IX. TIME-RESOLVED SPECTROSCOPY OF CONDENSED MATTER

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1. MICROVISCOSITY IN GELS AND POLYMER SOLS

David E. Cooper, J. David Litster

We have used the reorientation of molecules of the laser dye oxazine-4 per-
chlorate to probe the viscosity of interstitial water in both gel and sol phases
containing gelatine and agarose. Pulses (1 psec, 5 kW) from a mode-locked cavity-
dumped dye laser were used to preferentially bleach dye molecules whose transition
moments were oriented parallel to the light polarization. Reorientation times
were measured by decay of the resulting dichroism.

We found the reorientation times in bulk water to scale with the bulk viscos-
ity. Inside the polymer network of both gelatine and agarose sol and gel phases
we found the same temperature dependence of reorientation times as in bulk water,
and therefore the same activation energy. This indicates the same local structure
of water as in bulk and shows various hypotheses that the gel-sol phase transition
is associated with changes in the water structure are incorrect. We also found
in gelatine gels an increase in reorientation time of the dye probe as the polymer
concentration was increased. This resulted from interference of the polymers with
hydrodynamic back flow in the water; by calibration with known behavior in channels

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of Vycor glass we could estimate the effective pore size in the gel-polymer solution. This varies from 35 Å to 20 Å in 2% to 10% gelatine gels and is in good agreement with estimates by other methods.
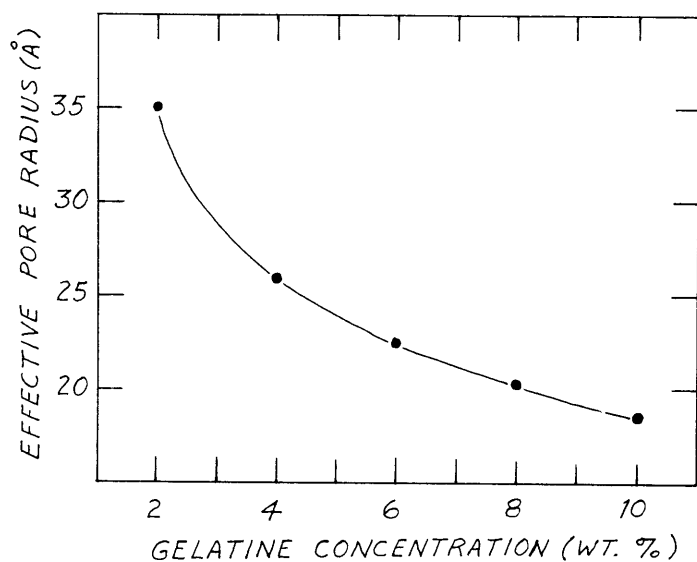

Fig. IX-1.

Figure IX-1 shows the effective pore radius deduced from the measurements. A short account of these results has been published[1] and a longer article is in preparation.

References

1. D.E. Cooper and J.D. Litster, "Molecular Orientation Dynamics in Gels and Critical Mixtures," in R.M. Hochstrasser, W. Kaiser, and C.V. Shank (Eds.), Picosecond Phenomena. II (Springer, Berlin, 1980), p. 115.

2. MOLECULAR REORIENTATION IN CRITICAL MIXTURES

David E. Cooper, J. David Litster

Nitrobenzene and n-hexane are mutually soluble in any concentration at temperatures greater than about 21°C. Below this critical temperature the contribution of the mixing entropy to the free energy is so small that the mixture separates into two phases, one rich in nitrobenzene, the other in hexane. This type of critical behavior is accompanied by divergences in such quantities as the osmotic compressibility and the coherence length for concentration fluctuations. We have used the electric field of the laser pulse to induce a small amount of orientation order (Kerr effect) of the nitrobenzene molecules and studied its relaxation by using a delayed probe pulse to measure the birefringence as a function of time. The order we induced and measured has quadrupolar symmetry and the orientational order parameter can be represented as a second-rank tensor

$$Q_{\alpha\beta} = \frac{1}{2} < 3\zeta_\alpha\zeta_\beta - \delta_{\alpha\beta} >,$$

where $\zeta_\alpha, \zeta_\beta$ are the Cartesian components of the symmetry axis $\vec{\zeta}$ of the molecules and the average is performed over a small but macroscopic volume. The anisotropy in the optical frequency dielectric constant tensor (the birefringence) is proportional to $Q_{\alpha\beta}$. A phenomenological model for the dynamical behavior of $Q_{\alpha\beta}$ predicts an exponential relaxation

$$Q_{\alpha\beta}(t) = Q_{\alpha\beta}(0) \, e^{-t/\tau},$$

where the relaxation time τ is given by

$$\tau = \nu\chi.$$

Here χ is a generalized susceptibility, expected to be only weakly temperature-dependent, and the transport coefficient ν may be expected to be proportional to the shear viscosity of the fluid. We find the reorientation time of nitrobenzene molecules varies from 6.5 psec to 11.1 psec as the reduced temperature $t = T/T_c - 1$

varies from 10^{-2} to 10^{-4}. A quantitative analysis of our data is consistent with a weak ($t^{-0.045}$) divergence in agreement with renormalization group calculations[1] for the temperature dependence of the shear viscosity. The data and theoretical expression are shown in Fig. IX-2.
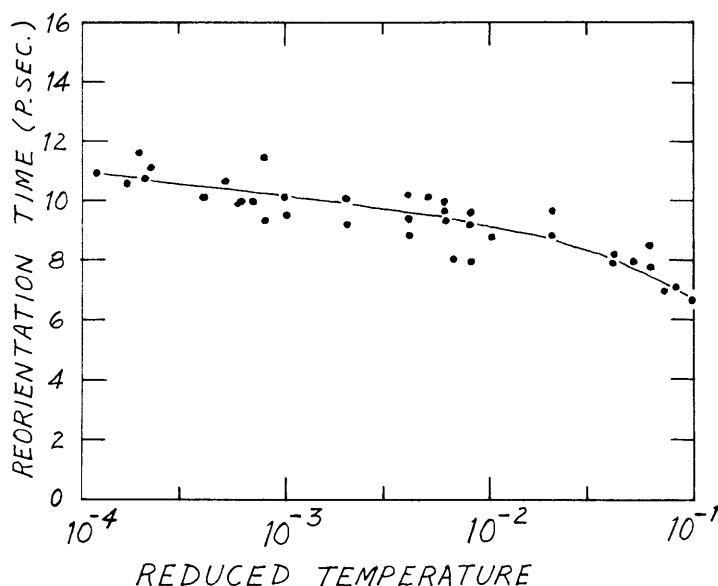

Fig. IX-2.

These experiments were extended to investigate the effect of restricted dimensions on the phase separation, by studying it in small-diameter pores in Vycor glass. They were unsuccessful because the glass provided too large an effective field on the sample and suppressed the phase transition. We are continuing by using suitable polymers to provide a random field. This is theoretically predicted to cause our three-dimensional system to behave as a one-dimensional system without the polymer would. Testing of these ideas is important to current developments in statistical mechanics.

References

1. D.E. Cooper and J.D. Litster, "Molecular Orientation Dynamics in Gels and Critical Mixtures," in R.M. Hockstrasser, W. Kaiser, and C.V. Shank (Eds.), Picosecond Phenomena. II (Springer, Berlin, 1980), p. 115.

3. TIME-RESOLVED SPECTROSCOPY IN LIQUID CRYSTALS

Lenn C. Kupferberg, Brent D. Larson, J. David Litster, Lorraine E. Solomon

We have used reorientation of dye probes in the isotropic and nematic phases of liquid crystals, and found no sign of the rapid (<10 ps) response reported by workers in France. We conclude the result was an artifact of their experiments.

Studies of nonradiative energy transfer in liuqid crystals and isotropic liquids continue, in order to elucidate both the energy-transfer mechanism and the short-range orientational order in these phases.