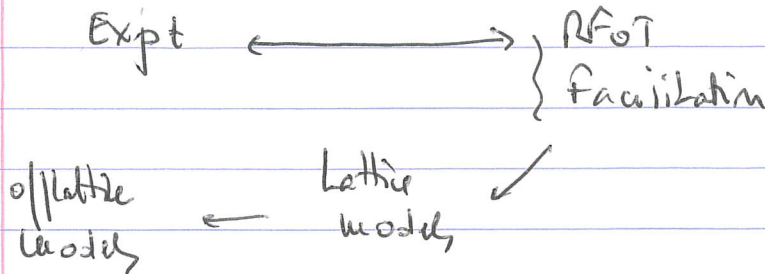


IV) Atomistic glass formers

a) Why doing simulation?

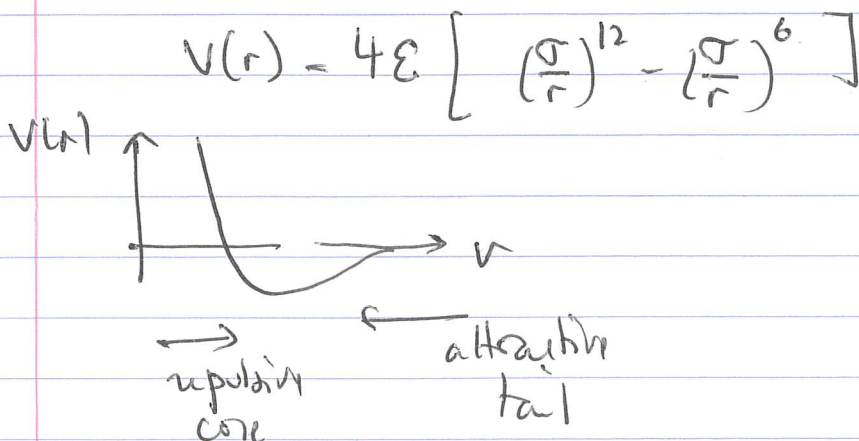


↓
~~Expt~~ Close to expt (realistic) but simpler + spatial resolution.
 | Easy to simulate
 | Not far from lattice models
 | Work with theory - TEST
 Change d towards d → ∞

Simple models: Classical pair interactions for point-like particles

$$H = \sum_{i \neq j} V(|\vec{r}_i - \vec{r}_j|)$$

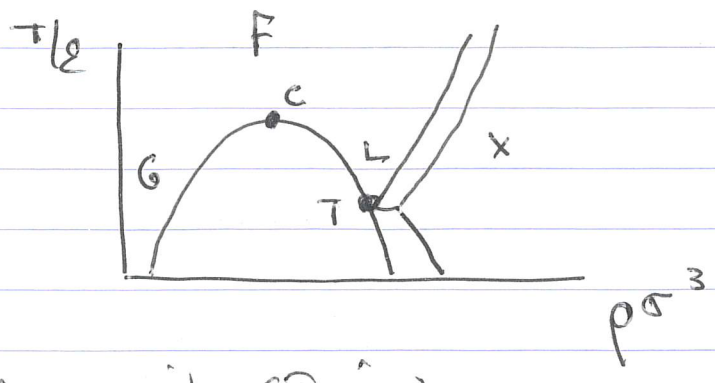
Canonical model for simple liquids = LJ potential



Phase diagram

$$\left(\frac{T}{\epsilon}, \rho \sigma^3 \right)$$

non-dimensional
control parameters

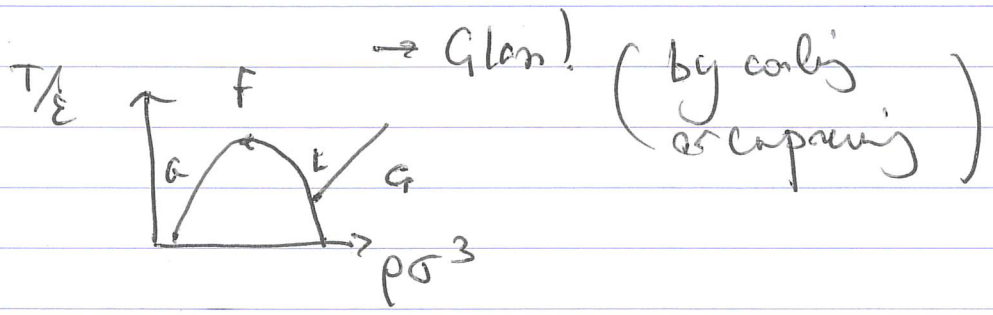


C = critical point (T_c, ρ_c)

T = triple point

NB also (P, T)

For size polydispersity \rightarrow xtal ~~is~~ disappears



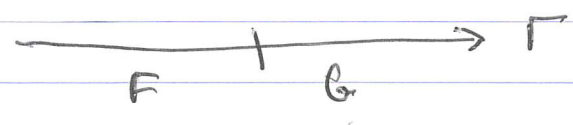
Even simpler: $V(r) = 4\epsilon \left(\frac{\sigma}{r} \right)^{12}$

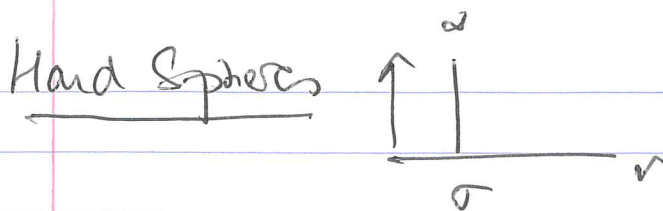
repulsive part of LJ potential = "soft spheres"

T and ρ are no longer independent variables!

A unique parameter $\Gamma = \rho T^{1/4}$

\rightarrow 1 dimensional phase diagram





the value of T no longer relevant

$\rho\sigma^3$ only control parameter

$$\phi = \frac{\pi}{6} \rho\sigma^3 = N \times \frac{4}{3} \pi \left(\frac{\sigma}{2}\right)^3$$

packing fraction.



NB also P or rather

$$z = \frac{P}{\rho k_B T}$$


can be used as
control parameter

many more models

WCA, HS, etc...

In all cases, well chosen polydispersity needed to prevent crystallisation.

- discrete mixtures (A, B); (A, B, C) ...

- continuous polydispersity $P(\sigma)$ 
(inspired by
colloidal physics)

b) Dynamical equations

For atoms: Newton's equations

$$m \frac{d^2 \vec{r}_i}{dt^2} = - \sum_{j \neq i} \frac{\partial V(|\vec{r}_{ij}|)}{\partial \vec{r}_i}$$

for given $\left\{ \begin{array}{l} \vec{r}_i(0) \\ \vec{v}_i(0) \end{array} \right\}_{i=1-N}$

Solving these equations is the core of Molecular Dynamics simulations

pbs to solve

- * discretize correctly
- * efficient for calculations
- * periodic boundary conditions
- * controlling (T, p) = | p is easy
T thermostat

Andersen JCP'84: one of the first serious MD simulations

N = 500 LJ particles
| 100 time step / minute.

35 years later $\sim 10^3 \cdot 10^6$ times faster.

CPU limit

$$10^3 \text{ steps / week} \rightarrow 10^7 \text{ t}_{LJ} \rightarrow T_{\alpha} \sim 10^5 \text{ t}_{LJ \text{ max}}$$

- * equilibration (slow)
- * crystallization

Other dynamics • Langevin equation (colloids)

$$m \frac{d^2 \vec{r}_i}{dt^2} + \gamma \frac{d \vec{r}_i}{dt} = - \sum_{j \neq i} \frac{\partial V}{\partial \vec{r}_{ij}} + \vec{g}_i$$

dissipation.
noise

$$\langle g_i^\alpha(t) g_j^\beta(t') \rangle = 2 T \gamma \delta_{ij} \delta_{\alpha\beta} \delta(t-t') \quad (FDT)$$

• Overdamped limit (big colloids)

$$\gamma \frac{d \vec{r}_i}{dt} = - \sum_{j \neq i} \frac{\partial V}{\partial \vec{r}_{ij}} + \vec{g}_i$$

• Monte Carlo dynamics: Markov process to sample configuration space with Boltzmann distribution.

Discrete jumps $C \rightarrow C'$ [eg move 1 particle]
+ rates satisfying detailed balance

$$\Rightarrow \text{at long times } P(C, t) \rightarrow P^{\text{ss}}(C) = \frac{e^{-\beta H(C)}}{Z}$$

A strong physical result

$$\tau_{\alpha}^{\text{MD}}(T) \propto \tau_{\alpha}^{\text{LD}} \propto \tau_{\alpha}^{\text{3D}} \propto \tau_{\alpha}^{\text{MC}}$$

All dynamics lead to similar physical results

Suggesting that at long times details of microscopic dynamics are not relevant -

c) Swap Monte Carlo algorithm

MC simulations allow to make unphysical moves $c \rightarrow c'$ = provided detailed balance is obeyed \Rightarrow equilibrium.

many attempts do not work; event chain cluster algorithms drifting ...

Swap MC works

In addition to whatever dynamics (MD, MC, ...)

Add swap moves

- pick 2 distinct particles at random
- try to swap
- accept/reject det. balance

Only works for discrete / continuous mixtures ... ie nearly all models!

Intuition for continuous size distributions

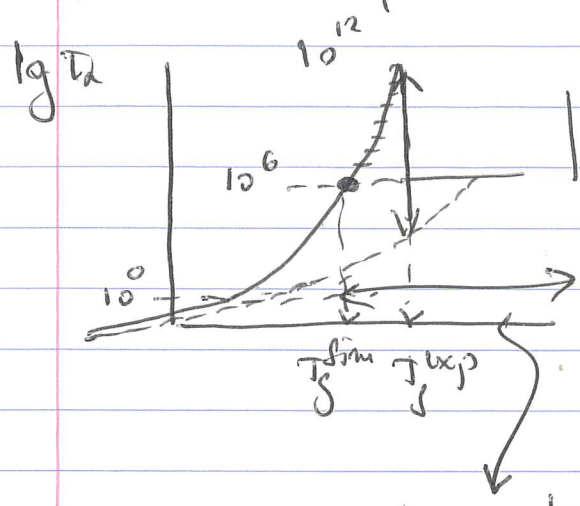
Swap = diameter change

From (x_i, g_i, z_i) to $(x_i, g_i, z_i, \sigma_i)$

MC
Swap MC

= 1 additional degree of freedom

For well chosen parameters we get large speedup:



Speedup at $T_g \sim \times 10^{10}$
 Some models: below T_g !
 → ultrastable
 glasses of Ediger

A new territory to explore glass physics

How to use it?

① Equilibrium study of liquids down to $T < T_g$

② Prepare glasses with very different preparation protocols
 → new control parameter
 → more realistic glasses

③ Equilibrate very low → launch MD simulations

$$10^9 \text{ steps} = 10^7 \tau_{LS} \approx \underline{\underline{1 \mu s}}$$

for arbitrary τ_α

d) Configurational entropy

Swamp MC allows measurements down to very low T (even better than experiments).

How to measure S_{conf} ?

① Removing vibrations

$$S_{conf} = S_{liq} - S_{vib}$$

• S_{liq} : obtained by thermodynamic integration from $T = \infty$ (ideal gas)

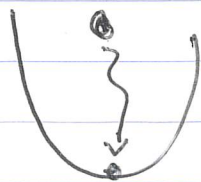
$$F = E - TS \rightarrow S = \frac{1}{T} [E - F]$$

| |
easy ?

$$F \Rightarrow P = - \left(\frac{\partial F}{\partial v} \right)_T$$

$$\Delta F = \int_1^2 dv (-P)$$

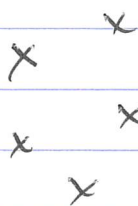
• S_{vib} ? Harmonic Approximation



- Find T_{co} (Tuberent Structure)
- diagonalise Hessian matrix \rightarrow normal modes
- Expand vibrations along eigenmodes

$$S_{vib} = \sum_i \left[1 - \frac{1}{2} \ln \left[\left(\frac{\beta \hbar \omega_i}{m} \right)^2 \right] \right]$$

② Frenkel-Ladd method



Study constrained system

$$H_\alpha = H(r^N) + \alpha \sum_{i=1}^N |\vec{r}_i - \vec{r}_i^{\text{ref}}|^2$$

instantaneous config
 $= \vec{r}_i^{\text{ref}}$

• α large: Einstein solid
 $\rightarrow S_{\text{Einstein}}$ known

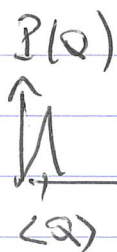
• Integration from $\alpha = \infty$ to
 $\alpha \rightarrow 0$

gives vibrational component
 $S_{\text{vib}}^{\text{FL}}(T)$

$$\underline{S_C} = \underline{S_{\text{rig}}} - S_{\text{vib}}^{\text{FL}} \quad (\text{mode by mode!})$$

③ Franz Parisi potential (= free energy $V(Q)$)

a normal simulation would probe $\langle Q \rangle \sim \exp^{-f_{\text{NV}}}$
 fluctuations around $\langle Q \rangle_0$



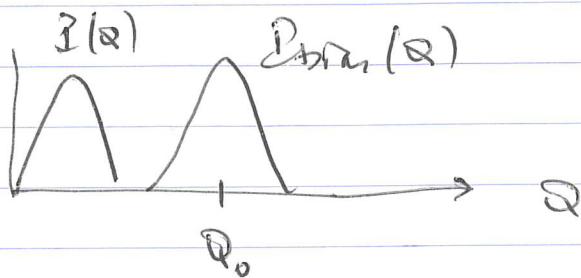
(you don't see ice in water at $0^\circ\text{C} + \epsilon$!)

first order phase transitions = explore unlikely
 fluctuations using
 biased simulations

$$H_{\text{bias}} = H_0(r^N) + \frac{k}{2} N [Q - Q_0]^2$$

with (k, Q_0) chosen; $Q_0 \gg \langle Q \rangle$

$$P_{bias}(Q) \propto P(Q) \times e^{-\frac{kN}{2} (Q-Q_0)^2}$$



$$\Rightarrow P(Q) \propto P_{bias} \times e^{\frac{kN}{2} (Q-Q_0)^2}$$

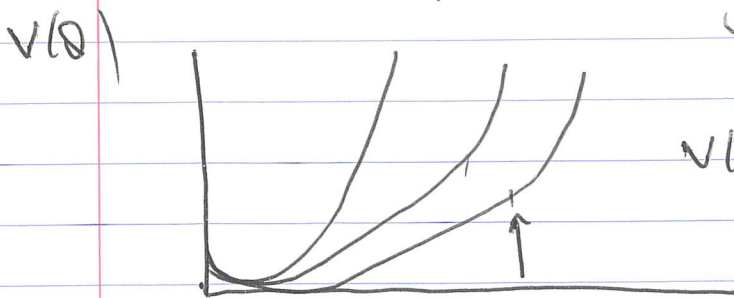
→ Do this for multiple (k, Q_0)

→ news but cube $P(Q) \rightarrow \overline{\log P(Q)}$

this is called utils sampling

$$V(Q) = -\frac{kT}{N} \overline{\log P(Q)}$$

(2013-2021) $N=32$ high T
 \downarrow
 $N=2000$ $T < T_g$



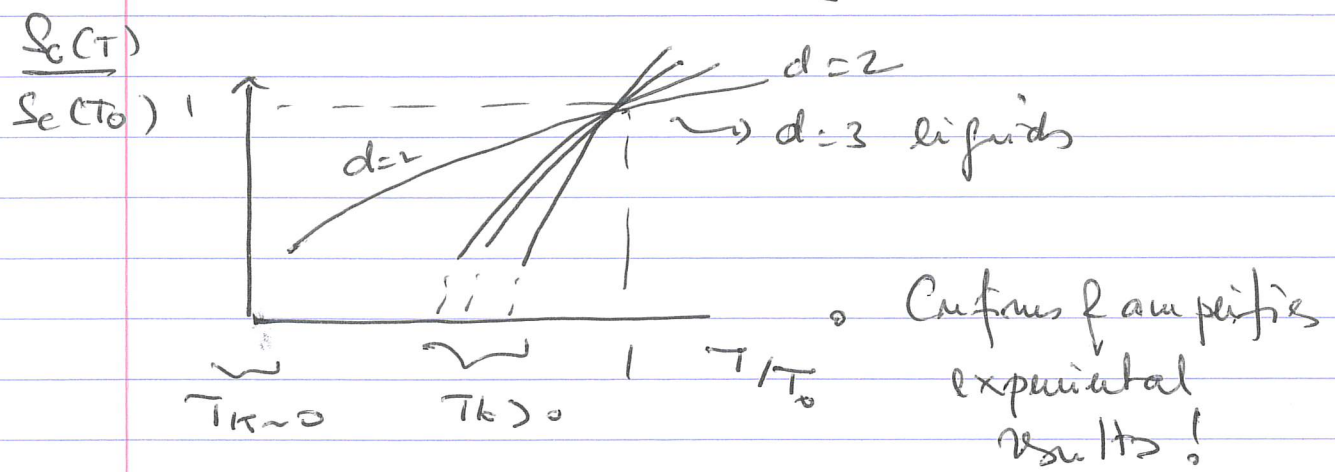
$$V(Q_h) - V(Q_l) = T \Delta$$

Results All 3 methods give consistent results for $\xi_{sc}(T)$

④ In addition: PT's length scale using cavity construction (again 2007-2020)

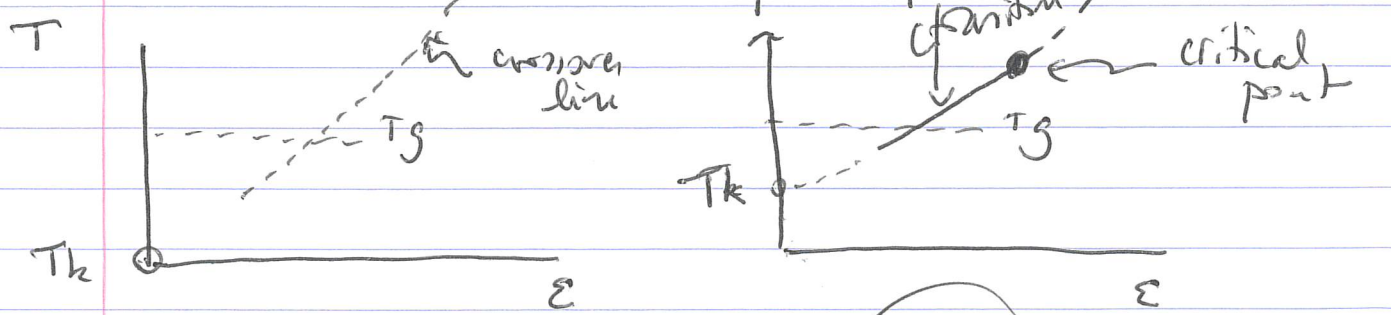
$$\xi_{PT's} \sim \frac{1}{\xi_c} \text{ seems to work}$$

decrease of ξ_c fits us to forming static correlation length scale -



Suggest $T_k > 0$ $d=3$
 $T_k = 0$ $d=2$

2) Phase diagram with ϵ -coupling



$d=2$

$d=3$

|| All measurements self consistent + agree well with RFT predictions