# Crossover from mean field to three-dimensional Ising critical behavior in a three-component microemulsion system

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Critical density fluctuations of water droplets in an oil-rich three-component microemulsion system have been studied by small-angle neutron scattering as a function of temperature near and far from the boundary of phase decomposition. The observed data in the one-phase region are well described in terms of the asymptotic crossover expression calculated by Belyakov *et al.* The data are found exclusively in the crossover region between the universality class of three-dimensional Ising and mean field regimes. The Ginzburg number is found to be between one and two orders of magnitude less than that for low molecular weight liquids. [S1063-651X(96)02207-6]

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## I. INTRODUCTION

The phenomenon of critical density fluctuations in micelles and microemulsions with droplet structure can be treated analogously to simple fluids. So far, researchers have tried to interpret their experimental data within one of the universality classes of critical phenomena, namely, of the mean field and of the three-dimensional (3D) Ising model [1–9]. The respective theoretical critical exponents of susceptibility and correlation length, which will be defined below, are $\gamma=1.0$ and $\nu=0.5$ for mean field, $\gamma\approx1.24$ and $\nu\approx0.63$ for 3D Ising. In two-component micellar systems, Corti and co-workers [1] showed experimental results of $C_iE_j$ (*n*-alkyl polyglycol esters) and water that indicated mean field behavior. These results were confirmed by several other experiments [2]; however, in the literature many more experimental findings are reported with critical exponents closer to the 3D Ising case [3]. Because of the nature of the droplet systems, most researchers expected that, within the experimentally accessible temperature range at the critical point, its critical behavior belongs to the 3D Ising universality class.

In multicomponent microemulsion systems, the obtained critical exponents do not always coincide with the exact values of the 3D Ising model [4–13]. On limiting to the well-known ternary system, an oil-rich AOT (dioctyl sulfosuccinate sodium salt), decane, and water mixture, there exist various experimental results. Kotlarchyk, Chen, and Huang [10] obtained $\gamma=1.61$ and $\nu=0.72$ by small-angle neutron scattering (SANS); Huang and Kim [11] observed $\gamma=1.22$ and $\nu=0.75$ by light scattering (LS); and, Honorat, Roux, and Bellocq [12] gave values of $\gamma=1.30,1.25$ and $\nu=0.76,0.71$ by LS. In order to understand such a complicated situation, Fisher tried to explain the observed critical exponents of two-component systems with the concept of crossover from mean field to 3D Ising behavior [14]. Alternatively, Martinez-Mekler, Al-Noaimi, and Robledo considered a correction to scaling with temperature dependent interactions [15]. Especially, in the multicomponent systems, an interpretation in terms of Fisher's renormalization of the 3D Ising model [16] has been a convincing candidate, because these multicomponent systems should have an extra degree of freedom in addition to the droplet density. Otherwise, no author has found the exact values of Fisher's renormalized 3D Ising case, where $\gamma\approx1.39$ and $\nu\approx0.71$.

Quite recently, Anisimov *et al.* [17] and Belyakov and Kiselev [18] proposed an analytical form of the susceptibility, which describes the fluctuations of the order parameter over the whole temperature range in the mixed state of the system. Their asymptotic regimes are the 3D Ising and mean field behavior near and far from the critical point, respectively. This theoretical expression successfully interpreted composition fluctuations in polymer blends [19,20]. One principal result of these studies was that previous interpretations with asymptotic scaling laws were quite misleading insofar as the validity of the Flory-Huggins mean field theory was very much overestimated. Thus for a reliable analysis of the experimental data one needs quite generally a theory which is valid over the whole crossover regime including the scaling limits both very near and very far from the critical point.

It is the aim of this paper to present SANS experiments that determined the susceptibility and correlation length on a three-component microemulsion of near critical composition, and to apply the above-mentioned extended crossover function [17,18] to our results. We used the well-known microemulsion system of an oil-rich mixture composed of water, AOT, and *n*-decane. The structure is known to be a simple water-in-oil type, homogeneous at room temperature, and decomposed in two phases at higher temperatures. As we described above, the associated critical phenomena were already studied by several authors using SANS and LS [10–13]. It was concluded that the system behaves as a

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quasi-one-component system whose critical phenomena could be described as the 3D Ising characteristics. However, the obtained critical exponents were not always in agreement with the exact 3D Ising values. On the other hand, in a recently published SANS study of this fluid [21] we saw that the density fluctuations of the droplets are sufficiently well described within the mean field approximation. This result can be understood spontaneously because the mean field theory is an extreme case, which is applicable when the temperature is far from the critical point and the correlation length of the droplet density fluctuation is smaller than the range of an interaction between droplets.

## II. THEORY

Within the range of mean field and 3D Ising behavior, the temperature dependence of the susceptibility $S_0$ and of the correlation length $\xi$ follow a scaling law according to

$$S_0 = C\tau^{-\gamma}, \quad \xi = \xi_0 \tau^{-\nu}, \tag{1}$$

where $C$ is a critical amplitude with $C = C_+$ in the 3D Ising range and $C = C_{\mathrm{MF}}$ in the mean field range, and $\tau = |T^{-1} - T_c^{-1}|/T_c^{-1}$ is the reduced temperature. Far from the critical point, a mean field temperature dependence of the susceptibility with $\gamma = 1.0$ is expected. On the other hand, in the nearest neighborhood of $T_c$ the susceptibility should be described by the scaling law of the 3D Ising model because of $\xi \to \infty$ at $T_c$. The transition between 3D Ising and mean field behavior is estimated by the Ginzburg criterion which gives for low molecular weight liquid systems a value of $\tau \approx 0.01$ [17]. This value of $\tau$ is defined as the Ginzburg number Gi.

As we mentioned above, Anisimov *et al.* [17] and Belyakov and Kiselev [18] proposed a new expression for the susceptibility describing the fluctuations of the order parameter over the whole one-phase regime including the asymptotic scaling laws of Eq. (1). Therefore the hitherto applied scaling theories are included in the crossover function. This function is based upon the renormalization group theory and an $\epsilon$ expansion with the 3D Ising and mean field behavior as asymptotic laws near and far from the critical temperature, respectively. They presented the following relationship between the renormalized susceptibility $\hat{S}_0 = S_0 a_0 \mathrm{Gi}$ and the renormalized temperature $\hat{\tau} = \tau/\mathrm{Gi}$, where $a_0$ is the coefficient of the second order term of the Landau free energy expansion of the system in terms of order parameter $\phi$ and is identical to the inverse of the critical amplitude $C_{\mathrm{MF}}$:

$$\hat{\tau} = (1 + 2.333\hat{S}_0^{\Delta/\gamma})^{(\gamma-1)/\Delta}[\hat{S}_0^{-1} + (1 + 2.333\hat{S}_0^{\Delta/\gamma})^{-\gamma/\Delta}]. \tag{2}$$

The critical exponents included are $\gamma = 1.24$ and $\Delta = 0.51$ of the 3D Ising model. For the classical limit with $\tau \gg \mathrm{Gi}$, this equation reads [17,18]

$$\hat{S}_0^{-1} = (\hat{\tau} - 1)[1 - 1.098(\hat{\tau} - 1)^{-0.411}], \tag{3}$$

which is the correction to scaling form of Eq. (1). For $\tau \ll \mathrm{Gi}$ one obtains from Eq. (2) the scaling form of Eq. (1) with $C_+ = 1.902\mathrm{Gi}^{0.24} C_{\mathrm{MF}}$ [17]. The Ginzburg number is then given by

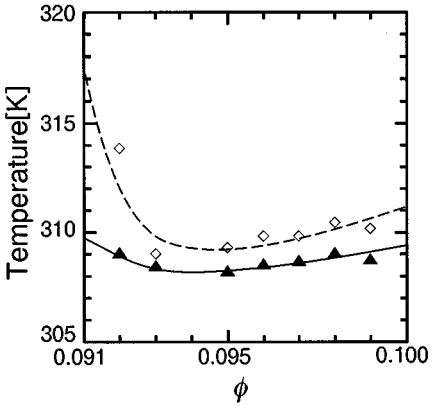


FIG. 1. Obtained binodal temperatures $T_B$ and spinodal temperatures $T_S$ for various droplet concentrations $\phi$. The concentration was varied using the dilution method from the batch of $\phi = 0.2$. The $T_B$'s were defined by the ''kink'' of the critical scattering divergence (see Ref. [15]) and the $T_S$'s were defined by the extrapolation of the critical divergence according to the mean field approximation. The solid and the dashed lines are the binodal and the spinodal lines, respectively, which are a guide for the eyes.

$$\mathrm{Gi} = 0.068(C_+/C_{\mathrm{MF}})^{4.17}, \tag{4}$$

in terms of the ratio of the critical amplitudes of $S_0$ of 3D Ising and mean field range [19].

## III. EXPERIMENT

SANS experiments were carried out at the SANS-U diffractometer in the JRR-3M reactor of Japan Atomic Energy Research Institute (JAERI). The experimental conditions were as follows. The incident neutron beam wavelength was $\lambda = 7$ Å with a resolution of $\Delta\lambda/\lambda = 10\%$. The covered $q$ range was $3 \times 10^{-3} \leqslant q \leqslant 8 \times 10^{-2}$ Å$^{-1}$ where $q$ is the scattering vector. Each sample was kept in a 1 mm thick niobium cell with a quartz window, placed in an electronic furnace controlled within $\pm 0.003$ K. All the samples were prepared with the same water to surfactant ratio of 5 ml of water to 3 g of AOT. This is the same ratio that was used in the previous experiments [10–13,21–23]. The volume fraction $\phi$ of both water and surfactant against the whole volume is defined as the order parameter. This value is proportional to the droplet number density. Amounts of 99% AOT (supplied by Fluka and Aldrich), 99% *n*-decane (by Katayama Chemical), and 99.9% $D_2O$ (by Isotec Inc.) were mixed without any further treatment and used within three days after opening the seal of the bottles. In this experiment, samples with $\phi = 0.096$, 0.098, and 0.099 were prepared because these compositions are rather close to the spinodal [21,22]. However, as we have already pointed out [22] the critical composition could never be achieved; i.e., we could not find any contact between the spinodal and binodal even though we studied samples at small concentration steps within $0.092 \leqslant \phi \leqslant 0.099$. (See Fig. 1.) The samples were prepared using the dilution method. Therefore the critical phenomena will be discussed on the basis that the critical droplet density fluctuations diverge at the spinodal temperature $T_s$ which plays the same role as the critical temperature $T_c$.

The measured two-dimensional data were radially inte-

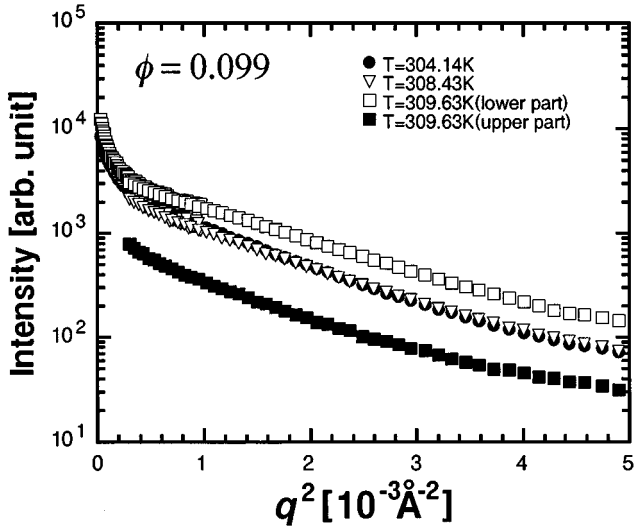


FIG. 2. Typical examples of the obtained scattering intensity presented in the Guinier plot. Most of the data could be approximated by Guinier formula Eq. (6) in the range $1.0\times10^{-3}\leqslant q^2\leqslant 2.5\times10^{-3}$ Å$^{-2}$, however, the profile from the upper part of the decomposed sample has no straight line region in this plot. This result suggests that the structural change of the droplet structure occurs at the decomposition temperature.

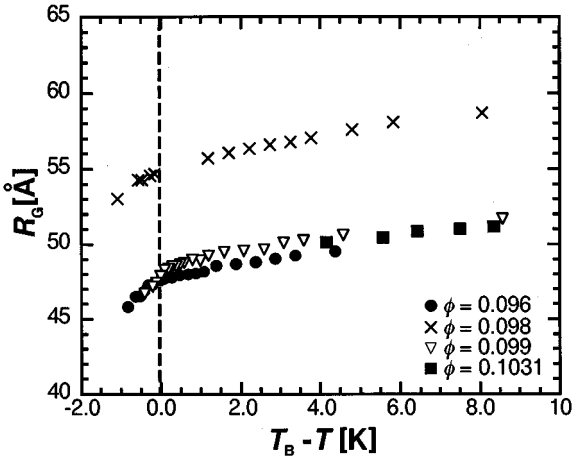


FIG. 3. The temperature dependence of the obtained radius of gyration for four samples. The horizontal axis indicates the temperature difference from the binodal temperature $T_B$.

grated and calibrated using the incoherent scattering standard of Lupolen. The total scattering cross sections

$$I^{\text{total}}=\int q^2 I(q)dq = 2\pi^2\phi_w(1-\phi_w)\Delta\rho^2 \qquad (5)$$

were calculated for each sample using the evidence that the scattering intensities followed the Porod law at high-$q$ region ($q\geqslant 4\times10^{-2}$ Å$^{-1}$). All the scattering intensities were normalized using $I^{\text{total}}$ in order to avoid artifacts. The details were described in our previous paper [21]. In Fig. 2, typical examples of scattering profiles are shown by a Guinier plot; i.e., the logarithm of scattering amplitude versus the square of $q$. In the one-phase region (solid circle, inverted open triangle), all the profiles could be approximated by the Guinier formula,

$$P(q)\propto\exp(-R_G^2q^2/3), \qquad (6)$$

in the range of $1.0\times10^{-3}\leqslant q^2\leqslant 2.5\times10^{-3}$ Å$^{-2}$. From this approximation, the radius of gyration $R_G$ of the droplets was obtained. In the same plot, one sees in addition the scattering profiles from the two parts of the decomposed phase: the upper (solid square) (droplet-poor) and the lower (open square) (droplet-rich) part. On the one hand, the scattering profile from the lower part also shows a straight line region in the Guinier plot. On the other hand, the scattering profile from the upper part of the decomposed sample is completely different so that the Guinier formula could not be applied any more.

The values of $R_G$ of the droplets in the one-phase region and the lower part of the decomposed sample are plotted in Fig. 3. $R_G$ decreases monotonously with increasing temperature up to the binodal point $T_B$. Above $T_B$, the system decomposes completely into two phases with a meniscus in between, and the radius of gyration decreases more steeply above $T_B$ (lower part). This evidence suggests that the droplet structure is not constant through the phase decomposition. So the ''quasi-one-component picture'' seems to break down near the critical point. This observation might mean a change of the hydrophile-lipophile balance with increasing temperature [24]. The quasi-one-component picture, however, might be realistic within the one-phase region below $T_B$, since $R_G$ changes only within 0.5 Å/K. Note that the droplet radius is quite sensitive to the composition fluctuations which occur in each mixing process, and $R_G$ for $\phi$=0.098 was a little different from others.

The form factor $P(q)$ of the droplets is described by the Guinier formula. The structure factor $S(q)$ describing the density fluctuations of the droplets was obtained by dividing the experimental scattering function $I(q)/I^{\text{total}}=P(q)S(q)$ with the form factor $P(q)$. In Fig. 4, typical examples of the

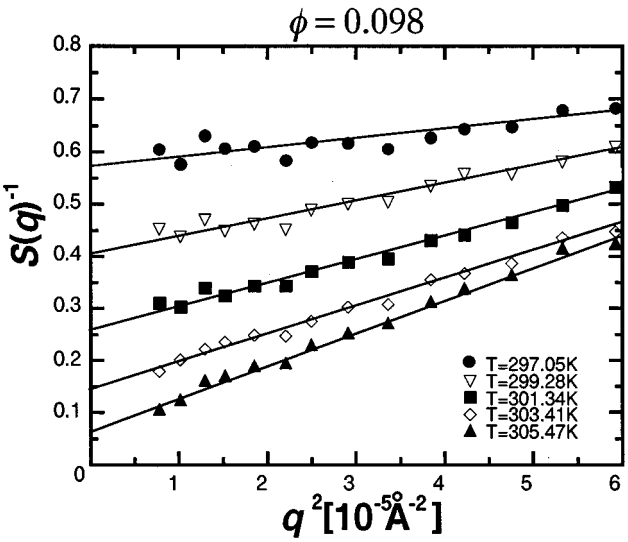


FIG. 4. Typical examples of the structure factor in Zimm representation. All the structure factor in this $q$ region can be approximated by the Ornstein-Zernike formula Eq. (7).

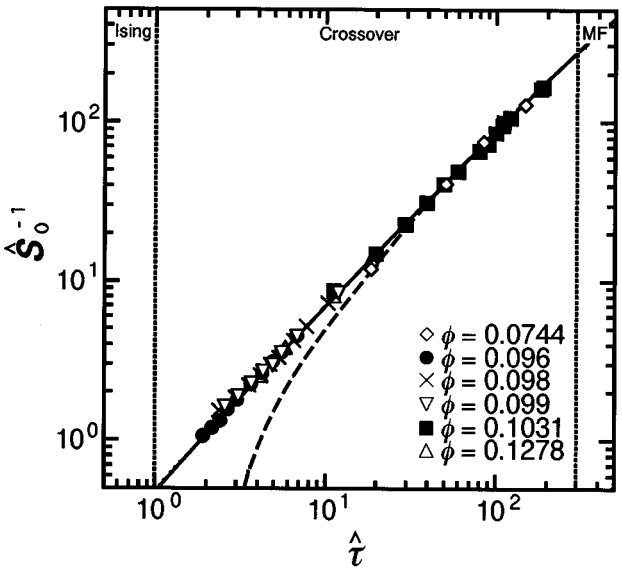


FIG. 5. The inverses of the renormalized susceptibility $\hat{S}_0^{-1}$ for all the samples are shown as a function of the renormalized temperature $\hat{\tau}$. The solid line represents Eq. (2), which completely explains the temperature dependence of the forward scattering in the one-phase region, and the dashed line indicates the mean field curve [Eq. (3)].

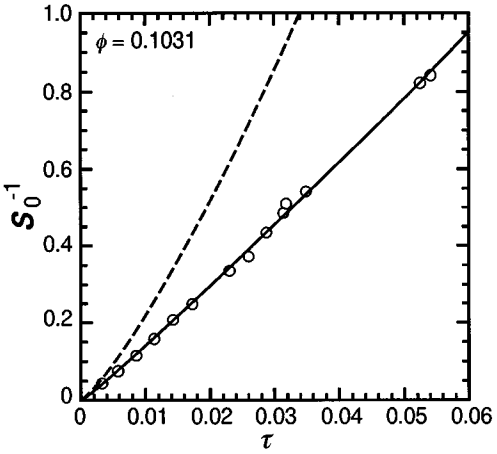


FIG. 6. A variation of the inverse of the forward scattering $S_0^{-1}$ for $\phi$=0.1031. The horizontal axis indicates the reduced temperature; $\tau=T_c^{-1}-T^{-1}/T_c^{-1}$. The solid line is the crossover equation [Eq. (2)] and the dashed line the scaling function [Eq. (1)].

obtained structure factor $S(q)$ are shown in the Zimm plot; the inverse of the structure factor versus the square of the momentum transfer. In the presented $q$ region ($3.0\times10^{-3}\leqslant q\leqslant 7.7\times10^{-3}$ Å$^{-1}$), $S(q)$ could be approximated by the Ornstein-Zernike law,

$$S(q)=S_0/(1+\xi^2q^2). \tag{7}$$

All the observed temperature variations of the susceptibility $S_0$ in the one-phase region, including the data already published [21], were fitted with Eq. (2). In this case, the fitting parameters were the spinodal temperature $T_s$, the Ginzburg number Gi, and the critical amplitude $C_{\rm MF}$. All the data are shown in Fig. 5 where the inverse of the renormalized susceptibility $\hat{S}_0^{-1}$ is plotted versus the renormalized temperature $\hat{\tau}$. The solid line indicates the theoretical curve according to Eq. (2) and the dashed line is that of Eq. (3). The resulting parameters are listed in Table I, in which the generalized Flory-Huggins parameters $\Gamma_s$ and $\Gamma_\sigma$ are also listed as calculated by [21]

$$\Gamma_s=\frac{1}{2\phi(1-\phi b')^2},\quad b'=4 \tag{8}$$

$$\Gamma_\sigma=-(a_0/2+\Gamma_s). \tag{9}$$

Note that the values of $\Gamma_\sigma$'s are consistent with our previous result. (See Table 1 of Ref. [21].) It is the main result of the present paper that the asymptotic crossover theory described the critical behavior of this microemulsion system successfully.

The Ising regime at $\tau<$Gi is determined from the definition of the Ginzburg criterion and the mean field regime is supposed to be at $\tau>$300Gi [19,20]. All the data are found exclusively in the crossover region, i.e., between the 3D Ising and mean field regimes. This figure clearly exhibits that the data are well described by the crossover formula proposed by Kiselev and co-workers [17,18]. The Ginzburg number Gi being around $10^{-3}$ is between one and two orders of magnitude less than that for low molecular weight liquids.

## IV. DISCUSSION AND CONCLUSIONS

In Fig. 6 the experimental $S_0^{-1}$ of the sample with $\phi$=0.1031 is plotted versus $\tau$ as a typical result. The solid line is according to the crossover function of Eq. (2), while the dashed curve is the calculated 3D Ising curve, where the critical amplitude $C_+$ was calculated by Eq. (4) (see Table I).

TABLE I. Results from the crossover function Eq. (2).

| $\phi$ | $T_s^{-1}$ ($10^{-3}$ K$^{-1}$) | Gi (units of $10^{-3}$) | $C_{\rm MF}$ (units of $10^{-2}$) | $\Gamma_s$ | $\Gamma_\sigma$ | $C_+$ (units of $10^{-2}$) |
|---|---|---|---|---|---|---|
| 0.0744 | 3.194±0.006 | 0.4±0.9 | 6.5±0.8 | 13.6 | −21.3±1.0 | 1.9±1.2 |
| 0.096 | 3.230±0.001 | 1.7±0.5 | 2.7±0.1 | 13.7 | −32.5±0.7 | 1.1±0.1 |
| 0.098 | 3.268±0.001 | 2.9±1.9 | 4.0±0.4 | 13.8 | −26.4±1.1 | 1.9±0.5 |
| 0.099 | 3.229±0.001 | 2.7±1.6 | 4.7±0.4 | 13.8 | −24.4±0.9 | 2.2±0.5 |
| 0.1031 | 3.208±0.001 | 0.3±0.2 | 5.6±0.2 | 14.1 | −22.9±0.3 | 1.5±0.3 |
| 0.1278 | 3.159±0.002 | 1.7±1.1 | 5.5±0.4 | 16.4 | −25.6±0.7 | 2.3±0.5 |

The dashed line would describe well the data below $\tau \leqslant 3\times10^{-4}$ if accessible by experiment. In the measured temperature range, however, the experimental data deviate appreciably from 3D Ising behavior. Since we were unaware of the crossover function at that time in our previous paper [21], the same data were interpreted quite satisfactorily in terms of the mean field approximation. This shows, as already discussed in Refs. [20, 25] that the analysis of the data with the scaling law of Eq. (1) is misleading, and that a reliable analysis of the data can only be performed with an expression that is also valid within the crossover range.

To summarize the main result of this paper, the density fluctuations in this microemulsion system, as measured by the susceptibility, can only be reliably interpreted in terms of the crossover function of Eq. (2). All experimental data were found within the crossover range with a Ginzburg number of the order of $10^{-3}$. The asymptotic 3D Ising range is essentially not accessible for the system studied because of the small value of Gi and the absence of the critical point. The Gi values found are about one order of magnitude smaller than the typical values for low molecular weight liquids [17,18]. This means that the temperature range of the investigated microemulsion is a respective order of one magnitude smaller and larger for the 3D Ising and mean field asymptotic behavior in comparison to low molecular weight liquids.

In this paper we have shown that the critical phenomena in the water-in-oil droplet structure microemulsion system can be explained by the asymptotic crossover model proposed by Belyakov and Kiselev. By applying their equation to our experimental results, the Ginzburg numbers were obtained for some mixtures. These values are one or two orders of magnitude smaller than simple fluids. Therefore most of the data were found in the crossover regime rather than in the scaling regimes, and the critical exponent cannot be defined exactly within the framework of one critical universality.

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