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Comment on "Spherical agglomeration of superconducting and normal microparticles with and without applied electric field"

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Ghosh and Hirsch [Phys. Rev. B **86**, 054511 (2012)] claimed that many micrometer-size particles in liquid nitrogen, as large as 25 to 32 μm, could be aggregated into balls by shaking. Ghosh and Hirsch performed their experiments with liquid nitrogen in open air; therefore, moisture condensed on the particle surface, leading to ball aggregation by shaking. This phenomenon has nothing to do with the electric field-induced formation of superconducting balls. In addition, their claim that a large electric field still exists in the interior of the capacitor when the electrodes are insulated is flawed. The electric field–induced superconducting ball formation reveals that the area of interaction between electric field and superconductors requires more investigation. However, the phenomenon can be explained within the BCS theory.

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I. WATER-INDUCED AGGREGATION

In their recent paper,[1] Ghosh and Hirsch claim that many micrometer-size particles in liquid nitrogen, as large as 25 to 32 μm, can be aggregated into balls by shaking. $Bi_2Sr_2CaCu_2O_{8+x}$, $YBa_2Cu_3O_{7-\delta}$, MgB_2, σ-powder, Pb powder, and Zn powder were all able to aggregate into submillimeter balls in liquid nitrogen by shaking. Meanwhile, they also found that they were unable to aggregate these particles in water, ethanol, or methanol by shaking.

It is well known that nanoscale particles suspended in colloidal suspension aggregate into clusters under the Van der Waals force. During this process, particles dispersed in the liquid phase stick to each other and spontaneously form irregular particle clusters, flocs, or aggregates. This phenomenon is very important for colloids since it is related to the colloidal stability.[2–4] On the other hand, as the particle size increases, such self-aggregation gradually disappears. For particles as large as 25 to 32 μm, it is normally impossible to aggregate them by shaking. Therefore, if the finding by Ghosh and Hirsch were true, this would indicate that liquid nitrogen is anomalous in causing suspended particles to aggregate, which is not the case for water, ethanol, and methanol.

After carefully examining their paper and communicating with the authors, however, we have learned that all of their experiments were conducted in open air, although the paper does not say so explicitly. It is known that when an experiment with liquid nitrogen is conducted in open air, the moisture and oxygen condense within. This occurrence is demonstrated in several educational videos on the Web[5] and explained in liquid nitrogen handling manuals.[6] Once these gases condense in the liquid nitrogen, an unexpected phenomenon occurs. Therefore, when we learned that Ghosh and Hirsch's liquid nitrogen experiments about superconductivity were performed in open air, we were surprised.

The phenomenon that small quantities of water on suspensions of solids having hydrophilic surfaces in organic media can induce aggregation of balls by shaking was reported as early as 1932 and afterward.[7–9] In 1951, Stock observed that shaking fine barium sulphate particles suspended in benzene formed spheres of 0.5–1.0 mm in diameter.[10] Later it was confirmed that water played a crucial role in Stock's experiment. Smith and Puddington[11] verified that the presence of a small quantity of water is necessary in shaking for the aggregation into spherical masses of barium sulphate particles suspended in organic media. When Stock's system was thoroughly dried, no ball formation occurred. In addition, Smith and Puddington also found that below the freezing temperature, water continued to induce ball aggregation of barium sulphate in organic media. Only under the temperature range of $-17\,^{\circ}\mathrm{C}$ to $-20\,^{\circ}\mathrm{C}$ is water no longer effective for ball formation in benzene.

The previous results suggest that Ghosh and Hirsch's aggregation by shaking in liquid nitrogen is also a result of moisture, which condenses on the suspended particle surface when they performed the experiment in open air. In order to verify it, we conducted the shaking experiment with Pb, YBCO, and BSCCO powders, respectively, in liquid nitrogen inside a glove bag filled with dry nitrogen gas. To avoid any interference from moisture, we thoroughly dried our samples first. We placed our sample in a small dry box, which contained an effective desiccant, and then we used a vacuum pump to suck air out of the dry box continuously for several hours. We placed the samples and all needed tools in a glove bag, used a vacuum pump to evacuate the bag, and refilled the bag with dry nitrogen gas. Two batches of powders were prepared for each sample: one batch had a particle size of 10 to 25 μm, and the other had a particle size of 25 to 32 μm. We followed the procedure described in Ref. 1 exactly and poured 60 mg of powder in a 80-mm-diameter container, which contained approximately 5 mm of N_2, and kept the container cold by submerging it in a container of larger diameter with substantially higher levels of N_2.

Our tests fully confirmed that the aggregation reported in Ref. 1 is due to the presence of moisture. When Ghosh and Hirsch performed their experiment with liquid nitrogen in open air, the moisture condensed on the particle surfaces and induced the microscale particles to aggregate by shaking. We found that dry BSCCO, YBCO, and Pb powders did not form any balls in the dry glove bag. As shown in Fig. 1, BSCCO powders did not aggregate no matter how much we shook the sample. However, when we opened the glove bag and let the

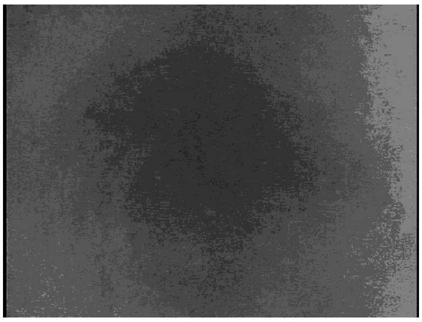

FIG. 1. Dry BSCCO powders of particles between 10 and 25 μm do not aggregate by shaking.

air in with the samples, BSCCO, YBCO, and Pb all formed some balls by shaking. As shown in Fig. 2, the same BSCCO particles formed balls by shaking in open air. When moisture is present in the surrounding liquid nitrogen suspension, water freezes on the surface of the particles, changing the particle aggregation dramatically.

It is the same as the ball aggregation of barium sulphate particles suspended in benzene by shaking that moisture must have condensed on the particle surface because water is not miscible with benzene. The hydrophobic effect of the base liquid forced the particles with a water layer on their surfaces to aggregate into small balls by shaking. There is no hydrophobic effect when the particles are suspended in water. In addition, when one conducts experiments with ethanol or methanol in open air at low temperature, moisture does not condense on the particle surface, as water is miscible with ethanol and methanol although water also adds to the sample. Therefore, there is no ball aggregation produced by shaking in water, ethanol, and methanol, as reported by Ghosh and Hirsch.

As the liquid nitrogen temperature is well below water-freezing temperature, someone might ask if the moisture condensed on the particles surface would become an ice layer. If there is no shaking, we believe so. However, the shaking raises the particle surface temperature well above the liquid nitrogen temperature because the kinetic energy becomes local heat. In addition, it is also speculated that the liquid oxygen condensed from the open air and mixed with moisture on the particle surface may also help the ball formation by shaking.

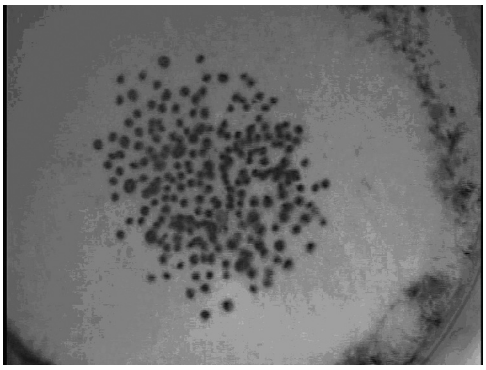

FIG. 2. When the glove bag was opened to expose the BSCCO sample to open air, the powder soon aggregated into small balls by shaking.

However, the most important issue is that the water induced ball formation by shaking has nothing to do with the electric field-induced superconducting ball formation.[12–16] When we used liquid nitrogen to work with high temperature superconducting particles, the particles were dried, and the experiments were always conducted in a glove bag with dry nitrogen. No open air was in contact with our particle samples.[12,14] This is the normal procedure, as conducting such experiments in open air would invite moisture and other gases to condense.[5,6] When we worked with Pb, other low temperature superconducting particles, and MgB_2, the experiments were performed in a helium dewer, which was completely isolated.[13,15] In addition, our experiments found that superconducting particles as large as 60 μm could be aggregated into balls under an electric field.

II. ELECTRIC FIELD WITH INSULATED ELECTRODES

Ghosh and Hirsch also conducted an experiment when either both electrodes or one electrode was insulated. They have found that when they applied up to 20 kV to the two electrodes that were insulated, the BSCCO particles did not move. Hence, Ghosh and Hirsch concluded that the motion and ball formation had nothing to do with the electric field.[1]

This conclusion, however, is incorrect. When the two electrodes are covered with insulating materials, the electric field between the insulated electrodes is considerably reduced. As the applied voltage is raised to 20 kV and while many insulating materials such as a layer of 1-mm-thick Teflon can sustain 60 kV, the electric field outside the insulated electrodes is almost vanishing.

Communication with Ghosh and Hirsch indicated that they believe that the electric field is increased, not reduced, when the electrodes are insulated. Dr. Hirsch stated, “If you insert an insulator between the electrodes, this will not weaken the electric field in the region between the electrodes not occupied by the insulator, rather it will strengthen it.” He further wrote, “I don’t believe that in a parallel plate capacitor the electric field in the empty part is decreased if you insert a dielectric slab occupying part of the empty space. On the contrary, the electric field in the empty part would increase. In the limiting case where the dielectric slab that you insert has infinite dielectric constant, i.e. is metallic, the electric field in the empty part would be increased from V/d to $V/(d\text{-}d')$, where d' is the thickness of the slab inserted” (Hirsch, personal communications with R. Tao).

These arguments are erroneous. The electric insulation is used everywhere to insulate electric wires in houses, working environments, and electric equipments, etc. If insulators could only increase the electric field outside, as Ghosh and Hirsch claim, there would be no safe environment. Therefore, we must clarify this issue here.

Insulators cannot be represented by a dielectric material with a uniform electric field inside. Insulators are materials with large band gaps; therefore, they have no conducting electrons. Let us consider the electric field between two insulated electrodes (Fig. 3). The gap between the two electrodes is d. The capacitor is immersed in liquid nitrogen (or in air) with dielectric constant ε_0. The positive electrode has

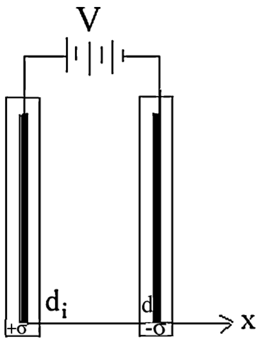

FIG. 3. The electric field with the two insulated electrodes.

surface charge density $+\sigma$, while the negative electrode has surface charge density $-\sigma$. We assume that each insulated slab covers the whole electrode with a layer thickness d_i, dielectric constant ε_i, and sufficient high dielectric strength. At $x = 0$, the electric field inside the insulated slab is $E(0) = 2\pi\sigma/\varepsilon_i$. However, if the insulation is perfect, at the other side of the insulated slab, $x = d_i$ the electric field inside the insulated slab,

$$E(d_i) = 0. \tag{1}$$

The electric field inside the insulated slab $E(x)$ is not uniform and there is bounded charge density inside the insulator $\rho = (dE/dx)/(4\pi)$. This is possible because insulators are materials with large band gaps, and they have no conducting charges to neutralize these bounded charges. In addition, we have

$$\int_0^{d_i} E(x)dx = \frac{1}{2}V. \tag{2}$$

The situation with the insulated slab near the negative electrode is similar. Inside the slab,

$$E(d) = 2\pi\sigma/\varepsilon, \quad E(d-d_i) = 0, \quad \text{and} \quad \int_{d-d_i}^{d} E(x)dx = \frac{1}{2}V. \tag{3}$$

The assumption that the electric field is uniform inside the insulated slab is incorrect. The previous analysis also clearly indicates that both electrodes still have high charge density. The weak electric field between the two insulated slabs does not mean that the charge on the electrodes is diminished.

If there is only one electrode insulated, the electric field is $2\pi\sigma/\varepsilon_0$ in the space between the electrode and the other insulated electrode.

To verify our previous analysis, we conducted an experiment. First, we used a bare wire to connect to a dc high of 1000 V. Then we used a surface dc voltmeter to measure the voltage at the position about 2.5 cm away from the wire. The reading on the meter showed that the electric potential on the bare wire was 1000 V. Then we replaced the bare wire with an insulated wire. The same meter showed almost zero voltage on the outside surface of the insulating wire, although the core of the insulated wire was still connected to 1000 V. After the high voltage was disconnected, we also found that the insulation material was negatively charged on its surface.

In summary, the liquid nitrogen experiments in Ref. 1 were performed in open air, and the moisture condensed on the particle surface, which led to ball aggregation by shaking. This phenomenon is irrelevant to the electric field-induced formation of superconducting balls. In addition, Ghosh and Hirsch's claim that insulating electrodes would increase the electric field outside the insulator is flawed.

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