Theory behind atomistic simulations

[main sources: Allen-Tildesley and Antti Kuronen's MD course]

- An atomistic simulation (MD or MC) gives atom positions and velocities $\{\mathbf{q}_i,\mathbf{p}_i\}$
- $\{\mathbf{q}_i,\mathbf{p}_i\}$ (or in cartesian coordinates $\{\mathbf{r}_i,\mathbf{p}_i\}$) => macroscopic quantities
- system Hamiltonian $H(\mathbf{q}, \mathbf{p})$
- equations of motion:

$$\dot{q}_k = \frac{\partial}{\partial p_k} H(\mathbf{q}, \mathbf{p})$$

$$\dot{p}_k = -\frac{\partial}{\partial q_k} H$$

- N particles => the system state at any given time is a point Γ in a 6N-dimensional phase space. The evolution of the system from one point Γ to another is determined by the MD equations of motion or a Metropolis Monte Carlo simulation.
- Let us denote one point in phase space $\{\mathbf{q}_i,\mathbf{p}_i\} = \Gamma$

If we in MD want some physical quantity $A = A(\Gamma)$ which should correspond to a measured quantity A_{obs} it can be obtained from the simulation as a time average:

$$A_{\text{obs}} = \langle A \rangle_t = \langle A(\Gamma(t)) \rangle_t = \lim_{t_{\text{obs}} \to \infty} \frac{1}{t_{\text{obs}}} \int_0^{t_{\text{obs}}} A(\Gamma(t)) dt$$

- All practical simulations are of course over discrete steps, so the integral has to be rewritten

$$A_{\mathrm{obs}} = \langle A \rangle_t = \frac{1}{\tau_{\mathrm{obs}}} \sum_{\tau = 1}^{\tau_{\mathrm{obs}}} A(\Gamma(\tau))$$

and because an MD simulation often fluctuates strongly in the beginning, we do not want to include the first, say, 5-50 time steps in the average and thus should use e.g.

$$A_{\mathrm{obs}} = \frac{1}{\tau_{\mathrm{obs}} - 100} \sum_{\tau = 100}^{\tau_{\mathrm{obs}}} A(\Gamma(\tau))$$

Relation between simulations and statistical physics

- So, in MD a time average gives the experimental quantity A. This is **not** the approach taken in statistical physics, however. In the classical theory, instead so called Gibbs ensembles are considered, that is, a set of points Γ in phase space. The likelihood of being in one point is given by some probability distribution $\rho(\Gamma)$.

  - the probability distribution $\rho(\Gamma)$ is different for different external conditions, ensembles:NVE, NVT, NPT. Let us denote these e.g. with $\rho_{NVE}(\Gamma)$ or generally, for any ensemble, $\rho_{\mathrm{ens}}(\Gamma)$.

- In statistical physics the time average is replaced by an ensemble average, that is, we go through **all** the points $\{\mathbf{q}_i,\mathbf{p}_i\}$ in the ensemble phase space.

- In a Monte Carlo simulations the time average is replaced by going through a **large set** of points in phase space. Then A_{obs} is given by

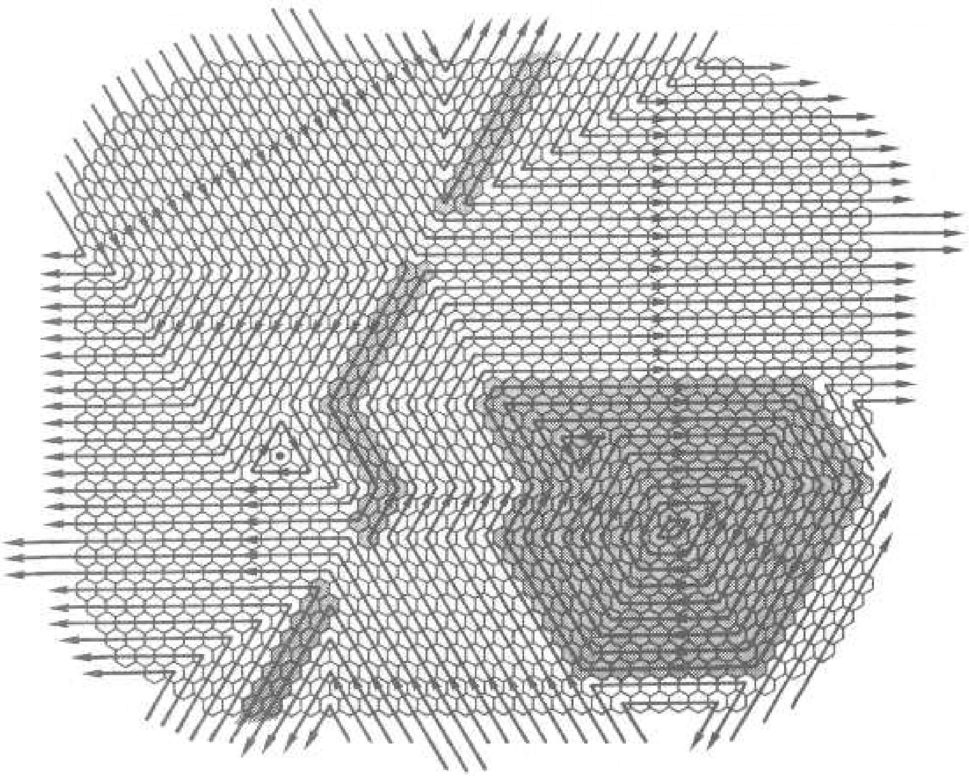
$$A_{\mathrm{obs}} = \langle A \rangle_{\mathrm{ens}} = \sum_{\Gamma} A(\Gamma)\rho_{\mathrm{ens}}(\Gamma)$$

- In case $\rho_{\mathrm{ens}}(\Gamma)$ is independent of time (that is, the system is in thermodynamic equilibrium), and the system is **ergodic**, this gives the same thing as $\langle A \rangle_t$

Ergodicity

- By an ergodic system, one means a system where a long enough simulation will go through all points in phase space $\{\mathbf{q}_i,\mathbf{p}_i\}$.

- An example of a *non-ergodic* system (each hexagon represents one point phase space$\{\mathbf{q}_i,\mathbf{p}_i\}$):



- In the darker area, the simulation moves in a close path, and can never get out of this area => the simulation does not test all of phase space, i.e. is non-ergodic.

- In case there would be a single path which would go through the whole system, the system would be ergodic.

- Is it possible to prove that some system is ergodic? Not in the general case, and even for a given system it is usually very difficult in practice.

- In practice the system may not only have regions which are impossible to reach, but also regions which are surrounded by a high potential energy barrier so that reaching them in a finite simulation may be very unlikely (such a barrier is illustrated by the grey thin regions in the figure). This may distort the simulation averages badly.

- A practical example: simulate diffusion in Cu at high temperature, around the melting point. In equilibrium the lattice has, say, 10 vacancies which cause diffusion at a rate of e.g. 1 atom/1 ps. Hence in a 100 ps simulation one gets about 1000 atom jumps, which appears to give a good time average of the diffusion constant.

  But: about once a ns a Frenkel pair, that is a pair of one vacancy and one atom at an interstitial position, may be created. Because the interstitial moves very much faster than the vacancy, it can cause thousands of atom jumps before it recombines with some vacancy. Because the interstitial causes a huge lot of diffusion, its presence can completely change the diffusion constant which would have been obtained in 100 ps.

  So the system must be simulated for tens of ns:s to get a reliable estimate of the diffusion coefficient - and if one does not realize the possibility of Frenkel pair formation, one would probably never notice this in a single 100 ps simulation.
  [Nordlund and Averback, Phys. Rev. Lett. 80 (1998) 4201]

- So: to get reliable results one not only has to burn away computer time, but also understand the physics in the system well!

- Sometimes (in MC simulations) it is useful to use a weighting function $w_{\text{ens}}(\Gamma)$ to weigh the ensemble and speed up getting the desired results:

$$\rho_{\text{ens}}(\Gamma) = \frac{w_{\text{ens}}(\Gamma)}{Q_{\text{ens}}}$$

$$Q_{\text{ens}} = \sum_{\Gamma} w_{\text{ens}}(\Gamma) \qquad \text{(partition function)}$$

$$\langle A \rangle_{\text{ens}} = \frac{\sum_{\Gamma} w_{\text{ens}}(\Gamma) A(\Gamma)}{\sum_{\Gamma} w_{\text{ens}}(\Gamma)}$$

• The reason this is useful is related to the theory of MC integration: the flatter the function, the faster it is to obtain a precise average

- Q_{ens} will depend on the macroscopic properties of the system.

- Connection to thermodynamics: $\Psi_{\mathrm{ens}} = -\ln Q_{\mathrm{ens}}$
  = thermodynamic potential

- In practice this is achieved by setting up the MC simulation such that it generates points according to the desired weighting function. A simple choice for the weighting function is simply

$$w_{\mathrm{ens}}(\Gamma) = \rho_{\mathrm{ens}}(\Gamma)$$

- How this is achieved in practice will be dealt with later on during the course

- So, to summarize the purpose of equilibrium simulations can be stated as:

  - go through phase space as efficiently as possible to get averages which correspond to experimentally observable quantities A_{obs}

  - molecular dynamics: $\langle A \rangle_t$

  - Monte Carlo: $\langle A \rangle_{\mathrm{ens}}$ (importance sampling)

- In MD only the NVE ensemble is obtained by solving the ordinary Newton/Lagrange/Hamiltonian equations of motion. For the other ones, one has to generate equations of motion which behave according to the desired ensemble $\rho_{\mathrm{ens}}(\Gamma)$

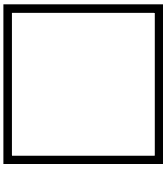
The most important ensembles

- As in thermodynamics, the ensembles are denoted by letters which indicate which physical quantities are conserved. The names are also the same.

1. microcanonical (NVE)
2. canonical (NVT)
3. isothermal-isobaric (NPT)
4. grand canonical (μVT)

- Here N is the number of atoms, V the system volume, T the temperature, P the pressure, and μ the chemical potential [cf. e.g. Mandl “Statistical physics” chapters 2 and 11].

- microcanonical: NVE constant (isolated)



$$\rho_{NVE}(\Gamma) = \delta(H(\Gamma) - E)$$

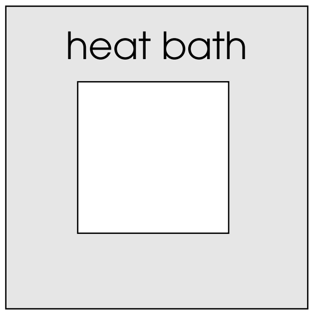
$$Q_{NVE} = \sum_{\Gamma} \delta(H(\Gamma) - E) = \frac{1}{N!}\frac{1}{h^{3N}} \int d\mathbf{r} d\mathbf{p} \delta(H(\mathbf{r},\mathbf{p}) - E)$$

the thermodynamical potential is the entropy: $\frac{S}{k_B} = \ln Q_{NVE}$

- the δ function selects the states Γ where the total energy = E

- natural in the sense that the total energy is conserved.

- canonical: NVT constant (closed but not heat-isolated)

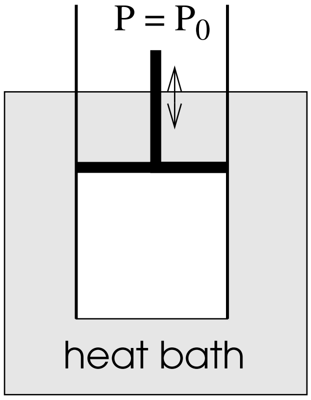


$$\rho_{NVT}(\Gamma) \propto \exp(-H(\Gamma)/k_B T)$$

$$Q_{NVT} = \sum_{\Gamma} \exp(-H(\Gamma)/k_B T) = \frac{1}{N!}\frac{1}{h^{3N}} \int d\mathbf{r} d\mathbf{p} \exp(-H(\mathbf{r},\mathbf{p})/k_B T)$$

- the thermodynamical potential is the Helmholtz free energy:

$$\frac{A}{k_B T} = -\ln Q_{NVT}$$



- isothermal-isobaric: NPT constant

$$\rho_{NPT}(\Gamma) \propto \exp((-H(\Gamma) + PV)/k_B T)$$

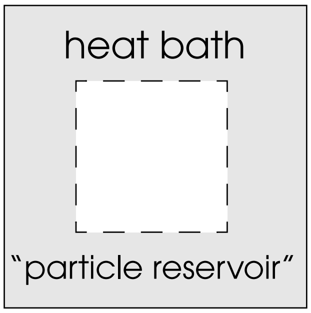
$$Q_{NPT} = \sum_{\Gamma} \exp((-H(\Gamma) + PV)/k_B T) =$$

$$\frac{1}{N!}\frac{1}{h^{3N}}\frac{1}{V_0}\int d\mathbf{r}\,d\mathbf{p}\exp((-H(\mathbf{r},\mathbf{p}) + PV)/k_B T)$$

- thermodynamical potential the Gibbs free energy:

$$\frac{G}{k_B T} = -\ln Q_{NPT}$$

- So in MD the volume has also to be made variable.



- grand canonical: μVT constant

$$\rho_{\mu VT}(\Gamma) \propto \exp((-H(\Gamma) + \mu N)/k_B T)$$

$$Q_{\mu VT} = \sum_{\Gamma, N} \exp((-H(\Gamma) + \mu N)/k_B T) = \sum_{N}$$

$$\frac{1}{N!}\frac{1}{h^{3N}}\exp(-\mu N/k_B T)\int d\mathbf{r}\,d\mathbf{p}\exp(-H(\mathbf{r},\mathbf{p})/k_B T)$$

the thermodynamic potential is the grand potential:

$$\frac{-\Omega}{k_B T} = -\ln Q_{\mu VT}$$

- now the number of atoms is changing: we have to have an algorithm to add or remove particles (not trivial in most practical systems)

- in the thermodynamic limit (system size => ∞) all the ensembles are equivalent (but the fluctuations around the average may not be)

Calculating thermodynamical quantities

- Internal energy, that is, total energy:
  (in the `mdmorse` code `Etot`)

  $$E = \langle H \rangle = \langle K \rangle + \langle U \rangle = \langle \sum_i \frac{|\mathbf{p}_i|^2}{2m_i} \rangle + \langle U(\mathbf{q}) \rangle$$

  *U(**q**)* is obtained directly from the potential energy calculation.

- Momentaneous temperature

  $$E_{kin} = \langle K \rangle = \frac{3}{2} N k_B T \quad => T = \frac{2K}{3Nk_B} = \frac{1}{3Nk_B} \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{m_i}$$

- So on average there is *kT/2* of energy per degree of freedom, as the classical equipartition theorem predicts.

- Pressure (refer to Hamiltonian equations of motion):

  - Generalized equipartition theorem for atom positions:

  $$\langle q_k \frac{\partial H}{\partial q_k} \rangle = k_B T$$

  $$=> \qquad -\frac{1}{3} \langle \sum_{i=1}^{N} \mathbf{r}_i \cdot (\nabla_{\mathbf{r}_i} U) \rangle = \frac{1}{3} \langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i^{\mathrm{tot}} \rangle = -N k_B T ;$$

  we can divide the force into two components: $\mathbf{f}_i^{\mathrm{tot}} = \mathbf{f}_i^{\mathrm{ext}} + \mathbf{f}_i$

  external pressure: $\frac{1}{3} \langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i^{\mathrm{ext}} \rangle = -PV$

  internal virial: $W = -\frac{1}{3} \sum_{i=1}^{N} \mathbf{r}_i \cdot (\nabla_{\mathbf{r}_i} U) = -\frac{1}{3} \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i$

hence $$\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i \right\rangle + \frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i^{\mathrm{ext}} \right\rangle = -Nk_BT$$

which can be rewritten $\langle W \rangle - PV = -Nk_BT$

which gives the desired pressure as $PV = Nk_BT + \langle W \rangle$

- for a pair interaction $V(r)$ and periodic boundaries it is best to calculate the virial as:

$$W = \frac{-1}{3}\sum_i \sum_{j>i} w(r_{ij}); \qquad w(r) = r_{ij}\frac{d}{dr_{ii}}V(r_{ij}) ;$$

So in practice it is best to calculate the virial in connection to the force calculation:

```
! dVdr is the derivative of V, i.e. the force
virial=virial+dVdr*(dx/r*dx+dy/r*dy+dz/r*dz)
```

Thermodynamic potentials (free energies)

- quantities which depend on the entropy. These can not usually be calculated directly.

- energy/potential differences can be ‘easily’ calculated by integrating over a reversible path:

$$\left(\frac{A}{Nk_\mathrm{B}T}\right)_2 - \left(\frac{A}{Nk_\mathrm{B}T}\right)_1 = \int_{\beta_1}^{\beta_2}\left(\frac{E}{Nk_\mathrm{B}T}\right)\frac{d\beta}{\beta} = -\int_{T_1}^{T_2}\left(\frac{E}{Nk_\mathrm{B}T}\right)\frac{dT}{T}$$

$$\left(\frac{A}{Nk_\mathrm{B}T}\right)_2 - \left(\frac{A}{Nk_\mathrm{B}T}\right)_1 = \int_{\rho_1}^{\rho_2}\left(\frac{PV}{Nk_\mathrm{B}T}\right)\frac{d\rho}{\rho} = -\int_{V_1}^{V_2}\left(\frac{PV}{Nk_\mathrm{B}T}\right)\frac{dV}{V}$$

- So one has to calculate a thermodynamic average for a large number of intermediate steps, then integrate over the path. Simple in principle, but can be a major pain-in-the-neck in practice.

Calculating absolute values with the Frenkel-Ladd method:

- construct a potential energy which is dependent on a parameter λ:
  $U = U(\mathbf{r}, \lambda)$

$$\Rightarrow \frac{\partial A}{\partial \lambda} = -k_{\mathrm{B}} T \frac{\partial}{\partial \lambda}[\ln \int d\mathbf{r} \exp(-U(\mathbf{r},\lambda)/k_B T)]$$

$$= \frac{\int d\mathbf{r} \frac{\partial V}{\partial \lambda} \exp(-U/k_B T)}{\int d\mathbf{r} \exp(-U/k_B T)}$$

$$= \langle \frac{\partial U}{\partial \lambda} \rangle$$

- we can calculate the absolute value of A, if we construct U so that some value of $\lambda = \lambda_0$ gives a system where the absolute value of A can be calculated analytically or numerically. This 'reference state' could be e.g. an ideal gas or a harmonic lattice. If this is possible, we can then get the absolute value of A for any λ using:

$$A(\lambda) - A(\lambda_0) = \int_{\lambda_0}^{\lambda} \langle \frac{\partial U}{\partial \lambda} \rangle d\lambda$$

- Let us say our real potential function, for which we want A, is U_0. We can then construct $U = U(\mathbf{r}, \lambda)$ to interpolate between U_0 and a harmonic lattice (Einstein's model) with

- $$U(\mathbf{r}, \lambda) = U_0(\mathbf{r}) + \lambda \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{r}_{i0})^2$$

$$=> \qquad A(\lambda = 0) = A(\lambda) - \int_0^{\lambda} \langle \frac{\partial U}{\partial \lambda} \rangle d\lambda'$$

- For large values of λ the system thus reduces to a harmonic lattice, for which many thermodynamic potentials are known analytically. For instance the Helmholtz free energy is:

$$A(\lambda) = \frac{3Nh\varpi}{2} - 3Nk_{\mathrm{B}}T\ln(1 - e^{-h\varpi/k_{\mathrm{B}}T}) + O(1/\lambda)$$

and hence the free energy for our 'real' system U_0 is $A(\lambda = 0)$ and can be calculated by integrating over $(\partial U)/(\partial\lambda)$.

[Frenkel-Ladd, J. Chem. Phys. **81** (1984) 3188]

Response functions

- How does the system react to a change in some thermodynamic variable?

- Some of the most important response functions:

constant volume heat capacity $C_V = \left(\frac{\partial E}{\partial T}\right)_V$

constant pressure heat capacity $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

thermal expansion coefficient $\alpha_P = V^{-1}\left(\frac{\partial V}{\partial T}\right)_P$

isothermal compressibility $\beta_T = -V^{-1}\left(\frac{\partial V}{\partial P}\right)_T$

bulk modulus $B = 1/\beta_T$

thermal pressure coefficient $\gamma_V = \left(\frac{\partial P}{\partial T}\right)_V$

- because $\alpha_P = \beta_T \gamma_V$ it is enough to get one of these three coefficients

- How can one get these from simulations? One approach is of course to simulate them directly. For instance the heat capacity C_V can be obtained by doing simulations at different temperatures, thus obtaining $E(T)$ =>

$$C_V(T) = \left(\frac{\partial E}{\partial T}\right)_V$$

This of course works if done properly. But many of these can be also obtained from the fluctuations in the system.

- For instance C_V can be derived from a single simulation in the canonical ensemble utilizing the following equality:

$$\langle \delta H^2 \rangle_{NVT} = k_{\mathrm{B}} T^2 C_V \quad (H \text{ is the momentaneous enthalpy})$$

- because $\langle \delta K \delta U \rangle_{NVT} = 0$, C_V can be separated into a kinetic and potential energy part:

$$\langle \delta H^2 \rangle_{NVT} = \langle \delta U^2 \rangle_{NVT} + \langle \delta K^2 \rangle_{NVT}$$

- we get the kinetic energy part easily,

$$\langle \delta K^2 \rangle_{NVT} = \frac{3N}{2}(k_B T)^2 = \frac{3N}{2\beta^2}$$

which gives us the ideal-gas part of the heat capacity $C_V^{id} = \frac{3}{2} N k_B$.

By combining these equations we get

$$\langle \delta U^2 \rangle_{NVT} = k_B T^2 \left(C_V - \frac{3}{2} N k_B \right)$$

- So we can calculate C_V solely from the fluctuations of the potential energy.

- Similar fluctuation identities can also be derived for many other response functions, see e.g. Allen-Tildesley chapter 2.5.

- Remember that these identities really depend on the ensemble used. In the microcanonical ensemble for instance the heat capacity is not obtained as above, but using

$$\langle \delta K^2 \rangle_{NVE} = \langle \delta U^2 \rangle_{NVE} = \frac{3}{2} N k_B^2 T^2 \left(1 - \frac{3 N k_B}{2 C_V} \right)$$

Structural quantities

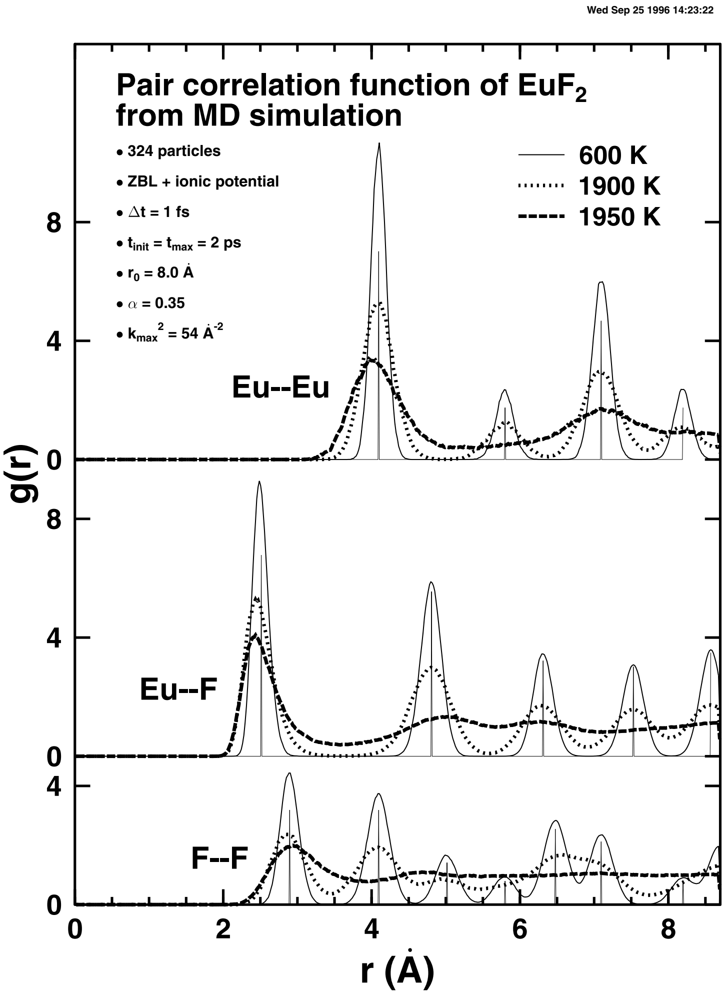
- pair correlation function

  $g_2(\mathbf{r}_i, \mathbf{r}_j) = g_2(r_{ij}) = g(r)$

  which tells at what distances atoms are from each other. Can be calculated as

$$g(r) = \rho^{-2}\langle\sum_i\sum_{j\neq i}\delta(\mathbf{r}_i)\delta(\mathbf{r}_j-\mathbf{r})\rangle = \frac{N^2}{V^2}\langle\sum_i\sum_{i\neq j}\delta(\mathbf{r}-\mathbf{r}_{ij})\rangle$$

- $g(r)$ gives information on the structure of the material. For instance melting:



• In practice it is of course not handy to use a delta function on a computer:

$$g(r) = \frac{N^2}{V^2}\langle\sum_i \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_{ij})\rangle$$

• So what is done instead is to collect statistics of what atom distances exist in some finite interval Δr:

integer stat(0:10000)

do i=0,10000
  stat(i) = 0
enddo

```
binwidth=0.01
do i=1,N
   do j=1,N
      if (i==j) cycle
      dx=x(j)-x(i);
      dy=y(j)-y(i);
      dz=z(j)-z(i);
      rsq=dx*dx+dy*dy+dz*dz
      r=sqrt(rsq)
      ir = int(r/binwidth+0.5)
      if (ir > 10000) ir=10000
      stat(ir) = stat(ir) + 1
   enddo
enddo
```

In this code periodics and checks that r is within the given interval are missing, and of course of N is large a linkcell method needs to be used.

• The normalization factor can be added afterwards, when printing the statistics

• The normalization factor volume for a bin of width Δr is $4\pi r^2 \Delta r$

• In practice if N is small (say 100 or less) the statistics will be poor, and it may be necessary to also perform a time average in the simulation.

- $g(r)$ is also useful because the average of any pair function can be given in the form:

  $$\langle a(\mathbf{r}_i, \mathbf{r}_j)\rangle = \frac{1}{V}\int d\mathbf{r}_i d\mathbf{r}_i g(\mathbf{r}_i, \mathbf{r}_j) a(\mathbf{r}_i, \mathbf{r}_j) \text{ or}$$

  $$\langle A\rangle = \langle\sum_i\sum_{j>i} a(r_{ij})\rangle = \frac{1}{2}N\rho\int_0^\infty a(r)g(r)4\pi r^2 dr$$

- for instance the energy (assuming a pair interaction $V(r)$)

  $$E = \frac{3}{2}Nk_{\mathrm{B}}T + 2\pi N\rho\int_0^\infty V(r)g(r)r^2 dr$$

  or the pressure

  $$PV = Nk_{\mathrm{B}}T - \frac{2}{3}\pi N\rho\int_0^\infty w(r)g(r)r^2 dr$$

- structure factor in reciprocal $\mathbf{k}$-space (Fourier transformation of positions):

  $$\rho(k) = \sum_{i=1}^{N}\exp(i\mathbf{k}\cdot\mathbf{r})$$

- The square of $\rho(k)$ gives the structure factor *S(k)*:

  $$S(k) = N^{-1}\langle\rho(k)\rho(-k)\rangle,$$

  which can be measured with x-ray or neutron scattering

- This quantity can be shown to be related to *g(r)* through a 3-dimensional Fourier transform:

  $$S(k) = 1 + \rho\hat{g}(k) = 1 + 4\pi\rho\int_0^\infty \frac{\sin kr}{kr} g(r)r^2 dr$$

  Because g(r) is a measurable quantity, it is often useful in testing how realistic a potential energy function is in describing some structure, especially a liquid or amorphous phase.

- However, this test is actually not all that sensitive to the detailed structure.

Transport coefficients

- The correlation between any two quantities A and B is

$$c_{AB} = \frac{\langle \delta A \delta B \rangle}{\sigma(A)\sigma(B)}$$

$$\sigma^2(A) = \langle \delta A^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2 \quad ; \quad \delta A = A - \langle A \rangle$$

$$0 \le c_{AB} \le 1$$

- the time dependent correlation function
  $c_{AB}(t)$: A and B at different times, e.g. *A(t)* and *B(0)*

- autocorrelation function $c_{AA}(t)$

- correlation time $t_A = \int_0^{\infty} c_{AA}(t) dt$

- these give information on
  - the dynamics of the material
  - transport coefficients
  - can be related to experimental spectra by Fourier transformations

- transport coefficients

  - system response to an external disturbance $\rho(t) = \rho_{\text{ens}} + \delta\rho(t)$

  - for instance diffusion coefficient:

    particle flux $\leftrightarrow$ concentration gradient

  - $\rho(t) \rightarrow$ time dependent averages

  - comparison to transport equations $\rightarrow$ transport coefficients

  - coefficients usually of the form $\gamma = \int_0^\infty \langle \dot{A}(t)(\dot{A}(0))\rangle dt$

  - for a large time there also always exists an Einstein relation

$$2t\gamma = \langle (A(t) - A(0))^2 \rangle$$

- some transport coefficients for the NVE-ensemble:

diffusion equation

$$\frac{\partial n}{\partial t} = D\nabla^2 n$$

- diffusion constant $D = \frac{1}{3}\int_0^\infty \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0)\rangle dt$

simple form to evaluate: $2tD = \frac{1}{3}\langle (\mathbf{r}_i(t) - \mathbf{r}_i(0))^2 \rangle$

heat conduction equation

$$\frac{\partial T}{\partial t} = \frac{\lambda_T}{\rho C}\nabla^2 T$$

- thermal conductivity

$$\lambda_T = \frac{V}{k_{\text{B}}T^2}\int_0^\infty \langle j_i^\varepsilon(t) j_i^\varepsilon(0)\rangle dt$$

$$2t\lambda_T = \frac{V}{k_{\text{B}}T^2}\langle (\delta\varepsilon_\alpha(t) - \delta\varepsilon_\alpha(0))^2 \rangle$$

where $\delta\varepsilon_\alpha = \frac{1}{V}\sum_i r_{i\alpha}(\varepsilon_i - \langle \varepsilon_i \rangle)$; $\quad j_i^\varepsilon = \frac{\partial \delta\varepsilon_\alpha}{\partial t}$; $\quad \varepsilon_i = \frac{p_i^2}{2m_i} + \frac{1}{2}\sum_{i \neq j} V(r_{ij})$

Algorithms for simulating ensembles

[most material from Allen-Tildesley ch. 7.4]

- pure NVE: see lectures 2-5

"NVE-scaling" or constraint methods:

- Often even in an NVE simulation one does some simple tricks to control temperature and/or pressure. This gives something of a NVT or NVP and NVE hybrid: T and P fluctuate, and the system does not behave as a true NVT or NVP ensemble in the thermodynamic sense. But on average T and P have the desired value. In true NVT or NPT algorithms it is possible to have T and P have exactly the desired value, and the simulation directly corresponds to the thermodynamic ensembles.

- Temperature scaling

- Trivial scaling: force during every time step the system temperature to be exactly T. This may be a rather severe perturbation of the atom motion especially if there are only a few atoms. It suppresses normal T fluctuations, and does still not correspond to a true NVT ensemble. But the error in ensemble averages usually is $O(1/N)$ so with a large number of atoms one may get away with it.

- The Berendsen method: essentially a direct scaling but softened with a time constant. [Berendsen *et al.* J. Chem. Phys. **81** (1984) 3684].

- Let T_0 be the desired temperature, Δt the time step of the system and τ_T the time constant of the control. In the Berendsen method all atom velocities are scaled at every time step with a factor λ, where

$$\lambda = \sqrt{1 + \frac{\Delta t}{\tau_T}\left(\frac{T_0}{T} - 1\right)}$$

- τ_T has to be > Δt. According to Berendsen if $\tau_T > 100\,\Delta t$ then the system has natural thermal fluctuations about the average.

- Pressure scaling (Berendsen):

  - In pressure scaling the system pressure is put to a desired value by changing the cell size during the simulation. If the desired pressure is P_0 and τ_P is the time constant, the scaling factor is

$$\mu = \sqrt[3]{1 - \frac{\beta \Delta t}{\tau_P}(P_0 - P)}$$

    where β is the isothermal compressibility of the system = 1/bulk modulus. Since β only occurs in the division over the time constant τ_P it is just a factor which makes the typical time constant values roughly independent of the material.

  - The scaling is implemented by changing all atom positions x and the system size S every time step

$$x(t + \Delta t) = \mu\, x(t)$$
$$S(t + \Delta t) = \mu\, S(t)$$

    whence also the system volume V changes:

$$V(t + \Delta t) = \mu^3\, V(t)$$

  - The pressure scaling should be done after the solution of the equations of motion. τ_P usually has to be > 100 Δt

- The Berendsen scaling can be used to control T and P. If the system is in equilibrium the total energy E should still be conserved, but if phase transitions, such as melting occur, E does not necessarily stay conserved until equilibrium is reached again.

- In the Berendsen method P, T, V and E_{pot} all fluctuate, and because the time constants τ have to be fairly large it can take quite a while to reach a desired pressure or temperature.

- But in equilibrium and with large enough time constants, the method gives quite realistic fluctuations in T and P. And it is almost as trivial to implement as direct scaling. Hence it is much to be preferred over direct scaling.

True NVT algorithms

- The Andersén method:

  [H. C. Andersén, J. Chem. Phys. **72**, 2384 (1980)].

  - Give the atom with some probability a new velocity which corresponds to a desired heat bath temperature T_0

  - Physical interpretation clear: connection to external heat bath

  - Suitable for calculating thermodynamic averages, but not for looking at atomic processes in detail, since the random velocity is obviously an unphysical perturbation on the motion of a single atom.

- Nosé-Hoover-method, a.k.a the Nosé-Hoover thermostat:

  [W. Hoover, Phys. Rev. A **31**, 1695-1697 (1985).]

  - A fictional degree of freedom s which has its own kinetic and potential energy is added to the system, and this degree of freedom controls the temperature. The system total energy, i.e. Hamiltonian:

$$H = \sum_i \frac{\boldsymbol{p}_i}{2m_i} + V(\boldsymbol{q}_i) + \frac{Q}{2}p_s^2 + qkT\ln s$$

where p_s is the momentum associated with the degree of freedom. Now the Hamiltonian equations of motion become:

$$\frac{d\boldsymbol{q}_i}{dt} = \frac{\boldsymbol{p}_i}{m_i}$$

$$\frac{d\boldsymbol{p}_i}{dt} = -\frac{dV}{d\boldsymbol{q}_i} - p_s\boldsymbol{p}_i$$

$$\frac{dp_s}{dt} = \frac{\sum_i \frac{\boldsymbol{p}_i}{m_i} - gkT}{Q}$$

which can be solved with some suitable algorithm. Q is a fictional mass related to the extra degree of freedom, which describes the rate at which the temperature changed. Nosé suggested $Q \sim gkT$ where g is the number of degrees of freedom in the system, typically $6N$. For large Q the connection to the heat bath weakens, and for small Q the energy E may oscillate too much.

((KN Internal note: above taken from Insight mnualhttp://www.csc.fi/chem/msimanual/doc/insight970/forcefields/FFBSim/5_Dynamics.html#349710))

- Nosé-Hoover chains
  [Tobias, Martyna, Klein, J. Phys. Chem. **97** (1993) 12959]

  - Also control the new degree s of freedom with another Nosé-Hoover-algorithm and so forth, i.e. form a chain of these.

  - At least in simulations of proteins this can give a very good temperature control.

  - "Massive" Nosé-Hoover-chain: add a Nosé-Hoover thermostat chain to every degree of freedom (!)

  - Advantage: as Nosé-Hoover, but in addition very efficient in equipartitioning the energy and thus getting the system into equilibrium.

  -Disadvantage: even more coding

True NPT algorithms

- Andersén pressure control
  [H. C. Andersén, J. Chem. Phys. **72**, 2384 (1980)]

  - The cell size V a dynamic variable, but the system shape may not change. The size is controlled by a fictional piston ("mäntä" in Finnish) which has a mass Q (in units of m/l^4). The kinetic and potential energy of the piston are:

$$E_{kinV} = \frac{1}{2}Q\dot{V}^2 \quad \text{and} \quad E_{potV} = PV$$

and if the atom positions $\boldsymbol{r}$ and velocities $\boldsymbol{v}$ are written in reduced units $\boldsymbol{s}$ such that $\boldsymbol{r} = V^{1/3}\,\boldsymbol{s}$ and $\boldsymbol{v} = V^{1/3}\,\dot{\boldsymbol{s}}$ we get the equations of motion

$$\ddot{s} = \frac{f}{mV^{1/3}} - \frac{2}{3}\dot{s}\frac{\dot{V}}{V}$$

$$\ddot{V} = \frac{P_t - P}{Q}$$

where $\boldsymbol{f}$ are the forces acting on atoms, P_t is the momentaneous pressure and P the desired pressure.

- Parrinello-Rahman-pressure control
  [Parrinello and Rahman, J. Appl. Phys. **52** (1981) 7182]

  - This method also allows a variable simulation cell shape, that is, the angles between the axes do not have to be 90^{o}.

  - The cell size and shape is given by vectors **a, b** and **c**. If we form a 3x3-matrix **h** out of these the atom positions **r** can be written in the form

$$\mathbf{r} = \mathbf{h}\mathbf{s}$$

where **s** is an ordinary vector. The equations of motion can be derived to be:

$$\ddot{s}_i = -\sum_j \frac{dV}{dr}\frac{1}{m_i r_{ij}}(s_i - s_j) - \frac{\dot{\mathbf{G}}}{\mathbf{G}}\dot{s}$$

$$W\ddot{\mathbf{h}} = (\mathbf{P} - p\mathbf{I})\sigma - \mathbf{h}\Sigma$$

where $\mathbf{G} = \mathbf{h}^{\mathbf{T}}\mathbf{h}$, σ is a tensor which defines reciprocal space, and **P** is the generalized 3x3 pressure tensor.

$$\mathbf{P} = \frac{1}{V}\left[\sum_i m_i \mathbf{v}_i \mathbf{v}_i - \sum_i \sum_{j>i} \frac{1}{r_{ij}} \frac{du}{dr_{ij}} \mathbf{r}_{ij} \mathbf{r}_{ij}\right]$$

The diagonal elements of **P** are the pressures in *x*, *y* and *z*, the other elements are shear elements. The hydrostatic "ordinary" pressure *P* is = 1/3 (P_{11}+P_{22}+P_{33}). Σ is a quantity which depends on the external pressure tensor **S:**

$$\Sigma = \mathbf{h_0}^{-1}(\mathbf{S} - p)\mathbf{h_0}^{\mathbf{T}-1}\Omega_0$$

where $\mathbf{h_0}$ and Ω_0 are the original (reference) shape and volume of the system. *W* is a fictional "mass" which is used to control the rate of change of the pressure (compare with *Q* in the NVT algorithms above).

- This allows us to simulate a system which changes shape, for instance a cubic to hexagonal phase transformation

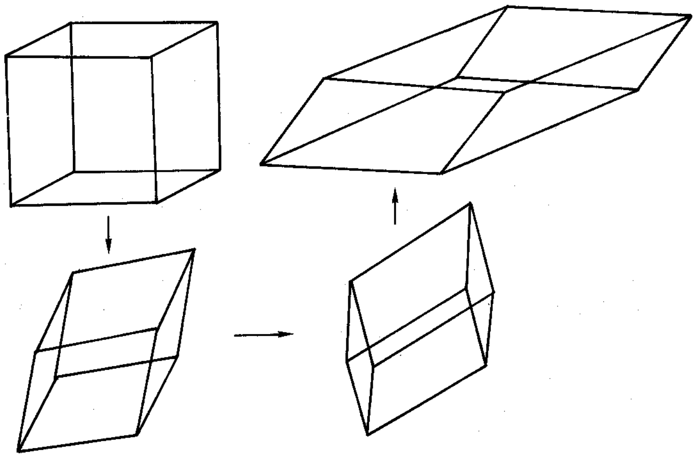
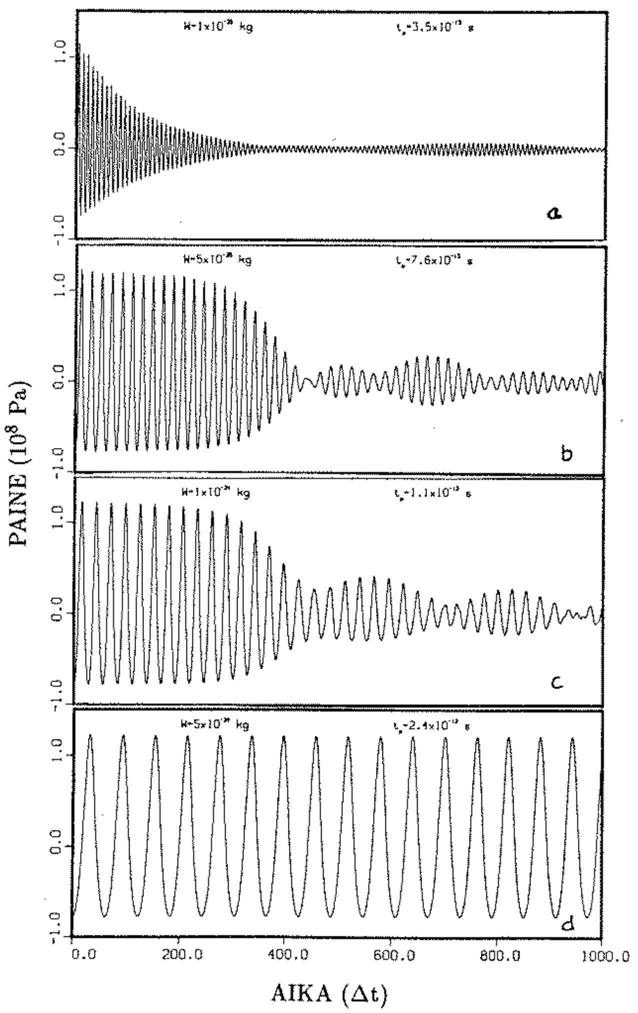


Fig. 7.3 Changing box-shape.

- An example of the effects of the mass parameter Q:

  A Lennard-Jones-system (Ne); T=0.1 K; constant pressure-MD



Kuva 4.1 *Massaparametrin W vaikutus paineen fluktuaatioihin. Aika–askeleen Δt pituus on eri ajoissa vaihdellut välillä 30 – 40 fs. t_p on painevärähtelyn lyhimmän jakson pituus.*

μVT-methods

- To simulate this ensemble, where the chemical potential stays constant, the number of atoms has to be able to fluctuate
- Fairly rarely used in MD, more often in MC simulations where it is more natural to add and remove atoms from the system. An alternative to adding or removing atoms is to add or remove "control volume".
- In MD the problem of course is that just adding an atom on a random place can easily lead to completely unphysical configurations (say 2 atoms separated by only 0.1 Å which is senseless in an equilibrium simulation). Also adding or removing control volume without distrorting the system state too much may be tricky.

  If you need this, see e.g. [Lynch, Pettitt: J. Chem. Phys. **107** (1997) 8594] or [Heffelfinger, J. Chem. Phys. **100** (1994) 7548].

A (semi-subjective) recommendation on what T and P control to use:

- For *T* or *P* scaling: Berendsen is fast to implement, and does work well provided the time constants are large enough.
- If one wants accurate *T* control or needs to do NVT thermodynamic averaging, one of the Nosé-Hoover methods is probably best
- For orthogonal box *NPT* simulations: Andersén
- If one wants needs to deal with shear pressure => Parrinello-Rahman

Other types of MD simulations

- MD is nowadays something of an industry in research, and it is natural that there are about a zillion variations on how to do MD. We only mention here some common variations; more information and references on the three first topics can be found from Allen-Tildesley.

- Non-equilibrium MD

  - In general means any MD simulation of a system which is not in thermodynamic equilibrium. Usually some perturbative term is added to the equations of motion.

  - For instance for simulating viscosity, heat conductivity and atomic diffusion there are special NEMD algorithms.

  - At its simplest, the perturbation can be an external force acting on some of the atoms.

  - The external force heats the system up, which can be compensated by temperature control.

- Brownian dynamics or Langevin dynamics

  - Random forces are let to act on some atoms some of the time. This can be useful e.g. in speeding up infrequent events.

  - This can also correspond to e.g. a large protein molecule in a liquid solvent. If the protein atoms do not react with the solvent atoms, and the solvent atoms are not interesting in themselves, their effect on the protein can be thought to reduce to random Langevin forces.

- "Multiple time step"-methods

  - In these methods the simulation is sped up by using different time steps for different atoms or parts of the system.

  - A simple example of where this may be useful: a molecule which has light and much heavier particles. The light particles move much faster, so their motion can be simulated with a short time step Δt_1 and the heavy ones with a longer time step Δt_2.

  - Another possibility: count near interactions acting on atom *i* with a short time step Δt_1 and those farther away with a longer one Δt_2. In here, we assume the movement of the atoms far away is so small that they do not move significantly with respect to atom *i* during the shorter time $\Delta \mathrm{t}_1$.

- MD far from equilibrium

  - Many processes of modern interest involve physical interactions which occur very far from thermodynamic equilibrium. Consider for instance what happens when two nanoparticles collide in vacuum, or an energetic ion from an accelerator hits a material. In both cases very violent interactions occur over ps timescales, and the surrounding medium does not have time to equilibrate the system into anything close to thermodynamic equilibrium during the time when the interesting processes occur.

  - Simulating such a system is simple: simply use ordinary NVE algorithms with no *T* or *P* scaling.

  - Much of what is said before in this package on the theory of MD is irrelevant in this case: the desired physically observable quantity is the process itself, and no thermodynamic average needs to be performed (in fact it should not even be performed, since the system is entirely out of equlibrium and equilibrium thermodynamics does no apply)