Colloidal Arrested States of Matter

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Lectures 1+2

0) Introduction:

*Glasses* and *Gels*; *Tools* to investigate theoretically and numerically colloidal arrested states:

- the ideal Mode Coupling Theory of the glass transition
- numerical simulations (Molecular or Brownian Dynamics)

1) Hard-sphere Glasses:
*monodisperse* and *polydisperse* hard spheres

2) Hard spheres plus short-range attraction:
*attractive glasses*, “melting by cooling”, *glass-glass transition*
Arrested states: generic features

We are talking about metastable states (out-of-equilibrium), often interfering with underlying equilibrium phases.

The transition is not in terms of thermodynamics (i.e. all thermodynamic functions are continuous crossing the arrest transition) but it is a kinetic transition: the system becomes so slow that it does not relax to equilibrium anymore.

Importance of timescales: need for an operational definition of arrest, e.g. when the relaxation time $\tau$ exceeds 100s (or viscosity exceeds $10^{14}$ poise)
**SIMILARITIES:**
Both are **disordered solids:**
- they do not flow, large viscosity, 
- finite elastic modulus

**Differences:**
Gels are **dilute;** Glasses are **dense.**
Gels need inter-particle attraction; glasses do not.

**Very large timescales.**
No long-time diffusion….*

**Bond-driven** versus **Cage-driven** arrest
(*at short scales gels are still mobile:
  e.g. vibrations of gel chains)

**Long-range disorder.**
Structure close to that of a liquid, but…**

**Aging** (history-dependence)

**large differences **for small
**wave-vectors** (gels are **compressible**)
GLASSES

“Easier” to predict/interpret**: thanks to the *Mode Coupling Theory* for the glass transition of Götze and coworkers

*Physical picture*: the nearest-neighbour *cage effect*

*Prototype glass-former*: colloidal **HARD SPHERES**

(** but still very challenging from a conceptual point of view)**
The simplest colloids: hard spheres

- steric stabilization of vdw attraction
- screening of electrostatic interactions with salt

Thermodynamic phase diagram

- Hard spheres show a fluid–solid transition due to entropic effects
Sterically stabilized PMMA particles: Experimental realization of hard spheres

confirmation of fluid-solid phase transition

But at large $\phi \sim 0.58$ amorphous solids are observed!

Hard sphere glasses

How can we explain the HS glass transition?
Physical picture: the cage effect

at high enough packing fraction

\[ \langle r^2(t) \rangle = \frac{1}{N \alpha} \sum_{i=1}^{N \alpha} \langle |r_i(t) - r_i(0)|^2 \rangle \]

diffusion \( \sim 6Dt \)

mean-squared displacement

transient plateau

cage effect

microscopic regime

trapping by nearest-neighbors due to large density defining a cage or localization length
Two-step relaxation of density correlators

Upon lowering $T$

1) microscopic relaxation down to an intermediate plateau

2) slower and slower second relaxation ($\tau_\alpha$)

$F(q,t) = \langle \rho_q(0) \rho^*_{q(t)} \rangle / N$

$T_g$: operative definition $\tau_\alpha \sim 100$ s
Mode Coupling Theory (MCT)

It is (up-to-date) the only first-principle theory of the glass transition

i.e. starting from the microscopic interactions --- interaction potential $V(r)$ ---
it predicts whether and how a system becomes non-ergodic:

$\tau_\alpha \rightarrow \infty$
long-time plateau $f_q > 0$

(non-ergodicity parameter)
How does it work?

It requires as *only inputs* thermodynamic and static properties in particular

the number density $\rho$

and

the static structure factor $S(q)$

e.g. from $V(r)$ through liquid state theories (or simulations or even experiments)
MCT equations of motion
for the density autocorrelation functions

\[ \ddot{\phi}_q(t) + \Omega^2_q \phi_q(t) + \int_0^t M_q(t - t') \dot{\phi}_q(t') dt' = 0 \]

\( \phi_q \) either self or collective:

\[ \rho_q(t) = \sum_{i=1}^N e^{i\mathbf{q} \cdot \mathbf{r}_i(t)} \quad \rho^s_q(t) = e^{i\mathbf{q} \cdot \mathbf{r}_i(t)} \]

\( \Omega \) characteristic frequency

\( M \) memory function

MCT approximations lead to:

\[ M_q(t) = \sum_k V(k, q-k) S(q) S(q-k) \phi_k(t) \phi_{q-k}(t) \]

- bilinear in the correlator
- coupling of all modes
Solving the long-time limit of MCT equations

$$\frac{f_q}{1-f_q} = M_q(\infty) = \sum_k V(k, q-k) S(q) S(q-k) f_k f_{q-k}$$

Hence $f_q=0$ (ergodic state) is always a solution.

For certain values of the thermodynamics parameters there appears bifurcations of the solutions, so that non-ergodic solutions $f_q>0$ appear. The transition is DISCONTINUOUS.

Solving the long-time MCT eqns in the control parameter space provides an estimate of the liquid-glass transition line.
Solving the Full MCT equations

\[ \partial_t^2 \Phi_q(t) + \Omega_q^2 \Phi_q(t) + \int_0^t [M^{reg}_q(t-t') + \Omega_q^2 m_q(t-t')] \partial_{t'} \Phi_q(t') \, dt' = 0 \]

initial conditions \( \Phi_q(0) = 1, \partial_t \Phi_q(0) = 0 \)

The full relaxation of the system can be obtained \textit{except for the microscopic dynamics} (microscopic timescale to be determined as a fit parameter)

\[ M^{reg}_q(t) = \nu_q \delta(t-0), \nu_q > 0 \quad \quad m_q(t) = F_q(\Phi(t)) \]

For colloidal suspensions, the equations are modified as:

\[ \tau_q \partial_t \Phi_q(t) + \Phi_q(t) + \int_0^t m_q(t-t') \partial_{t'} \Phi_q(t') \, dt' = 0 \]

initial conditions \( \Phi_q(0) = 1 \quad \quad \tau_q = S_q/(D_0 q^2) \)

\( \Phi_q(t) = 1 - (t/\tau_q) + O(t^2) \)
Remark: Predictive power of MCT

From thermodynamics only \( \rightarrow \) Prediction of full dynamic behavior

It implies a link between structure and dynamics! Although structure is *boring*, dynamics is NOT!
Summary of basic MCT predictions

• Power law forms of the correlators close to the plateau

• Power law scaling of relaxation time, diffusion coefficient, viscosity, etc.

• Relation between different power law exponents

• Time-temperature scaling
Power law forms of the correlators close to the plateau

approaching the plateau: $\phi \sim t^{-a}$

leaving the plateau: $\phi \sim -t^b$

N. B. $a, b$ not universal but independent of q-vector
Power law scaling of relaxation time, diffusion coefficient, viscosity, etc.

\[ \tau_x(T) = C_x(T - T_c)^{-\gamma} \]

\[ D^{-1}(T) \propto \tau_x(T) = C_x(T - T_c)^{-\gamma} \]

\[ \eta(T) = C_x(T - T_c)^{-\gamma} \]

N. B. \( \gamma \) not universal but the same for all quantities
Relation between different power law exponents

\[
\frac{\Gamma(1-a)^2}{\Gamma(1-2a)} = \frac{\Gamma(1+b)^2}{\Gamma(1+2b)} = \lambda
\]

\[
\gamma = \frac{1}{2a} + \frac{1}{2b}
\]

N. B. \( \lambda \) “the exponent parameter” has a microscopic expression and determines all the others.
Time-temperature scaling

\[ \Phi(t, T) = \hat{\Phi}(t/\tau(T)) \]

MCT does not provide an analytic form of the final form of the \(\alpha\)-relaxation, although this can be phenomenologically fitted with a stretched exponential function (Kohlrausch-Williams-Watts - KWW - law)

\[ \Phi(t) = A \exp \left( -\left( t/\tau \right)^\beta \right) \]

but it can be shown that for large q-vectors \(\beta \rightarrow b\)
Rheological properties according to MCT

MCT provides also an expression for the stress correlation function and through it of the viscosity and elastic moduli.

Zero-shear viscosity:

\[ \eta = \frac{1}{3V} \int_0^\infty dt \sum_{\alpha<\beta} \langle \sigma^{\alpha\beta}(t)\sigma^{\alpha\beta}(0) \rangle, \]

MCT stress correlation function

\[ C_{\sigma\sigma}(t) = \frac{k_B T}{60\pi^2} \int_0^\infty dq q^4 \left[ \frac{d \ln S(q)}{dq} \Phi_q(t) \right]^2 \]

at long times

\[ C_{\sigma\sigma}(\infty) = \frac{k_B T}{60\pi^2} \int_0^\infty dq q^4 \left[ \frac{d \ln S(q)}{dq} f_q^c \right]^2 \]

Elastic moduli

\[ G(\omega) = i\omega \tilde{C}(\omega) \]
Hard sphere glass transition: MCT vs experiments

MCT transition

\( \phi_c \sim 0.52 \)

Exp transition

\( \phi_g \sim 0.58 \)

*Once the location of the glass transition is rescaled, MCT accurately describes experimental data.*

W. van Megen &
S.M. Underwood

*Phys. Rev. Lett.*

70, 2766 (1993)
MSD of HS close to the glass transition

EXP: W. van Megen et al. PRE 58, 6073 (1998) (symbols+lines)
MCT: M. Sperl, PRE 71 060401 (2005) (red dashed lines)

FIG. 3. (Color online.) Fit of the mean-squared-displacement data from [11] (full circles and curves) by the solutions of MCT (dashed)
Throughout the years, the existence of a true HS glass transition has been questioned by various groups.

The question is:

**Do HS really form a glass below Random Close Packing ($\phi \sim 0.64$)?**

Main evidence against it:

Crystallization in experiments in microgravity (Zhu et al Nature 1997)

More recently, a new experimental work has put forward the same hypothesis

Brambilla et al. PRL 102, 085703 (2009)

PMMA 260 nm (grafted polymer)
10% polidispersity (no cryst over several months)
Two main problems:

**Proper definition of Packing Fraction**
see Poon, Weeks and Royall Soft Matter 8, 21 (2012)

**Polydispersity**: often not properly taken into account

Brannilla et al.

\[ \tau_\alpha(\varphi) = \tau_\infty \exp \left[ \frac{A}{(\varphi_0 - \varphi)^\delta} \right] \]

\[ \delta = 2.0 \pm 0.2 \]

(Vogel-Fulcher law \( \delta = 1.0 \))

\[ \varphi_0 \approx 0.637 \pm 0.002 \]
Back to experiments: interplay between crystals and glasses and the role of intrinsic polydispersity $S$

$S \sim 5\%$

Phase diagram of polydisperse hard spheres


• Packing fraction is usually defined by the fluid-crystal boundary
Phase diagram of polydisperse hard spheres

Sollich & Wilding  PRL 104, 118302 (2010)
from MC simulations
polydispersity suppresses crystal nucleation

\[ \Delta G^\times = \left( \frac{16\pi}{3} \gamma^3 \right) / (\rho |\Delta \mu|)^2 \]

Auer & Frenkel, Nature 413 711 (2001)

for small \( s \), the nucleation free energy becomes very small
Phase Diagram of slightly polydisperse HS

- Fluid
- Crystal

Fluid-crystal coexistence (single-phase crystal)

Fasolo & Sollich (2003)

High nucleation barrier

Slow dynamics

Dynamics is independent of polydispersity for all non-crystallizing state points.
Equilibrium states for $\phi \leq 0.58$ (no waiting time dependence)
Aging dynamics for $\phi > 0.58$

$\phi=0.60$

- $s=0.06; t_w=10^2$
- $s=0.06; t_w=1.2 \times 10^3$
- $s=0.06; t_w=2.5 \times 10^3$
- $s=0.06; t_w=10^4$
- $s=0.06; t_w=10^5$

Graph showing $\langle \tau \rangle / \sigma^2$ as a function of $t$.
Disordered state --- ideal glass

$\phi = 0.60$
Power-law dependence of self-diffusion coefficient $D$

\[ \gamma \sim 2.2; \phi_g \sim 0.585 \]
Phase Diagram and Isodiffusivity lines

- Fluid
- Crystal
- MCT binary mixture
- $D = 5 \times 10^{-3}$
- $D = 10^{-3}$
- $D = 5 \times 10^{-4}$
- $D = 5 \times 10^{-5}$
- Ideal glass line
- Fluid-solid coexistence

Parameters:
- $S$ vs. $\phi$
- Extrapolated ideal glass transition
...but aging dynamics is also invariant on polydispersity (before crystallization)

For $\phi > 0.58$ crystallization occurs from a glass!
There is no conceptual difference between monodisperse and polydisperse spheres.

Complex interplay between glass and crystal

Even for simple HS glasses, a lot of open questions!

Next we consider the effect of additional attraction (complementing the hard-core) e.g. **DEPLETION interactions** (Likos lectures)
Tuning interactions: **Depletion**

**Hard sphere colloids plus non-adsorbing polymers**

![Diagram](image)

**polymer available volume**

\[ \Omega(1) = \Omega(\text{TOT}) - 2 \cdot 4\pi(\sigma + \tau/2)^3/3 \]

\[ \Omega(2) = \Omega(1) + \Omega_{\text{overlap}} > \Omega(1) \]

**higher entropy configuration**

**Effective attraction**

Asakura and Oosawa (1957)
Asakura-Oosawa (AO) potential

- polymer size controls attraction range
- polymer concentration controls attraction strength
Role of the attraction on the phase diagram: importance of attraction range

Hard-Sphere

Large Range

Short Range

e.g Lennard-Jones (simple liquids)

e.g colloids, proteins

Noro-Frenkel law of extended corresponding states for short-ranged potentials: independence of thermodynamics from different potential shape and attractive range

\[ \Delta \lesssim 0.1 \sigma \]

How does attraction affects the dynamics?

1. What happens to glass transition?

2. What about gels at low densities?

(Lecture 4)
mean square displacement
(hard-sphere glass)

Particles rattle within nearest-neighbour cage
Adding a short-range attraction

Hard Spheres Potential

Square-Well short range attractive Potential

\[ T \gg \epsilon \]

\[ T \ll \epsilon \]
Two glasses!

Mean squared displacement

\begin{align*}
(0.1 \sigma)^2 & \\
\Delta^2 & \\
\end{align*}

Log(t)

How does the system change from one (glass) to the other one? Let’s ask MCT.

MCT predictions for HS plus short-ranged attraction

square-well potential

$V(r)$

HARD SPHERE LIMIT

narrow width

$\Delta=0.03\sigma$

hard-sphere glass

glass-glass transition

reentrant fluid region

melting by cooling

attractive glass

MCT: the role of the attraction range

square-well potential

HARD SPHERE LIMIT

Increasing the range of the square-well potential leads to a reentrant fluid region and a hard-sphere glass transition. Attractive glass is observed at lower densities.

MCT Predictions:
Wavevector dependence of the non ergodicity parameter (plateau) along the glass line

Fabbian et al PRE R1347 (1999)
Bergenholtz and Fuchs, PRE 59 5708 (1999)
Confirmation by Simulations: Isodiffusivity curves

How can we distinguish the two glasses:
Decay of correlation along an isodiffusivity line

EZ et al
Phys. Rev. E
66, 041402 2002
Non-ergodicity factors
(plateau height of density correlators)

Also rheology: attractive glass is stiffer

Experimental Verifications
Temperature

Glass samples

Fluid samples

Fluid-glass line from experiments

Multiple Glassy States in a Simple Model System

Pham et al Science 296, 104 (2002)
Reentrance and diffusivity maximum

FIG. 6: Collective dynamic structure factors at $qR = 1.50$ from samples A–H spanning the re-entrant region. The time axis is scaled to dimensionless length scale $(qR)^2$ and relative polymer solution viscosity $\eta_r$. The inset shows the same plots on an expanded vertical axis.

Pham et al Science 296, 104 (2002)
T. Eckert and E. Bartsch

Colloidal-Polymer Mixture with Re-entrant Glass Transition in a Depletion Interactions


FIG. 1. Comparison of the density autocorrelation functions \( f(q, \tau) \) of a hard sphere colloidal suspension (see text) before (thick solid lines) and after (thin solid lines) the addition of linear polymer chains (size ratio \( \delta = R_{g, \text{polymer}} / \langle R_{\text{colloid}} \rangle = 0.054 \)). The colloid volume fractions of each set of \( f(q, \tau) \) increase from left to right as indicated in the figure. The dynamics is probed at a scattering vector corresponding to the peak maximum of \( S(q) \) of the pure colloid suspension at its glass-transition volume fraction \( \phi_g \approx 0.595 \) [22].
FIG. 3. Effect of increasing the free polymer volume fraction $\phi_{\text{polymer}}$ on the dynamics of a colloid suspension in a state close to random close packing ($\phi_{\text{colloid}} = 0.67$) in the phenomenon of re-entrant melting. (a) Density autocorrelation functions $f(q, \tau)$ (probed at the same scattering $q$ as in Fig. 1). The polymer reservoir volume fractions indicated by the numbers at the curves. The thick lines correspond to nonergodic (glassy) samples. (b) Structural relaxations times $\tau_\alpha$ versus polymer volume fraction $\phi_{\text{polymer}}$. The vertical lines schematically indicate the transition lines to the respective nonergodic states.
Higher-order singularities
(i.e. where multiple MCT solutions coalesce)

and

anomalous dynamics
Back to MCT: two step relaxation

approaching the plateau:

\[ \phi(t) \approx f^c + \left( \frac{t_0}{t} \right)^a \]

leaving the plateau:

\[ \phi(t) \approx f^c - \left( \frac{t}{t_0} \right)^b \]

Von-Schweidler law
Exponents \( a, b \) are calculated from the asymptotic expansion of MCT solutions: two families of solutions

- negative exponent \( x = -b \)
- positive exponent \( x = a \)

respectively for approaching the transition from above and from below

\[
\frac{\Gamma(1-a)^2}{\Gamma(1-2a)} = \frac{\Gamma(1+b)^2}{\Gamma(1+2b)} = \lambda
\]

W. Gotze
*Complex Dynamics of Glass-Forming Liquids: A Mode-Coupling Theory*
Oxford Univ. Press (2009)
Higher-order singularities

They are defined by the condition

\[ \lambda = 1 \]

close to the singularity then

*a and b* becomes close to zero…

power-laws become logarithms…!

\[
\phi_q(t) = f_q^c + h_q \left[ -B \ln(t/\tau) \right]
\]
Tracing the $A_3$ & $A_4$ points: Theory and Simulation

\[ \phi_{MD} = 1.897\phi_{PY} - 0.3922 \]
\[ T_{MD} = 0.5882T_{PY} - 0.225 \]

MCT overestimates ideal attractive glass $T$ by a factor of 2

Approaching the A4 point

\[ \Phi_q(t) = f_q - h_q \left[ B^{(1)} \ln(t/\tau) + B^{(2)}_q \ln^2(t/\tau) \right]. \]

Logarithmic decay is enhanced at a characteristic \( q^* \).
MSD becomes sub-diffusive
Log-decay also seen experimentally
The MCT predictions of multiple glasses and reentrant melting (anticipating experiments) for HS with short-ranged attraction was one of the greatest success of the theory (2001-2002).

After that, it has been applied to several other soft matter systems with success (Lectures 3-5).

There is one aspect that the theory cannot fully capture: namely, the *long-time stability of attractive glasses* (i.e. importance of bond-breaking processes)
Long-time behavior of attaractive glasses

FIG. 6: Collective dynamic structure factors at $qR = 1.50$ from samples A–H spanning the re-entrant region. The time axis is scaled to dimensionless length scale $(qR)^2$ and relative polymer solution viscosity $\eta_r$. The inset shows the same plots on an expanded vertical axis.

Pham et al Science 296, 104 (2002)
FIG. 2. Top panel: density correlators predicted by MCT, $\phi_q^{MCT}(t)$, for a one-component SW system for different temperatures, crossing the glass-glass transition at $\phi \approx 0.54$, for $q \sigma = 14.5$. Such a $q$ value has been chosen to reproduce comparable differences in the nonergodicity parameters. The temperatures have been chosen such that $T/T_c$ ($T_c$ is the MCT transition temperature) is close to the simulation one for the reported $T$'s. Bottom panel: same curves from the simulation for $q \sigma_B \approx 25$. Temperatures from top to bottom: 0.1, 0.2, 0.35, 0.4, 0.5, 0.65, 0.9, 1.5. $t_w = 3754$. 

No sharp glass-glass transition 

Square-Well MCT Simulations

No sharp glass-glass transition

"attractive glasses"

attractive glass turning to repulsive

EZ & W. Poon PNAS 2009
Summary