Introduction to Molecular Dynamics II

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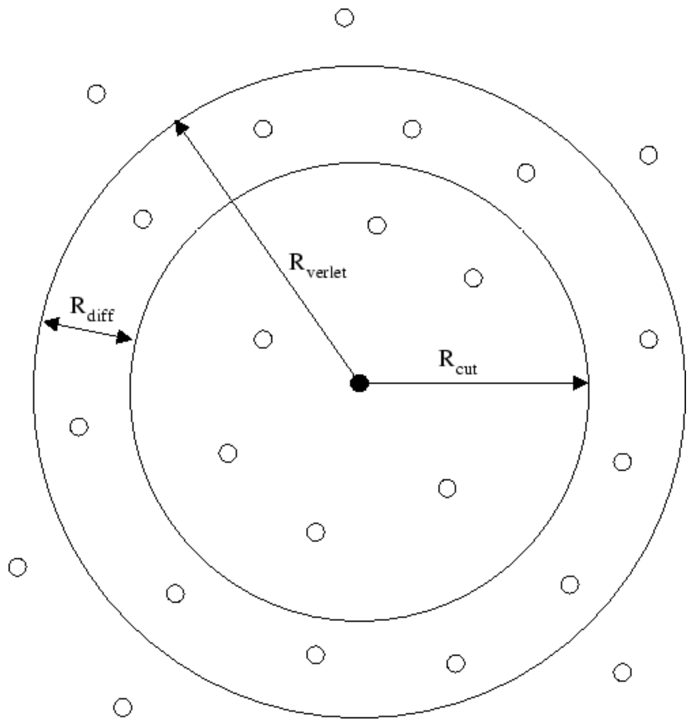
09 Force calculation: Verlet's list

Atomic forces exerted on atom i,

$$f_i = -\frac{\partial}{\partial q_i} V = \sum_{j \neq i} \varphi'(q_i - q_j).$$

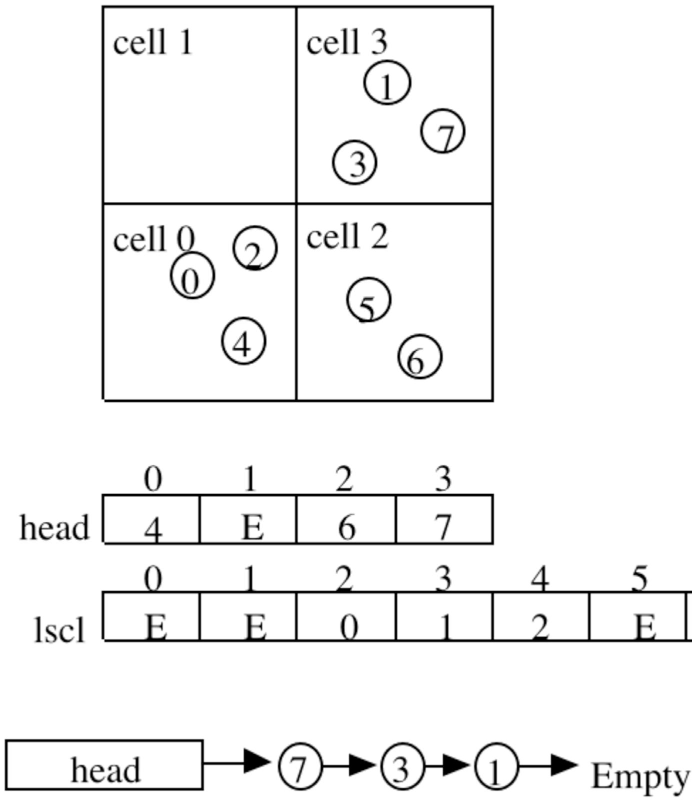
Main idea:

1. set up a list for the neighbors ($|q_i - q_j| < r_{cut}$).



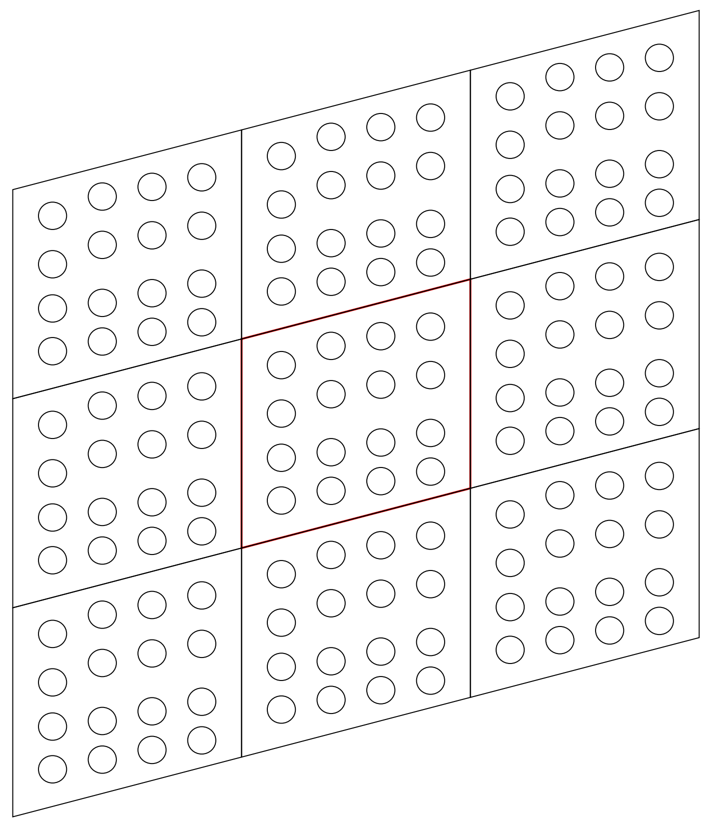
2. In the far field, use a mean field approximation.

Force calculation: Linked cell list



10 Boundary condition

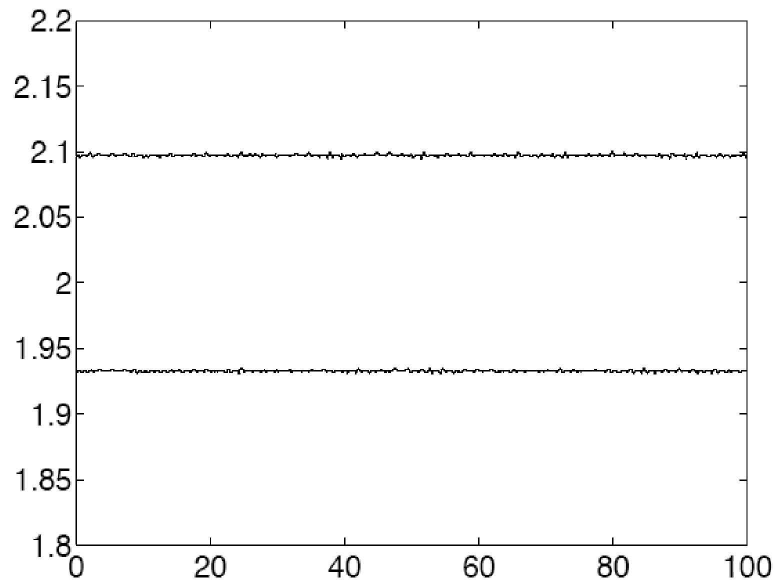
Use periodic boundary condition to mimic a large homogeneous sample



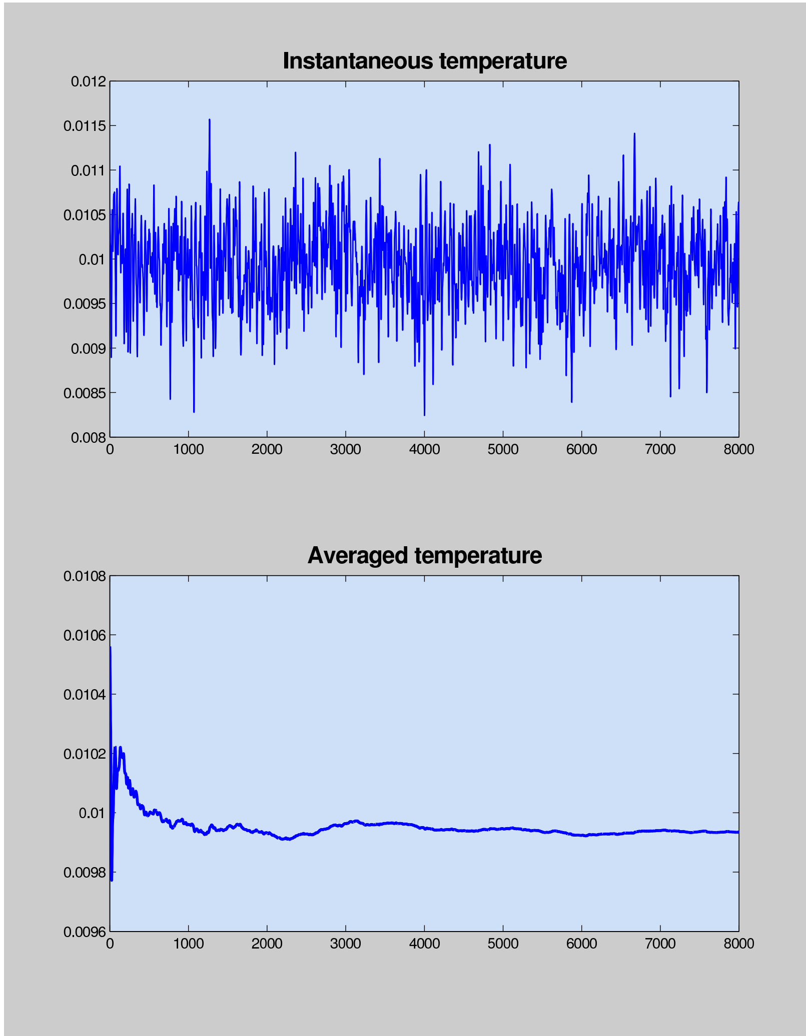
11 Example: Energy conservation of the Verlet's method

Molecular dynamics simulations are usually conducted for rather long period of time

Energy conservation is important to retain the right statistics.



Example: sample the temperature



12 Canonical ensemble

Consider a system with N particles, volume V at temperature T.

1. Total energy $E = E_1 + E_2$
2. Entropy $S = k_B \ln \Omega_1(E_1) + k_B \ln \Omega_1(E_2)$
3. Maximal Entropy Principle: $\frac{\partial S}{\partial E_1} = 0$, yielding,

$$\frac{\partial k_B \ln \Omega_1}{\partial E_1} = \frac{\partial k_B \ln \Omega_2}{\partial E_2}.$$

4. Canonical Distribution:

$$\text{Prob}(E = E_i) = \frac{e^{-\beta E_i}}{Z} \quad Z = \sum_j e^{-\beta E_j}.$$

Free Energy

1. Free energy

$$F = E - TS$$

2. From the second law of thermodynamics

$$E = \frac{\partial(\beta F)}{\partial \beta}, p = -\frac{\partial F}{\partial V}.$$

3. The average energy,

$$E = \frac{\sum_i e^{-\beta E_i} E_i}{\sum_i e^{-\beta E_i}} = \frac{-\partial \ln Z}{\partial \beta}.$$

4. The free energy:
   $F = -k_B T \ln Z = -k_B T \ln Q + const., Q = \int e^{-\beta V} d\mathbf{q}.$

Gibbs distribution

Partition function,

$$Z = \int e^{-\beta H} d\mathbf{q} d\mathbf{p}.$$

Gibbs Distribution

$$\rho = \frac{1}{Z} e^{-\beta H}.$$

13 Definition of pressure

1. The free energy: $F = -k_B T \ln Q$.

2. $\mathbf{q} \to (1+\epsilon)\mathbf{q}$, $V(\mathbf{q}) \to V((1+\epsilon)\mathbf{q})$.

3. $\frac{\partial F}{\partial \epsilon}|_{\epsilon=0} = -\frac{k_B T}{Q} \int (dN + \beta \mathbf{f} \cdot \mathbf{q}) e^{-\beta V} d\mathbf{q}$.

4. $\frac{\partial V}{\partial \epsilon}|_{\epsilon=0} = dV$.

5. The pressure,

$$
\begin{aligned}
p = -\frac{\partial F}{\partial V} \quad &= \quad \rho k_B T + \frac{1}{dV} \left\langle \mathbf{f} \cdot \mathbf{q} \right\rangle \\
&= \quad \rho k_B T + \frac{1}{dV} \left\langle \sum_{i<j} \mathbf{f}_{ij} \cdot \mathbf{r}_{ij} \right\rangle
\end{aligned}
$$

14 Sampling Error

Time-averaged value:

$$A(T) = \frac{1}{T}\int_0^T A(\mathbf{q}(t), \mathbf{p}(t))dt.$$

The average,

$$A = \langle A(T)\rangle.$$

The variance,

$$\begin{aligned}\left\langle A(T)^2\right\rangle - A^2 &= \tfrac{1}{T^2}\int_0^T\int_0^T \Big\langle (A(t) - A)(A(t') - A)\Big\langle dtdt' \\ &\approx \tfrac{1}{T}\int \phi(t)dt. \\ &= \tfrac{2\tau_A\phi(0)}{T}.\end{aligned}$$

The error estimate,

$$\frac{\sigma^2(A(T))}{A^2} = \frac{2\tau_A}{T}\frac{\sigma^2(A)}{A^2}.$$

15 Time correlation function

Stationary Stochastic Processes in the wider sense:

$$E(u(t)) = m, E\big((u(t) - m)(u(s) - m)\big) = \phi(t - s).$$

Examples:

1. $u(t) = a\cos t + b\sin t,\ a, b \in N(0, 1)$.
2. White noise
3. Solution of MD, with initial data drawn from the canonical distribution.

16 Linear response

Consider a system under external force initially,

$$A + \langle \Delta A \rangle = \frac{\int e^{-\beta(H-\lambda B)} A(t) d\mathbf{q} d\mathbf{p}}{\int e^{-\beta(H-\lambda B)} d\mathbf{q} d\mathbf{p}}.$$

To leading order,

$$\langle \Delta A \rangle = \beta\lambda \langle B(0) A(t) \rangle, as \lambda \to 0.$$

16 Dynamic quantities

Static quantities

1. temperature
2. pressure
3. stress

Dynamic quantities

1. diffusion constant
2. viscosity
3. heat conductivity

Velocity auto-correlation

Einstein relation

$$2D = \lim_{t \to +\infty} \frac{\partial \langle \Delta x(t)^2 \rangle}{\partial t}.$$

Mean square displacement

$$\begin{aligned} \langle \Delta x^2 \rangle &= \int_0^t \int_0^t \langle v(t')v(t'') \rangle dt' dt'' \\ &= 2 \int_0^t \int_0^{t'} \phi(t' - t'') dt' dt'' \end{aligned}$$

The diffusion constant

$$D = \int_0^{+\infty} \phi(t) dt.$$

Shear Viscosity

The Green-Kubo formula,

$$\eta^{\mu\nu} = \frac{1}{k_B T V} \int_0^{+\infty} \phi(t) dt.$$

The correlation function,

$$\phi(t) = \left\langle \sigma^{\mu\nu}(t) \sigma^{\mu\nu}(0) \right\rangle.$$

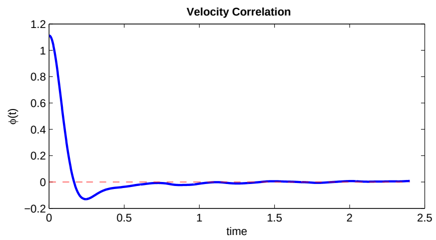
where,

$$\sigma^{\mu\nu} = \sum_i m_i v_i^\mu v_i^\nu + \frac{1}{2} \sum_{j \neq i} f_{ij}^\mu r_{ij}^\nu.$$

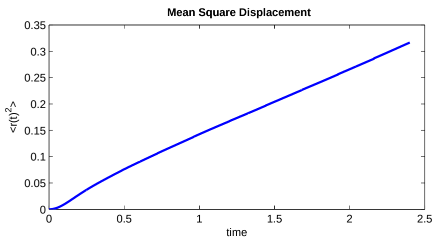
17 Pair correlation function

- $g(\mathbf{q}_1, \mathbf{q}_2) = \frac{N(N-1)}{\rho^2} \frac{\int e^{-\beta V(\mathbf{q})} d\mathbf{q}_3 \cdots d\mathbf{q}_N}{Q}$.
- $g(\mathbf{q}_1 - \mathbf{q}_2, 0) = g(\mathbf{q}_1, \mathbf{q}_2)$.
- $g(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{\rho^2} \Big\langle \delta(\mathbf{r}_1 - \mathbf{q}_1) \delta(\mathbf{r}_2 - \mathbf{q}_2) \Big\rangle$.
- $g(\mathbf{r}) = g(\mathbf{r}, 0) = \dfrac{1}{\rho^2} \Big\langle \sum_i \sum_{j \neq i} \delta(\mathbf{q}_i) \delta(\mathbf{q}_j - \mathbf{r}) \Big\rangle =$
  $\dfrac{V}{N^2} \Big\langle \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_{ij}) \Big\rangle$

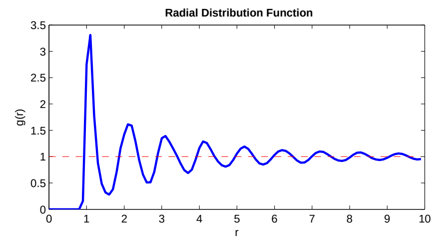
Examples



Velocity Correlation
φ(t)
time



Mean Square Displacement
<r(t)^2>
time



Radial Distribution Function
g(r)
r

The radial distribution function

If

$$A = \langle \frac{1}{N} \sum_{i \neq j} a(r_{ij}) \rangle.$$

Then, using the RDF,

$$A = \int_0^{+\infty} a(r) g(r) 4\pi r^2 dr.$$