

Temperature dependence of the diffusion coefficient in a solution with a singularity

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1. Among the wide variety of binary liquid solutions there are so-called critical solutions with “upper” and “lower” stratifications points (critical points) and also solutions having some closed region in which the two components exist separately.

Yet another group of solutions have a "singularity." In such solutions there is no stratification of the components at any concentration or temperature, but there are a particular concentration and a particular temperature at which the light scattering intensity goes through a rather narrow maximum^{1,2} (this is the singularity), implying anomalously large fluctuations. Use of the Brillouin (or "Mandel'shtam—Brillouin") scattering spectrum to study the propagation of hypersound has revealed some interesting features and has shown that the anomalous fluctuations have their greatest effect on the central or Rayleigh line of the scattered light.²⁻⁴

In particular, study of the angular distribution of the intensity of the scattered light in a solution of β -picoline and water, which exhibits a singularity, has revealed that the intensity is very asymmetric, implying the formation of large clusters near the singularity.

No theory has so far been derived for the effect which explains the behavior of the solution near the singularity, but it has been suggested that the singularity is a drawn-out second-order phase transition.¹

The most effective way to study the nature of the singularity would seem to be to use correlation spectroscopy to study the temperature dependence of the mutual diffusion coefficient near the singularity. In this letter we are reporting the first results of such a study in a solution of β -picoline and water, which has a singularity.

2. The experiments were carried out with a Malvern Instruments K7023 correlator. The scattered light was excited by the $\lambda = 6328 \text{ \AA}$ line from an LG-52-1 He—Ne laser. A cell holding the test solution was placed on a G1-5 goniometer in a constant-temperature chamber. The cell was positioned and oriented very precisely by a method developed especially for this purpose, which uses an optical observation system. The goniometer and the adjustment system made it possible to set the desired angles and to measure them precisely. The temperature was held constant within 0.02°C . The samples were purified, and all dust was carefully removed from them in order to suppress parasitic scattering.

From the correlation functions obtained from the K7023 correlator we determined the half-width $\Gamma = q^2 D$ of the Rayleigh line,⁵ where $q = 4\pi n/\lambda \sin \theta/2$, n is the refractive index of the solution, λ is the wavelength of the exciting light, θ is the scattering angle, and D is the mutual diffusion coefficient. At a constant value of q , the mutual diffusion coefficient can be determined directly from the correlation functions. The presence of Brillouin components does not interfere with measurements of the Rayleigh line, since the widths of the Brillouin components are several orders of magnitude larger than that of the Rayleigh line. The diffusion coefficient was determined within an error of about 1.5%. A detailed description of the apparatus, all its characteristics, and the measurement procedure will be reported elsewhere.

3. The experimental results on the temperature dependence of the mutual diffusion coefficient D turned out to be surprising (Fig. 1). If the singularity actually is, to some extent, a characteristic of a second-order phase transition, then we would expect the diffusion coefficients to behave approximately as they do in, for example, an aniline—cyclohexane solution and similar solutions. In fact, we find nothing of the kind.

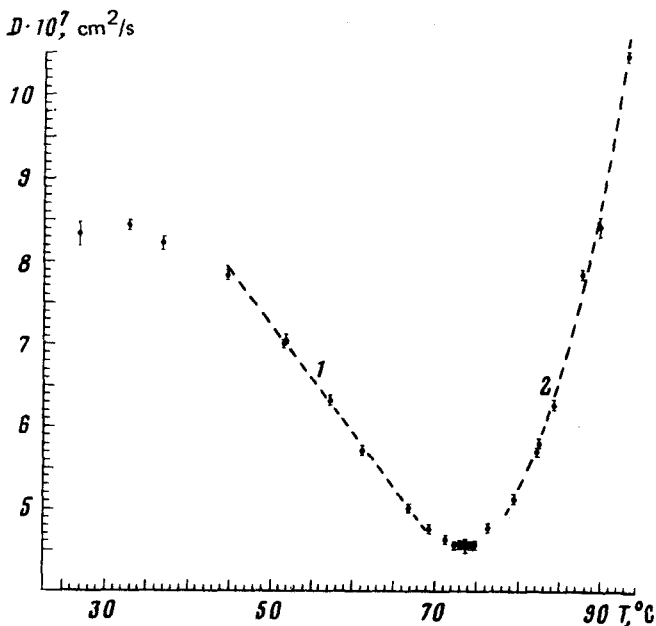


FIG. 1. Temperature dependence of the diffusion coefficient in a β -picoline–water solution, which has a singularity.

Figure 2 shows our measurements of the mutual diffusion coefficient of an aniline–cyclohexane solution, obtained with the same correlator; these data agree with those reported elsewhere. If we write the temperature dependence in the familiar manner $D = D_1 [(T - T_c)/T_c]^\nu$, then ν turns out to be approximately equal to the critical index of the correlation radius, $\nu = 0.63$. In the case of a singularity, the T dependence of D has a clearly defined minimum, where D has a value which is quite different from zero; this is a natural result, since no stratification occurs in the solution. The low-temperature and high-temperature branches of the curves, however (1 and 2, respectively, in Fig. 1), are different in nature.

We can attempt to describe both branches of the curve by an expression of the type

$$D = D_0 + D_i \left| \frac{T - T_i}{T_i} \right|^{x_i} \quad (1)$$

Holding D_0 constant for the two parts of the curve, 1 and 2, we can find D_i , T_i , and x_i by the method of least squares. It turns out that with $D = 3.58$ for curve 1 we have $D_1 = 50.8$, $T_1 = 350$ K, and $x_1 = 0.98$; for curve 2 we find $D_2 = 1.4 \times 10^{-6}$, $T_2 = 313$ K, and $x_2 = 5.35$. The temperature at the minimum of the curve (Fig. 1) is $T_{\min} = 346$ K. The x_i in expression (1) are so very different from the critical index ν and so very different from each other that at this point it is difficult to see how this effect could be directly related to a second-order phase transition. We must assume

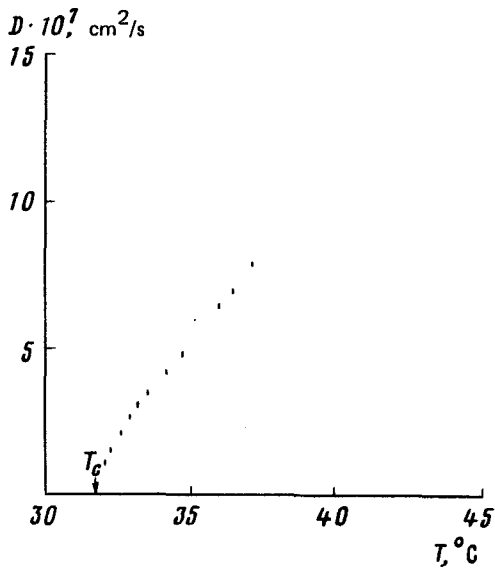


FIG. 2. Temperature dependence of the diffusion coefficient in an aniline-cyclohexane solution of the critical concentration.

that these quantitative results will serve as the starting point for the derivation of a theory for the effect.

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