ΥΠΟΛΟΓΙΣΤΙΚΗ ΜΑΘΗΜΑΤΙΚΗ ΧΗΜΕΙΑ

1ο ΣΕΜΙΝΑΡΙΑΚΟ ΜΑΘΗΜΑ

ΠΡΟΣΟΜΟΙΩΣΗ ΤΟΥ ΥΔΑΤΟΣ ΚΑΙ ΥΔΑΤΙΚΩΝ ΔΙΑΛΥΜΑΤΩΝ ΜΕ ΤΟ ΠΡΟΤΥΠΟ QM/MM

Βασικές έννοιες (Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

Με την παρούσα εισαγωγή επιθυμούμε να:

- **Παρουσιάσουμε τις δυνατότητες και τους περιορισμούς των MD προσομοιώσεων για επιστημονική και τεχνολογική έρευνα.**
- **Κατανοήσουμε τον συμβιβασμό ανάμεσα στην πολυπλοκότητα/ρεαλιστικότητα του μοντέλου και το υπολογιστικό κόστος.**
- **Δώσουμε τις απαραίτητες γνώσεις ώστε να κατανοούμε μελέτες που είναι διαθέσιμες στην βιβλιογραφία.**
- **Ερμηνεύσουμε τις θεωρητικές βάσεις των MDS**

Βασικές έννοιες (Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

Τι είναι η προσομοίωση MD;

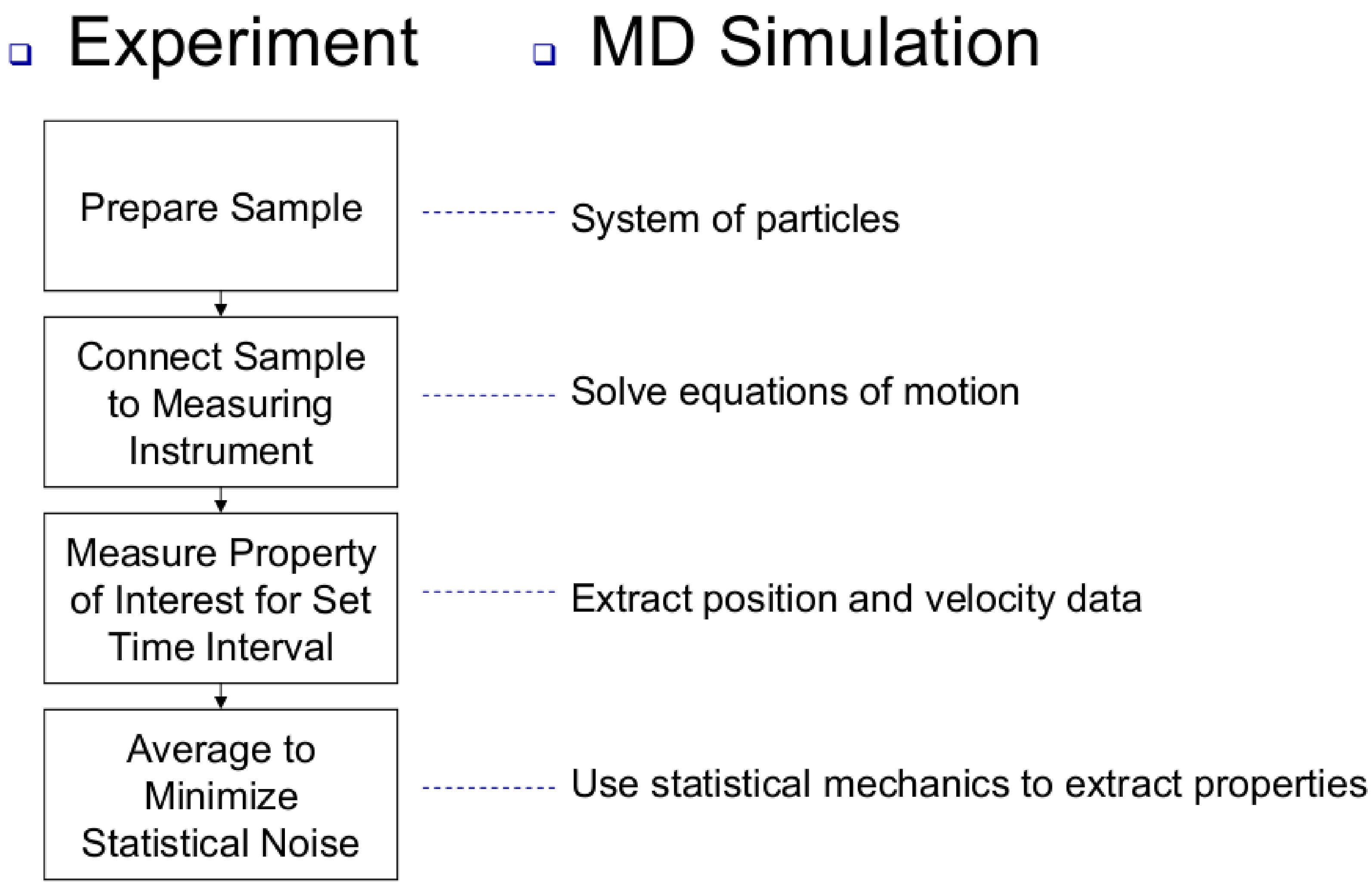
- **Είναι ένα υπολογιστικό εργαλείο που βοηθάει στον προσδιορισμό της θέσης, της ταχύτητας, και του προσανατολισμού σε διάφορες χρονικές στιγμές.**
- **Η προσομοίωση βασίζεται σε ένα σύνολο μοντέλων που περιγράφουν αλληλεπιδράσεις σε μοριακό επίπεδο.**
- **Αυτά τα μοντέλα αντιστοιχίζουν ενέργεια/δυνάμη στη διευθέτηση με σκοπό τον υπολογισμό της επιτάγχυνσης βάσει του νόμου του Newton**

Βασικές έννοιες (Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- **Η αριθμητική ολοκλήρωση μας δίνει τις ταχύτητες των σωματιδίων, και στη συνέχεια κάθε σωματίδιο μετακινείται σε απόσταση ίση με την ταχύτητά του επί το χρονικό βήμα.**
- **Εν ολίγοις μιλάμε για ένα υπολογιστικό “πείραμα” όπου ορίζουμε ένα σύστημα, το αφήνουμε να αναπτυχθεί, και εμείς καταγράφουμε την ανάπτυξή του.**

Βασικές έννοιες

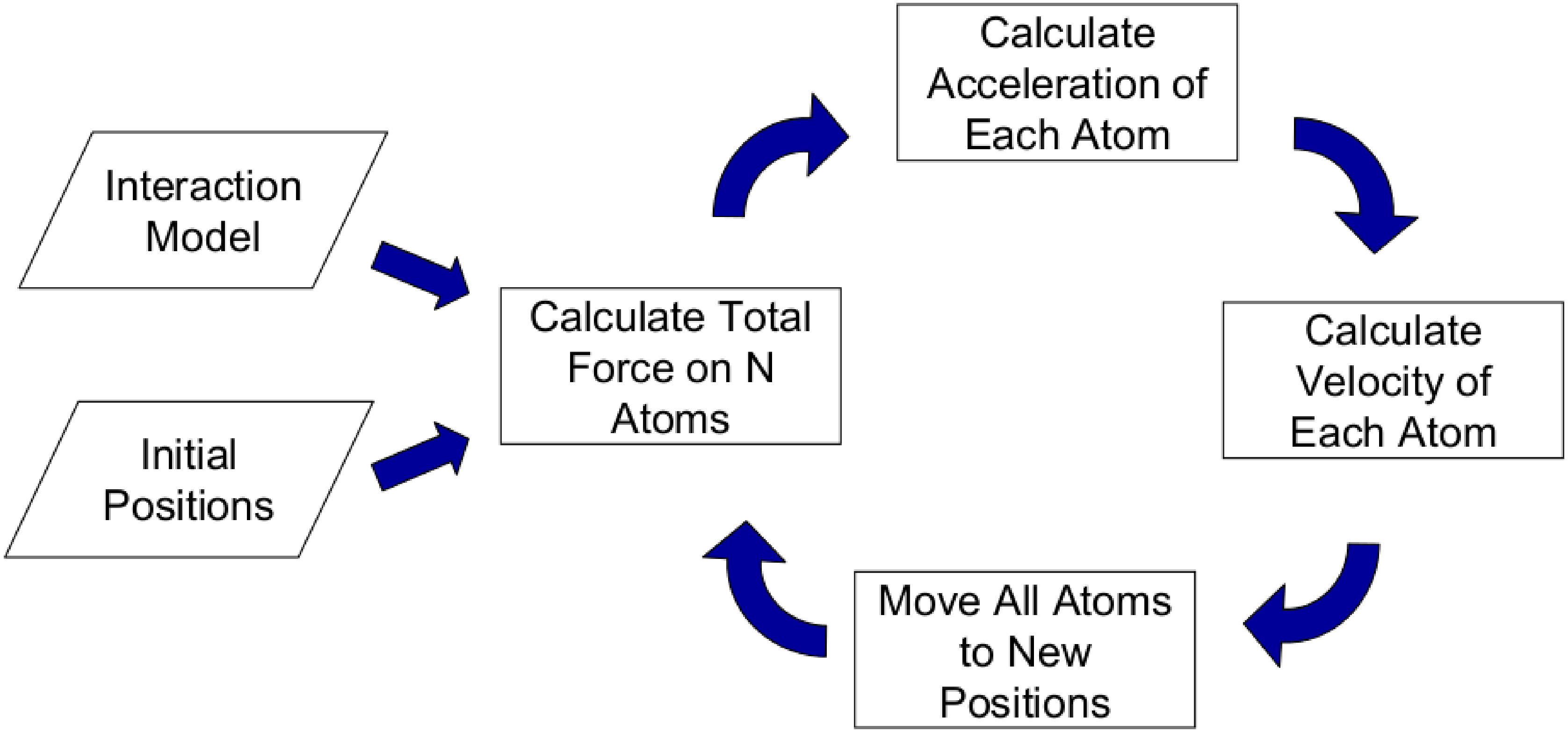
(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)



❑ Experiment	❑ MD Simulation
Prepare Sample	System of particles
Connect Sample to Measuring Instrument	Solve equations of motion
Measure Property of Interest for Set Time Interval	Extract position and velocity data
Average to Minimize Statistical Noise	Use statistical mechanics to extract properties

Βασικές έννοιες (Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- Process summary



Interaction Model

Initial Positions

Calculate Total Force on N Atoms

Calculate Acceleration of Each Atom

Calculate Velocity of Each Atom

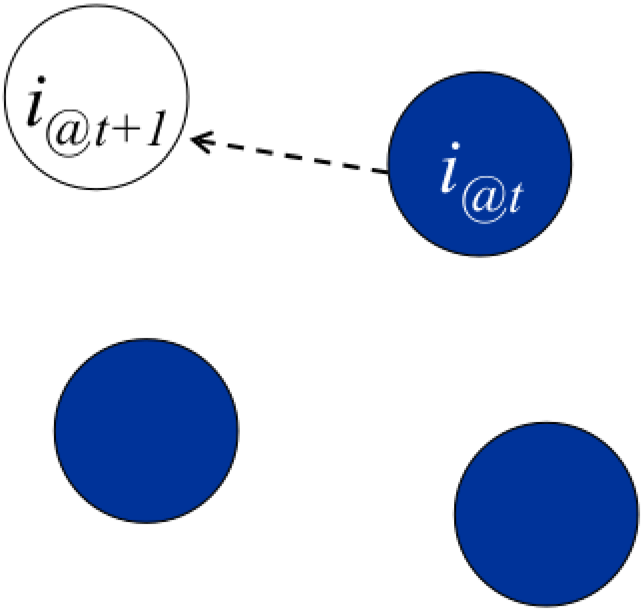
Move All Atoms to New Positions

Βασικές έννοιες

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

Δύναμη → Επιτάγχυνση → Ταχύτητα → Θέση

$$\vec{F}_i = m_i \vec{a}_i \qquad \vec{a}_i = \frac{d\vec{v}_i}{dt} \qquad \vec{v}_i = \frac{d\vec{r}_i}{dt}$$



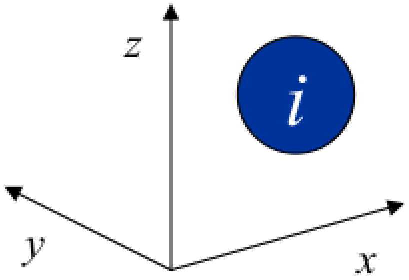
Βασικές έννοιες (Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

Στη διάρκεια της προσομοίωσης η ενέργεια διατηρείται

$$H(\vec{p}_i,\vec{r}_i)=\underbrace{\sum_{i=1}^{N}\frac{\vec{p}_i^{\,2}}{2m_i}}_{\text{KE}}+\underbrace{U(\vec{r}_i)}_{\text{PE}} \qquad \frac{dH}{dt}=0$$

Βασικές έννοιες (Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

Κάθε άτομο περιγράφεται από τα διανύσματα α) χρονικά εξαρτώμενης θέσης του, και β) ροπής του.



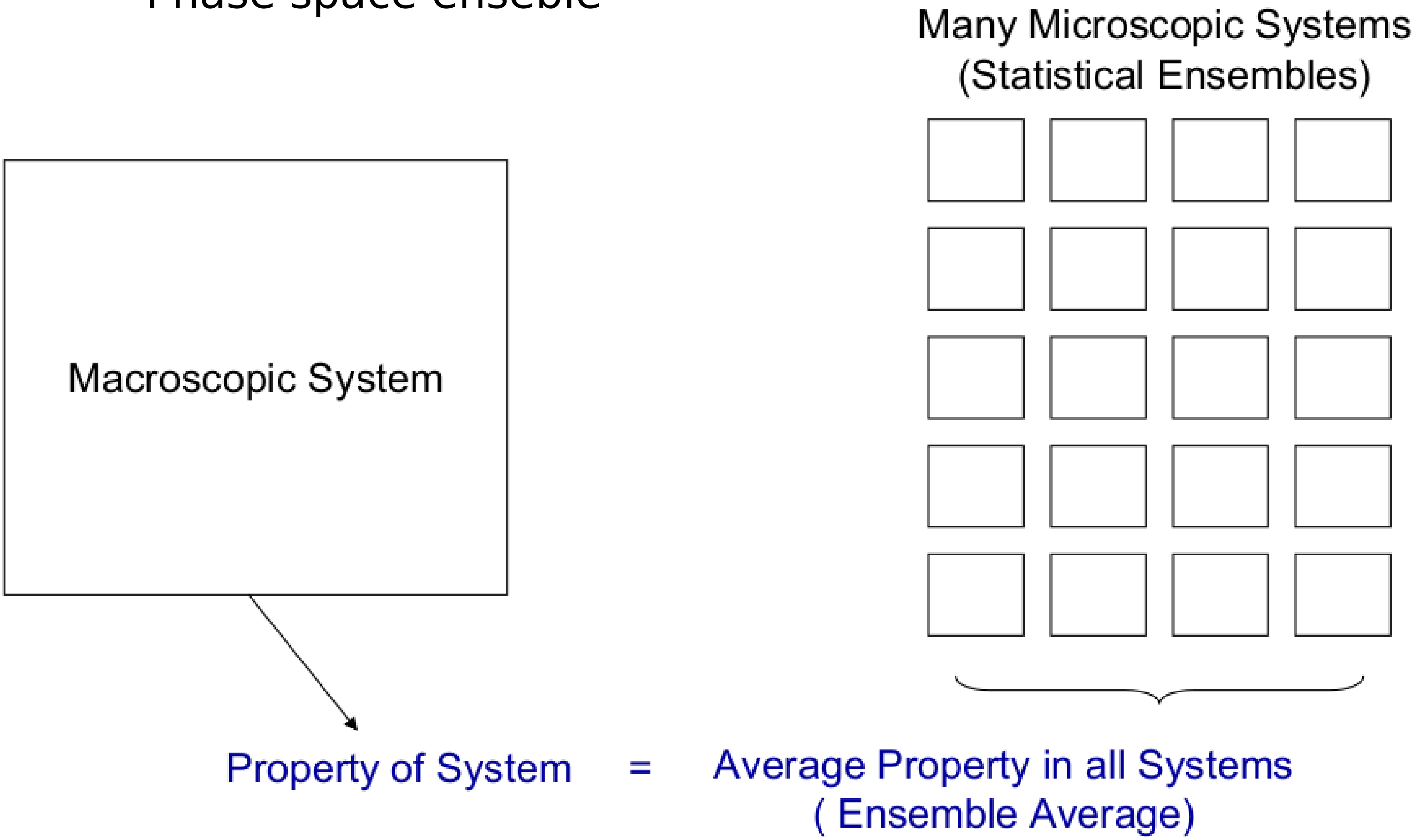
$$\vec{r}_i \qquad \vec{p}_i = m\vec{v}_i$$

Σε κάποια στιγμή το σύστημα περιγράφεται από τη θέση (3 διαστάσεις) και τη ροπή (3 διαστάσεις) των N σωματιδίων

Δλδ 6 N-διαστάσεων ..... Phase-Space

Βασικές έννοιες (Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

Phase space enseble



Many Microscopic Systems
(Statistical Ensembles)

Macroscopic System

Property of System = Average Property in all Systems
(Ensemble Average)

Βασικές έννοιες (Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- **Το σύνολο των εικόνων (δλδ θέσεων-ροπών στο χρόνο) χαρακτηρίζεται από θερμοδυναμικές μεταβλητές**

- ➢ **Ενεργεια**
- ➢ **Θερμοκρασία**
- ➢ **Όγκος**
- ➢ **Αριθμός σωματιδιών**
- ➢ **Χημικό δυναμικό**

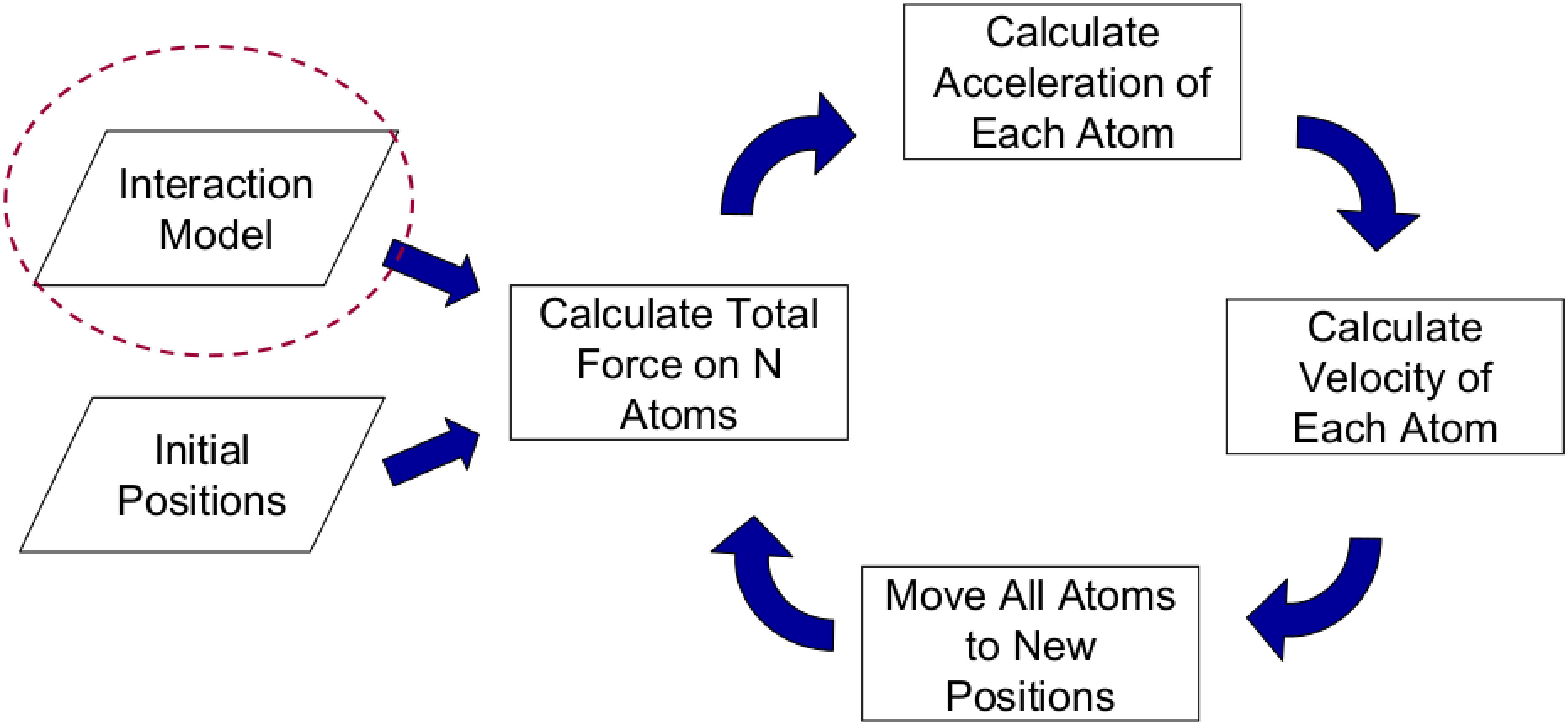
Μια προσομοίωση MD-NVE δίνει ένα *μικροκανονικό σύνολο.*

Ενώ NVT *κανονικό*, NPT *ισόθερμο-ισοβαρές*, μVT *μέγα-κανονικό*.

Συναρτήσεις Επιφάνειας Δυναμικού

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- Process summary



Interaction Model

Initial Positions

Calculate Total Force on N Atoms

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Calculate Velocity of Each Atom

Move All Atoms to New Positions

Συναρτήσεις Επιφάνειας Δυναμικού

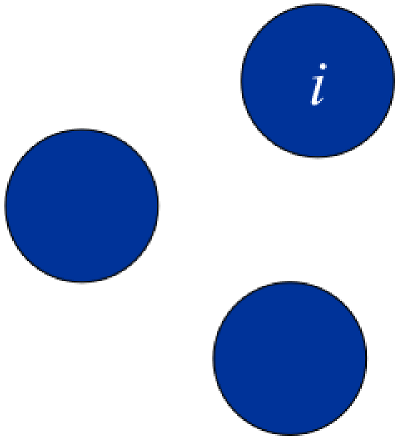
(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- **Αλληλέπιδραση…**

$$ma = F$$

$$a = \frac{dv}{dt} \qquad v = \frac{dr}{dt}$$

$$F = \frac{dU}{dr}$$

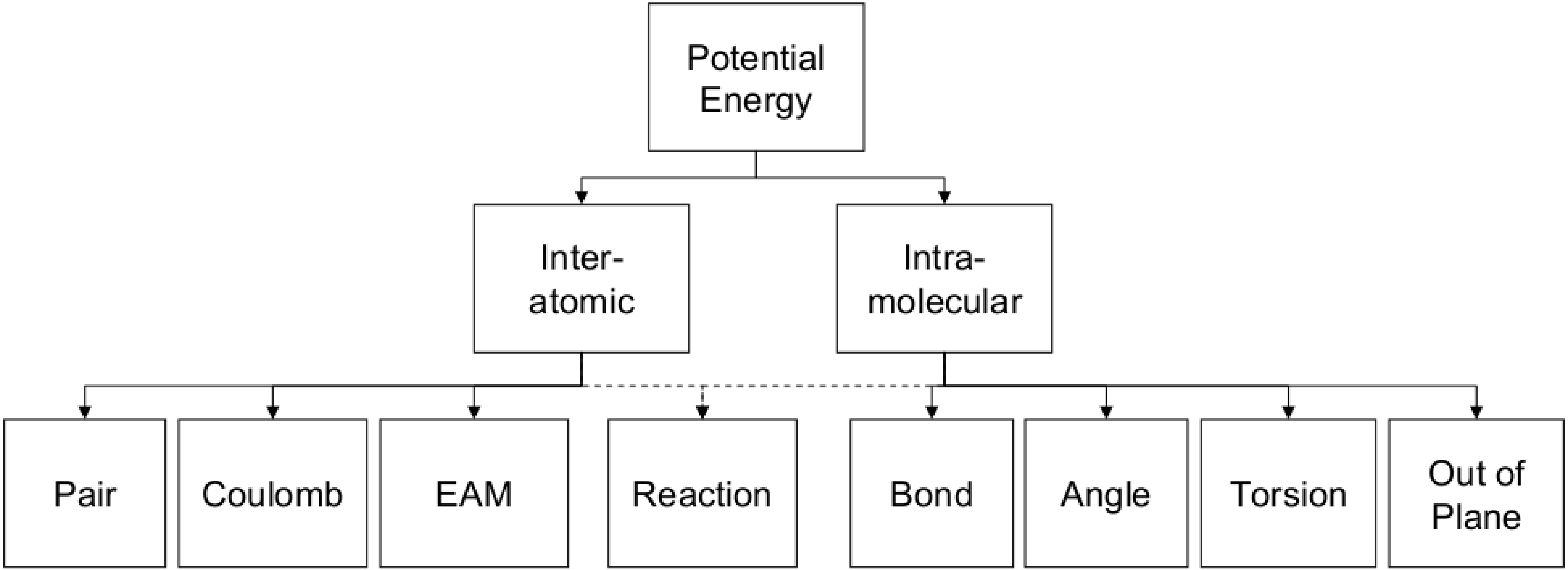


Interaction force is the spatial derivative of the potential energy

Συναρτήσεις Επιφάνειας Δυναμικού

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- **Αλληλέπιδραση...**



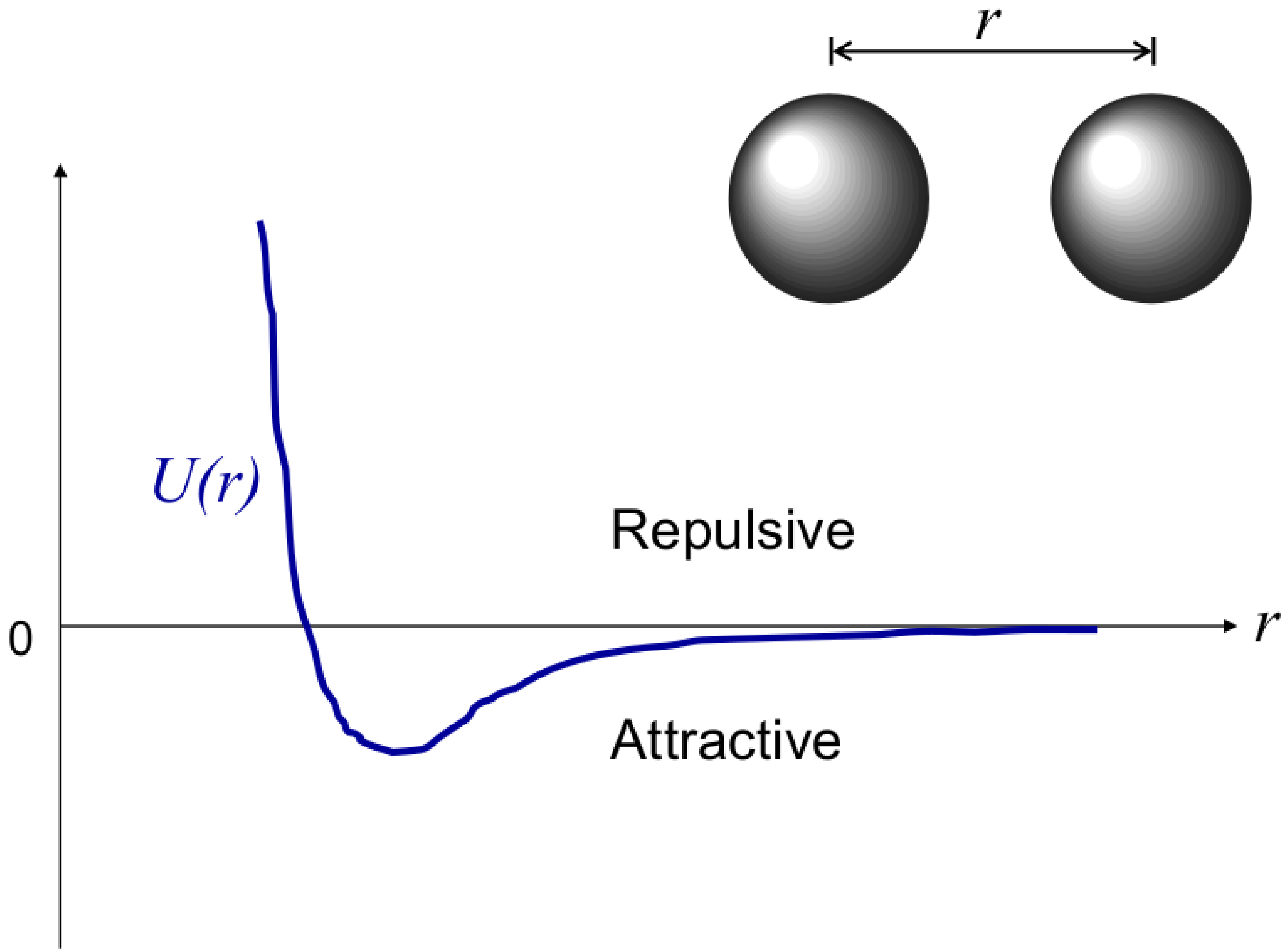
Δυναμικά Αλληλεπίδρασης

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- **Δυναμικά αλληλέπιδρασης- van der Waals αλληλεπιδράσεις**
- **Έλξη**
  - **Δρούν σε μεγάλες αποστάσεις**
  - **Dispersive δυνάμεις**
  - **Δημιουργούνται από δίπολα(όχι μόνιμα) που εμφανίζονται λόγω ανισοκατανομής τους φορτίου**
- **Άπωση**
  - **Δρούν σε μικρές αποστάσεις**
  - **Είναι δυνάμης ανταλλαγής ή αλληλεπικάλυψης**
  - **Αλληλεπικάλυψη ηλεκτρονιακού νέφους ώστε οι πυρήνες να νοιώθουν λιγότερο προστατευμένοι από τα ηλεκτρόνια…**

Δυναμικά Αλληλεπίδρασης

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)



Δυναμικά Αλληλεπίδρασης

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- Pair potentials
  - General Form

$$U(r) = k\varepsilon\left(\left(\frac{\sigma}{r}\right)^{n} - \left(\frac{\sigma}{r}\right)^{m}\right) \qquad k = \frac{n}{n-m}\left(\frac{n}{m}\right)^{m/(n-m)}$$

Repulsive Attractive

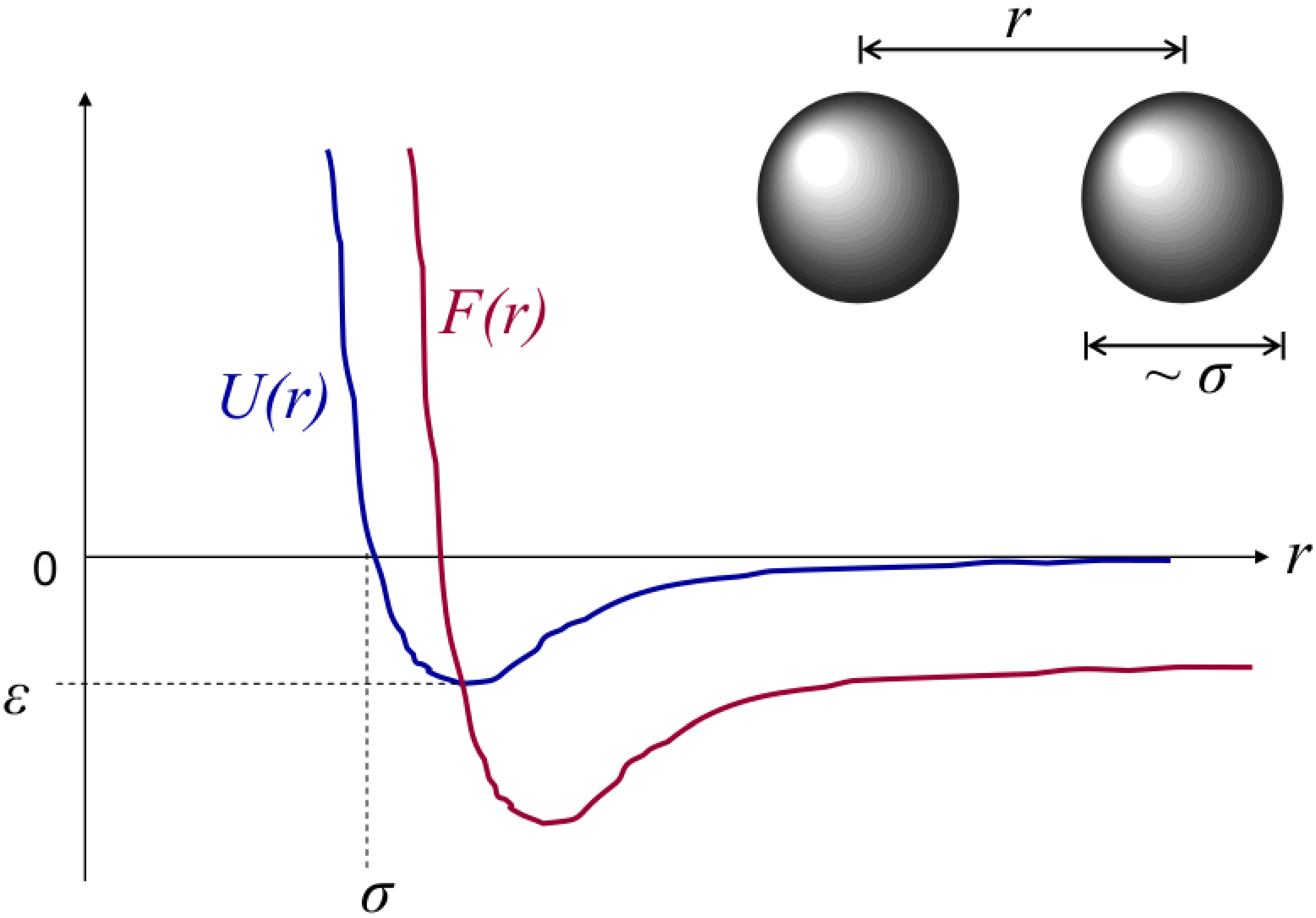
  - Lennard-Jones (n=12, m=6)

$$U_{LJ}(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

$$F_{LJ}(r) = -\frac{dU(r)}{dr} = 24\frac{\varepsilon}{\sigma}\left(2\left(\frac{\sigma}{r}\right)^{13} - \left(\frac{\sigma}{r}\right)^{7}\right)$$

Δυναμικά Αλληλεπίδρασης

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)



Δυναμικά Αλληλεπίδρασης

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- Truncation
  - The Lennard-Jones force (and similar models) decays rapidly with distance
  - Significant computation time can be saved by neglecting pair interactions beyond a cut-off

$$U_{LJ,t}(r) = \begin{cases} 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) & r \le r_c \\ 0 & r > r_c \end{cases}$$

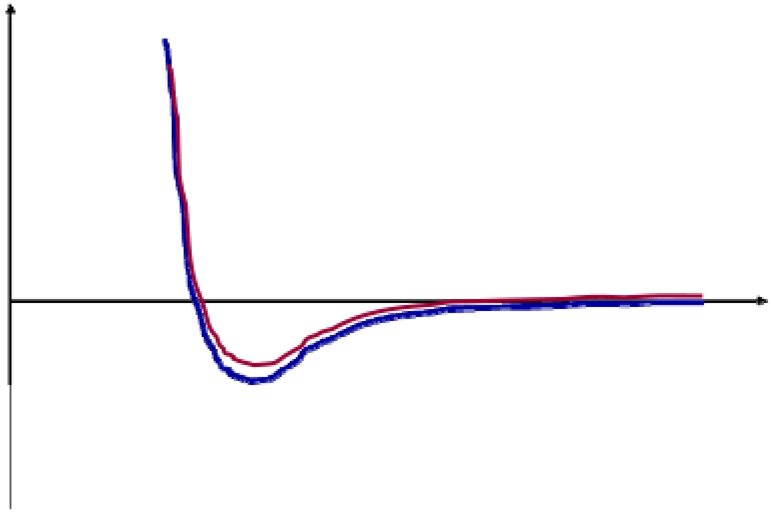
  - Commonly, $r_c = 2.5\,\sigma$

Δυναμικά Αλληλεπίδρασης

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- Truncated and shifted
  - The potential energy vanishes at the cut off radius
  - No discontinuity → no impulsive force

$$U_{LJ,t-s}(r) = \begin{cases} U_{LJ}(r) - U_{LJ}(r_c) & r \le r_c \\ 0 & r > r_c \end{cases}$$

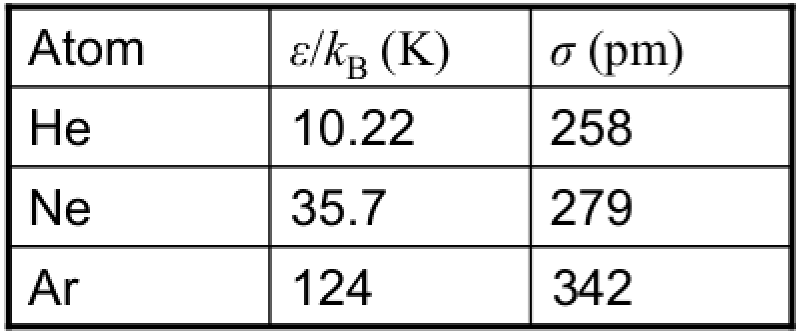


  - Shift must be taken into account in all post-processing calculations

Δυναμικά Αλληλεπίδρασης

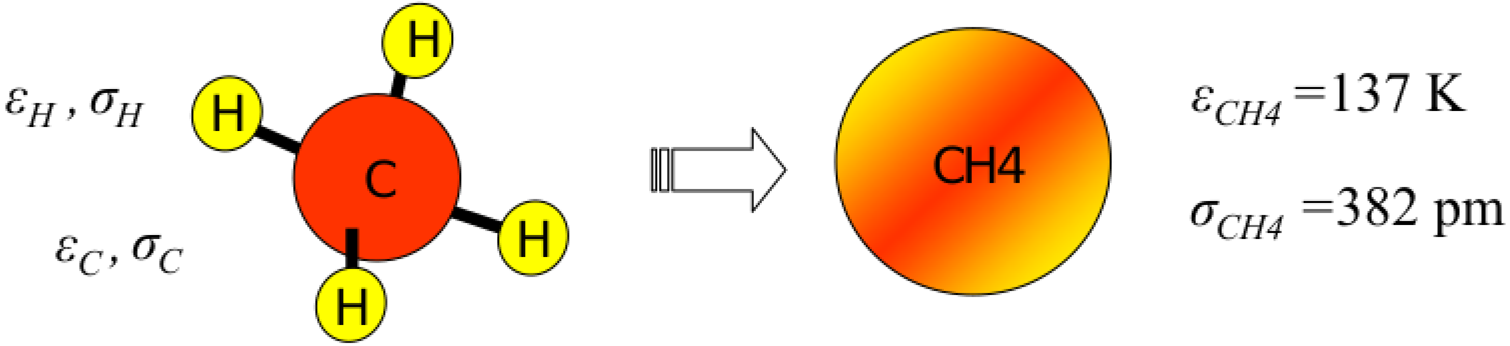
(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- Typical values of LJ constants



Atom	ε/k_B (K)	σ (pm)
He	10.22	258
Ne	35.7	279
Ar	124	342

- The united atom model



ε_{CH4} =137 K

σ_{CH4} =382 pm

Δυναμικά Αλληλεπίδρασης

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- Combination rules
  - Relate LJ parameters for an unlike pair (i-j) to the parameters of two like pairs (i-i and j-j)

1. $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ $\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$

2. $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ $\sigma_{ij} = \dfrac{\sigma_i + \sigma_j}{2}$

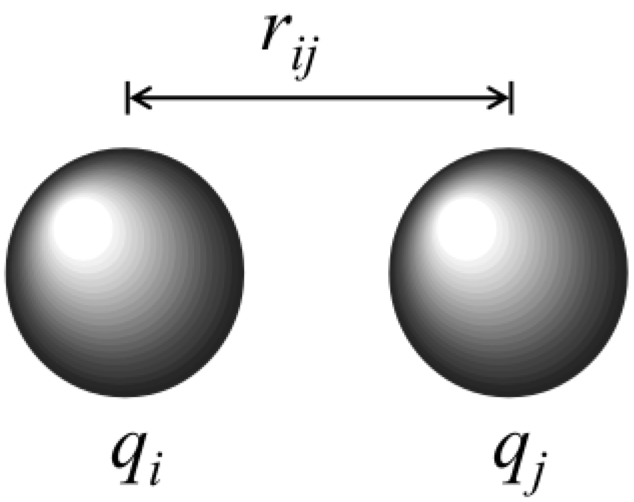
3. $\varepsilon_{ij} = \dfrac{2\sigma_i^3 \sigma_j^3 \sqrt{\varepsilon_i \varepsilon_j}}{\sigma_i^6 + \sigma_j^6}$ $\sigma_{ij} = \left(\dfrac{\sigma_i^6 + \sigma_j^6}{2}\right)^{1/6}$

Αλληλεπιδράσεις Coulomb

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- Coulombic interactions
  - Included if electrostatics between atoms are significant
  - Atomic charges q_i and q_j

$$U_{coulomb} = \frac{1}{4\pi\varepsilon_0}\frac{q_i q_j}{r_{ij}}$$



Αλληλεπιδράσεις Coulomb

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- In general, the contribution of the tail of a truncated potential is

$$U^{tail} = \frac{N\rho}{2}\int_{r_c}^{\infty} U(r)4\pi r^2 dr$$

- Coulombic force decays slower than r^{-3}
- Methods for calculating the long-range contributions
  - Ewald summation
  - Fast multipole methods
  - Particle-mesh-based methods

Αλληλεπιδράσεις Coulomb

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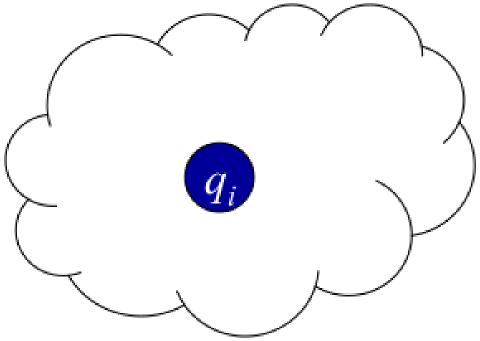
Αλληλεπιδράσεις Coulomb

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- **Ewald sums**
- **Υποθέτουμε ότι κάθε σωματίδιο “i” με φορτίο q_i περιστοιχίζεται από μια διάχυτη κατανομή φορτίου αντίθετου προσήμου.**



- **Το ηλεκτροστατικό δυναμικό λόγω του “i” οφείλεται αποκλειστικά στο μέρους του φορτίου που δεν “βλέπει” το νέφος**
- **Αυτό το μέρος γρήγορα τείνει στο μηδέν**

Αλληλεπιδράσεις Coulomb

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

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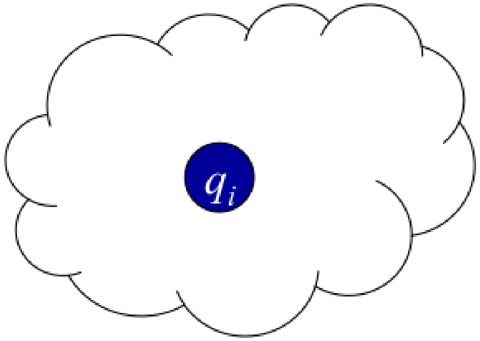

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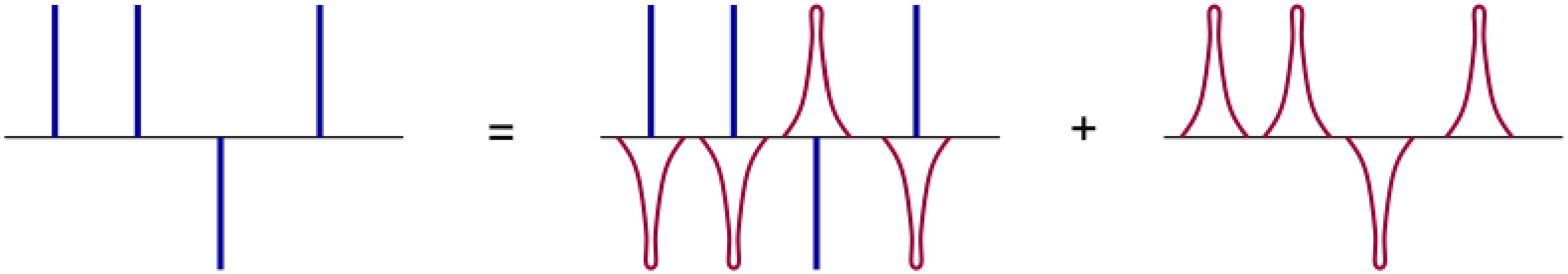
- **Αυτό το μέρος γρήγορα τείνει στο μηδέν**
- **Η συνεισφορά του ηλεκτροστατικού δυναμικού λόγω των φορτίων που “βλέπει” το νέφος μπορεί να βρεθεί με απεύθειας ολοκλήρωση**

Αλληλεπιδράσεις Coulomb

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- **Ewald sums**
  - **Βέβαια εμείς επιθυμούμε να μελετήσουμε την συνεισφορά σημειακών φορτίων**
  - **Οπότε εισάγουμε μια διόρθωση**

point charges = (point charges + screening cloud) + compensating cloud

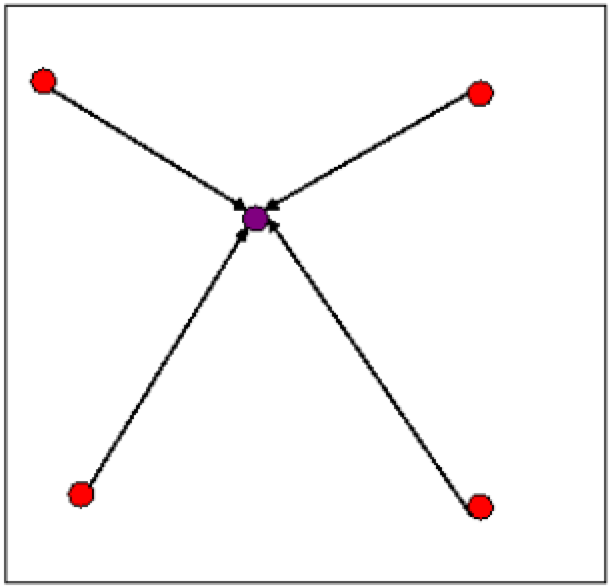


Embedded Atom Model

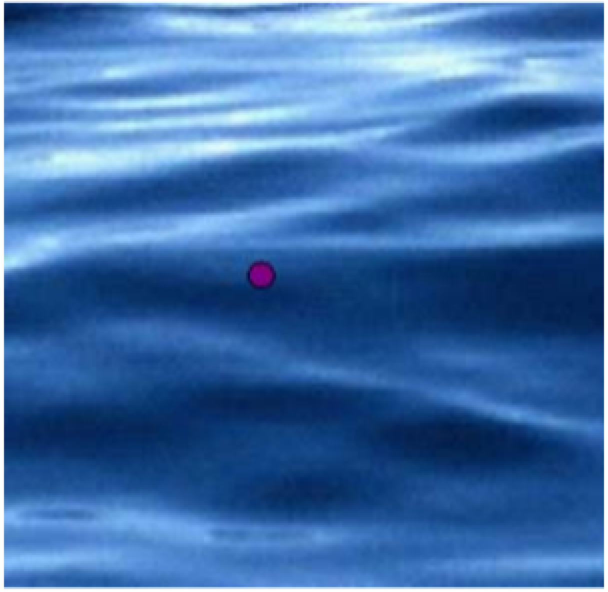
(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- Metals have ionized atom cores with a “sea” of delocalized valence electrons

Pair Potential



Electron Sea



Embedded Atom Model

(Prof. A. Martini, Purdue University, *Short Course on MD Simulation*)

- Model formulation

$$E_{total} = \sum_i F(\rho_i) + \frac{1}{2} \sum_{i,j(i \neq j)} \phi(r_{ij}) \qquad \rho_i = \sum_j f(r_{ij})$$

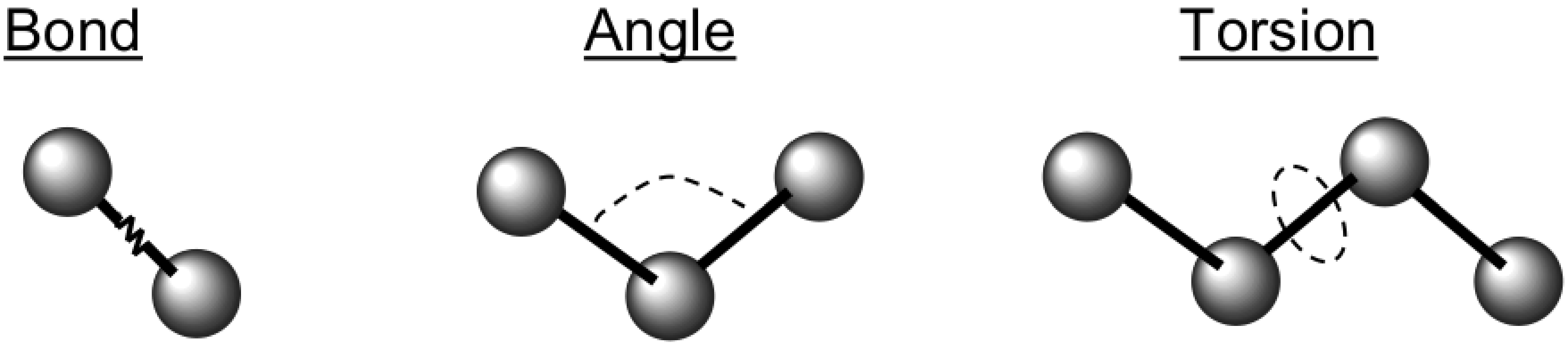
  - ρ_i : electron density at atom i
  - $F(\rho_i)$: embedding function
  - $\varphi(r_{ij})$: pair potential between atoms i and j
  - $f(r_{ij})$: electron density function at atom i due to atom j

- Three look-up tables

r_{ij}	$f(r_{ij}) - -electrondensityfunction$
ρ_i	$F(\rho_i) - -embeddingfuction$
r_{ij}	$\phi(r_{ij}) - -pairpotentialfunction$

Ενδομοριακές αλληλεπιδράσεις

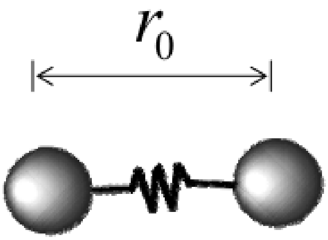
- **Για πολυατομικά μόρια, τα μοντέλα περιγράφουν τη συμπεριφορά ομοιοπολικών δεσμών**



Ενδομοριακές αλληλεπιδράσεις

- Bond stretching models
  - Harmonic bond model where k is the “spring constant”

$$U_{bond} = \frac{k}{2}(r - r_0)^2$$



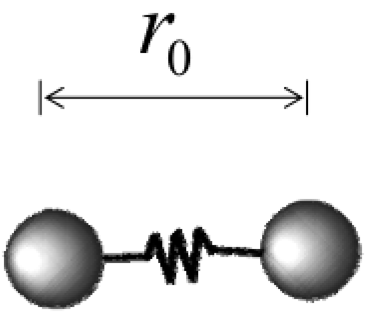
  - What is r_0
    - Reference bond length – value of bond when all other terms in the force field are zero
    - Equilibrium bond length – value when other terms contribute

Bond	r0 (A)	K (kcal/mol/A^2)
C-C	1.523	317
C=C	1.337	690

Ενδομοριακές αλληλεπιδράσεις-Δεσμός

- Bond stretching models
  - Morse bond potential where D is the potential well depth, α is a stiffness constant, and r_0 is the equilibrium bond distance
  - Better handling of large displacements

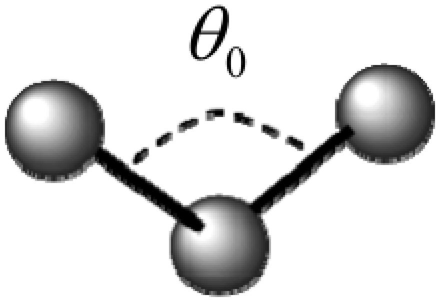
$$U_{bond} = D\left[1 - e^{-\alpha(r - r_0)}\right]^2$$



Ενδομοριακές αλληλεπιδράσεις-Γωνία

- Bond angle models
  - Harmonic angle model

$$U_{angle} = k(\theta - \theta_0)^2$$



  - Cosine angle models

$$U_{angle} = k[1 + \cos(\theta)]$$

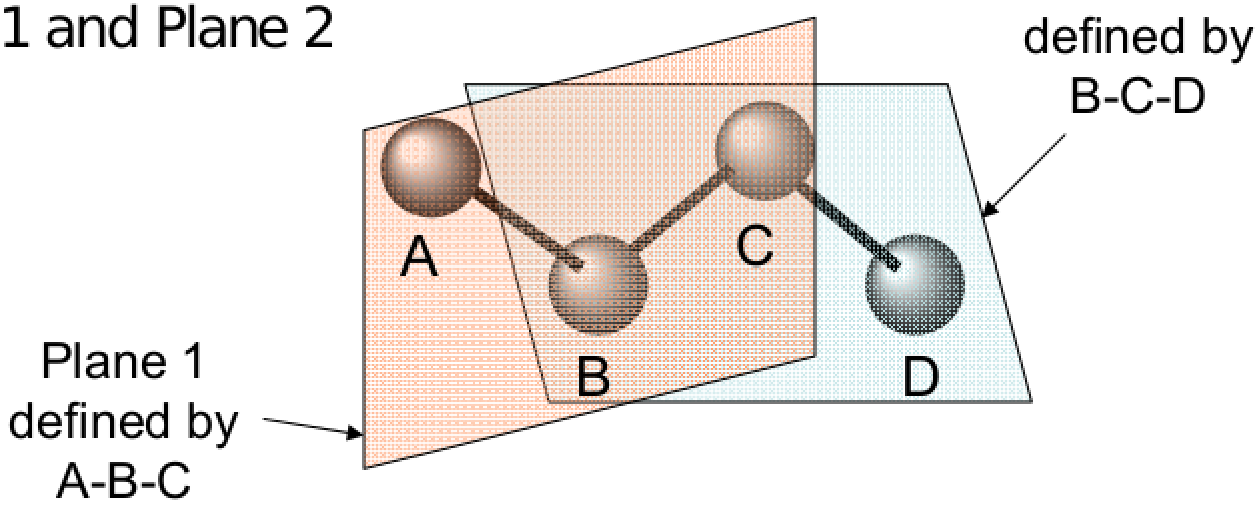
  - For all of these, k is energy constant and θ_0 is the equilibrium angle

Ενδομοριακές αλληλεπιδράσεις-Στρέψη

- Torsion models (dihedrals)
  - Harmonic torsion angle

$$U_{torsion} = k[1 + d\cos(n\phi)]$$

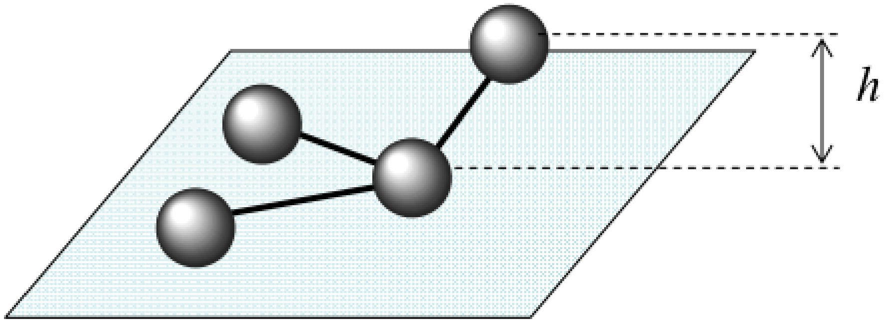
ϕ is the angle between Plane 1 and Plane 2



Ενδομοριακές αλληλεπιδράσεις- εκτός επιπέδου

- Out of plane models
  - The least common of the intramolecular potentials
  - Describes energy associated with the displacement of atoms out of their equilibrium plane
  - Relevant only to parts of molecules where atoms are known to lie in the same plane

$$U_{oop} = kh^2$$



Αλγόριθμοι Ολοκλήρωσης

- **Η δυναμική ενέργεια (ή δύναμη) είναι μια συνάρτηση των ατομικών θέσεων…αρα 3Ν μεταβλητών**
- **Δεν υπάρχει αναλυτική λύση των εξισώσεων κίνησης οπότε πρέπει να επιλυθούν αριθμητικά:**

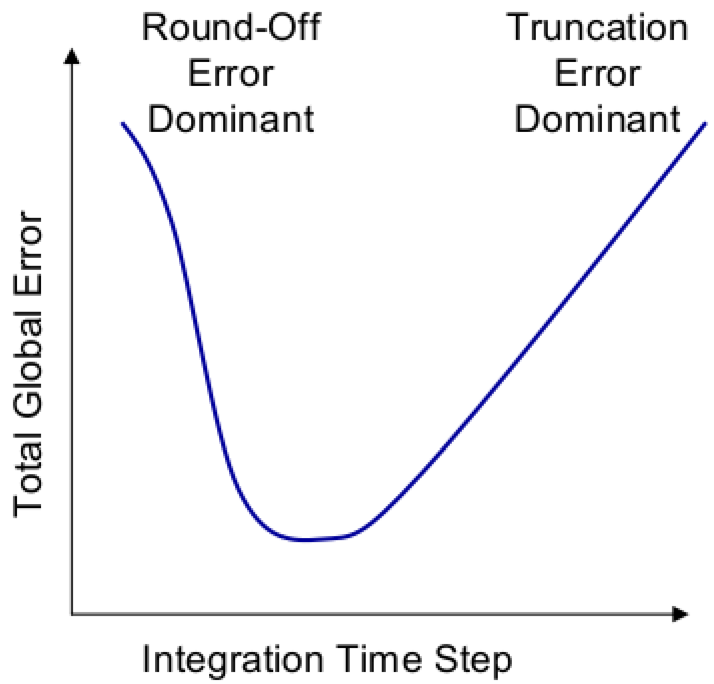
$$\vec{F}_i = m_i \vec{a}_i \qquad \vec{a}_i = \frac{d\vec{v}_i}{dt} \qquad \vec{v}_i = \frac{d\vec{r}_i}{dt}$$

Αλγόριθμοι Ολοκλήρωσης

- Γενικοί κανόνες
  - Διατήρηση της ενέργειας
  - Αντιστρέψιμη
  - Υπολογιστικά πραγματοποιήσιμοι
  - Να επιτρέπουν ένα “μακρύ” βήμα ολοκλήρωσης
  - Μόνο έναν υπολογισμό δύναμης σε κάθε βήμα
- Συχνά χρησιμοποιούμενοι ολοκληρωτές
  - Verlet
  - Velocity Verlet
  - Predictor-Corrector
  - Gear Predictor-Corrector

Αλγόριθμοι Ολοκλήρωσης

- Error:
  - Round off error vs. truncation
  - Local vs. global



Αλγόριθμοι Ολοκλήρωσης

- Verlet Algorithm:
  - Derived from two Taylor expansions

$$r(t+\delta t) = r(t) + \frac{dr(t)}{dt}\delta t + \frac{1}{2}\frac{d^2 r(t)}{dt^2}\delta t^2 + \frac{1}{3!}\frac{d^3 r(t)}{dt^3}\delta t^3 + O(\delta t^4)$$

$$r(t-\delta t) = r(t) - \frac{dr(t)}{dt}\delta t + \frac{1}{2}\frac{d^2 r(t)}{dt^2}\delta t^2 - \frac{1}{3!}\frac{d^3 r(t)}{dt^3}\delta t^3 + O(\delta t^4)$$

  - Add together and simplify

$$r(t+\delta t) = 2r(t) - r(t-\delta t) + \frac{d^2 r(t)}{dt^2}\delta t^2 + O(\delta t^4)$$

Αλγόριθμοι Ολοκλήρωσης

- Notes on Verlet:
  - Velocities not explicitly solved, calculated typically from first order central difference

$$v(t) = \frac{r(t+\delta t) - r(t-\delta t)}{2\delta t}$$

  - Position vector at $t+\delta t$ requires positions previous two time steps; a two-step method; not self starting
  - Advantages: simplicity and good stability
  - Global error $O(\delta t^2)$

Αλγόριθμοι Ολοκλήρωσης

- Velocity Verlet Algorithm:
  - Improved accuracy compared to standard Verlet
  - Start with position and velocity expansions

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

$$v(t+\delta t) = v(t) + \frac{1}{2}\delta t[a(t) + a(t+\delta t) + \ldots$$

Αλγόριθμοι Ολοκλήρωσης

- Velocity Verlet Algorithm:
  - Each integration cycle

1. Calculate velocities at mid-step $$v(t+\frac{\delta t}{2}) = v(t) + \frac{1}{2} a(t)\delta t$$
2. Calculate positions at the next step $$r(t+\delta t) = r(t) + v\left(t+\frac{\delta t}{2}\right)\delta t$$
3. Calculate accelerations at next step from the potential
4. Update the velocities $$v(t+\delta t) = v\left(t+\frac{\delta t}{2}\right) + \frac{1}{2} a(t+\delta t)\delta t$$

Αλγόριθμοι Ολοκλήρωσης

- Predictor-Corrector Algorithms:
  1. Predict positions and velocities at the end of the next timestep
  2. Evaluate forces at the next time step using the predicted positions
  3. Correct the predicted positions and velocities

Αλγόριθμοι Ολοκλήρωσης

- Predictor-Corrector Algorithms:

1. Predict the system configuration at the end of the next timestep using Taylor expansion

$$r(t+\delta t) = r(t) + \ldots$$

$$v(t+\delta t) = v(t) + \ldots$$

$$a(t+\delta t) = a(t) + \ldots$$

$$b(t+\delta t) = b(t) + \ldots$$

Αλγόριθμοι Ολοκλήρωσης

- Predictor-Corrector Algorithms:

2. Evaluate forces at the next time step using the predicted system state; difference between the predicted and newly calculated acceleration is the error

$$\Delta a(t+\delta t) = a^c(t+\delta t) - a^p(t+\delta t)$$

Αλγόριθμοι Ολοκλήρωσης

- Predictor-Corrector Algorithms:

3. Use the error calculated in the previous step to correct all next step values

$$r^c(t+\delta t) = r^p(t+\delta t) + c_0 \Delta a(t+\delta t)$$

$$v^c(t+\delta t) = v^p(t+\delta t) + c_1 \Delta a(t+\delta t)$$

$$a^c(t+\delta t) = a^p(t+\delta t) + c_2 \Delta a(t+\delta t)$$

$$b^c(t+\delta t) = b^p(t+\delta t) + c_3 \Delta a(t+\delta t)$$

  - Coefficients maximize stability and are dependant on the specific algorithm chosen

Αλγόριθμοι Ολοκλήρωσης

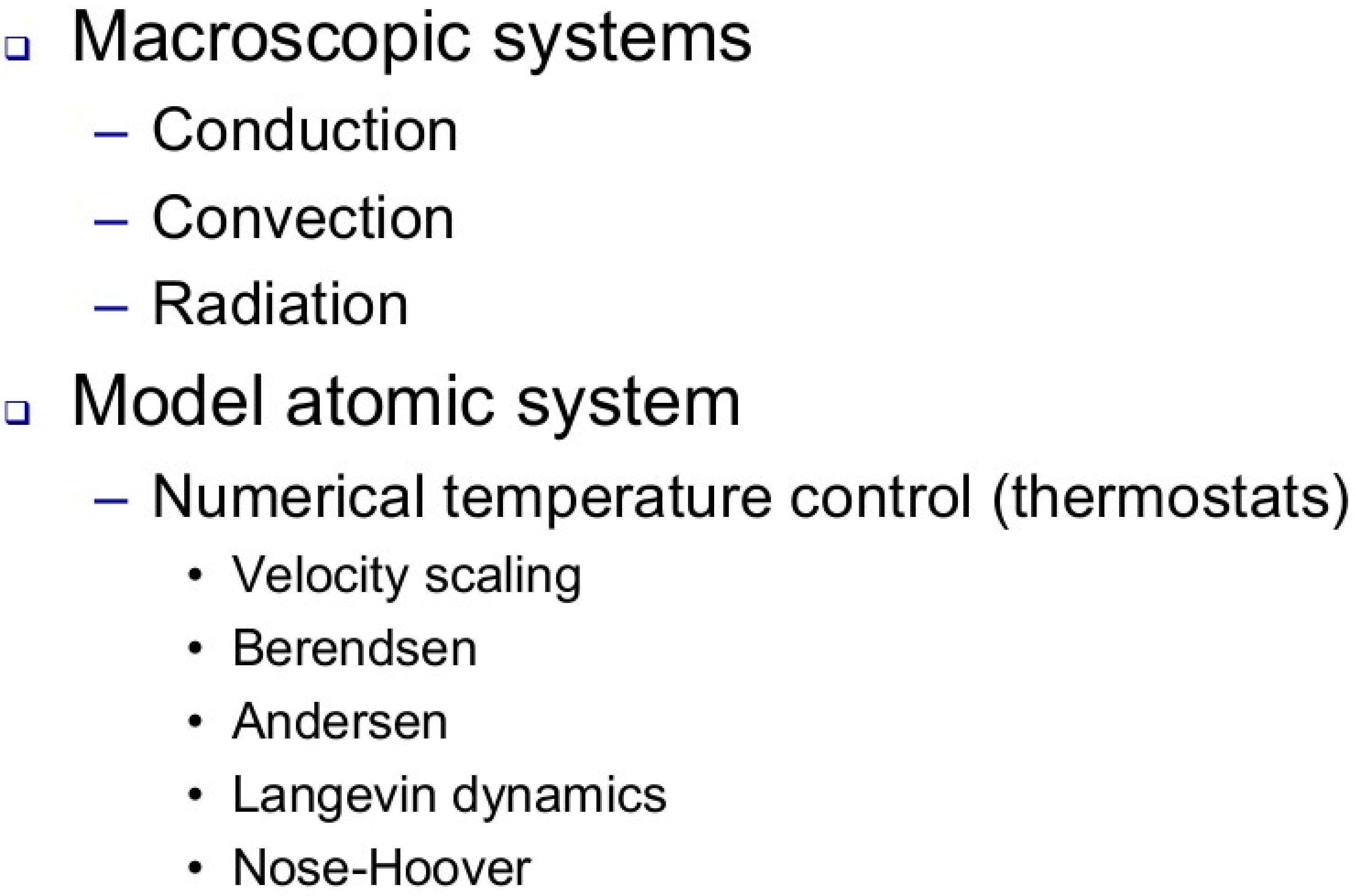
- Gear Predictor-Corrector Algorithms:
  - Predict using 5th order Taylor series
  - So need five derivatives of position at each timestep
  - Coefficients are tabulated for q-order predictors:
    - For example, with q=3
      - C_0=1/6
      - C_1=5/6
      - C_2=1
      - C_3=1/3
  - Error is $O(\delta t^{\mathrm{q}+1})$

Αλγόριθμοι Ολοκλήρωσης

- Choosing a time step
  - Too small → trajectory covers only a limited part of the phase space
  - Too large → numerical instability
  - Timestep should be ~ 1 order of magnitude smaller than the shortest motion time scale
  - In general:

System	Types of Motion	Time Step (s)
Atoms	Translation	10^{-14}
Rigid molecules	Translation and Rotation	$5x10^{-15}$
Flexible molecules, rigid bonds	Translation, Rotation and Torsion	$2x10^{-15}$
Flexible molecules, flexible bonds	Translation, Rotation, Torsion and Vibration	10^{-15} or $5x10^{-16}$

Θερμοστάτες



- Macroscopic systems
  - Conduction
  - Convection
  - Radiation
- Model atomic system
  - Numerical temperature control (thermostats)
    - Velocity scaling
    - Berendsen
    - Andersen
    - Langevin dynamics
    - Nose-Hoover

Θερμοστάτες

- Energy and temperature in an N-body system

$$H(p,r) = E_k(p_N) + U(r_N) = const$$

$$\langle E_k \rangle = \left\langle \frac{1}{2m}\sum_{i}^{N} \vec{p}_i^{\,2} \right\rangle = \frac{3}{2} N k_b T$$

$$\left\langle \sum_{i}^{N} (m_i \vec{v}_i)^2 \right\rangle = 3MNk_bT$$

$$M\left\langle \sum_{i}^{N} \vec{v}_i^{\,2} \right\rangle = 3Nk_bT \quad \Rightarrow \quad T = \frac{M}{3Nk_b}\left\langle \sum_{i}^{N} \vec{v}_i \cdot \vec{v}_i \right\rangle$$

Θερμοστάτες

- Controlling temperature during an NVE simulation

$$\frac{T^{new}}{T^{old}} = \frac{\dfrac{M}{3Nk_b}\left\langle \sum_i^N \vec{v}_i^{\,new} \cdot \vec{v}_i^{\,new} \right\rangle}{\dfrac{M}{3Nk_b}\left\langle \sum_i^N \vec{v}_i^{\,old} \cdot \vec{v}_i^{\,old} \right\rangle}$$

$$\frac{T^{new}}{T^{old}} = \frac{\left\langle \sum_i^N \vec{v}_i^{\,new} \cdot \vec{v}_i^{\,new} \right\rangle}{\left\langle \sum_i^N \vec{v}_i^{\,old} \cdot \vec{v}_i^{\,old} \right\rangle} \Rightarrow v_i^{new} = v_i^{current}\sqrt{T^{new}/T^{current}}$$

Θερμοστάτες (Berendsen)

- Berendsen; adjustable parameter determines how tightly bath and system are coupled
  - Simple velocity scaling as the coupling parameter approaches the integration timestep
  - Suggested value $\Delta t / \tau \sim 0.0025$

$$\frac{dT(t)}{dt} = \frac{1}{\tau}\left(T_{bath} - T(t)\right)$$

$$\Delta T = \frac{\Delta t}{\tau}\left(T_{bath} - T(t)\right)$$

Θερμοστάτες (Andersen)

- Andersen heat bath → stochastic impulsive forces acting on randomly selected particles
  - Coupling strength → frequency of stochastic collisions, ν

1. Start with a set of positions and momenta
2. Integrate equations of motion
3. Select particles to undergo collision with heat bath; probability of selection $\nu\Delta t$
4. The velocities of particles selected for collision are taken from a Boltzmann distribution at the desired temperature

Θερμοστάτες (Andersen)

- Coupling strength → frequency of stochastic collisions, ν
  - The value of ν is related to the intermolecular collision frequency ν_c (a function of the density and thermal conductivity)

$$\nu = \frac{\nu_c}{N^2/3}$$

  - For each particle, a random number is selected between 0 and 1
  - If that number is less than $\nu\Delta t$, its momenta are reset

Θερμοστάτες (Langevin Dynamics)

- Langevin method simulates interactions with a solvent
- Two terms added to the equation of motion
  - Friction term removes energy → frictional drag on the system moving through a solvent
  - Random term adds energy → collisions/interactions with solvent molecules

$$m\vec{a} = \vec{F} - m\gamma\vec{v} + \vec{R}$$

Θερμοστάτες (Nose-Hoover)

- Includes the heat bath explicitly as an additional degree of freedom
- Widely used algorithm
- Introduce an artificial variable s that plays the role of a time scaling parameter
  - "mass" Q
  - "velocity" $\dot{s}$

Θερμοστάτες (Nose-Hoover)

- Nosé-Hoover Hamiltonian

$$H_{Nose-Hoover} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2 m_i s^2} + U(\vec{r}^{\,N}) + \frac{p_s^2}{2Q} + (f+1) k_b T \ln s$$

- Magnitude of Q controls coupling strength
  - Too large → loose coupling → poor temperature control
  - Too small → tight coupling → high frequency temperature oscillation
  - Can be related to effective relaxation time

$$Q = C f k_b T$$

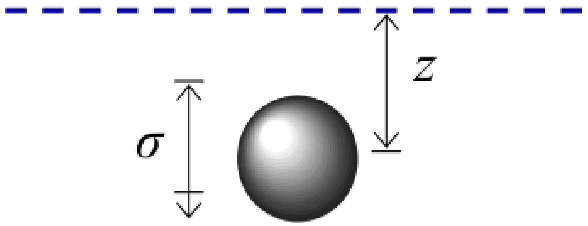
found by testing the system oscillation about a desired T

Συνοριακές Συνθήκες

- Fixed simulation cell boundaries
  - Repulsive boundary
  - Atomistic rigid walls
  - Atomistic semi-rigid walls
    - Massive boundary atoms
    - Spring potential
- Periodic boundary conditions
- Minimum image criteria

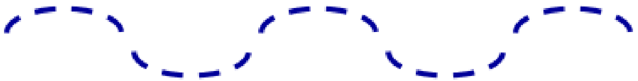
Συνοριακές Συνθήκες

- Continuous barrier potential
  - Simplest case, flat repulsive boundary



$$u(z) = \varepsilon \left(\frac{z}{\sigma} \right)^{-12}$$

  - Virtual barrier texture introduced through more complex expressions such as the (10-4-3) potential

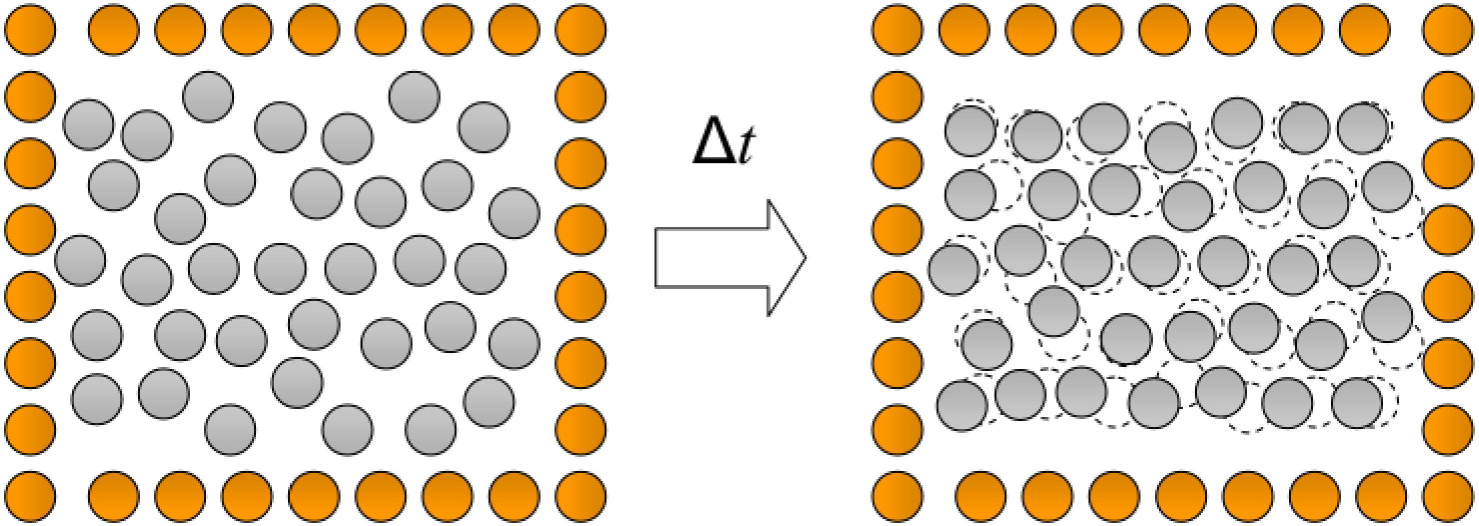


Continuous function representing the (100) face of an fcc lattice

$$u(z) = 2\pi \left[\frac{2}{5z^{10}} - \frac{1}{z^{4}} - \frac{1}{3/\sqrt{2}\left(z + 0.61/\sqrt{2}\right)^{3}} \right]$$

Συνοριακές Συνθήκες

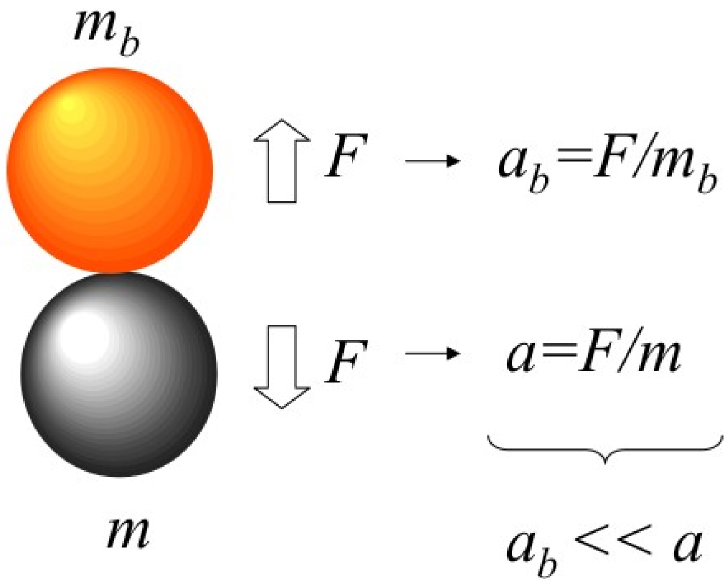
- Rigid atomistic walls



Συνοριακές Συνθήκες

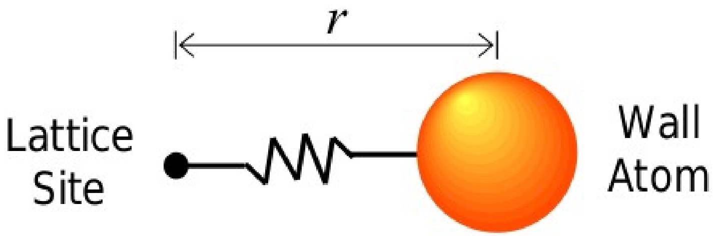
- Semi-rigid atomistic boundary → massive boundary atoms
  - Massive boundary atoms will be affected less by inter-atomic interactions
  - Consider the interaction between a boundary and a non-boundary atom where

$$m_b >> m$$



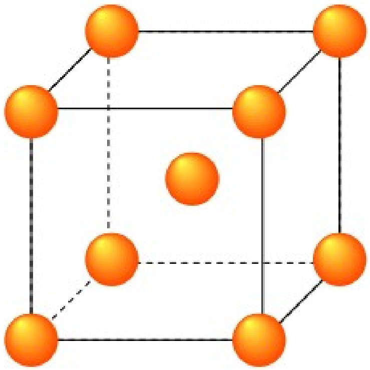
Συνοριακές Συνθήκες

- Semi-rigid atomistic boundary → spring potential
  - Boundaries both rigid enough to maintain structure and flexible enough to interact with the other atoms

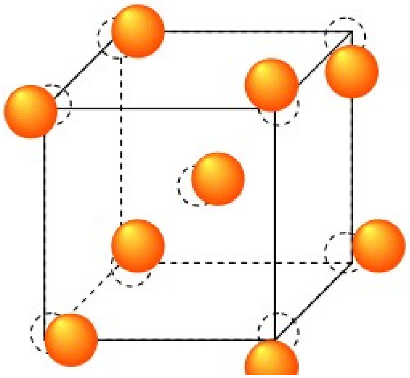


$$u(r) = \frac{1}{2}k\left(r - r_{lattice}\right)^2$$

Initial bcc configuration:

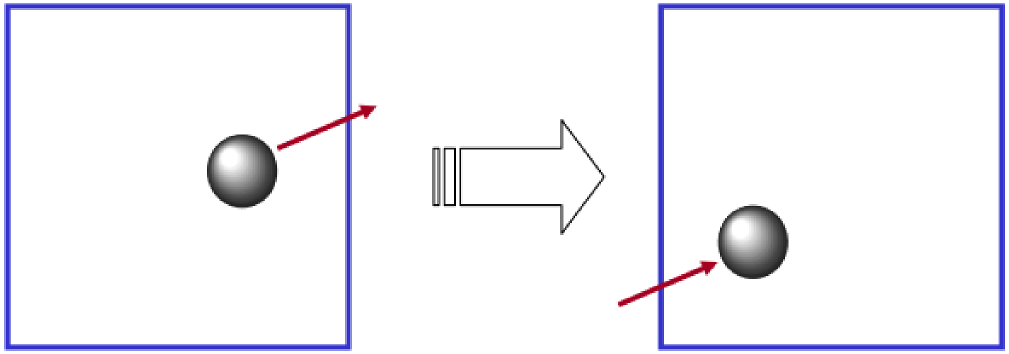


During MD simulation:



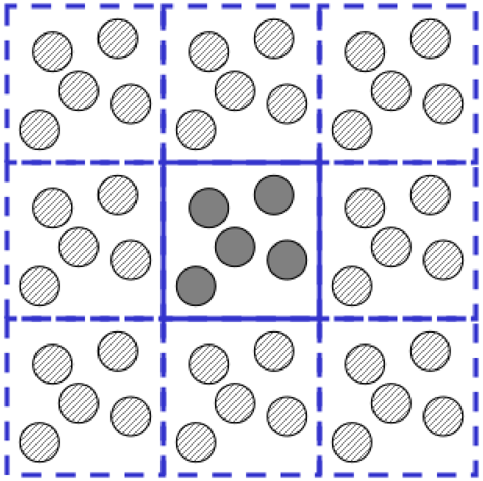
Περιοδικές Συνοριακές Συνθήκες PBC

- PBCs enable macroscopic properties to be calculated from fewer particles
- Simulated interactions of “bulk” material
- Out one side, in the other



Περιοδικές Συνοριακές Συνθήκες PBC

- The primary cell is replicated in all simulated direction as image cells
- Primary and image cells have the same
  - Number, position, momentum of atoms
  - Size
  - Shape



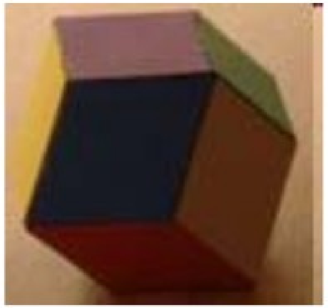
Περιοδικές Συνοριακές Συνθήκες PBC

- The shape of a periodic simulation cell must fill all space by translational operations of the central box in 3D


Cube

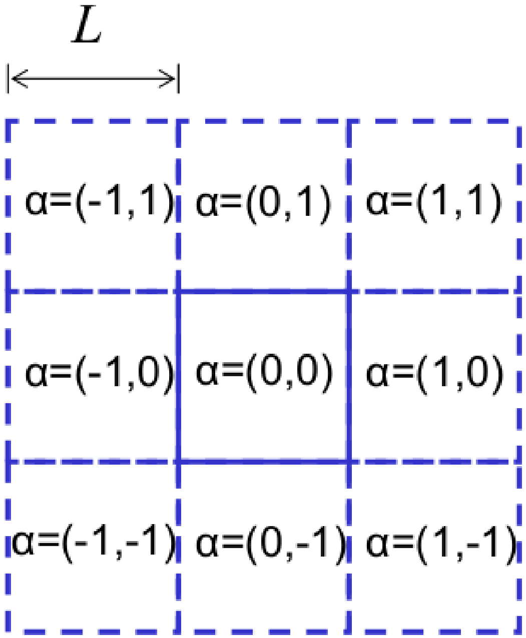

Truncated Octahedron


Hexagonal Prism


Rhombic Dodecahedron

Περιοδικές Συνοριακές Συνθήκες PBC

- Forces between primary and image atoms



If i and j are in the primary cell:

$$\vec{F}_i = -\frac{\partial U(\vec{r}_{ij})}{\partial \vec{r}_i}$$

If j is in an image cell:

$$\vec{F}_i = -\sum_{\vec{\alpha}} \frac{\partial U(\vec{r}_{ij} - \vec{\alpha} L)}{\partial \vec{r}_i}$$

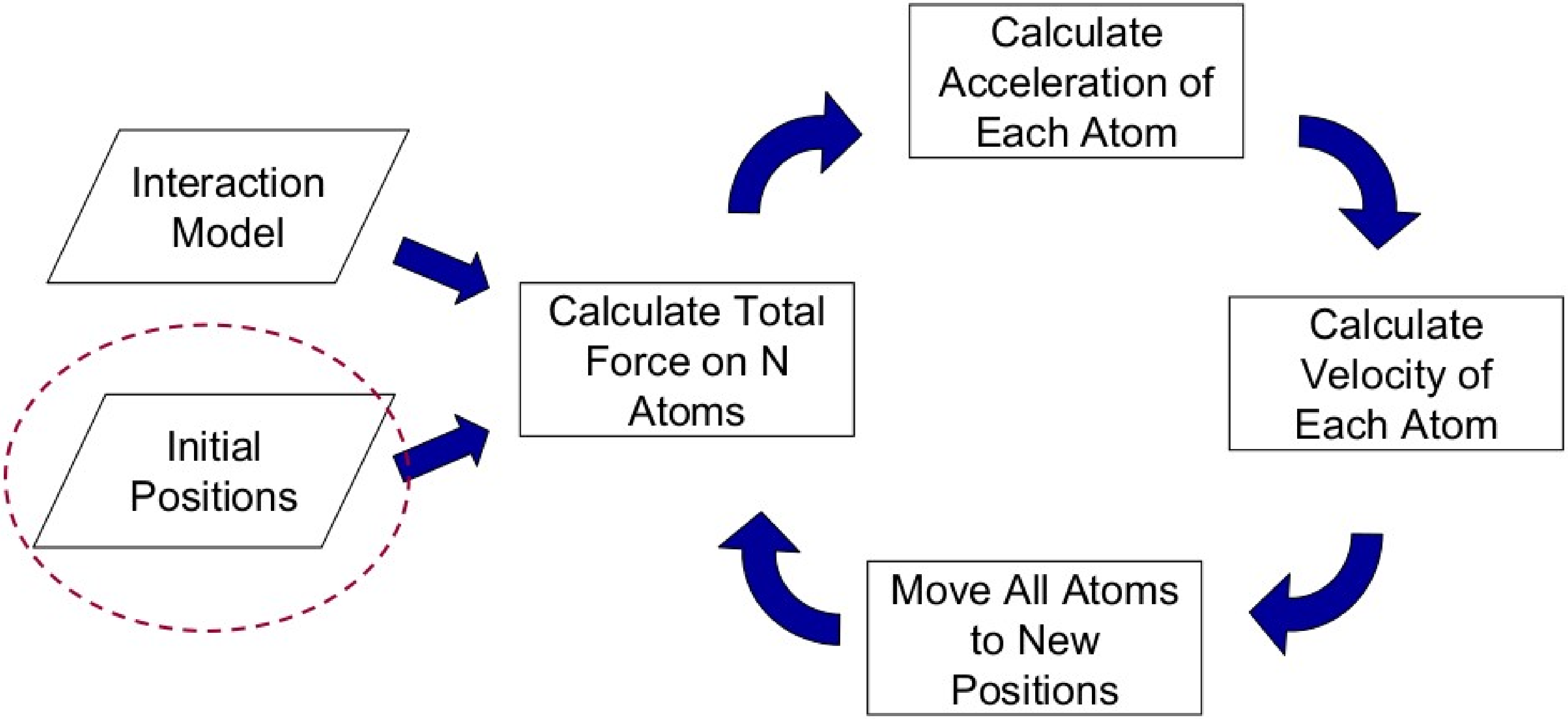
Περιοδικές Συνοριακές Συνθήκες PBC

$$\vec{F}_i = -\sum_{\alpha_x=-1}^{+1}\sum_{\alpha_y=-1}^{+1}\sum_{\alpha_z=-1}^{+1}\frac{\partial U(\vec{r}_{ij}-\vec{\alpha}L)}{\partial \vec{r}_i}$$

- Minimum image distance
  - Atom i can experience a force from atom j and its 26 images
  - But only one image is a distance less than ½L
  - So if the pair potential is truncated at $r_c \leq 1/2\ L$, either atom j or only one of its images can exert force on atom i
  - With PBCs, interactions are truncated *at least* to this minimum image distance

https://youtu.be/qO956ac-sEE

Εκκίνηση και “ισορροπία”



Interaction Model

Initial Positions

Calculate Total Force on N Atoms

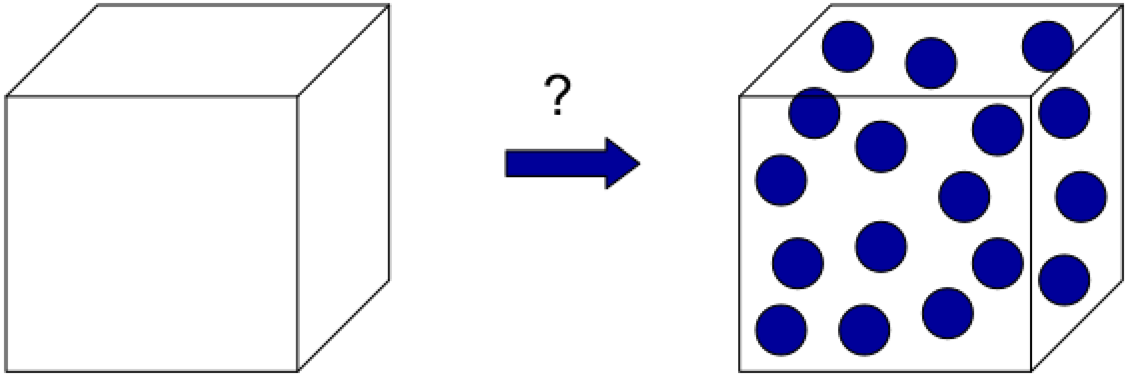
Calculate Acceleration of Each Atom

Calculate Velocity of Each Atom

Move All Atoms to New Positions

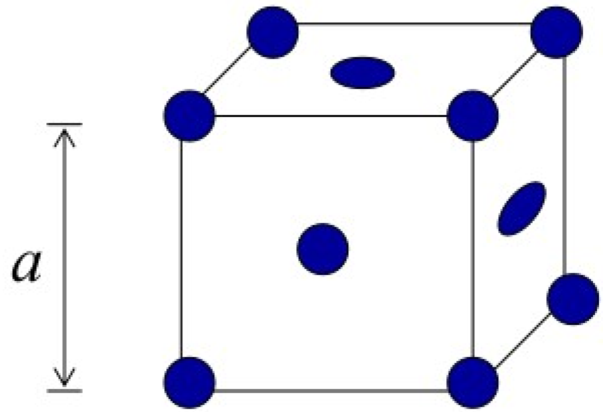
Εκκίνηση και “ισορροπία”

- Atomic positions
  - Experiment/theoretical modeling
  - Default lattice
  - Monte Carlo
- Atomic velocities
  - Randomization by temperature



Αρχικές Θέσεις

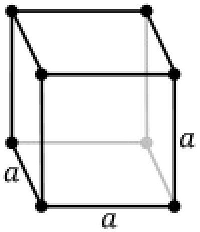
- Assign to lattice positions
  - Unit cell, typically fcc

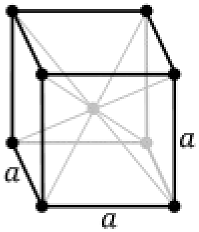


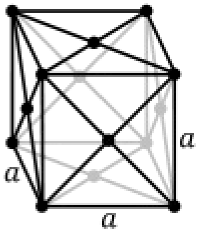
$$\rho = \frac{n}{a^3}$$

Bravais lattice

- **Primitive cubic Body-centered cubic Face-centered cubic**







The primitive cubic system (cP) consists of one lattice point on each corner of the cube. Each atom at a lattice point is then shared equally between eight adjacent cubes, and the unit cell therefore contains in total one atom (1⁄8 × 8).

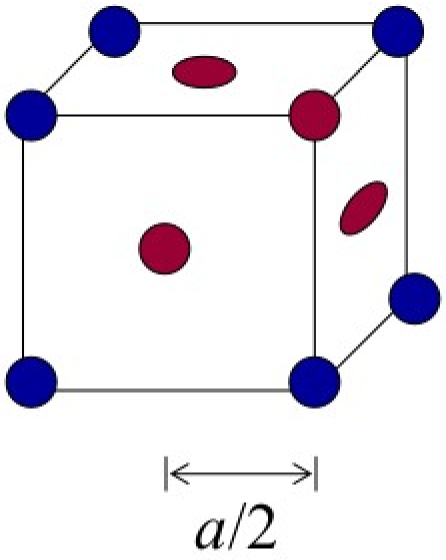
The body-centered cubic system (cI) has one lattice point in the center of the unit cell in addition to the eight corner points. It has a net total of 2 lattice points per unit cell (1⁄8 × 8 + 1).

The face-centered cubic system (cF) has lattice points on the faces of the cube, that each gives exactly one half contribution, in addition to the corner lattice points, giving a total of 4 lattice points per unit cell (1⁄8 × 8 from the corners plus 1⁄2 × 6 from the faces). Each sphere in a cF lattice has coordination number 12.coordination number is the number of nearest neighbours .12 is the coordination number of face centre cubic lattice.The no of second nearest neighbours are 6.third nearest neighbours are 24.

The face-centered cubic system is closely related to the hexagonal close packed (HCP) system, and the two systems differ only in the relative placements of their hexagonal layers. The [111] plane of a face-centered cubic system is a hexagonal grid.

Αρχικές Θέσεις

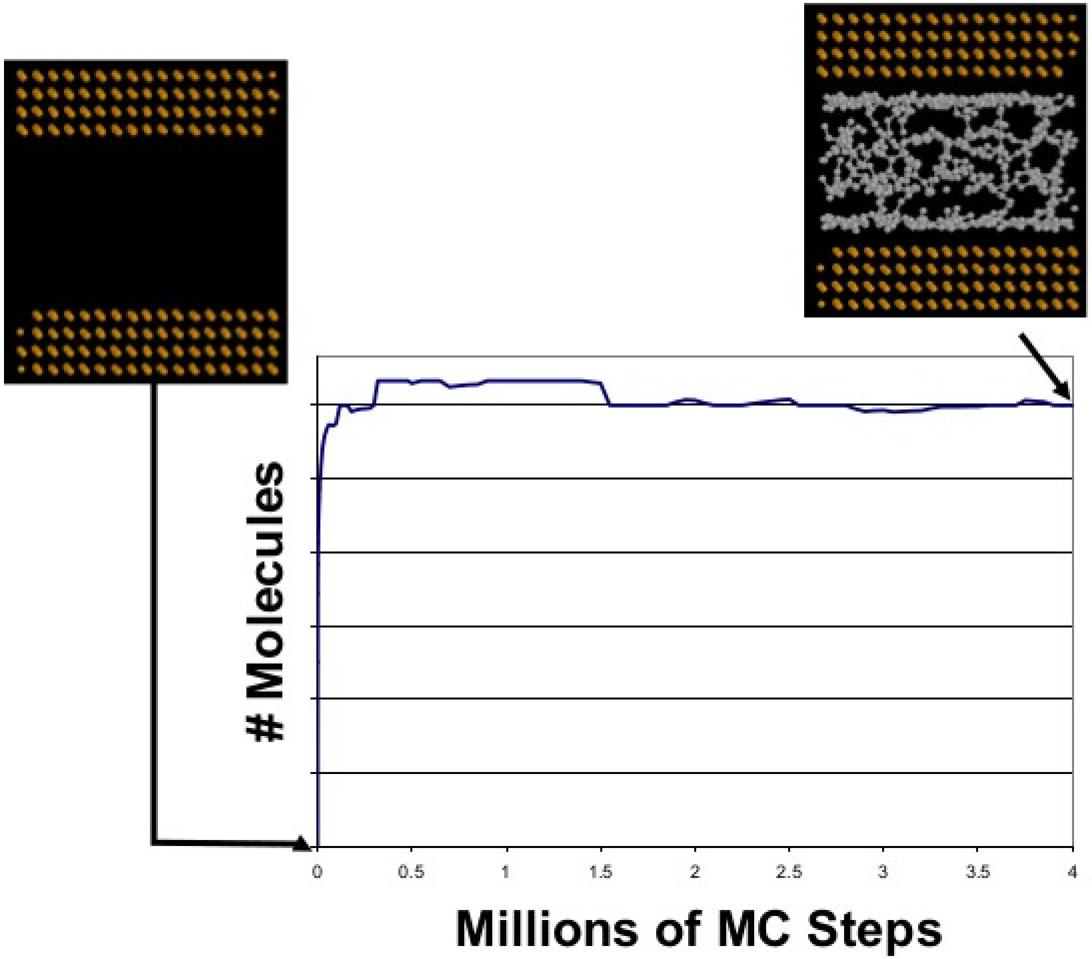
- Implementation
  - This approach requires an equilibration phase (called melting)



$$r_1 = (0,0,0)$$
$$r_2 = (0,\tfrac{1}{2}a,\tfrac{1}{2}a)$$
$$r_3 = (\tfrac{1}{2}a,0,\tfrac{1}{2}a)$$
$$r_4 = (\tfrac{1}{2}a,\tfrac{1}{2}a,0)$$

Αρχικές Θέσεις (Monte Carlo)

- Simulation "randomly" inserts/deletes/ translates molecules in the volume and then either accepts or rejects the move based on energy change criteria



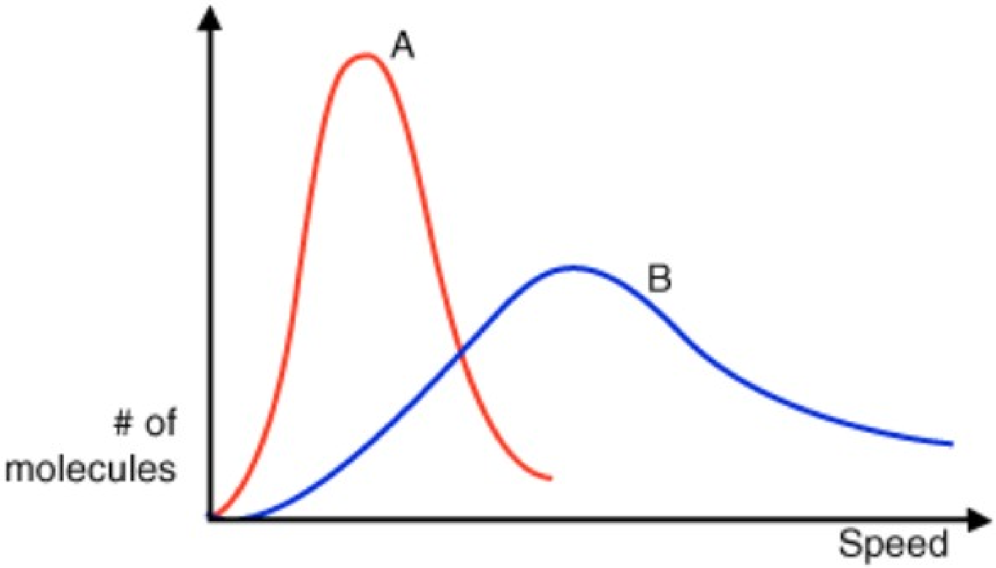
Αρχικές Ταχύτητες

- Initial velocities must be set such that
  - They comprise the desired temperature
  - The total linear momentum is zero
- Methods
  - Use trajectories from a previous simulation
  - Assign a uniform distribution
  - Assign a Maxwell-Boltzmann distribution

Αρχικές Ταχύτητες

- Maxwell-Boltzmann distribution

$$f_v(v_x) = \sqrt{\frac{m}{2\pi kT}}\exp\left[\frac{-mv_x^2}{2kT}\right]$$



Αρχικές Ταχύτητες

- Uniform distribution
  - Take random numbers r over the interval [-1,+1]
  - Scale to the desired temperature

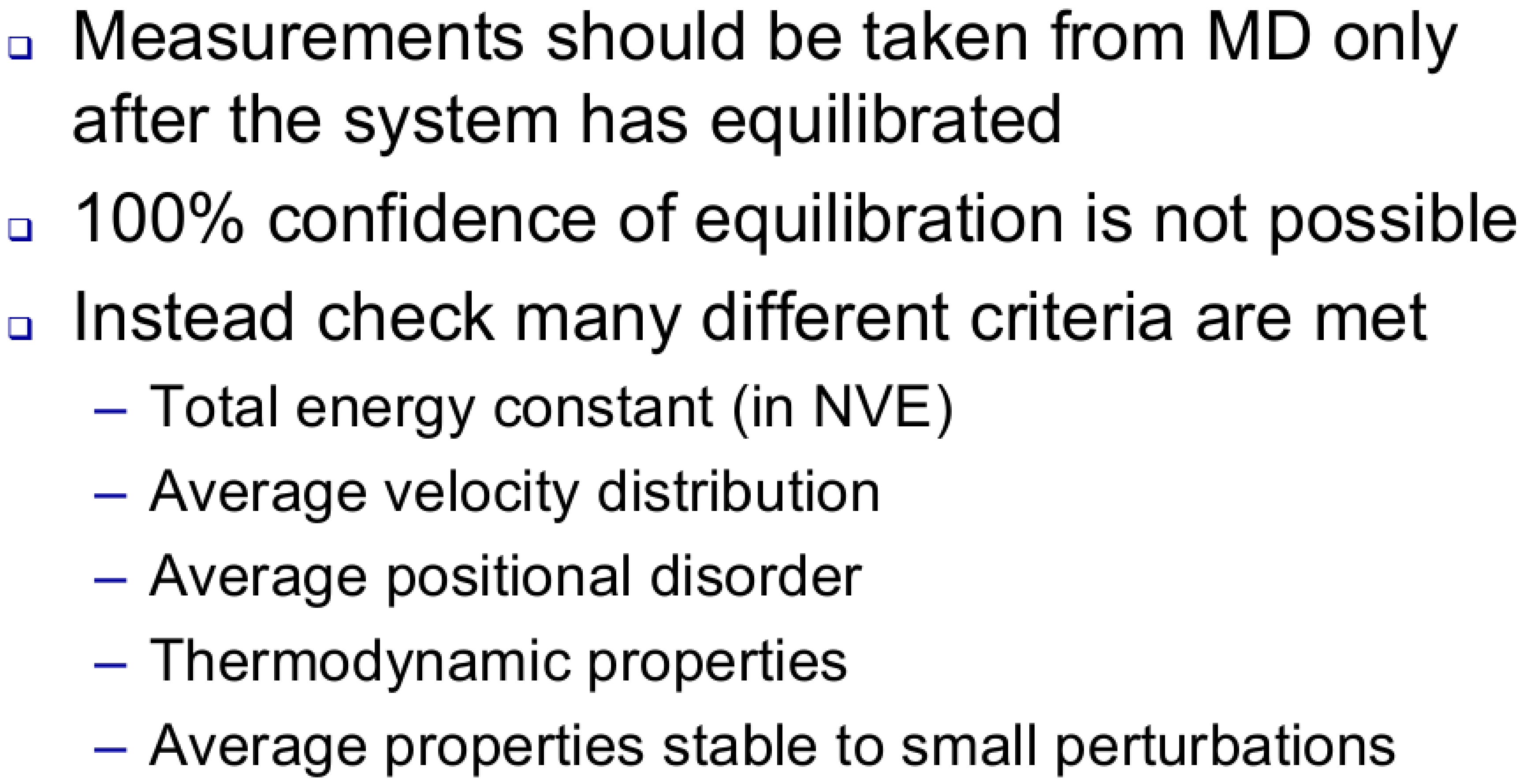
$$v_{reduced} = r\sqrt{T_{reduced}}$$

  - Scale to zero total linear momentum

$$v_i^{init} = v_i - \frac{1}{N}\sum_j v_j$$

  - Equilibrate

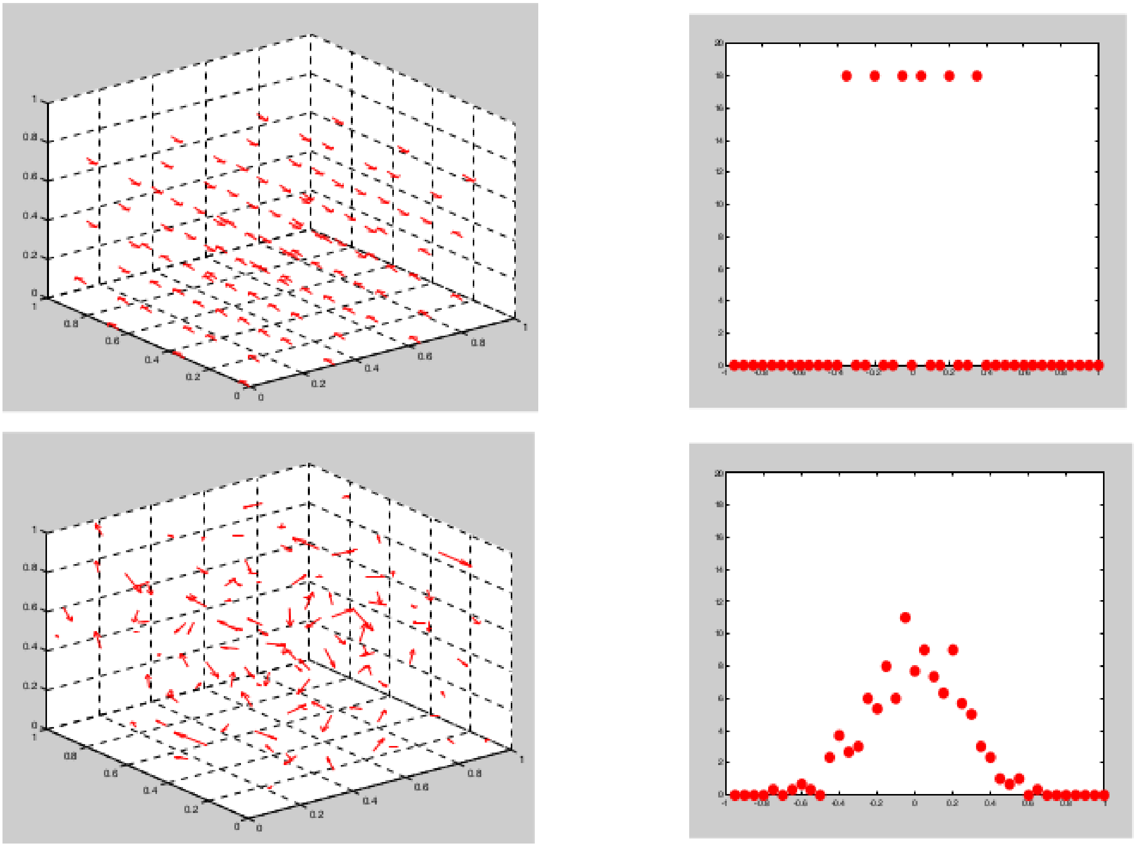
Equilibration



- Measurements should be taken from MD only after the system has equilibrated
- 100% confidence of equilibration is not possible
- Instead check many different criteria are met
  - Total energy constant (in NVE)
  - Average velocity distribution
  - Average positional disorder
  - Thermodynamic properties
  - Average properties stable to small perturbations

Equilibration

- Equilibration of initially assigned velocities



Instantaneous Velocity Vectors

Velocity Distribution

Initial Condition

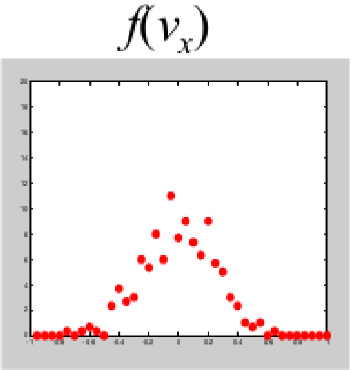
500 Collisions

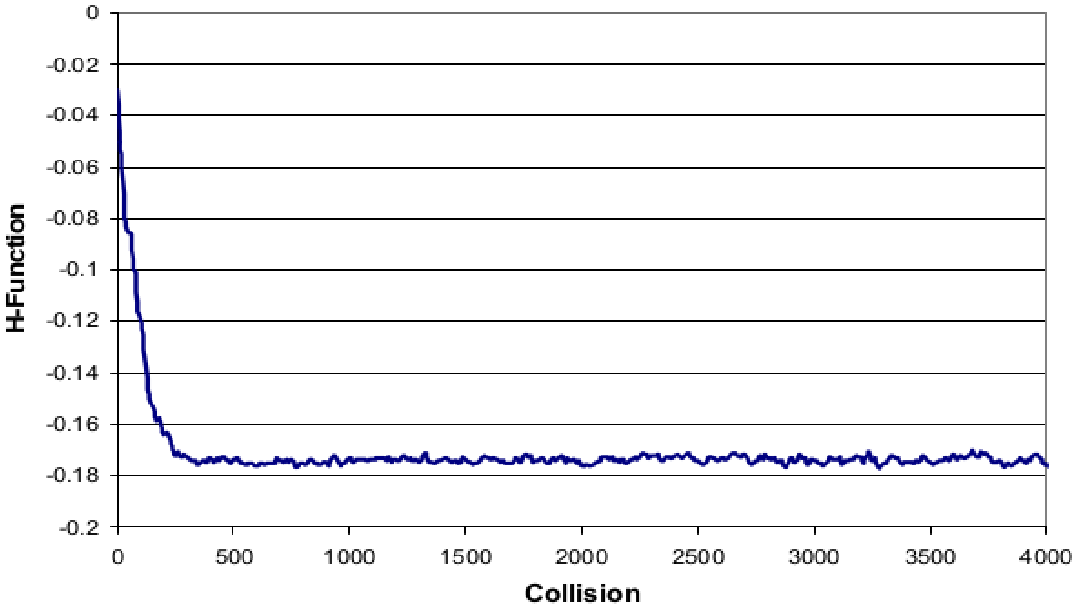
Equilibration

- Boltzmann's H-function

$$H_x = \sum_{\Delta v_x} f(v_x) \ln f(v_x) \Delta v_x$$

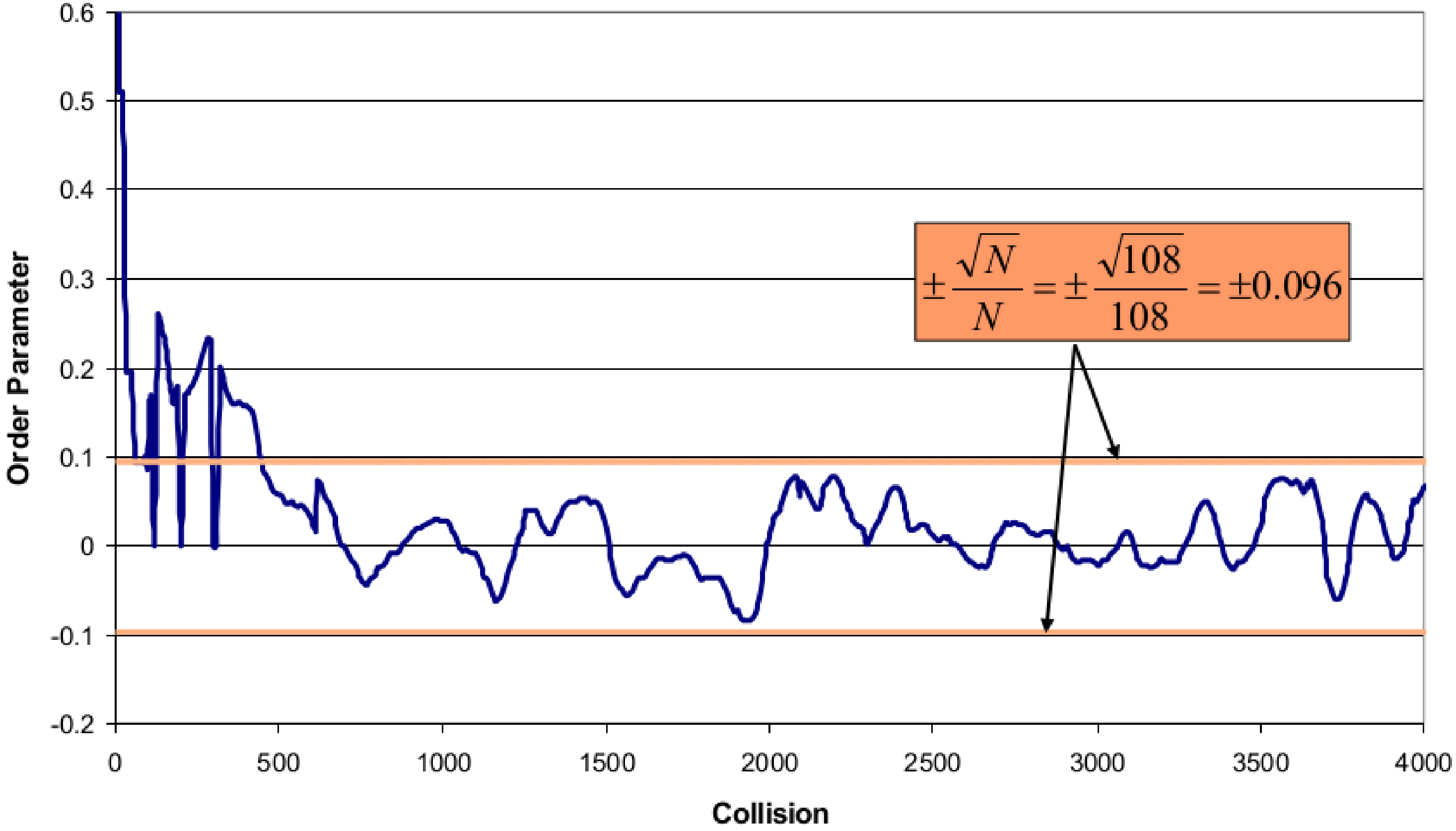
$$H = \tfrac{1}{3}\left(H_x + H_y + H_z\right)$$





Equilibration

- Positional disorder $\lambda_{x,fcc} = \frac{1}{N}\sum_{i}^{N}\cos\left(\frac{4\pi x_i}{a}\right)$ $\lambda = \frac{1}{3}\left(\lambda_x + \lambda_y + \lambda_z\right)$



$$\pm\frac{\sqrt{N}}{N} = \pm\frac{\sqrt{108}}{108} = \pm 0.096$$

Στατικές Ιδιότητες

- Thermodynamic properties
  - Simple functions of the Hamiltonian
  - Response functions
  - Entropic properties
- Static Structure
  - Radial distribution function

Απλές Θερμοδυναμικές Ιδιότητες

- Internal energy and temperature

$$H(\vec{r}^{\,N}, \vec{p}^{\,N}) = const$$

$$H = E_k + U$$

$$\langle E_k \rangle = \tfrac{3}{2} NkT = \frac{1}{2mt_\infty} \sum_{t'=1}^{t_\infty} \sum_{i=1}^{N} \vec{p}_i(t'\Delta t) \cdot \vec{p}_i(t'\Delta t)$$

$$\langle U \rangle = \frac{1}{t_\infty} \sum_{t'=1}^{t_\infty} \sum_{\vec{\alpha}} \sum_{i}^{N} \sum_{j>i}^{N} u\left(\left|\vec{r}_{ij}(t'\Delta t) - \vec{\alpha}L\right|\right)$$

Απλές Θερμοδυναμικές Ιδιότητες

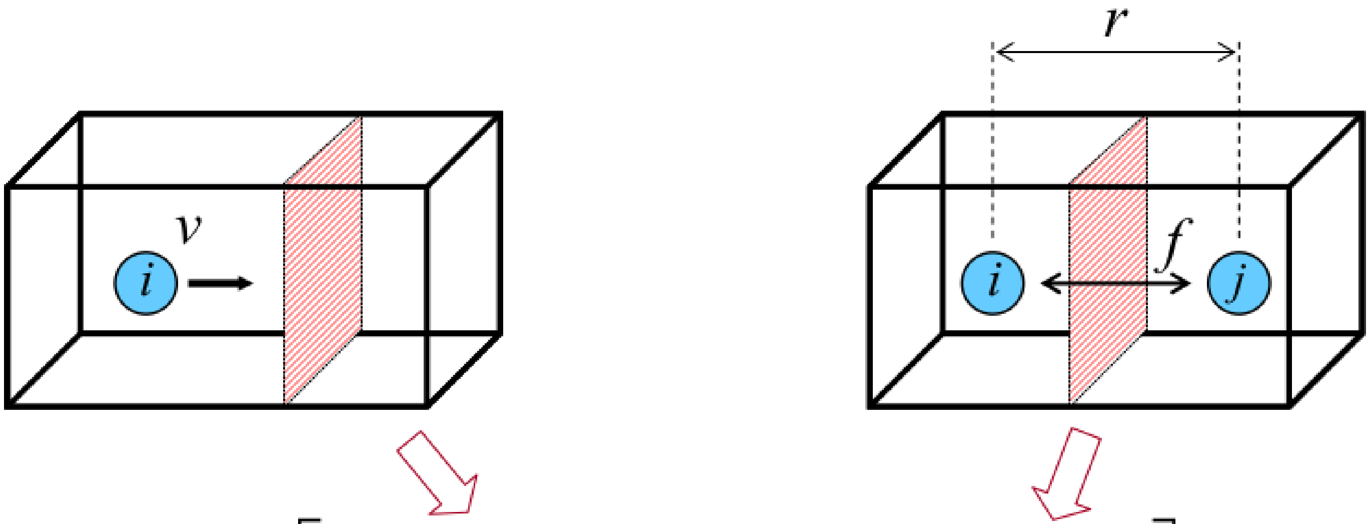
- Pressure
  - The continuum concepts of stress or pressure do not translate directly to the discrete particles of an MD simulation
  - Pressure is typically calculated using the pressure virial (also called the Irving-Kirkwood equation)
  - This expression is obtained by considering stress / pressure to be a momentum flux across an area

$$P = \frac{force}{area} = \frac{1}{area}\frac{d(mv)}{dt}$$

Απλές Θερμοδυναμικές Ιδιότητες

- Momentum transferred via two mechanisms

1. Carried across an area by a moving atom
2. Interaction between atoms on opposite sides of an area



$$P = \frac{1}{volume}\left[\sum_i m_i v_i^2 + \sum_i \sum_{j>i} r_{ij} \cdot f_{ij}\right]$$

Απλές Θερμοδυναμικές Ιδιότητες

- Irving Kirkwood / Pressure Virial
  - Used for all components of the stress tensor

$$\boldsymbol{\sigma}_{\alpha\beta} = -\frac{1}{V}\left\langle \sum_{i}^{N} m_i u_{i\alpha} u_{i\beta} + \sum_{i}^{N} \sum_{j>i}^{N} \mathbf{r}_{ij\alpha} \mathbf{F}_{ij\beta} \right\rangle$$

Απλές Θερμοδυναμικές Ιδιότητες

- Mean square force
  - Gives information about the shape of the repulsive part of the pair potential
  - Obtainable experimentally for comparison

On one atom: $$\left\langle F_1^2 \right\rangle = \left\langle \sum_{j \neq 1} \left(\nabla U(r_{1j}) \right)^2 \right\rangle$$

On all atoms: $$\left\langle F^2 \right\rangle = \frac{2}{MN} \sum_{k=1}^{M} \sum_{\vec{\alpha}} \sum_{i<j} \left(\nabla U \left[\left| \vec{r}_{ij}(k\Delta t) - \vec{\alpha} L \right| \right] \right)^2$$

Απλές Θερμοδυναμικές Ιδιότητες

- How do simple thermodynamic properties response to changes
  - Temperature
  - Pressure
- Two general methods
  - Use several simulations to determine values of a quantity as functions of the changing variable
  - Evaluate the derivative analytically using statistical mechanics

Απλές Θερμοδυναμικές Ιδιότητες

- How do simple thermodynamic properties response to changes
  - Temperature
  - Pressure
- Two general methods
  - Use several simulations to determine values of a quantity as functions of the changing variable
  - Evaluate the derivative analytically using statistical mechanics

Απλές Θερμοδυναμικές Ιδιότητες

- Example: Constant volume heat capacity

$$C_v = \left(\frac{\partial U}{\partial T} \right)_{V=const}$$

- Method 1
  - Begin with an initial configuration
  - Run simulation at temperature T1
  - Measure the internal energy U1
  - Repeat process at T2, T3, ….
  - Empirically fit simulation results for U(T)
  - Numerically or analytically take derivative

Απλές Θερμοδυναμικές Ιδιότητες

- Method 2

$$C_v = \frac{1}{kT^2}\left\langle (\partial U)^2 \right\rangle \qquad \partial U = U - \langle \partial U \rangle$$

Fluctuation of internal energy about its average

$$\left\langle (\partial U)^2 \right\rangle = \left\langle \left(U - \langle \partial U \rangle\right)^2 \right\rangle = \left\langle U^2 \right\rangle - \langle U \rangle^2$$

Mean-square fluctuation of internal energy

- Advantages
  - Only requires a single simulation
- Disadvantages
  - Typically less accurate than Method 1
    - Round off / small differences in big numbers

Απλές Θερμοδυναμικές Ιδιότητες

- Similar approaches are possible for
  - Adiabatic compressibility $\kappa = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_{S=const}$
  - Thermal pressure coefficient $\gamma = \left(\frac{\partial P}{\partial T}\right)_{V=const}$
  - Etc.

Εντροπικές Ιδιότητες

- Entropic properties are not simple time averages over a phase-space trajectory
  - Entropy
  - Gibbs free energy
  - Helmholtz free energy
  - Chemical potential
- Methods
  - Thermodynamic integration
  - Test particle method
  - Coupling parameter method

Εντροπικές Ιδιότητες

- Thermodynamic integration

Chemical potential

$$dS = \frac{dU}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN$$

  - Fix N and V, vary U, measure T

$$dS = \left(\frac{dU}{T}\right)_{N,V=const} \qquad S(U_2) - S(U_1) = \int_{U_1}^{U_2} \frac{dU}{T}$$

  - Fix N and V, vary T, measure U

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{1}{T}\left(\frac{dU}{T}\right)dT$$

Εντροπικές Ιδιότητες

- Thermodynamic integration
  - Fix two quantities, vary another, and measure the response of the last
  - For example,
    - Fix N and V
    - Perform a series of simulations at fixed energy
    - Calculate average temperature each time

$$S(U_2) - S(U_1) = \int_{U_1}^{U_2} \frac{dU}{T}$$

  - Typically very accurate method, but extremely time consuming because of the large number of simulations to obtain a single entropy difference

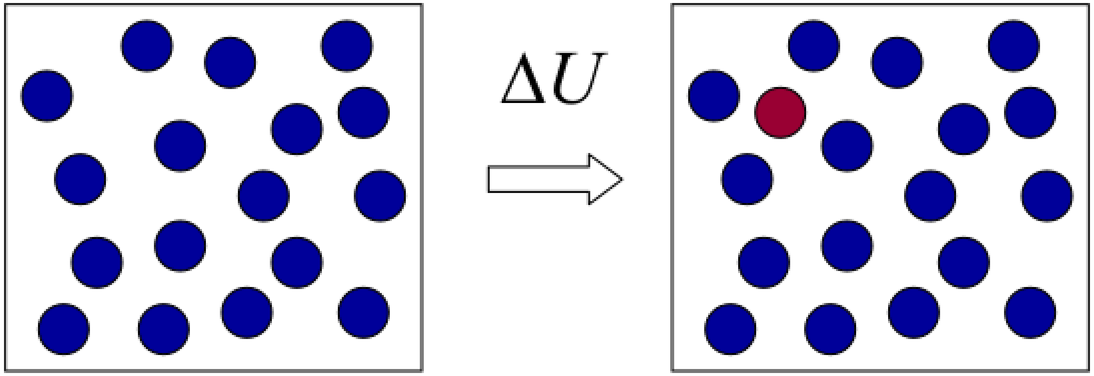
Εντροπικές Ιδιότητες

- Test Particle Method
  - Instead of varying the energy, temperature, or volume, alternatively vary the number of particles
  - Randomly insert a particle,
    - If it does overlap (i.e. large positive energy), its effect is ignored
    - If the placement is ok, we can measure the change in energy that results
  - Disadvantages
    - Implementation rather complex
    - Less successful at high densities (most insertions fail)

Εντροπικές Ιδιότητες

- Test Particle Method
  - Estimate the change in entropy due to a change in the number of particles, vary N

$$\mu = -T\left(\frac{dS}{dN}\right)_{U,V=const}$$



Στατική Δομή

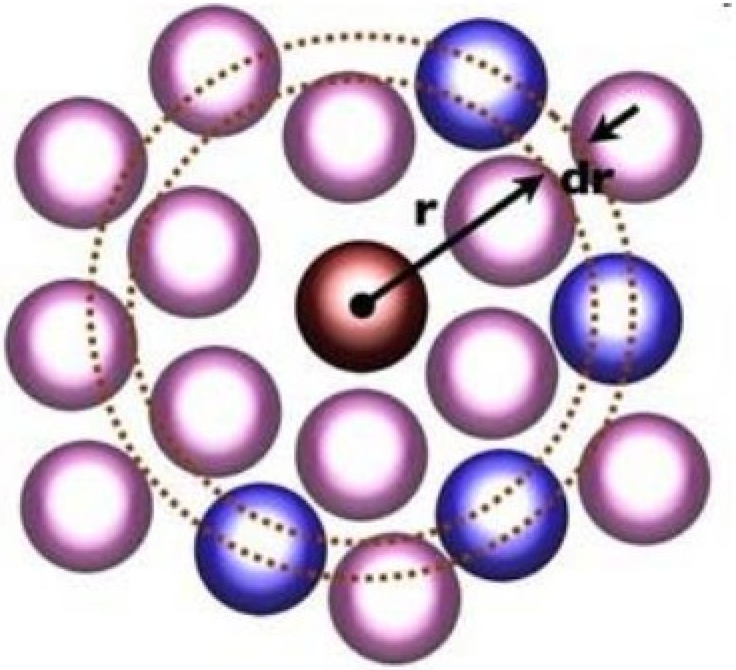
- Radial distribution function, $g(r)$
  - Measure of how atoms organize themselves around one another
  - Plays an important role in many statistical mechanics methods
  - Can be extracted from x-ray and neutron diffraction

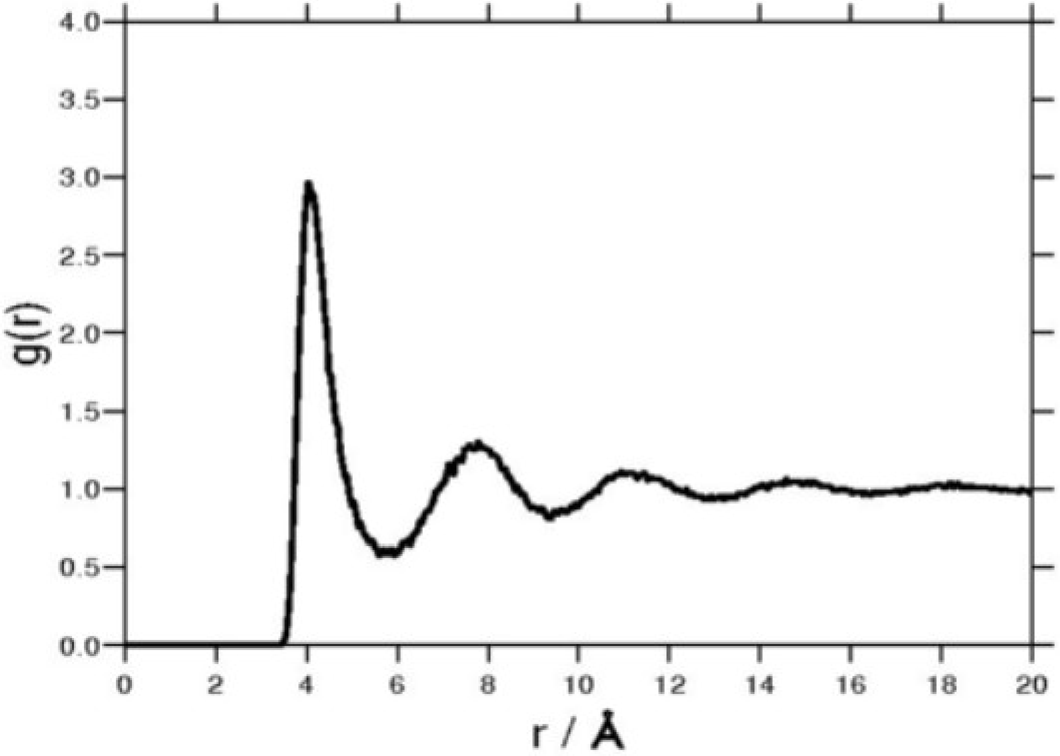
Ratio between the average number density at a given distance from any atom to the density at the same distance in an ideal gas

Necessarily, $g(r)=1$ in an ideal gas

Στατική Δομή

- Radial distribution function



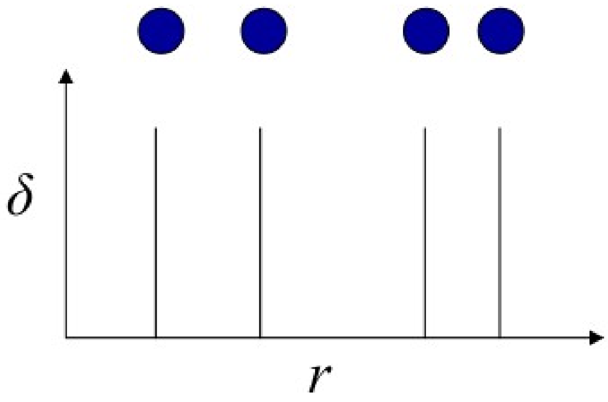


Στατική Δομή

- Radial distribution function from MD

$$\rho g(r) = \frac{1}{N}\left\langle \sum_{i}^{N}\sum_{j\neq i}^{N}\delta\left[r - r_{ij}\right]\right\rangle$$

$$\rho g(r) = \frac{2}{N}\left\langle \sum_{i}^{N}\sum_{j<i}^{N}\delta\left[r - r_{ij}\right]\right\rangle$$



  - Integrate over all possible two atom separations

$$\rho\int g(r)dr = \frac{2}{N}\left\langle \sum_{i}^{N}\sum_{j<i}^{N}\int\delta\left[r - r_{ij}\right]dr\right\rangle$$

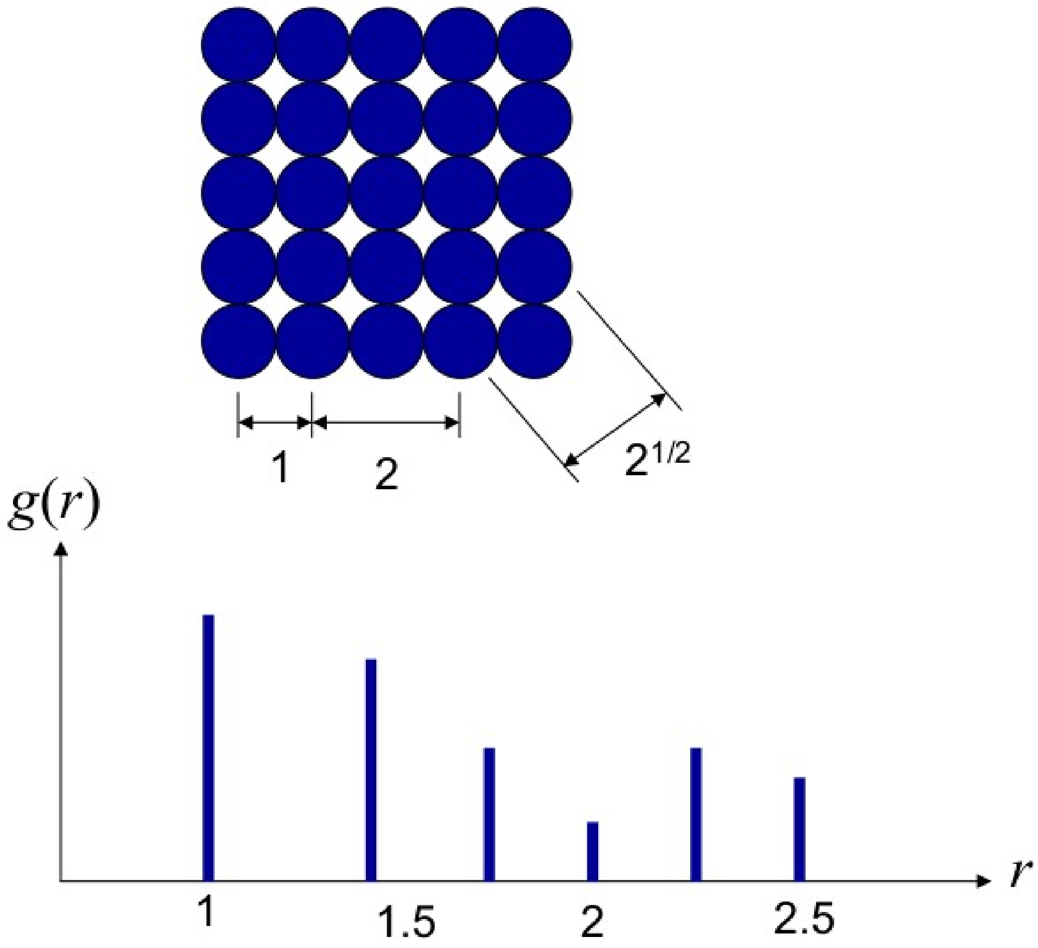
Στατική Δομή

- By definition $\int \delta\left[r - r_{ij}\right] dr = 1$
- So $\rho \int g(r) dr = N - 1 \approx N$
- Probabilitistic interpretation

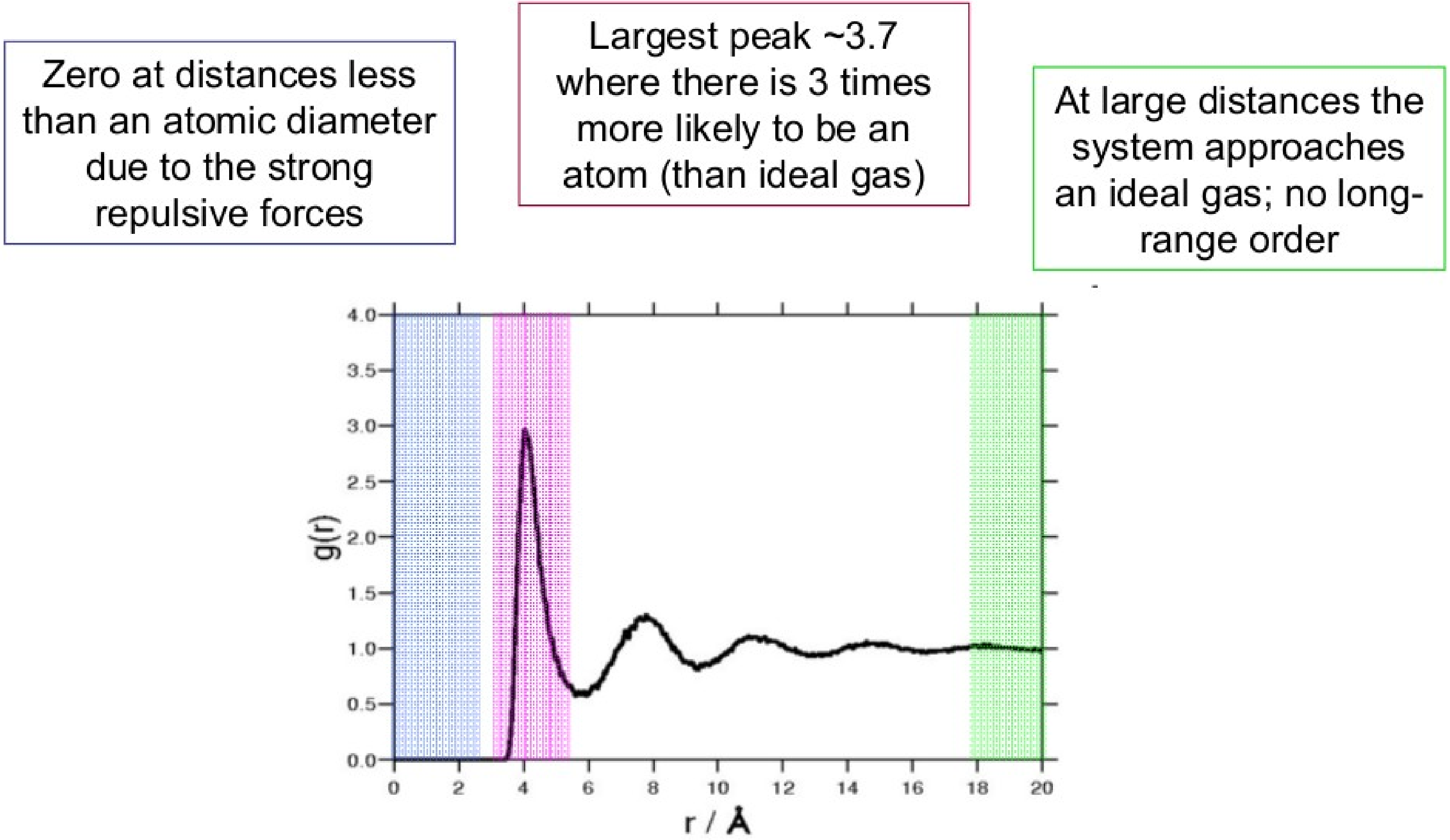
$$\frac{\rho}{N-1} g(r) V(r, \Delta r)$$

= probability that an atomic center lies in a spherical shell of radius r and thickness Δr with the shell centered on another atom

Στατική Δομή



Στατική Δομή



Zero at distances less than an atomic diameter due to the strong repulsive forces

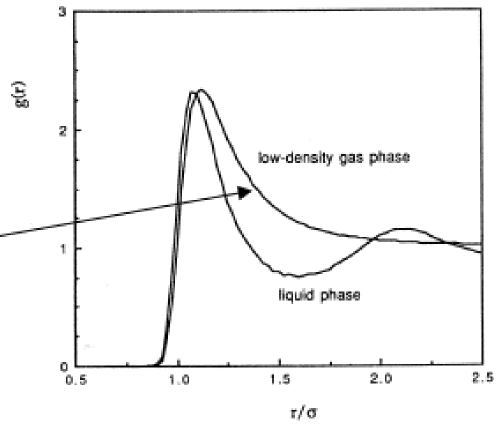
Largest peak ~3.7 where there is 3 times more likely to be an atom (than ideal gas)

At large distances the system approaches an ideal gas; no long-range order

Στατική Δομή

- Radial distribution function
  - In the low density (gas) limit

$$\lim_{\rho\to 0} g(r) = \exp\left[-\frac{U(r)}{kT}\right]$$



  - Discriminate between crystal structures
    - FCC lattice has fewer atomic pairs separated by sqrt(2) and more atomic pairs separated by sqrt(3) than a simple cubic lattice
  - Near fluid-solid boundaries, $g(r)$ used to determine phase
    - Crystalline solids will exhibit deeper valleys and higher, narrower secondary peaks liquids or amorphous solids

Time Correlation Function

- Two time dependent signals A and B; C quantifies the correlation between them

$$C(t) = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} A(t_0) B(t_0 + t) dt_0 = \langle A(t_0) B(t_0 + t) \rangle$$

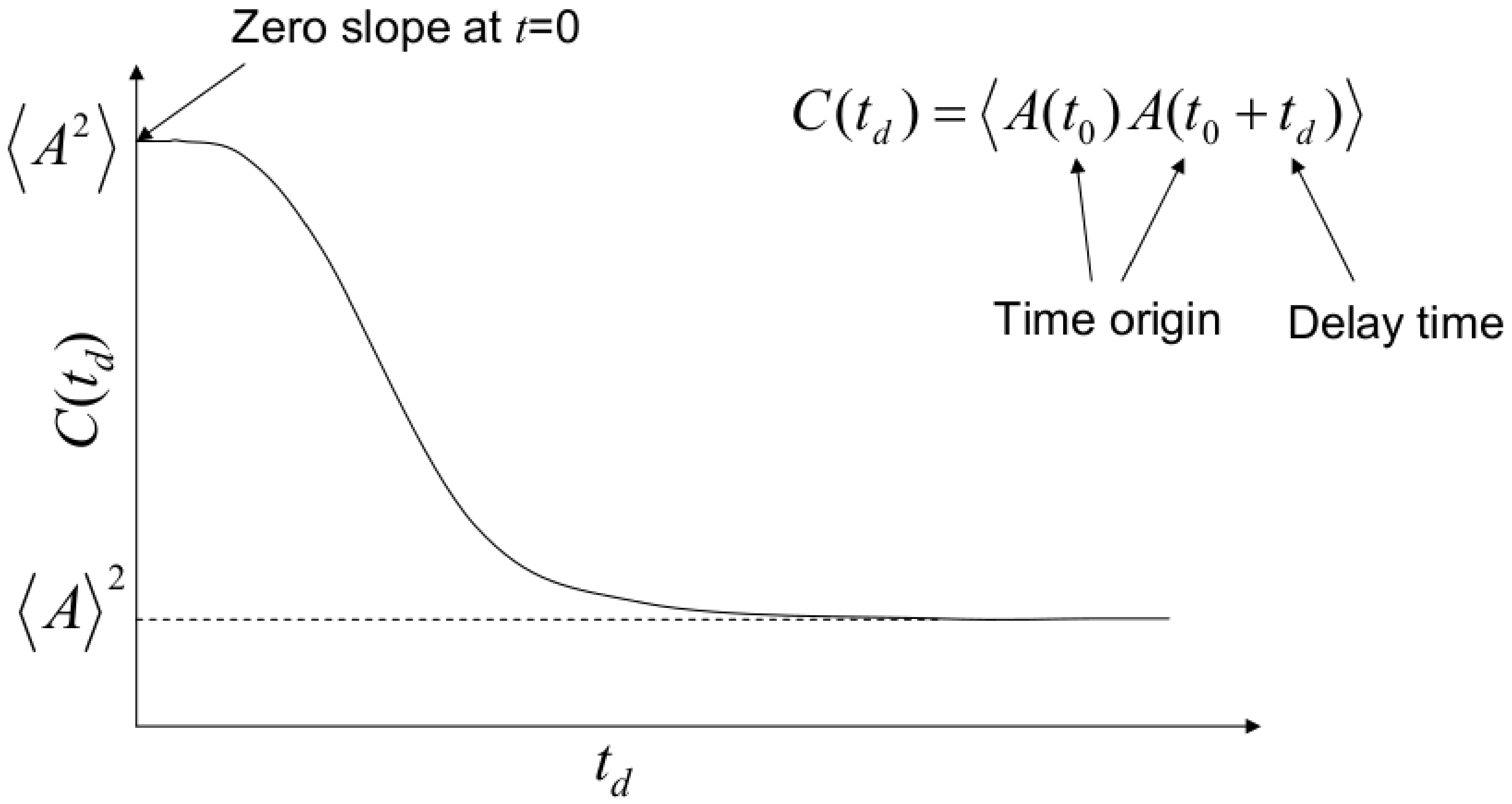
- A correlation function is invariant under translations of the time origin

$$C(t) = \langle A(t_0) B(t_0 + t) \rangle = \langle A(t_0 + s) B(t_0 + s + t) \rangle$$

  - A and B different: C is a cross-correlation
  - A and B the same: C is an auto-correlation

Time Correlation Function

- Characteristic features of an autocorrelation function



Time Correlation Function

- Implementation

$$C(t_d) = \frac{1}{t_{\max}} \sum_{t_0}^{t_{\max}} A(t_0) A(t_0 + t_d) \qquad t_{\max} = L - \frac{t_d}{\Delta t}$$

- Example

index	t	$A(t) = \sin\left(\frac{\pi}{2} t\right)$
1	0	0
2	.2	.31
3	.4	.59
4	.6	.81
5	.8	.95
6	1	1

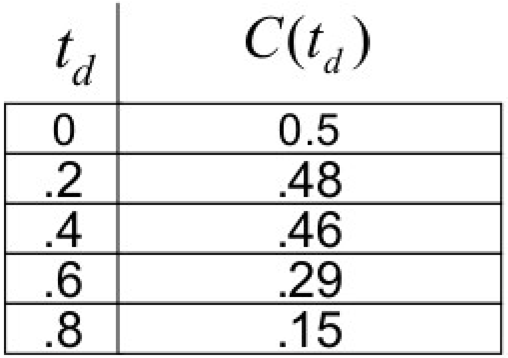
$$t_{\max}(t_d = .4) = 6 - \frac{.4}{.2} = 4$$

$$C(t_d = .4) = \frac{1}{4}\left[A(0)\cdot A(0+.4) + A(.2)\cdot A(.2+.4) + A(.4)\cdot A(.4+.4) + A(.6)\cdot A(.6+.4)\right]$$

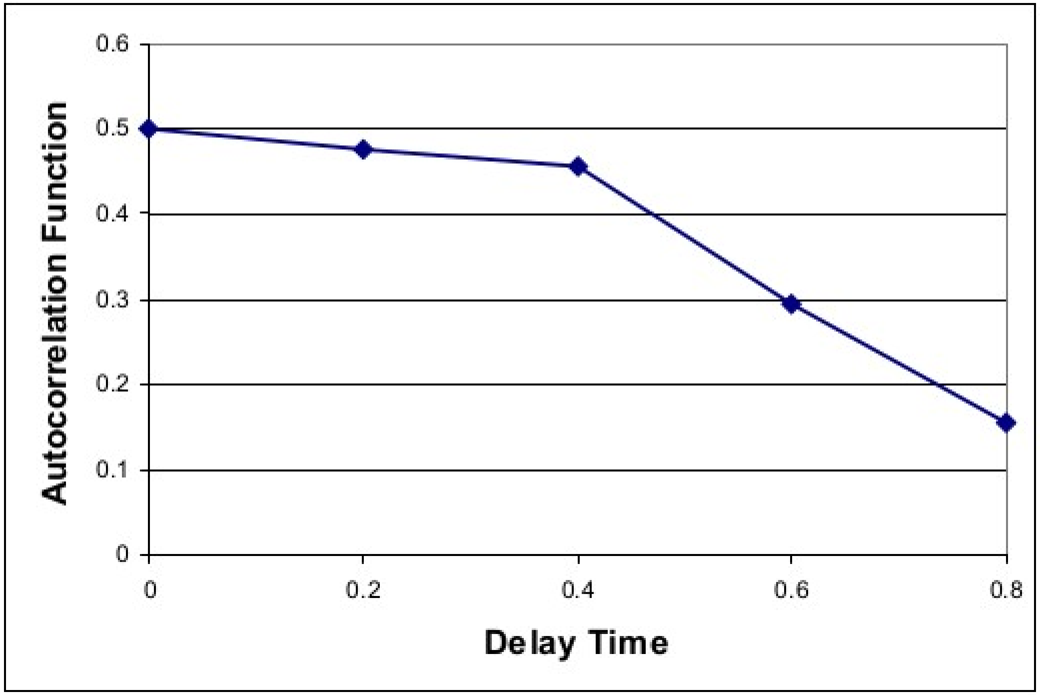
$$C(t_d = .4) = 0.46$$

Time Correlation Function

- Example cont.

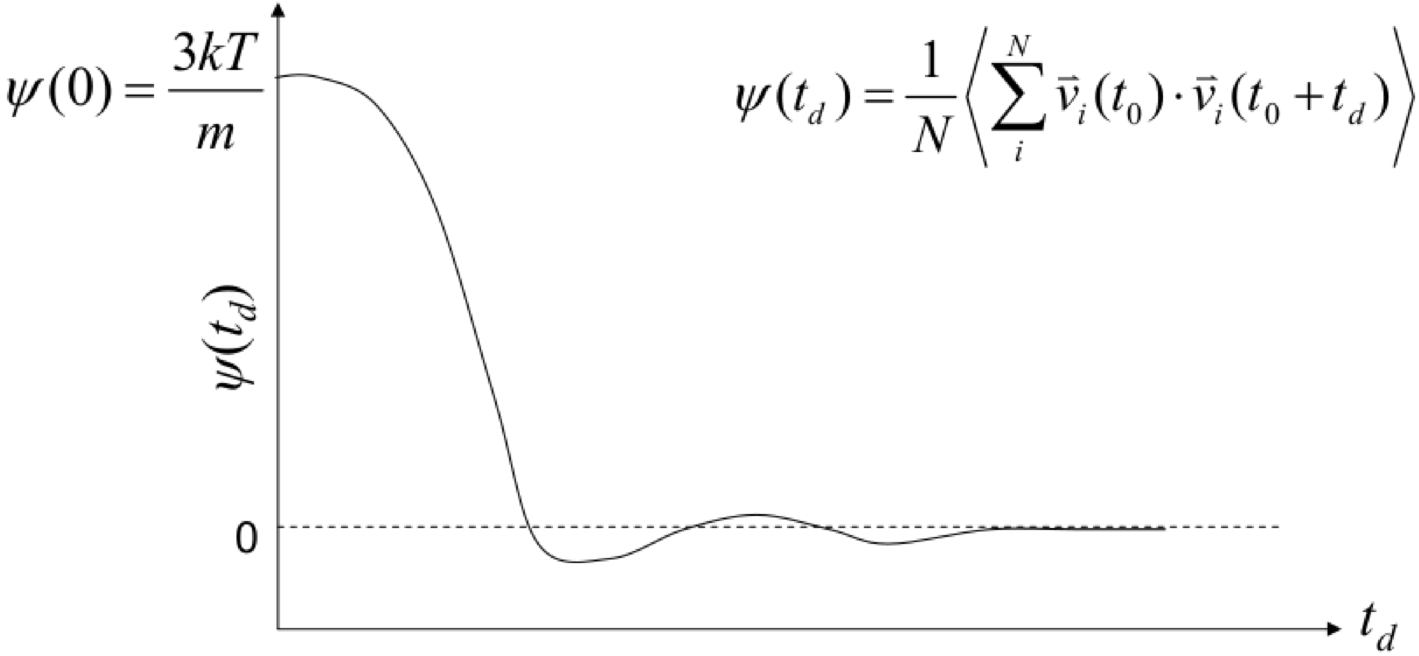


t_d	$C(t_d)$
0	0.5
.2	.48
.4	.46
.6	.29
.8	.15



Time Correlation Function

- Single particle correlations
  - Dynamic quantity is a property of individual particles
- Velocity autocorrelation function



$$\psi(t_d) = \frac{1}{N}\left\langle \sum_{i}^{N} \vec{v}_i(t_0)\cdot\vec{v}_i(t_0+t_d) \right\rangle$$

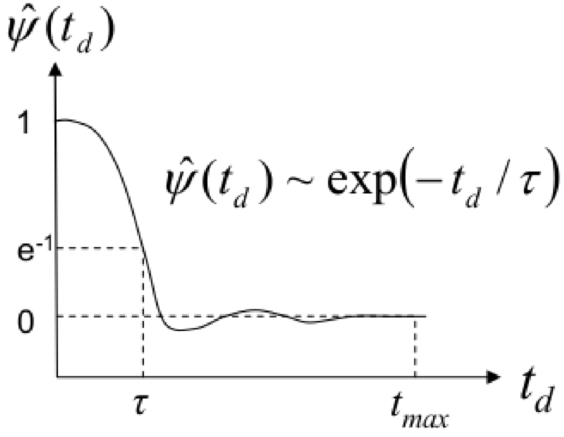
Time Correlation Function

- Uncertainty measurement
  - Equal Cartesian coordinate contributions

$$\langle \dot{x}_i(t_0)\dot{x}_i(t_0+t_d)\rangle = \langle \dot{y}_i(t_0)\dot{y}_i(t_0+t_d)\rangle = \langle \dot{z}_i(t_0)\dot{z}_i(t_0+t_d)\rangle$$

  - Statistical uncertainty

$$\varepsilon(t_d) \approx \pm\sqrt{\frac{2\tau}{t_{\max}}}\left[1-\hat{\psi}(t_d)\right] \qquad \tau = 2\int_0^\infty \left[\hat{\psi}(t_d)\right]^2 dt_d$$

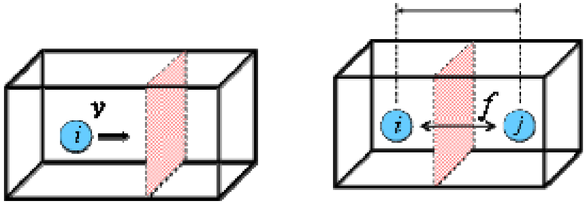


$\hat{\psi}(t_d) \sim \exp(-t_d/\tau)$ ➡ τ = time for $\hat{\psi}(t_d)$ to decrease from 1 to e^{-1}

Time Correlation Function

- Collective correlations
  - Properties of the whole system
    - Easier to compute
    - Less accurate
  - Stress autocorrelation function

$$J = \begin{bmatrix} J_{xx} & J_{xy} & J_{xz} \\ J_{yx} & J_{yy} & J_{yz} \\ J_{zx} & J_{zy} & J_{zz} \end{bmatrix}$$



$$J_{\alpha\beta} = m\sum_{i}^{N} v_{i\alpha} v_{i\beta} + \frac{1}{2}\sum_{i \neq j}^{N} r_{ij\beta} F_{ij\alpha}$$

$$\varphi(t_d) = \frac{\rho}{3kT}\frac{1}{N}\sum \left\langle J_{\alpha\beta}(t_0) J_{\alpha\beta}(t_0 + t_d) \right\rangle \qquad \text{for } \alpha \neq \beta$$

Transport Coefficients

- Einstein relations
  - Transport coefficients from differentiating a correlation function with respect time
- Green-Kubo relations
  - Transport coefficients from integrating a correlation function over time
- General concept
  - Flux = -coefficient x gradient

Transfer per unit area in unit time

Resistance to flow

Driving force for the flux

Transport Coefficients

- Example: 1D diffusion
  - Fick's law and conservation of mass

$$N\dot{x} = -D\frac{\partial N}{\partial x} \qquad \frac{\partial N}{\partial t} + \frac{\partial\left(N\dot{x}\right)}{\partial x} = 0$$

  - Combine and solve for N

$$\frac{\partial N}{\partial t} = D\frac{\partial^2 N}{\partial x^2} \qquad N(x,t) = \frac{N_0}{2\sqrt{\pi D t}}\exp\left[\frac{-x^2}{4Dt}\right]$$

  - Second moment of the distribution is the mean-square displacement

$$\left\langle [x(t) - x(0)]^2 \right\rangle = \frac{1}{N_0}\int x^2 N(x,t)\,dx$$

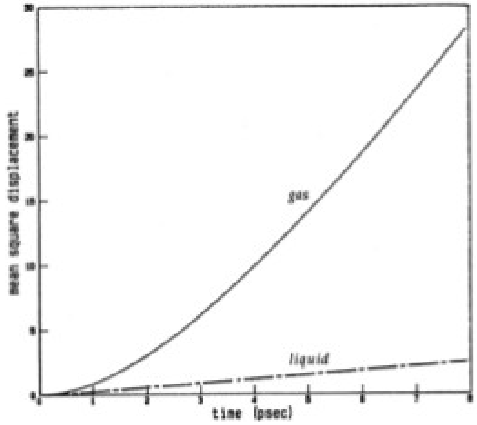
Transport Coefficients

- Example: 1D diffusion cont.
  - Combine

$$\left\langle [x(t)-x(0)]^2 \right\rangle = 2Dt$$

  - Applicable when the time is large compared to the average time between atomic collisions
  - Finally, Einstein's relation

$$D = \lim_{t\to\infty} \frac{\left\langle [x(t)-x(0)]^2 \right\rangle}{2t}$$


Mean-squared displacement

Transport Coefficients

- Example: 1D diffusion cont.
  - Time derivative

$$\dot{x}(t) = \frac{dx}{dt} \qquad x(t) - x(0) = \int_0^t \dot{x}(t')dt'$$

  - Square both sides and average over time origins

$$msd = \left\langle [x(t) - x(0)]^2 \right\rangle = \int_0^t dt'' \int_0^t dt' \left\langle \dot{x}(t')\dot{x}(t'') \right\rangle$$

  - Use integrand symmetry, shift the time origin, and change variables

$$msd = 2\int_0^t dt'' \int_0^{t''} d\tau \left\langle \dot{x}(\underset{\substack{\nwarrow \\ t''-t'}}{\tau})\dot{x}(0) \right\rangle$$

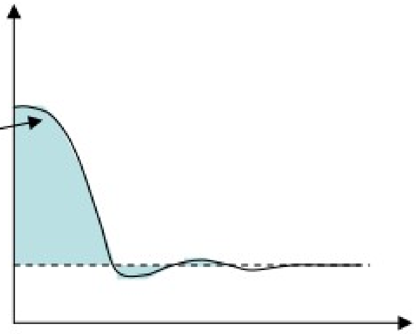
Transport Coefficients

- Example: 1D diffusion cont.
  - Integrate and solve for *msd*

$$\frac{\left\langle [x(t)-x(0)]^2 \right\rangle}{2t} = \int_0^t d\tau \left\langle \dot{x}(\tau)\dot{x}(0) \right\rangle \left(1-\frac{\tau}{t}\right)$$

  - Take the long-time limit

VACF



$$\lim_{t\to\infty} \frac{\left\langle [x(t)-x(0)]^2 \right\rangle}{2t} = \int_0^\infty d\tau \left\langle \dot{x}(\tau)\dot{x}(0) \right\rangle$$

  - Recall Einstein's relation

$$D = \lim_{t\to\infty} \frac{\left\langle [x(t)-x(0)]^2 \right\rangle}{2t}$$

$$D = \int_0^\infty d\tau \left\langle \dot{x}(\tau)\dot{x}(0) \right\rangle$$

Transport Coefficients

- Green-Kubo relations
  - Diffusion (3D)

$$D = \int_0^\infty \psi(t_d) \qquad \psi(t_d) = \frac{1}{3N}\left\langle \sum_i^N \vec{v}_i(t_0)\cdot\vec{v}_i(t_0+t_d)\right\rangle$$

  - Viscosity

$$\eta = \int_0^\infty \varphi(t_d) \qquad \varphi(t_d) = \frac{\rho}{3kT}\frac{1}{N}\sum\left\langle J_{\alpha\beta}(t_0)J_{\alpha\beta}(t_0+t_d)\right\rangle$$

Για να προσομοιώσω χρειάζομαι

α. Φυσικοχημεία
β. Ικανοποιητική γνώση Calculus
γ. Ευχέρεια στη χρήση υπολογιστή
δ. Υπομονή….