

Friday, July 7th Ludovic Berthier - Numerical Simulations I

I) Simulations of glass forming liquids
mostly classical fluids (no quantum)

- $\left. \begin{array}{l} \text{molecular} \\ \text{dynamics (MD)} \end{array} \right\} \text{Monte Carlo (MC)}$

↳ main methods.

- Could also do simulations of simple spin models (MC), spin-glass types or spin models without quench disorder.
- ab-initio simulations (describe the chemistry) \rightarrow not the topic.

■ Why doing simulations?

- Detailed theory for the glass transition is difficult.

Simulations can give a clue about the finite dimensional behavior.

- mostly empirical models: tested in simulations.

- simpler than experiments. Know exactly what are the ingredients that we put in.
(hard sphere used extensively)

- Have all molecules' positions at all times.

- we do the impossible things

↳ change dimensions d

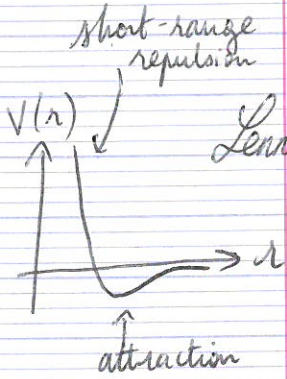
↳ very small / large systems

↳ curved space (hyperbolic)

↳ measure complicated functions.

ex. potential / free energy landscape

Simple models = isotropic pair interactions for point-like objects.



(a) Most common potential for 2 particles \vec{r}_i, \vec{r}_j
 Lennard-Jones: $V(|\vec{r}_i - \vec{r}_j|) = V(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$

ϵ : set energy scale
 σ : "size of particles"

Can study a fluid LJ changing $P, T, V \dots$

(b) Simplify LJ to soft sphere: $V(r) = 4\epsilon \left(\frac{\sigma}{r}\right)^{12}$
 Phase diagram simplified only depend on one parameter combining T, P .

(c) Hard sphere $V(r) = \infty$ for $r < \sigma$
 $= 0$ for $r > \sigma$

Only one parameter: density.

(d) Harmonic sphere $V(r) = \epsilon \left(1 - \frac{r}{\sigma}\right)^2$ for $r < \sigma$
 $= 0$ for $r > \sigma$

Used a lot in the context of jamming (A. Liu)

Other Real model for glass like SiO_2

Pair potential depend on molecule type (S_i, O), charges

Complicated!

$$V_{\alpha\beta}(r) = q_\alpha q_\beta \frac{e^2}{r} + A_{\alpha\beta} e^{-B_{\alpha\beta} r} - C_{\alpha\beta}/r^6$$

$\alpha, \beta = \text{Si}, O$

A, B, C fitted from experiments

■ Avoiding crystallisation: IS complicated

→ We use mixtures of particles to frustrate the appearance of crystallisation.

ex: binary sizes for hard-spheres.

Motivated by experiments in which crystallisation is avoided by binary, ternary etc. mixtures.

→ Continuous polydispersity (sizes of particles continuous). ex colloids are always polydisperse.

⇒ We do have glass-forming models that are good (no crystal. etc) but are perhaps far from real glasses in experiments. (Gilles, Mark's belief?)

■ Basic outcome of a simulation (MD or MC)

$$\left\{ \vec{r}_i(t) \right\}_{i=1 \dots N} \quad t = 0, \dots, T_{\text{sim}}$$

? viscosity, T_{PTS} , χ_4 etc? to study the glass transition

We need to extract the relevant information: thermodynamics, structure, dynamics etc.

■ Liquid state theory

• Density field
$$\rho(\vec{r}, t) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i(t))$$

average over sample:
$$\langle \rho(\vec{r}, t) \rangle = \frac{1}{V} \int d^d r \rho(\vec{r}, t) = \frac{N}{V} = \rho_0$$

ρ_0 number density

• fluctuations: $\delta\rho(\vec{r}, t) = \rho(\vec{r}, t) - \rho_0$

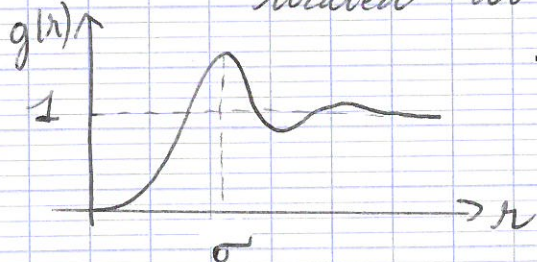
↳ 2 points $G(\vec{r}, \vec{r}', t) = \langle \delta\rho(\vec{r}, t) \delta\rho(\vec{r}', t) \rangle$ ensemble average
 isotropic, homogeneous etc. $G(|\vec{r} - \vec{r}'|, t)$

$$G = \langle \rho(\vec{r}, t) \rho(\vec{r}', t) \rangle - \rho_0^2$$

$$= \underbrace{\rho_0 \delta(\vec{r} - \vec{r}')}_{\substack{\text{single} \\ \text{particle} \\ \sum_{i=j}}} + \underbrace{\langle \sum_{i \neq j} \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) \rangle}_{\substack{= \rho_0^2 g(|\vec{r} - \vec{r}'|) \\ \text{pair correlation function}}}$$

$g(|\vec{r} - \vec{r}'|)$: proba of having particle i at \vec{r}
 j at \vec{r}'

↳ $\rho_0 g(r)$ = density at distance r from a particle located at $r=0$



$g(r)$: local structure of a dense disordered fluid

Thermodynamic properties

$$U = \sum \frac{1}{2} m \vec{v}_i^2 + \frac{1}{2} \sum_{i \neq j} V(|\vec{r}_i - \vec{r}_j|)$$

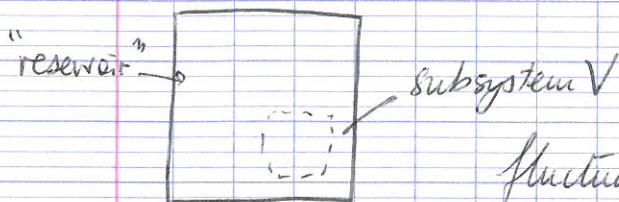
$$\langle U \rangle = \underbrace{\frac{3}{2} N k_B T}_{\text{equipartition}} + \langle \frac{1}{2} \int d\vec{r} d\vec{r}' V(\vec{r} - \vec{r}') \rho(\vec{r}) \rho(\vec{r}') \rangle$$

↓
~ $g(r)$



$$\langle U \rangle = \frac{3}{2} N k_B T + \frac{\rho_0 N}{2} \int d\vec{r} g(r) V(r)$$

thermodynamic fluctuations



fluctuations inside the subsystem.

$$\begin{aligned} \langle \Delta N^2 \rangle_V &= \left\langle \left(\int d\vec{r} \delta \rho(\vec{r}) \right)^2 \right\rangle \\ &= N \left[1 + \rho_0 \int d\vec{r} (g(r) - 1) \right] \\ &= N \rho_0 k_B T \chi_T \end{aligned}$$

isothermal compressibility = $-\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T$

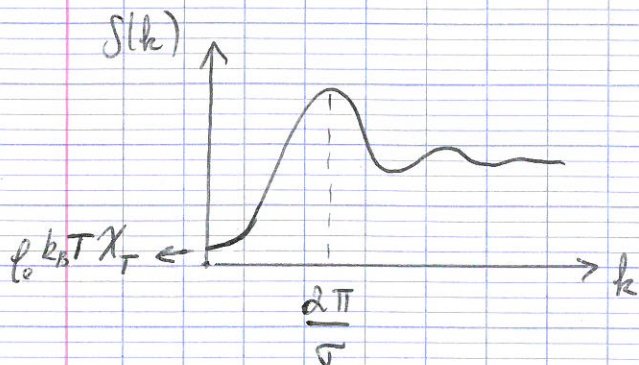
relevant experimental quantity obtained from $\{x_i\}$

Relation with Fourier-space measured quantities

Structure factor (neutron scattering at angle \vec{q}):

$$S(\vec{k}) = \frac{1}{N} \langle \rho_{\vec{k}}(t) \rho_{-\vec{k}}(t) \rangle$$

$$S(\vec{k}) = 1 + \rho_0 \int d\vec{r} e^{i\vec{k} \cdot \vec{r}} [g(r) - 1]$$



What do we learn from 2-pt correlation function?

Allen said none for glass transition.

• For jamming: encoded in the first peak of the pair correlation function when $r \sim \sigma$

• Torquato: Hyperuniformity: study of large scale density fluctuations ($q \rightarrow 0$).

Dynamics: Time correlation functions

Observable O $\langle O \rangle = 0$

$$C(t, t') = \langle O(t) O(t') \rangle$$

↑ ↗
computed at \neq times in the same trajectory ← ensemble average

At equilibrium steady state: $C(t-t')$
 $C(t, t')$ if non-eq (aging)

intermediate scattering function

$$F(\vec{k}, t) = \frac{1}{N} \langle \delta \rho(\vec{k}, t) \delta \rho(\vec{k}, 0) \rangle$$
$$= \frac{1}{N} \left\langle \sum_{ij} e^{i\vec{k} \cdot [\vec{r}_i(t) - \vec{r}_j(0)]} \right\rangle$$

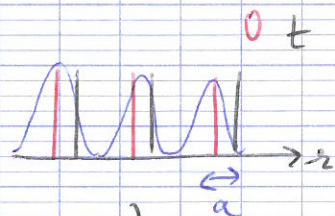
Self part $i=j$: $F_S(\vec{k}, t) = \left\langle \frac{1}{N} \sum_i e^{i\vec{k} \cdot [\vec{r}_i(t) - \vec{r}_i(0)]} \right\rangle$

mean-squared displacement $\langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle \sim 2d D_s t$
 $t \rightarrow \infty$ \uparrow self diffusion constant.

• Overlaps: $Q(t) = \frac{1}{N} \langle \sum_{ij} \Theta(a - |\vec{r}_i(t) - \vec{r}_j(0)|) \rangle$

time correlation of density profile.

Density profile = δ function.
 Coarse graining of density profile
 typically a is a fraction of σ ($a = 0.2\sigma$)



• Viscosity: $\eta = \frac{1}{\sqrt{k_B T}} \int_0^\infty dt \langle J(t) J(0) \rangle$

J is a current: $J = \sum_i \left[\frac{p_{xi} p_{yi}}{m} - y_i F_{xi} \right]$

Green-Kubo relation relating position/velocity to transport
 (a kind of fluct-dissip. theorem) coef.

Brief history of simulations

- 1985 - early studies
- 1995 - MCT ~ Dave Reichman.
- 2000 - Aging, effective temperatures, rheology
- 2005 - Dynamic heterogeneities
- 2010 - Static length scales, Kauzmann transition, config. entropy.

Slides: figures + ref.

II) Basic method: Molecular dynamics

Tricks:
Book
Allen-Tildesley

$$\left\{ \begin{array}{l} \{\vec{r}_i\}, V(r) \\ \frac{d\vec{r}_i}{dt} = \vec{v}_i \\ m \frac{d\vec{v}_i}{dt} = - \sum_j \frac{\partial V(\vec{r}_{ij})}{d\vec{r}_{ij}} \end{array} \right.$$

Start $\{\{\vec{r}_i(0)\}, \{\vec{v}_i(0)\}\} \xrightarrow{\text{qut}} \{\{\vec{r}_i(t)\}, \{\vec{v}_i(t)\}\}$ that's all

- discretize with timestep dt

Velocity-Verlet algorithm:

$$\left\{ \begin{array}{l} \vec{r}_i(t+dt) = \vec{r}_i(t) + \vec{v}_i(t)dt + \frac{1}{2}dt^2 \vec{a}_i(t) \\ \vec{a}_i(t+dt) \text{ computed from } \vec{r}_i(t+dt) \\ \vec{v}_i(t+dt) = \vec{v}_i(t) + \frac{1}{2}dt (\vec{a}_i(t) + \vec{a}_i(t+dt)) \end{array} \right.$$

- small system \rightarrow use periodic boundary conditions
- key step: i) for each i , sum forces over all j .
 \rightarrow compute forces $O(N^2)$ STUPID!

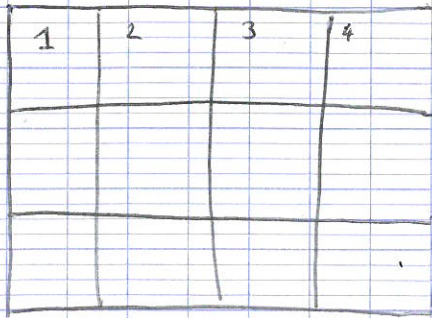


Only compute forces due to neighbor particles set by the cut-off of the potential.

Compute neighbor list costs $O(N^2)$ but then the computation is of order $O(N)$

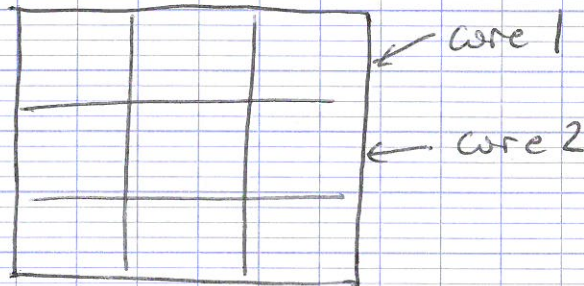
- ii) For much larger systems, the computation of neighbor is still too big.

Separate the system in cells.



Assign a cell to each particle $O(N)$
then in each cell compute
neighbor list.

iii) For even larger systems, parallel computing



iv) If you don't want to code: download LAMMPS

Thermostat

MD: control the temperature because equations
conserve Energy ($E_{kin} + E_{pot}$): NVE ensemble.

If you want to control temperature, should
kick particles (change velocities)
or change equations of motion.

For a simu. → [step 1) Use any thermostat T
equilibration → rescale velocity (NVT ensemble)
measurements → [step 2) Remove thermostat and
do NVE simulation.