The loss of signal does not mean the ensemble has returned to equilibrium. Recall, the $\pi/2$ pulse makes $\langle C_{11} \rangle = \langle C_{22} \rangle$, i.e., $\langle C_{22} \rangle = 0$. Often the $T_2$ decay is fast enough that $\langle C_{11} \rangle = \langle C_{22} \rangle$ after the signal has decayed. All that decayed was the coherence. The ensemble still has hidden order because there still exist definite phase relations between the systems whose $\vec{E}$ vectors were brought into phase by the $\pi/2$ pulse. That phase information can be reversed and ultimately refocussed by a $\pi$ pulse.
Consider first just two systems (or sub ensembles) $A$ and $B$ with $(\frac{H_{11} - H_{22}}{\hbar})_A = \omega_A$ and $(\frac{H_{11} - H_{22}}{\hbar})_B = \omega_B$, with $\omega_A < \omega_B$.

\[ t^* = 0 \]
\[ t^* = \tau \]
\[ t^* = 2\tau \]

where $\tau$ is an arbitrary time interval.

The $\pi_y$ pulse precesses the vectors by $180^\circ$ about $y$, putting $A$ ahead of $B$ by the amount $(\omega_2 - \omega_1)\tau$. Thus, after another $\tau$ of time interval, $B$ just catches up to $A$ as they both point in the $y$ direction again!
After time interval $\tau$ the A vector lags behind the B vector by the amount of angle $= (\omega_02 - \omega_01)\tau$.

This happens for all pairs of systems and the signal is completely regenerated, only to decay again.

![Graph showing signal decay over time with peaks at 0, $\tau$, and 2$\tau$.]

The following two pages show actual photon echoes recorded by the early pioneers of NMR.
Fig. 4. Effect of the homogeneity of the field on the widths of tails and echoes. The tails and echoes associated with a sample (1) in a very homogeneous field are wide compared to those associated with a sample (B) in a less homogeneous field.

*Bloembergen, Purcell, and Pound, Phys. Rev. 73, 679 (1948).*
FIG. 5. A tail and echo associated with an acetic acid (CH₃COOH) sample in a very homogeneous field. The nuclear signal displays modulation typical of the beating of two signals of nearly equal frequencies, the magnitude of one being three times that of the other. The beat frequency shown, corresponding to room temperature and 7000 gauss, is approximately 220 cps.
6. Comparison of the two free precession methods for measuring the decay time of the horizontal component of nuclear magnetic polarization. In "Method A" the sample must return to equilibrium condition each time an additional echo is to be viewed. In "Method B" the sample need only start from equilibrium once. The separate oscilloscope traces of "Method A" are usually displayed superimposed in a multiple exposure picture, whereas a single trace and hence a single exposure picture is required for "Method B." However, this latter method requires more than 80° pulse.
Fig. 7. (A) A "Method A" decay associated with water at 25°C. The time constant is approximately 0.2 sec. The decay is largely determined by the molecular diffusion through the 0.25 gauss/cm gradient. The decay is dominated by the factor exp(-kt).

(B) A "Method B" decay associated with water at 25°C. The time constant of the decay is approximately 2.0 sec. The effect of diffusion has been largely circumvented.
LONGITUDINAL RELAXATION ($T_1$)

On the previous page, it is seen that for longer $T_1$, less signal is recovered by the $T_1$ pulse. This decay is caused primarily by decay to the system back to thermal equilibrium, i.e., $\langle E_z \rangle$ decaying from 0 to $\langle E_z \rangle_0$. For this to happen, there must be some $H_2'$ coupling the states $|1\rangle$ and $|2\rangle$. This is often a fluctuating interaction provided by the thermal motion of the environment. It can differ from the effects that created the inhomogeneous broadening, discussed above, only by the property that a given system has $H_1'$-$H_2'$ changing in time randomly. Each system experiences exactly the same random fluctuations over the time scale of the observation, giving what is called homogeneous broadening.

Viewed another way, if the $H_1'$-$H_2'$ values change on a time scale similar to $\frac{1}{T_1}$, the $H_2'$ interaction could be thought of as an internal driving force, similar to electromagnetic radiation.
"Pure Dephasing Time" $T_2^*$

Usually both homogeneous and inhomogeneous mechanisms are present, giving another term to the observed transverse decay time: \( \frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*} \)

Why is $1/T_2 = 1/2T_1$???

$T_2^*$ is called the "pure dephasing time". This includes both molecular and magnetic effects.

Typically, homogeneous broadening gives Lorentzian line shapes \( \frac{A}{\omega_0^2 - \omega^2} \)

whereas inhomogeneous broadening gives Gaussian shapes \( \frac{A}{\text{Width}} \).

An ensemble exhibiting only homogeneous broadening will not give an echo following a $\pi/2$ ... $\pi$ ... $\pi/2$ sequence.

Why?
Why is $1/T_2 = 1/2T_1$? (when $H_{11} = H_{22}$, i.e., no pure dephasing)

**$T_1$ dephasing** happens only because of the transition between $|1\rangle$ and $|2\rangle$ during the process of *returning to equilibrium*.

\[
\dot{\rho} = \rho \times \Omega
\]

\[
\begin{align*}
\dot{\rho}_x &= \rho_y \Omega_z - \rho z \Omega_x \\
\dot{\rho}_y &= \rho_z \Omega_x - \rho x \Omega_z \\
\dot{\rho}_z &= \rho_x \Omega_y - \rho y \Omega_x \\
\end{align*}
\]

\[
\dot{\rho}_z = \rho_x \Omega_y - \rho y \Omega_x = \dot{\rho}_{11} - \dot{\rho}_{22} = i(\rho_{12} H_{21} - H_{12} \rho_{21}) - i(\rho_{21} H_{12} - H_{21} \rho_{12})
\]

In words, this says that the decay of population difference comes from the imaginary part of $H_{12}$ acting on the real part of the of $\rho_{12}$ minus the real part of $H_{12}$ acting on the imaginary part of $\rho_{12}$.

For the whole sample:

\[
\dot{\rho}_z = \dot{\rho}_{11} - \dot{\rho}_{22} = <\rho_x > \Omega_y - <\rho_y > \Omega_x
\]

Population decreases all the time from both components.

The "coherent packet" is directional, i.e., meaning its $\rho_x$ is large when its $\rho_y$ is small and vice versa. On average

\[
\dot{\rho}_z = \dot{\rho}_{11} - \dot{\rho}_{22} = \frac{<\rho_x >}{2} \Omega_y - \frac{<\rho_y >}{2} \Omega_x
\]

Thus, loss of the coherence is half as fast as the that of the whole ensemble.
The simple physics behind transitions between two states always comes down to the relative phase of the oscillating density from the superposition of the two states and the oscillating force coming from the Hamiltonian.

If they are in-phase, work can be done on the system and the amplitude of the higher state increases.

If they are out-of-phase, the system does work on the field and the amplitude of the lower state increases.

In between these two cases there is a phase difference for which nothing happens.