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Size evolution of onion structure under oscillatory shear flow

Zenji Yatabe [a*], Ruri Hidema [a], Chihiro Hashimoto [b],
Robert Bernard Pansu [c], Hideharu Ushiki [d]

[a] Laboratory of Molecular Dynamics and Complex Chemical Physics,
Department of Biochemistry and Biotechnology, United Graduate
School of Agricultural Science, Tokyo University of Agriculture and
Technology, 3-5-8 Saiwai-cho, Fuchu-shi, Tokyo 183-8509, Japan
[b] Department of Applied Chemistry and Biotechnology
Niihama National College of Technology
7-1 Yakumo-Cho, Niihama, Ehime, 792-8580, Japan
[c] Laboratoire de Photophysique et Photochimie Supramoléculaires et
Macromoléculaires UMR 8531 CNRS, D'Alembert Institute,
ENS Cachan, 61 av. President Wilson, 94230 Cachan, France
[d] Laboratory of Molecular Dynamics and Complex Chemical Physics,
Institute of Symbiotic Science and Technology, Division of
Ecosciences, Tokyo University of Agriculture and Technology, 3-5-8
Saiwai-cho, Fuchu-shi, Tokyo 183-8509, Japan
[*] Author to whom correspondence should be addressed.
E-mail: zenji@cc.tuat.ac.jp

Abstract

The formation process of onion structure in a quaternary mixture among water, NaCl, octanol and sodium dodecyl sulphate, have been investigated by two dimensional light scattering under oscillatory shear flow. In our experiment, we investigated the size evolution of onion structure estimated by light scattering data with a nonlinear least-squares curve fitting method. The time evolution of onion size showed a good agreement with a stretched exponential function. The effect of oscillatory shear flow on formation process of onions is briefly discussed from the viewpoint of the physical meaning of fitting parameters based on the integral transformation method.

Introduction

The behaviors of the lamellar structure and of the lamellar–sponge structures coexisting mixture under shear flow have been widely studied [1-15]. Above a critical shear rate typically of the order of few s^{-1}, lyotropic lamellar phase may form multilamellar vesicles known as onions [1-6]. Both nucleation process [1] and hydrodynamic instabilities known as buckling mechanism [2] were proposed for the transition of the shear-induced onion structure. In recent, the theoretical [3,4] and experimental works [5,6] supported the buckling mechanism based on the coupling between thermal undulations of the membranes and the flow. Once onion structure is formed under steady shear flow, this structure is comparative stable and their size slowly decreases with time course reaching to its final stationary state [5-7]. The stationary onion size R_f is expressed by $R_f \sim \dot{\gamma}^{-0.5}$, where $\dot{\gamma}$ is the applied shear rate [8,9]. Courbin et al. [10] showed that the temporal evolution of onion size in lamellar-sponge phases coexisting mixture under shear flow can be described by mono-exponential function. However, a shear-induced structural transition from lamellar structure to onion structure does not show a mono-exponential relaxation process [5,6,11]. In our previous work [11], we suggested that the time evolution of the Bragg peak $q_{\max}(t)$ can be expressed by the stretched exponential function. In fact, the mono and double-exponential function is not in agreement measured data, because the value of χ^2 is larger than stretched exponential function and also there are the meaningless fitting parameters in the sum of mono-exponential function [12]. Thus the stretched exponential function is appropriate to express the Bragg peak $q_{\max}(t)$.

Roux and co-workers [13,14] observed that the long-range order of onion structure was kept and improved after the small oscillations. Generally, onions are formed by applying a fixed shear rate to a lamellar structure. Recently, Fritz et al. [15] investigated the effect of an oscillating shear flow on the formation kinetics of onion structures. They could be controlled the kinetics of the transition with varying the stress amplitude of the oscillation and to determine a minimum strain amplitude needed to trigger onion formation. Further, Nettesheim et al. reported the process of onion formation in a flow reversal experiment is not only slowed, but the mesoscopic structures at the end of the flow reversal experiment most likely differ substantially in comparison to the continuous experiment [16].

In fact, very little is known on their behaviour during formation process of onion structure. There is difference between the study of the above researches [15,16] and the one presented here. Fritz et al. applied oscillatory stress [15] and Nettesheim et al. used a trapezoidal strain profile for [16], whereas we performed a triangular strain profile (see Fig.1). Since shearing was not stopped to between the forward and backward one, this triangular strain profile may be more effective than a trapezoidal one in the formation process of onion structure toward the stationary state. For instance, the triangular strain profile experiment is more likely to raise the frequency of collisions between onions.

In the field of complex fluids, many relaxation processes can be described by some power law functions in natural phenomenological facts [11,17-19]. In fact, these relaxation functions are empirical formula. Thus, it is still unclear the physical meaning of power law even after large theoretical [20,21] and experimental effort [22] was devoted to the understanding of the relationship between power low and fractal dimension. Hence, we proposed integral transformation method in order to clarify the mechanisms of complex fluids [11,23-26]. We have defined this method as follows:

$$I(t) = \int D(\tau) F(t,\tau) d\tau \qquad (1)$$

where $I(t)$, $F(t,\tau)$ and $D(\tau)$ are phenomenological, elementary and distribution functions, respectively. The phenomenological function $I(t)$ represents the gathered elementary function $F(t,\tau)$ having various τ values based on distribution function $D(\tau)$, namely, this integral formula indicates that the obtained phenomenological $I(t)$ functions are represented by the convolution integrals with the distribution functions $D(\tau)$ of parameters. Therefore integral transformation method is a powerful method to investigate relaxation process of complex fluids based on power law and distribution function [11,23-26]. We are make suggestion by integral transformation method to be available for research fields of complex fluid [11,23-26].

In this report, the formation process of the onion structure toward the stationary state under oscillatory shear flow in various frequencies at fixed shear rate $\dot{\gamma}$ = 47s^{-1} was measured by using two dimensional light scattering measurement. It is found the best fitting function in order to describe a position of the Bragg peak $q_{\max}(t)$ as function of time. Furthermore, the effect of oscillatory shear flow on kinetics of onion structure is briefly discussed from the viewpoint of integral transformation method.

2. Experimental

2.1. Materials

The system was studied a quaternary lyotropic lamellar phase, which was composed of sodium dodecyl sulfate (SDS), octanol, NaCl and water [27]. The sample preparation was the same in the previous paper [11]. The lamellar phase was prepared by dissolving 9% SDS and 11% octanol in brine (20g/L NaCl in distilled water). Experiments were performed after approximately two week, until the samples had reached steady state.

2.2. Measurements

The onion structures are micrometric size, therefore, the light scattering measurement were performed under oscillatory shear flow with 1 mm gap homemade plate-plate type cell, one of which is turned at periodic square wave. The schematic illustration of shear rate and strain profile is shown in Fig. 1. The shear rate was fixed $\dot{\gamma} = 47 s^{-1}$ with various periods of rotation T = 16 s, 32 s, 64 s, 128 s. The incident light (10mW He-Ne laser) was scattered in sample cell and the scattering light could be visualized by use of projection on a screen. All experiments were performed at room temperature (20℃). When onion structures were formed, the light scattered from the sample gave a characteristic ring in the forward direction. The position, $q_{\max}$, of the diffraction ring was related to the size R of the vesicle by the relation: $R = 2\pi/q_{\max}$ where $q_{\max}$ is the scattering wave vector. The images of the light scattering patterns were intermittently recorded using a CCD video camera. The decay curves of Bragg peak $q_{\max}(t)$ were fitted by our original fitting program as a software part of PLASMA [23-25], based on the quasi-Marquardt algorithm with nonlinear least square method. Detailed information about both the apparatus [11] and the curve fitting method can be found our previous paper [23-25].

3. Results and discussion

When lamellar structure are induced by oscillatory shear flow above the critical shear rate, the lamella structure undergoes a transition to the onion structure. A characteristic scattering ring suddenly appears on the screen. The wave vector corresponding to the maximum of the scattered intensity is $q_{\max}$ from which the size of the onion structure can be deduced by $R = 2\pi/q_{\max}$. A position of the Bragg peak slowly and continuously increases with time until the stationary state. This formation behaviour is also observed under steady shear flow [5-7,11]. The evolution of the Bragg peak $q_{\max}(t)$ under various oscillation frequencies, which is calculated from the scattering ring, are shown in Fig. 2. Assuming that the stretched exponential function could fit the time evolution of the Bragg peak

$q_{\max}(t)$ from the phenomenological viewpoint based on the integral transformation method [11,22-25].

$$q_{\max}(t) = q_1 + q_2\left[1 - \exp\left\{\left(\frac{t - t_0}{\tau_{kww}}\right)^{\beta}\right\}\right] \tag{2}$$

q_1 indicates the initial scattering vector when the onion structure is formed in the lamellar solution and t_0 is its time delay. And also the q_1+q_2 represents the scattering vector of the onion structure at stationary state. In case of steady shear flow, these values (q_1, t_0 and $q_1 + q_2$) have been extensively studied [2-6,8,9]. And τ_{kww} is the relaxation time and β is the power component. The details of meaning of fitting parameters were described in our previous paper [11]. Our experimental data agree with stretched exponential function (Eq.(2)) very well (see Fig. 2). Fitting parameters and χ^2 values of stretched exponential function (Eq.(2)) for various frequencies are listed in Table 1.

The plot of fitting parameters of stretched exponential function (Eq.(2)) against the frequency is shown in Fig. 3. The initial scattering vector q_1 the final scattering vector $q_1 + q_2$ and the power component increase with frequency. On the other hand, the time delay t_0 decreases with frequency. At lower frequencies the oscillatory flow have no influence on the formation process of onion structure.

In our previous paper [11], fitting parameters q_1, t_0, $q_1 + q_2$ and τ_{kww} under steady shear flow was experimentally found for $q_1 = 2.95 \times 10^{-1}\dot{\gamma}^{0.33}$, $t_0 = 6.11 \times 10^{4}\dot{\gamma}^{-1.1}$, $q_1 + q_2 = 4.54 \times 10^{-1}\dot{\gamma}^{0.48}$ and $\tau_{kww} = 4.37 \times 10^{4} - 1.86 \times 10\dot{\gamma}$, respectively. Using these equations, each fitting parameter at various oscillatory frequencies could be converted to the corresponding steady shear rate $\dot{\gamma}$, namely, q_1, t_0, $q_1 + q_2$ and τ_{kww} are substituted in above expressions for $\dot{\gamma}$. Fig.4 shows that a plot oscillatory frequency under $\dot{\gamma} = 47\ s^{-1}$ vs. its corresponding shear rates $\dot{\gamma}$ under steady shear flow for fitting parameters. The corresponding shear rate $\dot{\gamma}$ increases with increasing oscillatory frequency and approaches to a constant value at higher frequencies, namely, the effect of oscillation is saturated in the high frequency range. As shown in Fig. 3, the variation of q_1 is very small. In fact, Fig. 4 indicates that the effect of oscillatory flow is strongest for the relaxation time τ_{kww}. Current experimental works try to describe the formation of onions from lamella structure under oscillatory condition with parameters such as the strain, shear rate, and stress [15,16]. Since the influences of the various parameters (strain, shear rate, and stress) seem not to be independent of one another, the transition is still under debate. We hope that our experiments data will be useful to describe the formation of onions from lamella structure under oscillatory condition.

Meanwhile once onion structure is formed in lamellar structure under shear flow, their size slowly decreases with time course reaching to its final stationary state. Based on the integral transformation method [11,23-26], we can give a suggestion their relaxation process is gradually attained mono-exponential relaxation process with increasing frequency as follow. The kinetics of swelling and shrinking of PNIPA gels can be described by the collective diffusion equation, and the temporal change of gel size is expressed by a simple exponential function [25,28,29]. Thus in analogy with collective diffusion process of PNIPA gels, we deduced the β value as 0.5 on the assumption that the size decreasing of onion structure under steady shear flow undergoes by the collective diffusion and that the initial size of onions obeys the Boltzmann distribution of the surface free energy [11]. In case of oscillatory flow, β increases with increasing frequency (see Fig.3). Such behavior may be due to the fact that the characteristic relaxation time of the size decreasing τ_R is given by $\tau_R \sim R_0/D$, where R_0 and D are the initial single onion radius and the diffusion coefficient, respectively [11]. Then the temporal evolution of the average onion size $R(t)$ is given by a stretched exponential function as: $R(t) \sim \exp\left(-ct^{0.68}\right)$, where c is a constant [11]. Here, following mechanism is also possible. Let us imagine that the mechanism of the size decreasing of an onion is described by a mono-exponential function: $R(t,\tau) = \exp(-t/\tau)$. In fact, Courbin et al. proposed that the temporal evolution of onion structure of lamellar/sponge mixtures is described by mono-exponential function [10]. The stretched exponential function can be described by a superposition of mono-exponential function based on integral transformation method [22-25] as follow:

$$\exp\left\{-\left(t/\tau_{kww}\right)^{\beta}\right\} = \int_0^{\infty} D(\tau)\exp(-t/\tau)\,d\tau \qquad (3)$$

Since Eq.(3) means Laplace transform, the distribution function $D(\tau)$ can be derived by CONTIN program [30]. As shown in Fig. 5, the variance of $D(\tau)$ at oscillatory flow decreases with increasing frequency, namely, their relaxation process is gradually attained mono-exponential relaxation process with increasing frequency. On the other hand, β is close to 0.5 all over the shear rate range under steady shear flow [11]. Therefore the variance of $D(\tau)$ under steady shear flow is almost same all over the shear rate range (see Fig. 5).

4. Conclusion

In conclusion, we observed the size evolution of onion structures under oscillatory shear flow. We have shown for the first time that behaviour of the time evolution of onion size under oscillatory shear flow showed a stretched exponential function (Eq.(2)) with good agreement. The effect of oscillatory flow is not strong at low frequency. However, the oscillatory flow affect the formation process of onion structure with increasing frequency. Note that their relaxation process is gradually attained mono-exponential relaxation process with increasing frequency.

In general, the phase diagram of onion structure is expressed in the graph with volume fraction of component vs. shear rate. However the oscillatory flow is effective for formation process of onion structure. Therefore we can conclude that the third parameter in the phase diagram is needed to discuss the formation mechanism of onion structure. Theses researches are useful for controlling their size and texture.

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Caption

Table. 1 All fitting parameters and χ^2 values of the stretched exponential function (Eq.(2)) at various frequencies.

Figure 1 Schematic illustration of the oscillatory shear flow experiment.

Figure 2 Graph for the time vs Bragg peak $q_{\max}(t)$, observed two dimensional light scattering after a shear rate of $\dot{\gamma}$ = 47 s^{-1} with various oscillatory frequencies of (a) 0 Hz , (b) 7.81×10^{-3} Hz, (c) 1.56×10^{-2} Hz, (d) 3.13×10^{-2} Hz (e) 6.25×10^{-2} Hz.. The solid line is the best fit stretched exponential curve (Eq.(2)).

Figure 3 Graph for all fitting parameters in stretched exponential function (Eq.(2)) at various frequencies.

Figure 4 Graph for the oscillatory flow frequency at shear rate $\dot{\gamma}$ = 47 s^{-1} vs. its corresponding steady shear flow rate $\dot{\gamma}$ for q_1 (○)、t_0 (△), q_1+ q_2 (□) and τ_{kww} (×).

Figure 5 The distribution function $D(\tau)$ of relaxation time τ of both oscillatory flow and steady one.

Table 1

Frequency (Hz)	q_1	q_2	t_0	τ_{kww}	β	χ^2
0	1.03	1.75	1.05×10^{2}	3.39×10^{3}	4.55×10^{-1}	2.561×10^{-3}
7.81×10^{-3}	1.03	1.73	1.07×10^{2}	3.34×10^{3}	5.21×10^{-1}	1.322×10^{-3}
1.56×10^{-2}	1.10	2.00	8.94×10^{1}	2.51×10^{3}	5.86×10^{-1}	1.532×10^{-3}
3.13×10^{-2}	1.16	2.17	7.44×10^{1}	2.34×10^{3}	6.08×10^{-1}	1.845×10^{-3}
6.25×10^{-2}	1.18	2.30	6.60×10^{1}	2.12×10^{3}	7.70×10^{-1}	1.172×10^{-2}

Figure 1

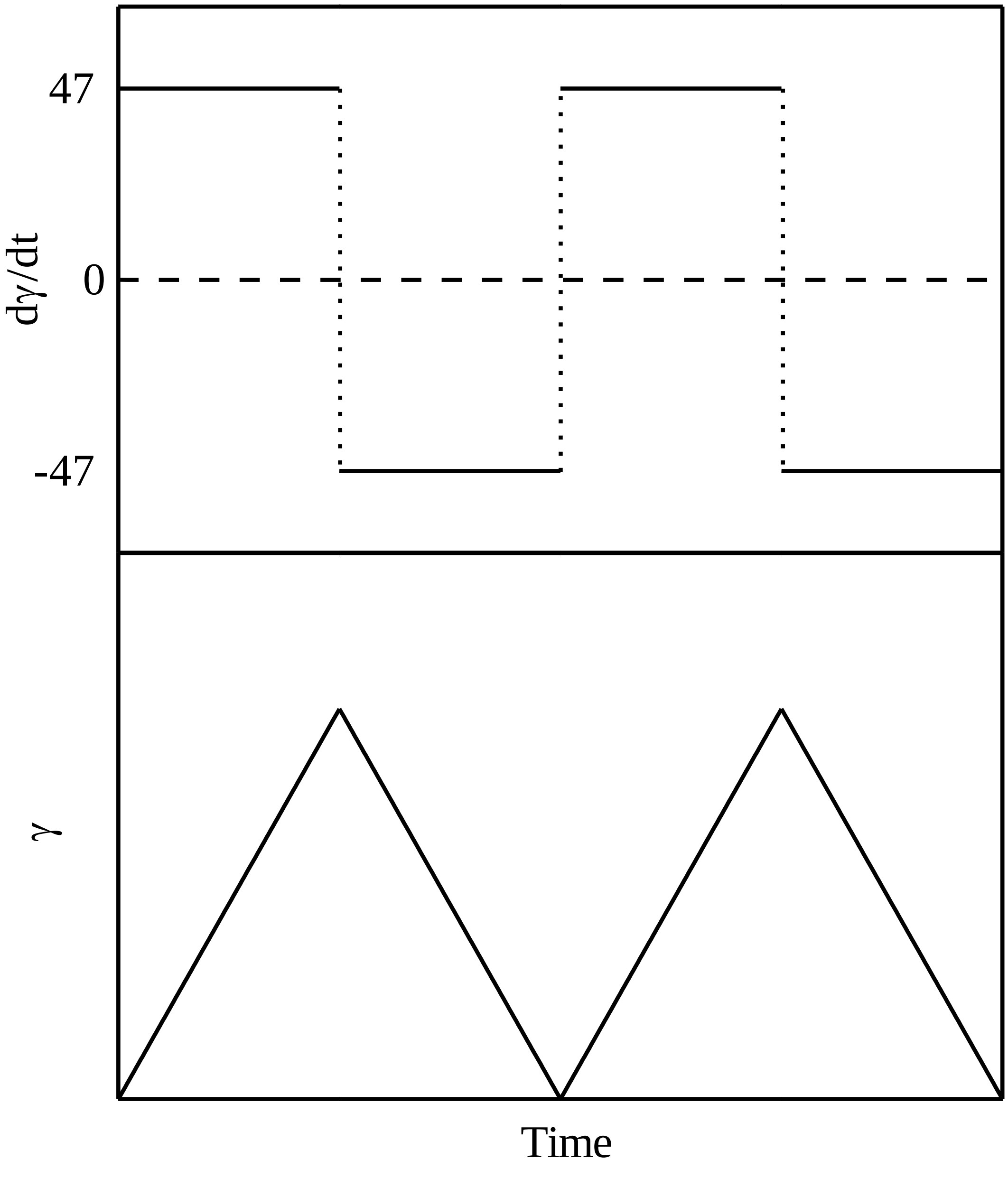


Figure 2

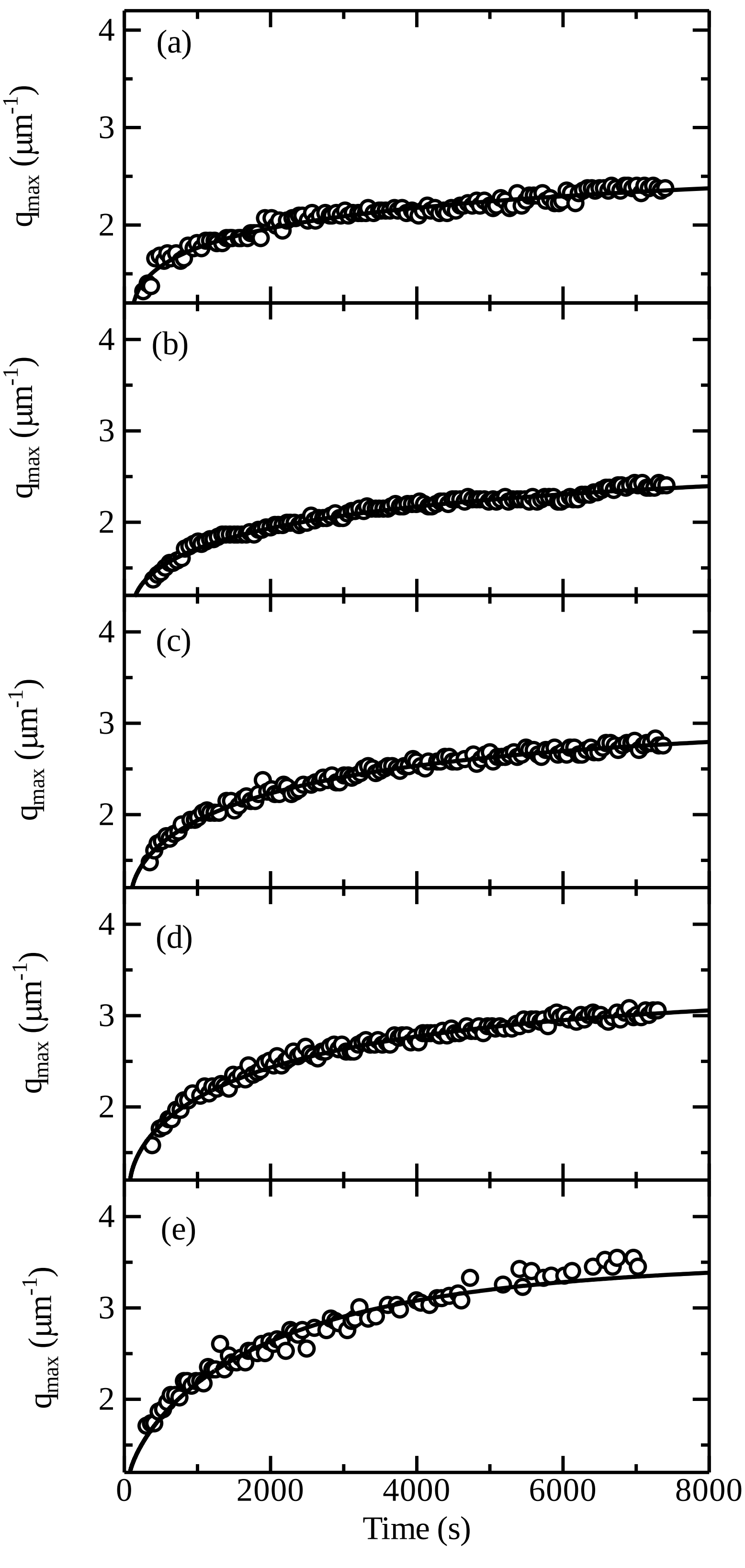


Figure 3

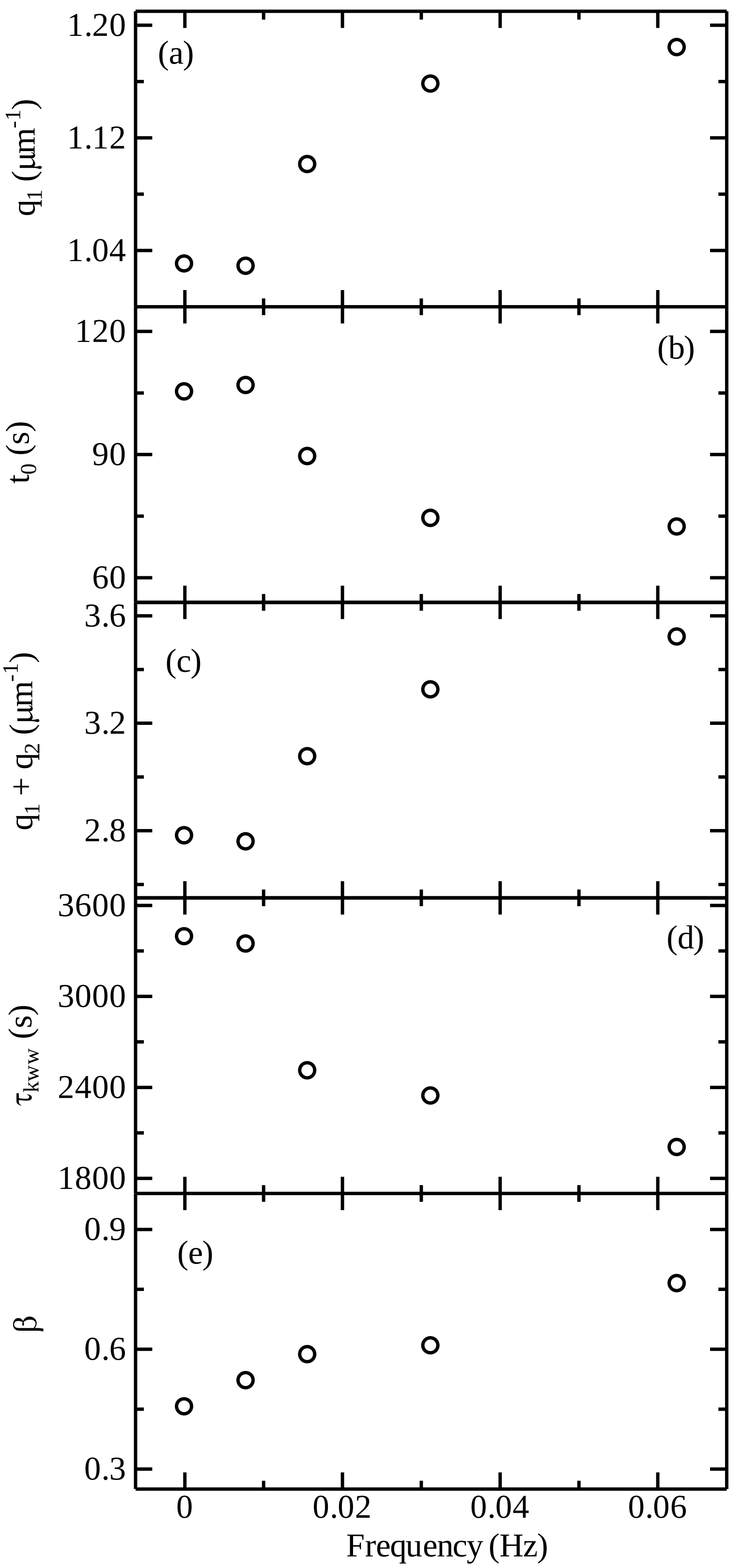

(a)
(b)
(c)
(d)
(e)
q_1 (μm^{-1})
1.20
1.12
1.04
t_0 (s)
120
90
60
$q_1 + q_2$ (μm^{-1})
3.6
3.2
2.8
τ_{kww} (s)
3600
3000
2400
1800
β
0.9
0.6
0.3
0
0.02
0.04
0.06
Frequency (Hz)

Figure 4

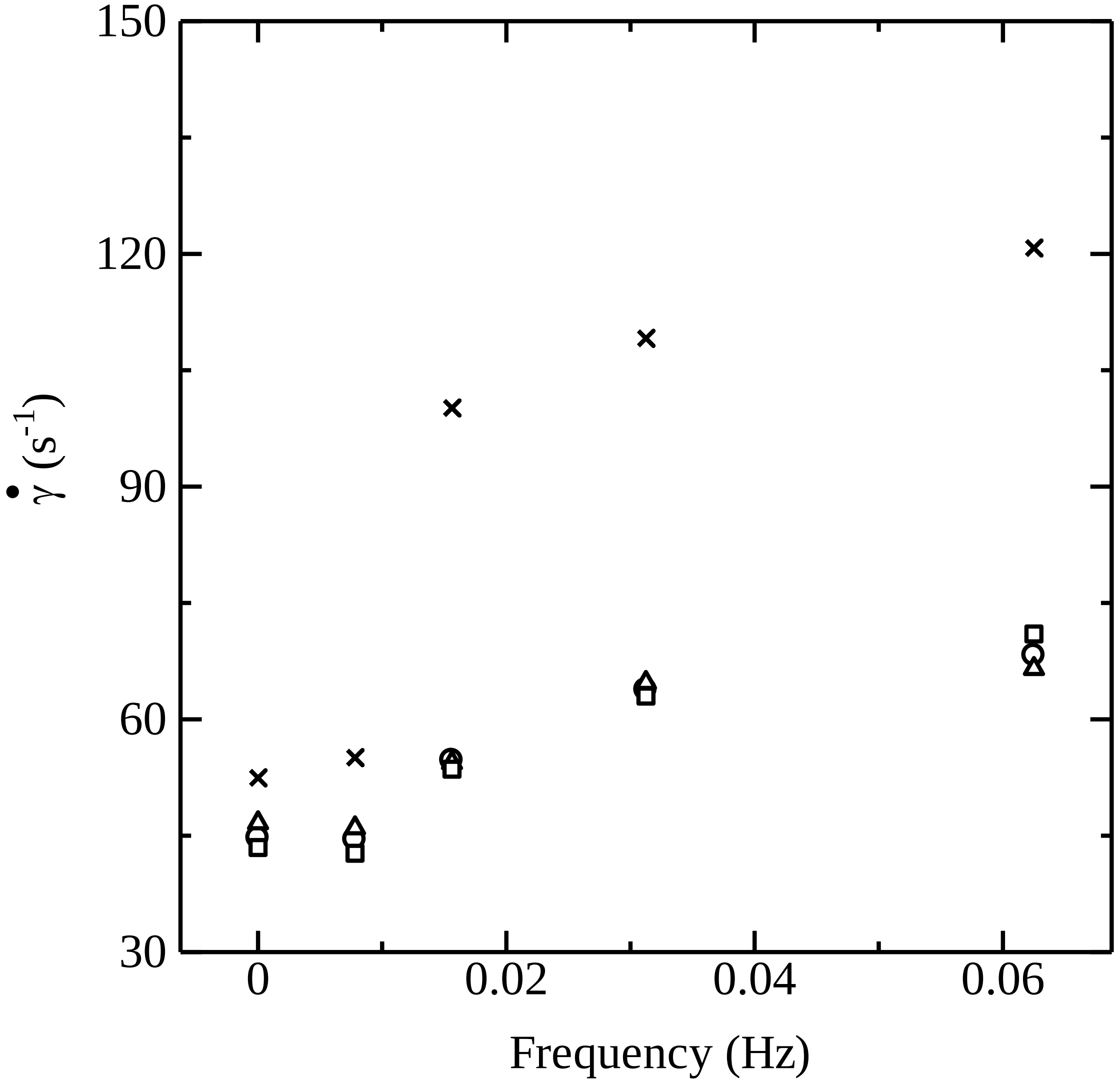
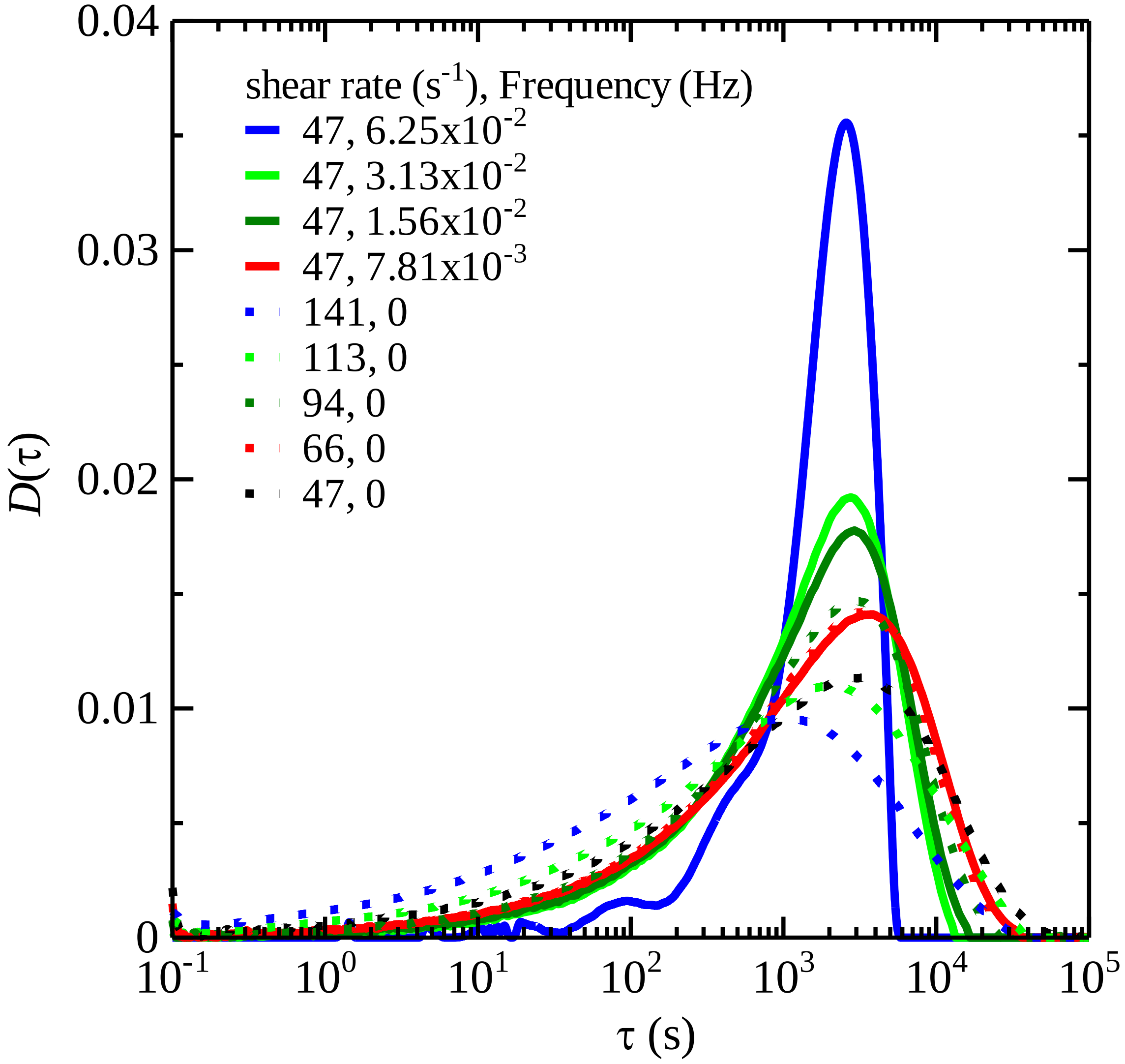


Figure 5


shear rate (s^{-1}), Frequency (Hz)
47, 6.25x10^{-2}
47, 3.13x10^{-2}
47, 1.56x10^{-2}
47, 7.81x10^{-3}
141, 0
113, 0
94, 0
66, 0
47, 0
0.04
0.03
0.02
0.01
0
$D(\tau)$
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
τ (s)