論文の内容の要旨

論文題目　Experimental Study on Nonequilibrium Physics using Self-Propelling Asymmetric Colloidal Particles

（自己駆動非対称粒子を用いた非平衡物理の実験的研究）

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Self-propelling phenomenon, especially on the dynamics and collective effects of self-propelling objects, has attracted considerable attention over the past decade for its ubiquity at all kinds of length scales, along with its nonequilibrium nature. However, insights into the physics of such self-propelling objects through experiments have been problematic owing to the difficulty in the realisation of a controllable experimental system, notably at a microscopic level. In this dissertation, self-propelling phenomenon at a microscopic scale is investigated experimentally by use of a novel experimental system consisting asymmetric colloids (Janus particles) under AC electric field, with an additional intention and interest in observing the effect of thermal fluctuations on the self-propulsion of such particles. For this reason, three main topics are studied experimentally; i) general features of particle motion and interaction, ii) application of fluctuation theorem to self-propelling objects, iii) collective behaviour of self-propelling objects at microscopic length scales.

For the experimental system used in the present study, when an AC electric field is applied to a suspension of Janus particles (polystyrene particle of few micrometres in size, half coated with gold), a two-dimensional motion of these particles perpendicular to the direction of the forcing is observed. The confinement of the particle motion to a two-dimensional plane is one of the novelties of the experimental system, where a realistic motion, *i.e.*, translational motion with the ability to change its direction of motion (albeit it not being intentional), is demonstrated and can be tracked simultaneously. The other novelty is the fact that the self-propulsion of the Janus particles can be controlled relatively well. Indeed, the self-propelling velocity of the particles show electric field squared proportionality, which is expected for ICEP (Induced-charge electrophoresis) generated by ICEO (Induced-charge electro-osmosis) flow in the vicinity of the particle surface.

Not only is the present Janus particle system beneficial for the experimental study of self-propelling objects, it displays a plethora of interesting behaviours that are purely phenomenal. The system shows an AC frequency dependence, having 3 characteristic frequency regions; *Aggregation* region, *Self-propelling* (SP) region, and *Inverse SP* region. Every region has its unique motion and interaction. In the *Aggregation* region (∼500Hz), particles do not self-propel. Strictly speaking, particles do not self-propel in the sense that the polarity of the Janus particle with respect to the direction of motion is random. Aggregation of particles and the motion of particles driven towards the aggregation can be expressed by dielectrophoresis. Whereas, in the *SP* (500Hz∼30kHz) and *Inverse SP* (30kHz∼) regions, particles self-propel and interact among themselves. Nevertheless, particles move in the direction of the polystyrene side and show repulsive interactions for the *SP* region, while the motion is in the direction of the metal side and the interaction is attractive for the *Inverse SP* region. Consequently, since the main interest is in the self-propelling objects, the general features of the two self-propelling regions are investigated in depth.

Self-propelling motion of the Janus particles is enhanced with the increase in the applied electric field, where the trajectories become straighter. Moreover, as mentioned above, the self-propelling velocity of the particles is attained via mean squared displacement, demonstrating proportionality to the applied electric field squared, as is expected by theory.

Furthermore, the AC frequency dependence of the particle velocity is examined. Switching of the direction of motion is observed, having no signs of hysteresis. ICEP velocity is calculated for a dielectric sphere with half metal coating, where a compact-layer model is also considered. Using appropriate physical values, the frequency dependence of the particle velocity similar to the experimental result is realised. This particular switching frequency can be estimated by considering a typical time necessary for the charging of the electric double-layer. Since the above frequency depends on the salt concentration of the medium and the particle size, the dependency is tested for different NaCl concentration and particle size, and show that it is sufficient in describing the approximate behaviour of the switching frequency.

In addition, the change in interaction between the *SP* and *Inverse SP* regions is scrutinised by regarding that the polarisability of dielectric material cannot follow the AC electric field when the frequency is to a certain degree too fast. At a characteristic frequency, *i.e.*, Maxwell-Wagner frequency, it can be predicated that the dipole configuration of the particle polarisation changes to a quadrupole configuration, which in turn induces attraction between particles. Actually, the Maxwell-Wagner frequency is calculated to be similar to the switching frequency.

Once the general features are known, a variety of experiments can be conducted with the Janus particles.

For small objects with length scales of the order of nanometre to submicrometre, precisely the size range in which the Janus particles belong to, the effect of thermal fluctuation cannot be neglected. The relation between such fluctuations and active self-propulsion is scarcely understood, especially from an experimental point of view. Accordingly, fluctuation theorem is applied to the Janus particle system in order to question how self-propelling force of the particles competes with thermal fluctuation and also to examine the validity of fluctuation theorem on self-propelling objects. In consideration of the above aims, experiments using Janus doublets are carried out in the *Inverse SP* frequency region. Since in this region, particles are able to attract each other and self-propel concurrently, rotating Janus doublet can be produced. The rotation demonstrates a continuous and fluctuating nature, having a probability of rotation counter to the main direction of rotation, *i.e.*, negative rotation. Increasing the applied voltage to the system causes the Janus doublets to rotate faster and the probability of negative rotation to decrease. This result is obvious though on the other hand very interesting. There is a probability of getting instantaneous negative entropy production, although on the average it is of course positive, as is stated by the second law of thermodynamics. Using only the rotation angle θ and fluctuation theorem defined for rotating Janus doublet, the torque acting on the Janus doublet is estimated. To confirm the validity of the estimated torque via fluctuation theorem, it is compared with another torque estimated by the rotating velocity and Stokes equation with near wall correction. Both estimated torques show good agreement with each other, evincing the validity of fluctuation theorem on self-propelling objects.

The other interest concerning self-propelling objects is the collective behaviour. This topic is extremely important especially from the standpoint of nonequilibrium statistical mechanics since collective behaviours exhibit macroscopic order despite having only relatively simple local rules that are under the effect of noises from the environment. Notwithstanding its importance, seldom has it been studied experimentally, for the difficulty in the realisation of controllable experiments. Therefore, it could be said that the present study is the first ever attempt to look into collective behaviour of self-propelling artificial (and controllable) particles at a *microscopic* scale. In the experiments, a few hundreds of particles self-propel in the region of observation, done in the *SP* region where the particles are able to move without the attraction of the particles.
Before studying the collective behaviour of the Janus particles in depth, an evaluation on the angular fluctuation with respect to the self-propulsion due to differences in applied electric field is done. Clearly, the fluctuation of the direction of motion weakens as the applied electric field is increased. This is important in the sense that it acts like some sort of noise in the system.
Next, experiments using many Janus particles are conducted. The first set of interest is in the manner in which the particles aligned during self-propulsion. Spatial correlation of the direction of motion is calculated, where it shows a short-range correlation of approximately a few particles' diameter in length. Despite the short-range nature of the correlation, interestingly enough, particles demonstrate the tendency of polar alignment at small distances (between the particles), *i.e.*, particles face more or less in the same direction locally. However, obvious to some extent, when the distance between the particles is large, the direction of motion is random. Such local alignment, though not very strong, induced a swirl-like structure.
The kind of structure mentioned above should in principle be initiated by collective motion, which exhibits anomalous density fluctuations that are not observed in equilibrium systems. For this reason, the next set of interest is in the density fluctuations, or strictly speaking the fluctuation in the number of particles in a given area of observation. In an equilibrium system with a mean number of particles N, the standard deviation of the number of particles ΔN is proportional to $\sqrt{N}$, as is stated by the central limit theory. Nevertheless, it is known that for a system that demonstrates collective motion, ΔN deviates from the $\sqrt{N}$ proportionality, where the scaling exponent α for $\Delta N \propto N^{\alpha}$ is larger than 0.5 (theoretically, for collective motion, it

should reach the value $\alpha = 0.8$). Consequently, ΔN and N is experimentally obtained for the many self-propelling Janus particle system for a wide range of area size within the region of observation. When the particle density is moderately high and the self-propulsion is relatively fast, a significant deviation of ΔN from $\sqrt{N}$ is seen, having a value of approximately $\alpha = 0.6$. On the other hand, when the surface fraction, namely particle density, and/or the particle velocity is low, the deviation is not apparent. The possible reasoning into the aforementioned deviation is scrutinised by discussing the distinctive change in both the spatial correlation and angular fluctuation for the experimental condition where such deviation is unique. However, according to theories, when the system is in the disordered phase, *i.e.*, the majority of the objects are not well aligned, which is the case in the present experiment (in the sense that long-range alignment is absent), ΔN should not deviate from $\sqrt{N}$. The discrepancy between the experiment and theory may probably be due to the following reasons. Firstly, finite size effect can be considered. Although there are no boundaries anywhere near the particles, some particles are pinned to the bottom electrode (which is inevitable) and they may act as a sort of boundary. Secondly, it may be caused by the complexity of the system, especially the fact that the system is at a microscopic length scale with hydrodynamic effects, which are not considered in the theories. Interestingly, such discrepancy mentioned above was observed experimentally for microscopic biological objects. Since experimental studies at a microscopic scale are extremely rare, all the results including the disagreement with theory is meaningful. Without doubt, more of such experimental investigation into collective behaviours is necessary in the future, especially at microscopic length scales.

The dissertation experimentally explores some of the fundamental aspects of not only nonequilibrium physics but also active and self-propelled matter system. A lot remains unclear, however, it is safe to say that this dissertation adds a new category in the "catalogue of generic behaviours" concerning physics of self-propelled objects, especially in the sense that experimental studies at a microscopic level had not been done prior to the present dissertation. Furthermore, the introduction and initiation of such experimental investigation regarding self-propelled objects seen in this dissertation, will surely benefit in driving the field of self-propelled/active matter to prominence and in appreciating the many wonders that nature displays.