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BROWNIAN MOTION NEAR THE CRITICAL POINT OF THE TWO-PHASE LIQUID-LIQUID EQUILIBRIUM

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Brownian motion of 0.23 micron mean radius particles near the critical mixing point is studied by dark-field microphotography. For a methanol-cyclohexane system, the Brownian particle diffusion coefficient decreases by a factor of two as the temperature approaches the critical point from the homogeneous region. The change of the system viscosity in the critical region is calculated. The results are discussed.

IN our previous work[1], we studied the Brownian motion of particles of mean radius roughly 0.8 μ in a phenol-water binary solution. A reduction of the Brownian particle diffusion coefficient by a factor 3–4 on approaching the critical mixing point was first brought to light there. In the discussion of those results, the question arose as to whether the observed effect might not be a consequence of the fact that the phenol-water system is a weak electrolyte, and the reduction of mobility of the Brownian particles be brought about merely by polarization of the solution and solvation formations.

In the present work, Brownian motion was studied at the critical point of the two-phase liquid-liquid equilibrium of the methanol-cyclohexane system, with upper critical mixing point (T_c = 45,33°C, C_c = 0.708 parts by weight of cyclohexane), which is not an electrolyte.

The Brownian particles were observed in a dark-field microscope. (see[1]). The thickness of the layer of solution in which the Brownian motion was observed was 0.2 mm. The solution was heated above the critical temperature, and thoroughly mixed to achieve homogeneity. Then the motion of the Brownian particles was photographed at various fixed temperatures. The system of thermostatic control enabled a given temperature of the solution to be maintained with accuracy ±0.005°C.

The mean square displacements of the Brownian particles in the horizontal plane were measured at regular intervals of time (2.5 sec.). Then the diffusion coefficient of these particles was calculated, using the Einstein-Smoluchovskii formula[2]

$$\langle(\Delta r)^2\rangle = 4D\Delta t; \tag{1}$$

Here, $\langle(\Delta r)^2\rangle$ is the mean square displacement in the horizontal plane at time Δt, and D is the diffusion coefficient.

We used a 0I-13 dark-field condenser with aperture 1.2, and an objective with magnification 58$^\times$ and aperture 0.85. This allowed us to observe finer particles. The Brownian particles on which observations were made were of glass, and had mean radius 0.23 μ. They were obtained by centrifugal fractionation of glass dust. The particle radius was determined by measuring their diffusion coefficients, and the viscosity of the solution, well away from the critical point, and using Einstein's formula[2]

$$D = kT / 6\pi r\eta, \tag{2}$$

where r is the particle radius, and η the viscosity of the solution.

The temperature dependence of the Brownian particle diffusion coefficient in the methanol-cyclohexane system is shown in Fig. 1. From the graph, it is clear that the diffusion coefficient of the system studied is reduced near the critical point by a factor of two approximately. At the present time, it is not possible to decide in favor of one or other of the mechanisms suggested to explain the observed reduction in diffusion. It is of interest, none the less, to examine them and to compare them with our experiment.

According to the fluctuation-dissipation theorem[3], the mean square displacement due to the Brownian motion after unit time is determined by the particle mobility alone. Assuming the absence of any frequency dependence of the mobility, and the applicability of the Einstein formula (2), we calculated the increase of viscosity of the investigated system from our data on the Brownian particle diffusion. We attempted to approximate the temperature dependence of the viscosity determined this way, in the range $T - T_c = 2°$ above the critical temperature, by the three functions:

$$\eta = A + Be^{-\gamma\tau}, \tag{3}$$

$$\eta = A - B\tau^{+\beta}, \tag{4}$$

$$\eta = A + B\tau^{-\alpha}, \tag{5}$$

where $\tau = (T - T_c)/T_c$, and A, B, γ, β and α are arbitrary constants, selected by a least squares method, in which all points have equal weight. Here A and B are measured in centipoise, while γ, β, and α are dimensionless constants.

It turned out that the function (3) is too crude an approximation, which cannot describe the behavior in any temperature interval adjoining the critical point.

The function (4) is a more suitable approximation. However, the temperature interval in which the approximation error is comparable to the dispersion of the data is only $T - T_c = 0.3°C$.

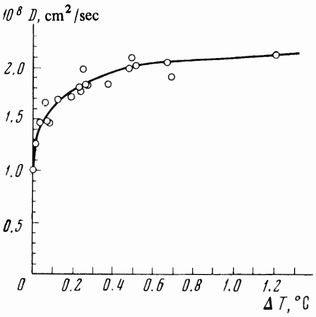

FIG. 1. The dependence on $\Delta T = T - T_C$ of the diffusion coefficient for Brownian particles of mean radius 0.23 μ near the critical mixing point of the methanol-cyclohexane system.

The function (5) is the nearest. This function approximates the data with mean square error, in ordinate, between 2.2 and 2.3%, throughout the temperature range in which measurements were taken. The error varies according as the exponent α varies between 0.15 and 0.25. In Fig. 2, the function (5) is plotted, in a logarithmic scale, for the exponent $\alpha = 0.20$ (A = 0.239 centipoise, B = 0.742 centipoise), which gives the least error in approximation, 2.2%. For values of α less than 0.15 and greater than 0.25, a significant systematic error appears.

The calculation shows that the greatest value of the viscosity, computed from the smallest experimental value of the diffusion coefficient, is twice as big as the regular part. Moreover, judging by the approximating function, the viscosity tends to infinity as T_C is approached. Such a conclusion is in sharp contradiction with the experimental measurements of viscosity by the capillary method[4] and the oscillating disc method[5], in which the observed increase in viscosity was not greater than 20%. If, in these works[4,5], the approach of the parameters T and C to the critical point, and the degree of thermodynamic equilibrium in the whole solution, were the same as ours, and not worse (which it is difficult to assess on account of the difference of methods), then another mechanism must be invoked to explain our results.

It is possible that a reduction of the mobility of particles of small dimensions arises, at constant viscosity, on account of an increase in the radius of correlation of fluctuations, in the critical region. In fact, we may suppose that a particle captures molecules, the motion of which is correlated at separations up to 1 μ, on our approach to the critical point.[6]. This is equivalent to an increase in the effective radius of the particle, and consequently, to a reduction of its mobility. Assuming that the inverse of the mobility depends linearly on the increment r_C to the particle radius, i.e., that $1/b \sim (r_0 + r_C)$, and that the regular part of the viscosity obeys Andrade's equation[4], we calculated the relative increase in the effective particle radius, r_C/r_0 (see Fig. 3).

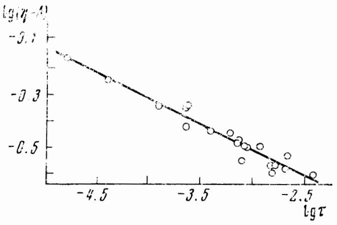

FIG. 2

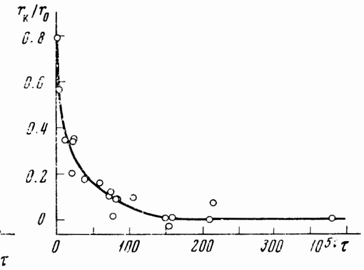

FIG. 3

FIG. 2. The dependenc of $ln(\eta - A)$ on $ln\,\tau$. The value A = 0.239 centipoise corresponds to a viscosity well away from the critical point for $\Delta T \sim 10°C$. The slope of the line is $\alpha = 0.2$, and $\tau = (T - T_C)/T_C$.

FIG. 3. The dependence of r_C/r_0 on $\tau = (T - T_C)/T_C$; $r_0 = 0.23 \times 10^{-4}$ cm is the mean radius of the particles, r_C the apparent increase of particle radius, connected with the radius of correlation of fluctuations.

In the capillary and oscillating disc methods, the characteristic dimensions are much greater than the radius of correlation, and therefore a large increase in viscosity is not observed.

So far, we have disregarded any frequency dependence of the mobility. The problem of the Brownian motion of particles near the critical point of a double solution has been considered, in a general form, by Patashinskiĭ et al.[7,8] In those papers, iterative calculation of non-linearity of the hydrodynamical equations revealed interference between the Brownian motion of a particle at different frequencies. Thus, it turns out that the mobility of such a particle is decreased even if the system viscosity remains constant. However, quantitative comparison of our results with the theory is not possible, owing to lack of the data needed in the computational formula[7,8] for the correction to the mobility of a Brownian particle.

In conclusion, we note that the results of our work on the Brownian motion in the phenol-water and methanol-cyclohexane systems do show that the reduction of mobility of the Brownian particles near the critical mixing point is not dependent on peculiar individual properties of the solutions, but, seemingly, depends on general properties of matter in the critical state.

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