

Ludovic Decker - Numerical Simulations II

Previously: Gap of 8 ord. of magnitudes between experiments and simulations.

Simulation: 1) Thermalize at T for "long enough"
 reach eq.

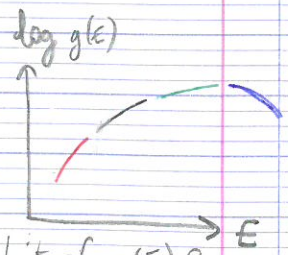
BIG QUESTION: how long is how long enough?
 When relaxation time increases, hard to simulate the system for longer times than several relax. time.

ANSWER: we don't know.

Tests for equilibration:

- 1-time quantities are stationary
- fluctuations of 1-time quantities:
 $\langle \delta p^2 \rangle = \frac{1}{V} k_B T \chi_T$ fluctuation-dissipation theorem should only work at equilibrium.
 Poor test because in the glass, the system is "equilibrated" inside the glass basin.
- distribution $P(E, T) \propto g(E) e^{-\beta E}$

(Werner Krauth 2000 only test)



bits of $g(E)$ for $\neq T$ but not the whole curve at each T

$g(E) \propto P(E, T) e^{\beta E}$ indep on temperature
 density of states counts # states at a given level

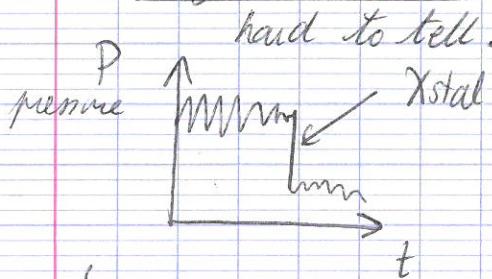
plot this for different temperatures \rightarrow should get the same $g(E)$

BAD TOO

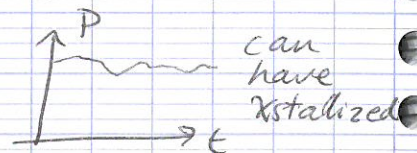
Dynamics: do particles move? If yes then

perhaps largely enough to sample phase space.
 measure τ_d^{self} , τ_d^{coll} , D_s .
 single particle diffusion

• crystallisation



} ideal scenario.
 in reality



Order parameters (local ordering)
 Structure $g(r)$, $S(k)$, ...

⇒ We are ready

(A) $S_c = S_{tot} - S_{liq}$

Hard spheres: $E=0$ $S_{tot} = -\beta F$

• $S_{tot} = \underbrace{S_{id}}_{\text{ideal gas entropy}} + \underbrace{S_{ex}}_{\text{excess}}$

de Broglie
 $\Lambda = \sqrt{\frac{2\pi\beta\hbar^2}{m}}$

$S_{id} = N \left\{ \frac{5}{2} - \ln \rho_0 - \ln \Lambda^3 + S_{mix} \right\}$
 mixing entropy (polydisperse system)

Thermodyn. integration

$S_{ex} = -\beta N \int_0^{p_0} dp \frac{p^{ex}(p)}{e^{\beta p}}$

$p^{ex} = P - p_{id}$

Mixing entropy: entropy coming from exchanging the identity of particles (different sizes)

$$X_m = \frac{N_m}{N} \leftarrow \begin{array}{l} \text{number of particles} \\ \text{of type } m \end{array}$$

Computing partition function: $Z = \frac{1}{\prod_{m=1}^M \frac{N_m! \Lambda^{3N_m}}{T^{N_m}}}$ $\int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}$

- pot $\xrightarrow{\log Z}$ $-\ln \left(\prod_{m=1}^M \frac{N_m!}{T^{N_m}} \right)$

Stirling's approximation:

$$-(N \ln N - N) - N \underbrace{\sum X_m \ln X_m}_{S_{\text{mix}}}$$

usual term S_{mix}

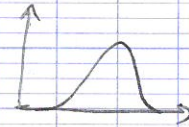
• BINARY MIXTURE : $X_1 = X_2 = 1/2$

$$\rightarrow S_{\text{mix}} = \ln 2 \sim 0.693$$

Estimates for config. entropy are of order 1-2 so if error of 0.7 then shifts $T_{\text{transition}}$ from a large amount.

• continuous polydispersity

$$P(\sigma)$$

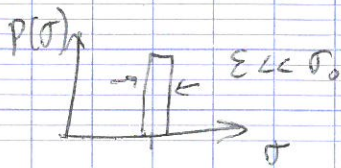


$$X_m = \frac{1}{N}$$

particles are now distinguishable.

$$N S_{\text{mix}} \sim \ln N \quad \text{diverges!} \quad ??$$

Suggests that there is no phase transition. If continuous but very narrow distribution, the physics should be the same as monodisperse.



How to estimate S_{vib} ?

III Potential energy landscape

Stillinger-Weber
(1984)



How to define free energy states?

→ replace by energy minima (well defined)
but what are their meaning (Gilles's lecture)

$$Z = \frac{1}{N! \Lambda^{3N}} \int dr^N e^{-\beta U(r^N)}$$

$$= \sum_{\alpha} Z_{\alpha}(T) \quad \text{a basin} \triangleq \text{"being close to an energy minimum } \alpha \text{"}$$

Suppose N identical particles $Z_{\alpha}(T) = \frac{1}{\Lambda^{3N}} \int dr^N e^{-\beta U(r^N)}$

In minima $U = E_{IS}^{\alpha} + \Delta U \approx E_{IS}^{\alpha} + \frac{1}{2} \sum_{ij} \frac{\partial^2 U}{\partial r_i \partial r_j} \vec{r}_i \cdot \vec{r}_j$

Hessian matrix

Assume harmonic approx (1st derivative = 0)

Diagonalize Hessian. Eigen values $\{\omega^{\alpha}\}$

$$U = E_{IS}^{\alpha} + \frac{1}{2} \sum_{a=1}^{3N} \omega_a^{\alpha 2} \delta r_a^2$$

$$Z_{\alpha}(T) = e^{-\beta E_{IS}^{\alpha} - \beta F_{vib}}$$

with $-\beta F_{vib} = -\frac{1}{2} \sum_a \ln \left(\frac{\beta \hbar \omega_a}{m} \right)^2$

$$Z = \sum_{\alpha} z_{\alpha} = \sum_{\alpha} \int dE_{is} \delta(E_{is} - E_{is}^{\alpha}) z_{\alpha}(E_{is}^{\alpha})$$

$$= \int dE_{is} \left(\underbrace{\sum_{\alpha} \delta(E_{is} - E_{is}^{\alpha}) z_{\alpha}(E_{is})}_{S_c(E_{is})} \right)$$

$$Z = \int dE_{is} e^{-\beta E_{is} - \beta F_{vib} + S_c} \quad \Omega(E_{is}) = e$$

Define $F_{vib} = E_{is} + F_{vib}$

$$Z = \int dE_{is} e^{S_c - \beta F_{vib}} \quad // \text{ saddle point}$$

$$\left. \frac{\partial S_c}{\partial E_{is}} \right|_{E_{is}^*} = \beta \left. \frac{\partial F_{vib}}{\partial E_{is}} \right|_{E_{is}^*} \quad \text{given by } \uparrow$$

Finally, $-\beta F = -\beta (F_{vib}(E_{is}^*) - T S_c(E_{is}^*)) = S_{tot}$

$$\boxed{S_c = S_{tot} - S_{vib}} \quad \text{explicit expression}$$

In practice? $S_{tot} \checkmark$

① Algorithm giving energy minimum $\xrightarrow[\text{MAGIC}]{\text{Algo}}$ IS

② Hessian \rightarrow eigenvalues (RPAC package) MAGIC

Group eigenvalues and compute density of states = $g(\omega)$
interesting for low-temperature physics of glasses.

- jamming (soft modes)
- Gardner transition.

We have the blue S_{conf} in the axis figure
for S_{conf} , we have a method for hard spheres.

IV Getting faster = Monte Carlo algorithm (MC)

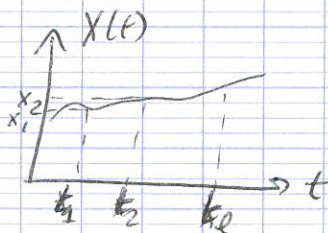
MD cannot get faster.

MC = stochastic Markov process to efficiently sample configuration space.

≠ non deterministic (unlike MD).

have a choice in the probabilities → way to get faster.

Markov



$$w_e(x_1, t_1; \dots, x_e, t_e)$$

Proba for next value:

$$w_{e+1}(x_1, t_1, \dots, x_{e+1}, t_{e+1}) = w_e(x_1, t_1, \dots, x_e, t_e)$$

$$\times \underbrace{P(x_e, t_e | x_{e+1}, t_{e+1})}_{\text{conditional proba}}$$

memory-less process.

In the limit of step going to zero:

Master equation ($\hat{=}$ equivalent of Newton's equation for MC)

$$\left\{ \begin{array}{l} P(x, t) = \text{probability} = \int dx_0 P_{\text{init}}(x_0, t=0) \underbrace{P(x_0, 0 | x, t)}_{\text{time}} \\ x(t) \text{ at } t \end{array} \right.$$

$$\left\{ \begin{array}{l} \text{Transition rate } R(x_0 | x) = \lim_{t \rightarrow 0} \frac{P(x_0, 0 | x(t), t)}{t} \quad x_0 \neq x \end{array} \right.$$

$$\frac{dP(x, t)}{dt} = \int dx' [P(x', t) R(x' | x) - P(x, t) R(x, x')]$$

discrete space $\int dx \rightarrow \sum_c$

• Equilibrium distribution $\frac{dP_S}{dt} = 0$.

• Detailed balance: each term in $\sum_c = 0$

$$\hookrightarrow \frac{R(C'|C)}{R(C|C')} = \frac{P_S(C)}{P_S(C')} = e^{-\beta(H(C') - H(C))}$$

One can prove $P(x,t) \rightarrow P_S(x)$

↑
canonical distribution

• Monte Carlo: transition rates obeying detailed balance
 \hookrightarrow sample config. space $P_S(C)$

• Algorithm for HS:

- Config \mathcal{C}
- pick at random 1 particle
- move from \vec{r} this particle
- if no overlap created ACCEPT MOVE
- get a new configuration.

Because of algorithm, you know that the canonical ensemble is sampled

• Dynamics is lost - unphysical in the way it's constructed.

• if $\vec{r} \rightarrow 0 \Rightarrow$ Brownian dynamics recovered
overdamped limit of Langevin equation.

• finite \vec{r} ? Compute relaxation times in MC approaching glass transition is equivalent to MD
(Strong result). Physics behind is the separation

of timescales (vibrations around minima & long jumps between minima)

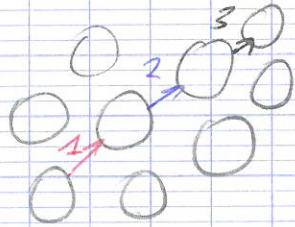
Same T -dependence as MD

• Faster than the physics:

To beat MD, invent more complicated moves.

Werner Krauth,
E. Bernard (PRE
109)

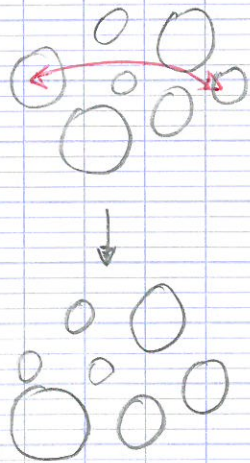
* Display many particles at one move. Each "event chain" | particle at a time until it touches another, that moves until touching the next etc...



Acceleration ~ 40 in dynamics (not even in glassy regime)

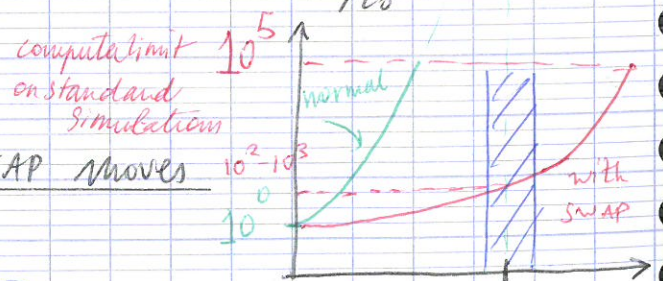
* SWAP Monte Carlo Algorithm

• 2-particle move (works with polydisperse systems)



- Pick 2 particles
- Swap their diameters
- accept or reject.

$\sim 10^{12}$
onset of glassy dyn.



Algo: Mix normal MC + SWAP moves

Acceleration - **BIG**

Good : algo. that closes the gap with experiments

Bad : the algorithm is "stupid" and local
that works very well \rightarrow our picture
of the glass transition was perhaps
much more complicated than in reality.