macromolecules in solution:

$$[T_1(\text{min})]^{-1} = \frac{\gamma^2}{\omega_0}[B_{xL}^0]^2 \tag{3-47}$$

Equation 3-47 makes it clear that at higher applied magnetic fields the minimum value of T_1 increases, as is shown in Fig. 3-17 and as may be deduced from Fig. 3-16.

As has been pointed out earlier, factors affecting spin–lattice relaxation will also cause transverse relaxation. However, whereas the non-secular contribution requires a fluctuating magnetic field, and thus depends on $J(\omega_0)$, the secular contribution involves no energy change, and the appropriate spectral density is $J(0)$. In fact the general expression for T_2 in the random-field model discussed in this section is

$$T_2^{-1} = (2T_1)^{-1} + \tfrac{1}{2}\gamma^2[B_{zL}^0]^2 J(0) \tag{3-48}$$

which is equal to T_1^{-1} provided $B_{zL}^0 = B_{xL}^0$ and $J(0) = J(\omega_0)$. The influence of the $J(0)$ term causes T_2 to decrease monotonically as τ_c increases in contrast to T_1, as is shown in Fig. 3-17 (but see Section 6-3). In fact at the T_1 minimum $T_2 = \tfrac{2}{3}T_1$. The concepts regarding relaxation, as given in the present section and as further elaborated for the dipolar relaxation mechanism in Section 4-3 and Appendix 3, were first described by Bloembergen, Purcell and Pound[14] and are frequently referred to as BPP theory. This is only valid in the so-called 'weak collision' case, where $\tau_c < T_2$. The situation in relatively rigid materials, where the extreme narrowing condition is usually not valid and where, in the limit, BPP theory is also not applicable, is further discussed in Chapter 6.

As noted in Section 3-14, the general requirement for spin–lattice relaxation is a magnetic interaction fluctuating at the resonance frequency. A nearly static component of the magnetic interaction is also effective for T_2. There are a number of physical mechanisms which provide the appropriate conditions, and at this point these are summarized, and the relevant equations given (Table 3-2), though in some cases more detail is supplied later.

(a) *Dipole–dipole interactions with other nuclei* (DD)

Dipolar interactions are of the same type as those observed macroscopically between two small bar magnets. They may be modulated by molecular tumbling (affecting intermolecular and intramolecular interactions) or by translational diffusion (intermolecular interactions), thus causing relaxation, and the equations for the two cases, given in Table 3-2, differ. There is also a difference of a factor of 3/2 between the case where the two nuclei under consideration both contribute to the magnetization being monitored (the homonuclear case) and that where one magnetization is under observation independently of the other (the heteronuclear case). Dipolar interactions are discussed in more detail in Chapter 4.

(b) *Shielding anisotropy* (SA)

The shielding at a nucleus, and therefore the magnetic field acting on it, varies with the molecular orientation in the static field B_0 (see

Table 3-2 Equations for spin–lattice relaxation rates, T_1^{-1}, of a spin-$\tfrac{1}{2}$ nucleus, A, for various mechanisms in the extreme narrowing approximation

Mechanism	T_1^{-1}	Notes
dd(intra)(homo)	$\left(\dfrac{\mu_0}{4\pi}\right)^2 \tfrac{3}{2} \gamma_A^4 \hbar^2 \tau_c / r^6$	for a single pair of spin-$\tfrac{1}{2}$ nuclei of separation r
dd(intra)(hetero)	$\left(\dfrac{\mu_0}{4\pi}\right)^2 \gamma_A^2 \gamma_X^2 \hbar^2 \tau_c / r^6$	for a single pair of spin-$\tfrac{1}{2}$ nuclei AX of separation r
dd(inter)(hetero)	$\left(\dfrac{\mu_0}{4\pi}\right)^2 \tfrac{2}{15} N_X \gamma_A^2 \gamma_X^2 \hbar^2 / Da$	for relaxation by a spin-$\tfrac{1}{2}$ nucleus X
ue(intra)(dipolar)	$\left(\dfrac{\mu_0}{4\pi}\right)^2 \tfrac{4}{3} \gamma_A^2 \gamma_e^2 \hbar^2 S(S+1) \tau_c / r^6$	for relaxation by unpaired electrons of total spin S at distance r
ue(scalar)	$\tfrac{8}{3}\pi^2 a_N^2 S(S+1) \tau_e$	for relaxation by unpaired electrons of total spin S
sr	$2 I_r k T C^2 \tau_{sr} / \hbar^2$	for isotropic molecular inertia
sa	$\tfrac{2}{15} \gamma_A^2 B_0^2 \Delta\sigma^2 \tau_c$	for cylindrical symmetry of shielding
sc	$\tfrac{8}{3}\pi^2 J_{AX}^2 I_X(I_X+1) \dfrac{\tau_{sc}}{1+(\omega_X-\omega_A)^2\tau_{sc}^2}$	relaxation by coupling to spin, X, of quantum number I_X

Meaning of symbols (where not otherwise defined in this Table or Section):

τ_c Correlation time for molecular tumbling

τ_e Correlation time related, *inter alia*, to the spin–lattice relaxation time for the unpaired electrons

τ_{sc} For scalar relaxation of the first kind this is the exchange lifetime; for scalar relaxation of the second kind this is T_{1X}

N_X Concentration of spins X (per unit volume)

D Mutual translational self-diffusion coefficient of the molecules containing A and X

a Distance of closest approach of A and X

γ_e Magnetogyric ratio for the electron

a_N Nucleus-electron hyperfine splitting constant (in frequency units)

C Spin–rotation interaction constant (assumed to be isotropic)

$\Delta\sigma$ Shielding anisotropy ($\sigma_\parallel - \sigma_\perp$; see Section 6-6)

Section 6-6), except for sites of very high symmetry. Molecular tumbling therefore modulates the local magnetic field, and can cause relaxation. The relevant equations are given in Table 3-2. It should be noted that the correlation time (in the case of isotropic motion) is exactly the same as that entering into the equations for dipolar relaxation caused by molecular tumbling. As shown by the equations in Table 3-2, the relaxation rate arising from shielding anisotropy is proportional to the square of the applied magnetic field B_0. This effect can cause unacceptable line broadening for some nuclei (e.g. ^{205}Tl) at high applied fields—for instance, the ^{205}Tl linewidth for Me_2TlNO_3 in D_2O in a magnetic field of $9\cdot40 T$ is 140 Hz, whereas in a field of $1\cdot41\ T$ it is 4 Hz.[15] The SA mechanism is unusual in that,