

* The main topic of the lecture is the simulations of classical fluids.

We'll introduce two methods:
 → molecular dynamics (≡ MD)
 → Monte Carlo (≡ MC)

* We could also consider simulations of simple spin models (≡ MC) with and without quenched disorder.

* People are also doing ab-initio simulations (chemistry quantum level)
 e.g. storage of nuclear waste in glasses -

I INTRODUCTION

WHY DOING SIMULATIONS?

→ it is difficult to obtain a detailed theory is difficult (mean field already complicated is hardly relevant in finite d)

→ many models, that are purely empirical → need to be tested

→ much simpler than experiments (very controlled framework, parameters, no interfering phenomenon = - impurities - vibrations)

↳ e.g. hard spheres simulations ≡ great simplification of real world systems.

→ very easy to measure: see all atoms at all times etc...

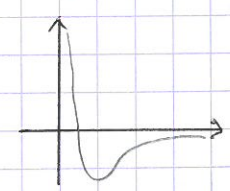
→ access impossible settings: - change dimensions to $d > 3$
 - small systems
 - curved space (hyperbolic)
 - measure complicated things (point-to-set, potential energy landscapes ...)

SIMPLE MODELS

= isotropic pair interactions for point-like objects.

energy + length scale

* Lennard-Jones \vec{r}_i, \vec{r}_j $V(|\vec{r}_i - \vec{r}_j|)$, $V(r) = 4\epsilon \left[\left(\frac{\epsilon}{r}\right)^{12} - \left(\frac{\epsilon}{r}\right)^6 \right]$
 ↑ repulsion short range ↓ weak attraction long range



* Soft sphere (get rid of attraction) $V(r) = \epsilon \left(\frac{\epsilon}{r}\right)^{12}$ → one dimensional phase diagram, only one effective parameter → much simpler.

* Hard sphere $V(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases}$ → only controlled by density

* Harmonic spheres $V(r) = \begin{cases} \epsilon (1 - r/\sigma)^2 & r < \sigma \\ 0 & r > \sigma \end{cases}$ soft interaction for overlap.
 no interaction if they don't overlap.

≠ Description of real material: e.g. SiO_2 → have to specify the interactions between different types of atoms.

↳ $\alpha, \beta = \text{Si, O}$: $V_{\alpha\beta} = q_\alpha q_\beta \frac{e^2}{r} + A_{\alpha\beta} e^{-B_{\alpha\beta} r} - \frac{C_{\alpha\beta}}{r^6}$ → with parameters determined in the lab -
 coulomb

PROBLEM OF CRYSTALLIZATION

↳ We want to study the disordered state so that we need to prevent crystallization and monitor that it does not nevertheless occur.

strategies: → mixtures (binary, ...)

↳ metallic glasses in experiments fall in that category

→ continuous polydispersity

↳ colloidal systems in real world

→ we do have some "good" glass models (to be challenged by MARK?)

WHAT COMES OUT OF THE SIMULATIONS? $\{r_i(t)\}$ for $i=1 \dots N$, $t=0, \dots, T_{\text{simulation}}$

We need to extract the relevant information

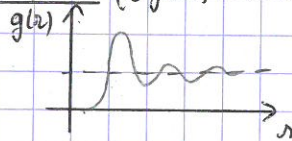
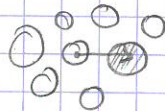
Density field $\rho(\vec{r}, t) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i(t)) \rightarrow \langle \rho(\vec{r}, t) \rangle = \frac{1}{V} \int d\vec{r}' \rho(\vec{r}', t) = \frac{N}{V} = \rho_0$

Fluctuations of the density: $\delta\rho(\vec{r}, t) = \rho(\vec{r}, t) - \rho_0$ ensemble, thermal average

2-point correlation: $G(\vec{r}, \vec{r}', t) = \langle \delta\rho(\vec{r}, t) \delta\rho(\vec{r}', t) \rangle = G(|\vec{r} - \vec{r}'|, t)$ (isotropic, homogeneous)

which can be written $G = \langle \rho(\vec{r}, t) \rho(\vec{r}', t) \rangle - \rho_0^2$
 $= \rho_0^2 \delta(\vec{r} - \vec{r}') + \langle \sum_{i \neq j} \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) \rangle - \rho_0^2$
 $\equiv \rho_0^2 g(|\vec{r} - \vec{r}'|)$ probab. to have 1 part at \vec{r} and 1 part at \vec{r}'

PAIR CORRELATION FUNCTION: $\rho_0 g(r) =$ density at distance r from a particle at $r=0$



← dense but disordered fluids.

Thermodynamic properties

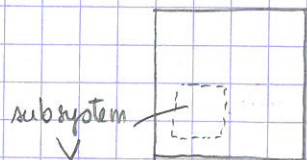
• Energy of the system → kinetic energy + potential

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

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

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

Thermodynamic fluctuations



fluctuations of e.g. number of particles:

$$\langle \Delta N^2 \rangle = \left\langle \left(\int d\vec{r} \delta\rho(\vec{r}) \right)^2 \right\rangle$$

$$= N \left[1 + \rho_0 \int d\vec{r} (g(r) - 1) \right]$$

$$\equiv N \rho_0 k_B \chi_T$$

↳ $-\frac{1}{V} \frac{\partial V}{\partial P}_T$ compressibility

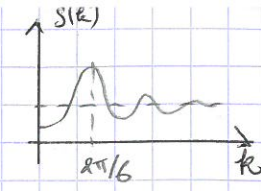
≡ macroscopic physical experimental

Structure fields \equiv

again experimental measure

$$S(\vec{k}) = \frac{1}{N} \langle \rho(\vec{k}, t) \rho(-\vec{k}, t) \rangle \quad \text{F.T.}$$

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



To sum up: what can we hope to learn from 2-point correlation function?

- physics of the jamming transition at $\nu \approx 0.6$
- medium range order at $\nu \approx 3-4.6$
- large ν , low k community as well...

DYNAMICS: Time correlation functions.

For an observable $O(t)$ we look at $C(t, t') = \langle O(t) O(t') \rangle$
 $\langle O \rangle = 0$

ensemble average

computed at \neq times on the same trajectory (otherwise uncorrelated).

- equilibrium: $C(t-t')$
- non eq. (e.g. aging): $C(t, t')$

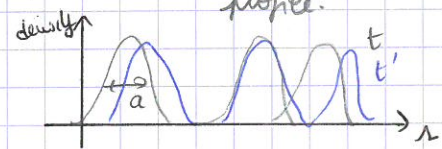
* Intermediate scattering function: $F(\vec{k}, t) = \frac{1}{N} \langle \delta \rho(\vec{k}, t) \delta \rho(-\vec{k}, 0) \rangle$
 $= \frac{1}{N} \langle \sum_j e^{i\vec{k}\cdot(\vec{r}_j(t) - \vec{r}_j(0))} \rangle$

self version: $F_s(\vec{k}, t) = \langle \frac{1}{N} \sum_i e^{i\vec{k}\cdot[\vec{r}_i(t) - \vec{r}_i(0)]} \rangle$

diffusion coefficient

* Mean squared displacement: $\langle (\vec{r}_i(t) - \vec{r}_i(0))^2 \rangle \sim 2d D_s t$

* Overlaps: $\Phi(t) = \frac{1}{N} \langle \sum_j \Theta(a - |\vec{r}_j(t) - \vec{r}_j(0)|) \rangle$ time correlation of the density people.
 course graining length ($\approx 0.2\sigma$)



* Viscosity: $\eta = \frac{1}{V k_B T} \int_0^\infty dt \langle J(t) J(0) \rangle$ current $J = \sum \left[\frac{p_{xi} p_{yj}}{m} - y_i f_{xi} \right]$

Fluctuation Dissipation Theorem \equiv GREEN-KUBO relation \rightarrow EXERCISE!
 response time integral of fluctuation

BRIEF HISTORY OF NUMERICAL SIMULATIONS -

- 1985 - Early studies, 1995 - Massive MCT (D. Reichmann),
- 2000 - Aging, Effective temperatures, rheology
- 2005 - Dynamic heterogeneities
- 2010 - Static length scales, Kauzmann theory

II BASIC METHOD: MOLECULAR DYNAMICS:

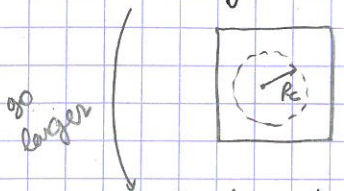
$\{ \vec{r}_i(t) \}$ fields that are simply related: $\left\{ \begin{array}{l} \frac{d\vec{r}_i}{dt} = \vec{v}_i \\ m \frac{d\vec{v}_i}{dt} = - \sum_j \frac{\partial V(\vec{r}_i)}{\partial \vec{r}_{ij}} \end{array} \right.$
 $\vec{r}(\vec{r}, t)$

\rightarrow initial conditions $\{ \vec{r}_i(0), \vec{v}_i(0) \} \rightarrow$ get $\{ \vec{r}_i(t), \vec{v}_i(t) \}$ that's all!

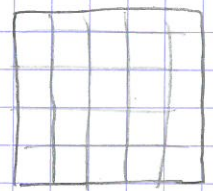
All the tricks (from ref Allen-Halesley)

- Consider small systems \Rightarrow periodic boundary conditions

- \rightarrow The key limiting step is the computation of the forces (pair interaction $\rightarrow O(N^2)$)
- Only restrict to nearest neighbors \rightarrow maintain a list of neighbors (at first $O(N^2)$)
- \rightarrow integration $O(N)$

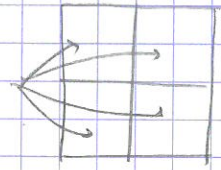


- Divide systems into cells \rightarrow assign cell to each particle $O(N)$
- \rightarrow easier to establish the neighbor list! $O(N)$
- \rightarrow integration $O(N)$



even larger

- Parallel computing one computer each
- not even of complexity $O(N)$



\rightarrow The key trick: Download open software: LAMMPS -

RK: THERMOSTAT \rightarrow to make sure total kinetic energy remain constant \rightarrow needs to change eq. motion (\checkmark forbidden?)

- (1) Use any thermostat T (rescale all velocities) \rightarrow "long enough"
- (2) Remove thermostat MD simulation \rightarrow should be fluctuating around chosen T - (N, V, E \rightarrow microcanonical)

10/07/2017

In the last lecture we finished on the question of being temperature. In the first phase of the computation we need to thermalize the system with a thermostat.

BIG QUESTION: How long is long enough? \rightarrow we don't know! No way to prove it, and it gets tricky close to the transition...

- list of necessary conditions: NOT SUFFICIENT
- 1-time quantities are stationary
 - fluctuations $\langle \delta p^2 \rangle = \frac{p^2}{V} k_B T \chi_T$ \rightarrow derivative
- It looks very demanding, a FDT! \rightarrow yet, within a basin of glassy system, verified \rightarrow NOT A GOOD TEST!

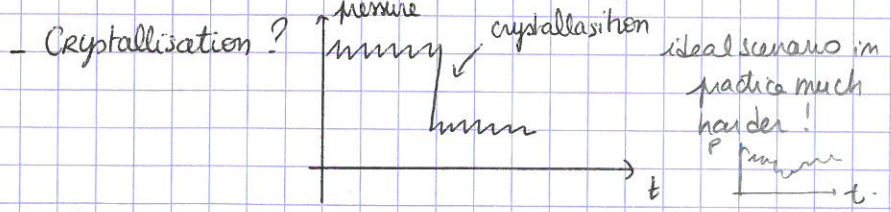
$P(E, T) = g(E) e^{-\beta E}$

density of state should not depend on the temperature $g(E) \propto P(E) e^{\beta E}$ (easy to compute at high temperatures)

YET, usually the effective span of energies probed at \pm temperatures do not overlap! so the smooth curve do not mean much!

problem to do parallel tempering, no access to dynamics, following trajectory

Dynamics: At equilibrium, particles should move $\tau_{\alpha}^{self}, \tau_{\alpha}^{coll}, \tau_s \rightarrow$ BEST TEST SO FAR.



\hookrightarrow need to monitor $g(r), S(k)$ specially designed order parameters

COMPUTING THE CONFIGURATIONAL ENTROPY:

$S_{cr} = S_{tot} - S_{vibration} \rightarrow$ Hard spheres $S_{tot} = -BF = S_{id} + S_{ex}$

with $\left\{ \begin{aligned} S_{id} &= N \left\{ \frac{5}{2} - \ln p_0 - \ln \Lambda^3 + s_{mix} \right\}$ mixing term $\Lambda = \sqrt{\frac{2\pi\beta\hbar^2}{m}}$ (from momenta int).

$S_{ex} = -N\beta \int_0^{\beta} dp \frac{p^{exc}(p)}{p^2}$ $p^{exc} = p - p^{hard sphere}$ → coming from the interaction between the particle.

↳ thermodynamic integration

mixing entropy: coming from interchanging the identity of the different particles.

mixture with M components:

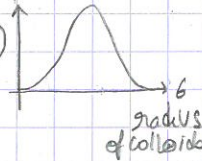
$$X_m = \frac{N_m}{N} \quad Z = \frac{1}{\prod_{m=1}^M N_m!} \frac{1}{\Lambda^{3N}} \int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}$$

$$-\beta F \rightsquigarrow -\ln \left(\prod_{m=1}^M N_m! \right) \rightarrow \text{stirling's} : - (N \ln N - N) - N \underbrace{\sum_{m=1}^M X_m \ln X_m}_{s_{mix}}$$

usual term.

e.g. for binary mixture: $X_1 = X_2 = 1/2 \rightarrow \Delta s_{mix} = \ln 2 \sim 0.693$

eg. for continuous polydispersity: $P(\epsilon)$

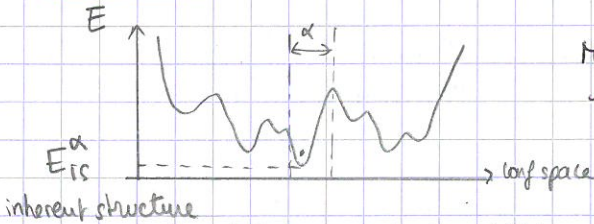


$$X_m = \frac{1}{N} \rightarrow \text{all different!}$$

$\Delta s_{mix} \sim \ln N \rightarrow$ diverges... problem with this blind application.

How could you find a transition marked by $S \rightarrow 0$ when defined $S = +\infty$, meaning that there could not be a Kauzmann transition in such system. Although it seems that for very narrow distribution $\uparrow \prod_{\epsilon} \epsilon$, the mixing entropy should not matter... so that there's something fishing about this entropy!

III POTENTIAL ENERGY LANDSCAPE



Metastable states actually exist, so one idea is to replace the free energy \rightarrow energy minima $\left\{ \begin{aligned} &\text{well-defined partition of conf. space.} \\ &\text{What is its meaning?} \end{aligned} \right.$

Idea of Stillinger-Weber 1984: Decompose over all basins (close to an energy minima in configuration space)

$$Z = \frac{1}{N! \Lambda^{3N}} \int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} = \sum_{\alpha} Z_{\alpha}(T)$$

↳ to be estimated with each basin

$$Z_{\alpha}(T) = \frac{1}{\Lambda^{3N}} \int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}$$

with $U(\mathbf{r}^N) = E_{is}^{\alpha} + \Delta U \approx E_{is}^{\alpha} + \frac{1}{2} \sum_{i,j} \frac{\partial^2 U}{\partial r_i \partial r_j} S_{r_i} S_{r_j}$

Hessian

no $N!$ \rightarrow we have $N!$ conf in a basin as we can exchange all the particles (assumed id.)

$$\approx E_{is}^{\alpha} + \frac{1}{2} \sum_{a=1}^{3N} \omega_a^2 S_{\omega_a}$$

eigenvalues of Hessian.

& that we can compute $Z_{\alpha}(T) = e^{-\beta E_{is}^{\alpha} - \beta F_{vib}}$, $-\beta F_{vib} = -\frac{1}{2} \sum_a \ln \left(\frac{\beta \hbar \omega_a}{m} \right)^2$

And the total partition function:

$$Z = \sum_{\alpha} Z_{\alpha} = \sum_{\alpha} \int dE_{is} \delta(E_{is} - E_{is}^{\alpha}) Z_{\alpha}(E_{is}^{\alpha}) = \int dE_{is} \underbrace{\frac{1}{\alpha} \delta(E_{is} - E_{is}^{\alpha})}_{\equiv \Omega(E_{is}) = e^{S(E_{is})}} Z_{\alpha}(E_{is}^{\alpha})$$

$$= \int dE_{is} e^{-\beta E_{is} - \beta F_{vib} + S_{\alpha}} = \int dE_{is} e^{-\beta E_{is} - \beta F_{basin}} \quad F_{basin} \equiv F_{vib} + E_{is} \quad (\sim \text{Gibbs})$$

→ explicit expression of the configurational entropy $S_c = S_{rot} - S_{vib}$

How is this performed in practice:

- S_{rot} ✓
- Algorithm ① find energy minima close to the equilibrium conf. $\xrightarrow[\text{"magic"}]{\text{"conjugate gradient"}} IS$

② estimate the Hessian → eigen decomposition ("magic" with already programmed recipe for large matrices)

↳ density of state of eigen values $g(\omega)$ → interesting to study:

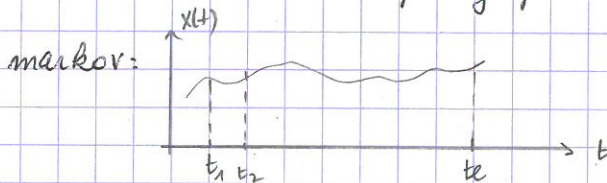
- low temperature physics
- Gardner transition
- jamming, soft modes

Rh: This is not possible as is for hard spheres, as there is no energy landscape. Nevertheless can be adapted.

II GETTING FASTER TO EQUILIBRIUM: Monte Carlo simulations - MC.

Crash course on MC: a stochastic Markov Process to efficiently sample configuration space.

↳ non deterministic ≠ Newton's equation behind MD
And it is this choice of the probability distribution that allows the speeding up.



We $(x_1, t_1, \dots, x_e, t_e)$ distribution

↳ non-memory:

$$W_{t+1}(x_{t+1}, t_{t+1} | x_t, t_t) = W_e(x_t) + P(x_{t+1}, t_{t+1} | x_t, t_t)$$
 key quantity to be studied

probabilities follow: $P(x, t) = \int dx_0 P_{init}(x_0, C) P(x_0, 0 | x, t)$
the master equation

↳ define the transition rate $R(x_0 | x) = \lim_{t \rightarrow 0} \frac{P(x_0, 0 | x, t)}{t}$

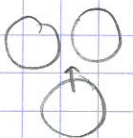
$$\frac{dP(x, t)}{dt} = \int dx' [P(x', t) R(x' | x) - P(x, t) R(x | x')] \quad (\text{discrete space } \int dx \rightarrow \sum_x)$$

↳ equilibrium distribution: $\frac{dP}{dt} = 0$ (one can prove $P(x, t) \rightarrow P_s(x)$)

↳ detailed balance: Each term in $\sum = 0 \Rightarrow \frac{R(x' | x) P_s(x)}{R(x | x')} = \frac{P_s(x')}{P_s(x)} = e^{-\beta(H(x') - H(x))}$
canonical

So that when using transition rates obeying detailed balance → sample config space $P_s(x)$.

→ algorithm for Hard spheres: configuration $C \rightarrow$ pick 1 particle
 \rightarrow sample a Sr_i
 \rightarrow accept if creating no overlap

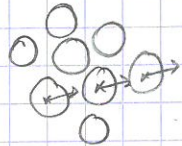


↳ check for equilibrium by checking for ergodicity → are particles traveling in the entire system - But still no way to prove that it is actually reached.

In the end, we sample $P_s(x)$ but! the dynamics is unphysical, lost in principle -
 Except when considering $Sr_i \rightarrow 0 \rightarrow$ BROWNIAN DYNAMICS (overdamped limit of Langevin).
 A strong result is the equivalence of MD \equiv MC → STRONG SEPARATION OF TIME SCALES

Going faster than the physics: The trick is to invent more complicated moves

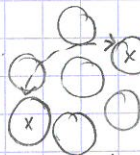
* KRAUTH-BERNARD '09: "event chain"



they move chains, and the claim is to gain 40 in acceleration
 ↳ yet not tested yet in glassy regime

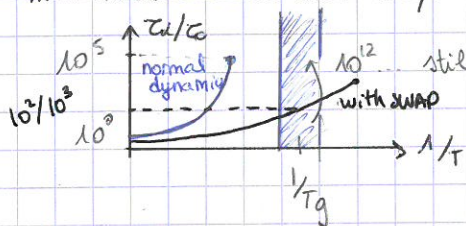
picking pairs at random
 ensures reversibility -

* SWAP MC algorithm: 2 particle move



- choose two at random
 - swap their diameters if not creating overlaps -

↳ mix translational and swap moves! → acceleration claimed to be BiG.



still need to get 7 order of magnitudes to
 ↳ make extrapolation → estimation of τ_g

Good: simulations comparing to experiments.
 Bad: it is a very local algorithm, not a complicated rearrangement corresponding to a jump from state α to state β . Would the physics of glass be actually much simpler??
 → big question -