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Direct observation of critical fluctuations

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Abstract. By performing careful observations very near the critical point of binary fluids or microemulsions using an optical microscope, it is possible to obtain a resolution of the order of the correlation length and observe fluctuations in the order parameter (concentration). The origin of these fluctuations is discussed by comparing the picture element to a spin block variable within 3D Ising model. It follows that the free energy of the configuration can be obtained from the histogram of the fluctuation amplitudes. Black and white domains can be defined by clipping these fluctuations relative to a mean value. Domains are seen to be self-similar in shape, with a fractal dimension of 2.8. The origin of this self-similarity is discussed and a possible relation with percolation models is envisaged.

1. Introduction

The behaviour of fluids and fluid mixtures, which belong to the same universality class as the 3D Ising model, has been much investigated and has led to a deep understanding of critical behaviour [1]. From experimental methods, however, only spatially averaged information can be obtained. The order parameter fluctuations are investigated through their correlation function or equivalently through their structure factor $S(\boldsymbol{k})$ (here $\boldsymbol{k}$ is a wavevector). The typical length ξ (the 'correlation length') at which $S(\boldsymbol{k}\xi)$ takes the value $\frac{1}{2}$ is used as a measurement of the approach of the critical point. Although the static statistical properties of critical fluctuations are well known, as are, to a lesser extent, the corresponding dynamical properties, no reliable local investigation method is available. A pioneering attempt by Debye and Jacobsen [2] was performed in the late 60s. They used a phase-constrast microscope to observe, in direct space, concentration fluctuations that develop near the critical point of a polymer–solvent system of polystyrene and cyclohexane. They immersed both the microscope and the sample in an air thermostat which was controlled to within ± 0.02 K; this thermal accuracy did not allow clear separation of the critical fluctuations from the onset of phase separation. No images were reported.

We believe that the local and direct observation of critical fluctuations should elucidate some aspects of critical phenomena. For instance, it becomes possible to study the statistics of such fluctuations, whose high degree of correlation would allow the Wilson effective free energy to be measured. The morphology of these fluctuations is striking, and the measure of a fractal exponent would provide new insight into the possible connection between thermal and percolation critical points, where the fluctuations are considered as domains percolating at T_c.

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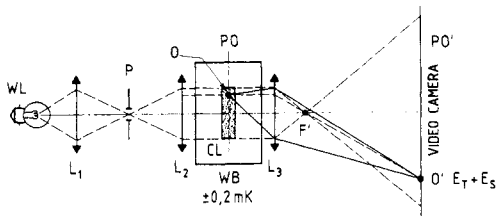

Figure 1. Schematic diagram of the apparatus. CL: sample cell containing the binary fluid; WB: water bath for temperature control; WL: white lamp source; L_1, L_2: lenses; L_3: high-quality, large-aperture objective; F': focus of L_3; P_1: pinhole; PO: plane of the object, whose image is in PO'; O: point object in PO, whose image is at O'; – – –: path of the direct light, with transmitted field E_T; ——: path of the scattered light, with scattered field E_S.

There are also a number of problems of current interest that could be studied. The two, four-point correlation functions could be determined; the statics and dynamics of fluctuations under an external field (shear flow, thermal gradient, gravity . . .), at a solid–mixture interface or between the two phases below T_c could be investigated. Dynamics related to a distribution of length scales (stretched exponential) could also be investigated [3].

2. Experimental details

Binary liquids were used because they allow a close approach to T_c to be made without noticeable gravity effects. Thermal stabilization was of the order ±0.2 mK over a few hours, and was provided by a water bath. A magnified image of the bulk system was directly formed on the sensitive photocathode of a video camera (figure 1). The ultimate optical resolution (one pixel) corresponds to 1 μm in the sample. For this resolution the field of view is of the order of 250 μm. The large aperture angle of the lens ($\simeq 90°$) ensured that the image was the projection of the bulk within a layer whose thickness was of the order of the resolution limit. The image was therefore simply a section of the bulk sample.

The cell was illuminated by a nearly parallel white light beam (figure 1), whose temporal coherence length was of the order of one μm. The image of the refractive index fluctuations $\delta n(\boldsymbol{r}, t)$ can be interpreted as being formed by the interference of the transmitted beam (E_T) with the light scattered by the above fluctuations (E_S).

The fact that $\langle \delta n^2 \rangle$ increases near T_c makes E_S increase, so the contrast $\mathscr{C}$ of the above fluctuations becomes larger. This contrast decreases with $T - T_c$. The intensity detected on the video camera plane (x, y) can be thus written as

$$i(x, y) \propto |E_0|^2 + E_0 E_S(x, y) \propto 1 + \mathscr{C}(T - T_c)\,\delta n(x, y, z = z_0, t). \tag{1}$$

Here $z = z_0$ denotes the coordinate of the section. Since the refractive index fluctations are proportional to the order-parameter fluctuations δM (here the concentration fluctuations), equation (1) becomes

$$i(x, y) = i_0 + \delta i(x, y, t) \tag{2}$$

with

$$\delta i(x, y, t) \propto \delta M(x, y, z = z_0, t) \tag{3}$$

where i_0 is the average intensity.

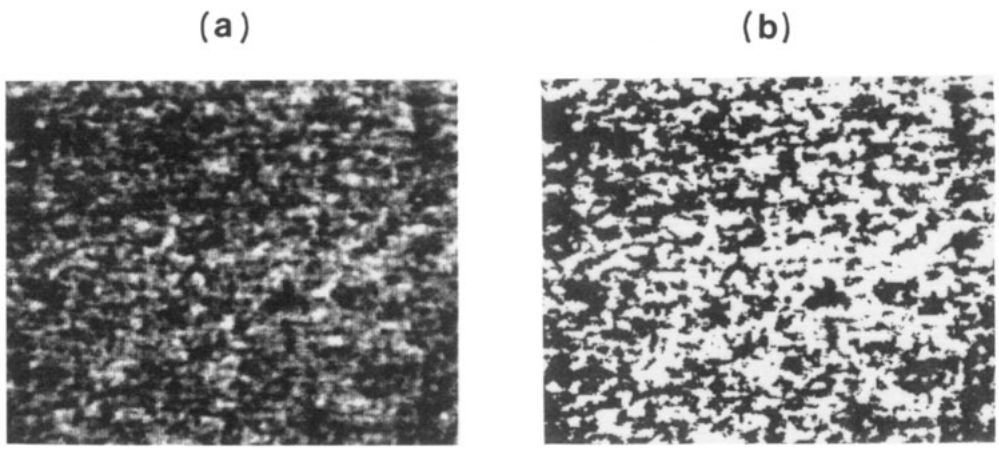

Figure 2. Fluctuation pattern (*a*) before and (*b*) after digitization at two levels ($T - T_c$ = 1 mK). The largest dimension corresponds to 600 μm.

In terms of image analysis, the signal that is obtained is discrete and corresponds to the integration of (2) over a volume element v. This volume v corresponds roughly to one pixel in the image and is of the order of a few pixels (depth of field) in the direction z. There is a time integration due to the video system during the scanning period τ = 40 ms. However, in the temperature range investigated, the minimum relaxation time is always larger than 40 ms, so the time integration has no influence. Therefore the useful signal at the pixel located at (x_i, y_i) is

$$\delta(x_i, y_i, t) \propto \langle \delta M(x, y, z = z_0), t \rangle_v \tag{4}$$

where $\langle\ \rangle$ denotes a spatial average.

The image, having been received by the camera, is stored on a videotape and later digitized with 64 levels (6 bits) and over 256 × 256 pixels. Typical images are shown in figure 2(*a*). A number of numerical treatments are then performed.

A number of binary fluids have been investigated: nitrobenzene–n-hexane, lutidine–water, isobutyric acid–water, methanol–cyclohexane and its deuterated derivatives, and also a microemulsion of dodecane–pentanol–water–sodium–dodecyl sulphate. Fluctuations can be seen only in a range of concentration and temperature close to criticality: $|c-c_c| \simeq 0$–0.03, $T - T_c$ (mK) $\simeq$ 1–25. The dynamics of such fluctuations are striking; they develop and vanish at a rate that is function of their size and of temperature, in full agreement with critical dynamics [1].

3. Statistics of fluctuations and free energy

On general grounds, the intensity distribution function $P(\delta i(x_i, y_i, t))$ of a given distribution $\delta i(x_i, y_i, t)$ at time $t = t_0$ (which we shall omit in the following since we deal

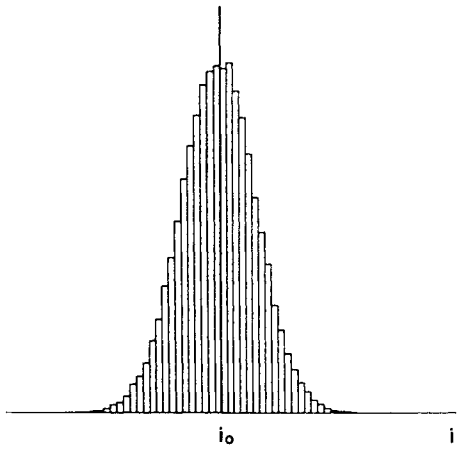

Figure 3. Histogram of a picture taken at $T - T_c = 1$ mK (isobutyric acid–water mixture).

only with statics) which corresponds to a partition function Z and a dimensionless free energy $F(\delta i(x_i, y_i))$ is defined as

$$P(\delta i(x_i, y_i)) = \frac{1}{Z} \exp\left(-\sum_i F(\delta i(x_i, y_i))\right). \tag{5}$$

This experimental quantity can be related to the singular free energy of the real system near T_c if one considers the renormalization trajectories in the renormalization-group theory [4]. Starting from a non-singular free energy, a renormalization over volume L^3 leads to an energy singular in $T - T_c$, and Gaussian statistics when $L \gg \xi$ (trivial fixed point), except for $T = T_c$. Our experiment, performed at a resolution $L \simeq 1$ pixel $\geq \xi$, therefore corresponds to an intermediate state on the renormalization trajectory. A deviation from the fixed point value can be reasonably expected.

The analysis of $P(\delta i)$, i.e. of the histogram in (figure 3), shows that the probability distribution is Gaussian, with a temperature-dependent first moment: $-\log P \sim F = \varepsilon(\delta i)^2$, with $\varepsilon = (T/T_c) - 1$, a prediction that can be compared with theory.

4. Morphology of fluctuations

Fluctuations can be considered as clusters or domains. A precise definition of these domains is not unambiguous, however (see below). The more obvious assumption is to call a domain the locus of connected pixels where the intensity $i(x_i, y_i)$ exceeds an arbitrary value i_1:

$$i(x_i, y_i) > i_1. \tag{6}$$

This will separate the image into 'white' clusters ($i \geq i_1$) and 'black' clusters ($i < i_1$). The more natural choice is, of course, to make $i_1 = i_0$, the average value of the histogram of intensity levels (figure 3).

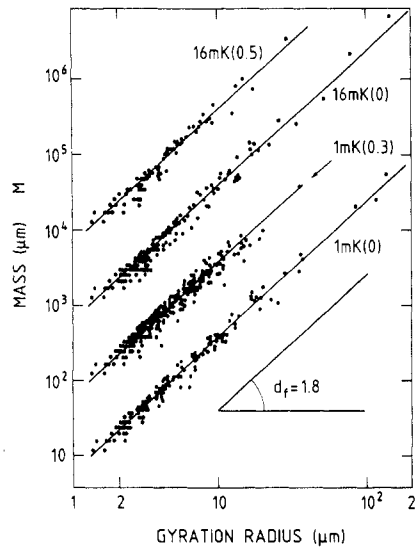

Figure 4. Self-similarity of fluctuation clusters: mass of clusters with respect to their gyration radii. Typical data at two temperatures are reported, with typical intensity thresholds in brackets. These are expressed as deviations from the average intensity in units of the fluctuation histogram full width. Because all data overlap, they have been shifted by one decade for clarity.

Such domains are reported in figure 2. Each domain (p) is characterized by its centre of mass (x_p, y_p), (i) its mass

$$m_p = \sum_{i \in p} 1 = n \text{ pixels} \tag{7}$$

and (ii) its gyration radius

$$R_p = \left(\frac{1}{m_p} \sum_{i \in p} (x_i - x_p)^2 + (y_i - y_p)^2 \right)^{1/2}. \tag{8}$$

The variation of m_p with respect to R_p is reported in figure 4. The fact that over more than three decades a linear relationship is obtained between $\log R_p$ and $\log m_p$ demonstrates self-similarity. The associated fractal exponent d_f defined by

$$m_p \sim R_p^{d_f} \tag{9}$$

has been found, for $i_1 = i_0$, to be $d_f = 1.8 \pm 0.1$. Small clusters (smaller than 5 μm) were ignored. The final error accounts for the known sources of uncertainties and is much larger than the statistical deviation. This value did not vary systematically with temperature. Changing the threshold (i_1) moves d_f to 1.7 and lowers the range of available gyration radius.

The domains that have been analysed are in fact the planar sections of 3D domains. The relationship between a 3D fractal object and its 2D section has been evoked by Mandelbrot [5]; the fractal dimension of the section (d_f) is related to the fractal dimension D_f of the 3D object through

$$D_f = 1 + d_f. \tag{10}$$

This relationship is obvious for dense domains. The fractal dimension of the 2D projection of a 3D object has been studied by Tence *et al* [6]. When the thickness of the projection tends to zero, one recovers the above result. The fractal dimension of the critical fluctuations according to (10) is therefore $D_f = d_f + 1 = 2.8 \pm 0.1$. That such fluctuations

are fractal objects might appear to be very surprising. But this is not really so, as we will explain below.

Fluctuations cannot be readily modelled by Ising clusters (i.e. a block of connected spins of the same magnetic sign). This has been proven by Coniglio and Klein [7]: Ising clusters can diverge as a result of a percolation mechanism, but the critical temperature of percolation differs from the thermal critical temperature and the exponents are not the same. In order to overcome this difficulty Coniglio and Klein have defined new clusters (called physical clusters) which obey new percolation rules and reproduce the usual Ising behaviour.

Two questions have to be answered in order to link our experimental findings with the above arguments. Firstly, what is the expected fractal dimension for the Ising clusters and/or the physical clusters? The simplest argument [8] gives

$$D_f = D - \beta/\nu \simeq 2.5 \tag{11}$$

where $D = 3$, and the values $\beta = 0.325$ and $\nu = 0.63$ are those of the 3D Ising model. This value is different from our result $D_f = 2.8$. Note that the existence of fractal fluctuations is not in disagreement with the form of the structure factor at large k

$$S(k) \sim k^{-(2-\eta)} \tag{12}$$

with $\eta \simeq 0.03$ the universal Fisher exponent. For monodisperse fractals

$$S(k) \sim k^{-D_f} \tag{13}$$

so a naive reasoning would give $D_f \simeq 1.97$. However, the distribution of mass of clusters $P(m)$ modifies this result. With τ the associated exponent

$$P(m) \sim m^{-\tau} \tag{14}$$

the structure factor at large k [9] is

$$S(k) \sim k^{-D_f(3-\tau)}. \tag{15}$$

Comparison with equation (12) gives

$$D_f = (2 - \eta)/(3 - \tau) \simeq 2.5 \tag{16}$$

when using the value $\tau \simeq 2.2$ which is generally found in the 3D percolation problems [10].

Equation (11), however, has been recently questioned (for $D = 2$) by Stella and Vanderzande [11] who have shown that more subtle arguments, relying on analogies with the Potts model, would invalidate $D_f = D - \beta/\nu$.

The second question is: are the clusters that we observe Ising clusters or physical clusters? The distinction between Ising and physical clusters shows that pure geometrical correlation effects have to be removed in order to obtain the true critical behaviour. Coniglio and Klein [7] took this into account for 3D clusters. In our case, the experimental definition of the 2D clusters mixes geometrical and thermal effects. Thus specific percolation effects in 2D should be relevant in our findings. The simplest fractal dimension for the $D = 2$ percolation problem is $d_f \simeq 1.9$ [8] which happens to be close to our experimental result $d_f = 1.8$.

Future experiments and theoretical work should clarify these points (more details can be found in [12] and [13]).

Note that the definition of a critical cluster is also an important problem for the new type of Monte Carlo simulations [14], whose dynamics does not rely on the flip of a single spin but on the flip of a whole critical cluster.

Acknowledgments

We are indebted to J Indekeu for having made us aware of the work by Stella and Vanderzande.

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