Spatial, Temporal, and Energetic Disorder in Microemulsions

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The relaxation of microemulsions has been studied by means of the pressure-jump relaxation technique with conductimetric detection. Kohlrausch-Williams-Watts stretched exponentials $\{\phi(t) = A\exp[-(t/\tau)^b]\}$ were obtained in which the parameter b increases with temperature from the percolation point of the microemulsions, attaining values greater than 1. These findings entail the existence of spatial, temporal, and energetic disorder associated with temperature-dependent anomalous (inhibited and enhanced) diffusion.

A microemulsion is a stable thermodynamically isotropic, single-phase fluid composed of water, oil, and a small quantity of a surface-active agent, or surfactant. If the amount of oil or water present is very small, droplets of this component are dispersed in the major component to give an oil-in-water or water-in-oil microemulsion, but there is considerable uncertainty as to the structure of microemulsions in which the two main components have similar concentrations, with bicontinuous,[1,2] chaotic,[3] and other models[4-8] having variously been proposed to explain the observed properties of such systems.

One means for the investigation of the structure and dynamics of complex systems is through relaxation experiments.[9] It has been found that the relaxation of many disordered systems does not exhibit simple exponential decay, but rather obeys a Kohlrausch-Williams-Watts (KWW) stretched-exponential law of the form $\phi(t) = A\exp[-(t/\tau)^b]$ ($0 < b < 1$), where b has been shown to be related to the spatial, temporal, and energetic disorder of the medium.[10] Assuming disorder decoupling, Blumen[11] has found that spatial and temporal disorder combine multiplicatively: $b = \gamma d_s/2$ for $d_s < 2$ and $b = \gamma$ for $d_s > 2$, where $0 < \gamma \leq 1$ is the degree of temporal homogeneity ($\gamma = 1$ for a temporally homogeneous medium) and d_s is the spectral, or fracton, dimension given by $d_s = 2d_f/d_w$, d_f being the fractal dimension of the medium and d_w the fractal dimension of a random walk within it.

We report here the results of a pressure-jump relaxation study of microemulsions comprising 7.5% of sodium bis-(2-ethyl,hexyl) sulphosuccinate (Aerosol-OT, or AOT), 46.25% of brine (3% of NaCl in H_2O), and 46.25% of n-decane. All chemicals were Merck p.a. products and were used without further purification. The employed pressure-jump technique with conductimetric detection (from DIALOG GmbH, Düsseldorf, West Germany) was similar to that developed by Knoche and Wiese.[12,13] This technique makes use of the fast pressure drop achieved by the blowing out of a rup-

ture membrane. Inside an autoclave filled with water and closed with a rupture membrane, two identical conductivity cells are mounted. One of these is filled with the solution to be examined and the second serves as reference to cancel disturbances caused by temperature fluctuations. The two cells form part of a Wheatstone bridge operated at a frequency of 40 kHz. The bridge is tuned at the ambient pressure of 1 atm, and the pressure is then increased slowly by our pumping more water into the autoclave, thereby shifting the thermodynamic equilibrium of the system (the microemulsion) and unbalancing the bridge. At 130 atm the rupture membrane bursts and the pressure in the cells drops to 1 atm within about 50 μs. The relaxation of the system to its thermodynamic equilibrium state is then recorded as an ac signal which is fed both to an oscilloscope and to a digited interface (DIA-RRC from DIALOG GmbH, Düsseldorf, West Germany), which after signal integration passes 1024 data to a computer for their conversion to electrical conductivity data, $\phi(t)$, and further processing. All such pressure-jump experiments were repeated 3-5 times and the $\phi(t)$ were averaged by the computer. The temperature of the autoclave was controlled to within ± 0.01 K.

The relaxation data were at first analyzed by an improved version of the method developed by Strehlow,[14,15] which has been proved to give satisfactory results in chemical relaxation experiments, i.e., for a discrete distribution of relaxation times.[16-19] However, systematic continuous variation of the relaxation times was observed; the relaxation process could only be described by a spectrum of relaxation times, i.e., by a distribution $P(\tau)$ of exponential relaxations with time constants τ. By means of a computer analysis similar to that described by Kronmüller, Mosser, and Henmeier,[20] the $P(\tau)$ were found to be Levy distributions, which clearly suggested the existence of a KWW relaxation law.[21-23] Because of their computational simplicity, the relaxation curves were therefore fitted directly with a KWW relaxation law. The goodness of fit was satisfactory in all the cases studied so long as the values of b were not restrict-
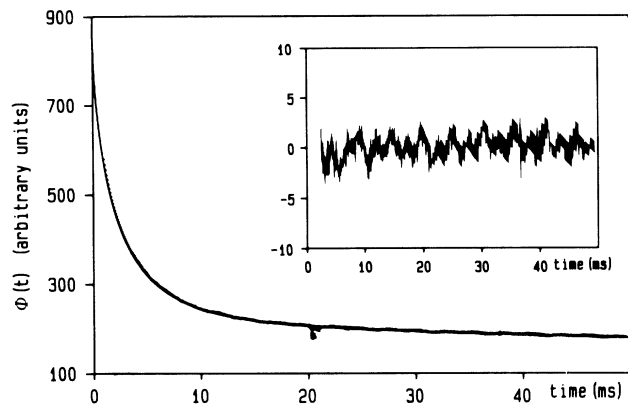
FIG. 1. Typical KWW relaxation curve fitted to 1024 experimental points ($T = 309.16$ K, $b = 0.64$, $\tau = 1.92$ ms). Inset: The random distribution of errors.

ed to the range $0 < b < 1$ (Fig. 1). The values of τ and b are listed in Table I for each of the temperatures at which experiments were performed. Similar results, with values of b likewise greater than 1, were obtained with AOT microemulsions of different compositions.[24] The increase in relaxation time with temperature confirms that critical slowing down occurred on approaching the temperature at which the microemulsion separated into two phases ($T_s = 312.16$ K), but the reader is referred elsewhere[25] for further discussion of τ; we concentrate here on the interpretation of b, whose observed temperature dependence (Fig. 2) is well fitted by the equation $b = A[(T_c - T)/T_c]^{-1}$ with $A = 9.83 \times 10^{-3}$ and $T_c = 313.65$ K.

Like other microemulsions of similar composition, that used in this study exhibits percolation,[24,26-31] for which Grest et al.[32] have recently suggested an explanation in terms of cluster formation. Since percolation clusters are self-similar, they can be modeled by fractal structures,[33] in which physical quantities obey scale-dependent laws; an example is the conductivity law $\phi \propto (p - p_c)^{t'}$, where p is the volume fraction of nanodroplets, p_c is the corresponding value for the percolation threshold, and t' is the critical exponent ($t' \approx 1.9$ for per-

TABLE I. Dependence of the KWW relaxation equation parameters on the temperature of the AOT microemulsion studied.

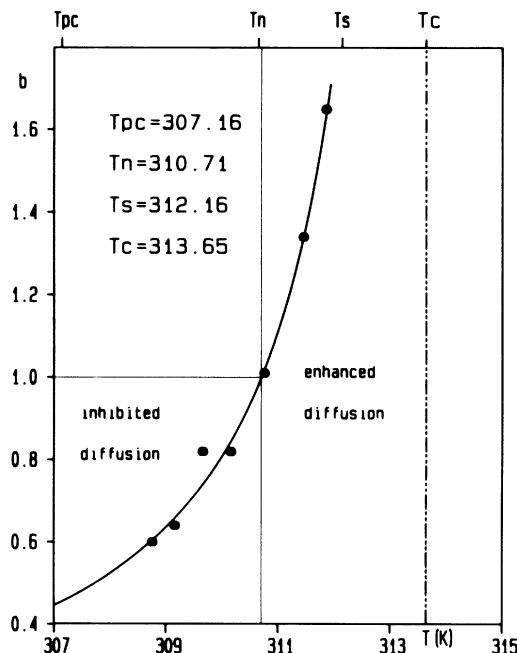| T (K)	b	τ (ms)
311.86	1.65 ± 0.03	34.3 ± 0.2
311.46	1.34 ± 0.04	28.2 ± 0.3
310.76	1.01 ± 0.05	19.1 ± 0.3
310.16	0.82 ± 0.05	11.9 ± 0.3
309.66	0.82 ± 0.06	5.18 ± 0.11
309.16	0.64 ± 0.07	1.92 ± 0.06
308.76	0.60 ± 0.07	1.28 ± 0.04

FIG. 2. Dependence of b on temperature. The solid line is the result of fitting the equation $b = A[(T_c - T)/T_c]^{-1}$ to the experimental data. T_{pc} is the percolation threshold temperature. T_n is the temperature for $b = 1$. T_s is the phase-separation temperature. T_c is the "effective" critical temperature for the scaling behavior of b.

colation in the Euclidean dimension $d = 3$). As the percolation threshold depends on the temperature and composition of the microemulsion, one can find a similar law relating conductivity to temperature or other parameters related with the composition, such as the volume fraction of water + AOT or the surfactant concentration.[26,27,32,34]

Diffusion in a fractal medium is anomalous,[35] i.e., $\langle r^2 \rangle \propto t^a$ ($a < 1$), where $\langle r^2 \rangle$ is the mean square displacement after time t; specifically, in a fractal medium, $a = d_s/d_f = d_w$, where d_w, the fractal dimension of the path of a particle in the medium, is given by $d_w = 2 + \theta$, θ being the exponent relating the diffusion coefficient in a fractal medium to the distance traveled $[D(r) \propto r^{-\theta}]$. Thus $a = 2/(2 + \theta)$ (and since $\theta \geq 0$, $a \leq 1$), and the parameters a and b are related by the expressions $b = \gamma d_f a/2$ (for $a d_f < 2$) and $b = \gamma$ (for $a d_f > 2$) with $a, b \in (0, 1)$.

For anomalous diffusion in a percolation lattice at the percolation threshold ($p = p_c$),[35] $\theta = (t' - \beta)/\nu$, $d_f = d - \beta/\nu$, and $d_s = 2(d\nu - \beta)/(t' - \beta + 2)$, where β is the critical exponent of the probability that a percolation lattice bond belongs to an infinite cluster $[P(p) \propto (p - p_c)^\beta]$ and ν is the critical exponent of the correlation length $[\xi(p) \propto (p - p_c)^{-\nu}]$; so for $d = 3$, for which $\beta \approx 0.4$ and $\nu \approx 0.8$ at the percolation threshold, $\theta \approx 1.88$, $d_f \approx 2.5$, $d_s \approx 1.29$, $a \approx 0.52$, and $b \approx 0.65\gamma$. Since the experimental temperature dependence of b (Fig. 2) points to a

value of $b = 0.46 \pm 0.05$ at the percolation threshold temperature $T_{pc} = 307.16$ K,[24,25] we may conclude that temporal "disorder" existed in the microemulsion at this temperature and that this disorder is characterized by the value $\gamma \approx 0.7$. At $p = p_c$, it thus transpires that spatial and temporal disorder were both important, the temporal disorder being explicable in terms of a distribution of waiting times for the breaking of droplet-droplet bonds within fractal nanodroplet clusters[36] embodying spatial disorder.

Away from the percolation point ($p > p_c$, i.e., $T > T_{pc}$), $\theta \rightarrow 0$ and $a \rightarrow 1$ as $p \rightarrow 1$; the percolation lattice becomes completely connected and ordinary diffusion takes place. In this case $b \rightarrow \gamma$, and if there is no temporal disorder in the completely connected lattice then $b \rightarrow 1$. Such changes of dimensionality and of the corresponding diffusion behavior with temperature have been supported both theoretically[37-43] and experimentally,[44,45] with all these studies agreeing that a transition from anomalous to normal diffusion can take place by an increase of the temperature. As Fig. 2 shows, the experimental value of b did indeed increase with temperature from the extrapolated value corresponding to $p = p_c$, and at $T_n = 310.71$ K the relaxation was purely exponential ($b = 1$), so that at this temperature diffusion can be considered as having been normal, with neither spatial nor temporal disorder present in the microemulsion (i.e., $\gamma = 1$ and $d_s = 2$). Away from the percolation point, however, values of b greater than 1 were attained as the phase-separation temperature T_s was approached; so far as we know, this is the first time that a KWW relaxation law with $b > 1$ has been reported.

With the assumption that $b \propto a$ and $b, a > 1$, the $b > 1$ phenomenon would be explained by the existence of diffusion processes which are faster than normal. Such processes have been claimed to occur in superconducting percolation networks[46] and other systems denominated "antifractals"[47] because they are associated with fractal structures whose diffusion properties are the opposite of those exhibited by normal fractals. However, a simpler and more elegant explanation for the appearance of enhanced diffusion would be the existence of energetic disorder, i.e., of an ultrametric space[48] for the energy barriers which can be associated with the breaking of droplet-droplet bonds within clusters. In this event, diffusion would be inhibited ($a < 1$ and $b < 1$)[37-41] or enhanced ($a > 1$ and $b > 1$)[42,43] depending on the parameters of the ultrametric space of the energy barriers. This hypothesis raises the questions of how the relaxation parameter b is related to the parameters characterizing diffusion through the ultrametric space, whether the temperature T_n is a borderline between compact and noncompact diffusion, and whether $b > 1$ reflects the existence of intrinsically nonlinear dynamics responsible for the synergetic phenomena which have been observed in microemulsions.[49,50] We hope that this Letter may

prompt more precise theoretical descriptions of diffusion in disordered systems and its relation to the relaxation parameters, which would allow a more quantitative analysis of the data reported here.

In conclusion, we have shown that the relaxation of some types of microemulsions is accurately described by a stretched-exponential law with an exponent b which, depending on the temperature, attains values less than, equal to, or greater than 1. The application to microemulsions of models similar to those developed in other fields (spin-glasses,[51] the dynamics of polymers[44] and proteins,[52] chaotic systems,[53] etc.) allows the existence of spatial, temporal, and energetic disorder to be deduced from this observed behavior.

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