An x-ray reflectivity study of surface layering in a magnetic fluid

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Abstract. By utilizing an x-ray diffractometer for the observation of liquid surfaces, the depth profile of the electron density of a magnetic fluid across the surface was studied. The observed x-ray reflectivity indicated oscillatory behaviour in the electron density along the surface-normal direction. The layer spacing is comparable to the dimensions of the magnetic fine particles. The temperature dependence of this long-range-ordered surface structure exhibited a distinctive feature: not only the period but also the amplitude and the decay length of the electron density oscillations increase with increasing temperature. The results are compared with features of the surface layering observed for metallic liquids.

1. Introduction

A variety of experiments have been performed within the analysis of the structural properties of liquids. Several of them have been dedicated to surface and interfacial structures [1]. However, information on the surface structure of colloidal solutions determined by diffraction techniques has remained scarce. We have chosen a magnetic fluid as an example of a complex fluid, and measured the x-ray reflectivity so as to clarify the surface structure. One of the aims of this study is to get a better perspective as regards the structures of non-crystalline materials under the boundary conditions of a named surface. Such information should also be very useful for industrial applications, since many useful and important properties are thought to be exhibited at the surfaces and interfaces of magnetic fluids.

Magnetic fluids are colloidal dispersions of magnetic fine particles. The magnetic fine particles, about 100 Å in diameter, are dispersed in a medium after coating them with appropriate surfactants. The direction of the magnetic moment of the fine particles is believed to fluctuate substantially as a result of thermal motion and a quantum effect. We can evaluate the volumetric packing fraction of the magnetic fine particles from the density of the magnetic fluid, the density of the magnetic fine particles, and that of the embedding medium. Then, we readily find that the volumetric packing fraction of the magnetic fine particles is about 0.1 for magnetic fluids. Therefore, we suggest that it might be reasonable to regard a magnetic fluid as a kind of gas state composed of magnetic fine particles. Owing to the fluctuations and owing to the low concentration, there would be no reason to expect any ordered structure at the surface, or in the bulk. The present work is intended to be an experimental study aimed at revealing the surface structure of the magnetic fluid.
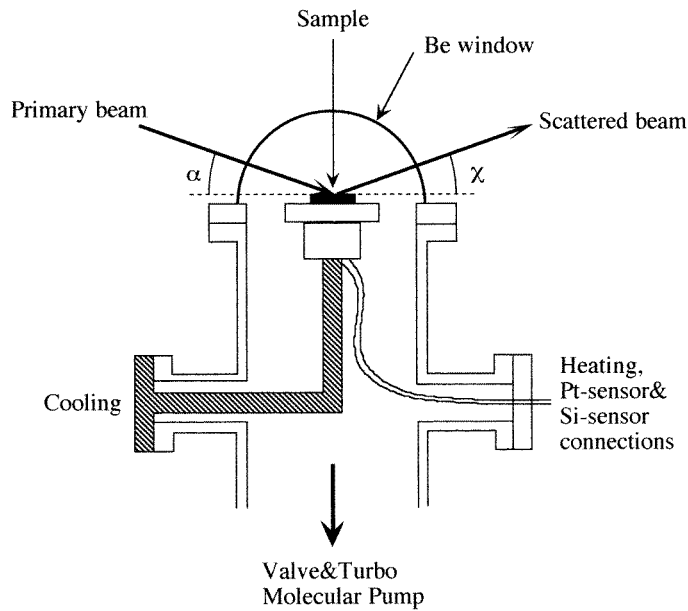
Figure 1. A schematic diagram of the apparatus and scattering geometry.

2. Experimental procedure

Figure 1 shows schematically an experimental apparatus in which a rotating-anode x-ray generator (18 kW) is installed. Cu Kα_1 radiation was monochromated by a Si(111) parallel-crystal monochromator. The beam size at the sample position was less than 0.2 mm $\times$ 2 mm (vertical $\times$ horizontal) (full widths at half-maximum). The angle of the primary beam with respect to the horizontal can be changed by rotating the x-ray source about the α-axis, which lies in the horizontal plane. Rotation of the scintillation detector is also allowed, around the χ-axis, which is also within the horizontal plane. An additional degree of freedom for the detector is employed: the axis is perpendicular to the surface, although this was not used in the present study. Moreover, the sample can be rotated around the surface normal by using a table. Therefore, we can observe scattering for any scattering condition without tilting the surface of the sample by utilizing the diffractometer. The details of the diffractometer used for observations of liquid surfaces will be published elsewhere.

The sample (Taiho Industry Incorporated, LS-40 [2]) filled a Pyrex sample cell of dimensions $40 \times 40 \times 0.5$ mm^3. The short dimension is vertical and along the common direction of the scattering vector. The x-ray reflectivity was measured by carrying out transverse scans at fixed diffraction angles: the angle of incidence α and the exit angle χ were changed, keeping $\alpha + \chi$ fixed. Background scattering was subtracted from each rocking curve so as to obtain the integrated intensity. The high and low temperatures were attained by a heating system and a refrigeration system; this set-up enables us to perform x-ray diffraction studies for temperatures between 15 K to 500 K. The sample temperature was controlled by a PID controller with a precision of better than 0.05 K. '2π' access of the x-ray beam to the sample surface was possible via a dome-shaped beryllium window.

The sample temperatures were between 250 K and 400 K. Below 250 K, the embedding medium congeals, and beyond 400 K, evaporation of the medium can hardly be ignored
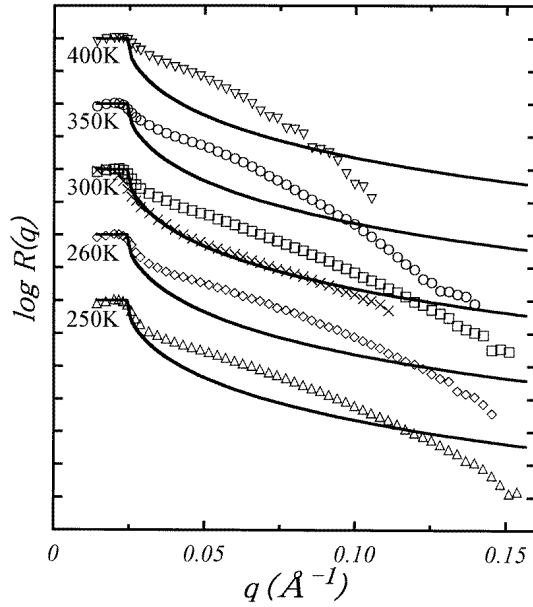
Figure 2. The x-ray reflectivity of the free surface of the magnetic fluid for different temperatures. For clarity, each reflectivity is displaced vertically by 0.01. The Fresnel reflectivity from an ideally flat surface is also shown, by solid curves. The crosses at 300 K indicate the reflectivity of silicone oil, used as an example of a non-colloidal liquid.
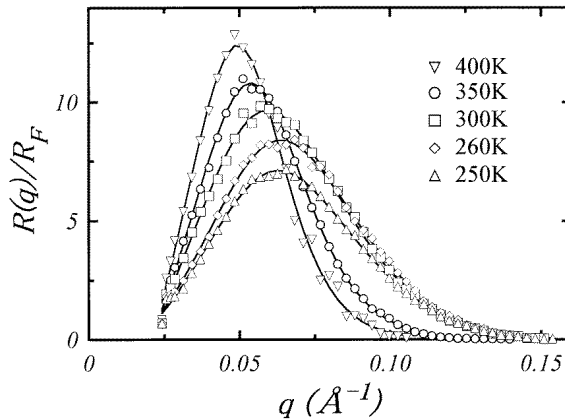

Figure 3. Reflectivity normalized with respect to the Fresnel reflectivity. The solid curves are the results of the fits to the model described in the present study.

with the base pressure of 10^{-5} Torr. We were not concerned about the vibration of the sample due to the vibration of the refrigerator because we chose viscous liquids, such as LS-40 [3].

Figure 2 indicates the observed reflectivity profile as a function of the momentum transfer q $(=4\pi(\sin\theta)/\lambda)$ and figure 3 shows the reflectivity normalized with respect to the Fresnel reflectivity. A broad peak is observed at around $q = 0.05$ Å^{-1} at each temperature.

The peak position shifts to a lower q-value and the peak height increases with increasing temperature.

3. Analysis

Within the kinematical theory, the reflectivity $R(q)$ is related to the average electron density along the surface normal, $\langle\rho(z)\rangle$, by the following expression [4]:

$$R(q) = R_F(q)\left|\rho_0^{-1}\int_{-\infty}^{\infty}[\mathrm{d}\langle\rho(z)\rangle/\mathrm{d}z]\exp(\mathrm{i}q_c z)\,\mathrm{d}z\right|^2 \tag{1}$$

where $R_F(q)$ and ρ_0 are the Fresnel reflectivity and the bulk electron density, respectively. A refractive index correction was applied to the normal component of the momentum transfer inside the medium, and it is denoted as q_c. Furthermore, we represent $\langle\rho(z)\rangle$ by an electron density function $\rho(z)$ under a flat surface and a probability function $p(z_s)$ which represents the probability of finding the surface at $z = z_s$:

$$\langle\rho(z)\rangle = \int_{-\infty}^{\infty}\rho(z-z_s)p(z_s)\,\mathrm{d}z_s. \tag{2}$$

Using equation (2), equation (1) is expressed as

$$R(q) = R_F(q)\left|\int_{-\infty}^{\infty}p(z)\exp(\mathrm{i}q_c z)\,\mathrm{d}z\right|^2\left|\rho_0^{-1}\int_{-\infty}^{\infty}[\mathrm{d}\rho(z)/\mathrm{d}z]\exp(\mathrm{i}q_c z)\,\mathrm{d}z\right|^2. \tag{3}$$

If $p(z)$ is the form of a normal distribution with standard deviation Σ, the reflectivity is finally given as

$$R(q) = R_F(q)\exp(-\Sigma^2 q_c^2)\left|\rho_0^{-1}\int_{-\infty}^{\infty}[\mathrm{d}\rho(z)/\mathrm{d}z]\exp(\mathrm{i}q_c z)\,\mathrm{d}z\right|^2. \tag{4}$$

The present formulation helps us to see what changes in electron density as a function of the temperature are intrinsic, and how the surface roughness Σ grows due to the capillary-wave fluctuations with increasing temperature.
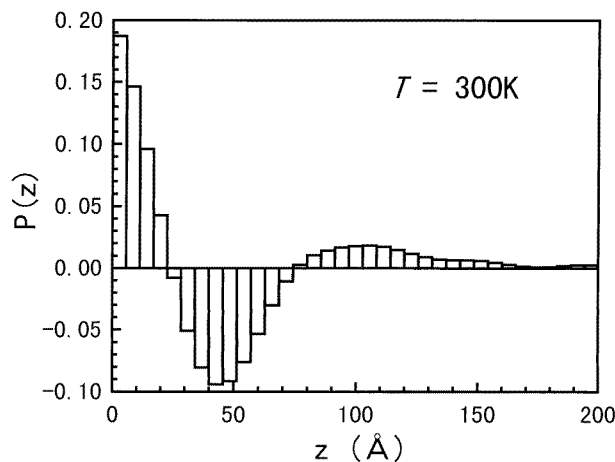

Figure 4. The correlation function $P(z)$ at $T = 300$ K, expressed as a series of narrow box functions (see equation (8)).

The peak seen in figure 3 seems to indicate a layering structure at the surface with a spacing of about 100 Å. We tried to check on the existence of the layering structure by evaluating a correlation function $P(z)$ defined by

$$R(q)/R_F(q) = \int_{-\infty}^{\infty} P(z) \exp(iqz) \, dz \tag{5}$$

$$P(z) = \rho_0^{-2} \int_{-\infty}^{\infty} \rho'(z+Z)\rho'(Z) \, dZ \tag{6}$$

where $\rho'(z) = d\rho/dz$. In the present study $P(z)$ was expressed as a series of narrow box functions, $s_n^N(z)$:

$$P(z) = \sum_{n=1}^{N} a_n s_n^N(z) \tag{7}$$

where a_n are coefficients to be determined, and

$$s_n^N(z) = \begin{cases} 1 & \text{for } (n-1)Z_M/N < z < nZ_M/N \\ 0 & \text{elsewhere.} \end{cases} \tag{8}$$

Since obtaining a_n is a linear problem, it is not very difficult to refine a_n, even if we make N a fairly large number—as long as it is less than the number of data points N_D. In the present analysis ($N_D = 48$ at 300 K), N and Z_M were chosen to be 35 and 200 Å, respectively [5]. Figure 4 exhibits the refined $P(z)$ at 300 K. On the basis of the maximum and minimum positions, oscillatory behaviour at the surface with a period of more than 100 Å is suggested. $P(z)$ at other temperatures also showed similar profiles.

Table 1. Refined parameters. The ESDs (estimated standard deviations) are given in parentheses. The discrepancy factors (R and wR) and χ^2 are defined as follows: $R = (\sum_{i=1}^{N_D} |I_i^{Obs} - I_i^{Cal}|)/\sum_{i=1}^{N_D} I_i^{Obs}$, $wR = [(\sum_{i=1}^{N_D} (I_i^{Obs} - I_i^{Cal})^2)/\sum_{i=1}^{N_D} (I_i^{Obs})^2]^{1/2}$, and $\chi^2 = (\sum_{i=1}^{N_D} (I_i^{Obs} - I_i^{Cal})^2)/(N_D - N_P)$, respectively ($I_i \equiv R(q_i)/R_F(q_i)$, N_D = number of data, N_P = number of parameters = 6 or 5). Σ at 250 K and 260 K was revealed to be very small and fluctuating throughout the least-squares fittings. Consequently, these values were fixed as zero.

T (K)	250	260	300	350	400
d (Å)	113(2)	110(2)	122(8)	119(5)	132(10)
A	2.9(1)	3.1(2)	4.3(7)	4.3(6)	4.5(1.7)
ξ (Å)	22(1)	23(1)	22(2)	30(1)	35(2)
σ (Å)	3.7(2.0)	0.9(6.1)	0.8(11.5)	0.2(3.6)	0.6(33)
z_0 (Å)	15(1)	15(3)	15(6)	16(1)	15(2)
Σ (Å)	0 (fixed)	0 (fixed)	6(5)	14(2)	17(4)
R	0.144	0.140	0.157	0.201	0.181
wR	0.125	0.126	0.135	0.154	0.157
χ^2	0.015	0.029	0.032	0.026	0.146
N_D	48	45	47	43	31

As a final stage of the analysis, $\rho(z)$ is determined. However, this is a non-linear problem. Many approaches have been reported for overcoming the lack of phase information. However, the inverse problem is sometimes quite difficult to solve due to the limited range of observed q-values. In the present study, with the help of information
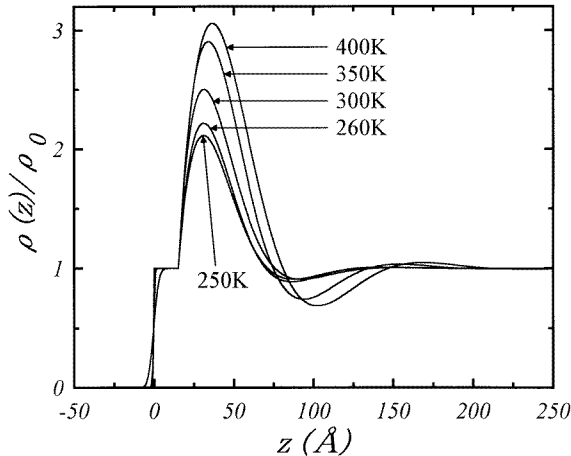
Figure 5. Normalized electron density profiles.

on $P(z)$, the following function was assumed as $\rho(z)$, and the parameters including Σ in equation (4) were refined by non-linear least-squares fitting:

$$\rho(z)/\rho_0 = \{\mathrm{erf}(z/\sigma) + 1\}/2 + \theta(z)A\sin(2\pi(z - z_0)/d)\exp(-(z - z_0)/\xi) \tag{9}$$

where $\mathrm{erf}(z)$ and $\theta(z)$ are the error function and the step function, respectively. Figure 5 shows $\rho(z)/\rho_0$ obtained, and the refined parameters are listed in table 1. The solid curves in figure 3 show the intensity calculated by using the refined parameters. The agreement between the observation and the calculation is satisfactory.

4. Discussion

As indicated in figure 5 and table 1, the oscillatory behaviour of the electron density rapidly decays, with a characteristic length of 20–35 Å. The period of the oscillation is about 110–130 Å which is almost the same as the average diameter of the magnetic fine particles [2]. Since the electron density of the medium is estimated to be about 25% of the electron density of the magnetic fine particles [2], we can regard the peak positions of $\rho(z)/\rho_0$ as the positions at which the magnetic fine particles agglomerate. Therefore, the function $\rho(z)/\rho_0$ obtained manifests the layering behaviour of the magnetic fine particles at the surface.

   The sudden drop of electron density at $z = 0$ Å indicates that the interface between the magnetic fluid and the vapour is quite sharp. The plateau for $0 < z < 16$ Å reflects the presence of surfactant molecules which cover the surface of the magnetic fine particles at the surface (figure 6), since the size of the molecule is about 20 Å and the surfactant molecules are usually stable between 250 K and 400 K [6].

   The values of Σ at 250 K, 260 K and at 300 K are reasonable: the value of Σ at 300 K agrees with the value predicted by the capillary-wave model, and that at low temperatures reflects the freezing of the medium. However, Σ grows much faster than would a value reflecting simply thermal fluctuation at high temperature. Evaporation of the medium at high temperature may be the reason for such a rapid increase of the surface roughness. The measurements were performed in low vacuum so as to avoid moisture at low temperature and to prevent oxidation at high temperature. After the measurement at 400 K, a slight decrease of the amount of sample present owing to evaporation was noticed. Therefore, the large magnitudes of the values of Σ at 350 K and 400 K probably reflect this evaporation.
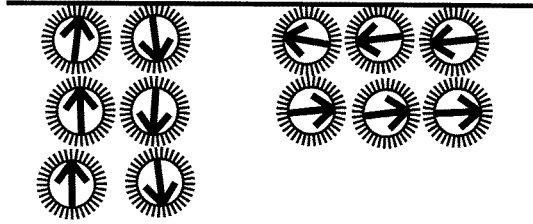
Figure 6. Possible structures at the surface of a magnetic fluid. Circles and arrows in the circles represent magnetic fine particles and magnetic moments, respectively. Surfactant molecules are represented by short lines. Surface-parallel and surface-normal arrangements are illustrated. The flat region in $\rho(z)$ at the surface (see figure 5) corresponds to the lengths of the surfactant molecules which impede the progress of the magnetic particles rising to the surface.

Since the period of the surface layering is almost the same as the average diameter of the magnetic fine particles, they would form short-chain structures as illustrated in figure 6. In this figure, an antiferromagnetic structure aligned parallel to the surface and a structure oriented toward the surface normal direction are shown schematically. Both structures might be acceptable, because they can each form a closed magnetic circuit to reduce the magnetostatic energy at the surface. A density-functional theory is presented in [7], in which the orientational profile as well as the density profile at the liquid–vapour interface are treated for fluids composed of molecules with strong permanent dipole moments. Therefore, it would be very interesting and informative to apply the theory to the present system. For the chain structure in the bulk, there are Monte Carlo simulations available [8, 9]. According to these, there is no long-range order in the bulk. However, chains lying along the field direction are formed in the presence of an external magnetic field. Therefore, the observed layering structure would seem to indicate the existence of a local magnetic field at the surface, although the average local field is zero in the bulk without an external field. We think that the local field might be generated as a truncation effect at the surface, and that the gradient of the local field is a driving force which yields a high density of magnetic fine particles near the surface. Once such a high-density state is realized, rearrangements of the magnetic moments readily occur in order to minimize the surface energy. The process of agglomeration and rearrangement of the magnetic moments would continue until the surface structure eventually stabilized. The surface-induced layering structure of magnetic fluids can be explained by the scenario described above. But it is still an open question; experiments under DC and AC magnetic fields, and simulations including surface effects might be helpful to resolve this problem.

The increase of the layer spacing with increasing temperature can be attributed to the increase of thermal motion and a decrease of the magnetic moment of the magnetic fine particles. However, the effects of the increase of the amplitude and of the decay length appear to act in opposition to the aforementioned thermal effect. The reasons for this peculiar temperature dependence are still unknown. Evaporation of the medium at high temperature might be one reason: it caused a high density of the magnetic fine particles at the surface. Consequently, evaporation would play a role in increasing the peak height of the electron density with increasing temperature. We also think that a frictional force between the magnetic fine particles due to the interaction between the surfactant molecules would reduce the free-rotational movement at low temperature. The ordering of the magnetic moment is hindered by the tangling collisions among the surfactant molecules especially at low temperature (figure 7(a)). When temperature increases, both the repulsion energy due
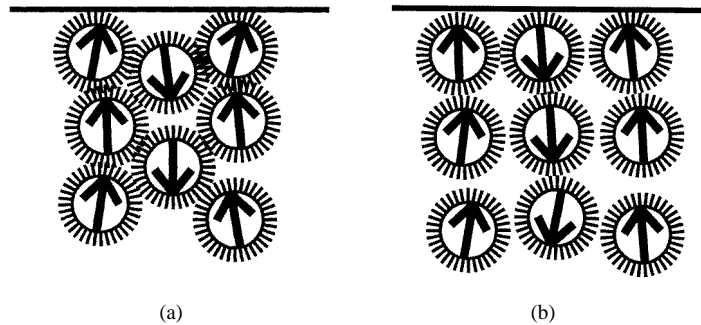
(a)   (b)

Figure 7. The surface structure of magnetic fluids at low temperature (a) and that at high temperature (b). The alignment of the magnetic moments is imperfect at low temperature. Condensation of the colloidal particles and a tangling interaction between the surfactant molecules could be the reason for the reduction of the ordering of the magnetic moments at low temperature. At high temperature, the increasing of the distance between the colloidal particles, due to increasing the thermal vibration and due to increasing the repulsive force, helps to align the magnetic moments.

to the interaction between the surfactant molecules [10] and the thermal vibration increase. Thus, the average distance between the magnetic particles also increases, and this change effectively acts to align the direction of the magnetic moments within the chains shown in figure 7(b), which eventually causes the increase of the peak heights and that of the decay length with increasing temperature.

It is interesting to compare the layering structure observed in the present study with the atomic surface layering of metallic liquids [11, 12]. Their normalized amplitudes show sharp contrast: the amplitude of the magnetic fluid is larger than that of metallic liquids (the height of the first peak is between 2.0 and 3.0 for the magnetic fluid, and it is about 1.2 for metallic liquids [11, 12]); in addition, the normalized electron density decays more drastically than in the case of Ga and Hg (ξ/d is about 0.3 for the magnetic fluid, but it is about 2.3 for Ga). The temperature dependence of the behaviour of magnetic fluids and that of Ga [13] also reveal a sharp contrast. For Ga, the peak height of the surface layering decreases with increasing temperature and the period remains constant, although both the peak height and the period increase for the magnetic fluid as indicated by the present study.

Experiments under magnetic fields and observation of the time evolution of the surface structure triggered by a change of the field are now in progress.

Acknowledgments

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[2] The information on LS-40 can be summarized as follows: the estimated volumetric packing fraction of the magnetic particles is 0.12; the estimated number density of the magnetic particles is 2.87×10^{22} m^{-3}; the

mean value of the magnetic moment of a single magnetic particle is 1.1×10^{-24} Wb m; the embedding medium is alkyl naphthalene ($C_{10}H_7(C_{20}H_{41})$). The electron densities of the magnetic fine particles and of the embedding medium are estimated as 12.5×10^{29} m^{-3} and 3.0×10^{29} m^{-3}, respectively. The electron density of the magnetic fluid is about 4.2×10^{29} m^{-3}. From the widths of the Bragg reflections of the magnetic fine particles, the average diameter—not including the surfactant layer—is estimated as 109 Å. Their value is in accordance with the range of the diameters of the magnetic particles (50–100 Å) obtained from a scanning electron microscopy (SEM) measurement (private communications from Taiho Industry Incorporated).

[3] The reflectivity of silicone oil had been measured so as to check the effects of vibration on this system. A typical reflectivity from a surface with roughness of about $\Sigma = 4.0$ Å was obtained. This value is consistent with the prediction of the capillary-wave theory [14]. Thus, it is concluded that the effect of vibration on the surface of the magnetic fluid is negligible, since the sample (LS-40) is apparently more viscous than silicone oil.

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[5] The authors were inspired by Pedersen's exhaustive study [15] regarding how to evaluate the correlation function.

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