Fluctuations in the Relaxation of Glasses

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Outline

1. Glass Transitions, aging, and dynamical heterogeneity
   - Glass transitions and aging
   - Dynamical heterogeneity
   - Probing glasses

2. Heterogeneous time evolution in spin glasses
   - Heterogeneous time evolution

3. Fluctuations in structural glasses
   - Scaling of probability distributions
   - Growing spatial correlations
   - Time fluctuations in structural glasses
   - Directly observing time fluctuations
   - Equilibrium vs out-of-equilibrium fluctuations
At the glass transition, the system “falls out” of equilibrium.

Viscosities and relaxation times increase dramatically as a material cools towards $T_g$. 

M.D. Ediger (2000)
Material in a glassy state

The two experiments give different results ≡ AGING !!
Aging in glassy systems

Spin glass (Svedlindh et al. 1987)

DLS colloidal gel (Cipelletti et al. 2000)

PVC (Struik 1978)
Dynamical heterogeneity: non-exponential relaxation

\[ C(t) = C_0 \exp\left(-t/\tau\right)^\beta = \int_0^\infty g(\tau) \exp\left(-t/\tau\right) d\tau = V^{-1} \int d^d r \exp\left(-t/\tau_\ell\right) \]

\(0 < \beta < 1\)

\((\text{Richert 2002})\)

\((\text{Ediger 2000})\)
Dynamical heterogeneity: viscosity - diffusion decoupling

\[
\frac{D\eta}{T} = \text{constant}
\]

(Angell et al. 2000)

(b) \(D_T \sim D_{\text{fast}}\)

(Ediger 2000)
Dynamical heterogeneity: particle tracking

Colloid: confocal microscopy (Courtland and Weeks 2003)

Figure 4. Locations of the 10% most mobile particles at three different ages $t_w$. For each picture, mobility was determined by calculating displacements $\Delta r$ over an interval $[t_w, t_w + \Delta T]$, with $\Delta T = 10$ min. Left: $t_w = 10$ min, and $\Delta r > 0.43 \mu m$ for the most mobile particles. Middle: $t_w = 55$ min, $\Delta r > 0.34 \mu m$. Right: $t_w = 95$ min, $\Delta r > 0.33 \mu m$. The data are the same as shown in previous figures, and the choices of $t_w$ correspond to local maxima of $\gamma$ in figure 2(a). The particles are drawn to scale (2.36 $\mu m$ diameter) and the box shown is the entire viewing volume (within a much larger sample chamber).
Probing freezing

- Glass $\leftrightarrow$ "random solid".
- Solid $\leftrightarrow$ "frozen", no/slow change in time.
- Two-time correlation $C(t, t_w)$:

$$C(t, t_w) \approx \begin{cases} 1 & : \text{unchanged between } t_w \text{ and } t \\ 0 & : \text{correlation lost between } t_w \text{ and } t \end{cases}$$

- Spin glass: $S_i = \pm 1 \rightarrow C(t, t_w) \equiv \frac{1}{N} \sum_i S_i(t)S_i(t_w)$.
- Structural glass:
  - $\vec{r}_i \rightarrow C(t, t_w) \equiv \frac{1}{N} \sum_i \cos(\vec{q} \cdot [\vec{r}_i(t) - \vec{r}_i(t_w)])$.

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Divide system in regions.

Compute $C_r(t, t_w)$ in each region.

Create a histogram of the results.
Probing fluctuations: spatial correlations

- Fluctuation respect to average:
  \[ \delta C_r = C_r - \langle C_r \rangle \]

- Correlation length \( \xi(t, t_w) \).
Can we understand dynamical heterogeneities?

A possible explanation: the time variables are fluctuating in space.
**Fluctuating times in spin glasses?**

- Continuous symmetry in Mean Field Theory (Sompolinsky; Dotsenko; Cugliandolo & Kurchan, 1981-1994).
  
  If “fast” terms neglected, $C(t, t_w)$ and $\tilde{C}(t, t_w) = C(h(t), h(t_w))$ are equally good solutions for almost any change of variables $t \to h(t)$. Not understood at the time.

- Long-time fully fluctuating dynamical theory invariant under $t \to h(t) \Rightarrow$ broken continuous symmetry.
  
  (Chamon, Kennett, HC and Cugliandolo; PRL 2002)
  
  (HC, PRB 2008) (Mavimbela and HC, JSTAT 2011)

- Broken continuous symmetries $\Rightarrow$ fluctuation modes (“Goldstone”).
  
  (HC, Chamon, Cugliandolo and Kennett, PRL 2002;
  HC, Chamon, Cugliandolo, Iguain and Kennett PRB 2003;
  Chamon, Charbonneau, Cugliandolo, Reichman, Sellitto, JCP 2004)
Broken continuous symmetry $\Rightarrow$ fluctuation modes

**Equilibrium ferromagnet**

"ground state" $\Rightarrow$ high probability

$\delta F$ small $\Rightarrow$ high probability

(direction of magnetization varies smoothly in space)

$$\vec{M}(\vec{r}) = R_\theta(\vec{r}) \vec{M}_0$$

small $\delta \mathcal{F} \Rightarrow$ high probability

$\delta S$ small $\Rightarrow$ high probability

**Dynamics of spin glass**

"ground state" $\Rightarrow$ high probability

$\delta S = 0$

"another ground state" $\Rightarrow$ high probability

(time coordinate varies smoothly in space)

$$C_\vec{r}(t, t') = C(\phi_{\vec{r}}(t) - \phi_{\vec{r}}(t'))$$

small $\delta S \Rightarrow$ high probability

(HC, Chamon, Cugliandolo, Kennett; PRL 2002)

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Fluctuations in the Relaxation of Glasses
A possible physical interpretation

\[ C(t, t') = V^{-1} \int d^d r \exp\left(-\frac{(t - t')}{\tau_r}\right) \]

But, regions change: slow ↔ fast

\[ C(t, t') = V^{-1} \int d^d r \exp\left(- \int_{t'}^t dt'' / \tau_r(t'')\right) \]

More general: \[ C(t, t') = V^{-1} \int d^d r \ C\left(\int_{t'}^t dt'' / \tau_r(t'')\right) \]

We have \( C_r(t, t') = C(\phi_r(t) - \phi_r(t')) \), with \( \phi_r(t) \equiv \int_{t'}^t dt'' / \tau_r(t'') \).

Recovered “time fluctuation” picture.
1. Goldstone modes at $t \to \infty \Rightarrow$
   Correlation length $\xi$ grows at long times.

2. Symmetry under $t \to h(t) +$ simplifying assumptions $\Rightarrow$
   In aging systems, $\rho(C_r)$ independent of $t_w$ for constant
   $C = C(t, t_w)$.

3. If we measure local quantities that probe the relaxation of the
   system, different regions will be at different points of a unique
   trajectory.

(HC, Chamon, Cugliandolo, Kennett, PRL 2002;
HC, Chamon, Cugliandolo, Iguain and Kennett PRB 2003)
Glass Transitions, aging, and dynamical heterogeneity

Heterogeneous time evolution in spin glasses
Fluctuations in structural glasses
Summary

Tests in spin glass simulations

Monte Carlo 3D Edwards-Anderson spin glass, $T = 0.72 T_g$.

(HC, Chamon, Cugliandolo, Kennett, PRL 2002; HC, Chamon, Cugliandolo, Iguain and Kennett PRB 2003)

Growth of correlation length $\xi(t, t_w)$

$\rho(C_r)$ collapses with $C(t/t_w)$

Heterogeneous time evolution
What about structural glasses?

- Proof of symmetry applies only to spin glass models.
- However, spin glasses and structural glasses have a lot in common: slow dynamics, aging, nonexponential relaxation, dynamical heterogeneities, etc.
- Could the same explanation for dynamical heterogeneities apply to structural glasses?
- Address the question using Molecular Dynamics simulations.
Aging: picking times with constant $C_{\text{global}}$, varying $t_w$

Binary LJ, $T >>> T_g \rightarrow T < T_g$, aging, $\sim 10^4 t_{\text{vib}}$

![Graph showing the decay of C(t,tw) with varying $t_w$](image_url)
Aging: scaling of local fluctuation distribution

Approximate collapse of distributions for constant $C_{\text{global}}$…

(HC and A. Parsaeian, Nature Physics 2007)
Aging: spatially correlated fluctuations

Measure of correlated fluctuations:

\[ \chi_4(t, t_w) \sim \left( \langle \int d^3r \ C(\vec{r}, t, t_w) \rangle \right)^2 - \langle \int d^3r \ C(\vec{r}, t, t_w) \rangle^2 \]

Scaling

\[ \chi_4(C = e^{-1}) \sim t_w^{0.35} \]

Old system \( \Rightarrow \) slower & correlated.

(A. Parsaeian and HC, PRE 2008)
Aging: correlation length

The plateau is higher and starts later for older systems.

(A. Parsaeian and HC, PRE 2008)
A more direct approach: fluctuations along trajectories

Use “triangular relations” (Jaubert et al., JSTAT (2007)):
\[ C(t_1, t_2), C(t_2, t_3) \Rightarrow C(t_1, t_3) \]

- Low temp, long times, large enough coarse graining:
  \[ C(t, t') \approx C(\phi(t) - \phi(t')) \]
- \( C(t, t') \approx \tilde{C}(\phi(t) - \phi(t')) \) fits the data well, for certain \( \tilde{C} \) and \( \phi(t) \).
- For 3 times \( t_1 > t_2 > t_3 \):
  \[ \phi(t_a) - \phi(t_b) \approx \Phi_{ab} \equiv \tilde{C}^{-1}(C(t_a, t_b)), \quad a, b \in \{1, 2, 3\} \]
  \[ \sigma \equiv \frac{1}{\sqrt{3}} (\Phi_{12} + \Phi_{23} - \Phi_{13}) \]
  \[ \sigma \approx \frac{1}{\sqrt{3}} (\phi(t_1) - \phi(t_2) + \phi(t_2) - \phi(t_3) - \phi(t_1) + \phi(t_3)) = 0 \]

K. E. Avila, HC, and A. Parsaeian PRL (2011),
K. E. Avila, HC, and A. Parsaeian in preparation
Global trajectory

\[ \pi_1 \equiv \frac{1}{\sqrt{2}} (\phi_{12} - \phi_{23}) \approx \frac{1}{\sqrt{2}} (\phi(t_1) - 2\phi(t_2) + \phi(t_3)) \quad \text{(transverse 1)} \]

\[ \pi_2 \equiv \frac{1}{\sqrt{6}} (\phi_{12,r} + \phi_{23} + 2\phi_{13}) \approx \sqrt{\frac{3}{2}} (\phi(t_1) - \phi(t_3)) \quad \text{(transverse 2)} \]

\[ \sigma \equiv \frac{1}{\sqrt{3}} (\phi_{12,r} + \phi_{23} - \phi_{13}) \approx 0 \quad \text{(longitudinal)} \]
Local fluctuations along the global trajectory?

Contours of constant $\rho(\sigma_r, \vec{\pi}_r)$, enclosing 25%, 50% and 75% of total probability. 125 part/coarse graining box.

K. E. Avila, HC, and A. Parsaeian PRL (2011),
K. E. Avila, HC, and A. Parsaeian in preparation
Longitudinal and transverse fluctuations

K. E. Avila, HC, and A. Parsaeian PRL (2011)
We expect \( C_r(t, t') = C(\phi_r(t) - \phi_r(t')) \), with \( \phi_r(t) \equiv \int_t^\infty dt'' / \tau_r(t'') \).

Data known for times \( t_1, t_2, \cdots, t_M \) \( \Rightarrow \) local two-time correlations calculated for \( M(M-1)/2 \) time pairs.

For each local region: fit \( C_r(t, t') \) by adjusting the \( M \) variables \( \phi_r(t_1), \cdots, \phi_r(t_M) \)

\( \Rightarrow \sim M/2 \) data points per fit parameter.
Fluctuations in the Relaxation of Glasses

$\phi_r(t)$ from data: convergence?

WCA particles, $T \approx 0.9 T_{MCT}$

WCA particles, $T \approx 1.1 T_{MCT}$
$\phi_r(t)$: does it describe the data?

WCA particles, $T \approx 0.9 T_{MCT}$

![Graph 1]

WCA particles, $T \approx 1.1 T_{MCT}$

![Graph 2]
$\phi_t(t)$: fluctuations

**WCA particles, $T \approx 0.9T_{MCT}$**

- History 1
- History 2
- History 3
- History 4
- History 5
- $\phi_{\text{global}}$

**WCA particles, $T \approx 1.1T_{MCT}$**

- History 1
- History 2
- History 3
- History 4
- History 5
- $\phi_{\text{global}}$

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Fluctuations in the Relaxation of Glasses
Fluctuations in $d\phi_r(t)/dt = 1/\tau_r(t)$

WCA particles, $T \approx 0.9T_{MCT}$

WCA particles, $T \approx 1.1T_{MCT}$
Summary

- Explanation of dynamical heterogeneities based on “time fluctuations” originated in spin glass models. It predicts:
  1. $\rho(C_r)$ collapses for fixed $C_{\text{global}}(t, t_w)$.
  2. Correlation length $\xi(t, t_w)$ diverges at long times.
  3. For two local quantities that probe the relaxation of the system, different regions will be at different points of a unique trajectory.

- Simulations in 3DEA spin glass support (1) and (3); allow (2).
- Does “time fluctuation” explanation apply to fluctuations in structural glasses? Simulations support (1) and (3); allow (2). Additionally:
  4. Scaling of spatial correlations vs $C_{\text{global}}(t, t_w)$.
  5. Triangular relations. $C_{\vec{r}}(t_1, t_2), C_{\vec{r}}(t_2, t_3) \Rightarrow C_{\vec{r}}(t_1, t_3)$
  6. Extracting $\phi_{\vec{r}}(t)$. Local relaxation times $\tau_{\vec{r}}(t)$?
In progress: Extracting $\phi_r(t)$ from data. (G. A. Mavimbela).

⇒ Describe the dynamics in terms of instantaneous quantities, instead of 2-time quantities.

Relate those instantaneous quantities describing local relaxation to instantaneous quantities describing local structure?
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  - Katharina Vollmayr-Lee

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  U. de Mar del Plata, Argentina
  Simon Fraser University
  Bucknell University
A toy example: Mean Field p-Spin Model

- Correlation and response: Cugliandolo and Kurchan, PRL 71, 173 (1993) \((\mu \equiv p\beta^2/2)\):

\[
\frac{\partial C(t, t')}{\partial t} = -(1 - p\beta \mathcal{E}(t)) C(t, t') + 2 R(t', t)
+ \mu \int_0^{t'} dt'' C^{p-1}(t, t') R(t', t'') + \mu (p - 1) \int_0^t dt'' R(t, t'') C^{p-2}(t, t'') C(t'', t')
\]

\[
\frac{\partial R(t, t')}{\partial t} = -(1 - p\beta \mathcal{E}(t)) R(t, t') + \delta(t - t')
+ \mu (p - 1) \int_{t'}^t dt'' R(t, t'') C^{p-2}(t, t'') R(t'', t')
\]

- Reparametrization invariance: in the limit of slow dynamics, the dynamical equations are still satisfied if \(C(t, t')\) and \(R(t, t')\) are replaced by:

\[
\tilde{C}(t, t') = C(h(t), h(t')) \quad \tilde{R}(t, t') = R(h(t), h(t')) \frac{dh}{dt'}
\]
Dynamical heterogeneity: polarization fluctuations

PVAc: dielectric fluctuations (Vidal Russell & Israeloff, Nature (2000))

Polymer glass, $T = T_g - 9K$
transient appearance of strongly fluctuating region under tip
Heterogeneity lifetime $\approx$ relaxation time
Can we understand dynamical heterogeneities?

**Equilibrium state of ferromagnet**

Rotations $R_{\theta}$ leave free energy $F$ unchanged
Minimization of $F[\vec{m}(\vec{r})]$ selects the (mean field approx.) physical magnetization

**Nonequilibrium dynamics of spin glass**

$\chi$

$C$

RG in time: reparametrizations $t \rightarrow h(t)$ leave “dynamical action” $S$ unchanged (irrelevant terms break symmetry at finite times) (C.Chamon, M.P.Kennett, H.E.C., L.F.Cugliandolo, PRL 89, 217201 (2002))

Minimization of $S[(C_{\vec{r}}(t, t_w), \chi_{\vec{r}}(t, t_w))]$ selects the (mean field approx.) physical evolution of $(C, \chi)$
Broken continuous symmetry $\Rightarrow$ fluctuation modes (ferromagnet)

**Equilibrium rotationally symmetric ferromagnet**

- "ground state"
- $\delta F = 0$
- $\delta F$ small
- high probability
- Goldstone mode
  (direction of magnetization varies smoothly in space)

- "another ground state"
Broken continuous symmetry $\Rightarrow$ fluctuation modes (spin glass)

Dynamics of spin glass

"ground state"

\[ \delta S = 0 \]

\[ \delta S \text{ small} \]

\textit{high probability}

"another ground state"

symmetry

Goldstone mode

(time coordinate varies smoothly in space)
Dynamical correlations: definitions


\[ w(r, t, t_w) = \begin{cases} 
1 & \text{if particle at } r \text{ has moved } < a_{\text{vib}} \\
0 & \text{otherwise}
\end{cases} \]

\[ g_4(r, t, t_w) = \text{spatial correlation of } w(r, t, t_w) \]

\[ \xi_4(t, t_w) = \text{correlation length for } g_4(r, t, t_w) \]

\[ \chi_4(t, t_w) = \text{dynamic density susceptibility} \]

\[ \propto \int d^3r \ g_4(r, t, t_w) \]

\[ \propto \left\langle \left( \int d^3r \ C_{\vec{r}}(t, t_w) \right)^2 \right\rangle - \left\langle \int d^3r \ C_{\vec{r}}(t, t_w) \right\rangle^2 \]
Relaxation to equilibrium for $T > T_g$

Binary system, purely repulsive Weeks-Chandler-Andersen (WCA) potential

(A. Parsaeian and HC, PRL (2009))
Aging vs equilibrium: distributions of local correlations

Identical probability distributions for aging ($t_w/\tau_\alpha < 1$) and equilibrium ($t_w/\tau_\alpha \gg 1$).
Aging vs equilibrium: distributions of particle displacements

Excellent collapse...

...except for the most mobile particles.

\[ \rho(\Delta x(t, t_w)) \]

\[ \Delta x(t, t_w) \]

\[ C=0.5 \]

\[ t_w/\tau_\alpha=0.31 \]

\[ T=0.4 \]

\[ C=0.5 \]

\[ t_w/\tau_\alpha=0.79 \]

\[ t_w/\tau_\alpha=11.5 \]

\[ t_w/\tau_\alpha=15.8 \]

\[ C=0.5 \]

\[ T=0.5 \]

\[ t_w/\tau_\alpha=0.31 \]

\[ t_w/\tau_\alpha=0.79 \]

\[ t_w/\tau_\alpha=11.5 \]

\[ t_w/\tau_\alpha=15.8 \]
More direct tests

- Use “triangular relations” (Jaubert et al., JSTAT (2007)):
  \[ C_\vec{r}(t_1, t_2), C_\vec{r}(t_2, t_3) \Rightarrow C_\vec{r}(t_1, t_3) \]
  Extract \( \phi_\vec{r}(t) \) and \( \tau_\vec{r}(t) \) from data.
**WCA particles, \( T \approx 0.9 T_{MCT} \)**

![Graph 1](image1)

**WCA particles, \( T \approx 1.1 T_{MCT} \)**

![Graph 2](image2)

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Fluctuations in the Relaxation of Glasses
Where are we so far?

Explanation of dynamical heterogeneities based on “time fluctuations” originated in spin glass models. It predicts:

1. $\rho(C_r)$ collapses for fixed $C_{\text{global}}(t, t_w)$.
2. Correlation length $\xi(t, t_w)$ diverges at long times.
3. For two local quantities that probe the relaxation of the system, different regions will be at different points of a unique trajectory

Simulations in 3DEA spin glass support (1) and (3); allow (2).

Does “time fluctuation” explanation apply to fluctuations in structural glasses? Simulations support (1); allow (2). Additionally:

4. Scaling of spatial correlations vs $C_{\text{global}}(t, t_w)$.
5. Equilibrium fluctuations $\approx$ out of equilibrium fluctuations.

However, all the evidence for structural glasses is pretty indirect so far.