Microscopic Observation of Order-Parameter Fluctuations in Critical Binary Fluids: Morphology, Self-Similarity, and Fractal Dimension

P. Guenoun, F. Perrot, and D. Beysens

Service de Physique du Solide et de Résonance Magnétique, Centre d'Etudes Nucleaires de Saclay-Saclay, 91191 Gif-sur-Yvette CEDEX, France

(Received 21 March 1988; revised manuscript received 1 June 1989)

We report what we believe to be the first direct visual observations of order-parameter fluctuations near a critical point. The observation has been made in a number of binary fluids which belong to the same universality class as the 3D Ising model. New properties can be investigated, in particular, the morphology of the fluctuations when they are considered as clusters. This analysis has demonstrated the self-similarity of the clusters and provided a measurement of a fractal exponent $D_f = 2.8 \pm 0.1$.

PACS numbers: 64.60.Ak, 05.40.+j, 05.70.Jk

A large number of experiments dealing with the critical behavior of gas-liquid and binary fluids systems (which belong to the same universality class as the 3D Ising model) has been performed and go back to over a hundred years. Many of them are scattering experiments. It is very surprising that, except for an attempt by Debye and Jacobsen,[1] no observation of the order-parameter fluctuations in direct space have been reported. However, the direct observation of critical fluctuations may help to answer basic questions such as, e.g., the possible correlation between thermal and percolation critical points. This connection rests on a precise criterion to define clusters starting from fluctuations, and this up to now is lacking. We present here the results of microscopic observations of concentration fluctuations in a number of binary fluids (Fig. 1). The concentration difference $M = c - c_c$, with c_c the critical concentration, is the order parameter. Fluctuations appear as domains whose intensity is different from the mean intensity of the picture. These fluctuations are detectable only when the system is close to criticality. The fact that the ultimate picture element (pixel) is greater, or at best equal, to the correlation length (ξ) of the critical fluctuations implies that the fluctuations extend on a range larger than ξ. However, this surprising observation agrees with critical-point phenomena as reported below. This justifies undertaking a detailed investigation of the fluctuations morphology which appear to be self-similar with a fractal exponent $D_f = 2.8$.

Experimental.—The binary mixtures are prepared at critical concentration by weighing the components directly in the experiment cell; the relative error on this concentration, including that on c_c, is of order 10^{-2}. The components are of the best available commercial quality. The cell is made of fused quartz, with two parallel 20-mm-diam optical windows separated by a 5.00-mm spacer for observation. It is immersed in a water bath with permanent filtration giving a temperature stable to within ± 0.2 mK over several hours. The optical setup is the same as already described in Ref. 2, however, the light scattering part was not used. It is basically formed of a white-lamp source which provides a nearly parallel beam at the level of the sample and of a high-quality photo lens (50- or 100-mm focal length, 1.0 or 2.0 aperture number). This lens directly forms a magnified image of the fluid on the sensitive surface of a video camera (Newicon). This camera is connected to a U-matic video tape and/or to a computer for image analysis. The analog-to-digital conversion is performed with 64 levels over 256×256 pixels. All further calculations are performed within 16 bits accuracy. The use of more monochromatic light by means of a yellow filter does not change the results; laser light, because of its large coherence length, blurs the image through many interference patterns. It must be noted that a study in direct space is hampered by specific problems. The resolution remains limited to a dimension of order the wavelength of light, that is of order 1 μm; complementarily the field of view is also limited, typically to a few 100 times the resolution. Moreover, the image that has to be analyzed is two dimensional, and can be, according to the depth field, either a section or a projection, or both, of the 3D object. In this study the large aperture angles of the lenses ensure that the depth of field remains of order of the resolution, and the image can be considered as a mere 2D section of the 3D system.

The formation of the image is due to the interference of the transmitted beam with the very intense light (Is) that is scattered by the refractive index fluctuations at small angle (θ). Indeed at the small angles Is varies with the transfer wave vector K as $\mathrm{Is}(K) \sim K^{-2} \sim \theta^{-2}$. The small refractive index modulations always remain proportional to the concentration fluctuations, that is to the order-parameter fluctuations $\delta M(\mathbf{r})$ (here $\mathbf{r}$ is the space variable). The above arrangement is called "heterodyne,"[3] and allows phase modulations to be converted into intensity modulations on the video tube plane (x,y). This interpretation of the image formation has been checked by comparing the same fluctuations pattern obtained this way and by using a strioscopic ar-

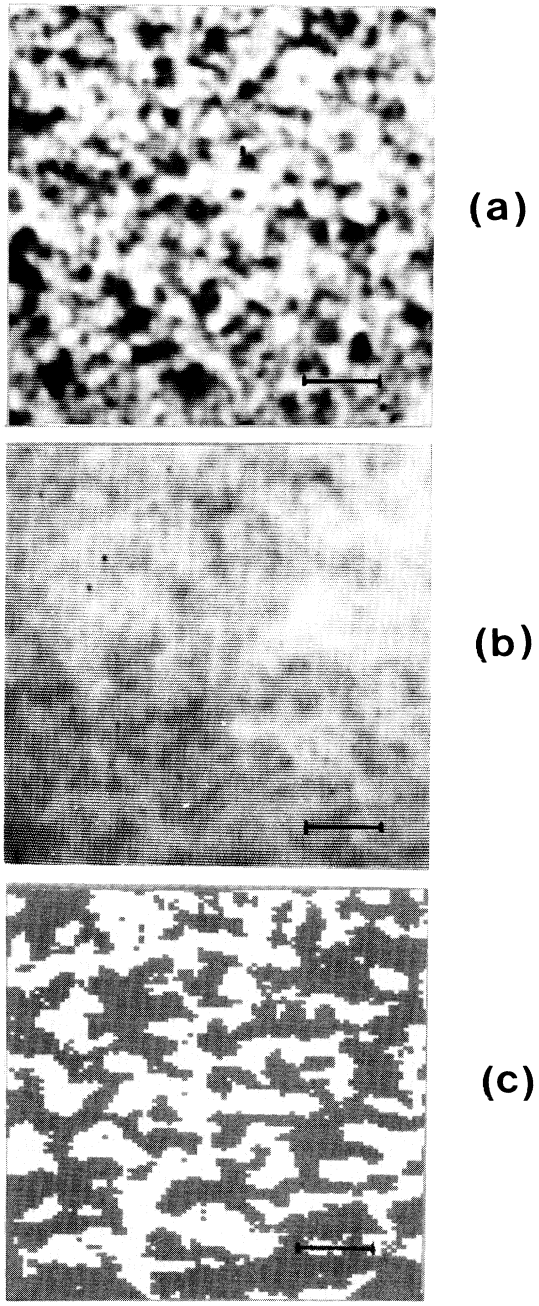

FIG. 1. Pictures of concentration fluctuations in a binary fluid of isobutyric acid and water: (a) photos at $T-T_c=1$ mK and (b) 16 mK (the bar corresponds to 40 μm); (c) a picture at 1 mK digitized with two intensity levels (black and white) around a threshold which is here the mean intensity. This method allows the fluctuations to be considered as (black and white) clusters.

rangement ("homodyne"), where it is the square of the fluctuations which is detected. With $i(x,y)$ the detected intensity, and $I(0)=|E(0)|^2$ the transmitted intensity at $K=0$, one can write $i(x,y)-I(0)\propto|E(0)|\delta M(x,y)$ at first order in δM. The fluctuations of intensity $[\delta i(x,y)]$ that are detected on the video tube therefore reproduce the fluctuations of the order parameter in the optically conjugated plane. These fluctuations are, however, integrated over a volume v defined by the product (pixel area)$\times$(depth of field). The intensity of a pixel is thus, $\delta i(x,y)\propto\langle\delta M(x,y)\rangle_v$. Here $\langle\rangle$ denotes a spatial average. Typical photos at different temperatures are shown in Fig. 1. Useful information can be obtained in a practical range $T-T_c=1$–20 mK, where T is the absolute temperature and T_c is the critical temperature. Although the contrast of these fluctuation patterns vanishes at large T, their aspect does not qualitatively change. Note that before analysis, each of these pictures has to be corrected for the parasitic modulations due to the spatial response of the tube, the inhomogeneity of the incident light, dusts on the windows, etc. Since the modulation by the fluctuations is small compared to the average intensity, a first-order correction consists in subtracting an image taken under the same conditions but at higher temperature ($T-T_c=40$ mK) where the fluctuations are no longer visible. Tests have been performed in a number of mixtures: nitrobenzene-*n*-hexane (NH), isobutyric acid-water (IW), lutidine-water (LW), deuterated cyclohexane-methanol (C*M), and cyclohexane-deuterated cyclohexane-methanol (CC*M). The refractive-index difference of these components varies over a large scale. All these systems supported, however, the same observations. We will report here only the results obtained with the IW system, whose relevant parameters are $T_c=299$ K, $c_c=0.389$ (mass fraction of acid), and correlation length $\xi=3.6[(T-T_c)/T_c]^{-\nu}$ Å.

Fluctuations and critical-point phenomena.—The contrast of the image modulations is very low, and we checked carefully that they were really caused by the order-parameter fluctuations. In order to demonstrate their bulk origin, we looked at different planes in the bulk and also stirred the system. We also systematically changed the concentration of the mixture around c_c; these fluctuations disappears when $|c_c|>5\times10^{-2}$. The dynamics of such fluctuations are striking; they develop and vanish at a rate which is a function both of their size and of the temperature. If one selects a fluctuation wavelength (Λ) by allowing only the light scattered at $K=2\pi/\Lambda$ to form the image (e.g., by putting a mask with an ex-centered pin hole in the focal plane of the lens), the corresponding typical frequency goes to zero with decreasing K and decreasing $T-T_c$. This is in full agreement with critical dynamics.[4] We did not investigate this aspect further because the information that can be obtained seemed to be the same as those inferred by light scattering techniques. We stress that the shortest relaxation time involved in our analysis (60 ms for Λ of the order the optical resolution and $T-T_c=16$ mK) remains larger than the integration time 40 ms. In fact, the quantity $\langle\delta M(\mathbf{r})\rangle_v$ can be considered as a "block spin variable" where the order parameter is averaged over v.

The fluctuations we observe are the remaining critical fluctuations once renormalized at the scale $v^{1/3}$, and since this scale is still of order ξ, it is not surprising that fluctuations are detected. Since the image intensity $\delta i(\mathbf{r})$ is proportional to the order-parameter fluctuations $\langle \delta M(\mathbf{r}) \rangle$, the probability distribution of δi, i.e., $P(\delta i)$, can be related to f through,

$$P[\delta i(\mathbf{r})] \sim P[\langle \delta M(\mathbf{r}) \rangle_v] \sim \exp\{-(1/k_B T) F[\langle \delta M(\mathbf{r}) \rangle_v]\}, \quad (1)$$

with k_B the Boltzmann constant and $F[\langle \delta M(\mathbf{r}) \rangle_v]$ the free energy in the volume of investigation (v). It thus becomes possible to directly determine the δM dependence of F. The result is that P is a Gaussian function, whose width is temperature dependent. 2D Fourier analysis of the pictures was also performed, giving access to the structure factor of the fluctuations. This quantity did not reveal any correlation length greater than ξ. The existence of nonrandom fluctuations on a scale larger than ξ might appear to contradict the ordinary notion of criticality. However, ξ is nothing else than the mathematical definition of the length over which the fluctuation correlation function has decreased by the factor $1/e$. Correlations at a scale larger than ξ exist, but they are rare. As an illustration of this remark, the reader should compare our Fig. 1 with the Figs. 4–8 of Ref. 5 where numerical simulations of the fluctuations in a 2D Ising model are reported. In particular, the dimension of the block spin variable is comparable to our experimental resolution. In these simulations, one or two fluctuations 20 or 50 times longer than the correlation length are clearly evidenced.

Fluctuations morphology.—Fluctuations are evidenced as local intensity deviations (δi) from the average intensity of the picture. This quantity is defined as the intensity for which the histogram is maximum. The shape of a fluctuation can be, therefore, determined by dividing the image into regions where $\delta i > 0$ (say white region) and regions where $\delta i < 0$ (say black region). In this case (Fig. 1), the black or white regions equivalently appear as being formed of highly interconnected domains. If one considers a partition of the picture with another threshold criterion, e.g., $\delta i > \delta i_0$, one forms a minority region (white if $\delta i_0 > 0$), where interconnectivity has been lowered, and a majority region (black if $\delta i_0 < 0$), where it has been increased. The choice of δi_0 defines a fluctuation as belonging to the minority region. This procedure has the advantage of allowing various definitions of clusters to be given, the number of clusters decreasing when δi_0 increases. A procedure of exploration of each domain has been developed, which determines for a domain including n pixels (x_i, y_i) of center of mass (x_G, y_G) a radius of gyration,

$$R = \left[\frac{1}{M} \sum_{i=1}^{n} [(x_G - x_i)^2 + (y_G - y_i)^2] \right]^{1/2} \quad (2)$$

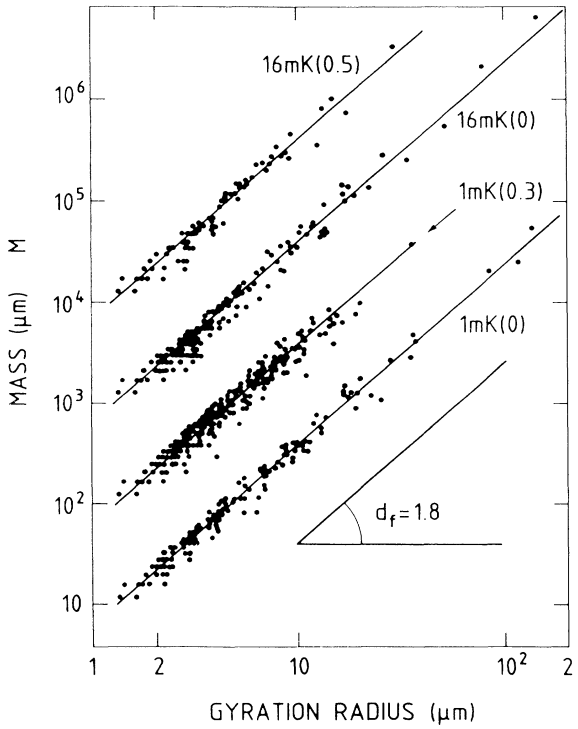

FIG. 2. Mass of clusters vs the gyration radius, showing the self-similarity of their morphology. Typical data at two temperatures are reported, with typical intensity thresholds in brackets. These are expressed as deviations from the average intensity in the units of the fluctuation histogram full width. All data overlap, and for clarity they have been shifted by one decade.

and its mass $M = n$. Self-similarity of the domains is related to the existence of a power-law dependence between R and M:[6] $M \propto R^{d_f}$, where d_f is a fractal dimension. In order to check our procedure, we considered self-similar compact domains where d_f was expected to be 2 (dimensionality of the image). We formed the image of a set of ten black disks of different radii, which was then submitted to the standard procedure (digitization, calculation). A power-law behavior has also been found and a least-squares fit provided the value for the exponent: $d_f = 2.00 \pm 0.05$. When $\delta i_0 = 0$, for all temperatures, a power law has been obtained over nearly four decades, the largest domain having a gyration radius of order of the field of view. One finds for $T - T_c = 1$–20 mK (Fig. 2): $d_f = 1.8 \pm 0.1$. Here the uncertainty has been estimated from the analysis of several independent pictures. It appears that the exponent is not temperature dependent. When $\delta i_0 \neq 0$, then the power law $M \propto R^{d_f}$ still holds, but the extension of the largest domain is reduced. For thresholds $\delta i_0 \in]0\text{–}0.5]$, in units of the full width of the fluctuation intensity histogram, a value slightly smaller is obtained, $d_f = 1.7 \pm 0.1$. Since the pictures that we have analyzed can be considered as

2D sections, we can deduce the fractal dimension (D_f) of the 3D fluctuations through the relation:[6] $D_f = d_f + 1 = 2.8 \pm 0.1$ ($\delta i_0 = 0$). Note that deviations from this relationship could be caused by the finite resolution of the optics and the fact that experimentally the section is not perfect. Its validity under our experimental conditions has been checked by varying the resolution and the depth of field by a factor of 4. No changes have been detected in the self-similarity of the domains and the value of d_f.

Discussion.— In terms of percolation phenomena, the occurrence of an infinite cluster can be associated with the divergence of the fluctuations near the critical point. For this purpose, a precise (and somewhat formal) definition of the clusters was made,[7-9] which allowed considering the fractal nature of fluctuations as resulting from the percolation behavior. The corresponding fractal exponent so deduced is $D_f = D - \beta/\nu = 2.5$ for the Ising model. (The classical Ornstein-Zernike form of the structure factor, with a tail in K^{-2}, is caused by the polydispersity of the clusters.[10]) The result $D_f = 2.5$ has been established at the critical point and cannot probably directly be compared with ours ($D_f = 2.8$), deduced in a kind of "crossover" range. Nevertheless this region keeps track of criticality, not only qualitatively, by making the order-parameter fluctuations observable, but also quantitatively, the fluctuation morphology being characterizable by a fractal exponent. Note that our procedure to determine fluctuations with respect to the threshold δi_0 means that we use a deterministic criterium that rejects the too big clusters. This is also the philosophy adopted by Coniglio and Klein[7] with the difference they have chosen a probabilistic criterium. Both analyses show that no single definition of fluctuation exists. We have chosen the simplest procedure but refinements can be found in the literature.[11]

P. Bonville is especially acknowledged for his help with computing. We gratefully thank C. K. Chan, E. Brezin, C. Bervillier, C. Bagnuls, H. Herrman, and M. Daoud for useful discussions.

[1]P. Debye and R. T. Jacobsen, J. Chem. Phys. **48**, 203 (1968).

[2]F. Perrot and D. Beysens, Rev. Sci. Instrum. **58**, 183 (1987).

[3]See, e.g., B. Chu, *Laser Light Scattering* (Academic, New York, 1974).

[4]K. Kawasaki, Ann. Phys. (N.Y.) **61**, 1 (1970); R. Perl and R. A. Ferrell, Phys. Rev. A **6**, 2358 (1972).

[5]A. Bruce and D. Wallace, in *The New Physics,* edited by P. Davies (Cambridge, England, 1989), pp. 236–267.

[6]See, e.g., B. B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, San Francisco, 1982).

[7]A. Coniglio and W. Klein, J. Phys. A **13**, 2775 (1980).

[8]K. Binder, Ann. Phys. (N.Y.) **98**, 390 (1976).

[9]F. Family, J. Stat. Phys. **36**, 881 (1984).

[10]J. F. Martin and B. J. Ackerson, Phys. Rev. A **31**, 1180 (1985).

[11]Z. Alexandrowicz, Phys. Rev. Lett. **60**, 669 (1988).

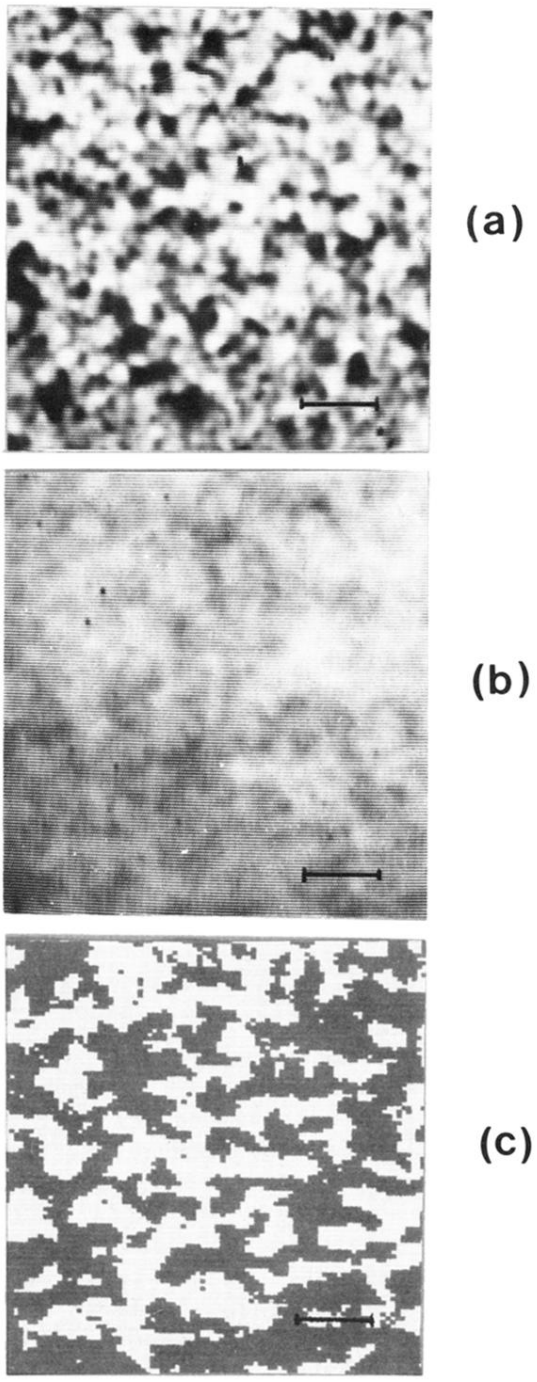

FIG. 1. Pictures of concentration fluctuations in a binary fluid of isobutyric acid and water: (a) photos at $T - T_c = 1$ mK and (b) 16 mK (the bar corresponds to 40 μm); (c) a picture at 1 mK digitized with two intensity levels (black and white) around a threshold which is here the mean intensity. This method allows the fluctuations to be considered as (black and white) clusters.