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# Thermally induced aggregation of rigid spheres on a liquid surface

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ABSTRACT

Fluids provide the optimal setting to explore natural patterns far from thermodynamic equilibrium. Experiments suggest that randomly dispersed particles on a liquid surface tend to aggregate on the surface of liquid over time, and the process is enhanced by an increase in the temperature of the liquid. We show that the agglomeration radii increases monotonically with temperature up until the point where all particles in the system form a single, large aggregate. The aggregation dynamics is related to changes in the material properties of the liquid including its viscosity and surface tension as well as the convection driven flow generated on the fluid surface. In this article we compare our experimental observations with analytical asymptotic results. The analytical arguments are seen to agree well with the experimental observations.



## 1. Introduction

Fluid dynamicists are well aware that the kitchen can be a fertile testing ground for important scientific discoveries. One such significant fluid dynamics phenomenon reveals itself in the simple act of making traditional Indian *chai* on the stove. Randomly distributed tea leaves on the surface of water are seen to aggregate into an increasingly compact configuration as the temperature of the water is increased (see Fig. 1). The temperature, although not the cause of the aggregation, serves to influence the time scale over which aggregation occurs. Indeed, aggregation has been noted to happen in cases when the system is in (or close to) thermal equilibrium.

The "cheerio effect" whereby cereal in a bowl of milk aggregates in a similar manner to the tea leaves has regained some recent attention in the literature [1]. The earliest contribution to the subject of aggregation of floating particles can be attributed to the 1949 paper by Nicholson [2]. Since then, the most pertinent analytical contributions to the subject are due to Gifford and Scriven [3], Chan, Henry and White [4] and more recently by Vella and Mahadevan [1]. Their analysis is based on asymptotic arguments for capillary forces between spheres and/or cylinders. Additionally, Singh and Joseph [5] and Dixit and Homsy [6] have conducted rigorous numerical simulations to capture the effect of aggregation between multiple floating bodies. All of these works however, disregard the effect of temperature.

Interfacial aggregation is fairly widespread and has been observed in a variety of other settings [7–12]. The solid state physics and biophysical communities have long been aware of the effects of temperature upon interfacial aggregation and are deeply interested in the regulation of this behavior. Self assembled monolayers (SAMs) involve the construction of highly ordered materials by utilizing the local forces between disordered molecules and are used in the design and production of semiconductor nano-electronic devices including nano-wires, nano-tubes and nano-sensors [13,14]. Several recent studies on SAMs report that temperature can be utilized to effectively control the topology of the networks formed [13,15–19], create more stable structures and prevent the formation of cracks by a suitable sintering pre-treatment which involves compactification and exposure to heat prior to the self-assembly process [20]. Temperature is also seen to impact the optical properties of the SAMs by suitable modification of their refractive indices [20]. While there is a lot written about aggregation and its potential applications, the effect of temperature on the aggregation process has never been explained in the literature from a fundamental physics perspective. Such a discussion is therefore significant and timely.

The current paper is devoted to the experimental study of interfacial particle aggregation under the influence of temperature. We hypothesize that the change in temperature of the fluid has a strong influence upon its material properties (viscosity and surface tension) thereby impacting the aggregation dynamics. Details of the experiments are explained in the proceeding sections. Our empirical models are used to extend the asymptotic expressions

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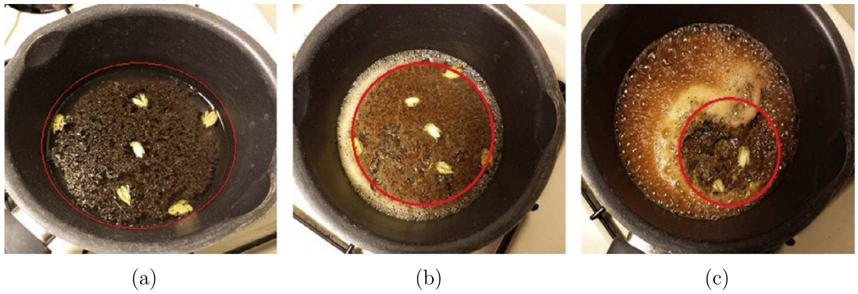

**Fig. 1.** Aggregation of tea leaves on heated water. The tea leaves evolve from (a) randomly distributed to (b) somewhat aggregated to (c) tightly aggregated very quickly as the water temperature is raised. It is noted that this was not a controlled experiment and that our observations with tea leaves are somewhat different from the investigation in the paper, due to the absorption properties of the tea leaves, lack of temperature control and low viscosity of water in which tea is prepared.

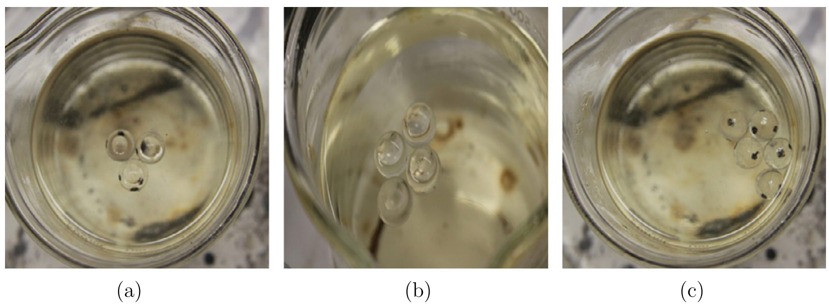

**Fig. 2.** Aggregation of multiple spheres on a heated liquid surface. In (a) the water–corn syrup mixture was heated to 60 °C while in (b) and (c) the mixture was heated to 70 °C.

for aggregation time and the analytical results are shown to agree well with the experimental observations.

## 2. Experiments

### *2.1. Methodology*

Our experiments were conducted in a beaker (diameter 4.0 in, height 4.75 in) filled with a solution containing equal volumes of water and corn syrup on a hot plate. In order to prevent heat loss, the beaker was immersed in a thermal bath. The beaker was then heated to a fixed temperature. After the desired temperature was reached, a number of acrylic spheres were placed into the solution and the time taken for the spheres to aggregate, henceforth denoted $t_a$, was recorded (see Fig. 2). Over the entire study the effect of temperature, sphere size and sphere quantity upon $t_a$ was investigated. In each experiment, the temperature was chosen to be within the range of 24 °C–100 °C; two, three and four spheres of diameters 0.635 cm, 1.27 cm and 2.54 cm were chosen for the study. The experiments were conducted with the spheres being placed at different initial positions in each of the experimental trials and each reported value of $t_a$ is the result of averaging three to five different trials.

The temperature distribution in the water–corn syrup sample was measured at various settings of the hot plate between 30 °C and 100 °C. Specifically, after setting the hot plate to a fixed temperature and upon reaching equilibrium, thermometers were placed at three different radii (center of the beaker, $\frac{r}{3}$ and $\frac{2r}{3}$, where $r$ is the radius of the beaker) and three different heights (3.18 cm, 6.36 cm, 9.52 cm) from the bottom. The observations revealed a very homogeneous distribution of temperature in the sample liquid with maximum standard deviation of 3 °C from the mean temperature measurement from all the trials. For the most part, the deviations were considerably lower than this.

The viscosity $\mu$ of the liquid was measured using a hand held rotational viscometer (Haake Rotational Viscometer). Viscosity is well known to be inversely proportional to the liquid's temperature [21]. Although we expected our sample solution to possess a similar profile, the exact nature of this dependence needed to be ascertained. Here as well, the liquid was maintained at different fixed temperatures and several repetitions of the viscosity measurements were made. All experiments yielded a consistently decaying profile with a rising temperature. A sample curve of viscosity versus temperature is shown in Fig. 3(a). A power law fit to the profile yields the relationship $\mu(\theta) = 3.16\theta^{-0.775}$, where $\theta$ is the temperature in °C, with a correlation coefficient of $R^2 = 0.99$ demonstrating an excellent fit.

We also measured the surface tension $\gamma$ of the liquid as a function of temperature. For this purpose, a tensiometer (DeltaPi model, Kibron Inc.) was employed. The instrument was calibrated with distilled water and measurements were made by placing the beaker containing the sample liquid on a hot plate in a thermal bath. The hot plate was heated to approximately 70 °C and the temperature and surface tension of the sample were simultaneously recorded (see Fig. 3(b)). Multiple measurements of the sample were made over a period of several months, and all measurements, for the most part, showed a declining trend in $\gamma$ as a function of temperature. The surface tension measurements were wrought with problems, including bubble formations, dust on the liquid surface, crystallization of corn syrup at higher temperature and possibly rapid evaporation, leading to errors in several attempts. Small variations between different samples of the liquid could also contribute to the observed variations. Precautions were taken to minimize the contributions of these factors. In particular, to minimize the negative and drastic impact of evaporation, it was deemed best to measure $\gamma$ in incremental ranges of temperature rather than considering the entire temperature range explored in the aggregation study. It is however, unclear to us if evaporation by itself is a problem or a natural route through which temperature impacts surface surface tension. Our repeated experiments did confirm an inverse relationship between $\gamma$ and $\theta$ with power law fit exponents ranging between $-0.0083$ and $-0.35$. In the sample shown in Fig. 3(b) the power law fit yields $\gamma(\theta) = 107.4\theta^{-0.183}$. Here, the rising trend beyond 50 °C is known to be erroneous and