# Cylindrical phase separation in colloidal suspensions

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When left overnight undisturbed in a covered beaker, suspensions of polystyrene microspheres were found to undergo a distinctive kind of macroscopically visible phase separation. Microspheres migrated radially, leaving a vertically oriented cylinder near the center of the beaker that was devoid of microspheres. Cylinder formation was preceded by formation of a microsphere-free plate at the suspension surface, which may be the precursor of the cylinder. The cylindrical phase separation was found to depend on illumination, which suggests that low-level photon energy from the laboratory environment is sufficient to drive this surprising pattern formation. So long as suspension parameters were set within certain ranges, the cylindrical pattern occurred regularly.

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## I. INTRODUCTION

Particles suspended in water exhibit Brownian displacements. The resulting net movements create diffusive actions, which tend to dissipate concentration gradients and maximize entropy. Except for gravitational settling, therefore, the second law of thermodynamics predicts a statistically uniform distribution as the final state in solutions and suspensions, although this prediction does not necessarily hold either for living systems that form structures by feeding on the free energy of the environment [1], or for nonliving dissipative systems fed by the energy of rhythmic chemical reactions [2].

Despite the straightforward expectation of uniform distribution, exceptions are legion, especially in colloidal suspensions [3,4]. It is known, for example, that for monodisperse latex microspheres, the transition from a homogeneous suspension to settled spheres leads to an iridescent state at the bottom of the chamber—the iridescence implying the presence of a crystalline sediment [5]. Successful attempts to observe the crystal under the light microscope have been made by Kose and co-workers [6–8], who showed that the ordered hexagonal sediment at the bottom excluded impurities.

Later, Ise and co-workers [9,10] found evidence of colloid crystal formation in the vertical plane. Attractive forces draw microspheres toward one another, creating dense crystallites in which constituent microspheres remain separated from one another by distances on the order of the microsphere diameter. Such crystallites coexist with the remainder of the suspension, forming scattered crystallite pockets. Also observed in such suspensions are voids—zones in which microspheres are absent [11,12]. Additional features of the anomalous attraction between like-charged microspheres were obtained by Grier and co-workers [4,13].

Another exception to the anticipated uniformity is the recently observed phase separation next to hydrophilic surfaces. Microspheres infused into the vicinity of hydrophilic surfaces including those of gels, biological tissues, and charged polymeric surfaces translate away from the surface, leaving large aqueous microsphere-free zones. Such zones can be hundreds of micrometers wide [14,15].

Nonuniform distributions of colloids have been observed in still other situations. In oil-water mixtures a single monolayer of particles surrounds the surface of each water droplet, whereas in the bulk oil phase, other particles self-assemble into body-centered-cubic crystals [16,17]. Nonhomogeneous distributions of micro- and nanobeads can also occur as a consequence of thermodiffusion [18]. And the expectation of ordinary barometric settling of colloids is contradicted in a number of important studies that report strong electrostatic effects [19–23], which may play a significant deterministic role in particle distributions.

Hence, many observations contradict the statistical uniformity anticipated from simple thermal motion considerations, and instead reveal heterogeneity and phase separation. Here we describe yet another unexpected separation. After standing undisturbed for several hours in a sealed beaker, aqueous microsphere suspensions develop large, vertically oriented, microsphere-free cylinders situated near the beaker's vertical axis. Although ephemeral when subjected to evaporative forces, these cylindrical zones are otherwise quite stable, and, paradoxically, their radial positions are sensitive to incident light. The low photon energy derived from the laboratory environment may indeed be critical for inducing this surprising formation, and by inference may play a role in other separations as well.

## II. METHODS

### A. Experiments

Aqueous microsphere suspensions were prepared, placed in Pyrex beakers, sealed with Parafilm (American National Can, Neenah WI), and left undisturbed for several hours. Formation of microsphere-free zones (MFZs) was documented with a digital camera (Scion Corporation, Model CFW-1308M) and Scion IMAGE software. If a MFZ had not formed within 24 h, the experiment was terminated. Experiments conducted in the dark were allowed to continue longer—up to four days.

To explore the factors responsible for MFZ formation, the beaker-microsphere system was systematically altered in a variety of ways. Parameters tested included the type, concen-

 

tration, and size of microspheres, the volume of aqueous suspension, and the beaker diameter and corresponding suspension height. Illumination of the beaker-microsphere system was also varied. And *p*H measurements were made both inside and outside the MFZs.

### B. Microspheres

Aqueous microsphere suspensions were freshly prepared, by adding the aqueous microsphere "concentrate" [2.5% solids (w/v)] to distilled water (ASTM Type II, VWR International), and mixing thoroughly. Final concentrations ranged from 0.001 to 0.02% v/v. For standard experiments unless otherwise stated, a microsphere concentration of 0.01% v/v was used. Two different types of microsphere were used in these experiments: Polybeadcarboxylate-functionalized microspheres (diameters 0.1, 2, and 10 $\mu$m) and amino-functionalized (1 $\mu$m diameter) microspheres (Polysciences, Inc., Warrington PA).

### C. Volumetric considerations

The ratio of liquid height to beaker diameter was varied. This was done by using beakers of different diameter, 5.1, 7.3, 8.4, 9.5, and 10.3 cm, which were filled with various volumes of suspension, ranging from 15 to 200 ml, to give height-to-diameter ratios ranging from 0.07 to 0.40.

### D. Illumination

To test the influence of light on MFZ formation, experiments were conducted under different illumination conditions. The two standard conditions used were ambient ceiling laboratory light and effectively total darkness. When ambient laboratory lighting was used, consistency was maintained by placing beakers at the same location for each experimental run, and by starting the experiments at the same time of day. Typically, multiple beakers were placed next to one another. For experiments requiring darkness, beakers were placed in a dark room, and the entire setup was covered with black felt material.

Additional experiments were conducted with a fiber-optic lamp (I-150, CUDA Products Corporation), which provided light through twin gooseneck guides. The fiber-optic lamp allows the illumination to be manipulated into various configurations and distances from the beaker by adjusting the gooseneck guides. In order to limit any effect of temperature increase generated by the light source, a setup was constructed to block much of the generated heat, by using reflected instead of direct lighting (Fig. 1).

### E. Open and closed systems

To test the effect of sealing the beaker, duplicate beaker-microsphere systems were set up side by side, identical in every respect except that one was sealed with Parafilm while the other was left open. The two systems were left until MFZs could be observed, at which point, in the closed system, the Parafilm was removed and documentation continued.

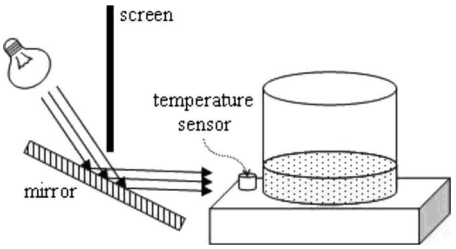


FIG. 1. Schematic of apparatus used to minimize the effect of heat on the microsphere suspension.

### F. *p*H measurement

Hydrogen-ion activity was measured in microsphere-containing and microsphere-free zones. Parafilm-sealed beakers containing 0.01% v/v microspheres were left until a MFZ had formed, or for 24 h if during that period no MFZ had yet formed. The Parafilm was removed and micropipettes were used to withdraw small amounts (10 $\mu$m) of fluid from each zone. A *p*H microelectrode (98 Series Micro-Combination *p*H/sodium electrode, Orion Research, Inc., Beverly, MA) was used to measure local *p*H.

## III. RESULTS

To explore the characteristics of the unexpected phase separation, more then 200 experiments were carried out under a wide variety of conditions. The first experiments were performed in order to establish the optimum conditions for the appearance of a cylindrical MFZ. Formation of a micrsophere-free cylinder was observed in 42% of these experiments, whereas in another 21% noncylindrical types of MFZ were found. Once the optimum conditions were established, then cylinders appeared more regularly, as described in detail below.

### A. Basic observation

A representative observation is shown in Fig. 2. A 0.01% v/v suspension of 2 $\mu$m carboxylated microspheres was placed in an 8.5-cm-diameter beaker and sealed with Parafilm. The height of the liquid was 1 cm. Initially, the entire suspension appeared cloudy as a result of light scattered by

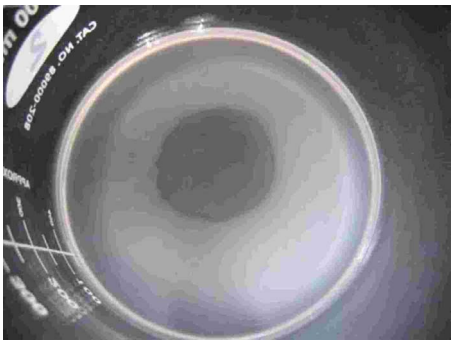

FIG. 2. (Color online) Appearance of a clear cylinder near the center of a glass beaker containing an aqueous suspension of microspheres. Photo taken from top of beaker.

the suspended microspheres. After 12 h the cloudy zone remained at the periphery, while the center had become clear, and devoid of microspheres.

In Fig. 2, the microsphere-free region corresponds to the dark circle near the center, while the lighter region beyond corresponds to the microsphere-containing zone. Often, an additional darker zone appeared just within the rim, as is apparent in the figure [also in Fig. 5(b)]. The latter regions were quite variable, and were established to correspond to accelerated sedimentation occurring along the rounded bottom edges of the beaker. Sedimentation left the peripheral zone more dilute and hence relatively clearer.

The central clear zone extended all the way from top to bottom: when newsprint was slipped beneath the beaker, it was possible to read the fine print. Whether the clear zone was cylindrical from top to bottom could not be ascertained, as it was not possible to focus at different levels. However, the MFZ appeared to be approximately cylindrical.

Removal of the beaker's cover had a profound effect. The image of Fig. 2 was obtained immediately after the Parafilm cover had been removed. Within several minutes after removal, the cylinder had noticeably changed shape and after approximately ten minutes it had vanished. Presumably, the strong convection currents arising out of evaporation were responsible for its disappearance.

Cylinder diameter was typically one-third of the beaker's diameter although in several cases we were able to obtain giant cylinders whose diameter exceeded half the beaker diameter. The variation might arise in part from variability of sealing efficacy, as the Parafilm does not provide an airtight seal. Indeed, when no cover was put on the beaker, the cylinder was much narrower then usual (see Fig. 6).

Cylinder position rarely coincided exactly with the beaker's central axis. Although neither the exact positions nor the consistency of shift directions were tracked, the typical shift was on the order of 1/6 of beaker diameter. Once the cylinder had formed, its center fluctuated slightly about its initial position for several hours.

Cylinders did not always form, and the conditions favoring formation are considered below. An interesting feature was that always, when several samples were placed next to one another and left overnight, when cylinders were found in one beaker they were found in all; and, when cylinders were absent in one, they were absent consistently. Hence, some feature of the environment appeared to play a role in their formation.

Another consistent feature was the presence of a clear zone at the top of the suspension (Fig. 3). After the microsphere suspension had been prepared and poured into the beaker, this MFZ became visible within approximately 10 min. It had a dark appearance, much the same as the cylindrical MFZ. At this 10 min stage, it was approximately 1 mm high.

The upper MFZ typically increased in depth by up to 2 mm over the following four hours. It then remained constant in size for another several hours until the cylinder formed. Once that happened, there was no longer any visible clear zone at the top, implying that the upper clear zone may have given way to the central cylinder.

Other types of phase separation were noted, with complex shapes too diverse to be easily classified. Examples are shown in Fig. 4. We assume that these shapes are variants of the default cylinder, and that they arose because some unforeseen environmental nonuniformity distorted the cylinder into some different shape.

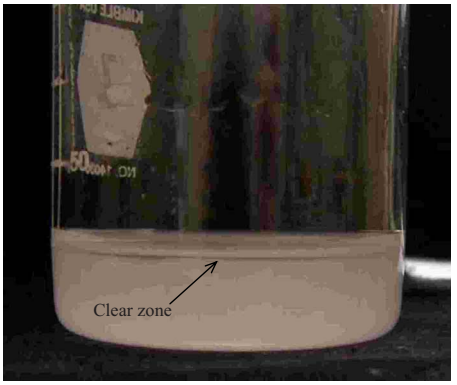


FIG. 3. (Color online) Shallow MFZ (dark) forming at the surface of the suspension. Suspension contained 0.01% v/v 2 $\mu$m carboxylated microspheres. Beaker size 600 ml. Photo was taken 10 min after preparation.

### B. Optimization of conditions

Having first observed the cylinder serendipitously, we set out to determine the optimum conditions for its appearance and the consistency with which it could be reproduced. In these studies we explored microsphere type and size; microsphere concentration; chamber volume and shape; effect of light exposure; role of evaporation; patterns of convectional flow; and, the impact of these parameters on the emergence of the cylindrical MFZ.

#### *1. Effect of microsphere polarity*

We first considered the effect of microsphere-charge polarity. Both negatively and positively charged polarities were studied. For negatively charged entities, polystyrene microspheres functionalized with carboxyl groups (so-called carboxylate microspheres) were used; for positively charged entities, polystyrene microspheres containing primary amine surface functional groups were used. Microspheres were monodisperse, nominally 1 or 2 $\mu$m in diameter, used here at concentration of 0.01% v/v.

Microsphere suspensions of one or the other polarity were placed in beakers, covered with Parafilm, left overnight on the laboratory bench (overhead lights remaining on), and examined the following morning and continuously during the day, for up to 24 h following preparation if no MFZ had yet formed. Laboratory temperature was well maintained at

FIG. 4. (Color online) Examples of noncylindrical types of separation.

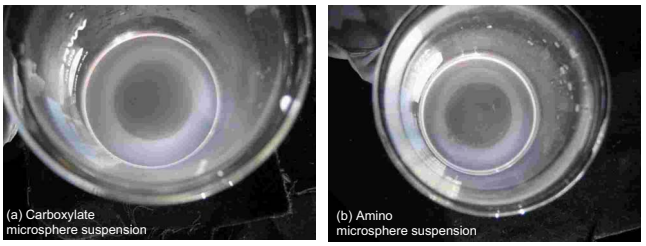


FIG. 5. (Color online) Appearance of cylinders formed in beakers containing suspensions of amino- (b) or carboxylate-coated (a) microspheres (0.01% v/v). Photos taken from top of beaker. Dark circle near center is the microsphere-free region. Cloudy peripheral region contains the microspheres. Image obtained after 9 h of rest in Parafilm-covered beaker, standing in room light. Beaker diameter was 8.5 cm. Because of camera perspective, the top of the beaker looks larger than the bottom.

$19 \pm 1$ °C throughout this period. Experiments were conducted in pairs: one beaker of each polarity. In total, 20 samples were studied over ten nights.

Results were similar for both polarities in all experiments (Fig. 5). When a cylinder was present in one beaker, it was present in the other, notwithstanding the polarity difference. When it was absent in one, it was absent in the other—although in the latter cases, noncylindrical microsphere-free zones were often observed. Hence, the results gave no reason to surmise that microsphere polarity played any significant role in cylinder formation.

#### 2. Effect of microsphere size

We tested carboxylate microspheres with diameters 0.1, 2, and 10 $\mu$m. They were studied at identical v/v concentrations, in 8.5-cm-diameter Parafilm-sealed beakers. Difficulties were encountered with larger microspheres because they settled to the bottom so rapidly that there was little time left for possible cylinder formation. As for the 0.1 and 2 $\mu$m microspheres, the number of cylinders found was similar for both types of microsphere. After 15 h in ten pairs of experiments, cylinders had formed in four 2 $\mu$m microsphere beakers and five 0.1 $\mu$m microsphere beakers; after 20 h there were five cylinders in 2 $\mu$m microsphere suspensions, and four, plus two noncylindrical separations, in the 0.1 $\mu$m suspensions. All the rest of the beakers contained seemingly uniform suspensions. Hence the likelihood of formation seemed relatively insensitive to microsphere size.

#### 3. Effect of microsphere concentration

Suspension-containing beakers with a series of different microsphere concentrations were covered with Parafilm, left in ambient laboratory conditions with lights on for up to 24 h, or less if the cylinder had formed.

Results are shown in Table I. Incidence of cylinders varied with concentration in a moderately predictable manner, the optimum lying at a v/v ratio of approximately 0.01%. Cylinders were never seen with microsphere concentrations above 0.03% or below 0.003%. The table shows that at optimum concentration, during 24 h, cylinders had formed in approximately 45% of samples.

TABLE I. Effect of microsphere concentration on incidence of cylinder formation. Experiments carried out in 8.5-cm-diameter sealed beakers, with 100 ml of 2 $\mu$m carboxylated microspheres, at room temperature.

| Concentration | | Number of samples | Number of cases with "cylinders" | Success rate (%) |
|---|---|---|---|---|
| Drops per 200 ml | % v/v | | | |
| 5 | 0.003 | 18 | 5 | 27.8 |
| 10 | 0.006 | 23 | 9 | 39.1 |
| 15 | 0.009 | 27 | 12 | 44.4 |
| 20 | 0.013 | 18 | 7 | 38.9 |
| 25 | 0.016 | 15 | 4 | 25.0 |
| 30 | 0.019 | 12 | 1 | 10.0 |

#### 4. Effect of geometric factors

To determine whether container diameter or suspension height played a role in cylinder formation, we examined a series of geometrical variants. Beakers of inner diameter 5.1 cm (140 ml), 7.3 cm (300 ml), 8.4 cm (500 ml), and 10.3 cm (1000 ml) were used, and heights were set at a variety of levels ranging from 0.6 to 4.0 cm. Carboxylate 2 $\mu$m microspheres at a concentration of 0.01% were used throughout. Beakers were covered with Parafilm, left overnight, and examined at a time point 24 h after preparation, or earlier if a cylinder had formed.

More than 50 experiments were carried out. We found that, irrespective of suspension volume, the optimum ratio of suspension height to beaker diameter for phase separation was approximately 0.21. At this ratio, phase separation—either cylindrical or other type—was found in six out of ten runs. The presence of phase separation was quite sensitive to this ratio: when the ratio rose from 0.21 to 0.27, no separation could be obtained in seven attempts. When it diminished to 0.15, no separation could be obtained in six attempts.

#### 5. Effects of evaporation

The evaporation experiments were always carried out in pairs. In each pair, one beaker was left uncovered, the other sealed with Parafilm. Suspensions of 2 $\mu$m carboxylate microspheres at concentrations of 0.01% were poured into 500 ml beakers, to a height of 1.5 cm. Samples were left overnight and examined 24 h after preparation. In the covered samples, cylinders were found in six out of 12 cases. In the uncovered samples, we found cylinders in only two out of 12 and they were much narrower than typical (Fig. 6). Hence, sealing seems important for cylinder formation, albeit not absolutely critical. We assume that evaporative forces create thermally driven convective flows that compromise the stability required for cylinder formation; but in occasional instances, such disturbances may be minor enough to allow some formation.

Indeed, when the covered samples were abruptly uncovered, the existing cylinders immediately began to disappear. Fluid movement could be seen in the beaker, and within three to four minutes the cylinders began to collapse either

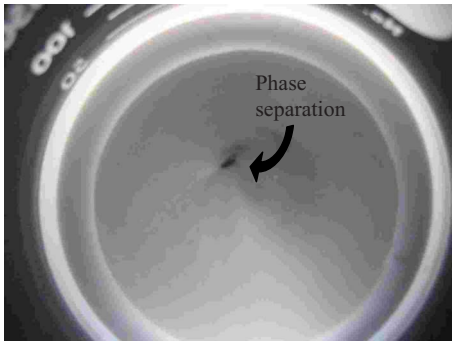


FIG. 6. (Color online) Relatively rare example of separation obtained in an uncovered beaker after 14 h.

through diameter decrease and/or by lateral shear-induced distortion and breakup. Within 10 min the cylinders were typically gone.

By contrast, when the covers had remained secure, the cylinders persisted for several hours at approximately the same size, fluctuating about their initial positions. Ultimately, they became progressively less distinct until they finally disappeared—at which time sedimentation had already progressed and the sediment layer was visible at the bottom.

#### *6. Effect of isolation*

Attempts were made to study cylinder formation under conditions in which the beaker was essentially isolated from the environment. Thus, each beaker was surrounded by a water bath set at the same temperature as the contents of the beaker. The bath jacket was made of expanded polyvinyl chloride, a material commonly used for ice buckets and other temperature-isolating applications. The sample, consisting of 0.01% v/v 2 $\mu$m carboxylate microspheres in a 7.3-cm-inner-diameter beaker filled to 1.5 cm and sealed with Parafilm, was immersed in the thermal jacket. The height of the jacket water was 2.5 cm, and the intervening annular width was 14 cm. The sample was observed 15 h later. In no case was a cylinder or other MFZ apparent ($n=10$).

On the other hand, it is noteworthy that when the samples were isolated from light alone, by carrying out the standard experiment in a darkroom, the results were different. Of 19 experiments, cylinders were found in ten, and MFZs in three. Hence, elimination of light alone did not prevent cylinder formation, whereas elimination of additional environmental influences stemming from the presence of a water jacket decisively eliminated the phase separation.

#### *7. pH measurement*

Because of previous results showing spatial distribution of charge [15,25], experiments were carried out to check whether the cylindrical and peripheral zones might have different *p*H. To carry out these experiments, micropipettes were used to withdraw small amounts (10 $\mu$l) of fluid from each zone. Pipette insertion induced some disturbance of the cylindrical zone; hence, because of likely inadvertent mixing, any measured difference between zones may underestimate the real difference.

TABLE II. *p*H values of samples taken from different regions of experimental suspensions.

| | Sample solution | | | |
|---|---|---|---|---|
| No. of experiment | Water for experiment | Suspension of water and microspheres | Liquid from cylinder | Liquid from microsphere zone |
| 1 | 6.8 | 6.5 | 5.2 | 5.6 |
| 2 | 6.3 | 6.7 | 5.6 | 5.7 |
| 3 | 6.2 | 7.2 | 5.4 | 6.1 |
| 4 | 6.7 | 7.5 | 5.1 | 5.5 |
| 5 | 6.9 | 6.8 | 4.9 | 6.0 |
| 6 | 6.1 | 7.4 | 5.4 | 5.9 |
| 7 | 6.2 | 7.1 | 5.5 | 5.5 |
| 8 | 6.6 | 6.9 | 5.3 | 5.8 |
| Mean | 6.5 | 7.0 | 5.3 | 5.8 |
| Standard deviation | 0.3 | 0.3 | 0.2 | 0.2 |

Table II shows the results obtained from eight experiments. Several features are of interest. First, the *p*H values of both zones were significantly lower than the *p*H of the original microsphere suspension; evidently, the *p*H values had diminished overnight, even though the samples had been isolated from the environment and hence not in communication with airborne carbon dioxide, which would act to lower the *p*H. The *p*H diminution probably arose from something other than $CO_2$ gas, although some gas can evidently pass through an imperfect seal. Second, the *p*H of the cylinder was lower than the *p*H of the peripheral zone. When paired values were considered, the change in *p*H appeared to be highly significant. Thus, spatial differences of *p*H may be involved in this unusual phase separation.

### C. Cylinder-formation dynamics

Time-lapse video was used to track the time course of cylinder formation. The experiments were carried out under standard conditions, using 0.01% v/v 2 $\mu$m carboxylated microspheres, in 7.3-cm-diameter beakers. To permit video recording from above, the cover was a clear Petri dish instead of Parafilm. The sample was then placed in an empty, opaque, ice-transport bucket in order to isolate the sample from occasional illumination inconsistencies. Video frames were recorded every 150 s, for a total of 432 frames.

Representative results are shown in Fig. 7. Only selected frames are shown. Although cylinder formation in this particular case required approximately 18 h, the figure shows that the actual formation was relatively rapid; it took place within a time window of 30–40 min, with little change thereafter. Five such experiments were carried out, and in all cases of cylinder formation, dynamics were similar to those shown in the figure. Relative to the extended latent period prior to cylinder emergence, actual formation was fairly rapid.

During these experiments, convectivelike spiral patterns were often seen within the microsphere zone. Since they

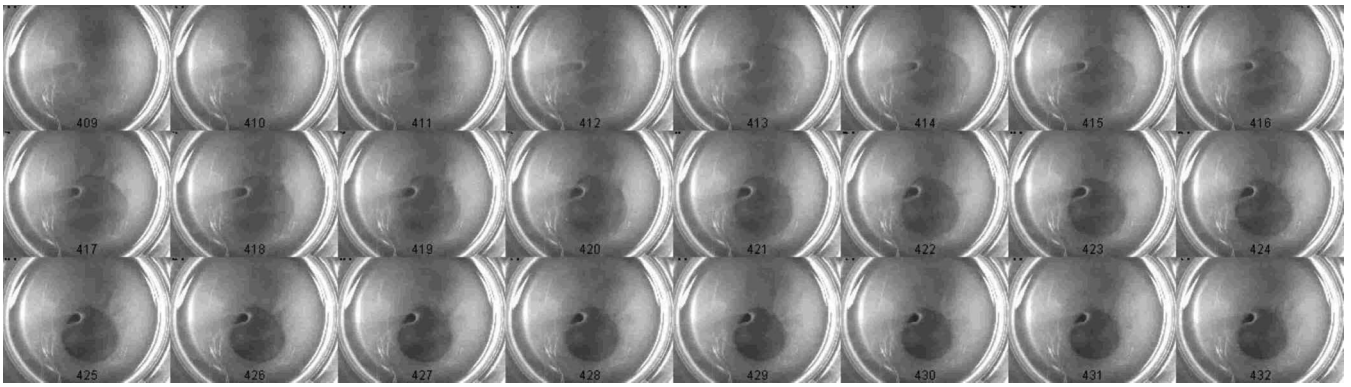


FIG. 7. Cylinder-formation dynamics, as observed from above the beaker. Frames were taken every 150 s. Only frames around the critical time are shown. Frame numbers are indicated on each panel.

were difficult to capture photographically, we simulated the behavior by carefully placing a small droplet of concentrated microsphere suspension into the center of a beaker partially filled with distilled water. Since their density was higher than that of the water, the microspheres immediately sunk. Instead of merely sinking to the bottom and remaining there, however, they formed spiral patterns (Fig. 8) reminiscent of Rayleigh-Bénard cells [26]. Although not identical to the weaker spirals sometimes seen during the experiments reported here, these spirals were nevertheless similar.

While it is not immediately obvious how these spiral currents might relate to cylinder formation, the important feature is the spirals' persistence; i.e., there is no ready mixing between the two fluids that create the visible spiral. It might be supposed that mixing of microsphere concentrate with water should occur uniformly, but the lingering presence of structure implies that it does not. The fact that spiral figures linger implies that the microsphere-containing suspension may have a different physical character, which could preclude easy mixing—much like egg white in water. The same may be happening during cylinder formation, the cylinder remaining phase-separated from the microsphere-containing zone because of the different physical character of one or the other component. Finally, the long persistence of these sprial figures implies that the system as a whole is out of equilibrium, and that it is fed by energy from outside.

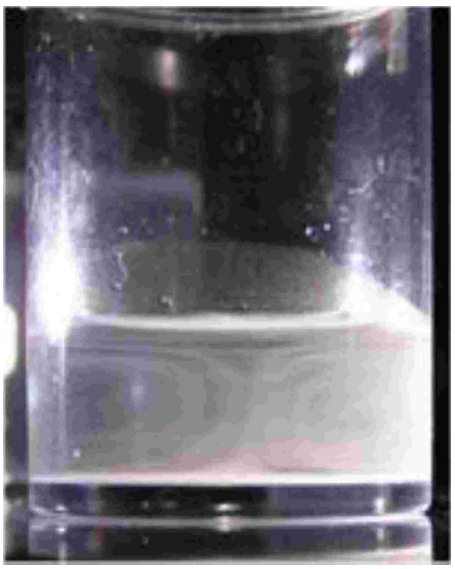

FIG. 8. (Color online) Dynamics of convection in water-microsphere suspension. Beaker diameter 2 cm. Suspension height approximately 1 cm. One drop of microsphere concentrate (2 $\mu$m, carboxylate, 2.5% w/v concentration) was dropped into distilled water, near the central axis. Image taken 15 min later. Note subtle pattern of spirals.

Finally, repeated examinations of the postsettling sediments showed an interesting feature. Rarely was the sediment uniform. The default pattern showed a central zone devoid of microspheres and a peripheral zone rich with microspheres. Quantitative measurements were not made, although this result was consistent over many observations.

### D. Effects of light

When the light source was placed off to one side, the phase-separation pattern was often noted to be asymmetric. Experiments were therefore undertaken to explore this effect in more detail.

The experiments were carried out under standard conditions, with 100 ml of a 0.01% v/v suspension of 2 $\mu$m carboxylated microspheres in an 8.5-cm-diameter beaker. Samples were placed in a photographic darkroom and illuminated only from a side-positioned fiber-optic light source, from a distance of 50 cm. Nine samples were tracked until the time the microspheres had finally settled. In no case had a cylinder formed. However, in five of the nine samples, a void structure appeared on the side away from the light. And, in those latter cases, the microspheres tended to settle in the zone closest to the light, as in the example of Fig. 9. From these results it appeared either that the microspheres were attracted toward the light, or that the void structure was repelled from the light.

As a control for any temperature-induced heating from the light source, we positioned the light higher than the chamber and used a mirror to deflect the light toward the sample (c.f. Fig. 1). A thermometer placed in the light path just outside the sample showed no significant difference ($\pm 0.5$ °C) from room temperature. Nevertheless, the sedimentation ring was consistently nonuniform. In all three cases studied, the patterns were similar to that of Fig. 9.

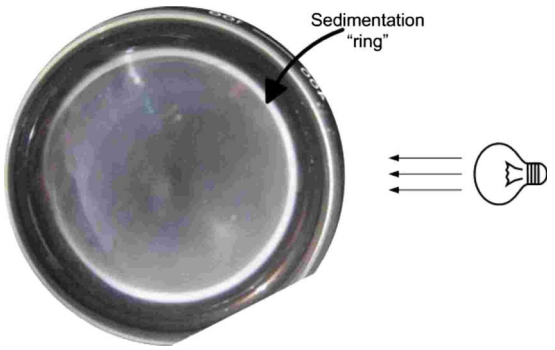


FIG. 9. (Color online) Sedimentation pattern observed following asymmetric illumination. Photo taken from top of beaker. Sedimentation ring is thinner on the side opposite the light source.

To follow up on this observation, we imposed side-directed incident light after the cylinder had already formed. The light source was again positioned 50 cm from the side of the beaker, which had remained covered. Immediately after the light was turned on, the cylinder began moving away from the light. In three attempts, this behavior was seen consistently. Velocity was approximately 0.5 mm/s. Typically, the cylinder grew smaller in diameter during the course of movement, and underwent shape change. The light-induced deflection supports the previous conclusion: either microspheres are attracted to the light, thereby "edging" the microsphere-free zone away, and/or, the microsphere-free zone is repelled from the light.

Another experiment along similar lines involved covering half the beaker's cylindrical surface with black paper, turning off the overhead light, and illuminating the uncovered portion from the side from a distance of 90 cm. In total, 16 such experiments were carried out. In four of the 16, no disturbance of uniformity was visually detectable. In nine out of the 16, after several hours, microspheres were observed to be distinctly more concentrated on the lighted side than the darker side. In the three remaining experiments, the cylinders that had formed were situated on the dark side. Hence, light-induced effects seemed once again to be apparent, although no serious attempt was made to quantify these effects.

In sum, the dynamics of phase separation observed here are sensitive to ambient light. The latter experiments imply that it is the microspheres themselves, perhaps including their hydration shells, that are somehow drawn toward the source of light.

## IV. DISCUSSION

We report here an odd but distinctive type of phase separation occurring in glass beakers under laboratory light. When aqueous suspensions of colloidal microspheres are poured into these beakers and left overnight, they separate into two phases: a peripheral zone containing microspheres and a central cylindrical zone devoid of microspheres. The central zone extends from the top to the bottom of the suspension, forming a clear, microsphere-free, cylinder. Such cylinders are observed regularly.

### A. Previous observations of microsphere-free zones

This is not the first report of colloid-free regions in suspensions, above and beyond those created by ordinary settling. In a series of studies designed to explore the dynamics of suspended microspheres, Ise and colleagues reported the existence of "voids," i.e., regions of the suspension devoid of microspheres [9–12]. Microspheres drawn from these regions would coalesce nearby to form colloid crystals, leaving the former regions free of microspheres. Such voids were large, fairly stable, and completely free of microspheres.

Whether those voids are similar to the microsphere-free zones found here is open to speculation. One argument in favor is that in our experiments, the microsphere-free zones were not always cylindrical; they were occasionally amorphous in shape, and thereby comparable to the zones seen by Ise and colleagues. Compared to those asymmetries, the symmetry of the cylinder may be merely a reflection of the inadvertent uniformity of some feature of the physical environment—realized here often, but perhaps not so often in the experiments of Ise *et al.* This conjecture is supported by the observation that in experimental pairs, both specimens either did form cylinders or did not. Behavior was consistently the same.

A second and perhaps implicitly obvious point of coincidence in both experiments is that microspheres must have been attracted to one another: without concentration increases in some regions, voids or clear zones could not form in other regions. In Ise's experiments such condensations appeared as crystallites; in our experiments crystallites might also have formed within the microsphere zone, but resolution was not high enough to investigate. At any rate, the microspheres in the peripheral zone must have become more concentrated; otherwise the cylindrical void could not have formed.

Another instance of large-scale phase separation is the so-called exclusion zone found next to hydrophilic surfaces. When an entity with a hydrophilic surface is inserted into a microsphere suspension, the microspheres translate away from the surface, leaving a substantial microsphere-free zone, often on the order of several hundred micrometers [14,15]. Such zones persist for extended periods, on the order of hours or days, and may reflect an altered state of water. In the experiments under discussion, hydrophilic surfaces are not present, except for the beaker itself; hence the relationship between exclusion zones and the microsphere-free zones found here remain speculative. Nonetheless, both the exclusion zone and the void are well-documented examples of large-scale phase separations with clear zones, quite distinct from the clear zones arising from ordinary settling. Hence, the large-scale phase separation reported here may be merely another example of already well-documented phenomena.

### B. Conditions required for appearance of cylinder

Cylinders did not form under all conditions. Several variables were particularly important for maximizing the likelihood of their appearance.

One of those variables was concentration. We found that concentrations on the order of 0.01% v/v were the most

likely to produce cylinders. The probability fell off considerably both at higher and lower concentrations; above 0.03% and below 0.003%, cylinders were never seen. Hence, cylindrical phase separation was dependent on a concentration window extending only one order of magnitude.

A second critical variable was solution stability. When evaporation was allowed to take place during the latent period, rarely did cylinders form even when the above-mentioned conditions had been satisfied. Sealing the beaker, either with Parafilm or with a Petri-dish cover, resulted in a qualitative increase of cylinder incidence.

A third critical variable was geometry: cylinders appeared most often when the ratio of suspension height to container diameter was on the order of 0.2. Larger containers could produce cylinders as commonly as smaller ones so long as suspension height was adjusted accordingly.

Finally, a yet to be identified fourth factor must have been at play. An extremely consistent finding was that when experiments were carried out in pairs, the presence of a cylinder in one sample almost guaranteed the presence of a cylinder in its partner; and, conversely, the absence of a cylinder in one almost guaranteed the absence in the other. The reason for this systematic pairing of results never became obvious, and warrants further study. It implies that some unidentified feature of the environment must be critical for cylinder formation.

### C. Origin of the cylinder

What creates the observed cylindrical phase separation? The most obvious candidate would seem to be thermally induced convection, or temperature-gradient induced heterogeneities due to the so-called Soret effect. This hypothesis is supported by the observation that cylinders failed to form when the beaker was surrounded by a water jacket. The jacket should have insulated the beaker from any thermal gradients, and when, apparently such gradients had been minimized or eliminated, cylinders did not form. Another observation that seems to fit this hypothesis is the height-to-diameter requirement. One may imagine that for thermal currents to create this characteristic separation, some geometric rules would need to apply; and, we found that indeed they did.

On the other hand, the thermal convection hypothesis seems inconsistent with a variety of observations. First, the cylinder did not form progressively; it appeared fairly abruptly relative to the latent period in advance of its formation. Commonly, the sample had to remain still for some 15 h, whereas the period of active cylinder formation was restricted to perhaps 30 min. Thus, creation occurred within a period of about 5% of the latency period. The abruptness of formation seems opposite to what might be anticipated from thermal gradients, which would be expected to be strongest early on, and weaker as the beaker contents progressively equilibrated with the environment.

A second inconsistency is that the likelihood of cylinder incidence was increased by sealing. According to the thermal convection hypothesis, evaporation-induced thermal currents ought to enhance convection and thereby promote cylinder formation. But the opposite was found: Only when thermal currents were minimized by sealing did the cylinders appear with any frequency.

A third argument is the finding that concentration was critical. Above and beyond fairly narrow limits, cylinders were never seen. If thermal currents were responsible, concentration dependence ought not to be as critical as it was.

Finally, it is not at all clear why any kind of thermal current would separate microspheres from water. Microspheres are denser than water, and if anything, they should settle at the bottom, leaving the bulk of the solution microsphere free. Eventually, they do settle. However, for creation of the central cylinder, they would need to translate radially, toward the periphery. Why such translation would result from thermal currents is not obvious; nor is it clear why the expected day-to-day and place-by-place randomness of thermal gradients should produce so consistent and geometrically symmetrical a pattern.

For all of the above reasons we think that the appearance of the clear cylinder is not easily explained by the presence of thermal gradients, although such gradients may indeed be present. Another possible origin may be the presence of electrostatic gradients. The finding of *p*H gradients between cylinder and bulk (Table II) implies that charges may somehow be involved. Such gradients create colloid-depleted zones at the oil/water interface [14,15]. Electrostatic gradients are also implicated in nonbarometric settling patterns of colloids [19–23]. Whether they play a role in aqueous systems such as those explored here, and especially in cylinder formation, remains to be explored.

A clue for the origin of the cylinder is that its formation was consistently preceded by a clear, platelike zone at the top of the suspension. This plate was microsphere-free. It formed shortly after pouring the suspension into the beaker, and then grew slowly with time up to a few hours. Because the clear plate vanished just as the cylinder formed, a possibility is that the plate is the cylinder's precursor. Indeed, the volume of the plate was of the same order of magnitude as the volume of the cylinder. Under standard conditions with beaker radius 42 mm and suspension height 15 mm, plate depth was approximately 2 mm—giving a plate volume of 11.1 ml. The cylinder radius under such conditions was typically 15 mm, giving a cylinder volume of 10.6 ml. Hence, plate and cylinder volumes were at least roughly comparable.

The reason for formation of the plate itself is not completely clear, but it may arise from phenomena similar to those seen adjacent to hydrophilic interfaces, where large, microsphere-free regions are abundantly seen [14,15]. The platelike zone is evident in many different chamber geometries. It appears to be sensitive to, and possibly a product of, ambient radiant energy [28]. Its appearance is currently under intensive study, and will be reported elsewhere [31]. Whatever the underlying mechanism, if this process requires time, then it may explain why cylinder formation is long delayed relative to other processes.

It is worth mentioning that the dynamics of formation of this plate differ from those expected from ordinary settling, although ordinary settling itself is far from barometric [19,21,22], and profiles can be light dependent [24]. The clear zone forms within minutes, and is fully developed

within several hours. After that, it remains stable for many hours, until the time of the instability that triggers the apparent conversion from plate to cylinder. Hence, the platelike separation is a complex matter involving physical processes not all of which are fully understood. Yet, the plate seems to precede the cylinder.

One possibility, then, is that as the plate matures, it gives way at or near its center point, and then flows downward, creating the cylinder. Once it reaches the bottom of the container, it can only flow radially, then upward, etc., creating the observed spirals. Whether the final cylinder is stable, or continues to flow downward as the plate replenishes, is not immediately obvious. We found that similar patterns could be created in chambers of various shape, especially narrow chambers built of two parallel glass plates. Hence, the central column and spirals are not unique to the beaker shape.

A distinct feature of the result is the separation of phases. Microspheres in the periphery do not mix with the water in the cylinder. Nor do elements of the spiral mix with contiguous elements of the spiral—for if they did, then the spiral figure would vanish; yet all separations are maintained. This implies that one is not dealing with a simple aqueous suspension, for if that were the case, then diffusion-induced mixing should soon blur the overall pattern. Hence, it appears that either the microsphere-water complex, or the cylinder water, was in some way constrained, producing physically distinct entities that might not easily mix. Indeed, the finding that there was a distinct *p*H difference between the phases implies some kind of physical difference between the separated entities.

Why the plate might suddenly give way to create the cylinder is not clear. One possibility is that the plate had slightly higher density than the suspension beneath. If so, it might eventually give way and flow downward. Why this would happen consistently near the center point is unclear; and why it would then turn upward to form spiral structures is again unclear. If higher density is the main feature, then the basis for upward flow is not obvious.

Another possibility is that the plate is charged. Although electrical aspects of the clear plate were not measured, the finding that the *p*H of the cylinder was different from that of the microsphere-containing region is consistent with such a possibility. Hence, a plausible hypothesis is that charge gradually builds within the plate. This is consistent with the findings of significant charge effects involved in the process of sedimentation [19–23]. As charge-based pressure grows too high to sustain, the fluid begins to flow downward to relieve the pressure. The downward flow would create a hole in the microsphere array, the fluid pushing its way down, then toward the sides, then upward to form the spirals. Testing of this hypothesis will require more detailed measurements within the plate and cylinder.

### D. Effect of light

One effect that at first seems difficult to fathom is that of incident light. Among the various observations we made, perhaps the most dramatic was that once the cylinder had formed and side-incident light was turned on, the cylinder moved resolutely away from the light source. This was seen not only in the present experiments but also in experiments in which cylinder-like phase separations were seen with other chamber geometries [29]. Incident light always pushed the cylinder away from the light source.

Incident light had a comparable effect as the cylinder was forming. Illumination from one side of the beaker enhanced the likelihood that the cylinder would appear on the opposite side. Hence, whether imposed during formation, or after formation, of the cylinder, light consistently drove the cylinder away. How this might integrate with the above-described scenario is the question at hand.

An interesting possibility is that incident photons attract microspheres to one another. In a study of colloid crystals, we found that incident light diminished the microsphere-microsphere spacing, by up to 25% [27]. If a similar effect were at play here, then microspheres would be drawn naturally toward the beaker's periphery, where incident light intensity would ordinarily be highest. This would create a central void, in the shape of a cylinder, possibly allowing the plate water to flow downward, the water from the platelike void mixing with water from the cylindrical void.

In this sense, results obtained with the water jacket are relevant. The jacket not only provided an insulating layer, but because the jacket container was not transparent, it also cut off much of the incident light. In the presence of this jacket, the cylinder did not form. Hence, the critical variable that allows the cylinder to form in the first place may indeed be incident radiant energy. The most relevant wavelengths are probably in the infrared. When only visible wavelengths were cut off by carrying out the experiments in the darkroom, cylinder formation was close to normal. The darkroom eliminates visible wavelengths, but not necessarily infrared wavelengths, whereas the thick water jacket absorbs all infrared. Hence, infrared seems particularly critical. The influence of incident infrared energy has recently been found in other types of microsphere experiments [30].

This influence of radiant energy may explain why the position of the cylinder was commonly slightly off center. If slightly more incident energy came from one side than from the other, then such asymmetry would be expected. Indeed, the various amorphous shapes seen occasionally instead of the cylinder might have arisen from incident energy that inadvertently had been especially nonuniform. Further, the fact that pairs of samples consistently showed the same results—either cylinders or no cylinders—adds credence to the critical role of ambient energy, which may be expected to vary over time in not always predictable ways.

Finally, what about incident light coming from overhead? Such light may have influenced the formation of the upper plate. Ordinarily, microspheres should have settled progressively toward the bottom of the beaker. However, incident light from above could present a retarding force, drawing microspheres upward and effectively inhibiting the downward settling (see also [24]). Indeed, the presence of the top plate itself might have derived from the balance between the downward pull of gravity on microspheres and upward force induced by incident light. Followup studies are necessary, but it seems clear that light, especially infrared components, must be a major player in all of these dynamics.

In sum, we report an unusual phase separation, which results in the appearance of a clear, microsphere-free cylinder penetrating vertically through a suspension of microspheres. Although originally found serendipitously, the cylinders were ultimately found to appear only when conditions are opportune; otherwise, they do not appear at all. And the energy driving this phase separation may arise from light. Indeed, it is possible that photonic energy may play a similarly unexpected role in driving other types of phase separation.

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