Supercooled liquids fall out of equilibrium in two distinct ways:

1) They have not been allowed to nucleate and crystallize (this is the more trivial way of being out of equilibrium)
2) Once cooled sufficiently far, the supercooled sample is no longer even in equilibrium with the liquid state. That is, the time scale for the relaxation in the sample ($\tau$) crosses the experimental time scales (set by either the cooling rate or the frequency of the probe.)

In glasses, cannot stay in equilibrium with the liquid down to a temperature close to the transition temperature, $T_0$, (if there is one) where the relaxation time diverges. What makes this different from ordinary critical slowing down associated with any phase transition is that even in the best of circumstances one can only get to about 45 K from $T_0$. This is very far away so one cannot probe close to the transition. Also, in e.g., a ferromagnet, when one cools below the Curie temperature one can again be in equilibrium. In a glass, one does not return to equilibrium at lower temperatures.
Susceptibility of Glasses

Dielectric susceptibility of liquids has 3 distinct frequency regimes.

At $T_o$, both $\nu_p$ and $\nu_T$ approach 0.

At the same temperature, $\sigma$ also approaches 0.

Thus $\varepsilon''$ is constant from $\nu = 0$ to $\nu_o$, a phonon frequency.

Kramers-Kronig implies $\Delta\varepsilon$ diverges at $T_o$:

$$\Delta\varepsilon = \frac{2}{\pi} \int_0^\infty \varepsilon''(\nu) \frac{d\nu}{\nu}.$$

$$\delta\Delta\varepsilon = \frac{2}{\pi} \int_{\nu_T}^{\nu_o} C_2 \nu^{-\sigma} \frac{d\nu}{\nu} \propto \frac{1}{T-T_o}.$$
Quenched vs. unquenched disorder

**Glass Transitions**

<table>
<thead>
<tr>
<th>Structural Glasses</th>
<th>Spin Glasses</th>
</tr>
</thead>
<tbody>
<tr>
<td>High temperature liquid: molecules become sluggish as the temperature is lowered.</td>
<td>High temperature disordered paramagnet: spins become sluggish as temperature is lowered.</td>
</tr>
<tr>
<td>At the glass transition: viscosity and relaxation times (e.g., rotation) appear to diverge, atoms freeze in position.</td>
<td>At the spin-glass transition: some relaxation times appear to diverge, spins freeze in orientation.</td>
</tr>
<tr>
<td>The glass is an amorphous solid with a structure that is like that of the liquid - but stationary.</td>
<td>In the spin-glass, spins point in random directions as in paramagnet - but stationary.</td>
</tr>
<tr>
<td>The disorder CAN anneal away to an ordered, crystalline phase.</td>
<td>The disorder CANNOT anneal away. It is quenched due to the initial placement of the spins.</td>
</tr>
<tr>
<td>Cannot get close to the transition temperature.</td>
<td>Can get much closer to the transition.</td>
</tr>
</tbody>
</table>
Susceptibility of Spin Glasses

Magnetic susceptibility of paramagnets above $T_{SG}$ also has 3 distinct frequency regimes.

$\log \chi''$

$\nu^\alpha$ $\nu^{-b}$ $\nu^{-\gamma}$

$\nu_P$ $\nu_T$ $\log \nu$

$\alpha$ and $\gamma$ depend on temperature (b does not).

As $T_{SG}$ is approached BOTH $\alpha$ and $\gamma$ approach 0.
$(\alpha \to 0$ has previously been used in studies of 1/f noise.)

Response above $\nu_P$ gives information about freezing in both structural glasses and spin glasses.
Susceptibility of Spin Glasses

Magnetic susceptibility of paramagnets above $T_{SG}$ also has 3 distinct frequency regimes.

![Graph showing log $\chi''$ vs. log $\nu$ with $\nu^\alpha$, $\nu^{-b}$, and $\nu^{-\gamma}$]

$\alpha$ and $\gamma$ depend on temperature (b does not).

As $T_{SG}$ is approached BOTH $\alpha$ and $\gamma$ approach 0. ($\alpha \to 0$ has previously been used in studies of 1/f noise.)

Response above $\nu_p$ gives information about freezing in both structural glasses and spin glasses.
Spin glass magnetic susceptibility: LiHo I Fl

(a) $\chi'(\text{emu/mol Ho})$ vs $\nu$ (Hz)

(b) $\Gamma$ (K) vs $T$ (K)

$H_L = 0$

$T_g \approx 0.13$ K
Normal modes in “normal” solid

Low-frequency normal modes are long-wavelength plane waves. Long wavelengths “average” over disorder.

Density of modes, $D(\omega)$, from counting waves:

$$D(\omega) \propto \omega^{d-1} \text{ in d-dimensions.}$$

All solids should behave this way.

Debye $T^3$ specific heat at low temperatures.
Low-temperature properties of glasses

Crystals: \( C_p = aT^3 + \ldots \)
\( \kappa = C_p \ V \ L \propto T^3 \)  \((V = \text{velocity}, \ L = \text{mean-free path are constant})\)
Quantum-mechanical two-level tunneling centers

In glass, particles can sit in more than one place. They tunnel between sites.

Creates two states split by tunneling matrix element.
Assume constant distribution of such energy splittings, \( n_0 \).
Leads to linear specific heat.

\[
C(T) = \int_0^\infty n_0 \left( \frac{E^2}{4k_B T^2} \right) \text{sech}^2 \left( \frac{E}{2k_B T} \right) \, dE
\]

\[
C(T) = \left( \frac{\pi^2}{6} \right) n_0 k_B^2 T
\]
\[ \begin{vmatrix}
E_1 + \langle \phi_1 | V - V_1 | \phi_1 \rangle & \langle \phi_1 | H | \phi_2 \rangle \\
\langle \phi_2 | H | \phi_1 \rangle & E_2 + \langle \phi_2 | V - V_2 | \phi_2 \rangle
\end{vmatrix} \]

\[
\frac{1}{2} \begin{vmatrix}
-\Delta & \Delta_0 \\
\Delta_0 & +\Delta
\end{vmatrix}
\]

\[
\Delta_0 = 2 \langle \phi_1 | H | \phi_2 \rangle
\]

\[
E = (\Delta^2 + \Delta_0^2)^{1/2}
\]

Figure 5. A double-well potential (a), together with the wavefunctions in the localised (b) and diagonal (c) representations.
Other consequences

Thermal conductivity: $\kappa \propto T^2$ (Because mean free path, $L \propto 1/T$)

Time-dependent specific heat (Because energy splitting is due to both tunneling matrix element and barrier asymmetry)

Get same $E$ by having different energy barrier combined with different asymmetry. But these have different tunneling times. Therefore specific heat varies with time.

Saturation (Because there are only two states)
Echoes
How about for metals? (They already have a linear term.)

Heat capacity of superconducting disordered metal Zr$_{0.7}$Pd$_{0.3}$. Components are: ..., electrons above $T_c$, --- electrons below $T_{cic}$, -.-. phonons, and --- extra contribution linear in $T$

Thermal conductivity of disordered metal Zr$_{0.7}$Pd$_{0.3}$

Graebner, Golding, et al. PRL 1977
Acoustic echoes in anomalous modes

At low $\omega$, modes highly anharmonic + localized

CLASSICAL echoes in simulations (w/o quantum 2-level systems).

Repulsive Hertzian potential

Time of echo = $\tau$

Cycles of driving frequency

Amplitude

Justin Burton
Localization of modes

Participation ratio:

\[ P_i = \frac{\left( \sum_{\alpha} |\epsilon_i(\alpha)|^2 \right)^2}{\sum_{\alpha} |\epsilon_i(\alpha)|^4} \]

High frequency modes are localized.
Localization vs. frequency in Lennard-Jones glass