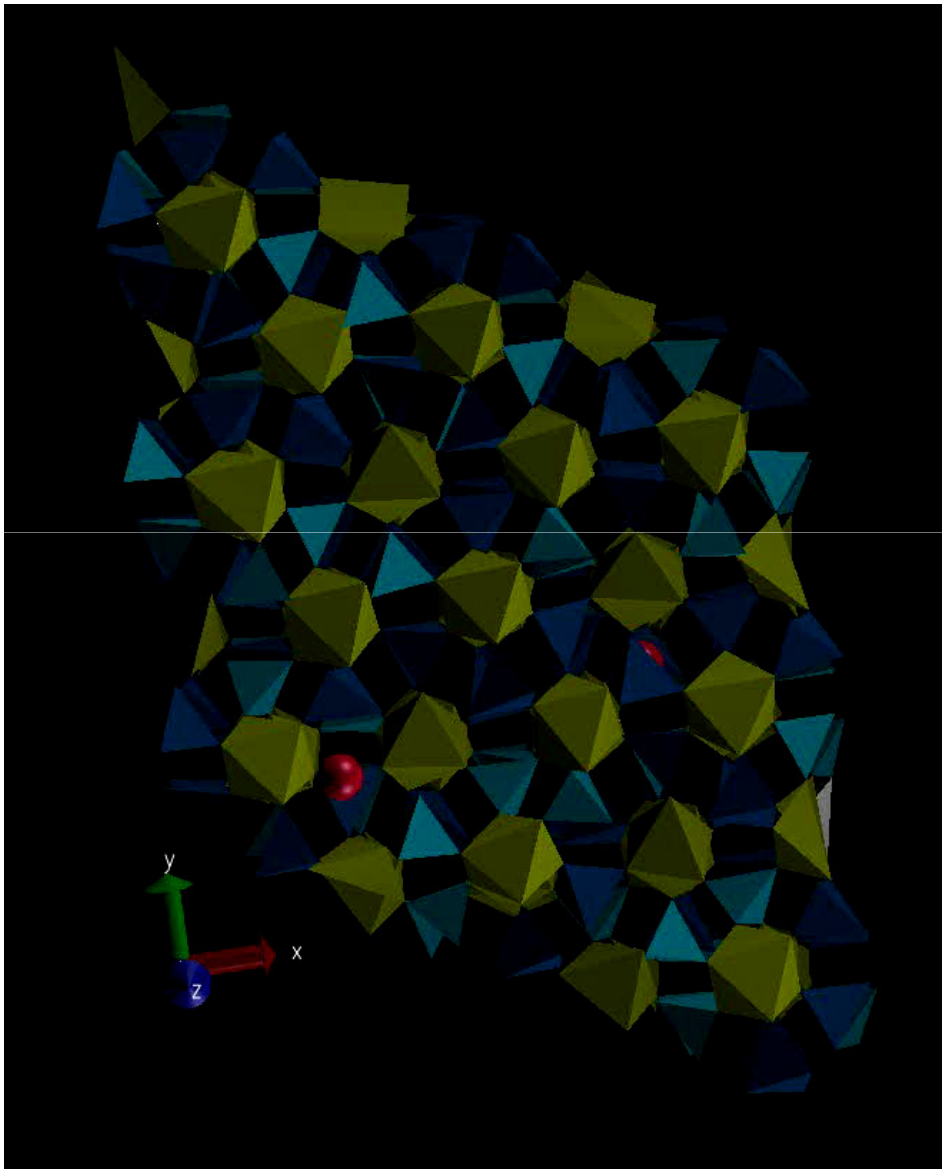
System:

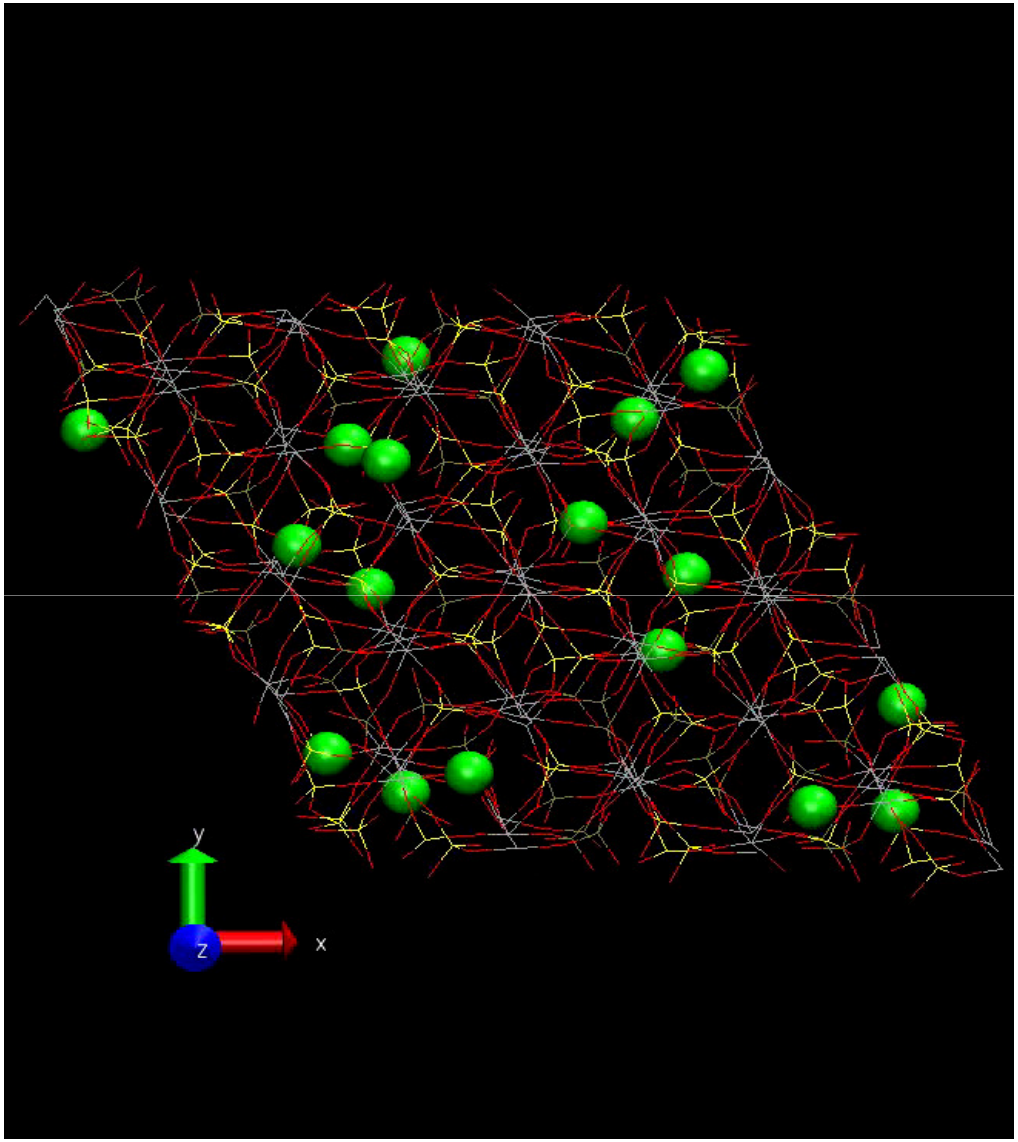
$Na_3Zr_2Si_2PO_{12}$

Na-SuperIonic Conductor

Na+ ions diffuse in the $[Zr_2Si_2PO_{12}]^{3-}$ matrix conducting electricity.

-A promising material for better batteries!




y
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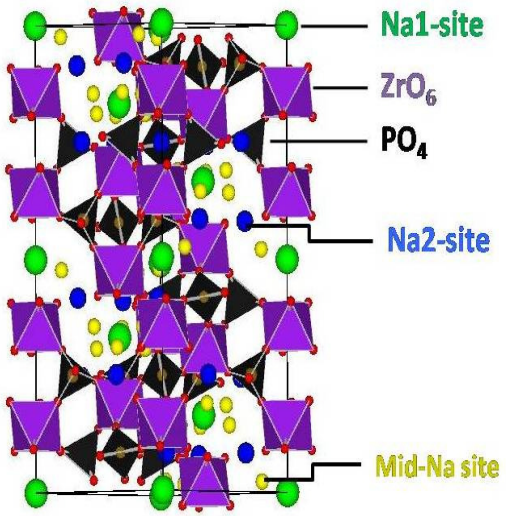
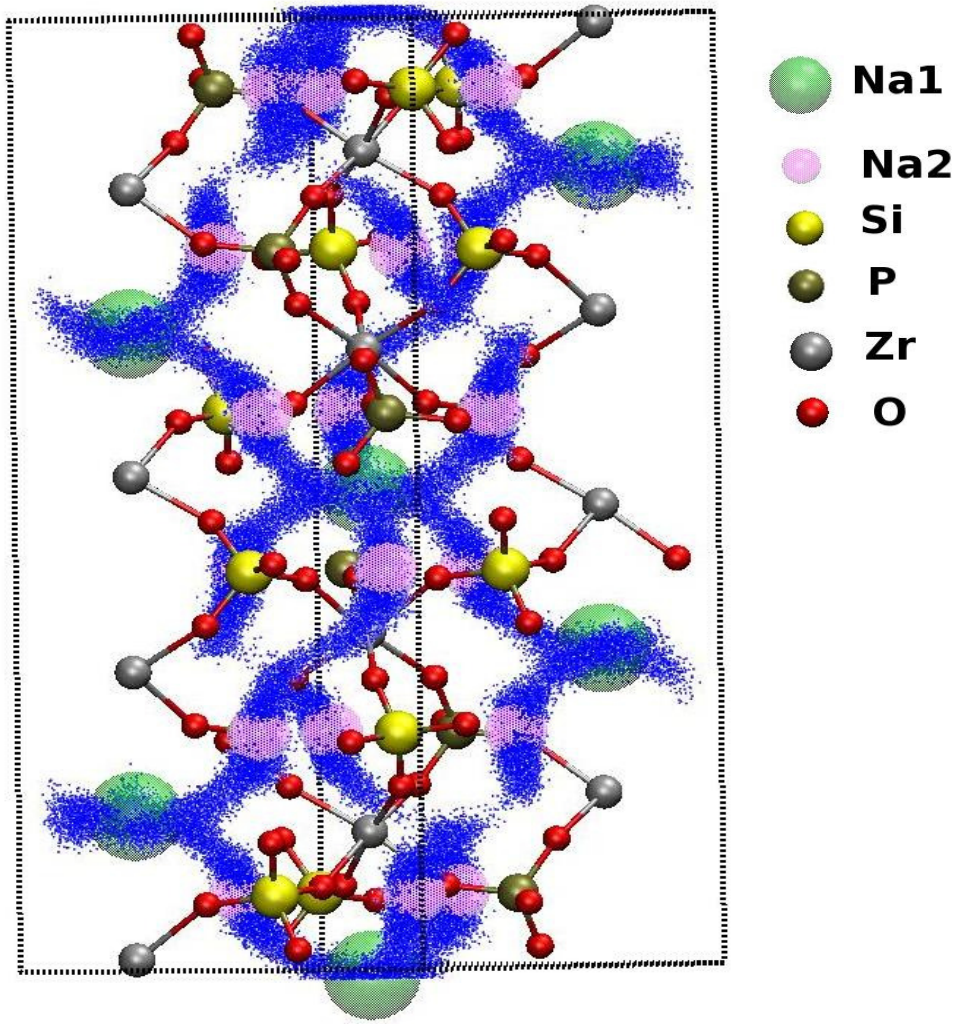
Ion Channel's In NASICON's

$Na_3Zr_2Si_2PO_{12}$





Supriya Roy and PKP to be published.

Ion Channel Recognized

System:

$Na_3Zr_2Si_2PO_{12}$

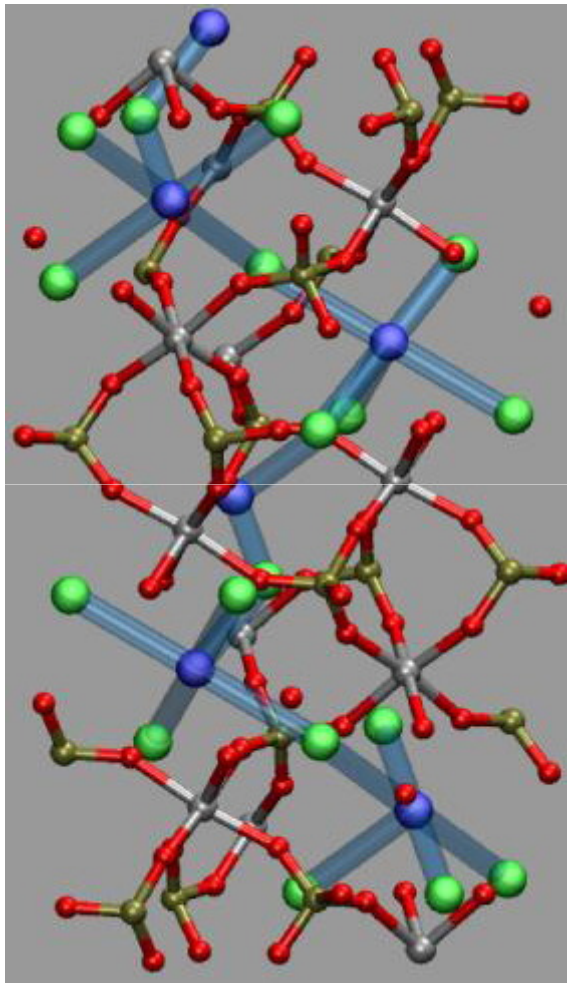
Na-SuperIonic Conductor

Na+ ions diffuse in the

$[Zr_2Si_2PO_{12}]^{3-}$ matrix

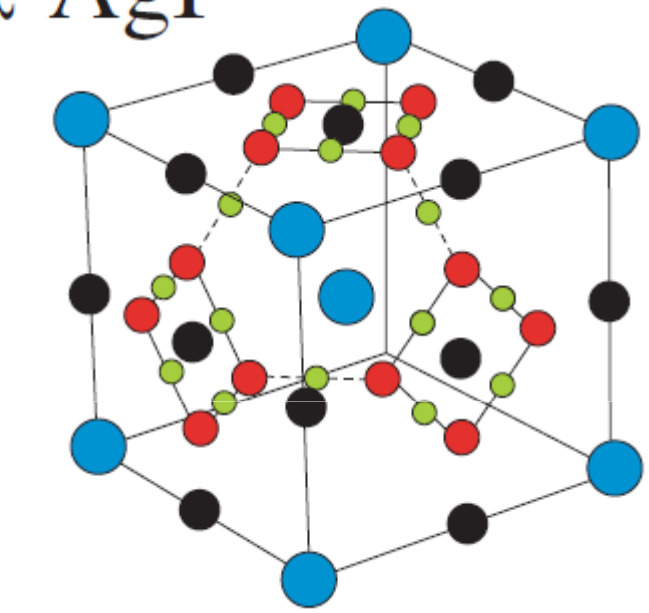
conducting electricity.

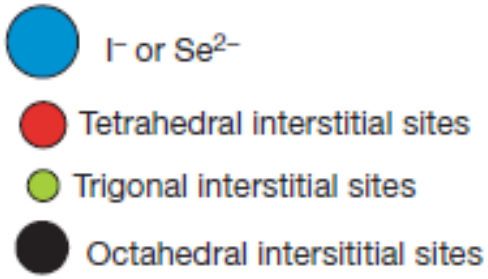
-A promising material for better batteries!

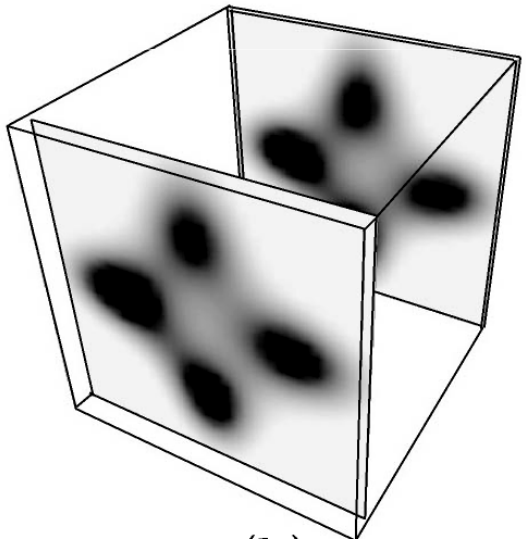


…Structural Properties: Site Occupancies

α-AgI $T > 420$ K

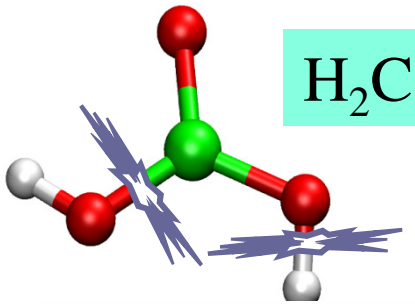




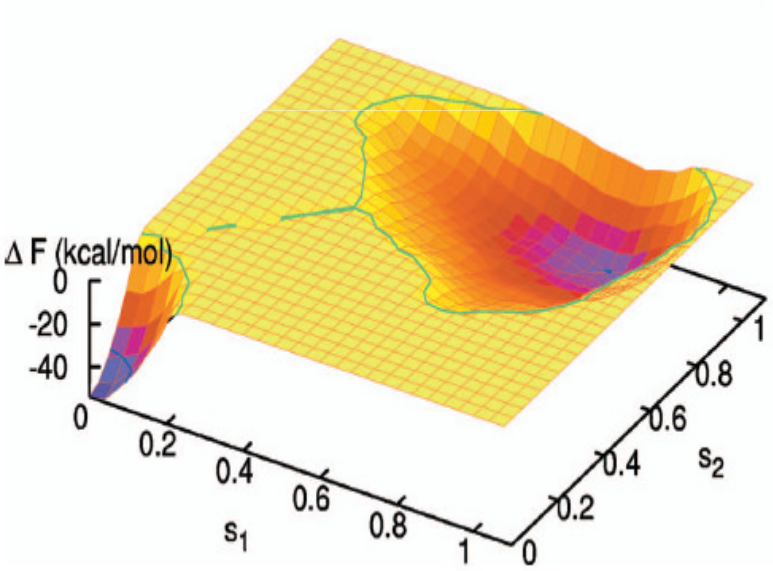


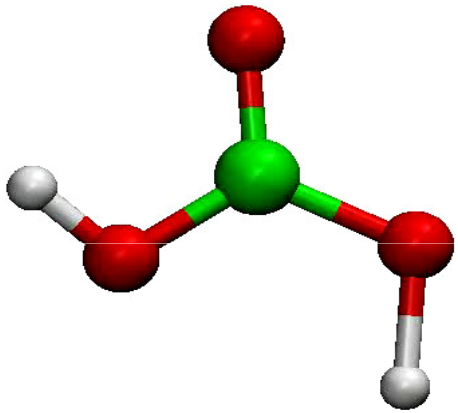
PRL **97, 166401 (2006)**

Advanced Simulation Techniques: Simulating Chemical Reaction Dissociation of H_2CO_3 in gas-phase



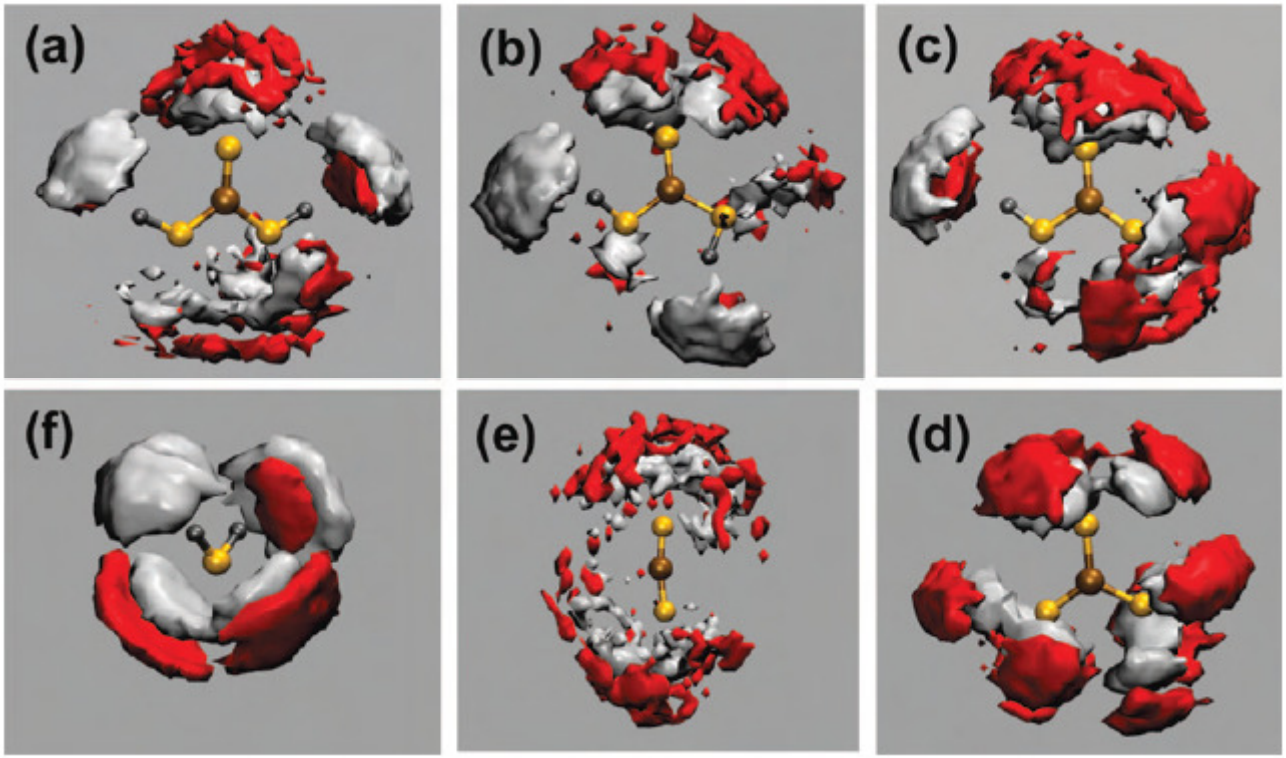
$$H_2CO_3 = H_2O + CO_2$$





P. Padma Kumar,[a] Andrey G. Kalinichev, and R. James Kirkpatrick
THE JOURNAL OF CHEMICAL PHYSICS 126, 204315 (2007)

Advanced Simulation Techniques: Understanding local structure and reactivity; Carbonates in Solution

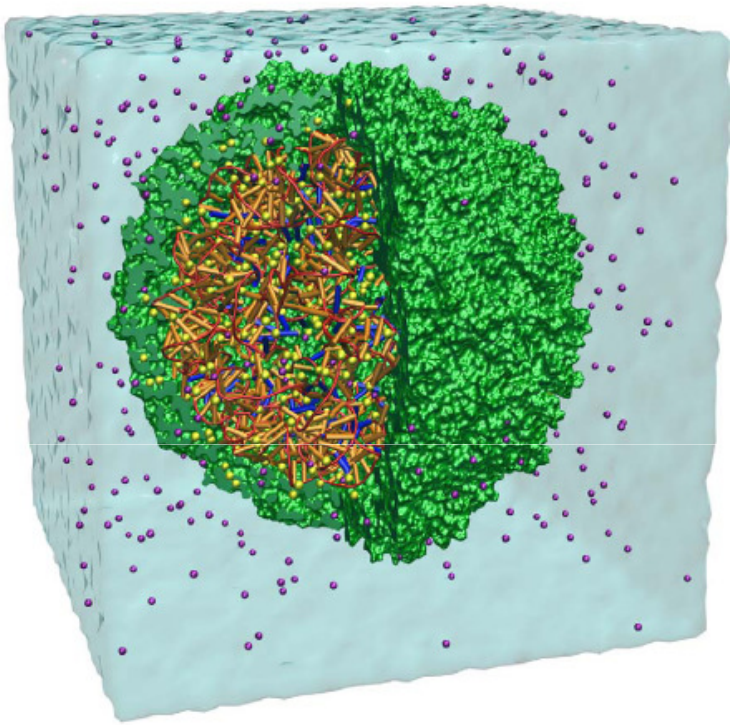


P. Padma Kumar,*,† Andrey G. Kalinichev,*,‡ and R. James Kirkpatrick§

J. Phys. Chem. B **2009**, *113*, 794–802

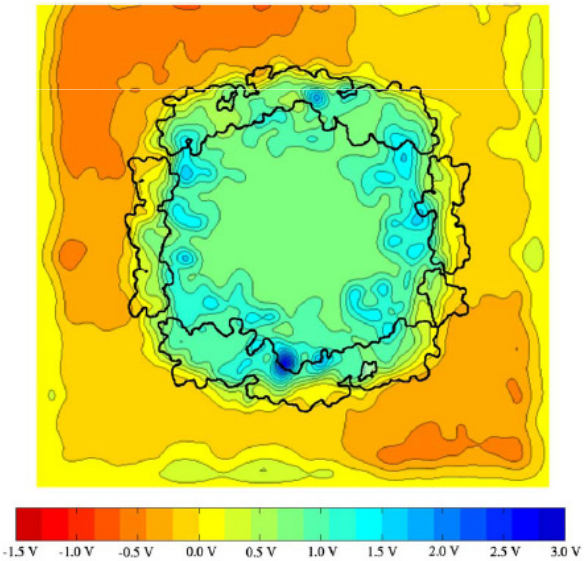
Simulation of Life!!

Satellite tobacco mosaic virus



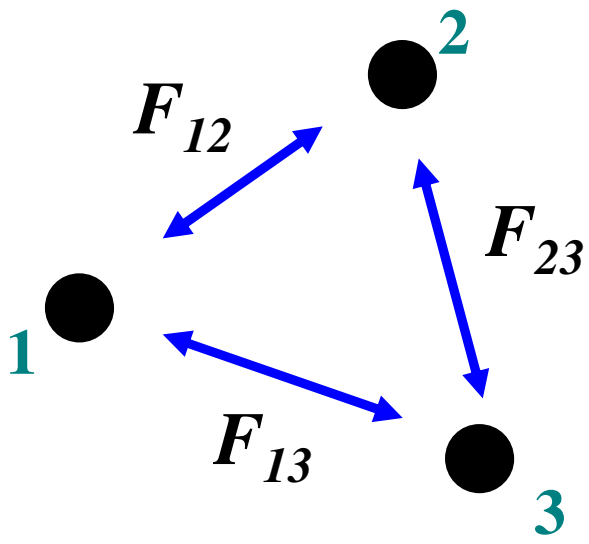
Peter L. Freddolino,[1,2,5] Anton S. Arkhipov,[2,3,5]
Steven B. Larson,[4] Alexander McPherson,[4]
and Klaus Schulten[1,2,3,*]

Structure 14, 437–449, March 2006



Charge distribution around the virus

Molecular Dynamics –The Basic Idea



$$F_i = \sum_{j \neq i} F_{ij}$$

$$F_1 = F_{12} + F_{13}$$

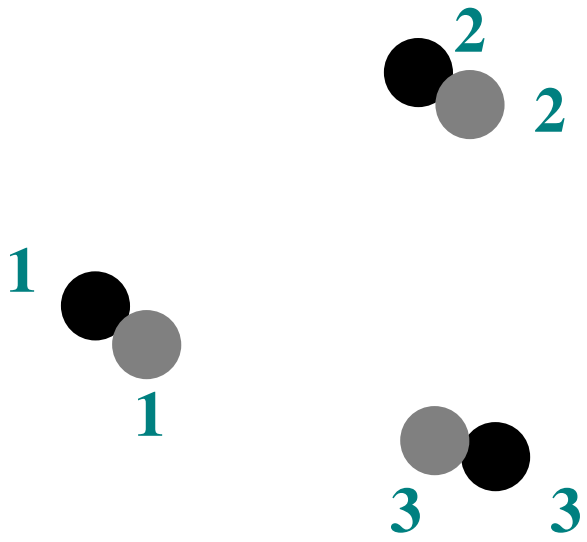
$$F_2 = F_{21} + F_{23}$$

$$F_3 = F_{31} + F_{32}$$

$$F_{ij} = -\nabla U_{ij}$$

Newton's IInd Law: $a_i = F_i / m_i$

Progress in time…



$$r(t) \longrightarrow r(t+\Delta t)$$

$$x(t) \rightarrow x(t+\Delta t)$$

$$y(t) \rightarrow y(t+\Delta t)$$

$$z(t) \rightarrow z(t+\Delta t)$$

Δt ~ 1-5 fs (10^{-15}sec)

Advance positions & velocities of each atom:

Taylor Expansion:

$$v(t+\Delta t) = v(t) + \Delta t \frac{f(t)}{m}$$

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2$$

too crude to use it as such!!

A good Integrator

Verlet Scheme:

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 + \frac{\Delta t^3}{3!}\dddot{r} + \mathcal{O}(\Delta t^4)$$

Newton's equations are time reversible,

$$r(t-\Delta t) = r(t) - v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 - \frac{\Delta t^3}{3!}\dddot{r} + \mathcal{O}(\Delta t^4)$$

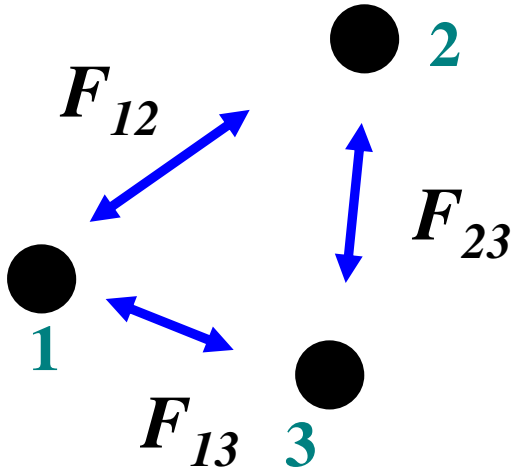
Summing the two equations,

$$\boxed{r(t+\Delta t) \approx 2r(t) - r(t-\Delta t) + \frac{f(t)}{m}\Delta t^2}$$

Now we have advanced our atoms to time $t+\Delta t$! !

Velocity of the atoms: $v(t) = \dfrac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t}$

…Atoms move forward in time!

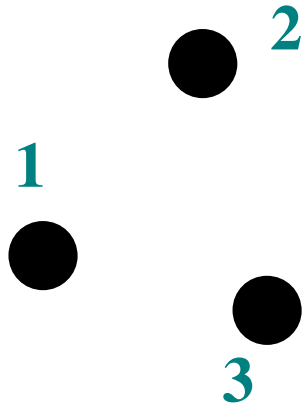


t+Δt

2nd MD Step

1. Calculate $f(t+\Delta t)$
2. Update $v(t+2\Delta t)$
3. Update $r(t+2\Delta t)$

Δt ~ 1-5 fs (10^{-15}sec)



t+2Δt

3rd MD Step

Continue this procedure for several lakhs of Steps.
Or as much as you can afford!

The main O/P of MD is the trajectory.

The missing ingredient… *Forces?*

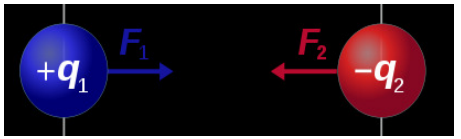
Force is the gradient of potential: $f_x(r) = -\frac{\partial u(r)}{\partial x}$

Gravitational Potential: $U = \frac{-Gm_1m_2}{r}$

too weak, Neglect it!!

The predominant inter-atomic forces are Coulombic in *origin!*

$$U = \frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{r}$$



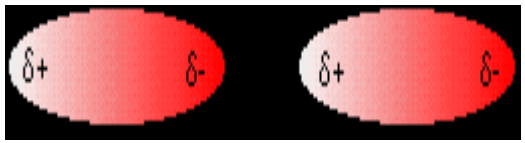
However, this pure monopole interaction need not be present**!**

Interatomic forces for simple systems

(non-bonded interactions)

1. Lennard-Jones Potential:

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



Instantaneous dipoles

Gives an accurate description of ***inert gases***
(Ar, Xe, Kr etc.)

2. Born-Mayer (Tosi-Fumi) Potential:

$$\mathcal{U}(r_{ij}) = \frac{q_i\, q_j}{r_{ij}} + A_{ij}\, exp(-r_{ij}/\rho_{ij}) - \frac{C_{ij}}{r_{ij}^6}$$

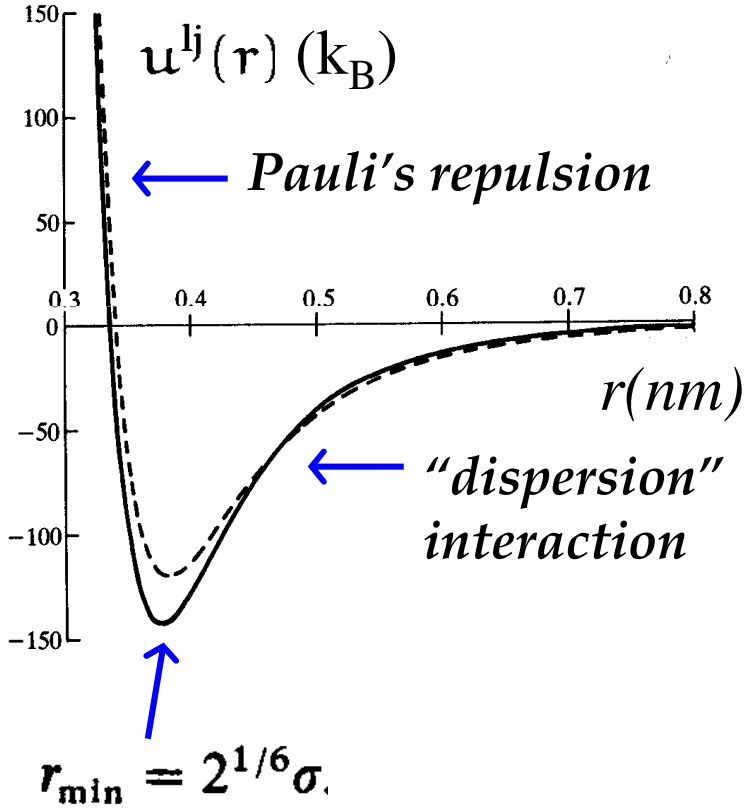
Faithful in describing ***pure*** ionic solids
(NaCl, KCl, NaBr etc.)

The Lennard-Jones Potential

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

for Ar : $\epsilon/k_B = 119.8\ \text{K}, \sigma = 3.405\ \text{Å}$

Should be known *apriori*.



$$F_{ij} = -\nabla U_{ij}$$

$$F_{ij}^{x} = -\frac{\partial U}{\partial x_i} = -\frac{\partial U}{\partial r_i}\frac{\partial r}{\partial x_i}$$

$$F_{ij}^{x} = 4\varepsilon\left(\frac{12\sigma^{12}}{r^{14}} - \frac{6\sigma^{6}}{r^{8}}\right)(x_i - x_j)$$

Length and Times of MD simulation

Typical experiment sample (**bulk**) contains **~ 10^{23}** atoms!

Typical MD simulations (on a single CPU)

a) Can include 1000 – 10,000 atoms (~20-40 Å in size)!

b) run length ~ 1 –10 *ns* (10^{-9} seconds)!

Consequence of system size:

Larger fraction of atoms are on the surface, $\frac{Ns}{N} = \frac{4\pi r^2 dr\ \rho\ /\ m}{\frac{4}{3}\pi r^3 \rho\ /\ m} = 3\frac{dr}{r}$

$$\frac{Ns}{N}(Expt.) \sim 3\frac{(3\text{A})}{10^8\,\text{A}} \sim 10^{-7}$$

Bulk system

$$\frac{Ns}{N}(MD) \sim 3\frac{(3\text{A})}{20\text{A}} \sim 0.45$$

Nano-cluster

Surface atoms have different environment than bulk atoms!

The Simulation Cell

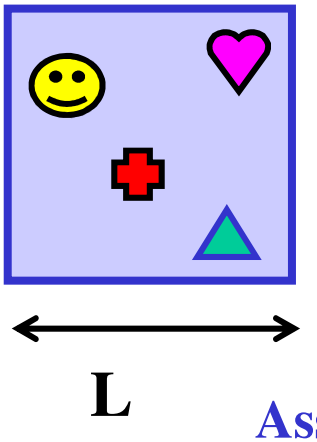
For Bulk systems!

Insert the atoms in a perfectly **porous** box – simulation super-cell.

If crystal structure/unit cell parameters are **unknown** (eg., liquids)

The length of the box is determined as, $\mathbf{L^3 = M/D_{exp} = N*m/D_{exp}}$

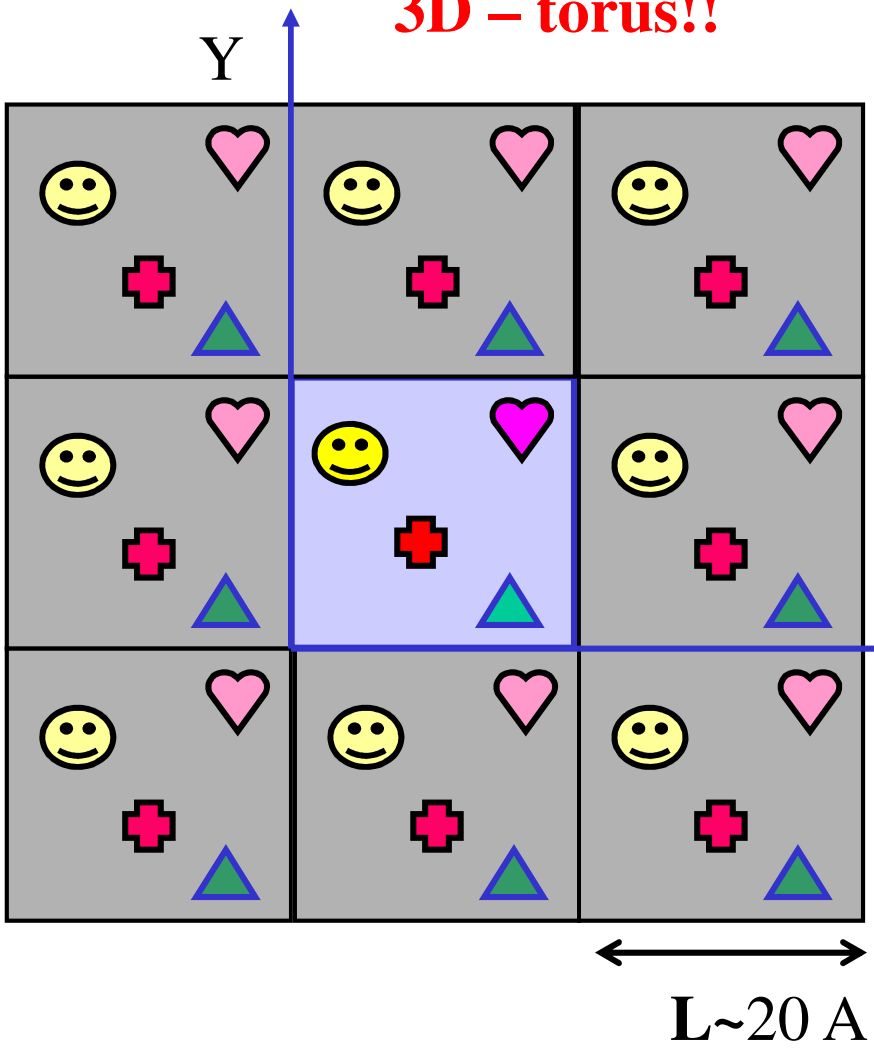
$\mathbf{D_{exp}}$ = Expt. density; **m** = At. mass; **N**= No. of atoms;



Assign positions and velocities(=0) for each atom.

Periodic Boundary Condition For Bulk systems!

3D – torus!!



~~Construct~~ Periodic Images:

In 3-D the simulation ***simulation-super-cell*** is surrounded by 26 **image cells!**

Image coordinates:

$$x' = x + \mathbf{n}_1 L$$

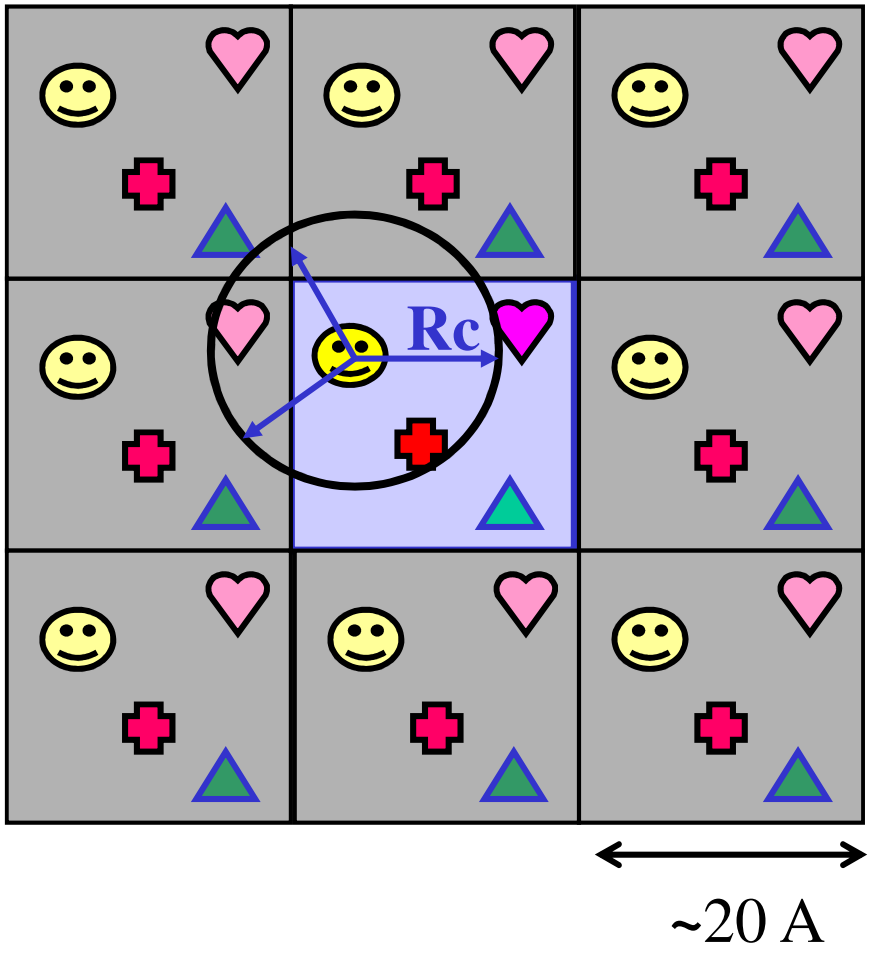
$$y' = y + \mathbf{n}_2 L$$

$$z' = z + \mathbf{n}_3 L$$

$$\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3 \in \mathbf{-1,0,1,}$$

Now, there are no surface atoms!

Minimum Image Convention



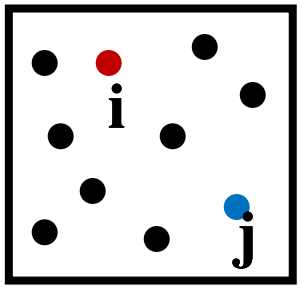
Interactions between atoms separated by a chosen cut-off distance (**Rc**) or larger (ie, $r_{ij} > Rc$) are neglected.

Rc is chosen such that **U(Rc)** ~ 0

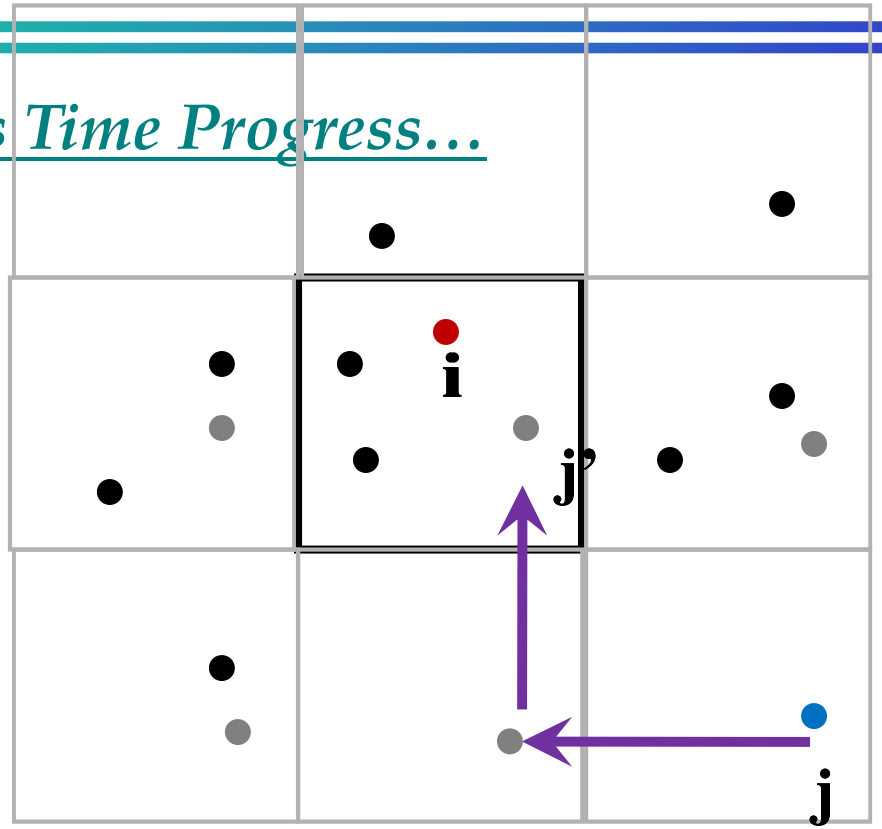
A large enough system (ie, bigger ***sim.-cell***) is chosen such that **Rc ≤ L/2.**

Thus particle **i** interact either with particle **j** or one of its images, **but not both**!

As Time Progress…



t = 0



t = 10 pico-sec

L

Force between **i** & **j** : $F_{ij}^{x} = 4\varepsilon(\frac{12\sigma^{12}}{r_{ij}^{14}} - \frac{6\sigma^{6}}{r_{ij}^{8}})(x_i - x_j)$

How to find the distance to the image of j that is nearest to i ?

The three lines of code…

Define,

dx = x(j) – x(i)

dy = y(j) – y(i)

dz = z(j) – z(i)

dx = dx – L***ANINT**(dx/L)

dy = dy – L***ANINT**(dy/L)

dz = dz – L***ANINT**(dz/L)

FORTRAN 77/90/95

ANINT(3.49) = 3

ANINT(1.51) = 2

ANINT(-3.51) = -4

ANINT(-11.39) = -11.0

$$F_{ij}^{x} = 4\varepsilon\left(\frac{12\sigma^{12}}{r_{ij}^{14}} - \frac{6\sigma^{6}}{r_{ij}^{8}}\right)(x_i - x_j)$$

rij_2 = (dx**2 + dy**2 + dz**2)

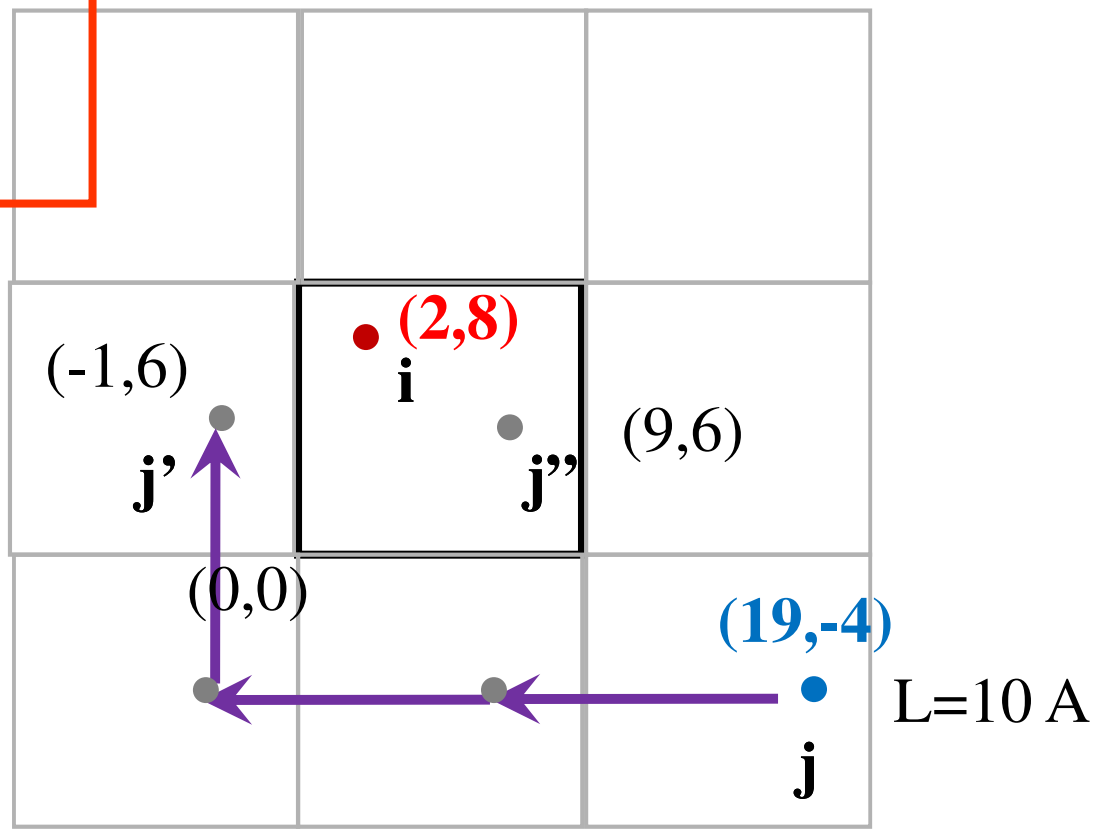
rij_8 = rij_2**4

rij_14 = rij_2**7

...demonstration

$$dx = dx - L*AINT(dx/L)$$
$$dy = dy - L*AINT(dy/L)$$

$$x' = x + \mathbf{n}_1 L$$
$$y' = y + \mathbf{n}_2 L$$



xi-xj=(2-19)-10*ANINT{(2-19)/10}= -17 - (-10*2)=3

yi-yj=(8+4)-10*ANINT{12/10}= 12 - (10*1)=2

The structure of a simple MD code

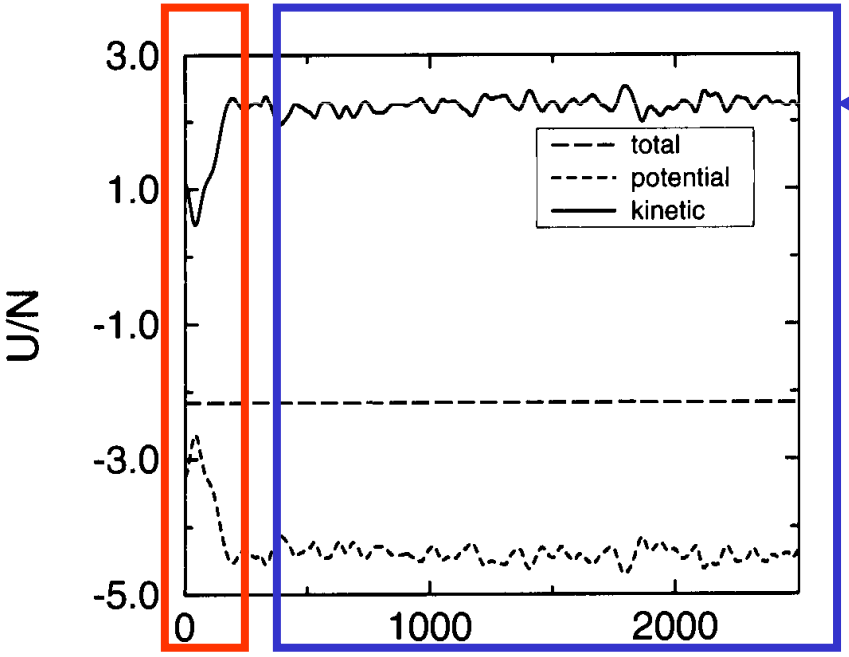
```
program md                          simple MD program

call init                          initialization
t=0
do while (t.lt.tmax)               MD loop
   call force(f,en)                determine the forces
   call integrate(f,en)            integrate equations of motion
   t=t+delt
   call sample                     sample averages
enddo
stop
end
```

Remarks on Statistical Ensemble

There is no energy coming in Or going out of our system of atoms: **micro-canonical (NVE)** ensemble.

Thus the **total energy (E)** and total linear momentum of the system should be conserved – through out our simulation!



$$K = \frac{1}{2}\sum_{i=1}^{N} m_i v_i^2$$ **(fluctuates)**

$$E = K + U$$ ***remain const.***

$$U = \frac{1}{2}\sum_{i=1}^{N} U_i$$ **(fluctuates)**

Transient phase **Equilibrated state**

Remarks on Energy

- Energy conservation,

$$\frac{\Delta E}{E} / ps \sim 10^{-6} / ps$$

-good check on your code!

-time integrator!

-on time step (Δt) used!

- Start from the expt. crystal structure if available.

- Else? Start from good guess! (like, in bio-systems, polymers, liquids)

  - And, perform an **energy minimization**!

    (Routines available in standard packages.

    Or, do an MD with constant velocity scaling.)

  - **Reaching a well equilibrated structure (from a random structure) can be very very costly!**

- Fluctuation of U(t) about a mean helps to identify equilibrated system.

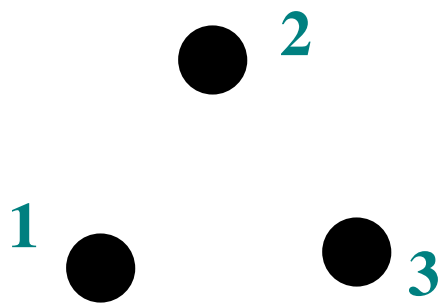
Calculating Temperature

Equipartition theorem: $\frac{3}{2}NkT(t) = \frac{1}{2}\sum_{i}^{N} m_i v_i^2$

Instantaneous temperature: $T(t) = \frac{1}{3Nk}\sum_{i}^{N} m_i v_i^2$

Average temperature : $< T >= \frac{1}{M}\sum_{m=1}^{M} T\,(t_m)$

M – no. of MD steps performed



Even if we start with $v_i = 0$, the system picks up non-zero v (hence **some T**) as time progress!

This **some T(!)** need not be what we want!

So how do we control T?

Controlling the Temperature ?

Velocity rescaling:

Actual temp. at some instant. $$T = \frac{1}{3Nk}\sum_{i}^{N} m_i v_i^2$$

If T is out side the fluctuation window around T_r: $$T_r - \Delta T < T > T_r + \Delta T$$

Then **scale** all velocities: $$v_r = \left(\frac{T_r}{T}\right)^{\frac{1}{2}} v$$

This instantly bring the $T = T_r$!

However to sustain the temp. around Tr we will need to do this procedure several times at intervals.

This phase of the simulation is should not be used for averaging!

Calculating thermodynamic quantities

Average Energy, $$< U >= \frac{1}{M} \sum_{i=1}^{M} U_i$$

Average Pressure, $$\langle \mathcal{P} \rangle = \frac{N k_B T}{V} + \frac{1}{3V} \sum_{i=1}^{N} \left\langle \vec{r}_i \cdot \vec{f}_i \right\rangle$$

Heat Capacity, Cv: $$\frac{[\langle T^2 \rangle - \langle T \rangle^2]}{\langle T \rangle^2} = \frac{2}{3N} \left(1 - \frac{3k_B}{2C_v} \right)$$

Reduced Units

- Length (m) → Å
- Mass (kg) → *a m u*
- ~~Time (s)~~ Energy → eV
- Charge (C) → e^-
- Temperature (K) → K
- Mole (mol) → mol
- Luminous Intensity (candela)

Hand-On-Session: 1 (Today! 2-4 pm)

Name your codes as "loginid_xy.c".
Name the output files of the code as "loginid_xy.out".
Have your **name, rollno, date of the session, and title of the assignment** as the first four lines of your code.
You may bring with you programming books.

- **Assignment a)**

  Title: Generation of FCC lattice

  Make 4x4x4 unit cells of the FCC lattice of Argon. Unit cell parameters 5.26 A (angstrom).

- **Assignment b)**

  Title: Calculation of total potential energy

  Argon atoms interact through Lennard-Jones potential with epsilon = 119.8 kB (kB - Boltzmann constant). Convert epsilon to eV before using it in the code (electron Volts). sigma = 3.4 angstrom.

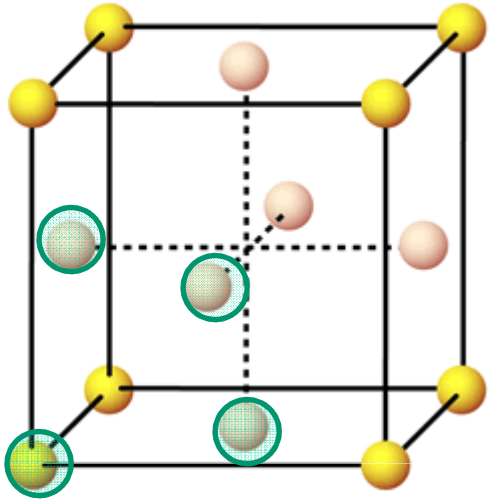
  Read the positions of the Ar atoms from the output of a) and calculate the total potential energy of the system (without any periodic boundary conditions or cut of distances imposed).

Lab session -I

!Generation of coordinates of FCC lattice (4x4x4 unit cells)

```
program fcc
implicit none
integer::i,j,k, n =4    !  No of unit cells
real::a=5.26
open(unit=1,file="fcc.dat")

do i =  0,  n - 1
do j =  0,  n - 1
do k = 0,  n - 1
        write(1,*) i*a + 0.0,   j*a + 0.0,   k*a + 0.0
        write(1,*) i*a + a/2,   j*a + a/2,   k*a + 0.0
        write(1,*) i*a + 0.0,   j*a + a/2,   k*a + a/2
        write(1,*) i*a + a/2,   j*a + 0.0,   k*a + a/2
end do
end do
end do
end program fcc
```



```
!Potential Energy of fcc lattice  (4x4x4 unit cells )
allocate(x(no_atom),y(no_atom),z(no_atom))
sigma6 = sigma**6;      sigma12 = sigma6**2;        eps4    = 4* eps;

pot_en =0.0
  do i=1,no_atom-1
     do j=i+1,no_atom
            dx = x(i) - x(j) ; dy = y(i) - y(j);  dz= z(i)-z(j);
             r2=dx**2+dy**2+dz**2
             r6= r2*r2*r2
            r12= r6 * r6
            fact= eps4*(sigma12/r12 - sigma6/r6)
            pot_en = pot_en + fact
       end do
     end do

print*,"potential energy=",pot_en
```

Integrating Equations of Motion

Verlet Scheme:

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 + \frac{\Delta t^3}{3!}\dddot{r} + \mathcal{O}(\Delta t^4)$$

Newton's equations are time reversible,

$$r(t-\Delta t) = r(t) - v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 - \frac{\Delta t^3}{3!}\dddot{r} + \mathcal{O}(\Delta t^4)$$

Summing the two equations,

$$\boxed{r(t+\Delta t) \approx 2r(t) - r(t-\Delta t) + \frac{f(t)}{m}\Delta t^2}$$

Now we have advanced our atoms to time $t+\Delta t$! !

Velocity of the atoms: $v(t) = \dfrac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t}$

Controlling the Temperature

Velocity scaling:

Actual temp. at some instant. $$T = \frac{1}{3Nk}\sum_{i}^{N} m_i v_i^2$$

If T is out side the fluctuation window around T_r: $$T_r - \Delta T < T > T_r + \Delta T$$

Then **scale** all velocities: $$v_r = \left(\frac{T_r}{T}\right)^{\frac{1}{2}} v$$

Though Good and simple algorithm,
Verlet Algorithm does not involve velocities explicitly!
- Not convenient in implementing velocity scaling!

30-1-12

"Velocity Verlet" Scheme

Calculate the positions at $t + \delta t$

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \delta t\,\mathbf{v}(t) + \tfrac{1}{2}\delta t^2\,\mathbf{a}(t)$$

Advance velocities by half-time step, $\frac{1}{2}\delta t$

$$\mathbf{v}(t+\tfrac{1}{2}\delta t) = \mathbf{v}(t) + \tfrac{1}{2}\delta t\,\mathbf{a}(t)$$

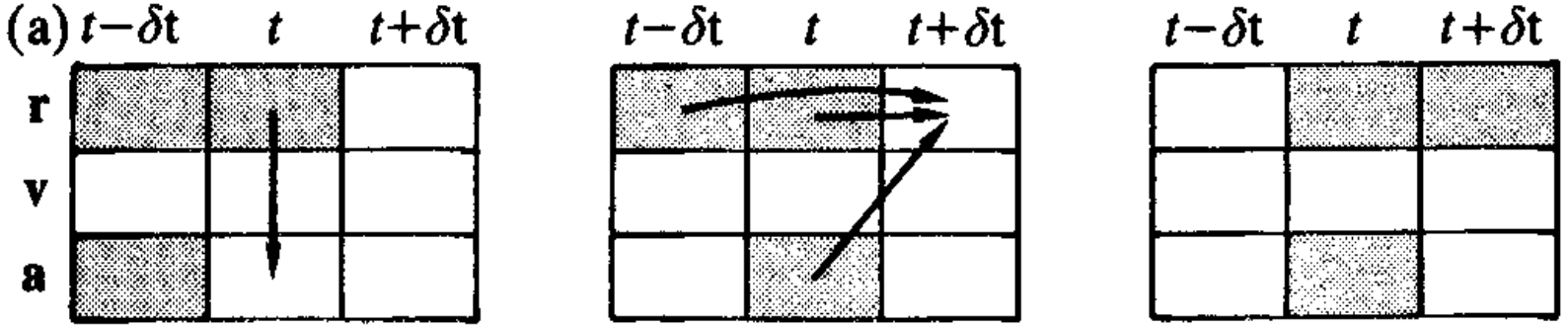
Calculate Forces

Complete the velocity-move,

$$\mathbf{v}(t+\delta t) = \mathbf{v}(t+\tfrac{1}{2}\delta t) + \tfrac{1}{2}\,\delta t\,\mathbf{a}(t+\delta t)$$

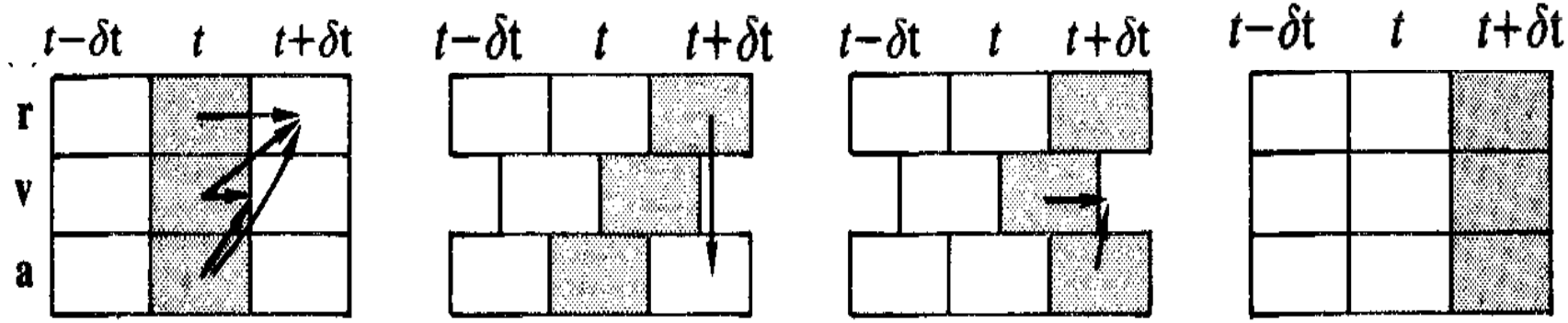
As good as the Verlet scheme in terms of numerical quality – energy conservation, storage (3N –words) etc., but has the advantage of having velocities explicitly in the equations.

Verlet scheme



$$r(t+\Delta t) \approx 2r(t) - r(t-\Delta t) + \frac{f(t)}{m}\Delta t^2$$

Velocity-Verlet scheme



$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \delta t\,\mathbf{v}(t) + \tfrac{1}{2}\delta t^2\,\mathbf{a}(t)$$

$$\mathbf{v}(t+\tfrac{1}{2}\delta t) = \mathbf{v}(t) + \tfrac{1}{2}\delta t\,\mathbf{a}(t)$$

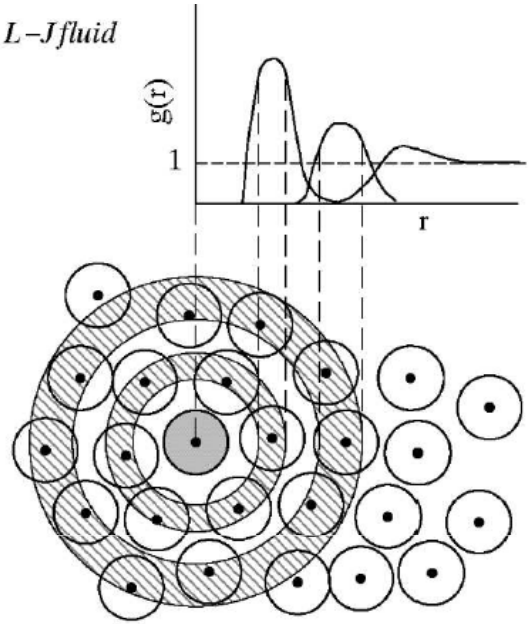
CALL FORCE

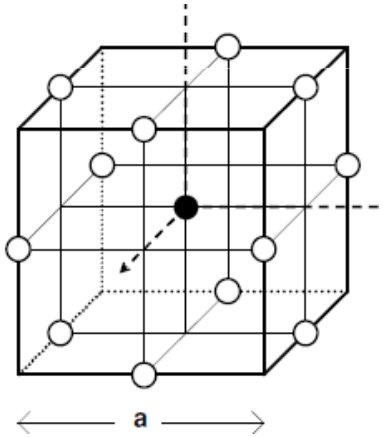
$$\mathbf{v}(t+\delta t) = \mathbf{v}(t+\tfrac{1}{2}\delta t) + \tfrac{1}{2}\,\delta t\,\mathbf{a}(t+\delta t)$$

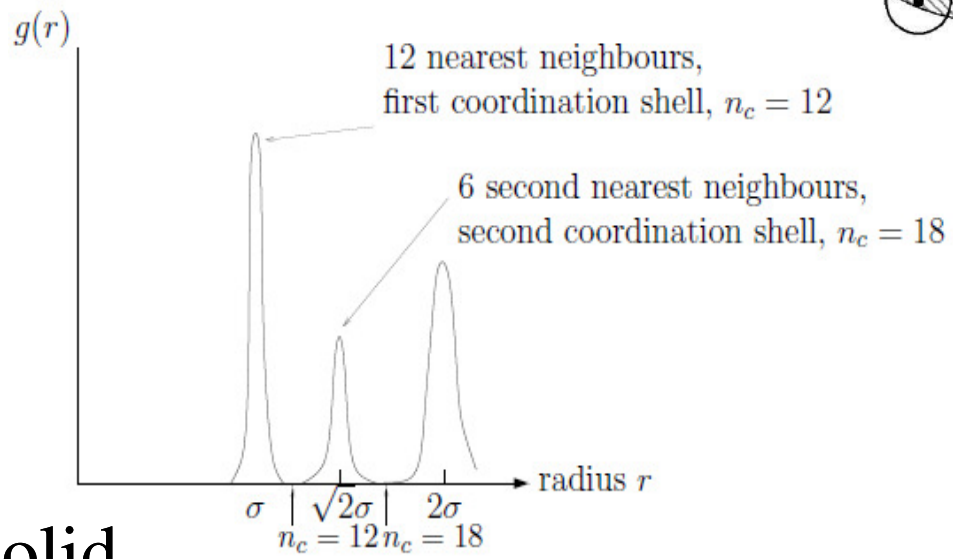
Structural Characterization

Radial Distribution Function (RDF)/ g(r)

$$g(r) = \frac{V}{4\pi r^2 \Delta r N^2} \sum_i^N n_i\,(r, \Delta r)$$





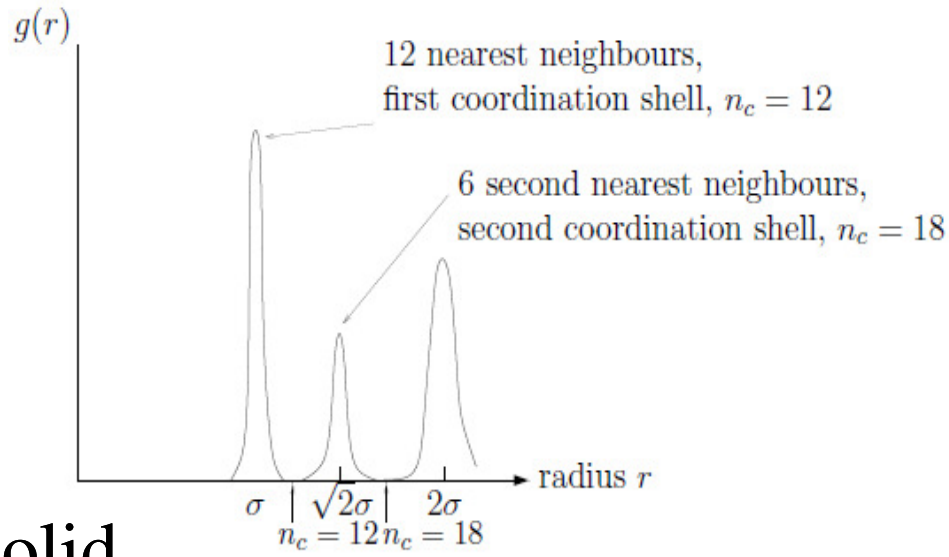


Rdf of fcc-solid

Structural Characterization

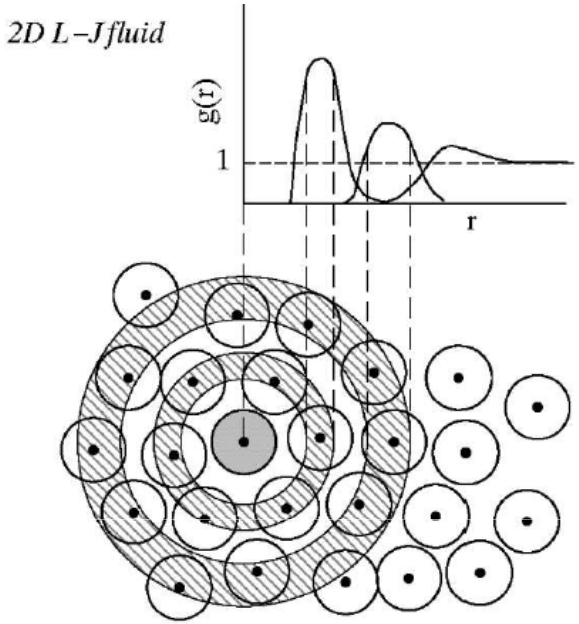
Running Coordination Number C(r)

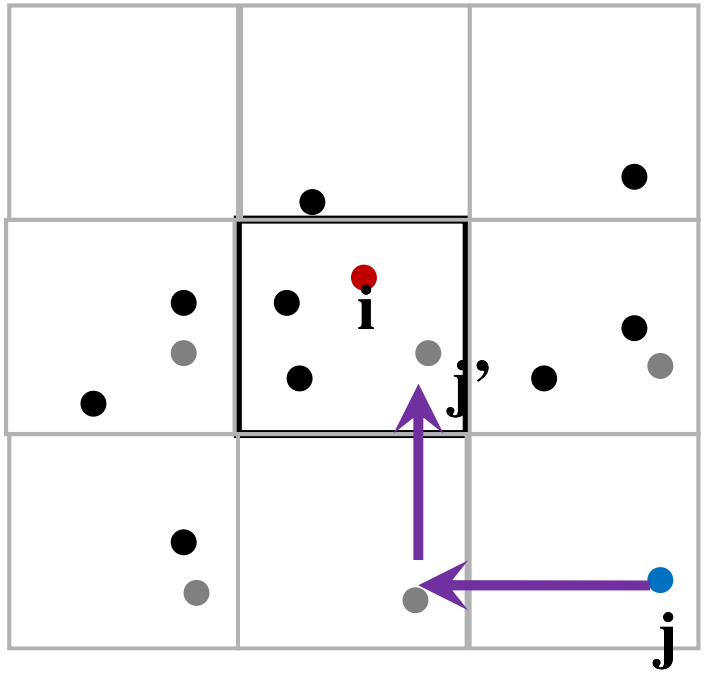
$$C(r) = \frac{4\pi N}{V} \int_0^r s^2 g(s)\, ds$$



Rdf of fcc-solid

Calculation of RDF and RCN



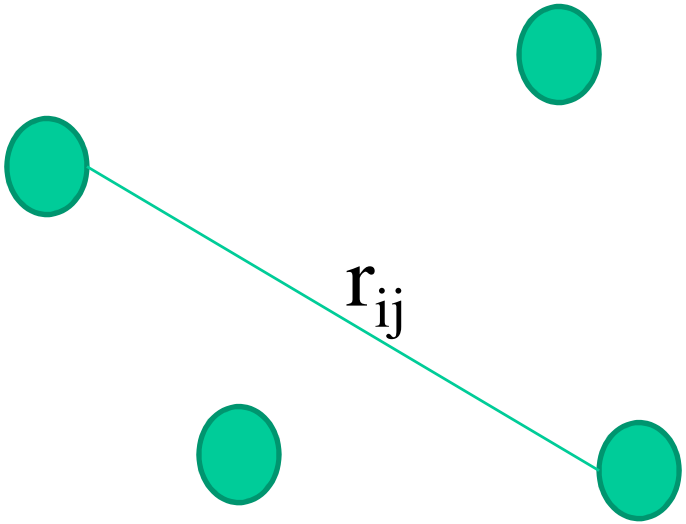


The same PBC as that used for MD should be be used in g(r) calculation!

dx = x(j) – x(i)
dy = y(j) – y(i)
dz = z(j) – z(i)

dx = dx – L***ANINT**(dx/L)
dy = dy – L***ANINT**(dy/L)
dz = dz – L***ANINT**(dz/L)

r2=dx2+dy**2+dz**2**



binsize ~ 0.02 - 0.1

k = **INT**(rij/binsize)

rdf (k) = rdf (k) + 1

Hands-On-Session –II (23/1/12) Time 2-4pm

Complete the assignments of Lab Session-I.

(Demonstrate running the code and the Pot. Energy obtained)

Make a new copy of your Pot. Energy Program &
Name it "loginid_2a.c" (retain your older version!!)

1. Read the fcc (4x4x4) positions *(**x**, **y**, **z** -already generated)*
2. Impose PBC & Minimum Image Convention
3. Calculate Pot. Energy U for different cutoff distances (Rc);
   (Find U for Rc=4.0 to 10 Å in steps of 0.5 Å)

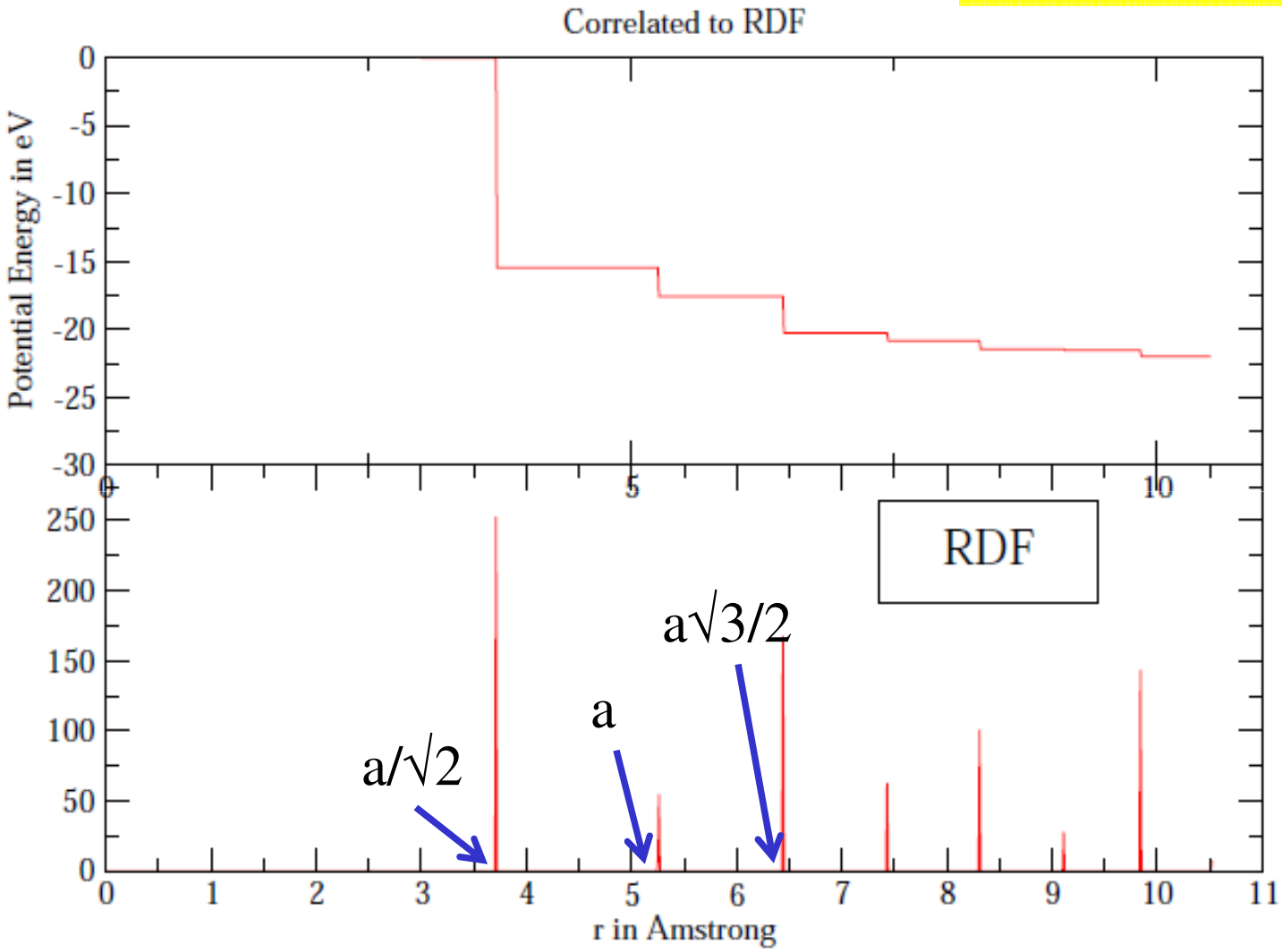
Bring Your Notebooks/C/Fortran- books;

Do not use internet!

FCC lattice + PBC

U

g(r)



1. Steps in U coincide with the g(r)!
2. U converges to as r increases.

Hands-On-session –III on Monday 30/01/12 **Time 2-4pm**

Complete the assignments of Lab Session-I & II.

Make a new copy of your Pot. Energy Program & name it "loginid_3.c" (retain your older version!!)

1. Read the fcc (4x4x4) positions *(x, y, z -already generated)*
2. Use a **fixed** cut_off distance of 10 A.
3. Impose PBC & Minimum Image Convention
4. Modify the code to calculate the forces on each atom due to the rest.

Please be prepared with the force expression between a pair of atoms for the Lennard-Jones Potential. Note that force being a vector need be dealt with component wise.

Bring Your Notebooks/C/Fortran- books;

Strictly do not open internet/ email accounts!

Initialization of Velocities (Random)

$$T = \frac{1}{3Nk}\sum_{i}^{N} m_i v_i^2$$

$$K.E = < \frac{1}{2}\sum_{i}^{N} m_i v_i^2 > = \frac{3}{2} N k T$$

```
sumv=0
sumv2=0
do i=1,npart
   v(i)=(ranf()-0.5)
   sumv=sumv+v(i)
   sumv2=sumv2+v(i)**2
enddo
sumv=sumv/npart
sumv2=sumv2/npart
fs=sqrt(3*temp/sumv2)
do i=1,npart
  v(i)=(v(i)-sumv)*fs
enddo
```

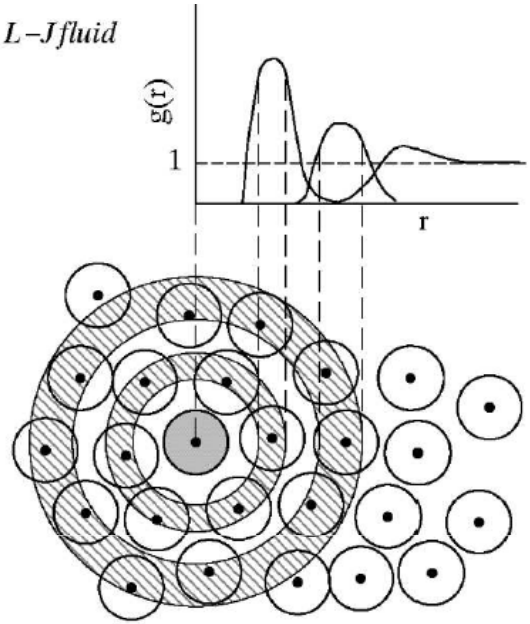
← Uniform random No (0-1)

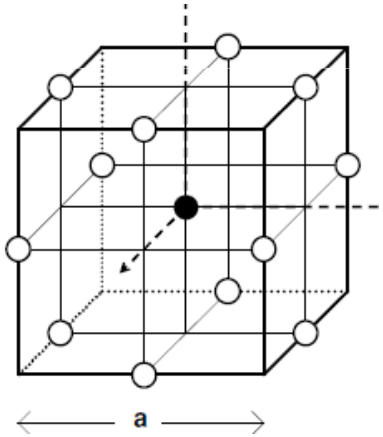
30-1-12

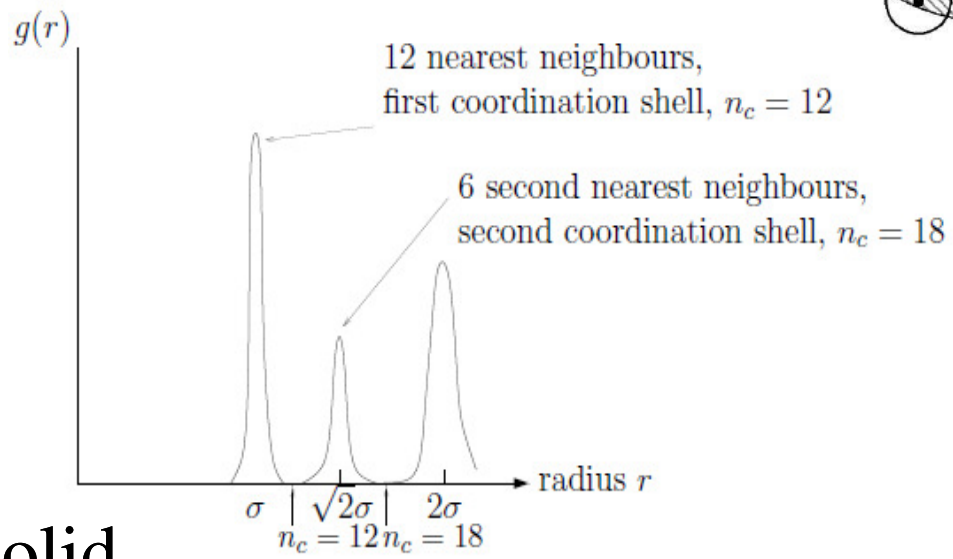
Structural Characterization

Radial Distribution Function (RDF)/ g(r)

$$g(r) = \frac{V}{4\pi r^2 \Delta r N^2} \sum_i^N n_i\,(r, \Delta r)$$







Rdf of fcc-solid

"Tail" Correction to Potential Energy!

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

$$u^{tail} \equiv (N/2)\int_{r_c}^{\infty} dr\, 4\pi r^2 \rho(r) u(r)$$

for $r \geq r_c$.

assuming $\rho(r)$ is equal to the average number density ρ.

$$\begin{aligned} u^{tail} &= \frac{N}{2} 4\pi\rho \int_{r_c}^{\infty} dr\, r^2 u(r) \\ &= \frac{N}{2} 16\pi\rho\epsilon \int_{r_c}^{\infty} dr\, r^2 \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \\ &= N\frac{8}{3}\pi\rho\epsilon\sigma^3 \left[\frac{1}{3}\left(\frac{\sigma}{r_c}\right)^{9} - \left(\frac{\sigma}{r_c}\right)^{3}\right]. \end{aligned}$$

Initialization of Velocities (Random)

!cmvx,cmvy,cmvz=0; sumvsq=0; rand(3)

```
do i=1,n
Call Random_Number(rand)
vx(i) = (rand( 1) -0.5);
vy(i) = (rand( 2) -0.5);
vz(i) = (rand( 3) -0.5);

cmvx = cmvx + vx(i);
cmvy = cmvy + vy(i);                    !For Centre of mass velocity
cmvz = cmvz + vz(i);
sumvsq = sumvsq + vx(i)**2 + vy(i)**2 + vz(i)**2
enddo

cmvx = cmvx/n; cmvy = cmvy/n; cmvz = cmvz/n;
```

! cmvx~0 cmvy ~ 0 cmvz ~0

```
do i=1,n
      vx(i) = vx(i) –cmvx;
      vy(i) = vy(i) –cmvy;
      vz(i) = vz(i) –cmvz;
enddo
```

$$\frac{3}{2} N k T = \frac{1}{2} \sum_i^N m_i v_i^2 \quad \Rightarrow \quad T = \frac{m}{3 N k} \sum_i^N v_i^2$$

Then **scale** all velocities: $v_r = \left(\frac{T_r}{T} \right)^{\frac{1}{2}} v$

```
fact = SQRT(3*n*kB* Tr / (m*sumvsq))
do i=1,n
      vx(i) = vx(i)*fact;
      vy(i) = vy(i)*fact;
      vz(i) = vz(i)*fact;
enddo
```

Dynamical Properties: Diffusion Coefficient

Fick's Law: $\vec{j}(\vec{r},t) = -D\nabla\rho(\vec{r},t)$

Continuity Eq.: $\partial\rho(\vec{r},t)/\partial t + \nabla\cdot\vec{j}(\vec{r},t) = 0$

Diffusion Eq.: $\partial\rho(\vec{r},t)/\partial t = D\nabla^2\rho(\vec{r},t)$

Einstein's relation: $D = \lim_{t\to\infty}\frac{1}{6t}\langle|\mathbf{r}(t)-\mathbf{r}(0)|^2\rangle$ ⟸ *Nr.* MSD

Nernst-Einstein's relation: $\sigma = Nq^2D\,/\,fk_BT$

06 Feb 2012

Dynamical Properties: Diffusion Coefficient

Fick's Law: $\mathbf{j} = -D\nabla c$

$\mathbf{j}(r, t)$ - **flux**

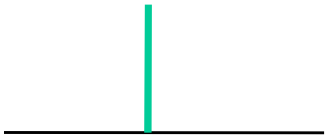
$c(r, t)$ - **concentration**

D – **self diffusivity (diff. coefficient)**

Continuity Eq.: $$\frac{\partial c(r,t)}{\partial t} + \nabla \cdot \mathbf{j}(r,t) = 0$$

Diffusion Eq.: $$\frac{\partial c(r,t)}{\partial t} - D\nabla^2 c(r,t) = 0$$

boundary condition $c(r,0) = \delta(r)$



($\delta(r)$ is the Dirac delta function)

$$c(r,t) = \frac{1}{(4\pi Dt)^{d/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$

$$\int dr\, c(r,t) = 1$$

Prob. Interpretation of c(r,t)

$$\frac{\partial c(r,t)}{\partial t} - D\nabla^2 c(r,t) = 0$$

by r^2 and integrating over all space

$$\frac{\partial}{\partial t}\int dr\, r^2 c(r,t) = D\int dr\, r^2 \nabla^2 c(r,t)$$

Einstein

$$\frac{\partial \langle r^2(t)\rangle}{\partial t} = 2dD$$

(Einstein's relation)

Frenkel & Smith

$$
\begin{aligned}
\frac{\partial \langle r^2(t) \rangle}{\partial t} &= D \int \mathbf{dr}\, r^2 \nabla^2 c(r,t) \\
&= D \int \mathbf{dr}\, \boldsymbol{\nabla} \cdot (r^2 \boldsymbol{\nabla} c(r,t)) - D \int \mathbf{dr}\, \boldsymbol{\nabla} r^2 \cdot \boldsymbol{\nabla} c(r,t) \\
&= D \int \mathbf{dS}\, (r^2 \boldsymbol{\nabla} c(r,t)) - 2D \int \mathbf{dr}\, \mathbf{r} \cdot \boldsymbol{\nabla} c(r,t) \\
&= 0 - 2D \int \mathbf{dr}\, (\boldsymbol{\nabla} \cdot \mathbf{r} c(r,t)) + 2D \int \mathbf{dr}\, (\boldsymbol{\nabla} \cdot \mathbf{r}) c(r,t) \\
&= 0 + 2dD \int \mathbf{dr}\, c(r,t) \\
&= 2dD.
\end{aligned}
$$

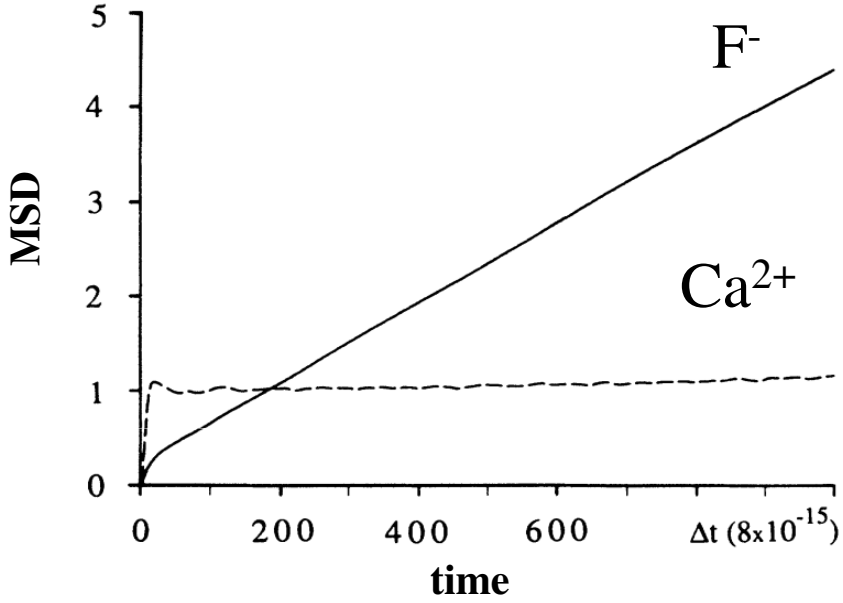
$$\frac{\partial \langle r^2(t) \rangle}{\partial t} = 2dD$$

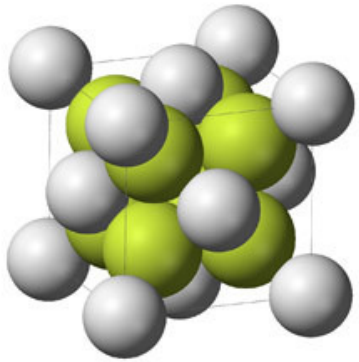
Einstein's relation: $D = \lim_{t \to \infty} \frac{1}{6t} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$ ⟸ *Nr.* M.S.D

(M. S. D – Mean Squared Displacement)

Nernst-Einstein's relation: $\sigma = Nq^2 D / fk_B T$

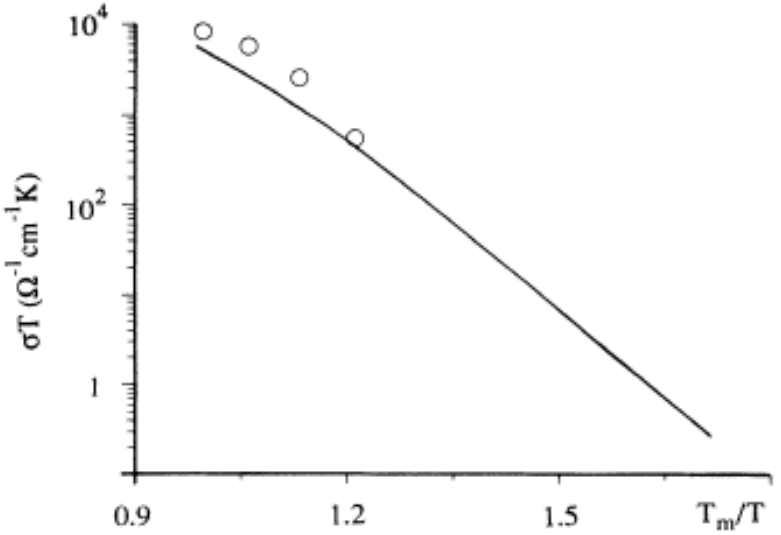
…Diffusion Coefficient: CaF2





CaF2

$$\sigma = Nq^2 D / fk_B T$$



PRB, **43**, 3180,1991.

In 1-Dimension

$$2D = \lim_{t \to \infty} \frac{\partial \langle x^2(t) \rangle}{\partial t}$$

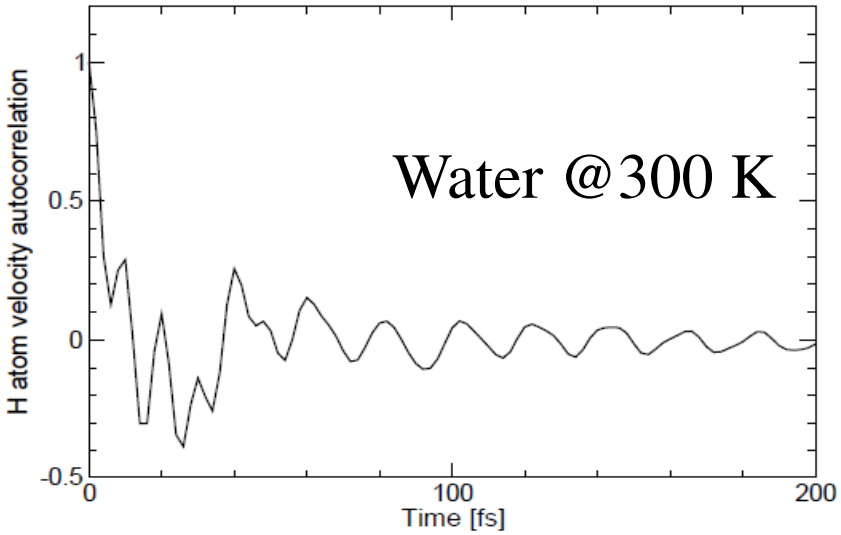
$$D = \int_0^\infty d\tau \, \langle v_x(\tau) v_x(0) \rangle$$

$\langle v_x(\tau) v_x(0) \rangle$ - Velocity auto correlation fn.

…Dynamical Properties: Vibrational Spectrum

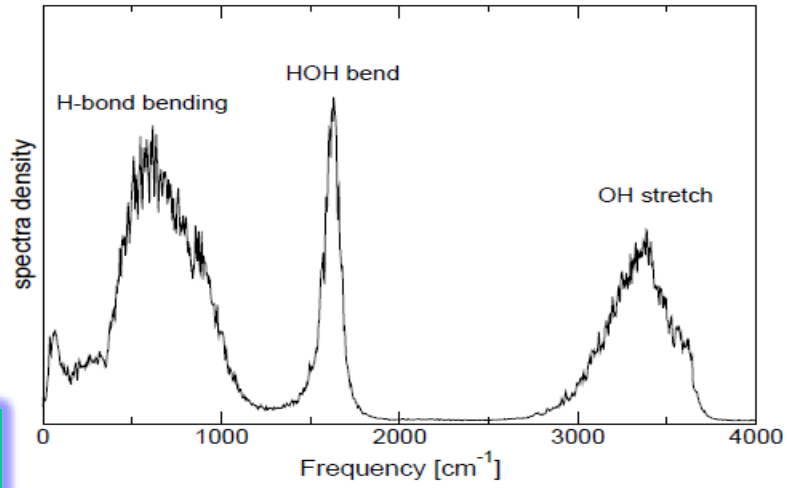
Velocity Autocorrelation Spectrum,

$$c_{vv}(\tau) = \langle \mathbf{v}_i(\tau)\mathbf{v}_i(0)\rangle$$



Power Spectrum,

$$\mathbf{c_{VV}(\omega)} = \int_{-\infty}^{\infty} d\tau\, e^{-i\omega\tau} c_{vv}(\tau)$$



Helps interpreting IR spectrum.

Hands-On-Session –IV (13/2/12) Time 2-4pm

Demonstrate the lab assignments of sessions-I, II, III.

Make a new copy of your Force Calculation Program &
Name it **"loginid_4a.c"** (retain your older version!!)

1. Read the fcc (4x4x4) positions *(**x, y, z** -already generated)*
   Keep (0, 0, 0) particle displaced at (-0.2, 0.3, 0.5).
2. Impose PBC & Minimum Image Convention (Rcut = 10A)
3. Use the forces to integrate the equations of motion using "velocity Verlet" algorithm. Use time step, dt = 1 fs.
   mass- that of argon. **(Workout the unit system!!!)**
   Perform 100 MD steps.

Bring Your Notebooks/C/Fortran- books;

Do not use internet!

Reduced Units

- Length (m) → Å
- Mass (kg) → *a m u*
- Time (s) / Energy → eV
- Charge (C) → e^-
- Temperature (K) → K
- Mole (mol) → mol
- ~~Luminous Intensity (candela)~~

time step = 1 fs = ?? (In reduced units)

Mid-Sem: 22nd Feb 2012 (10-12pm)

Bring Your Calculators.

Questions are based on NVE-MD of bulk Systems.

Total marks: 30 (6 x 5 marks)

Interatomic forces for simple systems

(non-bonded interactions)

1. Lennard-Jones Potential:

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

Instantaneous dipoles

Gives an accurate description of ***inert gases***
(Ar, Xe, Kr etc.)

2. Born-Mayer (Tosi-Fumi) Potential:

$$\mathcal{U}(r_{ij}) = \frac{q_i\, q_j}{r_{ij}} + A_{ij}\, exp(-r_{ij}/\rho_{ij}) - \frac{C_{ij}}{r_{ij}^6}$$

Faithful in describing ***pure*** ionic solids
(NaCl, KCl, NaBr etc.)

Issues with Coulombic Forces

(Ewald Summation technique)

$$\mathcal{U}_{\text{Coul}} = \frac{1}{2}\sum_{i=1}^{N} q_i \phi(r_i)$$

$$\phi(r_i) = \sum_{j,\mathbf{n}}{}' \frac{q_j}{|\mathbf{r}_{ij} + \mathbf{n}L|}$$

~~Minimum Image Convention~~

This sum is only Conditionally Convergent!

"Tail" Correction to Potential Energy!

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

$$u^{tail} \equiv (N/2)\int_{r_c}^{\infty} dr\, 4\pi r^2 \rho(r) u(r)$$

for $r \geq r_c$.

assuming $\rho(r)$ is equal to the average number density ρ.

$$\begin{aligned} u^{tail} &= \frac{N}{2} 4\pi\rho \int_{r_c}^{\infty} dr\, r^2 u(r) \\ &= \frac{N}{2} 16\pi\rho\epsilon \int_{r_c}^{\infty} dr\, r^2 \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \\ &= N\frac{8}{3}\pi\rho\epsilon\sigma^3 \left[\frac{1}{3}\left(\frac{\sigma}{r_c}\right)^{9} - \left(\frac{\sigma}{r_c}\right)^{3}\right]. \end{aligned}$$

Remarks on Interatomic Forces

- Development of good force fields (FF) can be a tough task!

FF's are developed by empirical methods or ab-initio calculations.

- FF assume that electronic clouds around the nucleus of atoms is intact irrespective of the environment around the atom!

This can be a poor assumption for highly polarizable atoms/ions!

Solution?

Develop a shell model of atoms/ions!

Or DFT-based *ab-initio* (Car-Parrinello) MD calculations !

Comments on Classical MD

Very powerful in studying a variety of physical phenomena and under several external conditions (T & P).

Extensively employed to understand Physical processes at atomic resolution

Phase Transitions,

Diffusion and transport properties,

Local structural and short-time relaxation of

- ✓ crystalline and amorphous solids
- ✓ liquids
- ✓ solid-fluid interfaces
- ✓ nano-clusters

And, serves a very useful bridge between experiment and theory!

Not useful in the study of electronic properties!

Not powerful enough to describe chemical reactions!

Hands-On-Session –V (05/03/12) Time 2-4pm

Complete the lab assignments of sessions-IV.

(Perform 1000 MD steps; with the particle positions, Potential Energy and Total Energy written at intervals of 10 MD steps; and demonstrate energy conservation.)

Use the positions to calculate the Radial Distribution Function (averaged over all particles and over 100 MD steps.)

Compare the same with the RDF of the static-FCC lattice.

Bring Your Notebooks/C/Fortran- books;

Do not use internet!

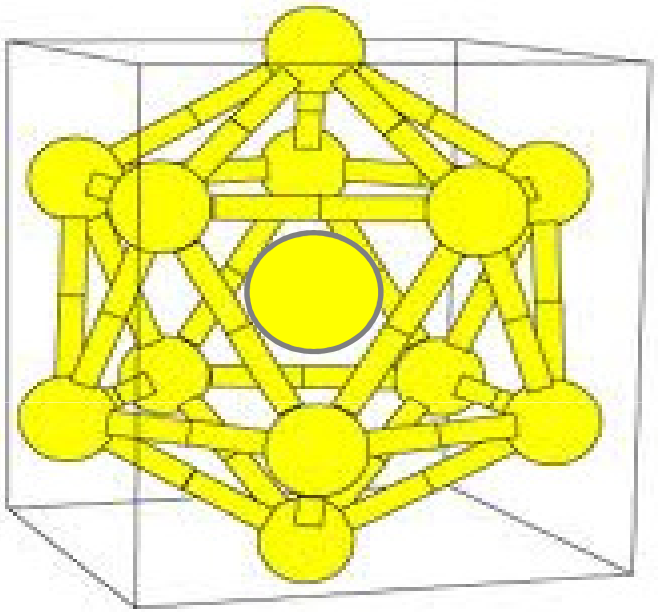
Translational & Rotational corrections

(from last class)

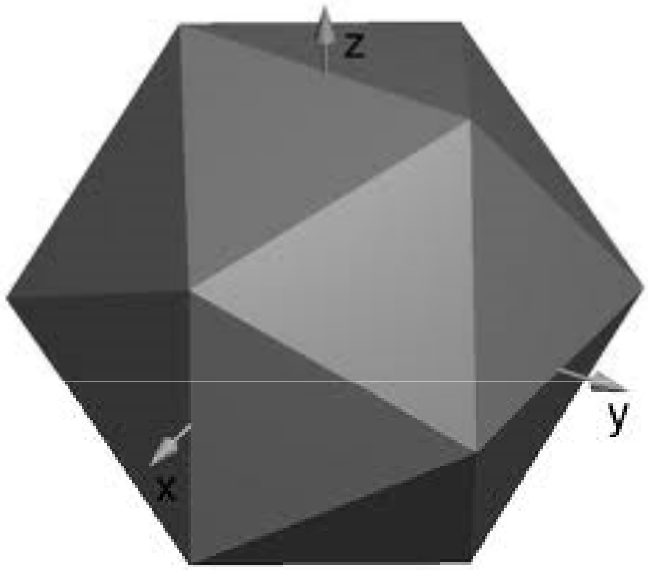
$$T = \frac{2}{(3N-6)} \frac{\overline{E}_{\text{kin}}}{k}$$

3 –translational and 3- overall-rotational DOF are to be subtracted.

Ar clusters: Structure



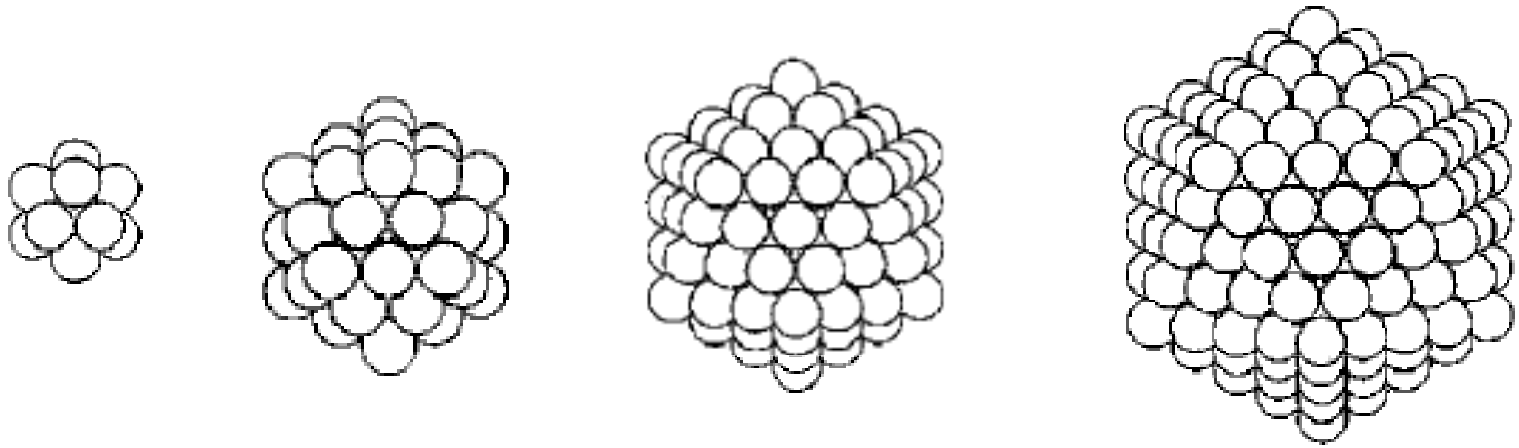
Ar_{13} Cluster



Icosahedron

Typically, clusters stabilize in different structures than their bulk counterparts.

Ar cluster Magic Numbers

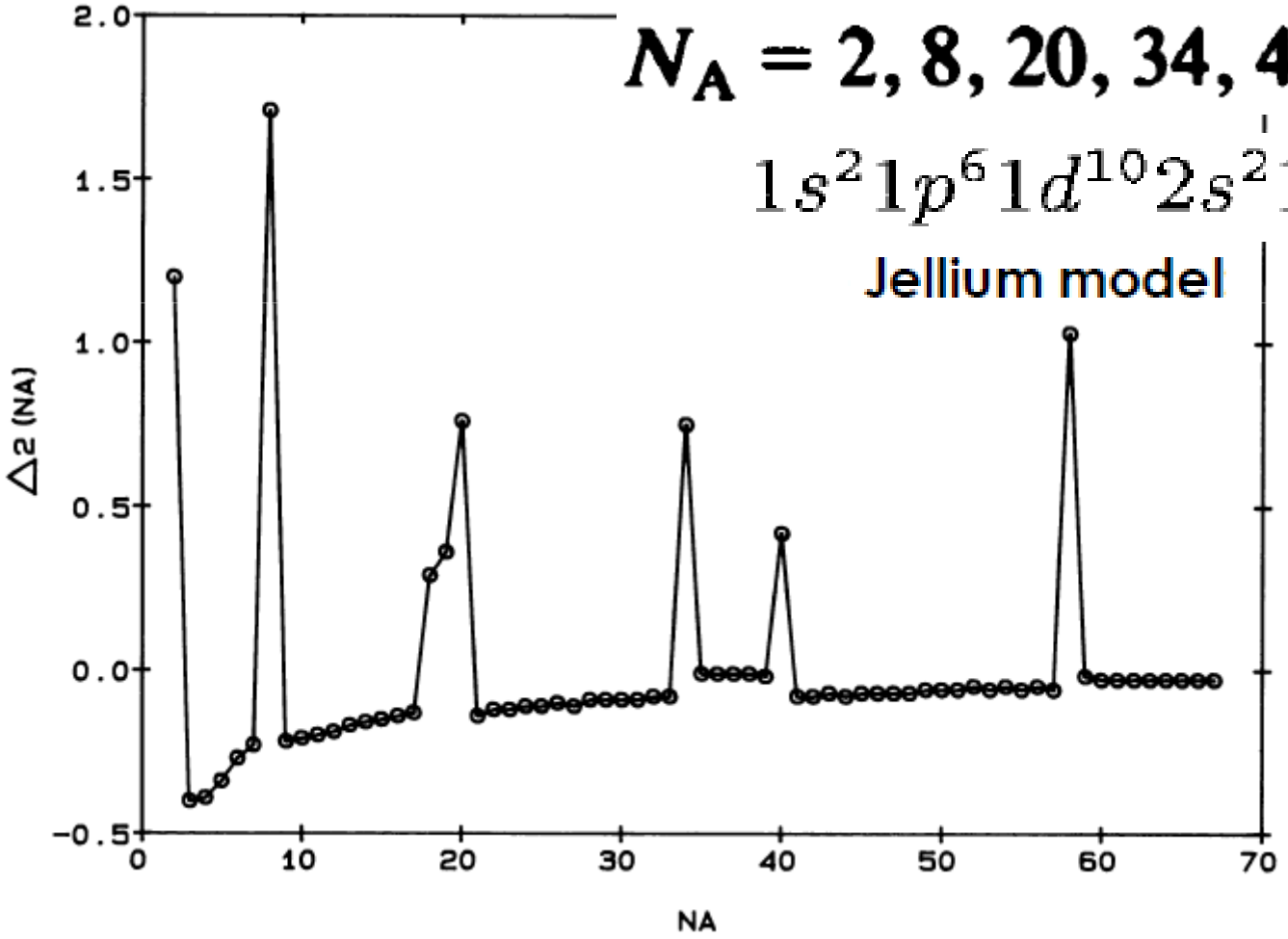


Ar_{13} **Ar_{55}** **Ar_{147}** **Ar_{309}**

Stability depends on completion of icosahedral shells.

Magic numbers of Na clusters

$$\Delta_2(N_A) = E(N_A + 1) + E(N_A - 1) - 2E(N_A)$$



N_A = 2, 8, 20, 34, 40, and 58

$1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^6$

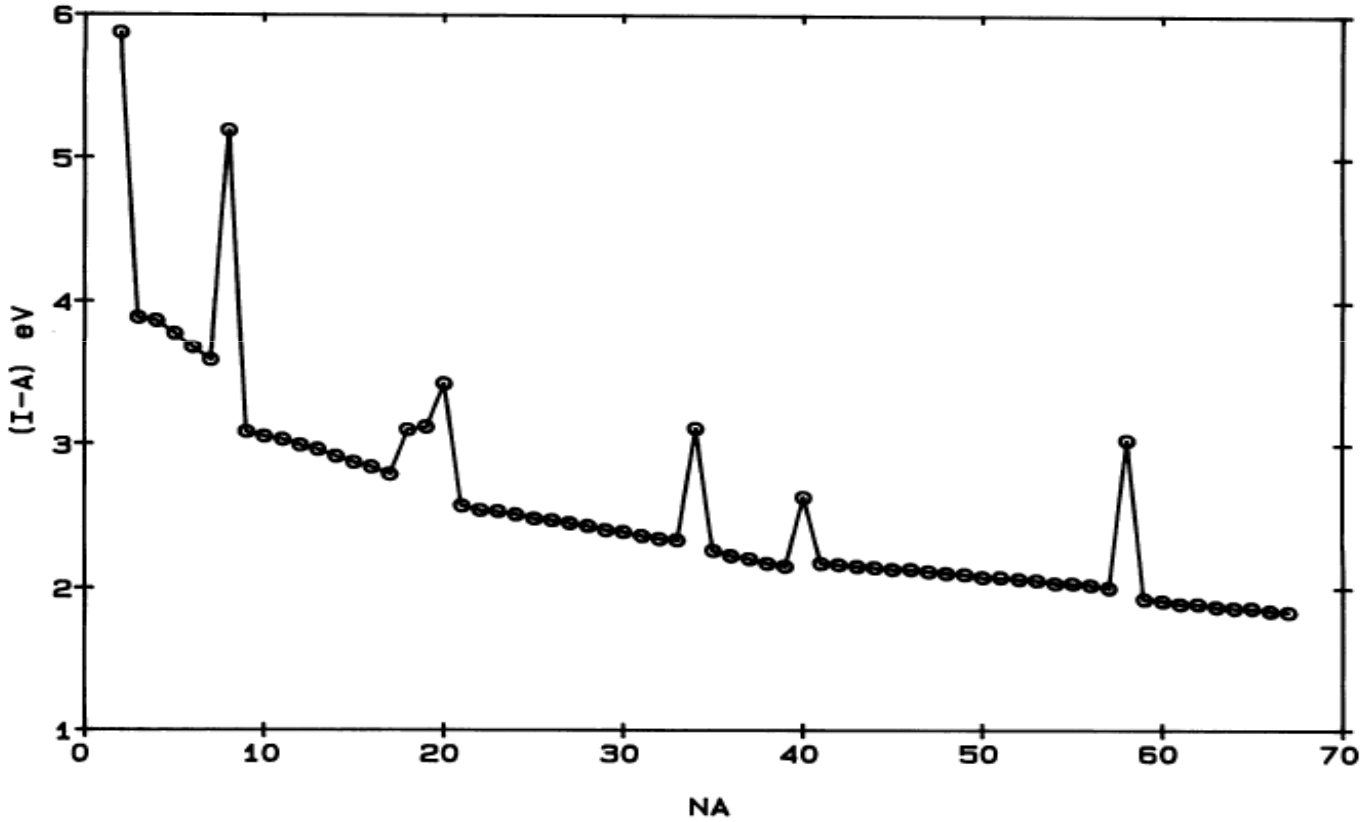
Jellium model

$l < n$

Stability of Na clusters?

Chemical Hardness, $\eta = \frac{I - A}{2}$

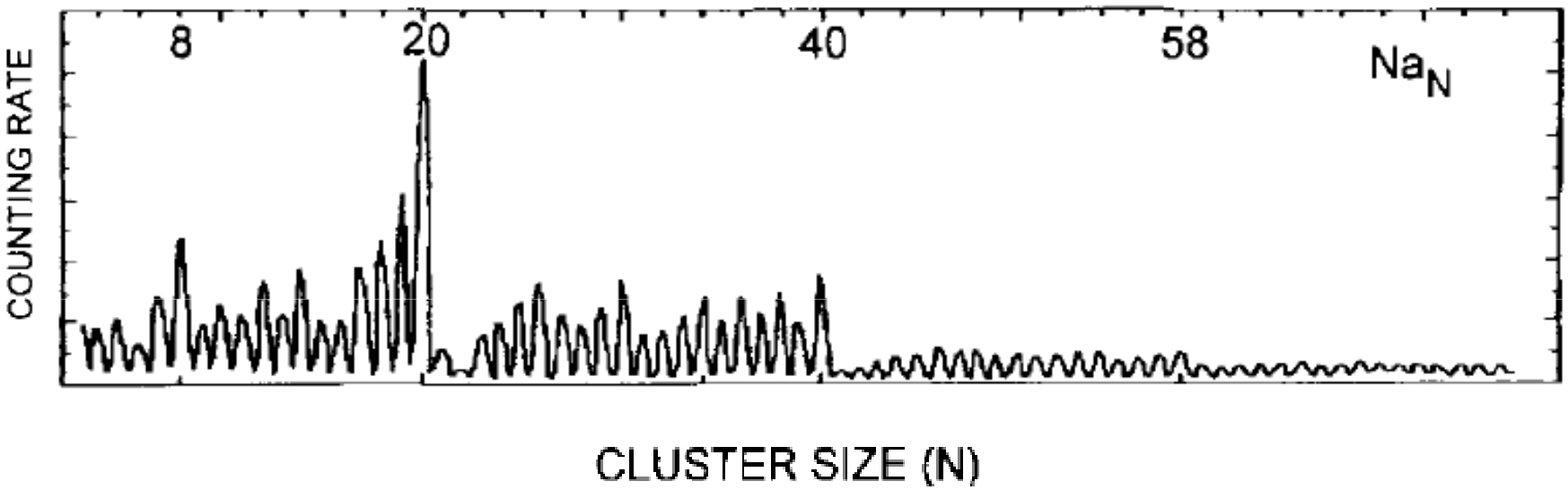
I- Ionization potential;
A-electron affinity



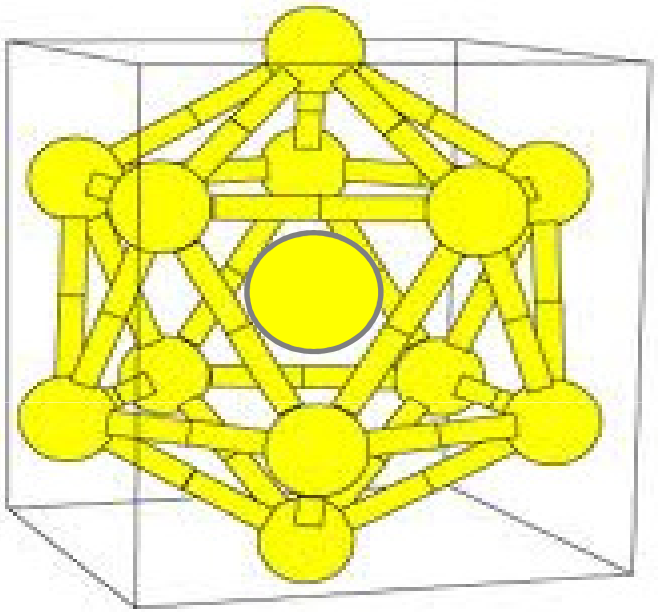
Chemical hardness (I–A) versus number of atoms (N_A) for lithium clusters.

Experimental evidence: Mass spectrometric data

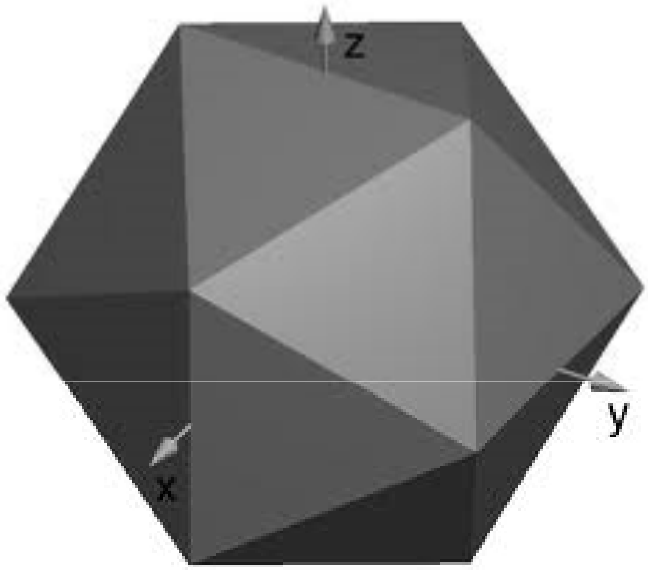
For Na cluster



Ar clusters: Structure



Ar_{13} Cluster



Icosahedron

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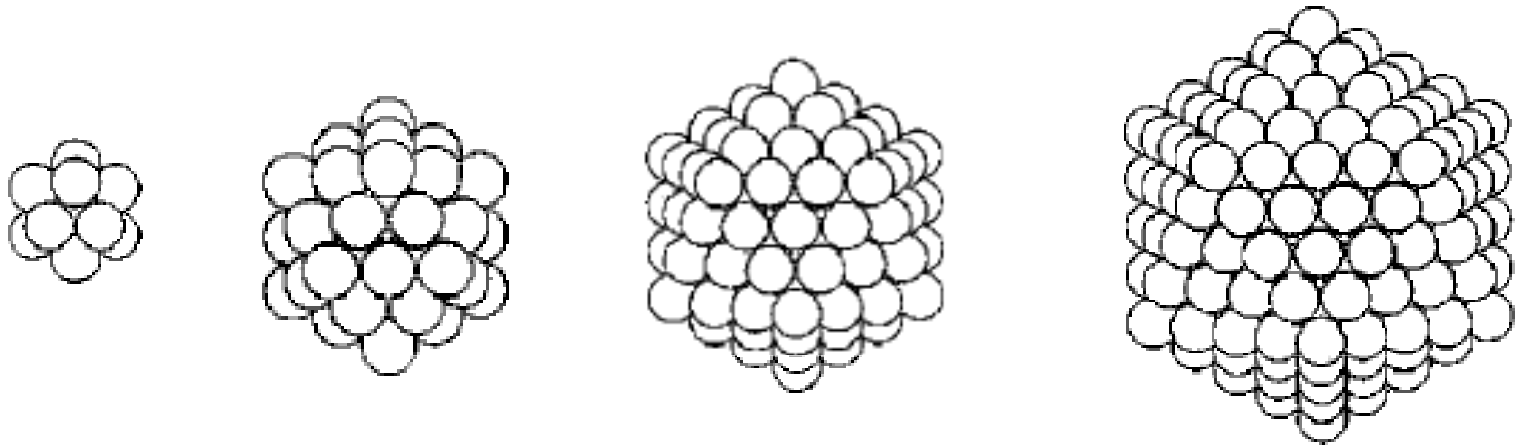
Ar cluster Magic Numbers

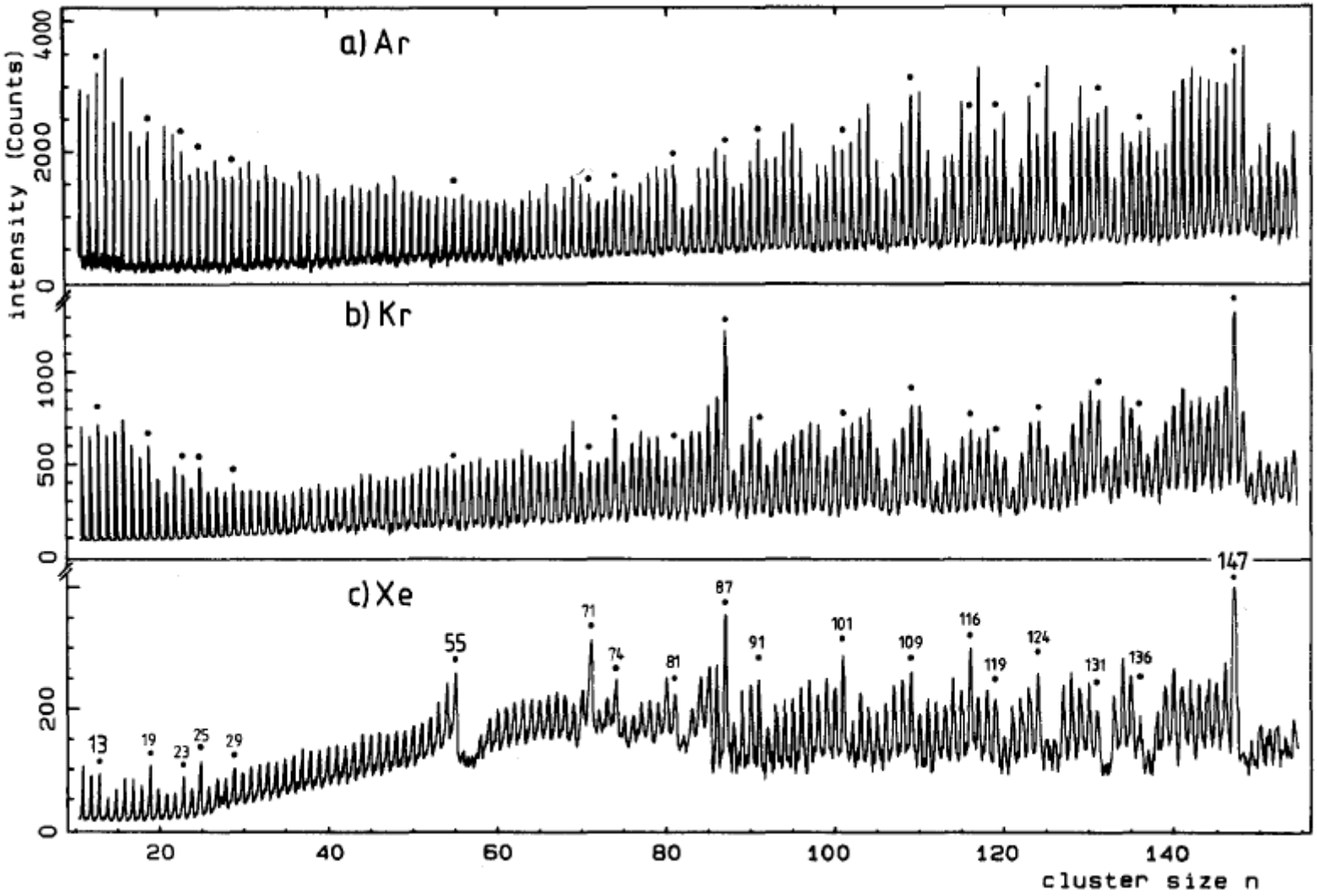


Ar_{13} **Ar_{55}** **Ar_{147}** **Ar_{309}**

Stability depends on completion of icosahedral shells.

Experimental evidence for magic clusters:

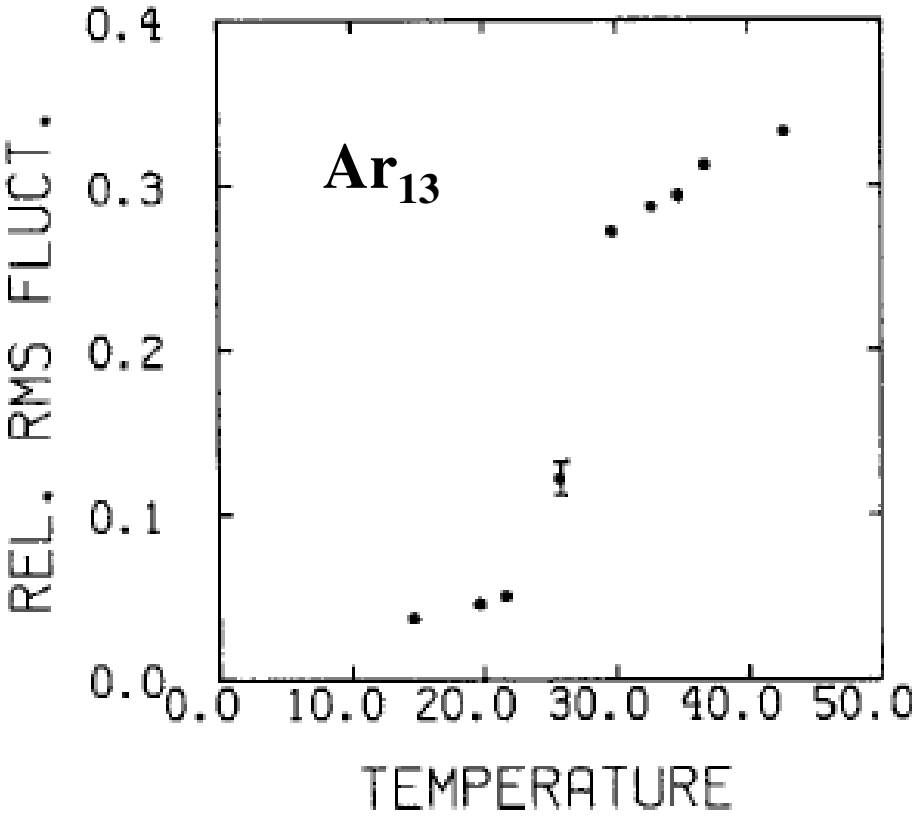
Mass spectrometric data for Inert gas clusters

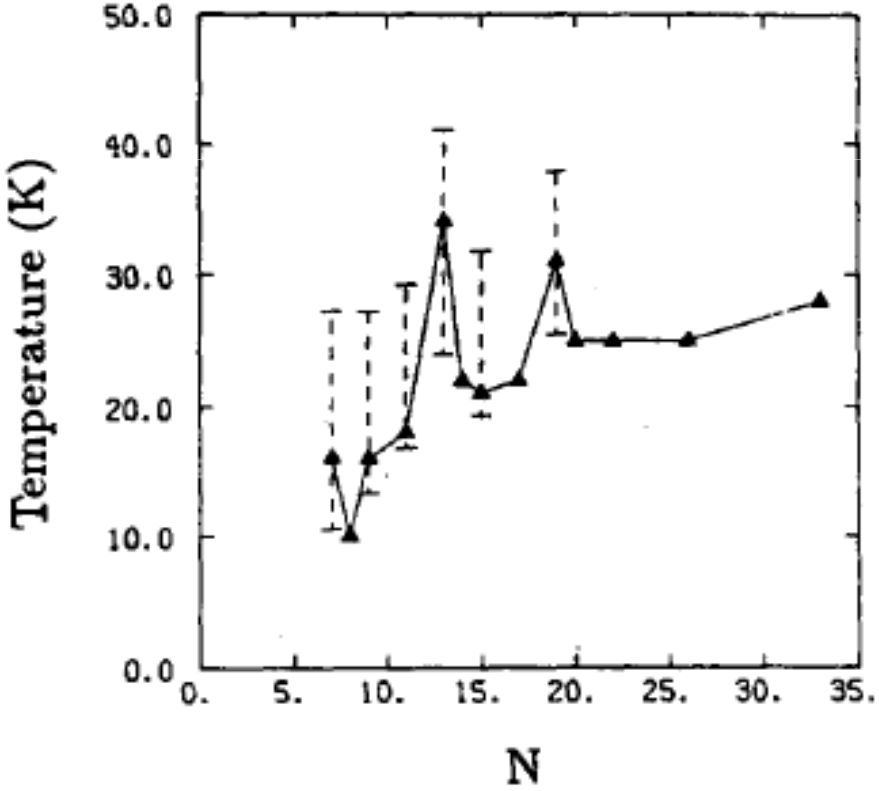


Solid – Liquid transition of Ar clusters

RMS bond length fluctuation, (Lindemann Criterion)

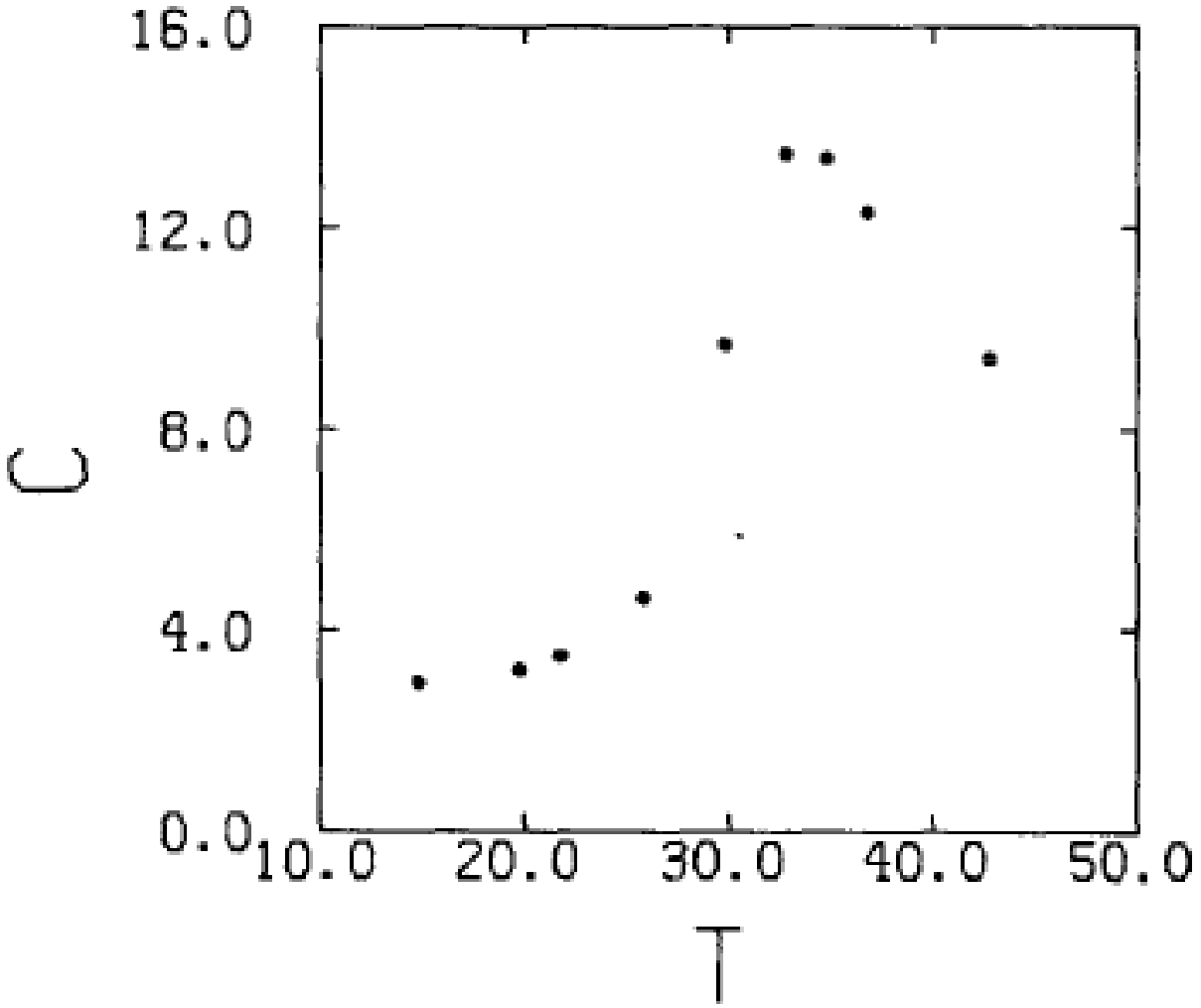
$$\delta = \frac{2}{N(N-1)} \sum_{i<j} \frac{(\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2)^{1/2}}{\langle r_{ij} \rangle}$$





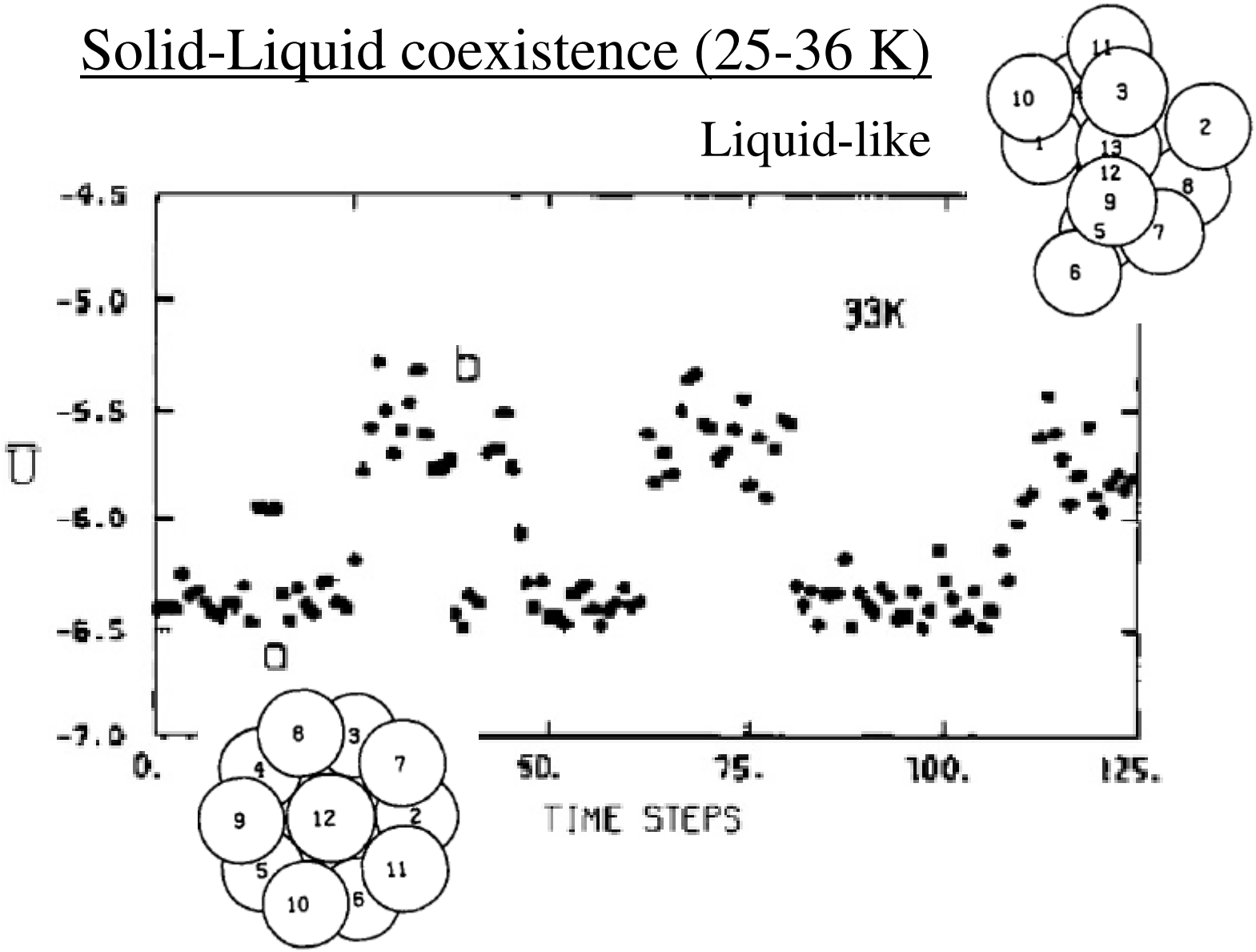
Solid – Liquid transition of Ar clusters

Heat Capacity Vs Temperature



Solid-Liquid coexistence (25-36 K)

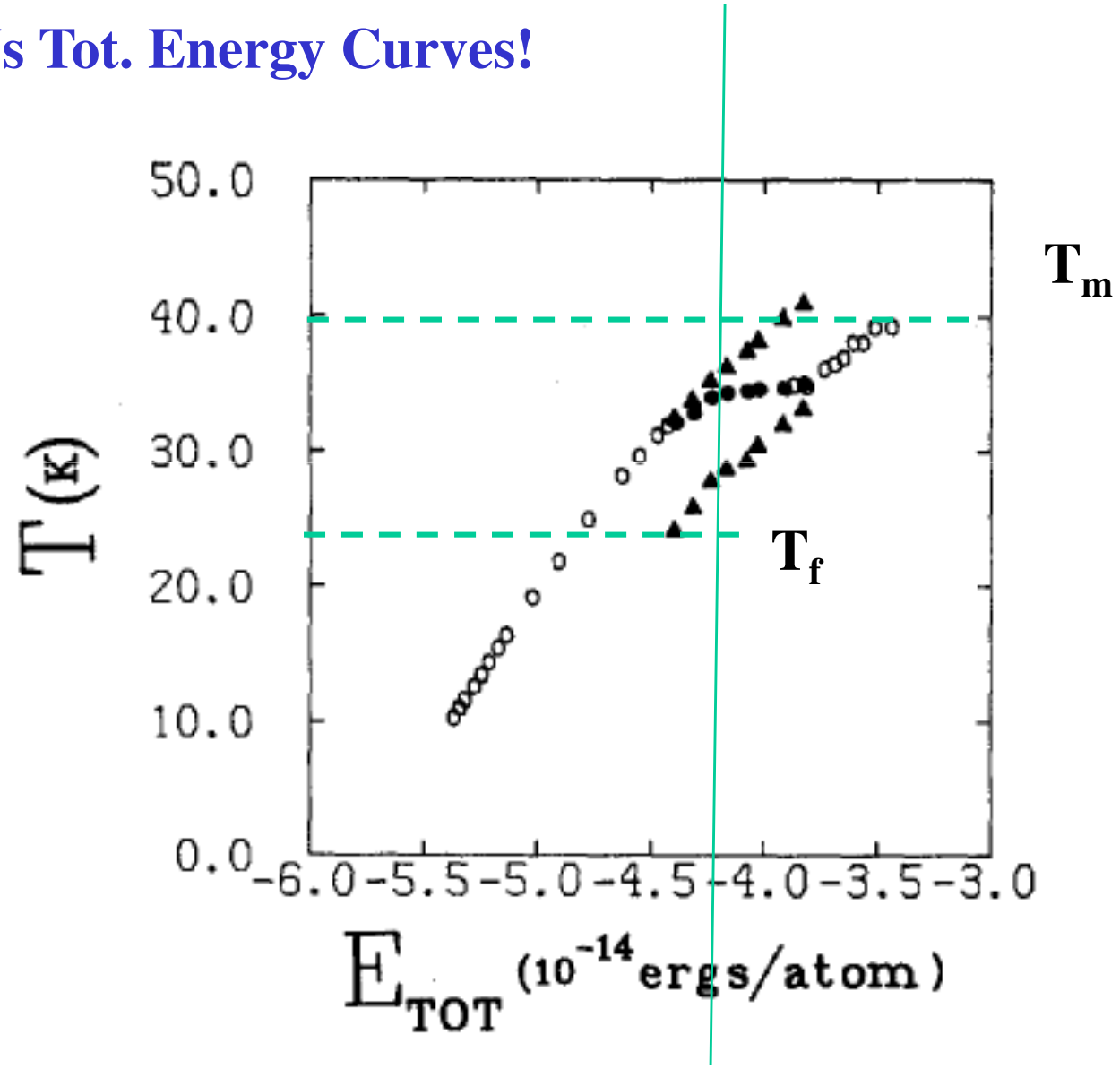
Liquid-like



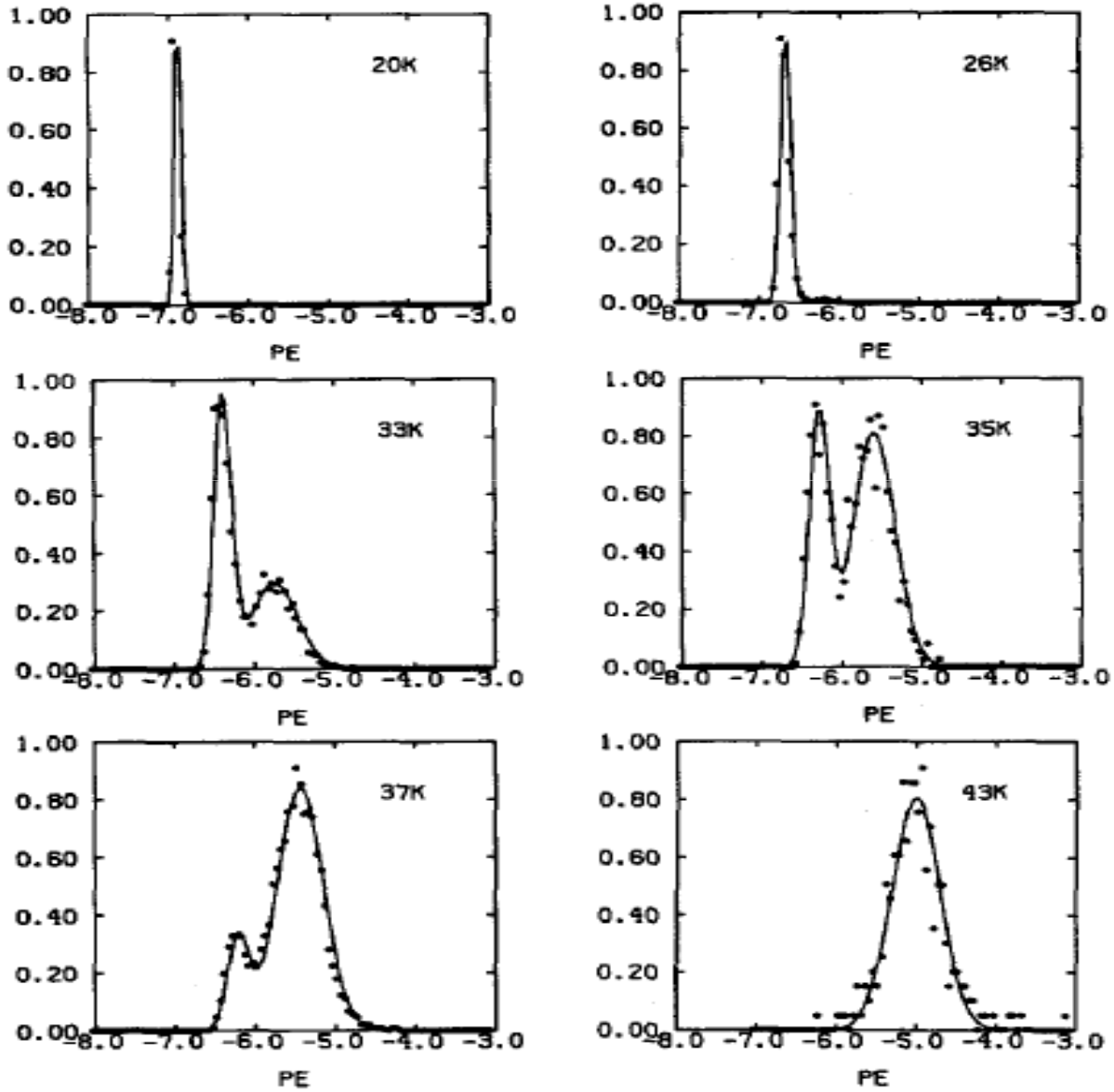
solid-like

Solid – Liquid transition of Ar clusters

Temp. Vs Tot. Energy Curves!



Bimodal distribution of U



Structure of $(KCl)_{32}$

Born-mayer potential

$$\Phi = \sum_{i<j} \Phi_{ij} = \sum_{i<j} \left[\frac{q_i q_j}{r_{ij}} + A_{ij} \exp(-r_{ij}/\rho) \right]$$

$$A_{++} = 1555.21 \text{ eV}$$

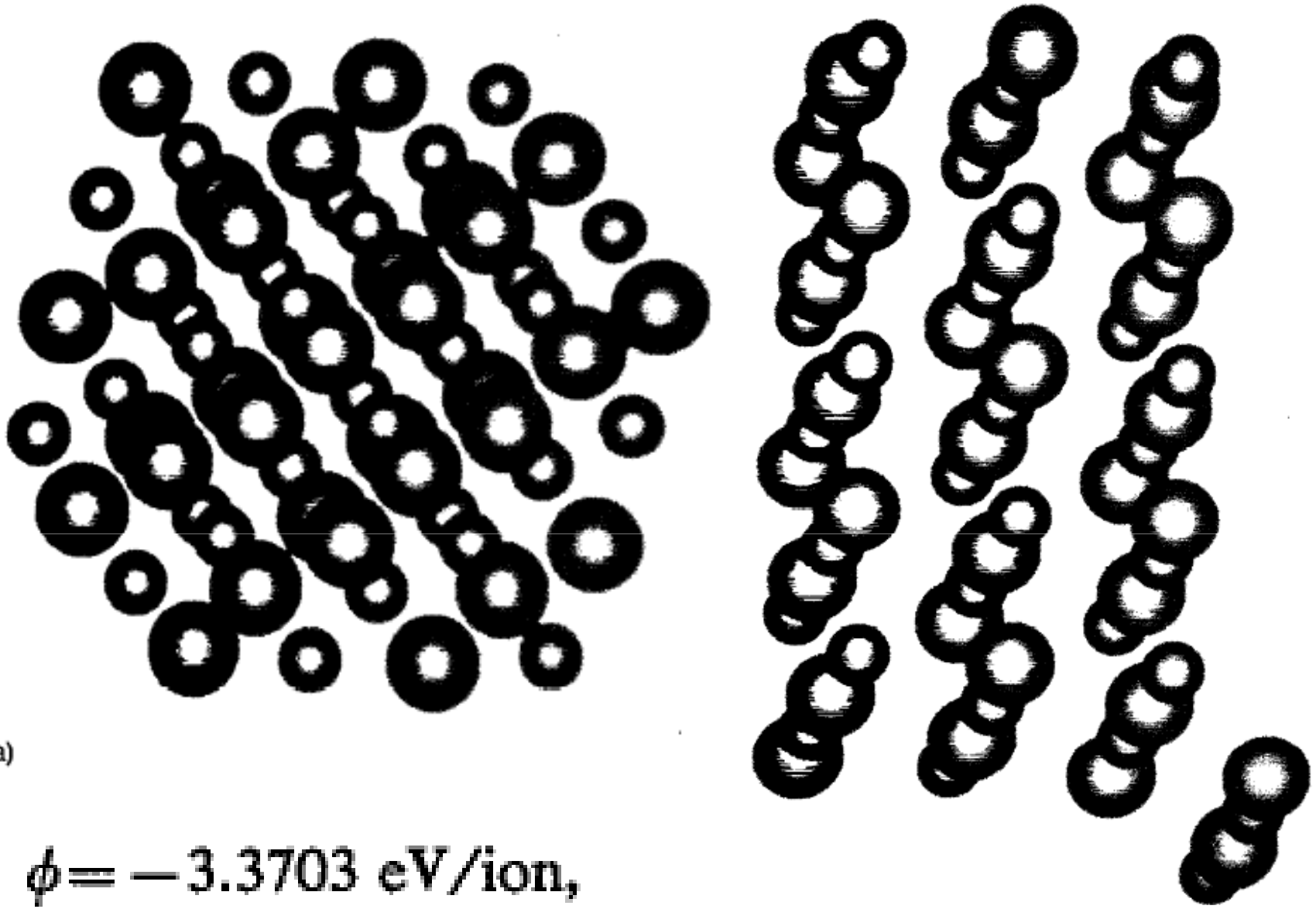
$$A_{+-} = 1786.91 \text{ eV}$$

$$A_{--} = 1924.80 \text{ eV}$$

$$\rho \ (0.337 \text{ Å})$$

time step of 3×10^{-15}

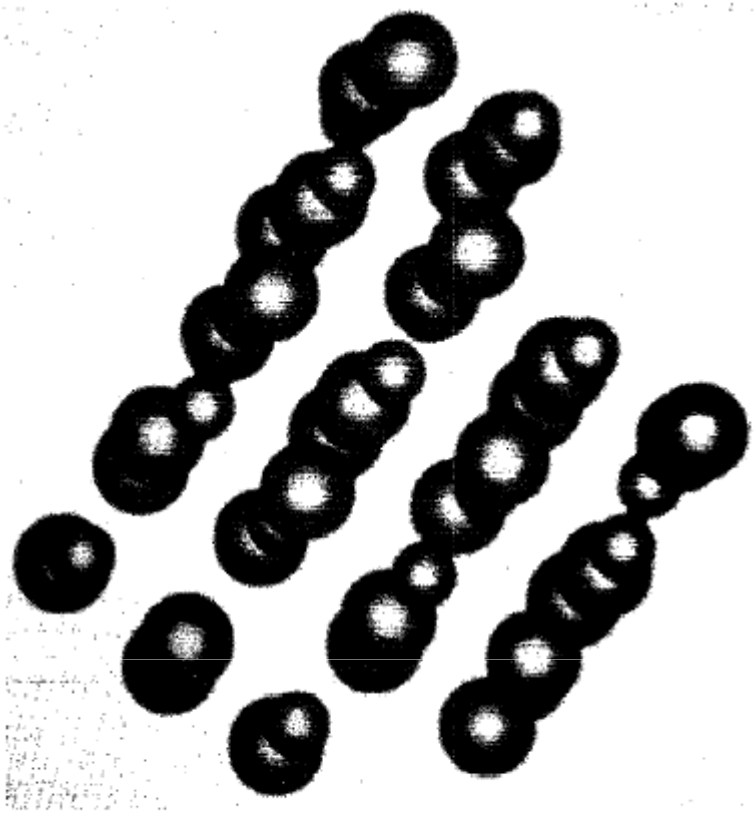
1.5×10^{6} time steps



(a)

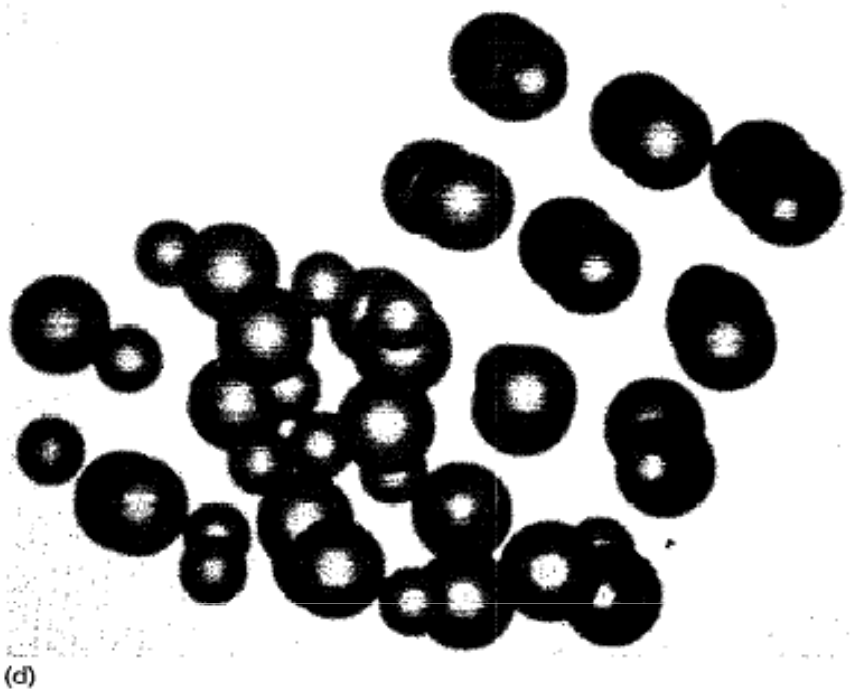
$\phi = -3.3703$ eV/ion,

$\phi = -3.3534$ eV/ion



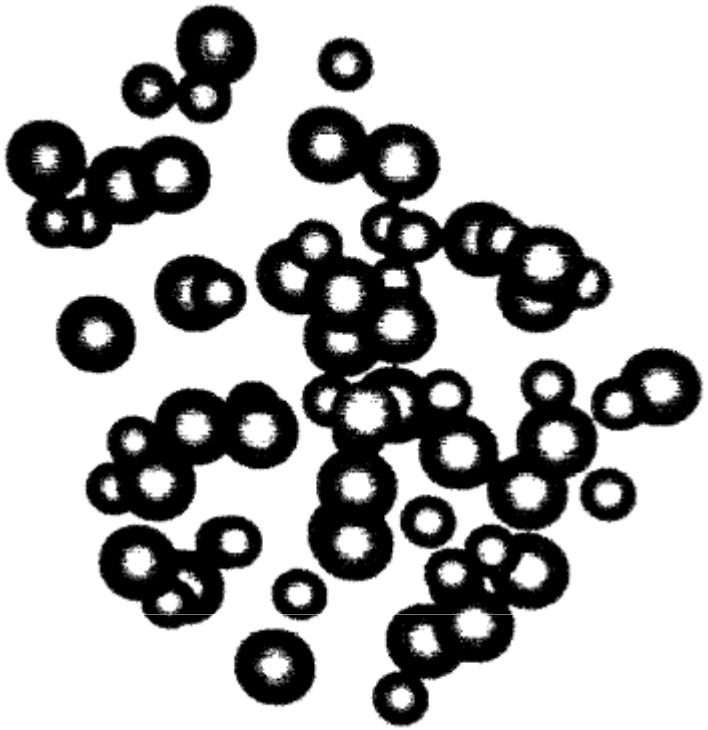
(c)

$\phi = -3.3465$ eV/ion,



(d)

$\phi = -3.3254$ eV/ion



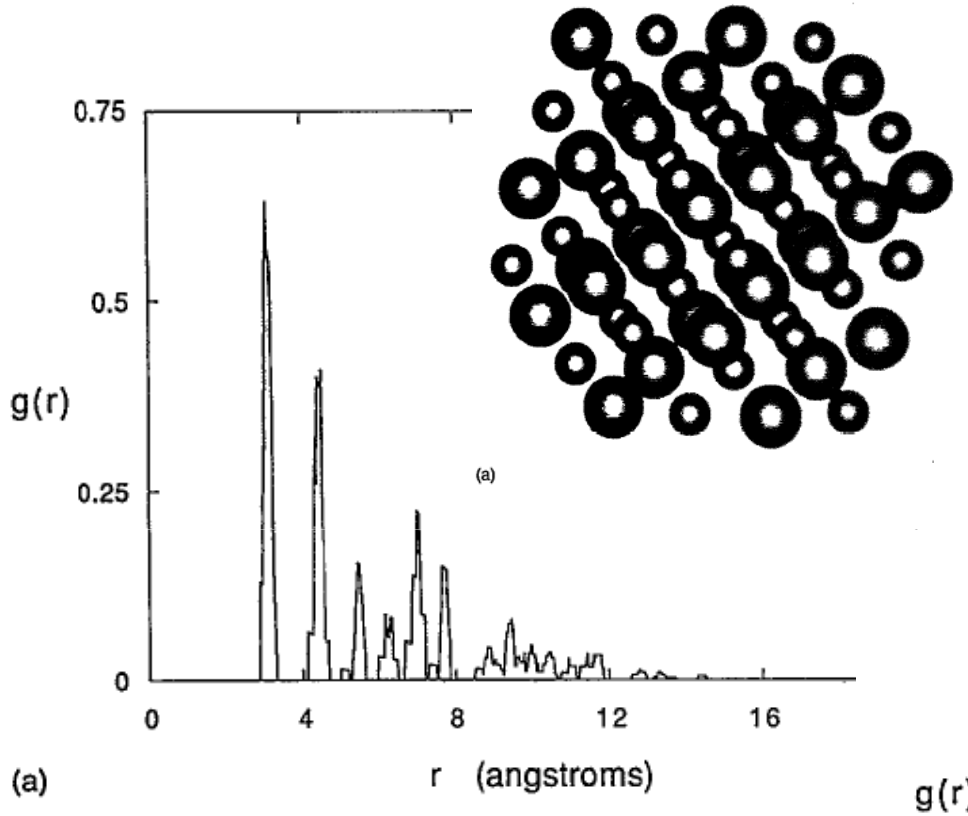
$\phi = -3.2993$ eV/ion

Quenching &
Steepest Descend - methods

$$\frac{dr}{dt} = -\nabla\Phi(r)$$

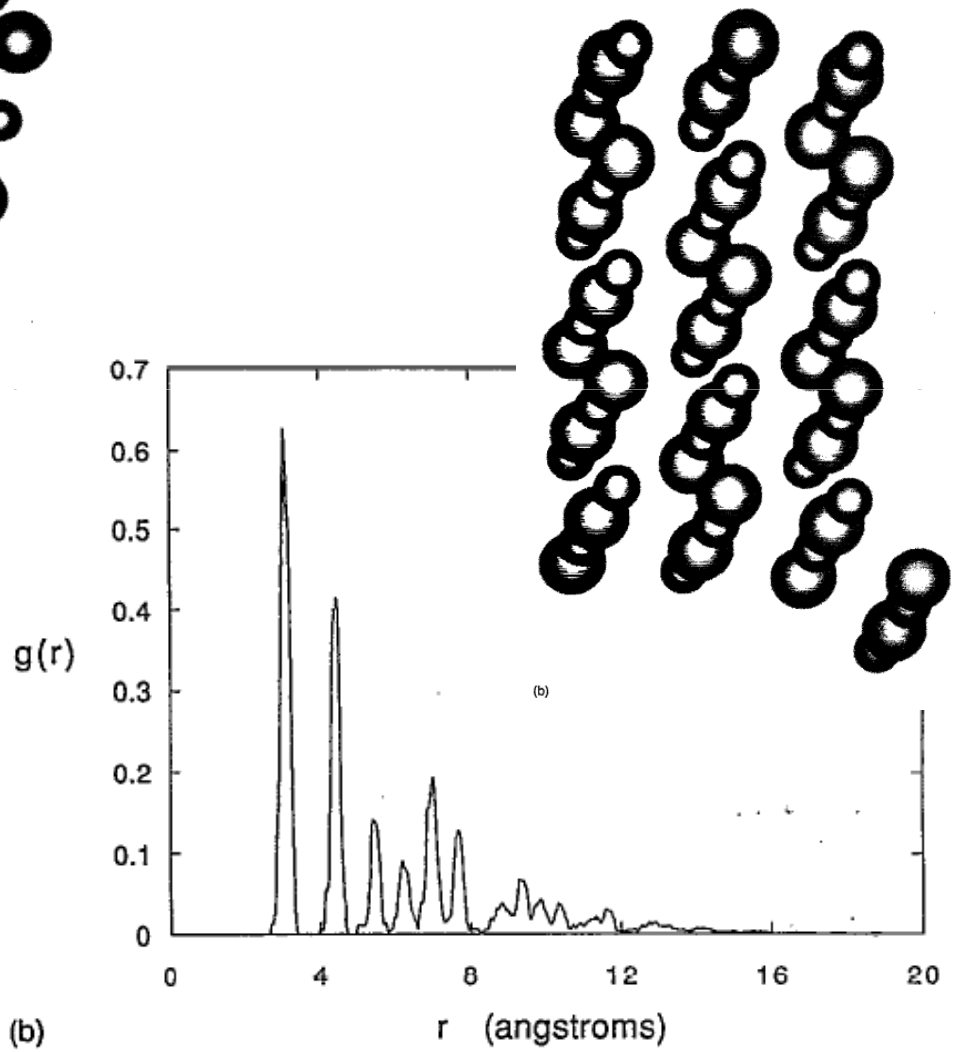
These are all stable (solid) structures corresponding to
"local minima" of the multi-dimensional Pot. Energy surface.

RDFs of Quenched Structures

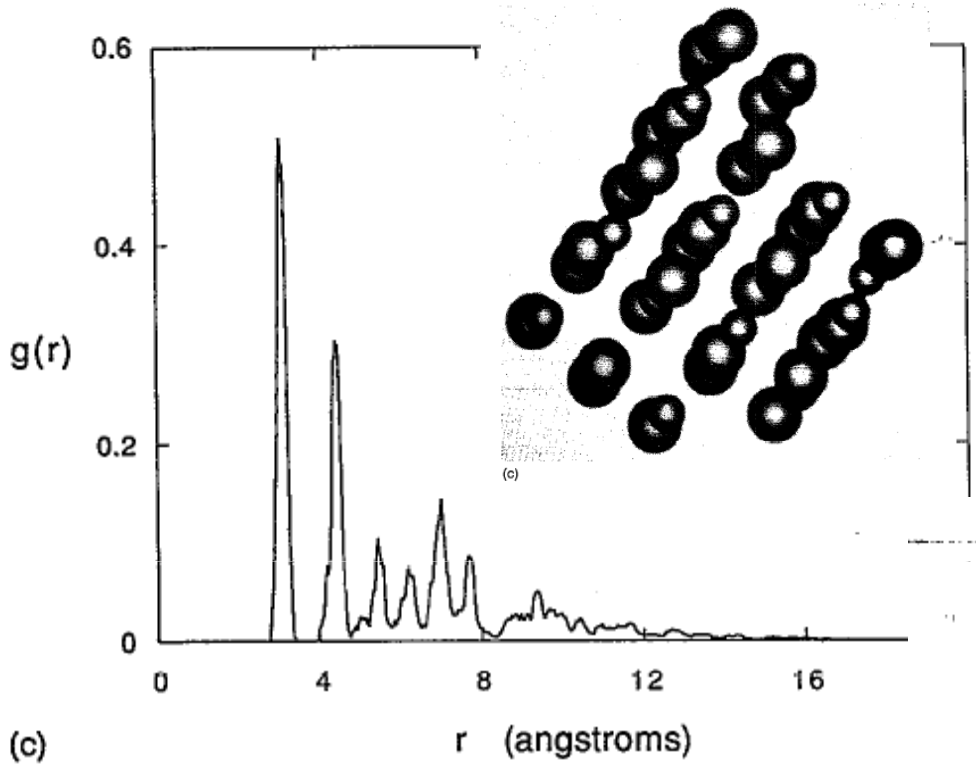


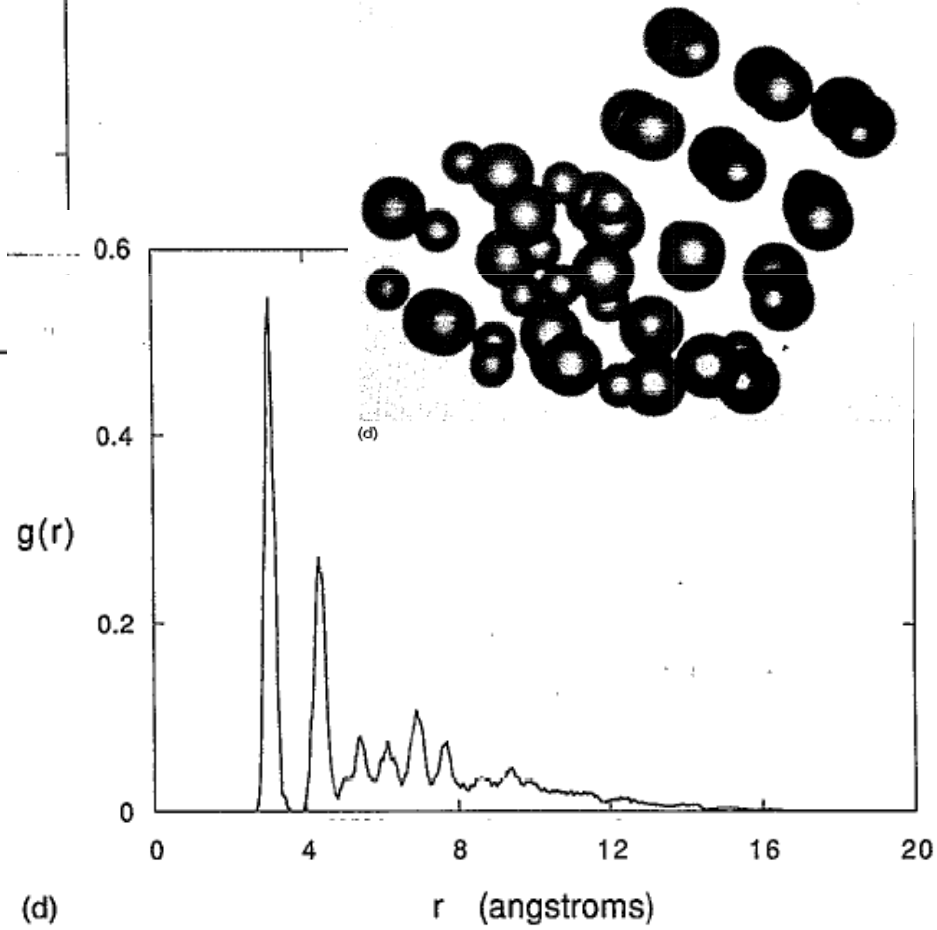
ground-state structure

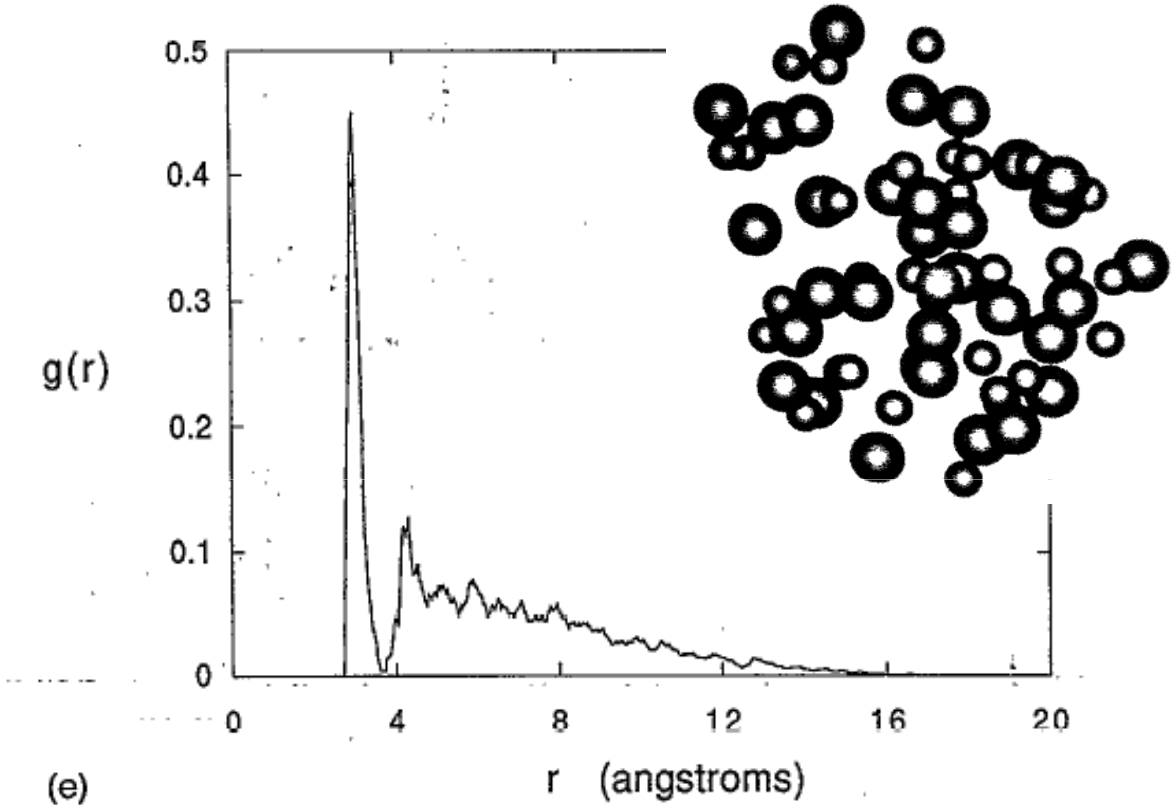
1st excited state



“non-wetted” structure

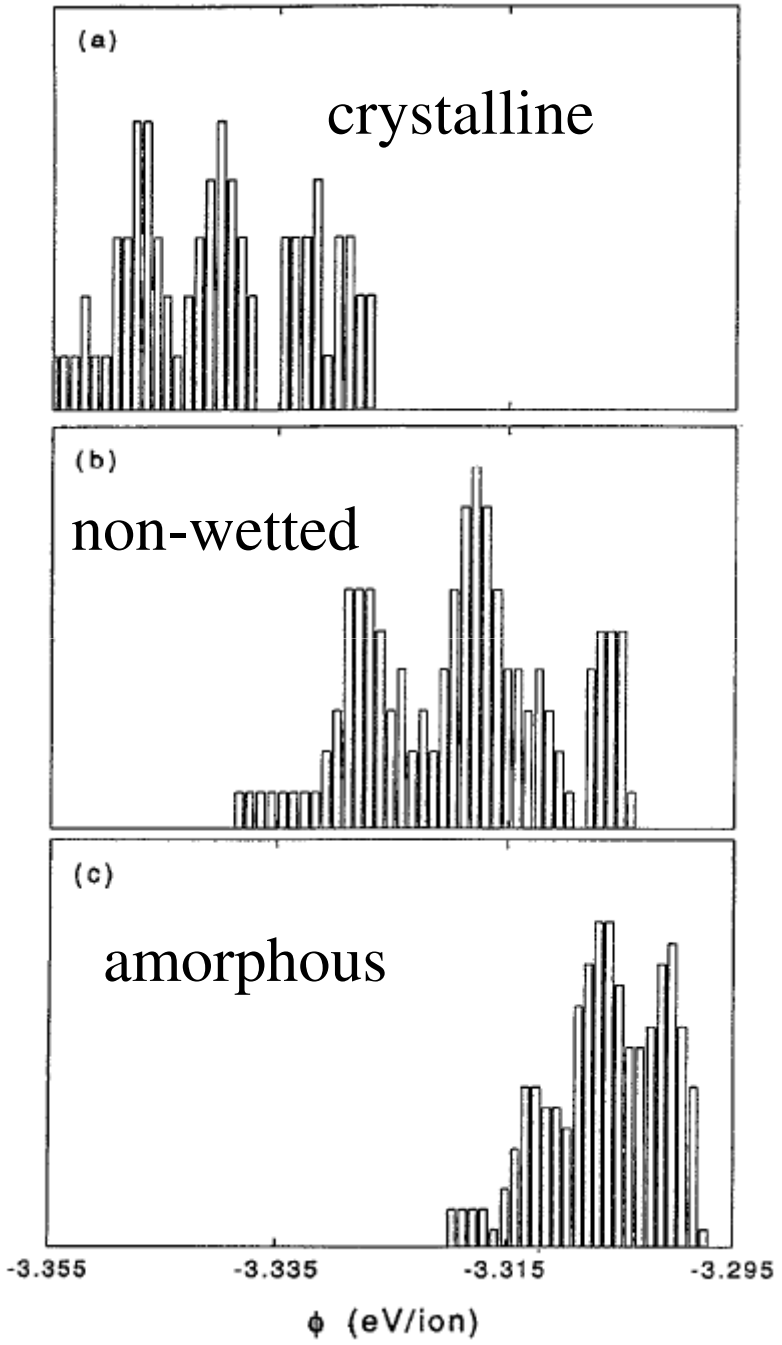






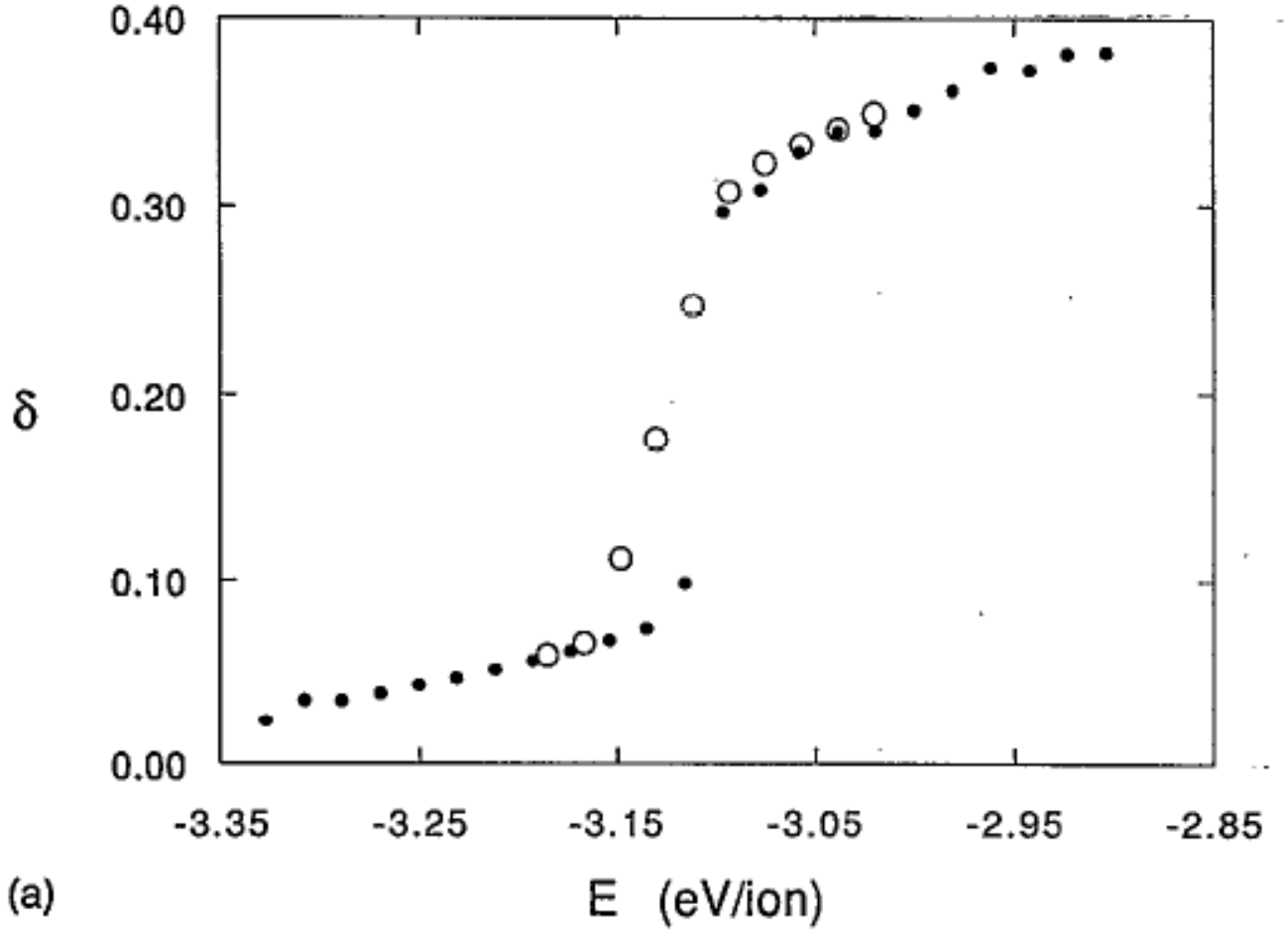
Amorphous/glassy phase

Statistics of quenched structures



RMS bond length fluctuation,

$$\delta = \frac{2}{N(N-1)} \sum_{i<j} \frac{(\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2)^{1/2}}{\langle r_{ij} \rangle}$$



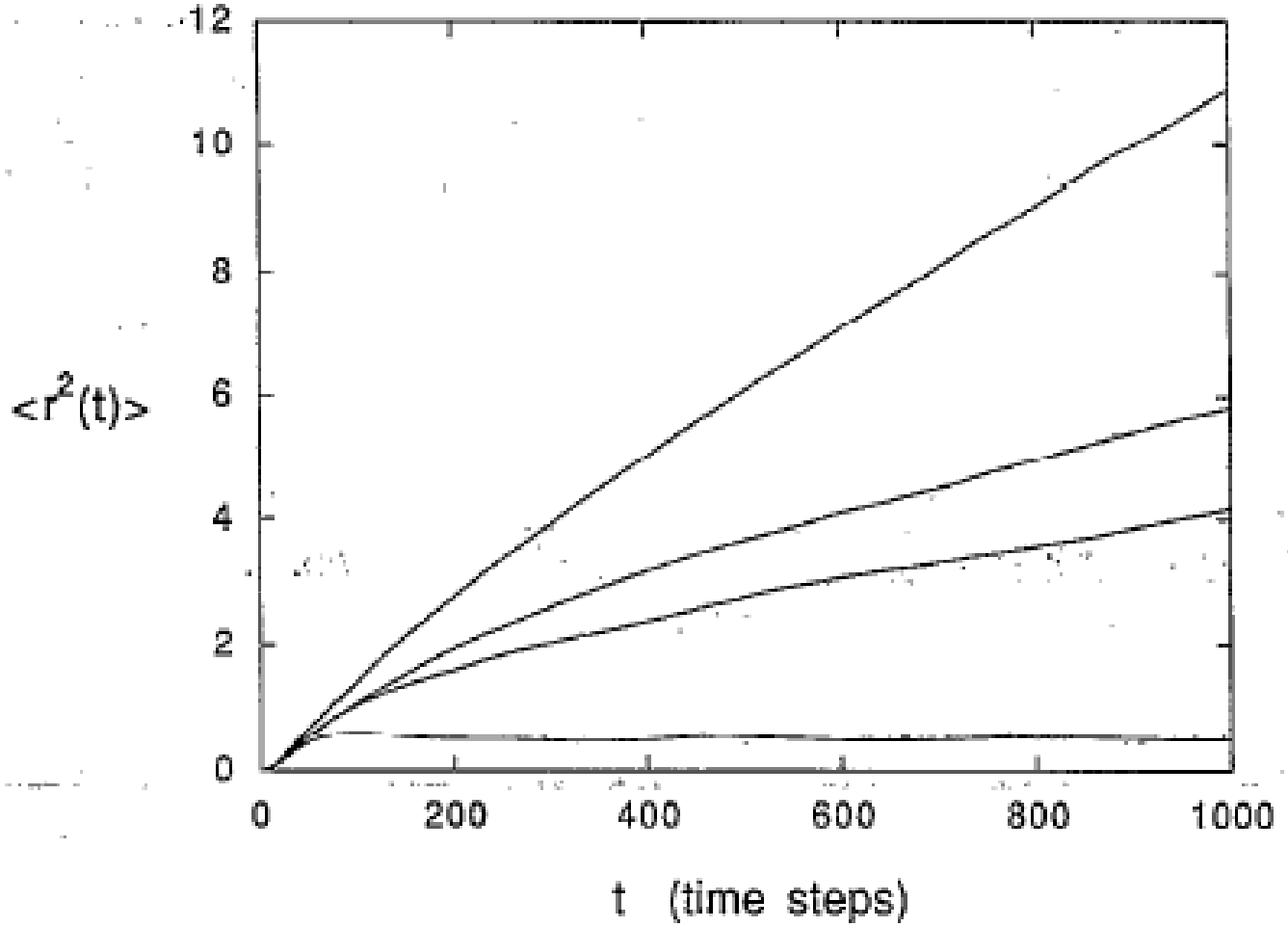


FIG. 6. Mean square displacement for $(KCl)_{32}$ at four energies; labeling from bottom to top, $E=-3.20$ eV/ion (solidlike), $E=-3.115$ eV/ion (melting region), $E=-3.107$ eV/ion (cold liquidlike) and $E=-3.05$ eV/ion (liquidlike).

Velocity Autocorrelation Spectrum,

$$c_{vv}(\tau) = \langle \mathbf{v}_i(\tau)\mathbf{v}_i(0)\rangle$$

Power Spectrum,

$$c_{VV}(\omega) = \int_{-\infty}^{\infty} d\tau\, e^{-i\omega\tau} c_{vv}(\tau)$$

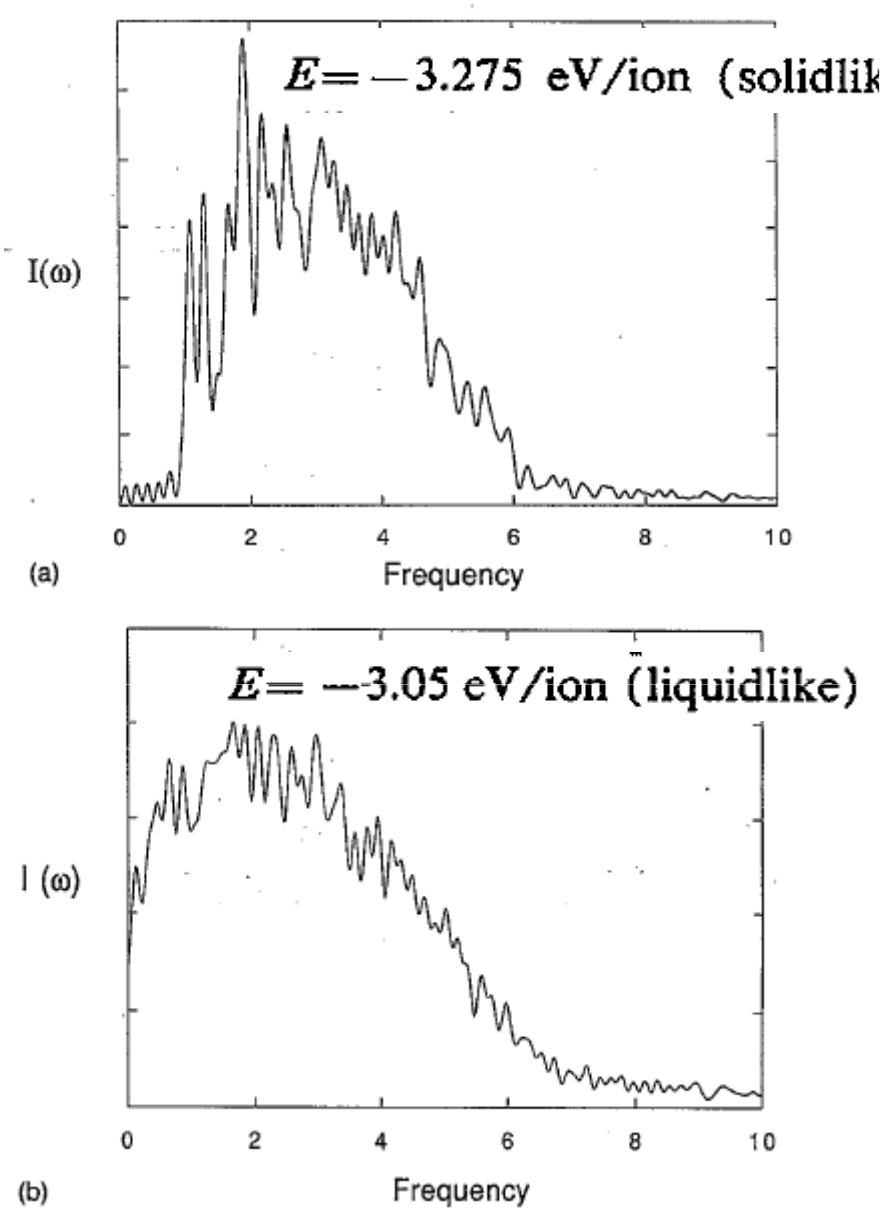


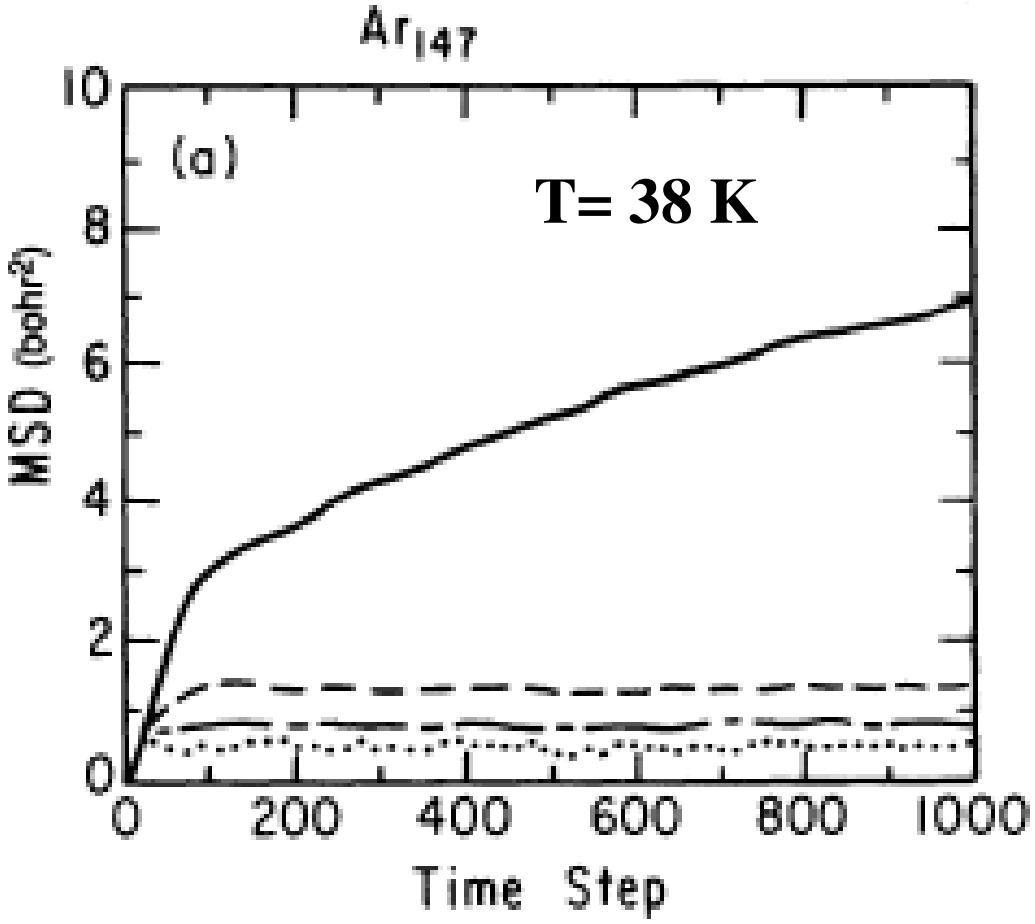
FIG. 7. Power spectra (a) $E = -3.275$ eV/ion (solidlike) and (b) $E = -3.05$ eV/ion (liquidlike). The units on the vertical scale are arbitrary and the frequency units on the horizontal scale are 10^{12} s^{-1}.

TABLE I. Representative self-diffusion constants D. The numbers for bulk KCl were calculated using Eq. (1) in Ref. 63 and the values for $(KCl)_4$ were taken from Ref. 24.

	Temperature (K)	D (10^5 cm^2/s)	Melting temperature (K)
Bulk KCl	1193	9.4[a]	1049
$(KCl)_{32}$	894	13.9	~750
$(KCl)_4$	1109	0.61	~700

[a]Average of the individual cation and anion self-diffusion constants.

Solid-Liquid Transition: Ar_{147} *vs* $(KCl)_{32}$

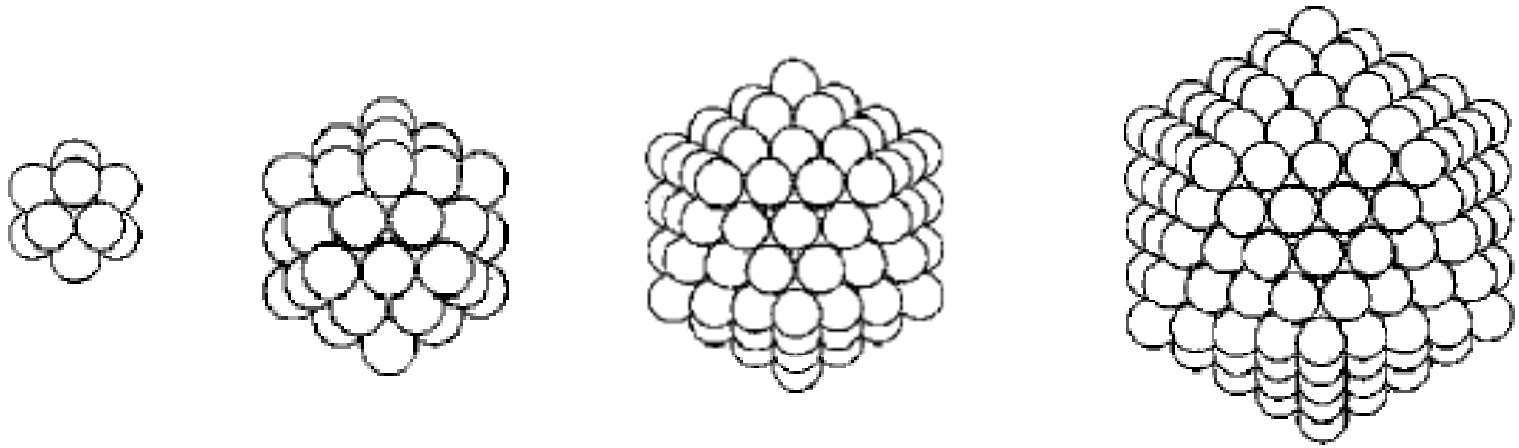


"Surface melting"
Inner core remains solid.

"wetting" phenomenon !
(in $\mathbf{Ar_{147}}$)

FIG. 4. Layer-by-layer mean-square displacements of atoms in Ar_{147} at two temperatures. The curves, top to bottom outermost, then successive layers moving inward. ~~Upper panel, 38.0~~,

Ar cluster Magic Numbers



Ar_{13} **Ar_{55}** **Ar_{147}** **Ar_{309}**

Stability depends on completion of icosahedral shells.

Solid-Liquid Transition in $(KCl)_{32}$

❑**No** evidence for a **"dynamical"** solid-liquid co-existence (**like in Ar_{13}**) is observed. *But still a possibility!*

❑ A crystal-like form co-existing simultaneously with a disordered structure is observed near the transition.

❑ However this transition is "**non-wetting**" in nature.
(the melted portion does not cover the solid portion uniformly).