Introduction to Computational Physics

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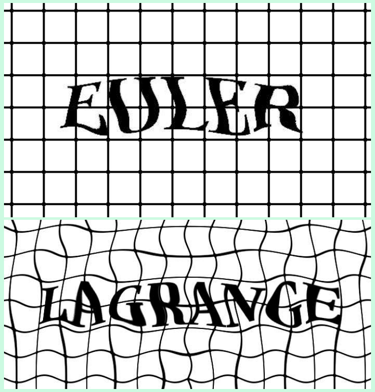
SELECTED APPLICATIONS

Section 6. Statistical-mechanical simulation

Section 7. Numerical quantum mechanics



Section 8. Computational hydrodynamics

6. Simulation and Statistical Mechanics

Ludwig Boltzmann would have loved simulation

A short tour takes us to:

- **Model Systems of Statistical Mechanics**
- **Tricks of the trade**
- **Monte Carlo simulation**
- **Molecular dynamics simulation**

Model Systems of Statistical Mechanics:

Hard spheres	$u(r) = \infty$ if $r < r_0$ $= 0$ if $r \geq r_0$	First approximation in many applications
Lennard-Jones	$u(r) = 4\,\epsilon \left[\left(\frac{r}{\sigma} \right)^{-12} - \left(\frac{r}{\sigma} \right)^{-6} \right]$	Noble gas atoms; nearly spherical molecules
Harmonic	$u(r) = A\,(r - r_0)^2$	Intramolecular bonds, if kT is small compared to the bond energy
Morse	$u(r) =$ $A \left[e^{-2b(r-r_0)} - 2e^{-b(r-r_0)} \right]$	Intramolecular bonds, if kT is comparable to the bond energy

Some isotropic model potentials: $u = u(r)$

Hard spherocylinders, etc.	$u(12) = \infty$ if overlap $= 0$ otherwise	First approximation to rigid molecules
Interaction site models	sum of isotropic pair energies between sites in molecules	Rigid and nonrigid molecules
Kramers-type	interaction site model with fixed internal bond lengths	Flexible molecules, from ethane to biopolymers
Stockmayer	Lennard-Jones + point dipoles	First approximation to small polar molecules
Gay-Berne	$4\,\epsilon(12)\left[\left(\frac{r_{12}-\sigma(12)+\sigma_0}{\sigma_0}\right)^{-12} - \left(\frac{r_{12}-\sigma(12)+\sigma_0}{\sigma_0}\right)^{-6}\right]$	Liquid crystal molecules of ellipsoidal shape

Some anisotropic models: $u(12) = u(\mathbf{r}_{12}, \mathbf{e}_1, \mathbf{e}_2)$

Spin models for solids:

Fixed positions on a lattice, but spins with varying directions:

Ising model – the spins may point either up or down,
Heisenberg model – all directions permitted.

2D Ising lattice: only the four nearest spins contribute to the energy of σ_i $(= \pm 1)$; in three dimensions the six nearest neighbors must be considered.

Total energy of the N spins:

$$E \;=\; -\frac{A}{2}\sum_{i=1}^{N}\sum_{j(i)=1}^{4 \; or \; 6}\sigma_i\sigma_{j(i)}$$

with A a coupling constant.

Simulation: General remarks

Let $\mathbf{\Gamma}_c \equiv \{\mathbf{r}_1 \ldots \mathbf{r}_N\}$ be a microstate in the $3N$-dimensional "configuration space" Γ_c, and let $p(\mathbf{\Gamma}_c)$ be its probability density.
(For spin models $\mathbf{\Gamma}_c$ is given by all *spins* on the lattice.)

Given some property $a(\mathbf{\Gamma}_c)$, the – observable – thermodynamic average of a is given by

$$\langle a \rangle \;=\; \int_{\Gamma_c} a(\mathbf{\Gamma}_c)\, p(\mathbf{\Gamma}_c)\, d\mathbf{\Gamma}_c$$

Examples:

$$U \;=\; NkT + \frac{1}{2}\langle \sum_i \sum_{j\neq i} u(r_{ij})\,\rangle \quad \text{Internal energy}$$

$$p \;=\; \frac{NkT}{V} - \frac{1}{6V}\langle \sum_i \sum_{j\neq i} r_{ij}\,\frac{du}{dr}\Big|_{r_{ij}}\rangle \quad \text{Pressure}$$

But: $\Longrightarrow$

$p(\mathbf{\Gamma}_c)$ is known only up to a normalizing factor:

e.g. $p_{can}(\mathbf{\Gamma}_c) \propto exp[-E(\mathbf{\Gamma}_c)/kT]$

But the *Partition Function* Q

$$Q \equiv \int e^{-E(\mathbf{\Gamma}_c)/kT} \, d\mathbf{\Gamma}_c$$

is not known.

$\Longrightarrow$How to compute thermodynamic averages?

– Ensemble average: Monte Carlo walk through phase space
– Time average: Molecular dynamics simulation

Tricks of the Trade

Units:

Choose appropriate units for three mechanical quantities, such as energy, mass, and length. The other units follow.

Example 1 – Lennard-Jones: $E_0 = \epsilon$, $m_0 = 1AMU = 1.6606 \cdot 10^{-27}\, kg$, $l_0 = \sigma$.

With $u^* \equiv u/\epsilon$ etc. the energy of a pair of particles is $u^*_{LJ} = 4\left[r^{*-12} - r^{*-6}\right]$ where all numerical values will be of order 1.

The unit of *time* is $t_0 = \sqrt{m_0\sigma^2/\epsilon}$.
Density (LJ): $\rho_0 = 1/\sigma^3$, thus $\rho^* \equiv N\sigma^3/V$.
Temperature (LJ): $T_0 = \epsilon/k$.

Example 2 – Hard Spheres: $E_0 = kT$, $m_0 = 1AMU$, $l_0 = d_0$ (diameter).

Time (HS): $t_0 = \sqrt{m_0 d^2/kT}$
Density (HS): $\rho_0 = \sqrt{2}/d_0^3$, thus $\rho^* = Nd_0^3/V\sqrt{2}$.
Temperature (HS): $T_0 = \epsilon/k$.

Exercise: Consider a pair of LJ “Argon” particles with $\epsilon = 1.6537 \cdot 10^{-21}\,J$ and $\sigma = 3.405 \cdot 10^{-10}\,m$. Let the two molecules be situated at a distance of $3.2 \cdot 10^{-10}\,m$ from each other, and calculate the potential energy of this arrangement. Now do the same calculation using ϵ and σ as units of energy and length.

Using the above units and $m_0 = 1AMU$, what is the metric value of the self-consistent unit of time? Let one of the particles have a metric speed $v = 500\,m/s$, typical of the thermal velocities of atoms or small molecules. What is the value of v in self-consistent units?

Periodic boundary conditions (PBC):

Instead of x_i, store $(x_i + 2L) \bmod L$ (with L the side length of the cell.)
$\Longrightarrow$Conservation of N and (in MD) $\sum \mathbf{v}_i$.

Nearest Image Convention (NIC):

Pair energy: if $\Delta x_{ij} \equiv x_j - x_i > L/2$, use $\Delta x_{ij} - L$ instead, etc.

A compact formulation of this rule is

$$\Delta x \;=\; \Delta x - L \cdot \mathrm{nint}\left(\frac{\Delta x}{L}\right)$$

(nint(a) ... rounded value of a.)

Starting configuration:

Place the particles on the vertices of an fcc grid and “melt” the lattice before the simulation. The fcc population numbers are $4m^3$, with $m = 1, 2, \ldots \Longrightarrow N = 32, 108, 256, 500$ etc.

Adjusting the temperature:

$$T^* = m^* \langle |\mathbf{v}^*|^2 \rangle / 3$$

$\Longrightarrow$Take the average of $|\mathbf{v}^*|^2$ over a number of MD steps, then scale each velocity component of every particle by $\sqrt{T^*_{desired} / T^*_{actual}}$

Exercise: Write a code to set up a cubic box inhabited by $N = 108$ or 32 particles in a face-centered cubic arrangement. Use your favourite programming language and make the code flexible enough to allow for easy change of volume (i.e. density). Make sure that the lengths are measured in units of σ_{LJ}. For later reference, let us call this subroutine STARTCONF.

By scaling all lengths, adjust the volume such that the reduced number density becomes $\rho^* = 0.6$.

Include a procedure that assigns random velocities to the particles, making sure that the total momentum is zero.

Exercise: Write a subroutine ENERGY that computes the total potential energy in a system, assuming a Lennard-Jones interaction and applying the nearest image convention:

$$E_{pot} = \frac{1}{2}\sum_{i}\sum_{j\neq i} u_{LJ}(r_{ij}) = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} u_{LJ}(r_{ij})$$

Use it to compute the energy in the system created by STARTCONF.

Monte Carlo Method

Generate a Markov chain of, say, K configurations $\{\mathbf{\Gamma}_c(k),\, k = 1, \ldots K\}$ such that the *relative frequency* of a configuration in the chain is proportional to the corresponding Boltzmann factor.
$\Longrightarrow$Estimate the mean value $\langle a \rangle$ from

$$\langle a \rangle \;=\; \frac{1}{K} \sum_{k=1}^{K} a \left[\mathbf{\Gamma}_c(k)\right]$$

The proven method for generating a suitable Markov chain of microstates is the *biased random walk* through configuration space: $\Longrightarrow$

Metropolis Monte Carlo for continuous potentials:

Let $\mathbf{\Gamma}_c(k) \equiv \{\mathbf{r}_1 \dots \mathbf{r}_N\}$ be given, with $E(k) \equiv (1/2) \sum_i \sum_j u(|\mathbf{r}_j - \mathbf{r}_i|)$.

1. Generate a "neighboring" configuration $\mathbf{\Gamma}'_c$ by randomly moving one of the N particles: $x'_j = x_j + d\,(\xi - 0.5)$ and similarly for y_j, z_j. Here, d should be adjusted such that $\approx$ 50% of the trials are accepted, and ξ is equidistributed in $(0, 1)$. The number j of the particle to be moved may either be drawn among the N candidates, or may run cyclically through the set of particle indices.
2. Determine the modified total energy E'; since displacing particle j affects only $N - 1$ of the $N(N - 1)/2$ pair distances, it is not necessary to recalculate the entire double sum.
3. If $E' \leq E(k)$, accept $\mathbf{\Gamma}'_c$ as the next element of the Markov chain:

$$E' \leq E(k) : \;\Rightarrow\; \mathbf{\Gamma}_c(k+1) = \mathbf{\Gamma}'_c\,; \;\text{ go to (1)}$$

If $E' > E(k)$, compare the quotient of the two thermodynamic probabilities, $q \equiv e^{-[E' - E(k)]/kT}$, to a random number $\xi \in (0, 1)$:

$$E' > E(k) :$$

$$\begin{aligned} \xi &\leq q : \;\Rightarrow\; \mathbf{\Gamma}_c(k+1) = \mathbf{\Gamma}'_c\,; \;\text{ go to (1)} \\ \xi &> q : \;\Rightarrow\; \mathbf{\Gamma}_c(k+1) = \mathbf{\Gamma}_c(k)\,; \;\text{ go to (1)} \end{aligned}$$

In the case of hard disks or spheres $E(k)$ and E' are either 0 or ∞, and the Boltzmann factors are either 1 or 0. Here is the MC procedure for hard particles.

Monte Carlo for hard spheres:

Let $\mathbf{\Gamma}_c(k) \equiv \{\mathbf{r}_1 \ldots \mathbf{r}_N\}$ be given.

- Trial move $\mathbf{\Gamma}_c(k) \longrightarrow \mathbf{\Gamma}'_c$:

$$x'_j \;\; = \;\; x_j + d\,(\xi - 0.5) \quad \text{etc., for } y_j,\, z_j$$

- If particle j now overlaps with any other particle, let $\mathbf{\Gamma}_c(k+1) = \mathbf{\Gamma}_c(k)$; otherwise let $\mathbf{\Gamma}_c(k+1) = \mathbf{\Gamma}'_c$.

Exercise: Write a subroutine MCSTEP which performs the basic Monte Carlo step as described above: selecting at random one of the LJ particles that were placed on a lattice by STARTCONFIG, displace it slightly and apply the PBC; then compute the new potential energy (using NIC!) and check whether the modified configuration is accepted or not, given a specific temperature T^*; if accepted, the next configuration is the modified one, otherwise the old configuration is retained for another step.

Write a main routine to combine the subroutines STARTCONF, ENERGY, and MCSTEP into a working MC program.

Molecular Dynamics Simulation

Different methodology for

– **Hard spheres**
– **Lennard-Jones and friends**

MD of Hard Spheres

– Given all positions and velocities, find for each pair (i, j) the time t_{ij} until they collide (if at all):

$$t_{ij} \quad = \quad \frac{-b - \sqrt{b^2 - v^2(r^2 - d^2)}}{v^2}$$

where r is the distance between the centers of i and j, and

$$b = (\mathbf{r}_j - \mathbf{r}_i) \cdot (\mathbf{v}_j - \mathbf{v}_i) \ , \qquad\qquad v = |(\mathbf{v}_j - \mathbf{v}_i)|$$

– For each i, find the smallest positive collision time $t(i) = min(t_{ij})$ and the corresponding collision partner $j(i)$. (If particle i has no collision partner at positive times, set $j(i) = 0$ and $t(i) = [\infty]$.

– Find the smallest of all N next-collision times, $t(i_0)$. Let the partners in this collision be i_0 and j_0.

– Increment all particle positions as

$$\mathbf{r}_i \longrightarrow \mathbf{r}_i + \mathbf{v}_i \cdot t(i_0)$$

and subtract $t(i_0)$ from all $t(i)$.

– Elastic collision between $i = i_0$ and $j = j_0$: $\Longrightarrow$

$$\mathbf{v}'_i = \mathbf{v}_i + \Delta\mathbf{v}\,, \qquad \mathbf{v}'_j = \mathbf{v}_j - \Delta\mathbf{v}$$

where

$$\Delta\mathbf{v} \;=\; b\,\frac{\mathbf{r}_{ij}}{d^2}$$

– Recalculate all collision times t_{ij} involving i_0 or j_0: only $2N - 3$ pairs have to be scanned.

Molecular dynamics simulation of hard spheres:

For all i, let the next-collision time $t(i)$ and the partner $j(i)$ be given.

1. Find the smallest positive $t(i_0)$, with partners i_0, j_0.
2. Perform free flight for $\Delta t \equiv t(i_0)$; subtract Δt from each $t(i)$.
3. Perform elastic collision between i_0 and j_0:
$$\mathbf{v}' \;=\; \mathbf{v} \pm \Delta\mathbf{v}\,, \quad \text{with } \Delta\mathbf{v} = b\,\frac{\mathbf{r}_{ij}}{d^2}$$
4. Recalculate all times $t(i)$ involving i_0 or j_0, ($i = i_0$, $i = j(i_0)$, $i = j_0$, and $i = j(j_0)$.)
5. Go to (1).

At low densities, limit the time allowed for free flight such that for all particles and each coordinate α $\Delta x_\alpha \equiv v_\alpha \Delta t \leq L/2 - d$.

Exercise: For a two-dimensional system of hard disks, write subroutines to a) set up an initial configuration (simplest, though not best: square lattice;) b) calculate $t(i)$ and $j(i)$; c) perform a pair collision. Combine these subroutines into an MD code.

Continuous Potentials

Particle i moves as

$$\ddot{\mathbf{r}}_i(t) = \frac{1}{m} \sum_{j \neq i} \mathbf{K}_{ij}(t) \quad \text{with} \qquad \mathbf{K}_{ij} \equiv -\nabla_i \, u(r_{ij})$$

Example – Lennard-Jones:
The pair force is

$$\mathbf{K}_{ij} \quad = \quad -24 \frac{\epsilon}{\sigma^2} \left[2 \left(\frac{r_{ij}}{\sigma} \right)^{-14} - \left(\frac{r_{ij}}{\sigma} \right)^{-8} \right] \mathbf{r}_{ij}$$

where $\mathbf{r}_{ij} \equiv \mathbf{r}_j - \mathbf{r}_i$.
(Don't forget to apply NIC!)

To solve the equation of motion, use the Verlet algorithm (or any competitor such as PC):

$$\mathbf{r}_i(t_{n+1}) \quad = \quad 2\mathbf{r}_i(t_n) - \mathbf{r}_i(t_{n-1}) + \mathbf{b}_i(t_n)(\Delta t)^2$$

Exercise: In the subroutine ENERGY, add a few lines to compute for each particle i the total force exerted on it by all other particles j: $\mathbf{K}_i \equiv \sum_{j \neq i} \mathbf{K}_{ij}$, with $\mathbf{K}_{ij}$ as above; remember to apply the *nearest image convention*.

Write a subroutine MOVE to integrate the equations of motion by a suitable algorithm such as Verlet's. Having advanced each particle for one time step, apply *periodic boundary conditions* to retain them all in the simulation box.

Write a main routine that puts the subroutines STARTCONF, ENERGY and MOVE to work. Test your first MD code by monitoring the mechanically conserved quantities.

Do a number of MD steps – say, 50-100 – and average the quantity $|\mathbf{v}^*|^2$ to estimate the actual temperature. To adjust the temperature to a desired value, scale all velocity components of all particles in a suitable way. Repeat this procedure up to 10 times. After 500-100 steps the fluid will normally be well randomized in space, and the temperature will be steady – though fluctuating slightly.

Beyond Basic Molecular Dynamics

Generalizations involve

– ionic and dipolar interactions

– orientation dependent potentials

– polymers or other complex molecules

– nonequilibrium dynamics

Evaluation of Simulation Experiments

Pressure:

$$p \quad = \quad \frac{NkT}{V} - \frac{1}{6V} \langle \sum_i \sum_{j \neq i} r_{ij} \, \frac{du}{dr}\bigg|_{r_{ij}} \rangle$$

Internal energy:

$$U \quad = \quad NkT + \frac{1}{2} \langle \sum_i \sum_{j \neq i} u(r_{ij}) \, \rangle$$

Exercise: In your Lennard-Jones MD and MC programs, include a procedure to calculate averages of the total potential energy and the virial,

$$W \equiv \sum_i \mathbf{K}_i \cdot \mathbf{r}_i = -\frac{1}{2} \sum_i \sum_j \mathbf{K}_{ij} \cdot \mathbf{r}_{ij}$$

From these compute the internal energy and the pressure. Compare with results from literature, e.g. Verlet*, McDonald**. Allow for deviations in the $5-10\,\%$ range, as we have omitted a correction for the finite sample size ('cutoff correction').

* Verlet, L., Phys. Rev. 159/1 (1967) 98; ibidem, 165/1 (1968) 201.
* McDonald I. R., J. Phys. C: Sol. St. Ph., 7 (1974) 1225.

Pair correlation function:

Local density at $\mathbf{r}$:

$$\rho(\mathbf{r}) \quad = \quad \langle \sum_i \delta(\mathbf{r}_i - \mathbf{r}) \rangle$$

In a fluid we usually have $\rho(\mathbf{r}) = const.$

More interesting: pair correlation function (PCF)

$$g(r) \quad = \quad \frac{V}{4\pi r^2 N^2} \langle \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \rangle$$

Probability of finding a particle at $\mathbf{r}$, given that there is a particle at the origin. $\Longrightarrow$Measure of spatial ordering.

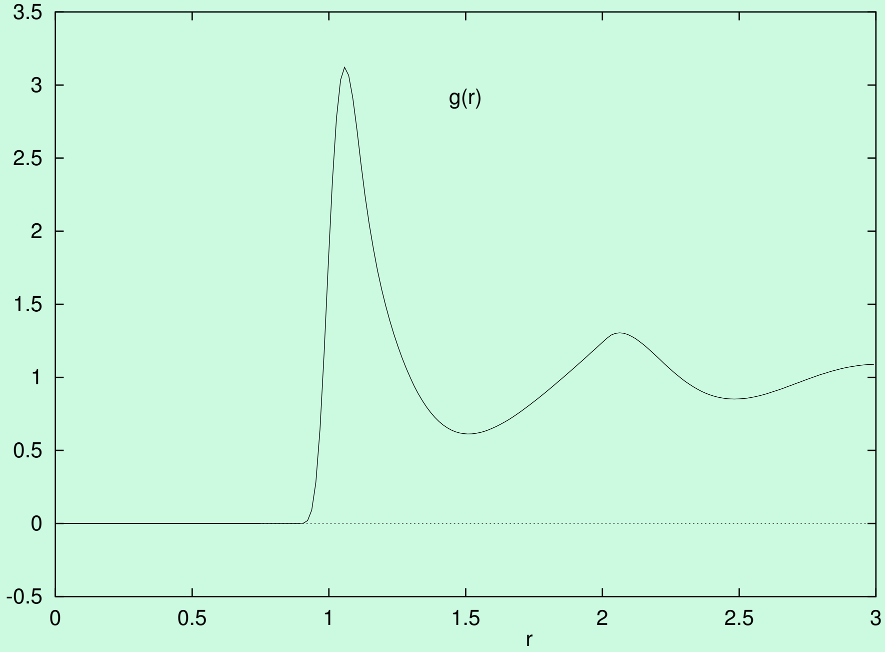
How to determine $g(r)$? $\Longrightarrow$

Calculation of $g(r)$:

– Divide the range of r (at most $[0; L/2]$) into $50 - 200$ intervals Δr.
– In a given configuration $\{\mathbf{r}_1, \ldots \mathbf{r}_N\}$, determine for each pair (i, j) a channel number

$$k = \text{int}\left(\frac{r_{ij}}{\Delta r}\right)$$

– Increment a histogram table $g(k)$.
– Finally, normalize $g(k)$ appropriately.



Pair correlation function of the Lennard-Jones liquid

Significance of $g(r)$;

– Thermodynamic averages:

$$p = \frac{NkT}{V} - \frac{N^2}{6V^2} \int_V r \frac{du}{dr} g(r)\, d\mathbf{r}$$

etc.

– Spectroscopy:

The Fourier transform of $g(r)$, the "scattering law"

$$S(k) = 1 + \frac{N}{V} \int_V [g(r) - 1]\, e^{i\,\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r}$$

is the relative intensity of neutron or X-ray scattering at a scattering angle θ which is related to k by $k \equiv \frac{4\pi}{\lambda} \sin\frac{\theta}{2}$

Exercise: Augment your Lennard-Jones MD (or MC) program by a routine that computes the pair correlation function $g(r)$; remember to apply the *nearest image convention* when computing the pair distances. As the subroutine ENERGY already contains a loop over all particle pairs (i, j), it is best to increment the $g(r)$ histogram within that loop.

Plot the PCF and see whether it resembles the one given in the Figure.

Autocorrelation Functions

The prime example is the velocity autocorrelation

$$C(t) \equiv \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle$$

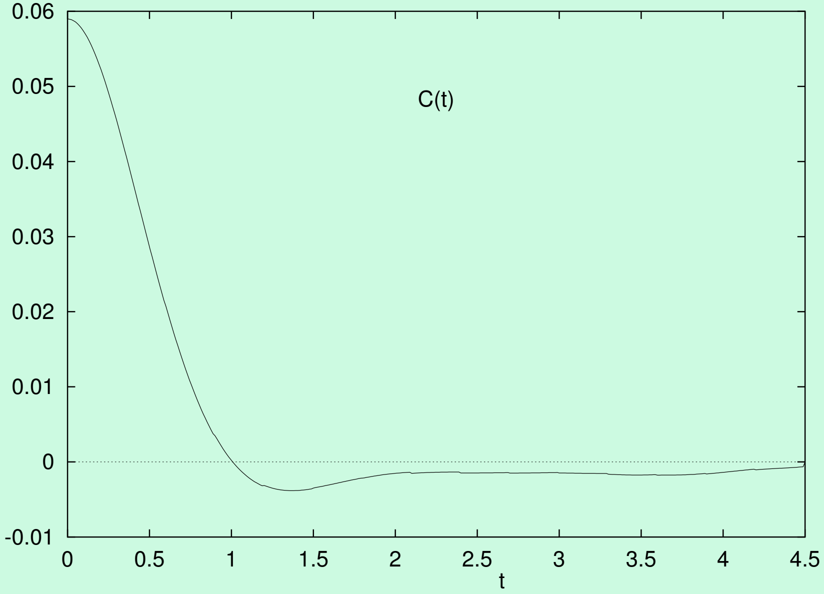
Simple kinetic theory predicts $C(t) \propto e^{-\lambda t}$; instead, Alder found $C(t) \propto t^{-3/2}$.

Significance:

The diffusion constant D of a liquid is given by

$$D = \frac{1}{3} \int_0^\infty C(t)\, dt$$

$\Longrightarrow$Strongly affected by the *long time tail* of $C(t)$: increase by 30% over kinetic theory.



Velocity autocorrelation function of the Lennard-Jones fluid

To calculate simple autocorrelation functions in a computer simulation, proceed as follows: $\Longrightarrow$

Calculation of the velocity acf:

- At regular intervals of $20-100$ time steps, mark starting values $\{a(t_{0,m}),\ m = 1,\dots M\}$. Since in the further process only the preceding $M \approx 10-20$ starting values are required, it is best to store them in registers that are cyclically overwritten.

- At each time t_n, compute the M products

$$z_m \;=\; a(t_n) \cdot a(t_{0,m})\,, \quad m = 1, \dots M$$

and relate them to the (discrete) time displacements $\Delta t_m \equiv t_n - t_{0,m}$; a particular Δt_m defines a channel number

$$k \;=\; \Delta t_m / \Delta t$$

indicating the particular histogram channel to be incremented by z_m. To simplify the final normalization it is recommended to count the number of times each channel k is incremented.

Exercise: Run your MD program for 2000 time steps and store the velocity vector of a certain particle (say, no. 1) at each time step. Write and test a program that evaluates the autocorrelation function of this vector.

Exercise: Using the experience gathered in the above exercise, write a procedure that computes the velocity ACF, averaged over all particles, during an MD simulation run.

Plot the ACF and see whether it resembles the one given in the Figure.

Stochastic Dynamics

Langevin's equation of motion for a heavy solute particle in a sea of light solvent particles:

$$\dot{\mathbf{v}}(t) = -\eta \mathbf{v}(t) + \mathbf{a}(t)$$

with

$$\begin{aligned} \langle \mathbf{v}(0) \cdot \mathbf{a}(t) \rangle &= 0 \qquad \text{for} \quad t \geq 0 \\ \langle \mathbf{a}(0) \cdot \mathbf{a}(t) \rangle &= 3 \frac{2\eta k T}{m} \, \delta(t) \end{aligned}$$

In addition to the autocorrelation of the quantity $\mathbf{a}(t)$ we need the statistical distribution of $|\mathbf{a}|$: $\Longrightarrow$assume Gauss distribution!

Using the definitions

$$e(t) \equiv e^{-\eta t}\,, \qquad f(t) \equiv \frac{1 - e^{-\eta t}}{\eta}$$

and

$$\mathbf{V}_n \equiv \int_0^{\Delta t} e(\Delta t - t')\,\mathbf{a}(t_n + t')\,, \qquad \mathbf{R}_n \equiv \int_0^{\Delta t} f(\Delta t - t')\,\mathbf{a}(t_n + t')$$

the stepwise solution to Langevin's equation may be written as

$$\boxed{\begin{aligned} \mathbf{v}_{n+1} &= \mathbf{v}_n\, e(\Delta t) + \mathbf{V}_n \\ \mathbf{r}_{n+1} &= \mathbf{r}_n + \mathbf{v}_n\, f(\Delta t) + \mathbf{R}_n \end{aligned}}$$

where the elements of the stochastic vectors $\mathbf{V}_n, \mathbf{R}_n$ are bivariate Gaussian variates with $\langle V_n \rangle = \langle R_n \rangle = 0$, $\langle V_n V_{n+1} \rangle = \langle R_n R_{n+1} \rangle = 0$, and

$$\boxed{\begin{aligned}
\langle V_n^2 \rangle &= \frac{kT}{m}\left[1 - e^2(\Delta t)\right] \\
\langle R_n^2 \rangle &= \frac{kT}{m\eta^2}\left[2\eta\Delta t - 3 + 4e(\Delta t) - e^2(\Delta t)\right] \\
\langle V_n R_n \rangle &= \frac{kT\eta}{m} f^2(\Delta t)
\end{aligned}}$$

– Remember? We know how to sample correlated Gaussian variates. (See Chapter 3. Stochastics)