Chemical Physics 513 (2018) 280–286

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Stretched exponential relaxation process of onion structures under various oscillatory shears with analysis using Shannon entropy

Hirokazu Maruoka[a,*,1], Akio Nishimura[a], Hideharu Ushiki[a,2], Keisuke Hatada[b,c,d]

[a] United Graduate School of Agricultural Science, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu-shi, Tokyo 183-8509, Japan
[b] Faculty of Science, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan
[c] Department Chemie, Physikalische Chemie, Ludwig-Maximilians-Universität München, Haus E2.033, Butenandtstrasse 11, 81377 München, Germany
[d] Physics Division, School of Science and Technology, Università di Camerino, via Madonna delle Carceri 9, I-62032 Camerino, MC, Italy

ARTICLE INFO

Keywords:
Onion structure
Oscillatory shear
Relaxation process
Stretched exponential
Shannon entropy

ABSTRACT

The relaxation processes of onion structure in sine-oscillatory shear in a quaternary mixture of water, NaCl, 1-Octanol and Sodium Dodecyl Sulfate, have been investigated by two dimensional light scattering. In this work, the relaxation processes of constant shear, oscillatory shear and sine-oscillatory shear are compared and evaluated by Shannon entropy. Shannon entropy is the function to estimate the statistical homogeneity. The relaxation processes of sine-oscillatory shear show the good fitness with the stretched exponential and the Shannon entropy of sine-oscillatory shear increases with frequency. The influence to the relaxation process reflected from the different manner of shearing is briefly discussed.

1. Introduction

The behavior of the lyotropic lamellar structures under shear flow has been widely studied [1–12]. Above a critical shear rate, the lamellar phase transform to the micro-size and monodisperse multilamellar vesicles phase. The size of vesicles, R, depends on the shear rate, $\dot{\gamma} = d\gamma/dt$, as follows, $R \sim \dot{\gamma}^{-0.5}$ [1,2]. The vesicles are sometimes referred to onion structure as it consists of multilamellar. The formation mechanism and the behavior of the stationary state are well studied [1–7,10–12]. The nucleation process[5] and the buckling model[6] are proposed for the formation process while the buckling model is supported experimentally[4,11] and theoretically[7]. Gentile et al. recently reported the detailed formation process from lamellar to onion structure using flow-SANS (Small angle neutron scattering) supporting buckling model.

Focusing on the relaxation process, firstly it was proposed that it was described by a single exponential. However, Yatabe et al.[8] showed that the formation process is better described by the stretched exponential,

$$I(t) = \exp\left[-\left(\frac{t}{\tau_K}\right)^{\beta}\right]. \quad (1)$$

Yatabe insisted that the process is described with the stretched exponential by supposing that the size decreasing is a collective diffusion equation and the initial size distribution is described by the Boltzmann equation [8,9]. He also found that the formation process of oscillatory shear is described with the stretched exponential while the fitting parameters depend on the frequency.

The stretched exponential is widely used in many areas including, glass transition [13–16], relaxation process [8,9,17,18], deformation of real materials [21,22], nucleation process [23], statistical analysis [19,20] and so on. It was discovered by Rudolf Kohlrausch in 1854 to describe the relaxation process of the residual charge of a glass Leyden jar while it was a phenomenological application[24]. Since the rediscovery by William and Watt [25] in 1970, the stretched exponential function has gained attention and started to be utilized for describing the relaxation phenomena, though it is even sometimes considered as a phenomenological tool without any fundamental significance [26].

Some models to obtain the stretched exponential function were proposed. Palmer et al. [27] obtained the stretched exponential function from the model of the hierarchically constrained dynamics in glassy relaxation. Trapping model [26,28], the survival time of Brownian motion in disorderly distributed traps, is also one of the major models for the stretched exponential decays. Phillips insisted that

* Corresponding author.
E-mail address: hmaruoka1987@gmail.com (H. Maruoka).
[1] Present address: Inorganic Functional Materials Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Anagahora, Shimo-Shidami, Moriyama-ku, Nagoya, Aichi 463-8560 Japan.
[2] Deceased 7 September 2016.

https://doi.org/10.1016/j.chemphys.2018.08.020
Received 4 May 2018; Accepted 12 August 2018
Available online 14 August 2018
0301-0104/

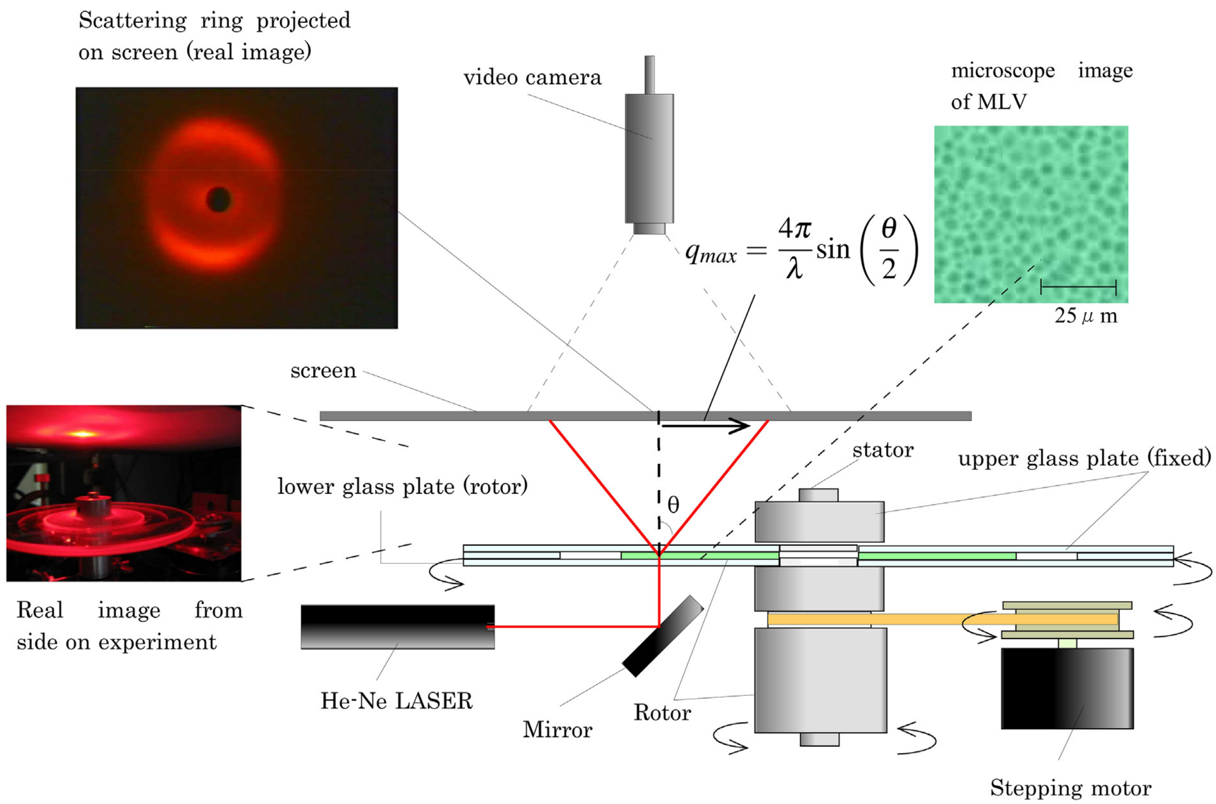

Fig. 1. The plate-plate type of glass cell was prepared and the sample (Sodium Dodecyl Sulfate/1-Octanol/Brine (20 g/L)) was induced between two glass plates. The upper side of plate was fixed and the lower side of cell was connected with the stepping motor which was controlled by PC, MS-Dos, programmed by Delphi. The experiment was performed at 20 °C, controlled by air conditioner. Once the program had started, the lower cell was rotated by stepping motor as it was programmed and the sample was sheared. For measurement, the He-Ne LASER (10 mW, λ = 632.8 nm) was radiated to the cell and the scattering light was projected on the screen. The scattering pattern was recorded by camera to VHS recorder, then later the movie is captured and analyzed. By fitting the scattering ring, the radius of scattering ring was measured and we obtain the scattering angle θ. Then we calculate the scattering vector $q_{max} = 4\pi/\lambda \sin(\theta/2)$.

molecular relaxation can be understood when one can separate extrinsic and intrinsic effects, and that the intrinsic effects are dominated by two magic numbers, β_{sr}, short range forces, and β_K for long range Coulomb force. These models suggested that the non-uniformity, constraint effects are the essential element to obtain the stretched exponential decays. An interesting result was reported by Bunde et al. [29]. They associated the power exponent β with the scale size effect. They found that the relaxation changes from the stretched exponential to a single exponential decays over a characteristic time which depends on the size of system. This report suggested that the power exponent was a relative, intermediate parameter which depends on the scale.

In our work, to develop the discussion of the relaxation process, we study the formation process in the sine-oscillatory shear flows, where the shear rate follows that of a sine function. We see how the way of shear influence the relaxation process. Furthermore, we propose the method to evaluate the processes. According to the integral transformation method, the relaxation is described as follows,

$$I(t) = \int_0^{\infty} D(\tau)F(t, \tau)d\tau \quad (2)$$

where $D(\tau)$ is distribution function and $F(t, \tau)$ is elementary function [8,9]. As mentioned above, several studies suggested that the power exponent is highly related with the non-uniformity of processes. In the integral expression of Eq. (2), this non-uniformity is expressed by $D(\tau)$. Here we estimate the non-uniformity by introducing Shannon entropy to $D(\tau)$. Shannon entropy is utilized for the probability density function to estimate the average amount of information content of the distribution, which reflects the statistical homogeneity. Bunde et al. suggested that the power exponent is not fixed number, but it is an intermediate exponent which depends on the size of system. Here we attempt to estimate how the non-uniformity of the process is reflected by the Shannon entropy.

2. Experiment

2.1. Materials

We prepared a quaternary lyotropic lamellar phase solution by mixing 9% Sodium Dodecyl Sulfate (Wako. Co. 97% purity), 11% 1-Octanol in brine (20 g/L NaCl in distilled water) by weight volume. Solution was mixed to reach the steady state and left for more than two weeks [8,9].

2.2. Measurements

The experimental system is sketched in Fig. 1. The shear rate is the rate at which a progressive shearing deformation is applied. In the experiment of a plate-plate type cell, the sample is bound between two plates and the shear rate $\dot{\gamma}$ is defined by the rotation speed of plate v divided by the cell gap h: $\dot{\gamma} = v/h$. We prepared the plate-plate type cell with 1 mm gap between two plates. We inserted the sample between plates. The sample was sheared by rotating lower side of plate. Upper plate was fixed and lower plate was rotated by the stepping motor. Stepping motor was connected with PC (MS-Dos) and we can control the velocity of rotation, the way of shear and frequency. The experiments were performed under 20 °C with air conditioner. We used the light scattering method for the measurements. He-Ne Laser (10 mW, λ = 632.8 nm) was directed to the sample and the scattering pattern was projected into the screen. The time evolution of scattering pattern was recorded to VHS recorder with CCD camera. Then we captured the