Nuclear magnetic relaxation spectroscopy of chain and headgroup fluctuations in Lecithin bilayers.

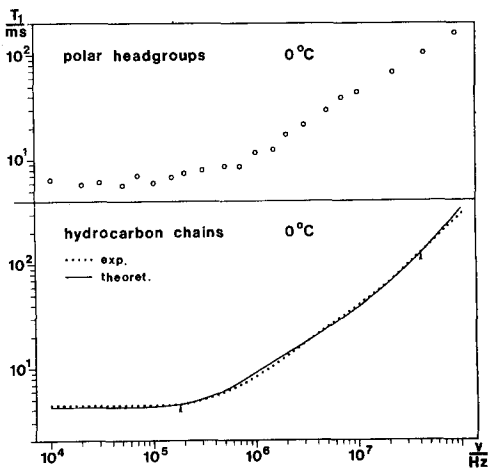
R. Kimmich, A. Scheuermann, G. Schnur, K.-H. Spohn,

Sektion Kernresonanzspektroskopie, Universität Ulm,
Postfach 4066, D-7900 ULM, W.-Germany

In a previous paper (1) we have investigated the proton relaxation dispersion (10^4 to 10^8 Hz) of Dipalmitoyl-L-α-lecithin (DPL) liposomes above and below the gel/liquid crystal phase transition. Using chain-deuterated lipids it was now possible to distinguish fluctuations in the hydrocarbon chains from those of the polar headgroup.

The figure shows the proton relaxation dispersion of the gel phase of a dispersion of 25 % DPL in D_2O as an example. The relaxation rate of the hydrocarbon chains has been obtained by the undeuterated DPL. The theoretical curve has been calculated by the aid of the limited defect diffusion model (2) assuming kinks ($gt\bar{g}$ sequences) which are reflected at the chain/headgroup interfaces. The frequency dependence of the longitudinal relaxation time T_1 is characterized by two bends at the positions $2\pi\nu\tau_d = 1$ and $2\pi\nu\tau_b = 1$ (arrows). τ_b is the mean diffusion time a defect needs to pass a reference segment, while τ_d is the mean diffusion time from polar headgroup to polar headgroup. Kink defects and the geometry of DPL bilayers lead to the ratio $\tau_d : \tau_b = 227$ used for the calculation of the theoretical curve. With the same model the transverse relaxation curves could be described using the Anderson-Weis-Kubo-Tomita theory (3).

Above the gel/liquid crystal transition at least one further process occurs which can be attributed to the fluctuations of the molecules perpendicular to the chain axis. The same finding holds for the polar headgroups. As possible mechanisms cooperative order fluctuations, lamellar modes and the lateral chain diffusion have been considered and discussed in the light of the longitudinal and transverse relaxation behaviour.



1) Kimmich, R. and Voigt, G., (1979) Chem. Phys. Letters 62, 181.
2) Kimmich, R., (1976) Z. Naturforsch. A, 31a, 693.
3) Abragam, A., (1962) Oxford, The principles of nuclear magnetism.