

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

Ya. A. BAL'TSEVICH, V. G. MARTYNETS, and E. V. MATIZEN

Siberian Division of the Institute of Physico-technical and Radiotechnical Measurements

Submitted to JETP editor February 11, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 51, 983-988, (October, 1966)

Brownian motion of particles of diameter approximately equal to one micron is investigated at the critical point of two-phase phenol-water equilibrium. A sharp drop of the diffusion coefficient is found and is connected with the decrease of the particle mobility at the critical point, provided the Einstein-Smoluchowski equation is valid up to time intervals on the order of $\Delta\tau = 0.2-0.5$ sec, and provided the elementary displacements are random. The causes of the decrease of diffusion, which are related to the increase of viscosity of the solutions at the critical point, are discussed.

INTEREST in the study of Brownian motion at critical two-phase liquid-liquid equilibrium is connected in the first place with the study of the critical state and was stimulated primarily by the work of Krichevskii and his colleagues (cf. for example,^[1]). There is still no satisfactory microscopic theory which explains at least the fundamental critical phenomena, and the experimental results in this field have been contradictory. The study of Brownian motion may give certain information about the microscopic characteristics of a system that is in the critical state. However, we know of only one paper dealing with an experimental study of Brownian motion, in which diffusion of iodine at the critical point of carbon dioxide gas was investigated visually^[2].

At the critical point of two-phase solutions, fluctuations strongly increase in connection with the vanishing of the first derivative of the chemical potential with respect to concentration. This increase in the fluctuations of concentration and density explains, in particular, the phenomenon of critical opalescence. Along with the increase of fluctuations, the effective radius of correlation increases. If at the critical point the correlation of fluctuations extends over dimensions comparable with the particle diameter, then changes in the Brownian motion can be expected. Since the estimated effective correlation radius at the critical point is $0.1-1 \mu$, changes can be observed in this case in the Brownian motion of particles that are visible in an optical microscope.

For the study of Brownian motion at the critical point we used the microcinematographic camera

MKU-1. The investigation was carried out in phenol-water solutions with the upper critical solution point ($T_c = 65.8^\circ\text{C}$, $x_c = 34.0\%$ phenol concentration by weight). For the preparation of the chemically pure solutions, phenol was distilled both in vacuum and in glass distillation apparatus in an atmosphere of dry air directly before dissolving. The water was distilled twice. The critical temperature of solutions prepared by us was reproducible within several hundredths of a degree.

The cell for the observation of Brownian motion is shown schematically in Fig. 1. The observation of the motion of a particle at the critical point is difficult because of strong scattering of light (opalescence). For the observation of the motion of a particle under these conditions we used an OI-10 dark-field condenser with aperture 0.65 and an objective with magnification $20\times$ and aperture 0.40. The height of the space in which the particle

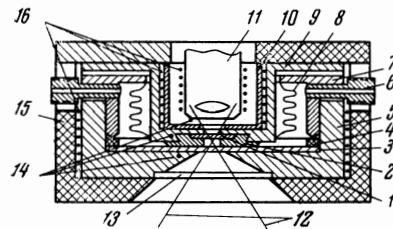


FIG. 1. Cell for the observation of Brownian motion at the critical point; 1—upper glass, 2—copper seal, 3—lower glass, 4—teflon spacer, 5—lower part of cell, 6—connecting pipe for filling, 7—insert, 8—sylphon bellows, 9—upper part of cell, 10—shell, 11—objective of microscope, 12—light rays from dark field condenser, 13—protective glass, 14—thermocouple junctions, 15—foam plastic box, 16—heaters.

moved was less than 0.3 mm. At such distances, opalescence no longer interferes substantially with the visibility of a particle illuminated by rays from the dark field condenser.

We could not introduce known suspensions of metals or particles of other substances into the phenol-water solution, owing to their coagulation and interaction with the studied solution. We observed, however, incidental particles present in the water after distillation. The particles settled down and we had to raise them from the bottom by stirring the solution. This was achieved by way of moving the upper part of the cell, which was connected with the lower part 5 by means of a siphon bellows 8.

Special attention was paid to attaining equilibrium in the investigated solutions. Thermostatic control was effected by proportional regulation of current of two heaters 16 in accord with the deviation of the temperature from the set value. Regulation was made automatic by using F-18 photoelectric amplifiers with accuracy $\pm 0.005^\circ$. To reduce the temperature gradients, the cell was made of copper and placed in a box of foam plastic. The body of the objective 11 was of bakelite with a wound-on heater 16 to prevent heat escape. Three copper-constantan thermocouple junctions 14, placed in the lower and upper part of the cell and in the objective, monitored the absence of any appreciable temperature gradients. To reduce the heating of the solution by the illuminating light, a water filter was placed in the path of the rays and proved to be sufficiently effective.

The time to adjust the temperature gradients and to establish equilibrium in the cell was no less than 30 minutes with stirring of the solution. The measurements themselves took on the average about 500 sec. The critical temperature was approached only from the homogeneous-region side. The onset of equilibrium was determined visually and photographically, from the absence of forced currents in the solution, which was revealed by the cessation of the drift of particles relative to one another and to the cell.

Measures were taken to get rid of the vibrations of the cell and to determine the effects of the vibrations. Thus, for example, the microscope was placed on a supporting plate weighing about 300 kg, and shock absorbers were used. The particles were observed following artificially produced vibrations and at the different times of the day. This ensured that the cell was well protected against practically all vibrations that could occur in our experiments.

The filling of the cell with homogeneous solution

of definite concentration was done through corresponding pipe connections, with its upper part raised. To equalize the pressure during the observations, the internal volume of the cell above the solution was vented to the atmosphere through a capillary of diameter 0.5 mm and length 150 mm. After filling the cell with the solution, the upper part of the cell was lowered until the copper seal was tight against the lower glass 3. The upper and the lower glasses and the annular copper seal between them, then formed a cylindrical volume of diameter 3 mm and height 0.3 mm, in which the motion of particles was observed.

The motion of one particle in the horizontal plane was recorded on motion-picture film and then projected on paper. The overall magnification was 2270. Four frames were photographed every 10 sec, and the exposures ranged from 1/25 to 1/50 sec. In 2.5 sec, a particle could undergo a displacement of several microns. The diameter of the particles was on the average 1–1.5 μ .

In our experiments we measured the projection of mean square displacement of a particle in Brownian motion on the horizontal plane in a unit time, and also the rate at which it settled down by gravity. Since some particles settled to a depth far greater than the mean-square displacement within the same time, it was possible, within the limits of error ($\sim 10\%$), to neglect the vertical Brownian motion and to calculate the rate of settling from the time and from the height to which the cell must be raised in order that the particle stay in the focus of the microscope's objective.

From the Brownian-motion data we determined the diffusion coefficient of a particle using the well-known Einstein-Smoluchowski formula:

$$\langle (\Delta r)^2 \rangle = 4D\Delta\tau, \quad (1)$$

where $\langle (\Delta r)^2 \rangle$ is the mean-square displacement in the horizontal plane within the time $\Delta\tau$. In the literature there are data on the measurement of viscosity^[3] and density^[4] of the phenol-water system in homogeneous state far from the critical point. Using these data and our values for the diffusion coefficient D and the settling rate v , one can determine the radius a and the density ρ_1 of the particles from Einstein's expression for the diffusion coefficient

$$D = kT / 3\pi a\eta$$

and from Stokes' law for the fall of a sphere

$$6\pi a\eta = \frac{4}{3}\pi a^3(\rho_1 - \rho_2)g / v$$

(the validity of these expressions for emulsions was verified by Perrin^[5]). The radius determined

in this way agreed within $\sim 30\%$ with the value obtained by direct comparison with an object-micrometer. This is evidence that we have observed the actual Brownian motion which is connected with thermal motion of molecules.

Near the critical point, the settling rate of particles diminishes sharply. The depth to which a particle settles becomes comparable with its mean free path in Brownian motion. In this case the accuracy of determining the settling rate decreased, and near the critical point we could not compare the values of the particle radius, as was done outside the critical region. Thus we could not confirm that in this region we were dealing with Brownian motion. However, it seems quite improbable that random displacements that are not connected with thermal motion are superimposed on the Brownian motion near the critical point, since we have shown that under the same conditions the motion of the particles is Brownian far from the critical point. Incidentally, we note that any random additional displacements can only increase the diffusion coefficient in the case of Brownian motion of a particle in our experiments.

Figure 2 shows the temperature dependence of the diffusion coefficient of a particle with diameter 1.4μ . From the diagram it is seen that if a homogeneous solution is cooled, the diffusion decreases to one-fourth its initial value, with a tendency to diminish to zero in the critical state. The decrease of particle diffusion begins at the temperature at which the opalescence seen in the microscope begins. The data pertain to the same particle. Qualitative observations made by us show that after the formation of phases ($T < T_c$) the coefficient of particle diffusion again increases sharply.

Figure 3 shows the time dependence of the rms particle displacement. The fact that the straight lines pass through the 0 means that the Einstein-Smoluchowski equation can be used for description of motion of Brownian particles with diameter about 1μ at the critical point, up to time intervals

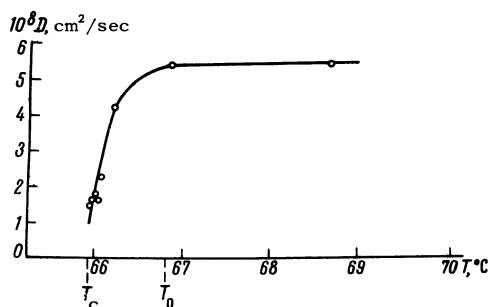


FIG. 2. Dependence of the diffusion coefficient D on the temperature T . T_c —critical temperature, T_0 —temperature of the beginning of visible opalescence.

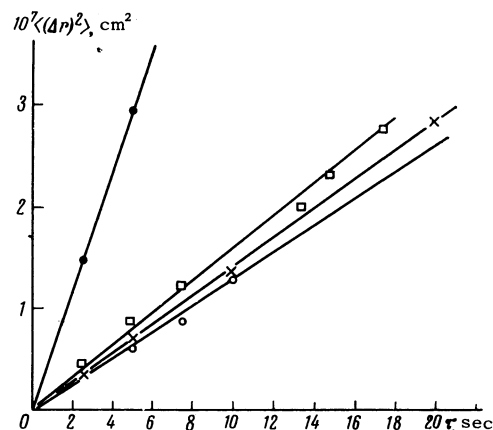


FIG. 3. Dependence of mean square displacement $\langle (\Delta r)^2 \rangle$ on the time τ . \circ , \times , \blacksquare —experimental points corresponding to Brownian motion in the critical region ($T - T_c < 0.1^\circ$) for various particles of different diameter in the range ($1.0 \mu < d < 1.5 \mu$), \bullet —the same far from the critical point ($T - T_c = 3^\circ$).

determined by errors of experiment.

To evaluate the reliability of these results, let us discuss the main errors of the experiment. We were measuring intervals of time, intervals of length, and temperatures. To determine the displacement of a particle, its image was projected on the screen in the form of a dark circular spot of diameter about 3 mm. The movement of the center of this spot could be measured accurate to ± 0.5 mm, which corresponds to an error of $\pm 0.25 \mu$ in the actual displacement of the particle. Thus, the displacement was determined inside the limits from r to $r \pm d/2$, where $d = 0.5 \mu$. This value corresponds to the resolving power of our optical system. The relative error of the smallest displacement fixed in our experiments was 10%. The minimum time intervals, $\Delta\tau = 2.5$ sec, were measured with a relative accuracy 2%.

The error in the measurement of temperature was mainly determined by nonuniformity of temperature distribution inside the volume in which the particle moved. This error can be estimated from the difference (not exceeding 0.02°C), in the indications of three thermocouples located in the cell at the locations shown in Fig. 1. The temperatures at these points themselves were maintained constant within $\pm 0.005^\circ\text{C}$.

The errors in the locations of the points in Fig. 3, which show the dependence of the mean square displacement on the time, increase with decreasing displacement and reach 20% for the point nearest to the origin, corresponding to $\Delta\tau = 2.5$ sec and $\Delta r = 1.9 \mu$. Each point represents 100–200 measurements at the same time for a given temperature. Within the limits of these errors, Eq. (1) is

valid down to time intervals less than the minimal actual time of observation (2.5 sec), at least down to 0.2–0.5 sec., which corresponds to displacements 0.15–0.4 μ .

The diffusion coefficients shown in Fig. 2 were determined from the slopes of the straight lines $\langle(\Delta r)^2\rangle = 4D\Delta\tau$ and therefore the error in their determination, due to inaccurate measurement of displacement, was less than the maximum (20%) and was about 7%. However, in the measurement of the temperature dependence of the diffusion coefficient of the same particle we had to reduce greatly the total time of observation for a given temperature, because of the limited time of stay of the particle in the given volume. Therefore the coefficients in Fig. 2 were calculated from a comparatively small number of measurements of elementary displacements (about 40 for each point), with certain points near the critical temperature excluded. For these points the rms displacements was calculated from 100–200 individual displacements. Estimates show that, owing to the small amount of statistical material, the error in determining the temperature dependence of the diffusion coefficient is $1/\sqrt{40} = 15\%$. Hence the total error of the ordinates of the points shown on Fig. 2 is 22%.

The histogram presented on Fig. 4 was plotted from 192 observed particle displacements near the critical point. The length of a step along the horizontal axis is equal to the resolving power of our optical system (0.5 μ). The rms particle displacement needed for the construction of the smooth curve was determined with 20% accuracy. The

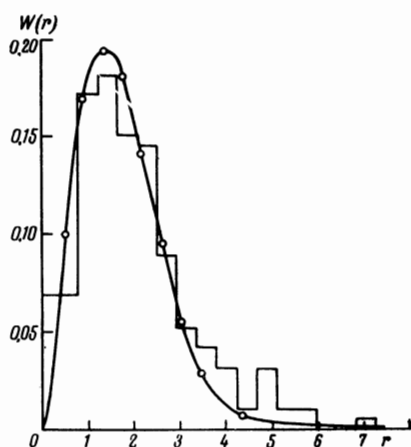


FIG. 4. Probability distribution of rms displacements of a Brownian particle with diameter about 1 μ near the critical point. The stepped line is the experimentally observed distribution. The smooth line is calculated according to the Gaussian distribution ($T - T_c = 0.07^\circ$, $[\langle(\Delta r)^2\rangle]^{1/2} = 1.9 \mu$).

above histogram illustrates very well the randomness of particle displacement, projected on the horizontal plane, in the critical region.

Since Eq. (1) holds in the critical point (as a consequence of the complete randomness of motion), it is natural to assume that the observed slowing down of diffusion is a result of the decrease of the particle mobility, in agreement with ideas of Leontovich^[6]. The decrease of mobility at the critical point may explain also the observed decrease of the rate of the particle settling by gravity.

Rough measurements of viscosity by the falling sphere method^[7] and by the capillary method^[8] show that the viscosity of a phenol-water solution and of a triethylamine-water solution increases by 30–40% at the critical solution temperature. It may be supposed therefore that the decrease of mobility of the particles at the critical point is due to the increase of viscosity, which is in reality greater than it was observed in the papers^[7,8] cited above. This conclusion is in agreement with the fact that near the critical point the particle settling depth h and its rms Brownian-motion displacement ($[\langle(\Delta r)^2\rangle]^{1/2}$) become commensurate at a certain temperature, since $h \sim 1/\eta$ and $[\langle(\Delta r)^2\rangle]^{1/2} \sim 1/\sqrt{\eta}$.

It is likewise not excluded that at the critical point the viscosity depends on the characteristic dimensions of experimental apparatus (on the radius of the falling sphere, the diameter of the capillary, etc). When the effective correlation radius becomes of the order of the characteristic dimensions (in our experiments it is the radius of the Brownian particles), an anomalous changes of viscosity can be expected, as was observed in our experiments. In the experiments of^[7,8] a relatively large characteristic dimension was chosen, hence the anomaly in the viscosity was by far less.

CONCLUSIONS

Experiments with Brownian motion have revealed that the diffusion coefficient of a particle with diameter of the order of 1 μ decreases by a factor of 4 at the critical point of a two-phase liquid-liquid equilibrium at rms mean free paths to 1.9 μ . It is shown that in this case Einstein-Smoluchowski equation is valid, at least down to intervals of time of the order of 0.2–0.5 sec., and that the particle displacements are random.

It is our pleasant duty to express our gratitude to the corresponding members of the U.S.S.R. Academy of Sciences, P. G. Strelkov and to Prof. I. R. Krichevskii for stimulating discussions.

¹I. R. Krichevskii, N. E. Khazanova, and L. S. Lesnevskaya, *Teplo- i massoperenos (Heat and Mass Transfer)* **2**, AN BSSR, 1962.

²I. R. Krichevskii, L. A. Rott, and Yu. V. Uspenskaya, *DAN SSSR* **163**, 674 (1965).

³A. M. Campbell and A. J. R. Campbell, *J. Am. Chem. Soc.* **59**, 2481 (1937).

⁴O. R. Howell, *Proc. Roy. Soc.* **A137**, 418 (1932).

⁵J. Perrin, *Atoms*, London, 1923 (Russ. Transl. Gostekhizdat, 1924).

⁶M. A. Leontovich, *JETP* **49**, 1624 (1965), *Soviet Phys. JETP* **22**, 1110 (1966).

⁷E. Matizen, *Dissertation, The Specific Heat and the Heat of Mixing of Double Liquid Solutions near the Critical Point*, 1957.

⁸V. K. Semenchenko and E. L. Zorina, *ZhFKh* **26**, 522 (1952).

Translated by O. Nankwo

115