

# Dynamic uniform fractals in emulsions

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The geometric structure of an emulsion mixture of two lyophobic liquids with a large concentration of the secondary component has been studied experimentally. A method of fast freezing was used. This method is based on the strong temperature dependence of the viscosity of the predominant (matrix) component. It is proposed for the first time here that high-temperature emulsions formed by mixing a low-viscosity melt of a glass-phobic liquid into molten glass be used for this purpose. An emulsion mixture unavoidably forms dynamic inhomogeneous (cluster) structures on small length scales. The geometry of these structures is fractal. The size of the elementary irregularities is governed by a universal function which depend on only the volume content of the components. The fractal dimensionality of these irregularities is  $2.5 \pm 0.1$ . The typical lifetime of the inhomogeneities in mixtures is estimated.

## INTRODUCTION

Substantial progress has recently been achieved in research on "soft matter." The interest in such materials is quite understandable in view of the complexity of real systems.<sup>1</sup> As examples we might cite emulsions, in particular, the water-oil microemulsions which have attracted particular interest.<sup>2,3</sup> The latter materials are thermodynamically stable two-phase systems consisting of an oil matrix in which water is dispersed in the form of tiny droplets from 10 to 100 Å in size. These droplets are coated with a saturated layer of surfactant molecules. Microemulsions arise spontaneously when a certain amount of surfactant is added to water and oil. There are also water-free microemulsions, in which the water is replaced by, for example, glycerine.<sup>4</sup> Of primary interest is the percolation transition observed in microemulsions. This transition occurs as the volume fraction of the disperse phase (water + surfactant) or the temperature is raised. The percolation transition is manifested in sharp changes in the properties of the microemulsions: their viscosity,<sup>4</sup> electrical conductivity, permittivity,<sup>5</sup> and luminescence quenching.<sup>6</sup>

No direct observation of the structure of microemulsions has been reported in the literature. Two models have been proposed for this structure. The static percolation model<sup>7</sup> involves the formation of open water channels. The dynamic percolation model<sup>8</sup> assumes that percolation clusters form closely spaced water droplets. Numerous studies show that the dynamic percolation model agrees best with experiment.<sup>5</sup>

Another pertinent topic is the more general question of the structure of a mixture produced by mixing two lyophobic liquids. The initial stage of the injection of a low-viscosity component into a viscous matrix has been studied thoroughly.<sup>9</sup> Some geometric structures ("viscous fingers") which form in the process are found to have a fractal dimensionality.

The final product of a sufficiently prolonged mixing of two lyophobic liquids is an emulsion consisting of a dom-

inant (matrix) component containing a secondary phase distributed in droplets. Just how valid are the ideas regarding the possibility for producing homogeneous emulsions? Since percolation transitions occur in microemulsions, one would expect that the answer to this question would by no means be trivial. It is quite likely that the structure of emulsions (including microemulsions) has features at length scales much larger than the dimensions of the droplets. Although emulsions have been studied quite thoroughly,<sup>10</sup> no studies of the distribution of phases have been reported.

The purpose of the present work was to directly study the geometric structure of an emulsion mixture of two lyophobic liquids for various degrees of filling of the matrix.

The results found here show that when the concentration of the secondary component is high, homogeneous mixtures can be achieved only in sufficiently large volumes: On short length scales, the droplets of the second phase unavoidably form cluster structures with a fractal geometry. On the other hand, the homogeneous fractal structure of the mixture is dynamic and can be observed if the observations are made over sufficiently short time intervals.

## FAST FREEZING METHOD

Many experimental and theoretical studies of two-phase solid disperse systems show that large-scale aggregations—macroscopic clusters of particles of the secondary phase in the host material—form in the course of percolation transitions (see Refs. 11 and 12 and the papers cited there). For liquid systems, the formation of cluster forms is prevented by rapid movements of droplets involved in a disordered Brownian motion. In addition, emulsions of lyophobic liquids are generally unstable: Phases separate after a certain length of time.<sup>10</sup> It is thus clear that if cluster forms do exist then they are dynamic entities in liquids. Such aggregates could apparently be observed directly only in the case of instantaneous freezing of all motions. For this purpose liquids whose viscosity has a

fast (sharp) temperature dependence are suitable. By quickly lowering the temperature of a sample, one can substantially slow all motions by virtue of the increase in the viscosity.

According to Frenkel's molecular-kinetics theory of liquids, the temperature dependence of the viscosity can be described by the function

$$\eta = A \exp\left(\frac{W}{kT}\right), \quad (1)$$

where  $A$  depends weakly on the temperature,  $W$  is the activation energy, and  $T$  is the temperature. If the change in the temperature of the liquid is small,  $\Delta T \ll T$ , the viscosity increases by a factor  $K$ :

$$K = \exp\left(\frac{W}{kT} \cdot \frac{\Delta T}{T - \Delta T}\right). \quad (2)$$

As the ratio  $W/kT$  increases, the increase in the viscosity becomes sharper at a given value of  $\Delta T/T$ . For rapid freezing, liquids with a large activation energy are therefore most suitable.

Let us formulate the requirements which the parameters of a system must satisfy if rapid freezing is to be possible. According to the dynamic percolation model, the droplets which belong to a percolation cluster are close together for a certain time  $\tau_R$ , called the "restructuring time." We denote by  $\delta$  the maximum displacement which results in the detachment of a droplet from a percolation cluster. The parameter  $\delta$  is obviously related to the restructuring time by

$$\delta = (D\tau_R)^{1/2}, \quad (3)$$

where  $D$  is the diffusion coefficient of droplets. Using the known expression

$$D = \frac{kT}{6\pi\eta R}, \quad (4)$$

to evaluate this diffusion coefficient ( $R$  is the droplet radius), we find the qualitative dependence of the restructuring time  $\tau_R$  on the parameters of the system:

$$\tau_R = \frac{6\pi\eta R\delta^2}{kT}. \quad (5)$$

By raising the viscosity of the matrix one can thus increase the time spent by the droplets in the cluster. If the viscosity of the matrix takes on large values, on the other hand, then the time  $\tau_R$  may be long enough for the necessary measurements. In addition, the restructuring time is longer for the large droplets. (From the last formula for microemulsions, setting  $R \sim 50 \text{ \AA}$  and  $\delta \sim 0.1R$ , we find  $\tau_R \sim 0.6 \text{ ms}$ . This figure is essentially the same as the experimental results.<sup>5</sup>)

The characteristic freezing time  $\tau_F$ , i.e., the characteristic time for lowering the temperature of the system by  $\Delta T \ll T$ , is governed by the dimensions  $L$  of the samples being cooled and by their thermal conductivity  $\kappa$ :

$$\tau_F = \frac{L^2 \Delta T}{\kappa T}. \quad (6)$$

A structure freezes if the droplets do not leave the percolation cluster over the characteristic time  $\tau_F$  of the temperature decrease, i.e., under the condition  $\tau_F < \tau_R$ . We thus find the following limitation on the parameters of the system during the freezing of the structure:

$$L < \delta \left(\frac{6\pi\kappa\eta R}{k\Delta T}\right)^{1/2}. \quad (7)$$

It can be seen from this inequality that freezing of the structure for water-oil microemulsions, even if possible in principle, would run into formidable technical difficulties because of the small values of  $L$ .

## EXPERIMENTAL PROCEDURE

The basic requirements for freezing the structure of liquid systems concern the viscosity of the matrix. According to Einstein's equation, the viscosity  $\eta'$  of a disperse mixture also depends on the volume fraction  $\Phi$  of the disperse secondary phase:

$$\eta' = \eta(1 + 2.5\Phi).$$

It is important to achieve long restructuring times  $\tau_R$  not only while the temperature of the mixture is being lowered but also for subsequent study of the mixture. Frozen mixtures with small values of  $\tau_R$  can change in structure even during the preparations and analysis. For this reason, high-temperature mixtures appear to be the best choice. After they are frozen, at ordinary (room) temperature, the structure does not change significantly over a macroscopically extremely long time.

For our experiments we selected high-temperature emulsion mixtures formed when a low-viscosity melt of a glass-phobic liquid is mixed in a melt of silicate glass. As the matrix for producing the emulsion mixtures we used a glass with the composition  $48\text{SiO}_2 \cdot 20\text{Na}_2\text{O} \cdot 15\text{CaO} \cdot 17\text{B}_2\text{O}_3$ . The viscosity of this glass has a very sharp temperature dependence, as is characteristic of molten silicates.<sup>13</sup> The activation energy of the viscosity for these materials is approximately  $W = 420 \text{ kcal/mole}$ . At room temperature, the solidified melt is an ordinary glass, which is highly stable and convenient to work with, as is well known. As the glass-phobic secondary phase for the emulsification we selected a melt of sodium sulfate, whose viscosity at the temperature at which the emulsion mixtures were prepared (1000–1100 °C) is about two orders of magnitude lower than that of the matrix phase,  $\eta \approx 75\text{--}125 \text{ P}$ . Direct substitution into the formula expressing the limitation on the dimensions  $L$  of the samples of the mixture to be frozen shows that the materials selected made possible a freezing of the structure for micron-size and even submicron-size droplets of the secondary phase.

High-temperature emulsion mixtures were prepared by the standard method of mechanical emulsification<sup>10</sup> ("standard" aside from the elevated temperature). For this purpose, a melt of the glass-phobic sodium sulfate was emulsified by means of a two-blade stainless steel stirrer into a melt of glass in small alundum crucibles. The degree of dispersity of the emulsions can be varied by varying the

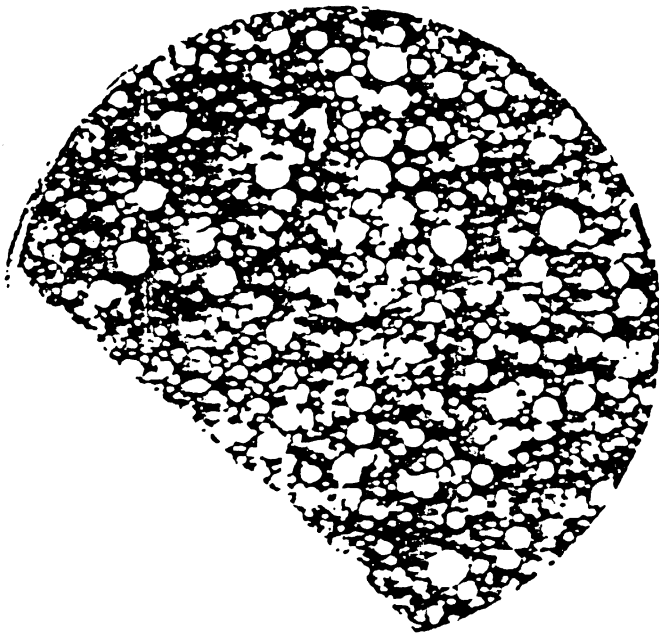


FIG. 1. Photograph of a frozen emulsion mixture (magnification  $4\times$ ).

operation of the stirrer.<sup>14</sup> The temperature of the resulting emulsion mixture was then rapidly lowered by  $70\text{--}100^\circ\text{C}$ . As a result the viscosity of the glass increased by about two orders of magnitude. Samples of the frozen emulsion mixture, cylinders 3 cm in diameter and 4–5 cm long, were cooled to room temperature. Flat plates were then cut from the cylinders for further analysis. The maximum concentration of the secondary component (sodium sulfate) in the glass matrix was  $\Phi_{\max}=0.20$ . A total of three lots of ten samples each were prepared, with volume fractions  $\Phi=0.10, 0.15$ , and  $0.20$ .

#### GEOMETRIC STRUCTURE OF THE FROZEN MIXTURE

Figure 1 is a typical photograph of a section of a sample of the frozen emulsion mixture.

First, photographic images of the frozen emulsion layer were studied by conversion to digital form. For this purpose, we used a VK-1 television camera. The information was then processed on a computer with the help of the SIAM software for morphographic image analysis.

Figure 2 shows a typical size distribution of the droplets of the disperse phase for an emulsion mixture with a secondary-component volume fraction  $\Phi=0.10$ .

To determine the geometric nature of the distribution of the secondary component, we plotted its specific mass content  $M$  versus the length of the side of the measurement cube,  $H$ . Figure 3 shows  $M(H)$  for the emulsion mixture with the secondary-component content  $\Phi=0.10$  and with a mean droplet radius  $\langle R \rangle = 160\ \mu\text{m}$ . The  $M(H)$  curves for the other mixtures are similar in shape. There are two regions, which differ in the power-law dependence: When

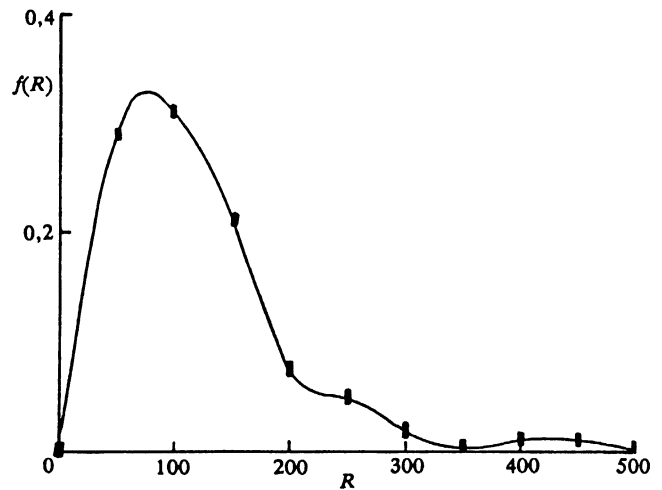


FIG. 2. Relative volume content of droplets with various radii in an emulsion mixture. The mean radius is  $\langle R \rangle = 160\ \mu\text{m}$ .

$H$  is smaller than certain lengths  $\zeta$ , we have  $M \propto H^{-0.5 \pm 0.1}$ , while we find  $M \propto \text{const}$  on large spatial scales,  $H > \zeta$ .

It is totally obvious that we would have  $M = \text{const}$  for a uniform distribution of droplets. This is precisely the behavior which we found at large values of  $H$ . The implication is that the emulsion layers of lyophobic liquids can be thought of as homogeneous materials at sufficiently large range. However, we see that as  $H$  is reduced below  $\zeta$  there is a different behavior:

$$M \propto H^{D-d}, \quad (8)$$

where  $d=3$  is the dimensionality of Euclidean space, and  $D < 3$  is the fractal dimensionality. The experimental data obtained for various samples differing in the mean droplet radius  $\langle R \rangle$  and in the volume fraction  $\Phi$  lead to the same fractal dimensionality:  $D = 2.5 \pm 0.1$ . (Interestingly, the fractal dimensionality of viscous fingers is close to this value. In the  $2D$  case for viscous fingers in a plane cell, for example, the figure is<sup>9</sup>  $D = 1.70 \pm 0.05$ .) On the other hand, the length scale  $\zeta$  at which the nature of the droplet distribution changes depends on the volume fraction of the secondary component,  $\Phi$  (Fig. 4).

We thus conclude that the emulsion mixtures have a structure which can be characterized as a uniform fractal: At large range these mixtures are uniform, while at short range they consist of a set of fractals of dimensionality  $D$  with a volume of order  $V_I = \zeta^3$ . This structure is a dynamic entity, but neither  $D$  nor  $\zeta$  varies in time. They remain constant for each emulsion mixture. The minimum volume  $V_I$  can be taken as an elementary irregularity of the emulsion mixture. These elementary irregularities have analogs in the blobs in polymer solutions.<sup>15</sup>

#### DISCUSSION OF RESULTS

We saw above that the structure of an emulsion mixture is homogeneous only at large range; over distances less than  $\zeta$ , the structure is fractal instead. However, this is just the structure which should be observed if the dynamic

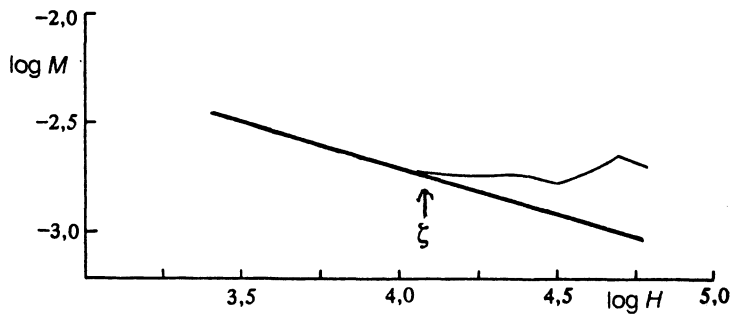


FIG. 3. Mass content of the secondary component,  $M$ , versus the length of the side of the measurement cube,  $H$ .  $\Phi=0.10$ ,  $\langle R \rangle = 160 \mu\text{m}$ ,  $\zeta = 18.6 \text{ mm}$ .

percolation model is valid. A percolation cluster is homogeneous only on length scales larger than the correlation length  $\zeta \propto |\Phi - \Phi_c|^{-\nu}$ , where  $\Phi_c$  is the percolation threshold, and  $\nu=0.88$  is a critical exponent. For dimensions less than  $\zeta$ , a percolation cluster is described by a fractal with dimensionality  $D=d-\beta/\nu$ , where  $\beta=0.4$  is the critical exponent. On the whole, the structure of a percolation cluster is described as a homogeneous fractal of dimensionality  $D$  (Ref. 11). According to theoretical predictions for  $d=3$ , the fractal dimensionality is  $D \approx 2.5$ .

A percolation cluster forms if the volume fraction of the droplets is sufficiently large. Ignoring the spread in the size of the droplets (Fig. 2), and assuming that all have the same radius  $R=\langle R \rangle$ , we conclude that the percolation threshold is reached when the volume fraction of the secondary component, along with the substance which forms the droplets at their distance of closest approach,<sup>1)</sup> is equal to the  $3D$  invariant  $\Phi_c=0.15$ . (In systems in which the sizes of the droplets span a wide range, the percolation threshold shifts toward larger values.<sup>16)</sup> We denote by  $\delta_1$  the thickness of the layer around the droplets. We then have the following expression for the percolation threshold for the emulsion system:

$$\Phi_0 = \Phi_c \cdot \frac{R^3}{(\langle R \rangle + \delta_1)^3}. \quad (9)$$

The quantity  $\delta_1$  can be found in two ways: by directly measuring the minimum distance between droplets or by analyzing the microscopic characteristics of the system,

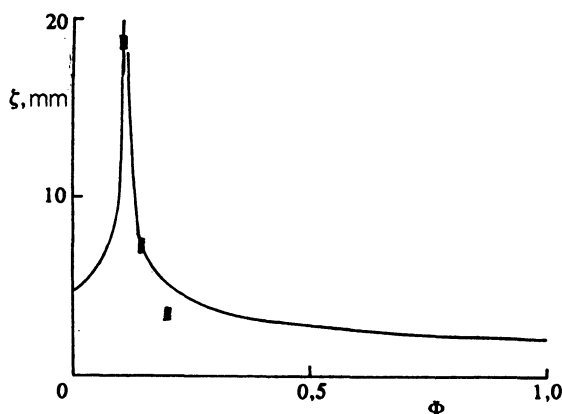


FIG. 4. Length scale above which the emulsion mixtures are homogeneous versus the volume fraction of the secondary component.

e.g., on the basis of the  $\zeta(\Phi)$  behavior.<sup>17</sup> For the mixture studied here, we find  $\delta_1 \approx 0.1 \langle R \rangle$  and correspondingly  $\Phi_0=0.11$ .

We write the  $\Phi$  dependence of the correlation length in the form

$$\zeta = \zeta_0 \cdot |\Phi - \Phi_0|^{-\nu}, \quad (10)$$

where the parameter  $\zeta_0$  is found experimentally for each mixture. In our own case we find the value  $\zeta_0 \approx 2 \text{ mm}$ . Figure 4 shows the  $\Phi$  dependence of the spatial scale  $\zeta$  above which these emulsion mixtures are homogeneous. In a narrow interval near the percolation threshold, at a secondary-component volume fraction on the order of 10–12%, the length scale  $\zeta$  takes on fairly large values—comparable to or even greater than the dimensions of the samples themselves. As was pointed out in Ref. 18, it is difficult to obtain reproducible results for such materials because of the random distribution of disperse inclusions.

An emulsion mixture of lyophobic liquids can be thought of as a close-packed system of elementary inhomogeneities—the fractals. However, in contrast with solid disperse systems, the inhomogeneous structure of liquid mixtures can be observed only over sufficiently short time intervals. The time  $\tau_I$  for observing inhomogeneities in liquid mixtures can be estimated from the diffusive nature of the motion of the droplets. We assume that there are no directed flows of material. Denoting the droplet diffusion coefficient by  $D$ , we can say that the following time is required for a change in density over a length scale equal to the size of an elementary irregularity in the mixture,  $\zeta$ :

$$\tau_I = \frac{\zeta_0^2}{D \cdot |\Phi - \Phi_0|^\nu}. \quad (11)$$

Consequently, the irregularities associated with the clustering of droplets can be observed most easily when the concentration of the secondary component is close to the percolation threshold.

## CONCLUSION

The results found here lend support to the dynamic percolation model for describing the structure of emulsions. One can verify that there are no continuous channels of secondary component by directly inspecting photographic images of the frozen structure (Fig. 1). With regard to the clustering of the droplets, it is necessary to

carry out a numerical analysis of the spatial distribution of droplets. It is possibly for this reason that the literature contains no information about the fractal behavior of emulsion systems, even though they have been under study for a long time now.

The method of freezing structure may be technically impossible for certain systems, e.g., water-oil microemulsions. Is it possible to analyze the geometric distribution of phases in such systems? In addition to the method proposed here, there is another method for finding the droplet distribution in emulsion mixtures, involving the scattering of electromagnetic radiation. This method is used to study the fractal behavior of solid substances.<sup>9</sup> For this purpose one could use small-angle scattering of x rays (for microemulsions) or of IR light (for emulsion mixtures). The intensity of the radiation scattered by the system of droplets of the emulsion mixture is given in the Born approximation by

$$I(q,t) = \frac{1}{N} S(q,t) |u(q)|^2. \quad (12)$$

Here, in contrast with the situation for solids, the structure factor  $S(q,t)$  depends on the time  $t$ ;  $q$  is the scattering wave vector, and  $u(q)$  is the form factor of an individual droplet. [The formula for Rayleigh scattering or the Guinier approximation<sup>19</sup> can be used for  $u(q)$ .] The structure factor can thus be determined experimentally by taking an average of  $I(q,t)$  over various time intervals  $\tau$ . The structure factor can then be expressed in terms of a time-dependent binary distribution function of droplets. After inversion, we find the following expression for the radial distribution of droplets,  $g(r,\tau)$ :

$$g(r,\tau) = 1 + \frac{1}{2\pi^2 \rho r} \int_0^\infty [S(q,\tau) - 1] \sin(qr) q dq, \quad (13)$$

where  $\rho = N/V$  is the density of droplets.

The limit  $g(r,\tau) \rightarrow 1$ , which corresponds physically to a transition to a homogeneous distribution of droplets, should be observed at large values  $r > \zeta$  if the time over which the scattered-radiation signals are averaged satisfies  $\tau < \tau_I$ .

If we instead use measurements of the intensity of scattered radiation over a sufficiently long time interval  $\tau > \tau_I$ , then the transition of the radial distribution of droplets,  $g(r,\tau) \rightarrow 1$ , should be observed considerably earlier, at a value of  $r$  equal to a few times the distance between particles.

In summary, emulsion mixtures of lyophobic liquids have a complex geometric structure which varies in time. This structure can be characterized as a dynamic homogeneous fractal. While these mixtures are homogeneous substances over long time scales  $t > \tau_I$  or in large volumes  $V > V_I$ , at small time and length scales they consist of a set of inhomogeneous elementary entities (of the blob type): fractals with the common dimensionality  $D = 2.5 \pm 0.1$ . The elementary inhomogeneities are dynamic entities, but for each emulsion mixture the fractal dimensionality and their volume remain constant in time. The lifetime of the elementary inhomogeneities,  $\tau_I$ , and their volume increase without bound when the concentration of the secondary component is close to the percolation threshold  $\Phi_0$ .

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<sup>1)</sup>For microemulsions, it is generally assumed that this is a layer of surfactant.

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