Presence of submicroscopic air bubbles in water. Small-angle neutron scattering experiment

N. F. Bunkin and A. V. Lobeev
Institute of General Physics, Russian Academy of Sciences, 117942 Moscow, Russia

O. I. Vinogradova and T. G. Movchan
Institute of Physical Chemistry, Russian Academy of Sciences, 117915 Moscow, Russia

A. I. Kuklin
Joint Institute for Nuclear Research, Frank Laboratory of Neutron Physics, 141980 Dubna, Moscow Region, Russia

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The Guinier regime was discovered in the long-wavelength region of the scattered-neutron spectrum in an experiment on small-angle neutron scattering in purified water. This observation is a direct proof of the fact that particles whose size is comparable to the wavelength of the neutron radiation are present in the water. © *1995 American Institute of Physics.*

One application of small-angle neutron scattering is investigation of the structure of microscopic objects (protein molecules, micelles, polymers, etc.) dissolved in a liquid.[1] This liquid must be transparent to neutron radiation and it must not contain foreign particles that could give a scattering pattern similar to that of the experimental object itself. Water is considered to be an ideal solvent. It is obvious that for neutron-scattering experiments the water must be extremely clean. This is achieved by deionization and filtering, which remove particles larger than 100 nm.

The present work was stimulated by experiments on the study of stable submicroscopic bubbles in a liquid—nuclei of acoustic and optical (stimulated by a laser pulse) cavitation. Since the rupture strength of a liquid is at least an order of magnitude lower than its molecular strength, it is believed[2] that extremely small gas bubbles, which form the cavitation nuclei, are present in the liquid (since the liquid is studied under normal conditions, it is extremely unlikely that vapor bubbles are present). Many experimental and theoretical studies have shown that such submicroscopic bubbles must be stabilized; otherwise, they would dissolve.[3] Here stabilization is understood to be some mechanism as a result of which the surface tension forces are canceled and the gas pressure inside a bubble is equal to the hydrostatic pressure. Among the possible stabilization mechanisms, we single out the mechanism based on the solution of the van-der-Waals equation for a gas bubble in a liquid,[4] as well as the mechanisms based on the adsorption of ions at the bubble wall[5] and trapping of gas bubbles inside cracks in the vessel walls or solid microparticles in the liquid.[6–8] All of these mechanisms are disputable: For example, if the liquid is contaminated with solid microparticles, it is natural to assume that cavitation should stop after the liquid is cleaned carefully enough; this, however, does not happen.

In Ref. 9 (where the model proposed in Ref. 5 is elaborated) it was shown qualitatively that far from the boiling point a liquid with a small ionic impurity contains submicroscopic bubbles which are stabilized by the adsorption of ions of one charge at the wall of such a bubble. This produces a negative Coulomb pressure that compensates for the surface tension and the bubble is stable (such bubbles were named bubbstons (bubbles stabilized by ions). In accordance with the estimates made in Ref. 9, the critical size of a bubbston in water is 100 Å . Objects of this size can be studied by means of small-angle neutron scattering, since neutron wavelengths lie in the range 1–10 Å and 100-Å objects can be observed at small angles in the scattering spectrum.

The experiment on small-angle neutron scattering was performed on the IBR-2 facility at the Joint Institute for Nuclear Research in Dubna. The diameter of the neutron beam in the cell was 2 cm. This setup has a number of advantages over other setups: Specifically, normalization is performed periodically, which eliminates different factors associated with the change in beam power in the course of the experiment.[10] In the experiments on small-angle neutron scattering, there arises the question of the contribution from the quartz glass used for the cell, since the glass can make both incoherent and coherent contributions to the spectral pattern. Inelastic neutron interactions in the quartz glass can also make a contribution. It is very important, therefore, that the quartz used to make the cell windows be pure. We employed a cell manufactured by the HELMA Company. The cell was 1 mm long in the direction of the beam. This length eliminated multiple scattering. We note that the cells manufactured by this company are widely employed in neutron-scattering experiments. Preliminary measurements showed that in the long-wavelength region the scattering spectrum of an empty cell contains only an incoherent component (isotropic background not associated with the specific atomic configuration). It is wrong to simply subtract out the spectrum obtained with an empty cell, since the contribution from the cell wall farthest from the reactor to the scattering pattern depends on the beam power and therefore it is different for the empty and filled cells. As follows from what we have said above, however, the error associated with the incorrectness of subtracting the contribution from the empty cell can affect only the determination of the incoherent component of the spectrum. As will be shown below, the incoherent background is not important for us.

The experiments were performed with light water (H_2O) and heavy water (D_2O), which was purified by using the standard "Millipore" purifier (the resistivity of the water was 18 $M\Omega \cdot cm$). After purification, the water was subjected to vacuum degassing for several days. Unfortunately, we were not able to check the gas content during the degassing process. However, the degassing procedure itself does not contribute additional contaminants, as can be verified by comparing the scattering spectra for the degassed and ordinary water. The gas content in the water did not increase appreciably in the process of filling the cell (several seconds duration) with the degassed water. After the spectrum of the degassed water was obtained, the same cell was used to obtain the spectrum of ordinary (not degassed) water. In so doing, the position of the cell relative to the beam axis was not changed. Next, the spectrum of the empty cell was obtained. Both the empty and filled cells were exposed to the beam for 3 h.

Figure 1 shows the logarithm $\ln I$ of the normalized scattering intensity versus the squared scattering vector $Q^2=[(4\pi/\lambda)\sin(\theta/2)]^2$ (measured in $Å^{-2}$) in a wide range of

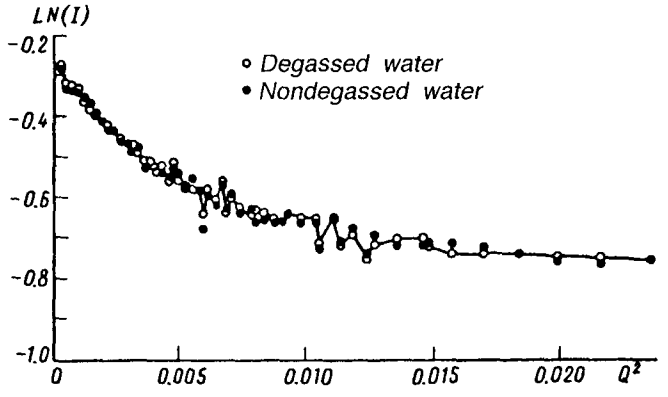

FIG. 1. Logarithm $\ln I$ of the small-angle neutron-scattering intensity versus Q^2 (Å^{-2}) for degassed and not degassed H_2O. The Guinier regime is characterized by the sharper drop of the curve in the long-wavelength region.

scattering angles for degassed and not degassed H_2O; the contribution from the empty cell is subtracted out. The so-called Guinier regime[11] can be easily identified in the plot. This regime is characterized by the fact that in the long-wavelength region the slope of the curve obtained is different from the slope of the rest of the spectrum (estimates show that this section cannot be associated with the inelastic contribution to the small-angle scattering pattern). This attests to the presence in the liquid of particles whose size is unequivocally characterized by the so-called gyration radius. The gyration radius corresponds to the boundary of the Guinier regime on the abscissa. The section of the spectrum, which corresponds to the Guinier regime, is approximated well by a straight line $y=ax+b$ with the parameters $a=-63\pm2$ and $b=-0.291\pm0.005$ for water which has not been degassed and $a=-59\pm2$ and $b=-0.295\pm0.004$ for degassed water. Extrapolation gives for the gyration radius the value 14 Å; in the approximation of a spherical object, we find that its diameter $d \simeq 36$ Å . A similar procedure for D_2O gives $d\simeq40$ Å. The size of the objects which give rise to the Guinier regime in the neutron scattering spectrum is thus close to the theoretical size of a bubbston.

The theoretical estimate in Ref. 9 gives for the bubbston concentration in water $C\sim10^{11}$ cm^{-3}. Since the density of nuclei in a liquid is higher than in microscopic gas bubbles, it is natural to expect that the incoherent component of the spectrum (determined by the scattering by spatially uncorrelated nuclei) should be higher after degassing. We assume that as a result of degassing, the bubbstons vanish completely (although this assumption is certainly incorrect, since it is impossible to remove dissolved air completely during degassing and, in addition, the Guinier regime occurs for both degassed and not degassed water) and bubbstons do not contain nuclei which scatter neutrons. Estimating C and knowing d, we can then easily see that the scattering volume occupied by the neutron beam inside the cell should increase by 10^{-9} cm^3 as a result of degassing. It is impossible to observe such a small change in the scattering volume in the incoherent component. As one can see from the figure, the difference in the spectra for the degassed

and not degassed water is very small, which could be evidence in support of the model considered here. However, this difference falls within the statistical error and cannot be used for estimates.

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