

Important for Integration Algorithms

- For the general case, we want a simulation algorithm that should: (please, debate)
- a) be computationally *fast*
 - b) permit *long* time step dt
 - c) duplicate classical *trajectories* as close as possible
 - d) satisfy known *conservation laws* for energy and momentum
 - e) be *time reversible*

43

Which one to choose?

For the general case, we want a simulation algorithm that should:

- Compared to the time-consuming force calculations, the raw speed of the integration algorithm is not important. Rather want bigger dt , but this will decrease accuracy!
- a) be computationally *fast*
 - b) permit *long* time step dt
 - c) duplicate classical *trajectories* as close as possible
 - d) satisfy known *conservation laws* for energy and momentum
 - e) be *time reversible*

44

Which one to choose?

- For the general case, we want a simulation algorithm that should:
- But, how important are points c), d), and e)?
- a) be computationally *fast*
 - b) permit *long* time step dt
 - c) duplicate classical *trajectories* as close as possible
 - d) satisfy known *conservation laws* for energy and momentum
 - e) be *time reversible*

45

Divergence of Trajectories

Get over it!

Computers are far from perfect and anyway we are dealing with approximate algorithms...

But even two classical trajectories that are close to each other will eventually diverge exponentially with time.

After all, we are dealing with non-linear diff. equations!

46

Divergence of Trajectories

Let the position of particle i be

$$\mathbf{r}_i(t) = f[\mathbf{r}(t), \mathbf{p}(t)]$$

And the perturbed position

$$\mathbf{r}'_i(t) = f[\mathbf{r}(t), \mathbf{p}(t) + \epsilon]$$

The difference between both at short times is linear in ϵ

$$|\Delta\mathbf{r}(t)| \sim \epsilon \exp(\lambda t)$$

This is the so-called Lyapunov instability

47

Divergence of Trajectories

Lyapunov instability:

$$|\Delta\mathbf{r}(t)| \sim \epsilon \exp(\lambda t)$$

is responsible for our inability to accurately predict a trajectory beyond a certain small time.

Suppose bound \mathbf{r} to Δ_{max} for $t < t_{max}$. What is the max. error ϵ that we can afford? From above:

$$\epsilon \sim \Delta_{max} \exp(-\lambda t_{max})$$

Thus, max error decreases with length or run t_{max}

48

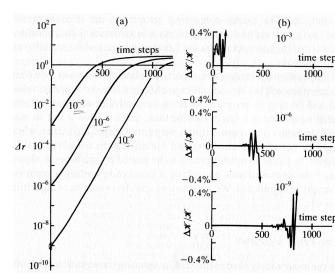
Divergence of Trajectories

- Compound that with other errors, such as the one associated with finite precision arithmetic.
- Take as an example a simulation of a dense liquid. Consider one unperturbed system and three perturbed systems with $10^{-3}\sigma$, $10^{-6}\sigma$, and $10^{-9}\sigma$ displacements (σ diameter). Define distance between systems as:

$$|\Delta\mathbf{r}|^2 = (1/N)\sum|\mathbf{r}_i(t) - \mathbf{r}_i^o(t)|^2$$

49

Divergence of Trajectories



- It only takes a few hundred steps for the perturbed trajectories to diverge from the unperturbed one
- Note kinetic energy also loses correlation with original

50

Going back to Importance

For the general case, we want a simulation algorithm that should:

- a) be computationally fast
But, how important are points c), d), and e)?
- b) permit long time step dt
- c) duplicate classical *trajectories* as close as possible – **CANNOT** for $t > t_{corr}$
- d) satisfy known *conservation* laws for energy and momentum – **E YES, P CAN BE ARRANGED**
- e) be *time reversible* – **CANNOT**

51

So, what is important?

- Exact solutions for times up to the correlation times desired
- Need energy conservation because we will sample from the microcanonical ensemble
- Does not need exact trajectories (in contrast to satellites in orbit)
- Big enough dt but small enough that preserve time correlations and energy conservation
- Note: High T, light molecules, rapidly varying potentials demand low dt

52

Checks on accuracy

After a simulation is coded and ran for the first time, the answer to “Is my simulation running correctly?”

is usually NO!

Check:

- That there are no *catastrophic* errors...
- Conservation laws, E should be a constant
- No drifts in energy

53

Checks on accuracy

Catastrophic errors come usually from:

- Incorrect force calculation
- Overlapping particles
- Wrong units for physical constants
- Wrong size for potential cutoff distances

54

Checks on accuracy

Conservation of energy:

- Should be a *constant*, but for simple LJ, 1 part in 10^4 is generally ok. Reduce dt if necessary.
- Run same simu for different dt , but same t_{\max} , and plot energy RMS vs dt . For Verlet should be dt^2

55

Checks on accuracy

Drifts in energy:

- Could be from a too big dt or truncation in potential
- Perform same test as above. If drift is unchanged with dt then the drift has a *physical* origin not based on dt . Otherwise, decrease dt .

56

Once the simulations runs...

- We want to measure:
 - Thermodynamics properties: T, P, E
 - Response functions: C_v
 - Structural Quantities: $g(r)$
 - Transport Coefficients: D
- They have to be obtainable using only $r(t)$ and $v(t)$.

57

Thermodynamic Quantities

- Temperature comes from Kinetic energy:

$$T(t) = \frac{1}{k_B N_f} \sum_{i=1}^N \frac{m_i v_i^2(t)}{2}$$

- Where N_f = num. degrees of freedom (3N-3 for fixed c.m.)

- Pressure comes from the virial (in 3D):

$$PV = Nk_B T + \frac{1}{3} \left\langle \sum_{i < j} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \right\rangle$$

58

Response Functions

- Specific heat, a consequence of energy fluctuations (defined as $C_v = (\partial E / \partial T)_v$):

- Microcanonical Ensemble (NVE)

$$C_v = \frac{3}{2} k_B \left(1 - \frac{2N(\langle E_k^2 \rangle - \langle E_k \rangle^2)}{3k_B^2 T^2} \right)^{-1}$$

- Canonical Ensemble (NVT)

$$C_v = \frac{N}{T^2} (\langle E^2 \rangle - \langle E \rangle^2)$$

Could also solve by plotting $E(T)$ and obtaining the slope.

59

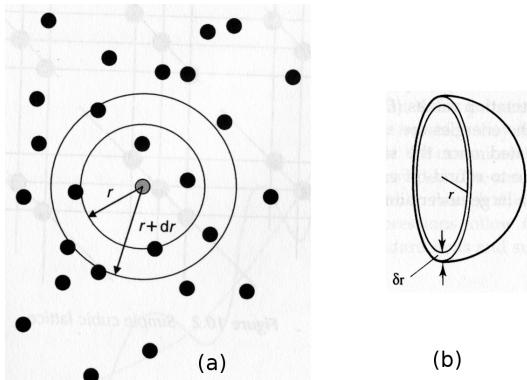
Structural Properties

Pair Correlation Function:

- Measures probability of finding a molecule at distance r from a reference molecule
- Is defined as the ratio between $\langle \rho(r) \rangle$ and $\langle \rho_{ideal}(r) \rangle$ - dimensionless
- Is related to, e.g.:
 - neutron and X-ray scattering in liquids
 - Light scattering in colloidal suspensions

60

Pair Correlation Function



61

Pair Correlation Function

- Create average histogram of particle pairs with separation distance between r and $r+dr$

$$n(r) = n_{his}(r)/l(N \cdot t_{total})$$

- Calculate same number but for ideal gas

$$n^{ideal}(r) = 4\pi \frac{\rho}{3} [(r + \delta r)^3 - r^3]$$

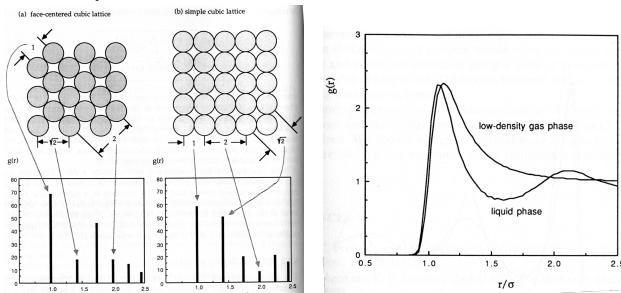
- Define pair corr. function

$$g(r) = n(r)/n^{ideal}(r)$$

62

Pair Correlation Function

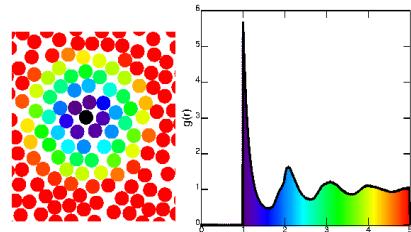
- Example:



63

Pair Correlation Function

Correspondence between peaks and neighbor shells:



64

Pair Correlation Function

- Useful to verify other properties:

$$U/N = 2\pi\rho \int_0^\infty dr r^2 u(r) g(r)$$

$$P = \rho k_B T - \frac{2}{3}\pi\rho^2 \int_0^\infty dr r^3 \frac{du(r)}{dr} g(r)$$

65

Transport Coefficients

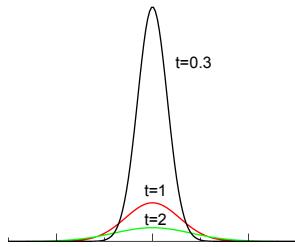
- Diffusion Coefficient, D
- Combining Fick's law on particle flux
 $\mathbf{j} = -D\nabla c$
- with conservation of mass, where c is particle concentration:
$$\frac{\partial c(r,t)}{\partial t} + \nabla \cdot \mathbf{j}(r,t) = 0$$
- get
$$\frac{\partial c(r,t)}{\partial t} - D\nabla^2 c(r,t) = 0$$

66

Transport Coefficients

- With solution

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



With BC: $c(r, 0) = \delta(r)$

67

Transport Coefficients

Going back to the differential equation:

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

Multiplying by r^2 and integrating

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

And identifying the mean-square distance over which molecules have moved in time t

Second moment of concentration

$$\langle r^2(t) \rangle \equiv \int dr c(r, t) r^2$$

68

Transport Coefficients

get:

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

It can be shown to get

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

obtaining a relationship between D and the width of the concentration profile (slope of rms of r^2).

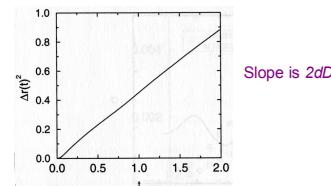
Relates microscopic to macroscopic

69

Transport Coefficients

To calculate: for every particle i , calculate distance traveled $\Delta r_i(t)$

to get: $\langle \Delta r(t)^2 \rangle = \frac{1}{N} \sum_{i=1}^N \Delta r_i(t)^2$



70

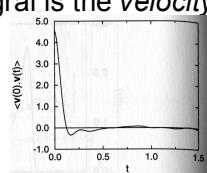
Transport Coefficients

Alternative formulation of the Diffusion Coefficient D

$$D = \frac{1}{d} \int_0^\infty d\tau \langle \mathbf{v}(\tau) \cdot \mathbf{v}(0) \rangle$$

The argument of the integral is the *velocity autocorrelation function*

e.g. for dense liquid



71

Transport Coefficients

Start from definition of displacement,

$$\Delta r(t) = \int_0^t dt' \mathbf{v}(t')$$

Consider 1D and substitute in previous result

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

72

Transport Coefficients

substitute: $2D = \lim_{t \rightarrow \infty} \frac{\partial \langle x^2(t) \rangle}{\partial t}$ ← $\Delta r(t) = \int_0^t dt' v(t')$

$$\begin{aligned}\langle x^2(t) \rangle &= \left\langle \left(\int_0^t dt' v_x(t') \right)^2 \right\rangle \\ &= \int_0^t \int_0^t dt' dt'' \langle v_x(t') v_x(t'') \rangle \\ &= 2 \int_0^t \int_0^{t'} dt' dt'' \langle v_x(t') v_x(t'') \rangle\end{aligned}$$

73

Transport Coefficients

Vacf (velocity autocorrelation function):

$$\langle v_x(t') v_x(t'') \rangle$$

Measures correlations of velocities at different times of the same particle.

Equilibrium property, thus invariant to time translations:

$$\langle v_x(t') v_x(t'') \rangle = \langle v_x(t' - t'') v_x(0) \rangle$$

74

Transport Coefficients

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

$$\langle x^2(t) \rangle = 2 \int_0^t \int_0^{t'} dt' dt'' \langle v_x(t' - t'') v_x(0) \rangle$$

$$2D = \lim_{t \rightarrow \infty} 2 \int_0^t dt'' \langle v_x(t - t'') v_x(0) \rangle$$

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

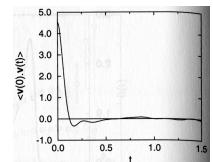
Example of a Green-Kubo relation:
relation between transport coeff. and
integral over a time-correlation function

75

Transport Coefficients

Velocity autocorrelation function.

- Time t to lose correlation is called the **correlation time or relaxation time**
- Neg. value → cage
- Low density fluids, it just decays monotonically



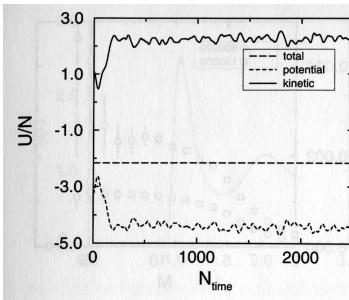
76

Error Analysis

- Different measurements in experiments are usually independent
 - Can use the usual statistical data analysis
- In MD, “measurements” are not necessarily uncorrelated
 - Averages of quantities may not suffer too much from correlations
 - Estimates of error, however, are sensitive to these correlations

77

Error Analysis



- Typical simulation: after an **equilibration** time, normal fluctuations settle in
- How do we calculate the error from these fluctuations?
- Answer depends on length of correlations

78

Error Analysis

In a simulation of some length, take several measurements of some quantity at different points of the trajectory.

- Mean value of the fluctuating property:

$$\langle A \rangle = \frac{1}{M} \sum_{\mu=1}^M A_\mu$$

A , property; A_μ , measurement of the property;
 M , number of measurements

79

Error Analysis

- If each A_μ is independent, get the variance

$$\sigma^2(A) = \frac{1}{M} \sum_{\mu} (A_\mu - \langle A \rangle)^2 = \langle A^2 \rangle - \langle A \rangle^2$$

with variance of the mean

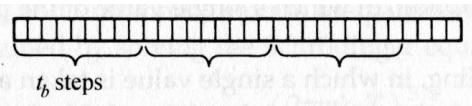
$$\sigma^2(\langle A \rangle) = \frac{1}{M} \sigma^2(A)$$

Note: if the A_μ are not independent (usual in MD), then the variance of the mean will be underestimated – (num. meas. < M)

$$\langle A \rangle = \frac{1}{M} \sum_{\mu=1}^M A_\mu$$

Error Analysis

- Soln: Use *block averages* method

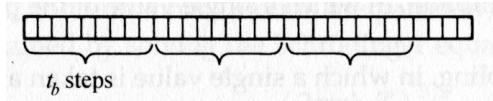


- divide trajectory into groups of time length t_b (coarse grain) and get the average per group
- Use these averages as the new data points and get variance

81

Error Analysis

- There is a t_b big enough beyond which the points will be uncorrelated



- For bigger blocking sizes, the error will then be independent of the size of the blocks
- Just have to find the value of t_b

82

Error Analysis

- For each size of block t_b and number of blocks M_b calculate

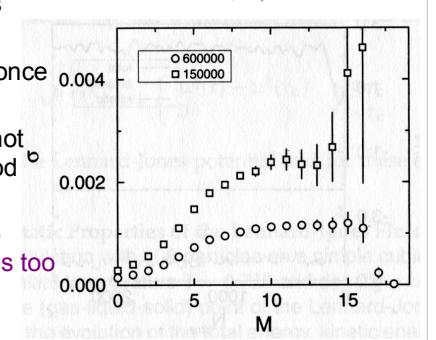
$$\sigma^2(\langle A \rangle_b) = \frac{1}{M_b - 1} \sum_{\beta=1}^{M_b} (A_\beta - \langle A \rangle_b)^2$$

- Plot as a function of size of blocks, M

83

Error Analysis

- For small M , error is underestimated
- Plateau is reached once data is uncorrelated
- At large M there is not enough data for good estimates of error
- Bonus: if there is no plateau, simulation is too short!



84

Setup of Simulations

At this point:

- We know how to calculate forces, potentials
- We know how to solve eqns of motion
- We know how to characterize structure and measure thermodynamic properties
- But, we do not know how to setup the simulation yet!

1

Periodic Boundary Conditions

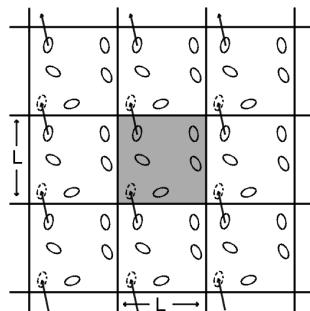
- For small systems, surface effects (e.g. on cubic box) are too big
 - (e.g. of 1000 particles in a $10 \times 10 \times 10$ box, 488 may be at interaction distance from one of the walls)
- Soln.: eliminate surfaces
- How: have “replicas” or mirrors of the original system surround and extend the system
- Condition: mirror atoms move in identical manner
- If an atom leaves the system, a mirror atom enters it from the opposing face

2

Periodic Boundary Conditions

Notes:

- Density in central box is conserved
- No need to store coordinates for all images



3

Periodic Boundary Conditions

How accurate is this:

- Depends on:
 1. Range of intermolecular potential (affect itself)
 2. The physics of the problem
- In LJ, $L \geq 6\sigma$ is sufficient

4

Periodic Boundary Conditions

Caveats:

- Inhibits occurrence of long-wavelength fluctuations (larger than L), thus:
 - Difficult to simulate close to liquid-gas critical point
 - 1st order transitions (that need long fluctuations) appear as higher order transitions

5

Periodic Boundary Conditions

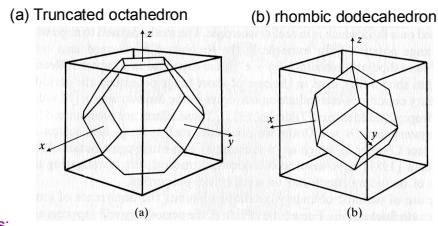
At the end of the day:

- Simulations show that away from phase transitions PBCs have little effect on equilibrium thermo. properties and structure

6

Periodic Boundary Conditions

Other geometries:



Features:

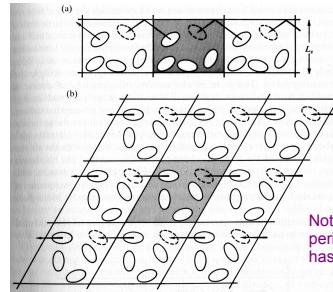
- (1) they are more spherical than cube;
- (2) distance between periodic images is larger than in the cube

7

Periodic Boundary Conditions

Mixed cases (adsorption on graphite surface):

- Rhombic PBC in the x-y plane
- Reflecting boundary in the z direction



Note: the graphite imposes a rhombic periodicity (external potential) that the PBC has to follow; could not do a square!

8