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Catalysis of impurities coalescence by quantized vortices in superfluid helium with nanofilaments formation

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The dramatic effect of quantized vortices in superfluid helium on the rate of coalescence of suspended impurities has been predicted; such catalytic process should result in formation of fiber-like structures having primarily nanothickness. That should be valid for any impurity and it may be used as a base for the universal method of nanowires and nanotubes producing. The experiments on molecular hydrogen imbedding into liquid helium supported these conclusions. They showed that: (i) in normal liquid He the coalescence led to formatting spherical microparticles carried by turbulent motion of a liquid; (ii) in the superfluid only very long filaments were observed, they behaved as quantized vortices should do. These filaments are fiber-like hydrogen crystals and they survived liquid helium transition to normal state. The promises for using this phenomenon in basic and applied sciences have been outlined.

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61.46.Km Structure of nanowires and nanorods (long, free or loosely attached, quantum wires and quantum rods, but not gate-isolated embedded quantum wires);
67.63.Cd Molecular hydrogen and isotopes.

Keywords: liquid helium, quantized vortices, molecular hydrogen, nanowire, flow tracer.

1. Introduction

Liquid and solid helium are the quantum liquid and crystal correspondingly, thus all their characteristics are spatially delocalized. The important and surprising exclusion is the quantized vortices appeared in superfluid helium in response to its excitation. Though a vortex occupies whole liquid bulk its potential described by formula

$$U \approx \ln \frac{r}{r_0}$$

is noticeably distinguished from zero only in a vortex core, its characteristic size $r_0 = 0.7$ Å is even less than the size of an atom. The quantized vortex length may be meantime rather long and comparable with a vessel size [1]. Any impurity including light helium isotope ^{3}He, from one side, and rather large clusters, from another side, tends to be placed in a vortex core because the energy for a particle possessed the finite viscosity is minimal at the axis of a vortex [2]. However the affinity of these impurities to the vortex is rather small amounting for atoms and small molecules to 3–10 K [1,3]. It means that for the temperatures 1.5–2 K the probability to find them inside of vortices is only weekly larger than outside, though at $T = 0.1$ K practically all of them should be finally attached to vortices. There are still no calculated energies for binding larger features to a vortex in literature but the authors of Ref. 4 found experimentally that the preliminarily grown micron-size grains of molecular hydrogen were concentrated steadily in quantized vortices even in the very vicinity of λ point, i.e., at temperature around 2 K [4]. The problem the authors of this paper put for themselves consisted in revealing the possible role of quantized vortices not in alignment of already prepared clusters, as it was already done in Ref. 4 for visualization of quantized vortices in superfluid helium, but in the very process of impurity condensation into agglomerates and clusters.

A linear molecule of course tends to align along the vortex axis [3]; this evidently should be true for a dimer of atoms or molecules as well and the binding energy of a dimer with a vortex has to be approximately twice as more than for monomer. In general one could suppose that the energy of small cluster pinning to a vortex is defined by cluster length – for n links it will be n times more than for individual particle. If so for the clusters or chains having 5–10 links the preference of their finding inside vortices will be strongly dominant already at $T \approx 2$ K. Every guest particles in liquid helium excluding ^{3}He stick together practically at every collision, and the rate of condensation governs by the rate of mutual collisions. The last is proportional to square of impurity local density and thus it much higher inside of vortex. The motion of captured particles along the vortex core has no restriction; this additionally enhances the rate of collisions because inside of a vortex the particles can move only towards each other, contrary to the bulk liquid helium where the particle velocities are chaotically directed.

Such a way the presence of quantized vortices results in sudden effect of catalysis of sedimentation for the impurities — atoms, molecules and clusters — suspended in superfluid helium. Provided the number of vortices is sufficient the rate of the process as a whole should grow at many orders of magnitude, and filament-like structures should appear as a product of condensation.

2. Experimental evidences

These considerations were confirmed by our experiments on imbedding the molecular hydrogen significantly diluted by helium gas directly into superfluid helium; the powerful gas jet provided a short time of mixture transport to gas–liquid interface. This study has been performed in Tokyo Institute for Physics and Technology [5]. The ^{4}He cryostat has been equipped by two pairs of optical windows and the inner diameter of its central bath was 160 mm and the distance between the inner optical windows was 220 mm, the superfluid was achieved by pumping liquid helium in the bath. The use of so large cryostat allowed to be sure that both the vessel walls and liquid helium surface were enough far away. To provide the reliable and fast transport of impurity to liquid helium surface in the presence of large counterflow of evaporating helium we applied gas helium jet technique [6]. Since the nearly equimolecular mixture of hydrogen and deuterium formed the particles which levitate in liquid helium the preliminarily prepared gas mixture H_2:D_2:He = 1:1:200 was used in the most of our experiments, though some sets were performed for H_2:He = 1:100 and D_2:He = 1:100 mixtures. A mixture at pressure of 3–6 bar was allowed with using of electromagnetic valve to put into inlet capillary at pulses of 80 ms duration with repetition rate 6 Hz, 30–40 bursts in each injection series. The total number of hydrogen introduced into a fridge in sequence of pulses has been chosen not so high to restrict the overlapping the structures in the field of view. The molecular source was Dewar tube with central capillary of 1 mm inner diameter and a nozzle of about 300 μm at its bottom. The distance between the nozzle and the surface of superfluid helium was 3–7 cm.

The sequence of pulsed jet entering liquid helium significantly distorted its interface; the height of surface waves was several mm and one could be positive that a lot of quantized vortices appeared in He II just in the place where density of guest particles was maximal. The optical technique has been chosen for registration from the consideration of reliability of interpretation. We understood of course that because the spatial resolution of an optical method can not be better than 1 μm, our observations would start only when the formed features became to be of this size and the most interesting initial stage of the condensation process would be hidden. It turns out anyway that even the last pages of scenario contained important and unambiguous information. Since hydrogen is transparent in optical range and absolute difference between refraction index of solid hydrogen and liquid helium is not large the method based on the schlieren photography [7] with the sensitive and high-resolution CCD camera has been used. The spatial resolution of the particle registration system was 20–30 μm and depth resolution was about 3 cm.

While liquid helium was in normal state even at temperatures close to λ point the spherical particles with diameter around 10 μm appeared in a field of view in several minutes after the injection termination. The particles were obviously made of hydrogen; for equimolecular hyrogen-deuterium mixture in average there were no definite direction of their motion, whereas for pure deuterium whole pattern moved temporarily to the bottom. As it is seen from Fig. 1 the particles move along slightly curved trajectories with lateral velocities projections of few tenths of cm per second. The particles were obviously entrained by convective flows in liquid helium. Sometimes they changed sharply the direction of their motion as if they jumped from one flow to another one. Such a behavior is the ready solution for the problem of making quantitative measurements of local flow velocities in turbulent liquid helium using tracer particles [8]. Indeed the space resolution of the observation technique and the size of the fridge windows are close. Thus by focusing the schlieren system to the cryostat axes and observing simultaneously the central area through reciprocally perpendicular pairs of windows one could restore the trajectories for all particles and such a way obtain the field of flow velocities in liquid helium.

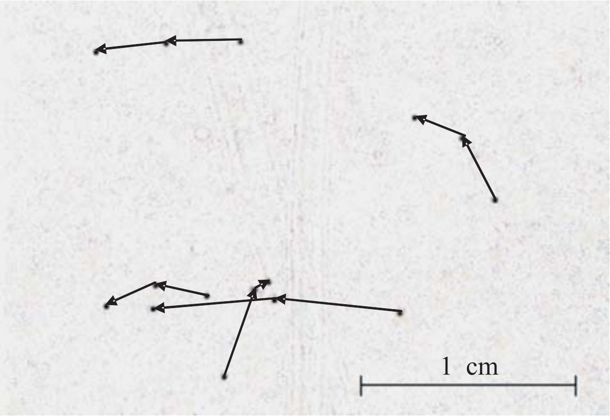

Fig. 1. The displacement of micron-size H_2–D_2 particles drifted with turbulent flows in normal liquid helium, background is subtracted. The time between successive frames is 0.5 s, the maximal projection of particle velocity to the plane perpendicular to the observation axis is 0.5 cm/s.

Completely different behavior took place in the case when the hydrogen injection proceeded into superfluid helium even if the liquid temperature decreased only a little below 2.19 K. Almost just after termination of H_2:D_2:He mixture injection the very long hairs often being longer than the window size appeared throughout the superfluid; this was proven by changing of the focusing area of the observation technique. Such filaments were observed for H_2:He mixture as well, though they moved randomly but predominantly upward to the surface. In the case of H_2:D_2 equimolar mixture the motion was predominately in horizontal direction without any sign of upflow. The example of the filament is shown in Fig. 2. Sometimes the filaments were rather short, only few mm long and practically linear. They had a predominantly vertical position and in the case of H_2:He mixture they moved up with velocity about 0.5 cm/s. The number of hairs slowly decreased with time and in 20 min they disappeared from the field of view.

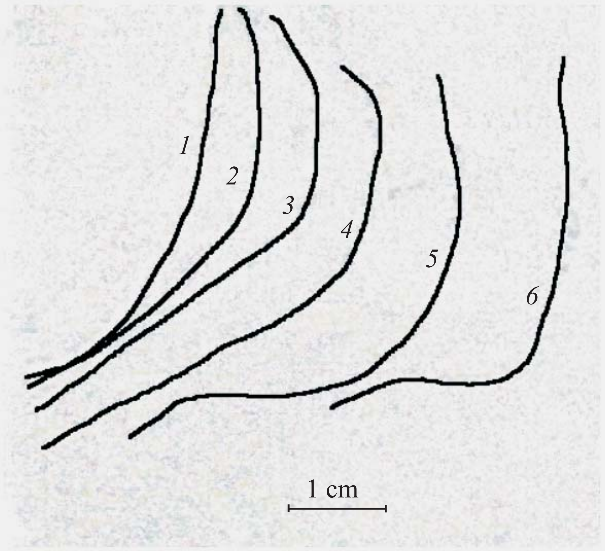

Fig. 2. The motion of H_2–D_2 long filament in superfluid helium. The time between successive frames is 1 s.

Surprizing and important for applications property of quantized vortices is their ability of pinning to different protuberances in apparatus [9]. We used this property for fixing the formed in superfluid helium filament in a field of view in order to follow its evolution in time and under change of conditions. The registration system has been focused for that purpose to the spot where the low-temperature optical window's tube was connected with the inner wall of a cryostat LHe bath. The example of the filament «caught» by this way is shown in Fig. 3. This filament had the length around 3 cm and the diameter, being the same along whole thread, less than 50 μm. The temporal behavior of the filament was the same as it has been theoretically predicted for quantized vortex [9]. Though the filament swung strongly in the flow of the normal component, its ends were immovable and perpendicular to the place of pinning. It was clearly seen that the filament was levitated in the liquid helium, i.e., it was consisted of hydrogen-deuterium mixture.

Nevertheless the dilemma still existed, whether the filaments observed were quantum vortices captured and kept together separate hydrogen grains as it was considered recently in Ref. 10, or the quantum vortices enveloped the fiber-like hydrogen crystals grown inside a vortex; the enveloping the 16 μm diameter wire by quantized vortex has been considered in Ref. 11. The solution was simply to heat liquid helium with filaments suspended in it by pulses of pure warm helium gas up to the temperatures above 2.2 K and to watch what happened with filaments. The transition to normal state of liquid helium was easily observed as the start of boiling. It was stated the hydrogen filaments already grown in superfluid helium didn't decay if quantum vortices disappeared, it allowed to consider them as one-piece fiber-like hydrogen crystals.

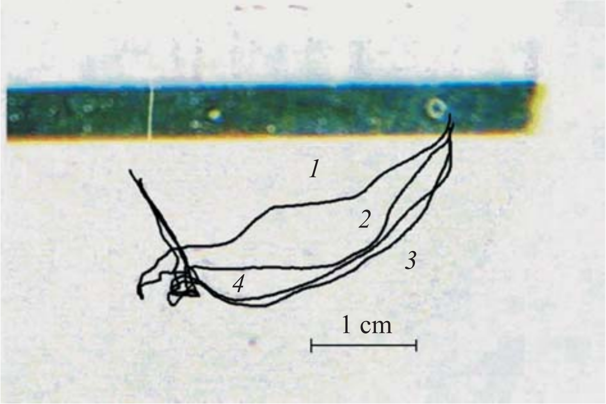

Fig. 3. The motion in superfluid helium of H_2–D_2 pinned to protuberance long filament. The time between successive frames is 1 s.

The aging both in superfluid and in normal states revealed a tendency to filament thickening and lengthening. However at temperatures higher than T_λ the ends of filaments were not pinned to some places anymore and they were moving in a liquid freely. Eventually the fibers spliced to «rope» up to 150 μm thick and it survives liquid helium evaporation being seen by unaided eye after that [5].

3. The peculiarities of fiber-like crystal growth in superfluid helium

According to considerations developed in colloidal chemistry and valid for every dispersed particles suspended in a liquid the maximal size of separate particles formed in a liquid is defined by balance between the coalescence forces in the spot of particles mutual contact and the fluctuations of liquid action to particles destroying such a contact (see Fig. 4,*a*). The fluctuations which values are governed by the ratio of particle's surface to its volume are responsible for Brownian motion in liquid. For nonspherical, prolonged particles the limiting volume of particle should be even less because the surface-to-volume ratio for them is more than for spherical ones (Fig. 4,*b*). For this reason even dendrite crystals in normal liquid have to grow from the end appending step-by-step the short fragments (Fig. 4,*c*). In quantum vortices the prolonged particles are kept directed along the vortex axes, i.e. coaxial to each other, thus even for the compounds of isotropic nature the formation of fiber-like structures from long enough fragments is quite possible (Fig. 4,*d*).

As for the condensation of small particles — atoms, molecules and agglomerates — from liquid helium bulk on the surface of filaments, there are no specificity of helium here because the impurity–impurity interaction ever stronger than impurity–helium interaction. The same one may say about interaction of two filaments originated from different vortices, the crossing them is to be followed by their reciprocal rotation up to splicing along their total length because that will gain a lot of energy. That is the reason for appearance of more thick and more long (last is due to mismatching the fragments lengths) fibers.

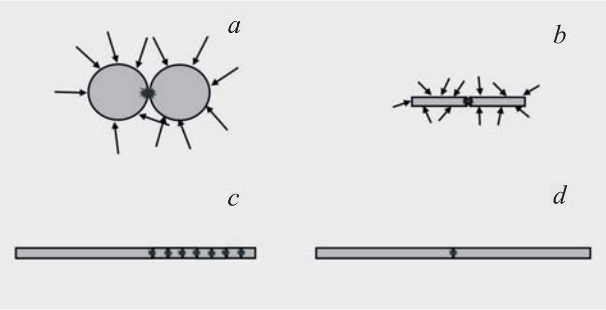

Fig. 4. To the explanation of mechanism of fiber-like crystals growth.

It is worth to say that filament-like structures (worms) made of impurities have been already observed in superfluid helium [for instance, 12] but nobody connected their appearance with quantized vortices so far.

4. The promises

One of the declared promises for nanowires and nanotubes applications is the production of superstrong ropes from them. The idea is taken from silk and spider's web and it is based upon as the practical absence of the crystal structure faults in nanoobjects as the strong, due to small radius of curvature, lattice squeezing by surface tension preventing dislocation exit to a surface, i.e. microcrack formation. In our experiments such a rope has been already produced. Though the rope described above was made of weakly bound hydrogen in the absence of structural faults it should lift the weight of 50 g and its length is already sufficiently long both for study and for applications.

The creation of superstrong ropes is important but far from being only stimulus for nanowires study. Quantum wires and quantum dots are attractive objects for basic science [13]. From the viewpoint of applied science nanowires can be used to build the next generation of computing devices. Chemically doped semiconductor nanowires of *p* type and *n* type have already been created. The conducting nanowires offer the possibility of connecting molecular-scale entities in a molecular computer as well as in flexible flat-screen displays.

The progress in study and application of nanowires is restrained by their high price, low productivity of manufacturing and difficulties of manipulations. A suspended nanowire used to be produced by chemical etching of a bigger wire, or bombarding a bigger wire with some highly energetic particles (atoms or molecules). Another way to produce a suspended nanowire is to indent the tip of a scanning tunneling microscope in the surface of a metal near the melting point, and retract it. Of course, such a limited production can not be a base for industrial method.

Nanowire growth in quantized vortices makes it possible not only to do their production cheaper and more productive but due to its universality may substantially expand the variety of these promising objects of nanotechnology. The vortex ability of pinning to any protuberance allows growing the wires attached to the tips of needles intentionally installed in active zone; these needles would be served as pincers for manipulation by nanowires. Important advantage of given approach is the feasibility to grow a few cm long wires.

As it was already stated the quantized vortices play a specific role only at first stage of the impurity coalescence process. It is profitable at that stage to use small densities of source material — atoms, molecules and agglomerates in order to keep the rate of filaments growth inside quantum vortices much larger than the rate of filament thickening as at the account of an impurity sedimentation from the bulk of liquid on their surface as due to entangling the separate filaments into the rope. In this case up to the exhaust of initial material the filaments will remain thin. To realize what method one has to apply for supply the material for nanowire production into superfluid helium let estimate with what amounts of matter we should deal. Let we are going to grow 10 filaments of 3 cm length with 10^3 atoms in a cross-section, that corresponds to diameter about 10 nm. Thus, we should embed to superfluid helium about 10^{12} atoms; that amount can be ablate from solid target placed inside of liquid by laser pulse with the energy around 1 μJ. At any case that is no problem to create so small number of particles.

It is difficult to say something definite about the crystalline structure of thin filaments formed such a way, but one could expect the enhanced probability for amorphous structure appearance. Both low temperature of coalesced particles and abnormally high removal of coalescence heat by superfluid helium promote stabilization particles just at the place of primary contact.

The further thickenning of filaments is convenient to carry out in normal liquid helium to prevent the new quantized vortices appearance. The particles neccessary for that could be introduced either by embedding atoms and molecules from a gas as we did in Ref. 6 or by laser ablation from target submerged in liquid helium; in the case of metals the effective method of cathode sputtering in the spark organized in liquid can be used. It is important that the material sedimented to filament primarily grown in a core of quantized vortex could be different from filament material, and multi-layer filament-like structure being one-dimensional analog of epitaxial film may be created. Besides the primary nanofiber could be built up from volatile material, hydrogen for example, in order to obtain, after the core evaporation, the nanotube made of given material.

Impurity particles stabilization in a core of quantized vortex lengthens the time of their possible contact, that facilitates low-temperature tunneling chemical reactions proceeding in case of chemically active species. If the impurity fragments captured to vortex have enough large length the time of contact may be indefinitely large. In principle an aligned polymer may be grown in quantized vortex such a way.

The experiments on nickel wires growth seems to be of top-priority. Nanowires made of nickel widely studied [13]; nickel ferromagnetism allows wire levitation in liquid helium with using magnetic field: as it follows from barometric formula at temperature 1.5 K the ensembles consisted of less than 10^4 atoms are insensitive to gravity, whereas bigger agglomerates of nickel display already ferromagnetism and can be suspended by magnetic field. Such experiments are in progress in Chernogolovka group. The fact of nickel nanowire formation at the top of each from four steel needles mounted near the zone of a spark disrupted from nickel cathode will be registered by leakage current from the needle.

5. Conclusion

Above suggestions and experimental results confirm the existence of new phenomenon of catalysis of impurities condensation in superfluid helium by quantized vortices. That phenomenon results in increasing by many orders of magnitude the rate of coalescence process and in formation of filament-like structures having primarily nanothickness. Since that fact should be valid for any impurity the phenomenon may be used as a base for the universal method for nanowires and nanotubes producing. Due to small matter consumption — 1 cc of the material is sufficient for the production of nanowires with total length of 10^7 km — the usage of principally expensive low-temperature technique is competitive with other methods, especially if one keeps in mind that liquid helium gives itself deep cryogenic purification from any contamination, usually that is realizes by expensive high-vacuum chambers and pumps applications.

Apart from the possible applications in industry the phenomenon under consideration is of significant interest for basic problems of low temperature physics and chemistry. The possibility to rule the loaded by impurities quantized vortices by using outer fields — magnetic, gravitational, etc. — seems attractive. The feasibility to create in quantized vortex at very low temperature the linear chain of spin-aligned atoms, in particular hydrogen atoms, makes it possible to elongate the ensemble lifetime at the account of three-body recombination retardation. Nowadays there are many speculations on existence at very low temperature of liquid and even superfluid state in small hydrogen clusters [14]. The creation of thin but simultaneously long hydrogen fibers where such a phenomena should take place together with real mass transfer will give a chance to reveal real fingerprints of superfluidity or simply fluidity provided they will take place. The core of quantized vortices is unique nano-reactor for low-temperature tunneling chemical reactions.

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