Computer simulation methods

(1)

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To understand and predict the properties of complex systems (many degrees of freedom): liquids, solids, adsorption of molecules onto surfaces and into solids, macromolecules, etc….

In practice such systems are not tractable by exact methods, and many straightforward approximations simply do not work.

Computer simulation methods allow us to study and predict structural and thermodynamic properties of such complex systems through the use of techniques that generate representative configurations of small replications of the macroscopic system with manageable numbers of particles.

Simulation techniques also enable us to determine the time-dependent behavior of atomic and molecular systems.

Computer simulations offer a test of theories and may assist experimentalists in the interpretation of new results.
Computer simulations generate information at the microscopic level (atomic and molecular positions, velocities, etc.) which is converted into macroscopic terms (pressure, internal energy, etc..) using statistical mechanics.

In the following we will summarize some concepts of statistical mechanics which are of most interest for the computer simulator.
Let us consider a system of $N$ particles.

$A(t) = A(p^N(t), r^N(t))$ is a generic property (pressure, heat capacity, etc.) varying over time and depending from the $N$ momenta $p^N(t)$ and positions $r^N(t)$.

**Time average**: average quantity of a single system over a time interval (directly related to a real experiment)

$$A_{\text{ave}} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t=0}^{\tau} A(p^N(t), r^N(t)) \, dt$$

integrating the equation of motion of the system to determine $A(p^N(t), r^N(t))$

**WARNING:**

- ! the typical number of simulated particle ($\sim 10^6$) is much smaller than in a “macroscopic system”.
- ! the typical trajectory length ($\sim 10^{-6}$ s) is relatively short.
Questions:

Does the method allow a sufficient exploration of phase space to yield satisfactory time averages within a feasible amount of computer time?

How critical is the choice of the initial conditions (positions and velocities)?

😊 Numerical simulations are within the power of modern computer.

😊 Thermodynamically consistent results can be obtained provided that initial conditions are carefully chosen.

$$\langle A \rangle = \frac{1}{M} \sum_{i=1}^{M} A(p^i, r^i)$$

where M is the number of time steps.
Because of the complexity of the evolution over time of $A(t)$, in conventional statistical mechanics the time average is replaced by ensemble average: a system evolving in time is replaced by a large number of replications of the system that are considered simultaneously.

**ensemble**: collection of points $\Gamma = \{r^N, p^N\}$ in the 6-dimensional phase space. Each point represents a typical system at any particular time. The points are distributed according to a probability density function (pdf) $\rho(\Gamma)$, which is determined by the chosen fixed macroscopic parameters defining the system (NPT, NVT, NVE, etc.). Each system (=point) evolves in time according to the standard equations of motion, quite independently from each other.

$$
\langle A \rangle = \int d\mathbf{p}^N d\mathbf{r}^N A(\mathbf{p}^N, \mathbf{r}^N) \rho(\mathbf{p}^N, \mathbf{r}^N)
$$

the ensemble average is defined by the integral over all possible configurations of the system at a fixed time, using the pdf $\rho(\Gamma)$ as measure.

ex.: in NVT conditions $\rho(\mathbf{r}^N, \mathbf{p}^N)$ is the familiar Boltzmann distribution:

$$
\rho(p^N, r^N) = \exp(-E(p^N, r^N)/k_B T)/Q
$$

where $Q$ is the partition function («sum over states», it provides the normalization of the probability distribution $\rho(p^N, r^N)$. It is function of the macroscopic parameters which define the ensemble)

$$
Q_{\text{NVT}} = \frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{p}^N d\mathbf{r}^N \exp \left[-\frac{\mathcal{H}(p^N, r^N)}{k_B T} \right]
$$

the system is called «ergodic» if time average = ensemble average

in an ergodic system all the trajectories would be different sections of a single long trajectory
Molecular dynamics (MD) vs Monte Carlo (MC)

**Molecular dynamics**: by numerically integrating the Newton’s equation of motion, MD calculates the “real dynamics” of the system (evolution of atomic positions and velocities over time) from which time averages of properties can be calculated. MD method is deterministic: the state of the system at any future time can be predicted from its current state. Successive configurations are connected in time. 

\[
\langle A \rangle = \frac{1}{M} \sum_{i=1}^{M} A(p_i, r_i) \quad \text{where} \ M \text{ is the number of time steps}
\]

**Monte Carlo**: In MC simulation each configuration depends only upon its predecessor and not upon any other previously visited configurations. MC method generates configurations randomly and uses a special set of criteria to decide whether or not to accept each new configuration. These criteria ensure that the probability of obtaining a given configuration is equal to the Boltzmann factor: 

\[
\exp\{-\frac{V(r^N)}{k_B T}\}
\]

The underlying idea is to generate a complete set of states in the phase space in accordance with the probability density. The ensemble average is then replaced by a trajectory average-like equation.

\[
\langle A \rangle = \frac{1}{M} \sum_{i=1}^{M} A(r_i) \quad \text{where} \ M \text{ is an index over all the sampled configurations}
\]

1. New configurations are generated by randomly moving a single particle or several particles.
2. Using the potential energy function \(V(r^N)\), the energy of the new configuration is calculated.
3. If \(V_{\text{new}} < V_{\text{old}}\) → the new configuration is accepted. Else, 
   
   if \(V_{\text{new}} > V_{\text{old}}\) → \(\exp\left[-\frac{V_{\text{new}}(r^N) - V_{\text{old}}(r^N)}{k_B T}\right]\) is compared to a random number sampled from a uniform distribution between 0 and 1. If the random number is higher, then the move is rejected. Otherwise the move is accepted. This procedure allows also moves to states of higher energy. 

The smaller is the difference \(V_{\text{new}}(r^N) - V_{\text{old}}(r^N)\), the greater is the probability that the move will be accepted.
### Some differences:

<table>
<thead>
<tr>
<th>MD</th>
<th>MC</th>
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<tbody>
<tr>
<td>• provides information about the time dependence of the properties of the system;</td>
<td>• there is no temporal relationship between successive MC configurations;</td>
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<tr>
<td>• has a kinetic contribution to the total energy;</td>
<td>• the total energy is determined from the potential energy;</td>
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<tr>
<td>• samples the 6N-dimensional phase space.</td>
<td>• samples the 3N-dimensional position space =&gt; provides deviations of thermodynamic properties from ideal gas behavior</td>
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Calculation of simple thermodynamic properties

Comparison between computed and measured thermodynamic properties allows the simulation and the underlying energy model to be tested.

Simulations allow predictions of the thermodynamic properties for which experimental data are not available or difficult to obtain.

Simulations provide information on the conformational changes in molecules and distributions of the molecules in a system.

**energy:**

\[ U = \langle E \rangle = \frac{1}{M} \sum_{i=1}^{M} E_i \]

**heat capacity:** (monitored to detect phase transitions) \( C_V = \left( \frac{\partial U}{\partial T} \right)_V \)

1. by performing a series of simulations at different T and then differentiating the energy with respect to T
2. from one simulation at fixed T by considering the instantaneous fluctuations in the energy:

\[ C_V = \{ \langle E^2 \rangle - \langle E \rangle^2 \} / k_B T^2 \]

or

\[ C_V = \langle (E - \langle E \rangle)^2 \rangle / k_B T^2 \]

more accurate due to round-off error

see note 1 for derivation
**temperature:** (calculated via the *equipartition theorem*)

The energy is shared equally amongst all energetically accessible degrees of freedom of a system (a system will try to maximize its entropy by distributing the available energy evenly amongst all the accessible modes of motion)

In particular: each quadratic degree of freedom will on average possess an energy $1/2 \ K_B \ T$

**Quadratic degree of freedom:** the energy depends on the square of some property:

- Translational degrees of freedom
  $$K = \frac{1}{2}mv^2$$

- Rotational degrees of freedom
  $$K = \frac{1}{2}I\omega^2$$

- Vibrational degrees of freedom
  $$K = \frac{1}{2}mv^2$$

At room T many rotational and translational d.o.f. are occupied (treated classically)

At room T most molecules are in their ground vibrational state $\Rightarrow$ equipartition contributions from vibrational d.o.f. need only to be considered at very high $T$.

**see note 2 for derivation**

**calculating $T$:**

According with the theorem of equipartition of energy each d.o.f. contributes $1/2 \ K_B \ T$. A system of $N$ particles has $3N$ translational d.o.f. If the total linear momentum is constrained to zero, 3 d.o.f. have to be removed.

$\pi_i$ is the total momentum of particle $i$ and $m_i$ is its mass

$N_c$ is the total number of constraints
**pressure**: (calculated via the virial theorem)

**virial theorem**: provides a relation between the time average of the total kinetic energy and the expectation value of the sum of the products of the coordinates of the particles and the total forces acting on them.

\[
P = \frac{1}{V} \left[ N k_B T - \frac{1}{3} \sum_{k=1}^{N} \sum_{j<k} \frac{dV(r)}{dr} r_{jk} \right]
\]

for a system at equilibrium

3N is the number of translational degrees of freedom

V(r) is the interaction potential between two particles function of the distance r

see note 3 for derivation
radial distribution function

the structure of a system, particularly of liquids, can be described by a set of distribution functions for the atomic positions. The simplest is the pair distribution function:

$$g_2(r_i, r_j), \text{ or } g_2(r_{ij}) \text{ or simply } g(r)$$

probability of finding a pair of atoms a distance \( r \) apart, relative to the probability expected for a completely random distribution at the same density (no interactions between particles).

$$P^{(N)}(r_1, \ldots, r_N) \, dr_1 \cdots dr_N = \frac{e^{-\beta U_N}}{Z_N} \, dr_1 \cdots dr_N$$

probability of an elementary configuration for a system of \( N \) particles. \( Z_N \) is the configurational integral.

$$P^{(n)}(r_1, \ldots, r_n) = \frac{1}{Z_N} \int \cdots \int e^{-\beta U_N} \, dr_{n+1} \cdots dr_N$$

probability of a reduced configuration, where the positions of only \( n < N \) particles are fixed, in \( r_1, r_2, \ldots, r_n \), with no constraints on the remaining \( N-n \) particles.

Since particles are identical, it is more relevant to consider the probability that any of them occupy positions in any permutation:

$$\rho^{(n)}(r_1, \ldots, r_n) = \frac{N!}{(N-n)!} P^{(n)}(r_1, \ldots, r_n)$$

\( n \)-particle probability density. For \( n = 1 \) is the one-particle density.

if the atoms are independent from each other \( \rho^{(N)} \) would simply equal \( \rho^N \), then \( g^{(n)} \) accounts for the correlations among atoms.

$$g^{(n)}(r_1, \ldots, r_n) = \frac{V^n N!}{N^n (N-n)!} \cdot \frac{1}{Z_N} \int \cdots \int e^{-\beta U_N} \, dr_{n+1} \cdots dr_N.$$  \( g^{(n)} \) is dimensionless.

For \( n=2 \)

$$g(r_1, r_2) = \frac{N(N-1)}{\rho^2 Z_{NVT}} \int dr_3 \, dr_4 \cdots dr_N \exp (-\beta \mathcal{V}(r_1, r_2, \ldots, r_N))$$
radial distribution function (continue)

operative definition: how many particles are within a distance of \( r \) and \( r + dr \) away from a particle with respect to a uniform distribution?

1. Calculate the distance between all particle pairs and binning them into a histogram.
2. The histogram is then normalized with respect to an ideal gas, in which particles’ histograms are completely uncorrelated (uniform distribution). In 3 dimensions, the normalization is the number density of the system multiplied by the volume of the spherical shell, \( \rho \times 4\pi r^2 dr \).

![Graph showing radial distribution function](image)

- At this distance the probability to find a particle is \( \sim 3 \) times larger than in ideal gas.
- At long distances \( g(r) \) tends to the ideal gas values: no long-range order.

*Fig 6.2: Radial distribution function determined from a 100 ps molecular dynamics simulation of liquid argon at a temperature of 100 K and a density of 1.396 g cm\(^{-3}\).*
radial distribution function (continue)

Assuming pairwise additivity, the $g(r)$ can be used to calculate thermodynamic properties:

$$4\pi r^2 dr = \text{volume of a spherical shell}$$

$$\rho g(r)4\pi r^2 dr = \text{number of particles inside a spherical shell}$$

$$v(r) = \text{pair interaction potential at distance } r$$

$$\rho g(r)v(r)4\pi r^2 dr = \text{interaction energy between the particles in the shell and the central particle}$$

$$E = \frac{3}{2} N k_B T + 4\pi N \rho \int_0^{\infty} r^2 v(r) g(r) \, dr$$

$E$ = energy of an ideal gas

potential contribution due to the interactions among the particles

= potential energy of a real gas

we count each interaction only once.

$$PV = N k_B T - \frac{2\pi N \rho}{3} \int_0^{\infty} r^2 r \frac{dv(r)}{dr} g(r) \, dr$$

$PV$ = kinetic contribution

kinetic contribution from the equipartition theorem

=energy of an ideal gas

virial contribution due to the interaction forces among the particle
**remarks: Sampling the phase space**

If it were possible to sample all the points in the phase space, than the partition function could be calculated by summing the values of $\exp(-E/k_B T) \rightarrow$ ergodic trajectory: the thermodynamic properties would be independent of the initial configuration.

In practice for the typical system studied by simulations methods the phase space is immense! and an ergodic trajectory is not achievable $\rightarrow$ A simulation can only provide an “estimation” of the true energies and thermodynamic properties, and different simulations with different starting points will provide similar but different results.

**thermodynamic properties:**

- **mechanical properties**: (related to derivative of the partition function)
  - internal energy, pressure, heat capacity
  - standard simulations provide reasonable estimations

- **entropic or thermal properties**: (directly related to the partition function)
  - free energy, entropy, chemical potential

...difficult to determine accurately by standard simulations!

see note 4 for more explanation
the content of notes 1 to 4 is shown on the whiteboard