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Kohlrausch Explained: The Solution to a Problem That Is 150 Years Old

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We construct a bridge between the standard diffusion-to-traps mathematical model of stretched exponential relaxation and the modern experimental database on both electronic and structural relaxation.

KEY WORDS: Diffusion; traps; stretched exponential; relaxation; Kohlrausch; electronic; structural.

Stretched exponential (Kohlrausch, 1847) relaxation, $\exp[-(t^{\beta})]$, fits many relaxation processes at intermediate frequencies (below and near the primary relaxation peak frequency) in disordered electronic and molecular systems, but it is widely believed(1,2) that no microscopic meaning can be assigned to $0 < \beta(T) < 1$ even at $T = T_g$, a glass transition temperature. We show that $\beta(T_g)$ can be understood, providing that one separates extrinsic and intrinsic effects, and that the intrinsic effects are dominated by two magic numbers, $\beta_{SR} = 3/5$ for short-range forces, and $\beta_K = 3/7$ for long-range Coulomb forces, as originally observed by Kohlrausch for the decay of residual charge on a Leyden jar.(3) Our mathematical model treats relaxation kinetics using the Lifshitz–Kac–Luttinger diffusion-to-traps depletion model,(4) which gives $\beta = d/(d+2)$. Here the effective dimensionality d of the configuration space in which relaxation takes place must be analyzed in the context of a theory which is capable of defining the glassy state and which has proved its physical relevance by predicting the composition dependence of the glass-forming tendency in simple systems. That theory is Phillips–Thorpe constraint theory, which is based on elastic

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stiffness percolation, and which correctly predicts the glass-forming tendency and related stiffness thresholds in chalcogenide alloy network glasses.(5) The central concept which motivates the Phillips–Thorpe analysis is axiomatic set theory, which leads to the two values of β quoted above.

Within the last decade there has been a rapid and impressive expansion of the database on Kohlrausch relaxation parameters in a wide range of physical systems. The older broad-band macroscopic relaxation experiments (dielectric and mechanical) have been systematically organized from a phenomenological point of view by Böhmer *et al.*(2) In these experiments the intrinsic behavior can be masked by extrinsic effects associated with surface contacts, especially for dielectric relaxation. Another source of extrinsic effects is partial submicrocrystallization. The extent of the intrinsic/extrinsic content of macroscopic relaxation data can now be determined because microscopic experiments, without contacts in noncrystallized materials and on time scales typically 10^6 faster, have been completed on many systems. The most direct data have been obtained using time-resolved spin-echo techniques with spin-polarized neutrons, which provide pulses of energy and momentum and which also monitor the ensuing relaxation.(1)

The data examined span about 1000 papers on both electronic materials, such as a-Si:H, a-C_{60}, TaS_3, spin glasses, and vortex glasses in high-temperature superconductors, as well as molecular materials, encluding include polymers, network glasses, alcohols, van der Waals supercooled liquids and glasses, and fused salts. In the intrinsic cases the theory of $\beta(T_g)$ is often accurate to 2%, which is often better than the quoted experimental accuracies of $\sim$5%. The extrinsic cases are identified by explicit structural signatures which are discussed at length. The discussion also includes recent molecular dynamical simulations, which have achieved the intermediate relaxed Kohlrausch state and which have obtained values of β in excellent agreement with the prediction of the microscopic theory.

REFERENCES

1. W. Götze and L. Sjögren, *Rep. Prog. Phys.* **55**:241 (1992).
2. R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, *J. Chem. Phys.* **99**:4201 (1993).
3. R. Kohlrausch, *Ann. Phys.* (Leipzig) **12**:393 (1847); G. Williams and D. C. Watts, *Trans. Faraday Soc.* **66**:80 (1970); J. Jackle, *Phil. Mag. B* **56**:113 (1987).
4. I. M. Lifshitz, *Vsp. Fiz. Nauk* **83**:617 (1964) [*Sov. Phys.-Vsp.* **7**:549 (1965)]; R. Friedberg and J. M. Luttinger, *Phys. Rev. B* **12**:4460 (1975); P. Grassberger and I. Procaccia,

J. Chem. Phys. 77:6281 (1982); see also M. D. Donsker and S. R. S. Varadhan, *Commun. Pure Appl. Math.* **28**:525 (1975); J. C. Rassiah, J. Zhu, J. B. Hubbard, and R. J. Rubin, *J. Chem. Phys.* **93**:5768 (1990).

5. J. C. Phillips, *Non-Cryst. Solids* **34**:153 (1979); *Physics Today* **1982**(February):1; G. H. Döhler, R. Dandoloff, and H. Bilz, *J. Non-Cryst. Sol.* **42**:87 (1980); I. P. Swainson and M. T. Dove, *Phys. Rev. Lett.* **71**:197 (1993).

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