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Experimental studies of the transient fluctuation theorem using liquid crystals

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Abstract. In a thermodynamical process, the dissipation or production of entropy can only be positive or zero, according to the second law of thermodynamics. However, the laws of thermodynamics are applicable to large systems in the thermodynamic limit. Recently a fluctuation theorem, known as the transient fluctuation theorem (TFT), which generalizes the second law of thermodynamics to small systems has been proposed. This theorem has been tested in small systems such as a colloidal particle in an optical trap. We report for the first time an analogous experimental study of TFT in a spatially extended system using liquid crystals.

Keywords. Nonequilibrium fluctuations; transient fluctuation theorem; liquid crystals.

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1. Introduction

The laws of thermodynamics describe the physical behaviour of macroscopic systems. The second law of thermodynamics states that when such a system is taken from one equilibrium state to another, the change in entropy can only be positive or zero depending on whether the process is irreversible or reversible respectively. For macroscopic systems, the effect of thermal noise on physical quantities is negligible except under special conditions such as near phase transitions. However, when the system size is small or more precisely the change in the relevant energy of the system in a process is of the order of the thermal energy $k_{\mathrm{B}}T$, k_{B} being the Boltzmann constant and T being the absolute temperature of the system, thermal noise is expected to play an important role. In particular, the validity of the second law of thermodynamics for small systems is under considerable debate since the time of Boltzmann. Recently, a nonequilibrium fluctuation theorem (FT) known as the transient fluctuation theorem (TFT) has been proposed to generalize the second law of thermodynamics for small systems [1]. In its most general form, TFT not only predicts transient violation of second law of thermodynamics when the

dissipation is comparable to the thermal energy $k_{\mathrm{B}}T$ but also it provides an expression for the probability that a dissipative flux flows in a direction opposite to that required by the second law of thermodynamics. More precisely, for a thermostated system at temperature T, this theorem states that in a time interval τ, the probability $P(\Omega_\tau)$ of a dissipation Ω_τ being positive and the probability $P(-\Omega_\tau)$ of the same dissipation Ω_τ being negative satisfies the following condition:

$$\frac{P(\Omega_\tau)}{P(-\Omega_\tau)} = \exp\left[\frac{\Omega_\tau}{k_{\mathrm{B}}T}\right]. \tag{1}$$

Dissipation being an extensive quantity, it increases when either the system size or the observation time is increased. Then the above theorem implies that the production of entropy will be overwhelmingly more likely its consumption in an irreversible process for large systems or for large observation time in accordance with the second law of thermodynamics. In this way the TFT generalizes the second law of thermodynamics to small systems. Physics of such small systems has recently gained wide interest in the scientific community [2,3]. Examples include nanomaterials, biological molecular machines, quantum dots etc. In particular, physics of such small systems when driven out of equilibrium is of paramount importance in technological applications such as solar energy conversions.

Though considerable theoretical and simulation studies [4–9] on FTs have been reported in literature, only a few experimental studies have been performed. The validity of the fluctuation theorems have been probed experimentally in small systems such as a colloidal particle in an optical trap [10,11], in two-level system [12], torsion pendulum immersed in a viscous fluid [13] and unfolding dynamics of single RNA molecule when stretched [14]. In fact these theorems have been used to measure the folding free energy of a single RNA molecule when stretched [15] by an external applied force. However, all these experiments have been performed on relatively small systems. Recently, nonequilibrium fluctuations in a sheared micellar gel in a jammed state has been studied experimentally [16] and found to obey the Gallavotti–Cohen steady state fluctuation relation [4]. Validity of these theorems for spatially extended systems, where the physical properties are described by an effective order parameter which varies in space has not yet been probed experimentally. In this letter, we report experimental studies of TFT for a spatially extended system of nematic liquid crystals.

Liquid crystals (LC), usually made of rod-like organic molecules, lack three-dimensional periodicity of crystals, but have anisotropic physical properties [17]. The simplest LC, viz. nematic LCs, which are used in practically all commercial LC displays (LCD) have a long-range orientational order of the long axes of the molecules. The orientational order described by the director $\mathbf{n}$ can be easily deformed using external perturbations such as electric and magnetic fields. The distortion-free energy of the director field can be described in terms of three elastic constants corresponding to splay-, bend- and twist-types of distortions of the director field [17]. In our experiments, a nematic liquid crystal is sandwiched between two appropriately treated tin oxide-coated glass plates. The transparent tin oxide coating acts as electrode for the application of an electric field without obstructing the optical measurements. The glass plates are coated with polyimide and rubbed along a certain direction to align the long axes of the rod-like molecules parallel to

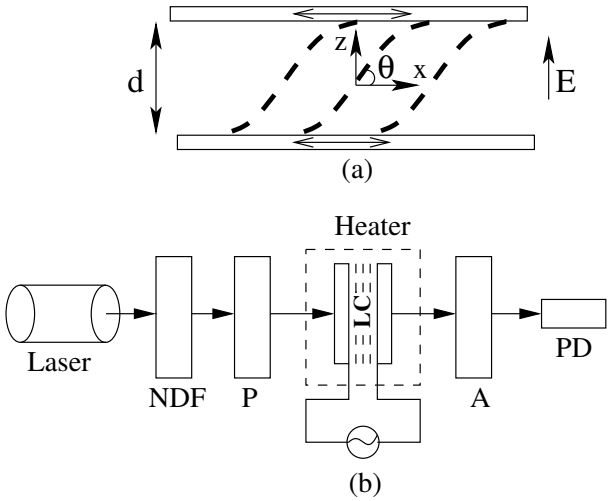

Figure 1. Schematic representation of the experimental set-up. (**a**) The distorted director configuration in the nematic liquid crystal between two plates for applied electric field above Frederiks threshold. The dashed lines represent the local orientation of **n** which makes an angle θ with respect to the x-axis. The double arrow represents the rubbing direction on the plates. (**b**) Schematic experimental set-up where the He–Ne laser beam passes through a neutral density filter (NDF) and then through the LC sample held between crossed polarizers (P) and (A). The intensity of the light passing through the sample is monitored using the photodiode (PD).

the rubbing direction. When such homogeneously aligned nematic liquid crystals having positive dielectric anisotropy are subjected to an applied voltage between the plates, they exhibit a second-order transition to a distorted structure (figure 1a) above a threshold voltage. This is known as the Frederiks transition [17]. This transition occurs due to the quadratic coupling of the applied electric field to the director **n**, arising from the anisotropy of the dielectric constant in the nematic liquid crystals. Thus the equilibrium state of the nematic liquid crystal above the Frederiks transition is determined by the square of the applied voltage difference between the plates.

As liquid crystals have anisotropic physical properties, the refractive index n_e for light polarized parallel to the director **n** (extraordinary ray) is different from n_0 which corresponds to light polarized perpendicular to **n** (ordinary ray). This anisotropy in the refractive index gives rise to a phase difference (Φ) between the extraordinary and ordinary rays of the light beam passing through the sample. The phase difference Φ depends on the orientations of the director **n** between the plates. In the absence of an applied voltage between the plates, the director **n** is parallel to the x-axis and $\Phi = 2\pi\Delta nd/\lambda$ for light propagating along the z-axis, where $\Delta n = n_e - n_0$ is the birefringence of the LC sample, d is the thickness of the LC sample and λ is the wavelength of the light. When the applied voltage is increased beyond the Frederiks threshold, the director **n** progressively becomes parallel to the electric field (z-axis) and Φ decreases with increasing voltage. Thus

the change in the director configuration can be monitored by measuring the change in Φ using an interferometric technique under crossed polarizers. As the response of the liquid crystal depends on the square of the applied voltage, we use a bipolar square wave voltage of frequency 1 kHz to drive the sample from one equilibrium state to another by changing it's amplitude. Use of this AC voltage minimizes the effects of charge impurities, invariably present in the liquid crystals. We have experimentally studied the dissipative relaxation dynamics of Φ when the liquid crystal is driven from one equilibrium state to another by a step change in the amplitude of applied AC voltage. The change in the amplitude is made sufficiently small such that the free energy difference between the initial and final states of the system is comparable to the thermal energy $k_{\mathrm{B}}T$ thus facilitating the study of validity of TFT. We study the TFT associated with the longest wavelength deformation of the director **n** even though the system consists of many molecules.

2. Experimental set-up

A schematic of the experimental set-up is shown in figure 1b. A homogeneously aligned liquid crystal cell is placed between two crossed polarizers with the director **n** making an angle 45° with respect to the polarizer. The intensity of a stabilized He–Ne laser ($\lambda = 632.8$ nm) beam passing through the sample is monitored using a high gain low noise photodiode. The output of the photodiode is digitized using a 16-bit data acquisition board at the rate of 1 kHz. The experiments are performed on nematic liquid crystal (5CB) for sample thickness $d = 27.0$ μm at 30°C which is about 5°C below the nematic–isotropic phase transition temperature (35.1°C). The sample is thermostated in a heater with a temperature stability of 5 mK. For a given temperature, we hold the sample with the amplitude of the applied square wave voltage at a certain value (V_{i}) for 2 s; then the amplitude of the applied voltage is changed in a step to a slightly lower value (V_{f}) and held at that value for subsequent 2 s. The normalized phase difference $\chi = (\Phi - \bar{\Phi}_{\mathrm{i}})/\bar{\Phi}_{\mathrm{i}}$, where $\bar{\Phi}_{\mathrm{i}}$ the equilibrium value of Φ at the initial voltage V_{i}, is monitored as it relaxes from it's initial equilibrium value of zero to the final equilibrium value $\bar{\chi}_{\mathrm{f}}$ at voltage V_{f}. This cycle is repeated 3000 times to find the probability distributions of dissipation. The instrumental error in the measurement of Φ is found to be less than 2%. Figure 2 shows a typical fluctuating dynamics of χ when the amplitude of the applied voltage is changed from $V_{\mathrm{i}} = 1.490$ V to $V_{\mathrm{f}} = 1.488$ V and the average relaxation dynamics of χ averaged over 3000 such curves. The average dynamics of χ is described by a single exponential decay from the initial value to the final value with a characteristic relaxation time $\tau_{\mathrm{r}} \sim 362$ ms. The evolution of χ after the step-like change in the amplitude of the applied voltage in this system is analogous to the overdamped Langevin-type dynamics of a particle from the initial equilibrium position of zero to a final equilibrium position $\bar{\chi}_{\mathrm{f}}$, when the harmonic potential felt by the particle is shifted from zero to $\bar{\chi}_{\mathrm{f}}$ (see inset of figure 2). The effective strength (k_χ) of the harmonic potential associated with χ for a given applied voltage can be determined by measuring the thermal fluctuation of χ and by the application of the equipartition theorem $k_\chi = k_{\mathrm{B}}T/\sigma_\chi^2$ where σ_χ^2 is the variance of χ. Equipartition theorem has been used extensively for the study of thermal fluctuations of the

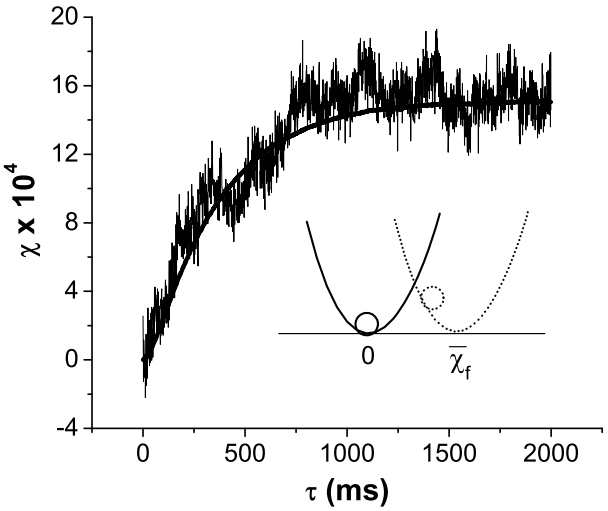

Figure 2. The wiggly line shows the typical fluctuating relaxation dynamics of χ when the amplitude of the applied square wave voltage is changed from $V_\mathrm{i} = 1.490$ V to $V_\mathrm{f} = 1.488$ V. The smooth line shows the average relaxation dynamics of χ averaged over 3000 such curves. The average dynamics is well-described by a single exponential decay to the final value with the relaxation time 362 ms. The time evolution of χ is analogous to the dynamics of a particle when the harmonic potential felt by the particle is shifted from position zero to $\bar{\chi}_\mathrm{f}$ as shown in the inset.

director field which give rise to strong scattering of light in nematic liquid crystals [17]. To determine k_χ, we sample χ in the initial and final equilibrium states of the system for 40 s and determine k_χ from the measured values of the variance σ_χ^2 in these states. The measurement of σ_χ^2 is repeated 10 times at each voltage and averages of σ_χ^2 are used for the determination of k_χ at the respective voltages. We find that on the average, $\sigma_\chi^2 \sim 1.31 \times 10^{-7}$ both at the initial ($V_\mathrm{i} = 1.49$ V) and final ($V_\mathrm{f} = 1.488$ V) applied voltages although 25% fluctuations of σ_χ^2 about the average values are observed. σ_χ^2 is expected to be inversely proportional to the square of the applied voltage [17]. Thus the values of σ_χ^2 at V_i and V_f are almost equal as the difference $V_\mathrm{i} - V_\mathrm{f} = 0.002$ V is small compared to the applied voltages in our experiments.

3. Results and discussions

Using the simple analogy of a particle in a harmonic potential which is shifted at time zero from equilibrium position zero to $\bar{\chi}_\mathrm{f}$ keeping the strength of the potential k_χ the same, the dissipation Ω_τ in time τ can be defined in terms of the probabilities of observing the forward trajectory and anti-trajectory of the particle [11,18]. These can be obtained from the Green's functions of the Langevin dynamics. The

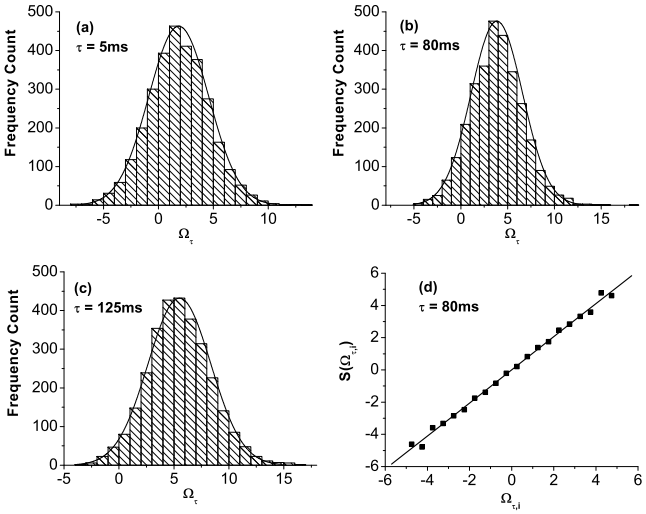

Figure 3. Histograms of the dissipation Ω_τ obtained from an ensemble of 3000 experiments at different τ (**a**) 5 ms, (**b**) 80 ms and (**c**) 125 ms. The bin size $\Delta = 1.0$. The solid lines are the fit to the normal distributions. (**d**) The corresponding plot of $S(\Omega_{\tau i})$ vs. the the dissipation $\Omega_{\tau i}$ associated with the ith histogram bin for $\tau = 80$ ms. The solid line is the best linear fit with slope 1.02 which agrees very well with the TFT predicted value of one.

dissipation Ω_τ, in our system can be written as

$$\Omega_\tau = \frac{k_\chi \bar{\chi}_{\rm f}}{k_{\rm B}T}(\chi_\tau - \chi_0), \tag{2}$$

where χ_0 and χ_τ are the values of χ at time zero and τ respectively. We calculate Ω_τ from eq. (2) for 3000 repetitions of the experiment to get the desired histogram of Ω_τ. The histograms of Ω_τ for $\tau = 5$ ms, 80 ms and 125 ms are shown in figure 3. For small τ, the average dissipation is small. Therefore, the probability distribution of Ω_τ is peaked near zero with a considerable probability of observing negative dissipation as can be seen from figure 3a. As τ increases, the average dissipation increases and the peak of the probability distribution of Ω_τ shifts toward positive values of Ω_τ (figures 3b and 3c) and the probability of observing negative dissipation decreases. For very large τ, the dissipation is much larger than $k_{\rm B}T$ and the probability of observing negative dissipation becomes negligible as required by the second law of thermodynamics.

To test the validity of the TFT, we evaluate the function $S(\Omega_\tau) = \ln[P(\Omega_\tau)/P(-\Omega_\tau)]$ from the experimentally measured probability distribution function of Ω_τ. Then, according to the TFT, $S(\Omega_\tau)$ should be a linear function of Ω_τ, i.e. $S(\Omega_\tau) = \alpha\Omega_\tau$ with slope $\alpha = 1.0$ for all τ. We find from the experimentally measured histogram of Ω_τ the probability count ($N_{\rm i}$) for dissipation between $\Omega_{\tau i} - \Delta/2$ and $\Omega_{\tau i} + \Delta/2$ corresponding to the ith histogram bin $\Omega_{\tau i} = i\Delta$, Δ being the bin size. Then the experimental analog of the function $S(\Omega_{\tau i})$ is $\ln(N_{\rm i}/N_{-{\rm i}})$. We find that the experimentally determined $S(\Omega_{\tau i})$ can be fitted well by a linear

function of $\Omega_{\tau i}$ for all τ. In figure 3d, we show the plot of $S(\Omega_{\tau i})$ vs. the dissipation $\Omega_{\tau i}$ for $\tau = 80$ ms. The straight line in figure 3d shows the corresponding linear fit to the data with slope $\alpha = 1.02$ agreeing very well with the prediction of TFT. Though the experimental results agree very well with the prediction of TFT for τ close to 80 ms, we find that in this system the value of the slope α is not equal to one for all τ but it varies slowly with τ. We have repeated the experiments at different temperatures and for different applied voltages and we have observed similar trends. If the dynamics of χ is analogous to the first-order Langevin dynamics of a particle in harmonic potential, it can be shown theoretically [6] that TFT is satisfied for all time τ. Thus we speculate that the possible origin of the discrepancy between the theoretical predictions and the experimental results may be due to not taking into account the contributions from the higher-order terms involving χ in the dissipation function in eq. (2). Further experimental and theoretical investigations are in progress to account for these effects.

4. Conclusion

In conclusion, we have experimentally studied the validity of the TFT in the spatially extended system using liquid crystals. The TFT is studied for the dissipative dynamics of a macroscopic order parameter, viz. the orientational order of the liquid crystals when driven from one equilibrium state to another. The experimental results are compared with the predictions of the TFT. We find agreement between the experimental observations and the predictions of TFT only for particular values of the observation time τ. Simulation studies of spatially extended systems may shed further insight into the validity of TFT in these systems.

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