

Torrey H C. Nuclear spin relaxation by translational diffusion.

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Nuclear spin relaxation rates are calculated for the process of modulation of dipolar interactions by thermally activated relative motions. These are treated by a general random-walk theory applied to isotropic diffusion and to jumps to nearest-neighbor sites on a crystal lattice. [The SCI® indicates that this paper has been cited in over 470 publications since 1955.]

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"In 1951, when I started this work, it was known from the work of Bloembergen that the dipolar interaction modulated by diffusion was a potent relaxing mechanism for nuclear spins, but the theory was only semi-quantitative and I resolved to try to put it on a sounder basis. I first tried to use the diffusion equation, Fick's law, to find the spectral density functions for dipolar interactions, but the results did not agree with experiments in the realm of low temperatures and high frequencies. Since Fick's law is known to describe the limiting case of a random walk when there are many small steps over a long time, I decided to apply general random-walk theory, hoping to discern the effects of longer steps in a shorter time. I succeeded in deriving a distribution function and spectral density functions for the relative motion of two interacting spins that were sufficiently general to be adapted to various models of random walk. I settled on two such models. One was applicable to fluids and amorphous solids and the other to random walks on a crystal lattice.

"For many years, the only applications of my work were to crystals. Ten years after my paper, Eisenstadt and Redfield¹ pointed out that, in the case of vacancy diffusion, atoms do not jump until a vacancy diffuses into their vicinity and in such encounters considerable activity can take place: bunching of jumps and correlated jumps. They showed how to make corrections for such effects. Their work was extended by Wolf, who has given an extensive review² of relaxation in crystals.

"Sixteen years elapsed before an effective attempt was made to apply my jump model to liquids. Harmon and Muller,³ in a carefully planned and executed study, measured the relaxation rate in ethane and related the part of it attributable to translational diffusion to my theory. They used a more realistic pair-correlation function than my simple step function and found finite jumps of the size of the molecular diameter. Six years later, Hwang and Freed⁴ poured cold water on this conclusion by showing that the data were consistent with a refined theoretical model without the need to postulate finite jumps. However, the issue cannot be said to be settled at this time. I have been stimulated by my review of this field at the behest of ISI® and hope to raise some questions and make some suggestions soon in a new paper.

"It is gratifying that my ideas of 1953 have stimulated much new work and progress. In citing my old paper, several authors have called it 'pioneering,' 'classic,' and 'classical' even when they have made suggestions for emendations and new departures. My simple jump model for liquids has been used in fields other than spin relaxation, such as chemical kinetics. It was apparently independently discovered much later by Egelstaff (see equation 10.14 in *An Introduction to the Liquid State*)."⁵

1. Eisenstadt M & Redfield A G. Nuclear spin relaxation by translational diffusion in solids. *Phys. Rev.* 132:635-43, 1963. (Cited 105 times.)
2. Wolf D. *Spin-temperature and nuclear-spin relaxation in matter: basic principles and applications.* Oxford: Clarendon Press, 1979. 462 p.
3. Harmon J F & Muller B H. Nuclear spin relaxation by translational diffusion in liquid ethane. *Phys. Rev.* 182:400-10, 1969. (Cited 105 times.)
4. Hwang L P & Freed J H. Dynamic effects of pair correlation functions on spin relaxation by translational diffusion in liquids. *J. Chem. Phys.* 63:4017-25, 1975. (Cited 50 times.)
5. Egelstaff P A. *An introduction to the liquid state.* New York: Academic Press, 1967. 236 p. (Cited 500 times.)