The superfluidity role in impurities condensation in liquid helium

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Tuapse,

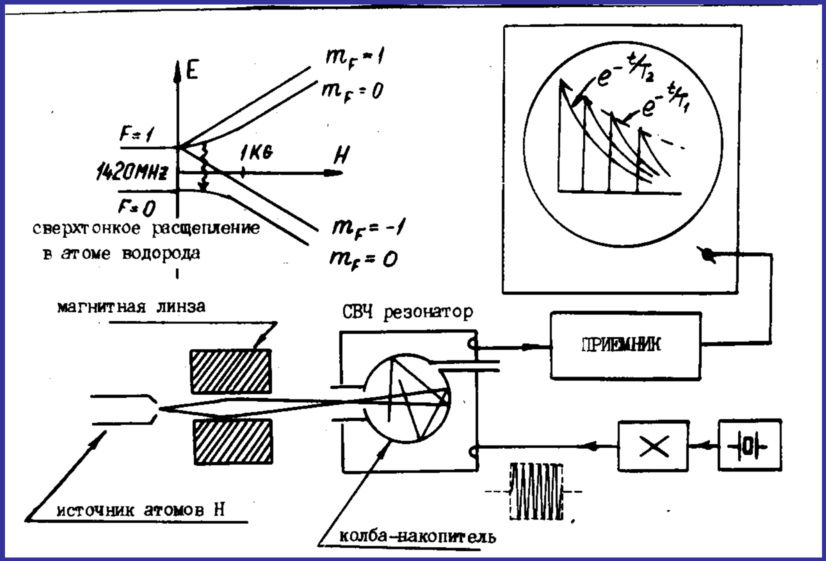
September 14, 2012

Arrennius idea that decrease in temperature can arbitrarily retard chemical reactions periodically attracts the researchers dreaming of super-explosives and propellants containing high concentrations of the active atoms, especially Hydrogen ones, stabilized at a low T.

In 1972, I was an employee of the Division of Free and Condensed Radicals and Ions in Chemical Physics Institute created just for development such a work (HEDM).

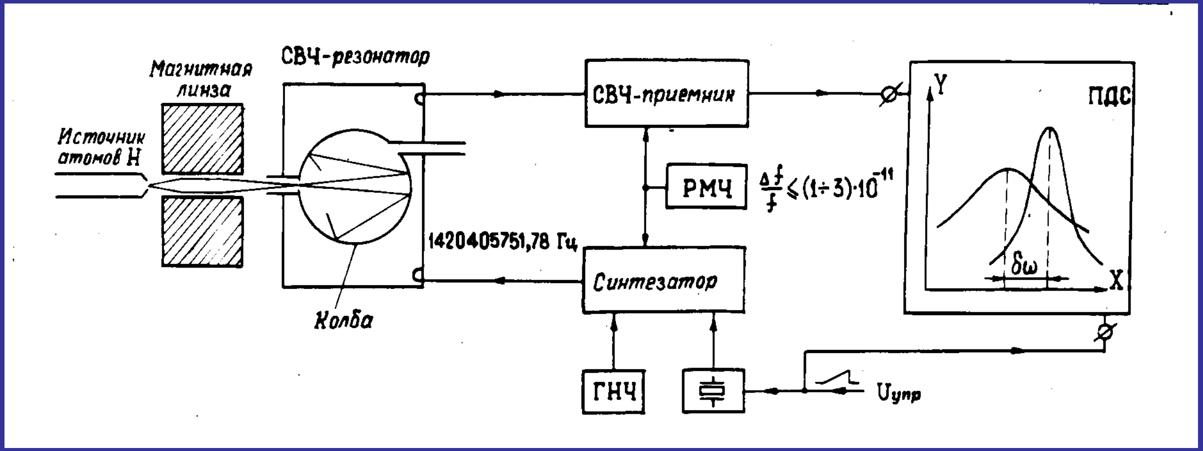
Metallic hydrogen was our goal as well.

My PhD study: Hydrogen Maser Application for Chemical Reactions Study



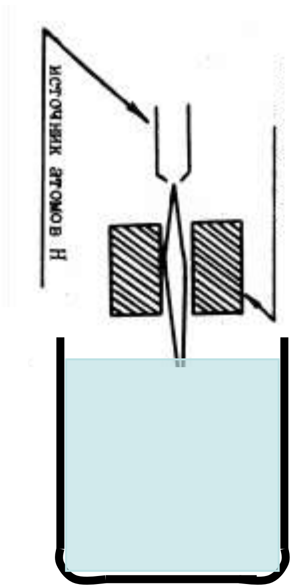
Amplifier: time domain

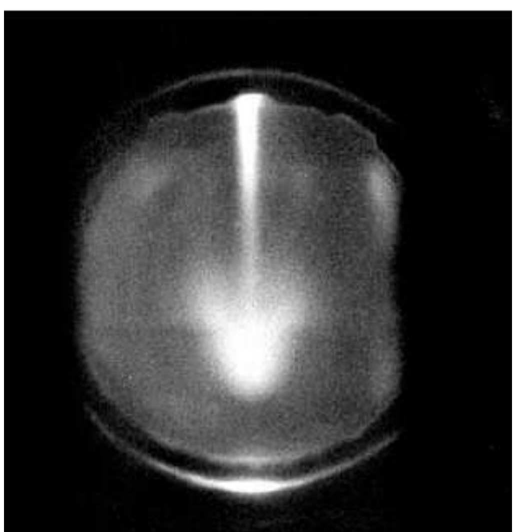
Collimated beam of atomic hydrogen !!!!



Generator: frequency domain

The idea was to direct H atom beam to the LHe surface





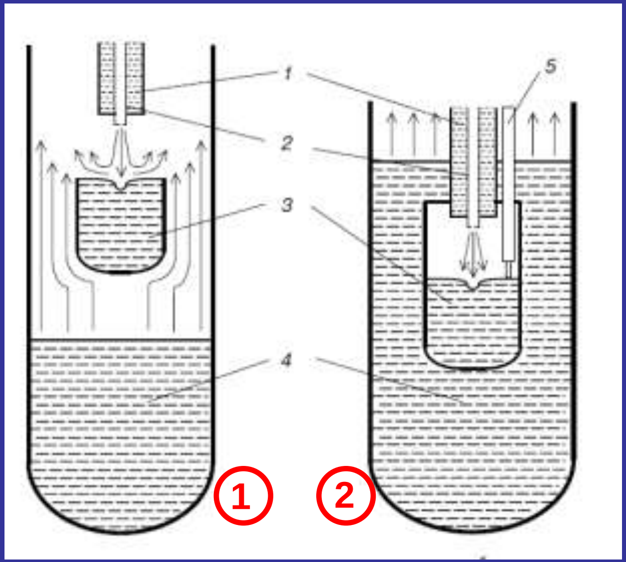
Liquid helium is just only substance being liquid at T = 0 and it is possible to reduce its vapor pressure by pumping in oder to allow the beam reach the liquid surface.

My neighbor at home L. P.Mezhov-Deglin being the expert in LT supported the idea. Moreover, he noted that in this case the liquid becomes superfluid and therefore efficiently remove any heat from the active area.

The idea seemed attractive because a "soup" of atoms in an isothermal liquid looks much more promising than the common approach where the atoms were deposited in solid matrix poorly conducting a heat.

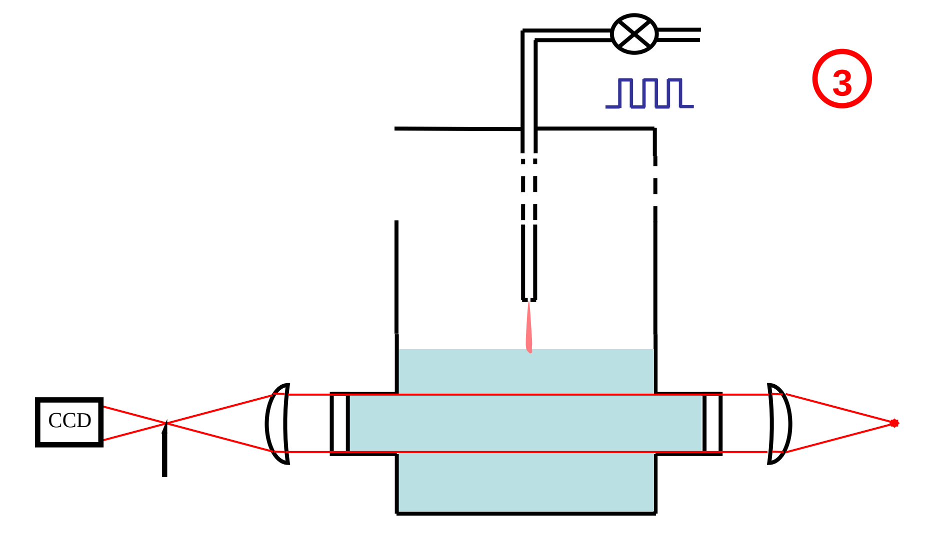
Intensive atomic jet directed to LHe surface

is necessary because under cooling by helium vapor pumping the inflow of “hot” gas should be 60 times less than counter-flow



1. *E. B. Gordon, L. P. Mezhov-Deglin, and O. F. Pugachev, JETP Lett.* ***19(2)*** *, 63 (1974)*

2. *R. E. Boltnev, G. Frossati, E. B. Gordon, I. N. Krushinskaya, E. A. Popov, and A. Usenko. J. Low Temp. Phys. 127, 245 (2002)*

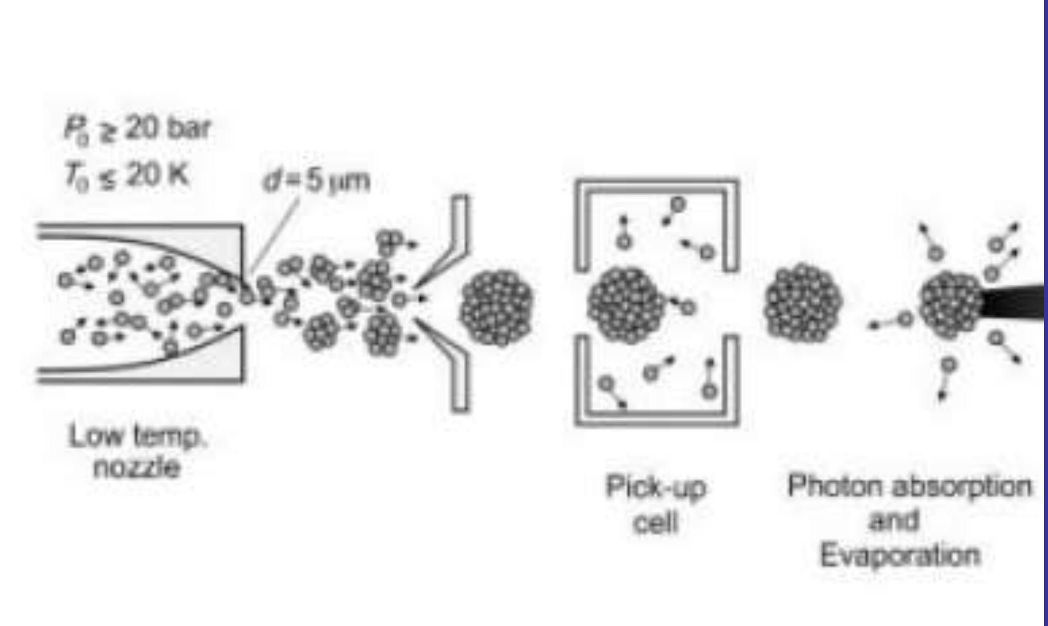


3. *V. Ghazarian, J. Eloranta, and V. A. Apkarian, Rev. Sci. Instr. 73, 3606 (2002).*
E.B. Gordon, R. Nishida, R. Nomura, Y. Okuda, JETP Lett. ***85(11),*** *581 (2007).*

The gas jet introducing into liquid helium allows the preliminary exposition of species to HF electric discharge and further fast transport of atoms, free radicals and metastable particles to the surface of liquid.

However, the only *superfluidity fingerprint* was the explosion of active nitrogen sediment stabilized inside HeII under its transition from superfluid to normal state at λ-point. This effect was explained *by thermal explosion of energy-rich medium due to retardation of heat release* from sediment grains surface.

Capture of impurity particles in superfluid helium droplets



The main goal was the low-temperature spectroscopy of matrix-isolated atoms and molecules.

J.P. Toennies, A.F. Vilesov, ANGEWANDTE CHEMIE-INTERNATIONAL EDITION 43(20), 2622 (2004)

The observed change of the rotational constant in molecular spectra were intrepreted as the *manifestation of superfluidity* in the nanoscale. Theoretically some influence on the rate of superfluidity particle condensation in HeII has been predicted due to lengthening free pass of impurity particles

The total conclusion:

1. The process of atom and molecule coalescence in liquid helium as in common liquid rare gases should obey the diffusion-controlled reaction approach developed by P.Debye for colloid solutions:

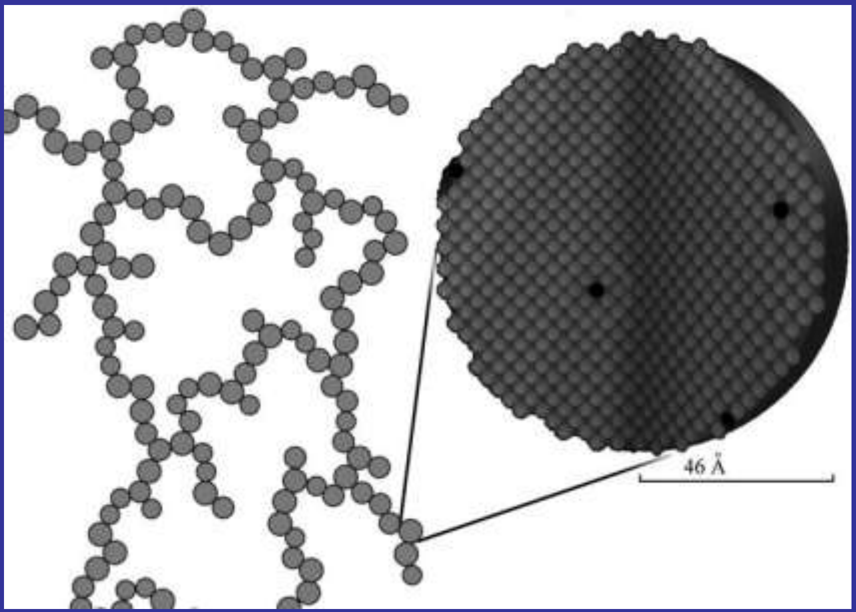
$$\frac{dn}{dt} = -k_D n^2; \quad k_D = 4\pi DR \qquad \tau \approx (4\pi DR)^{-1} N$$

2. The size of colloid is about 3 nm.

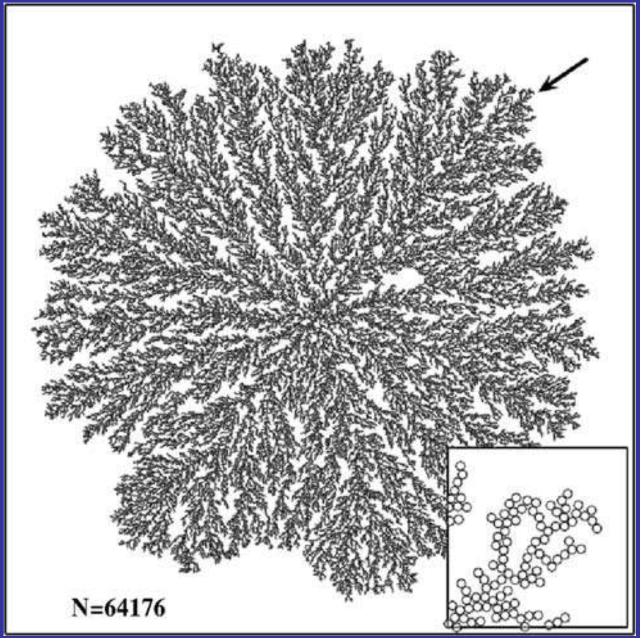
*V. Kiryukhin, B. Keimer, R.E. Boltnev, V.V. Khmelenko, E.B. Gordon, PRL **79**, 1774 (1997).*

2. **The process should be strictly isothermic**.

The supposed structure of condensates in superfluid helium



V.V. Khmelenko ,· H. Kunttu, · D.M. Lee
J Low Temp Phys (2007) 148: 1–31



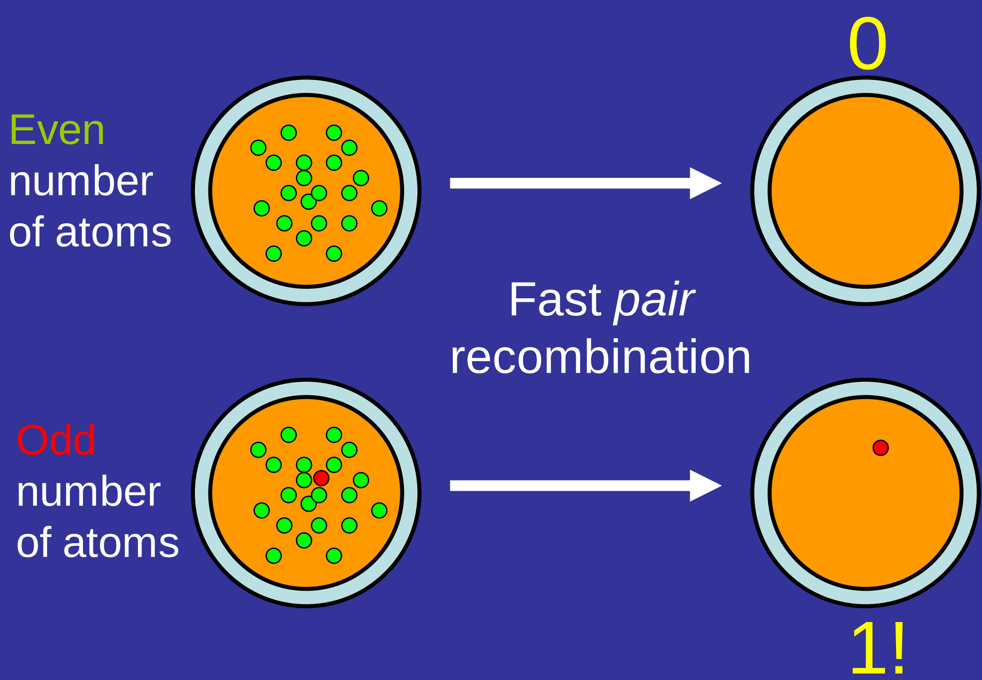
S.G. Alves, A. F.Vilesov, S.C. Ferreira, Jr.,
J.Chem.Phys. ***130****, 244506 (2009).*

Quasi spherical colloid-like clusters with amorphous or fractal structure !!!

Every impurity nanocluster is insulated from others by the film of solidified helium,
E.B. Gordon, A.F. Shestakov, LTP 26 (1),1 (2000)

“Odd” Low Temperature Chemistry

E.B.Gordon, Doklady Physical Chemistry ***378 (4-6)****,* ***156 (2001)***



Transition of an atom stabilized in a grain to another grain is much more difficult than its diffusion inside it.

After fast decay induced by self-heating the “odd” grains contain (for very long time) *one* atom

In “odd” clusters further chemical reaction maybe stimulated by temperature or by light.

The concentration of active particles for 3 nm clusters is reasonable for chemical syntesis -10^{-3} mol / mol or $3 \cdot 10^{19}$ cm^{-3}.

This plausible scenario turns out to be wrong due to two peculiarities of superfluid helium

1. Famous but rather weak excitations – quantized vortices –long quasi-1D features having the affinity to any guest particles in HeII.

2. The huge sensitivity to overheating – above heat flow of 10 W/cm^2 HeII practically jump-likely converts from perfect heat-conductive (by the second sound) media to good thermo-insulator.

Quantized vortices in He II

- They appear only in superfluid phase assuring the superfluidity existence. Any perturbation of HeII causes the vortices, then they decayed very slowly.

- They either form closed loops (smoker) or they are *pinned to protuberances (tornado).*

- *! They are practically one-dimensional features*

$$U = \ln(r/a)\ ,$$

where $a = 0.7$Å,

whereas their length is up to few cm !

Quantized vortices capture any impurities

L.S.Reut, I.Z. Fisher, Sov. Phys. JETP – USSR 28(2), 3758 (1969).

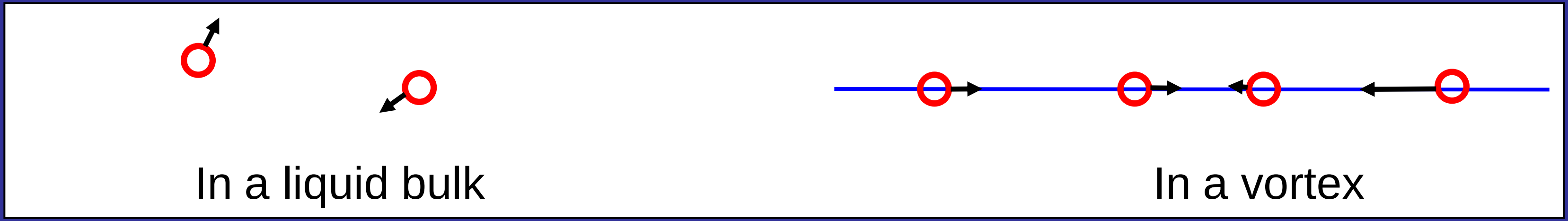
However,

the binding energy is rather small –

- 20 – 40 K for ions
- 3 –10 K for atoms and small molecules

Our suggestion #1

1. The impurity atoms or molecule density in a vortex is not so much - in (*exp (E/kT) = 10 – 20* times higher than that in the rest liquid,
 but the rate of their collisions is much higher there due to the collinearity of their velocities

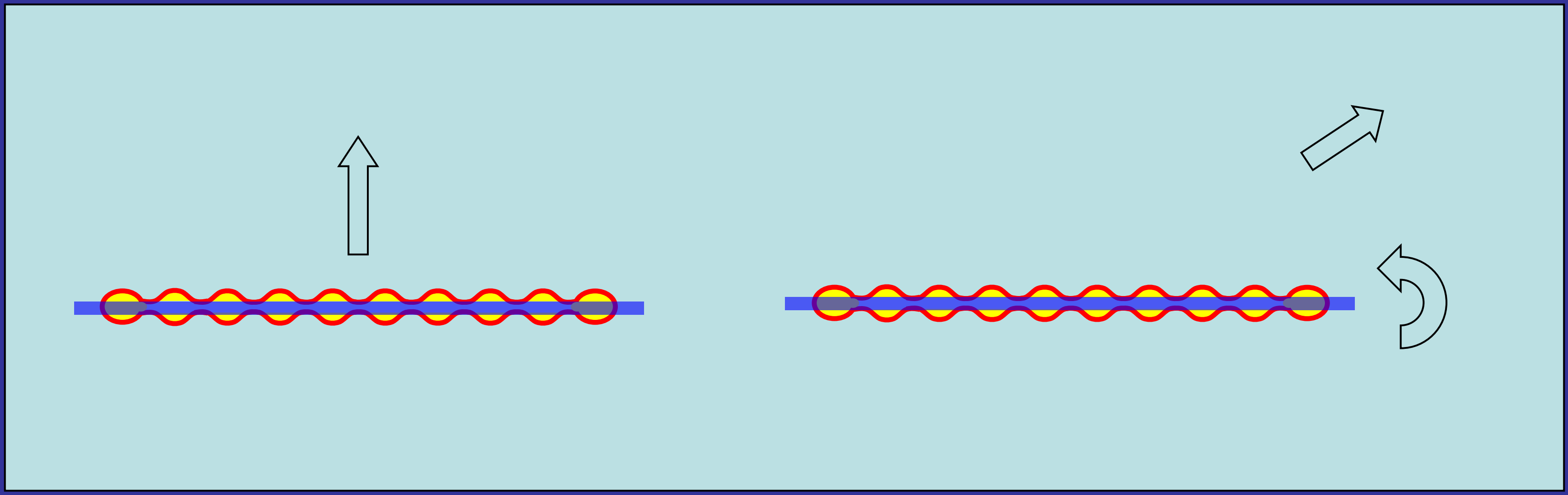


2. The growth of cluster from the merging atoms takes place along the vortex core forming the chain by such a way; and if it even leaves vortex it lines up the core coming back to it.

Our suggestion #2

Any prolonged feature tries to align along the quantized vortex axis and energy of small cluster affinity to vortex core is proportional to impurity length – for ***n*** links it should be ***n*** times more than for single one.

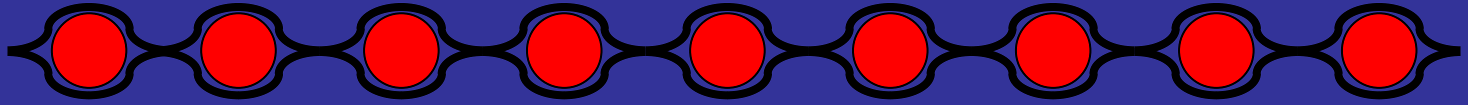
Simple considerations



Our suggestion #3

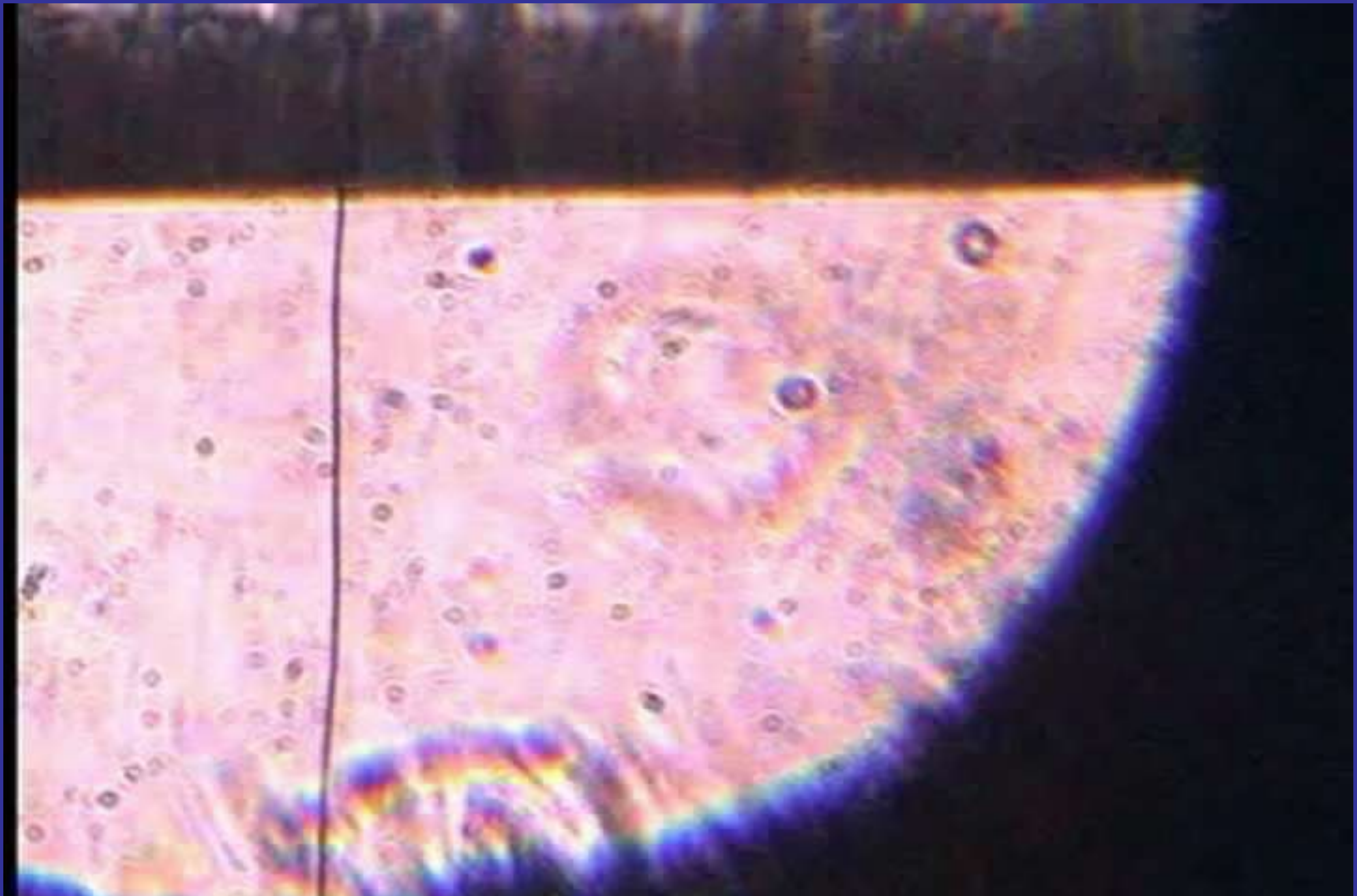
1. Nanoparticles freely collide in a vortex core merging together into continuous wire

2. Microparticles repulse each other in a vortex core forming chain of separate grains by this way



The vortex "pinned to protuberances"

E.B.Gordon, R. Nishida, R. Nomura, Y. Okuda. JETP Lett. ***85(11),*** *581 (2007).*



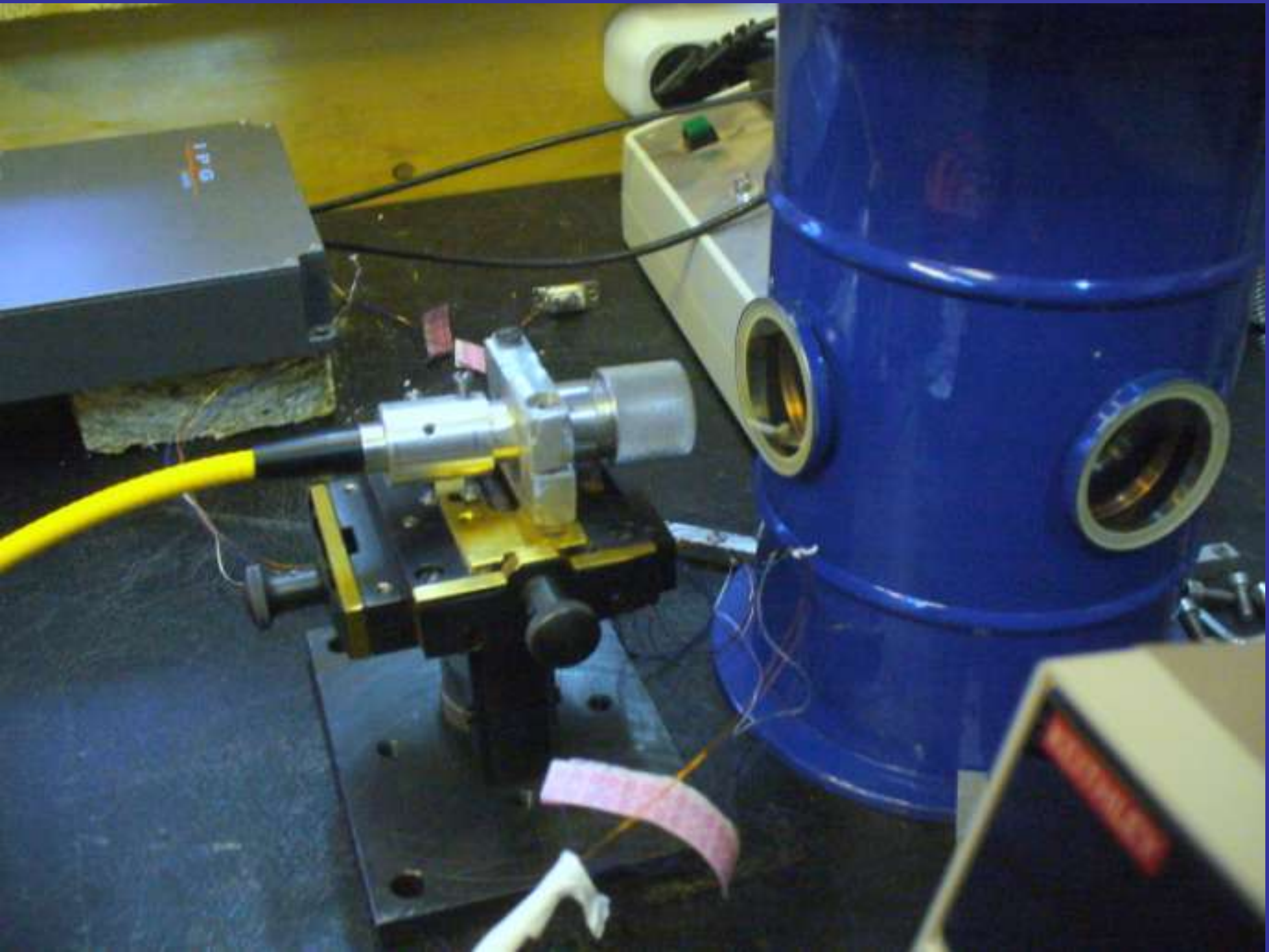
- В нормальном жидком гелии образовывались исключительно сферические крупинки водорода
- В верхтекучем гелии наблюдались исключительно длинные нити, ведущие себя подобно квантованным вихрям

New mechanism for impurities condensation in superfluid Helium

E. B. Gordon, Y. Okuda, JETP Letters, 85, 581 (2007), JLTP, 35, 209 (2009)

- Any guest particles have affinity to the core of quantized vortex.
- The particles captured there have enhanced rate of mutual collisions leading to coagulation.
- Resulting growth in its size increases the cluster lifetime in a vortex core and consequently their local density.
- Such self-accelerating catalytic process of condensation becomes to be prevailing .
- Due to the small (<1Å) thickness of a vortex core the primary condensation products should be extremely thin long filaments.
- Quantized vortex willingness of pinning to any protuberance may cause the filament growth just at needle electrodes

Nanowires needs so small amount of material that using of small power fiber laser is sufficient



Yitrrbium laser

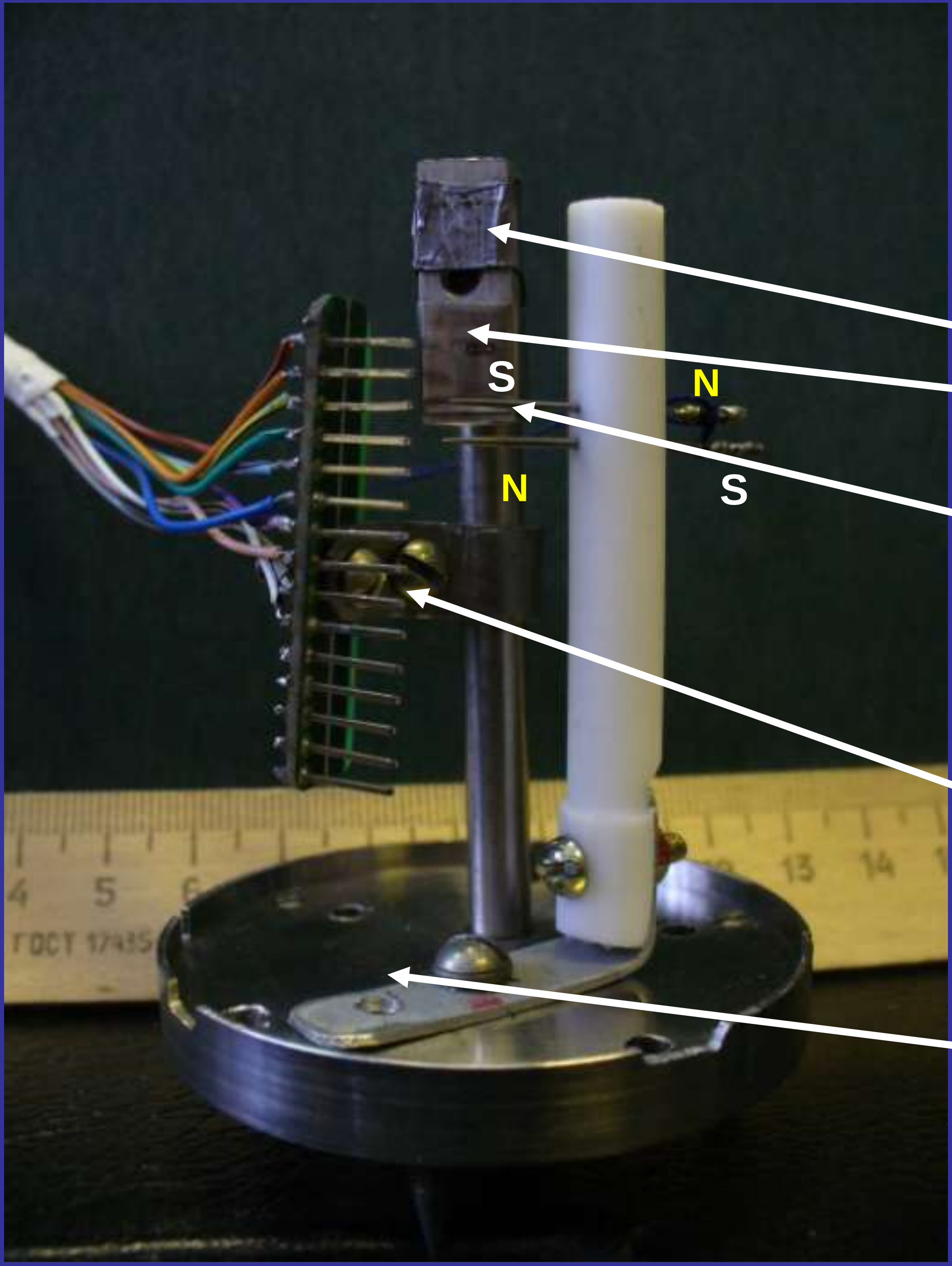
λ= 1.06 μ

E = 10^{-4} J

τ = 25 ns

f = 0.5 – 2 kHz

Experimental cell

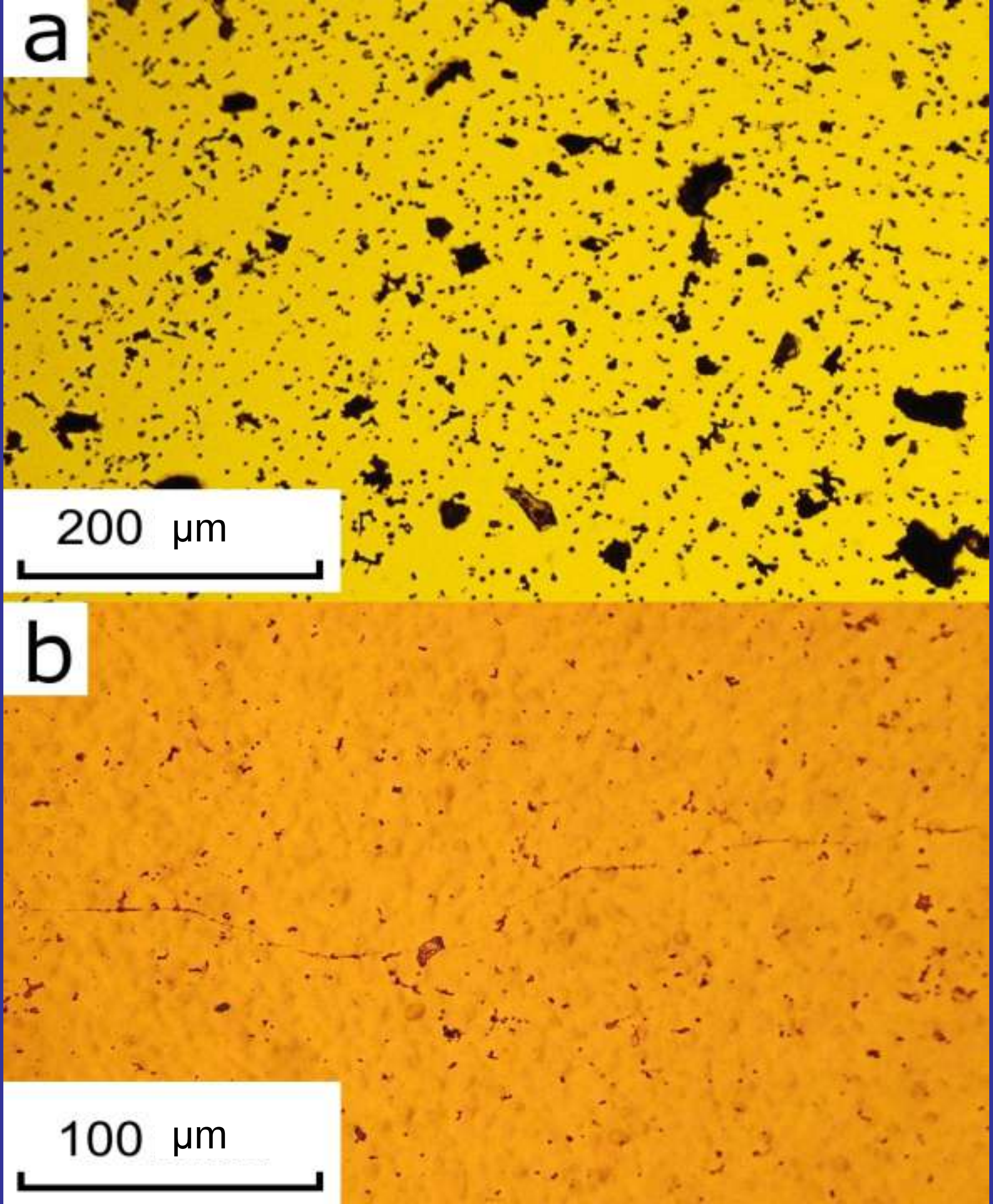


Metallic targets, the craters in laser focuses are seen

The pair of oppositely magnetized sewing needles are seen

Vertical row of gilded contacts, interelectrode distances are 3 mm each

Bottom, where fragments of filaments where collected

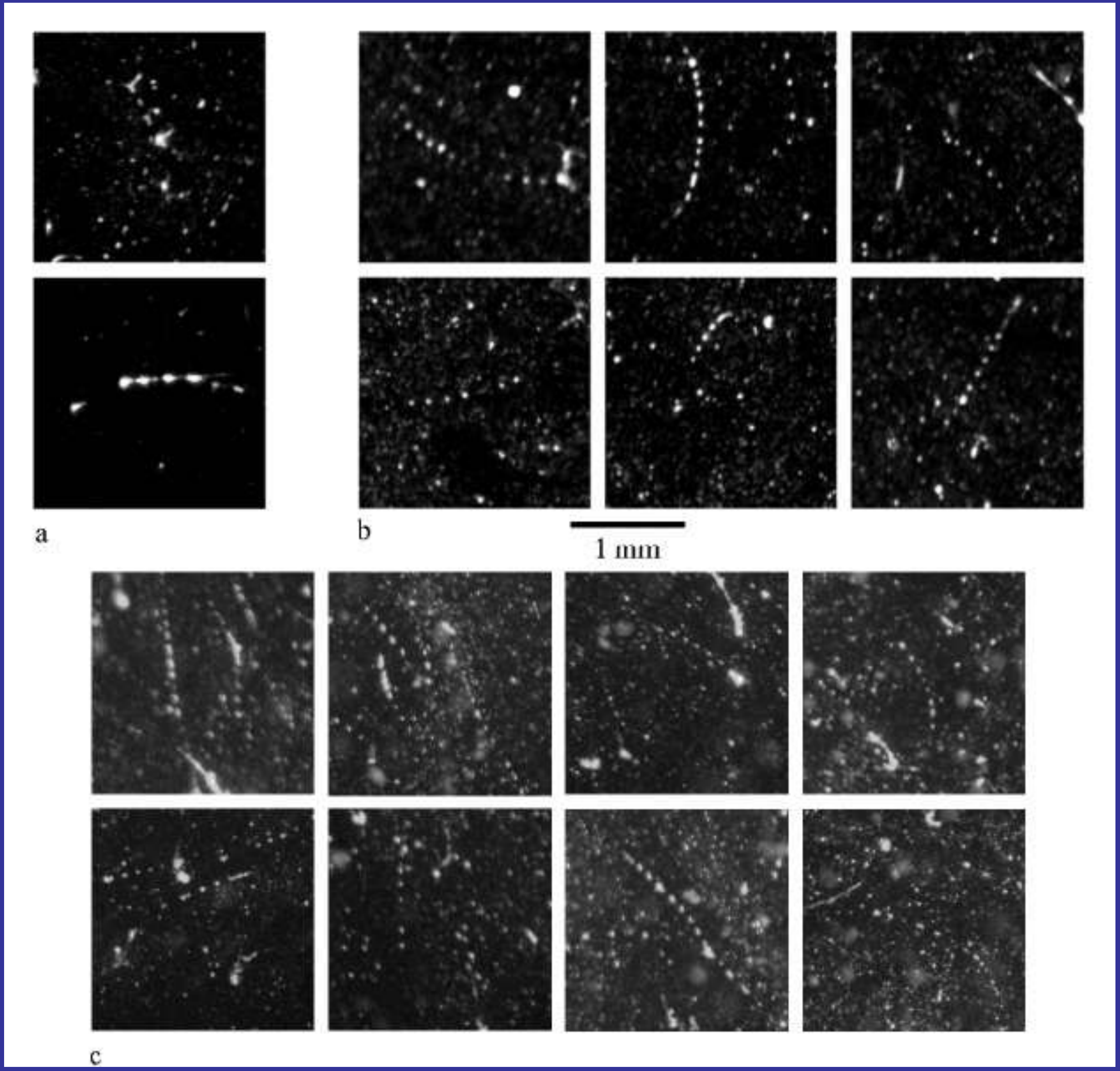


OM: Sediment just beneath the target

A lot of large (2 μm) metallic balls united to the beads –

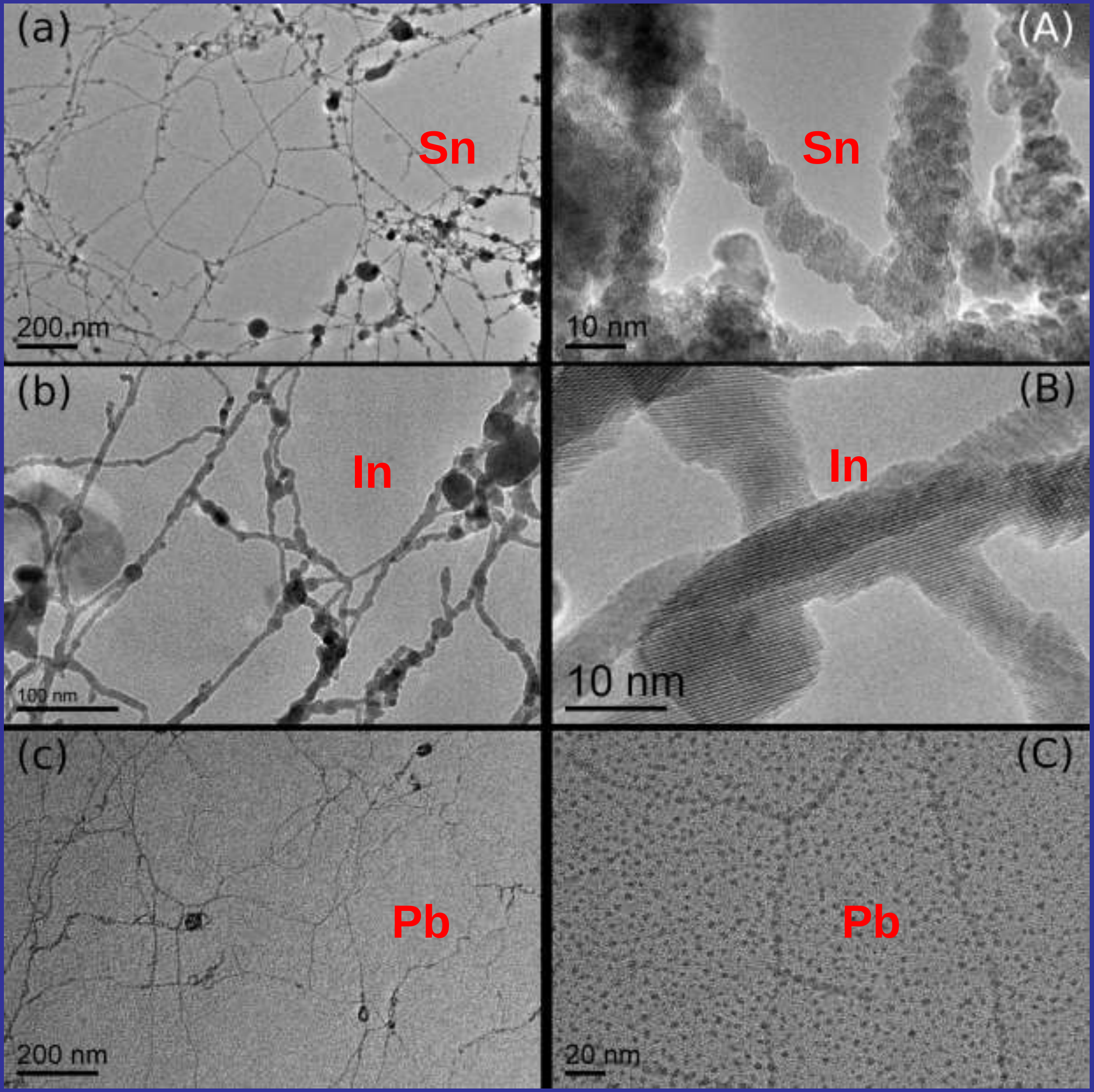
possibly due to mutual repulsion as hydrogen large grains

Bewley thesis: dotted lines



The hydrogen micron–sized grains in a vortex core seemed to repulse each other

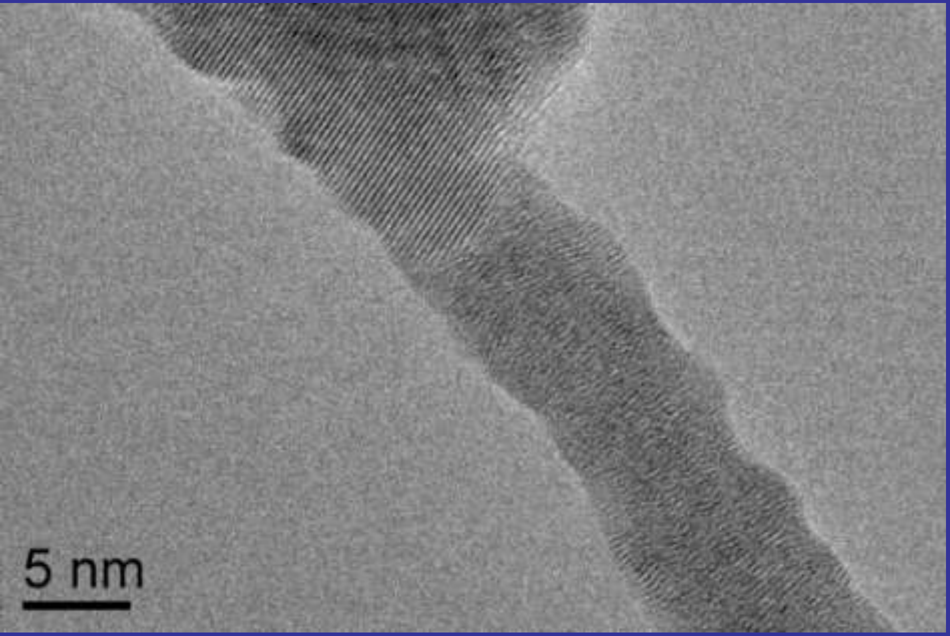
Nanowire bundles morphology and structure

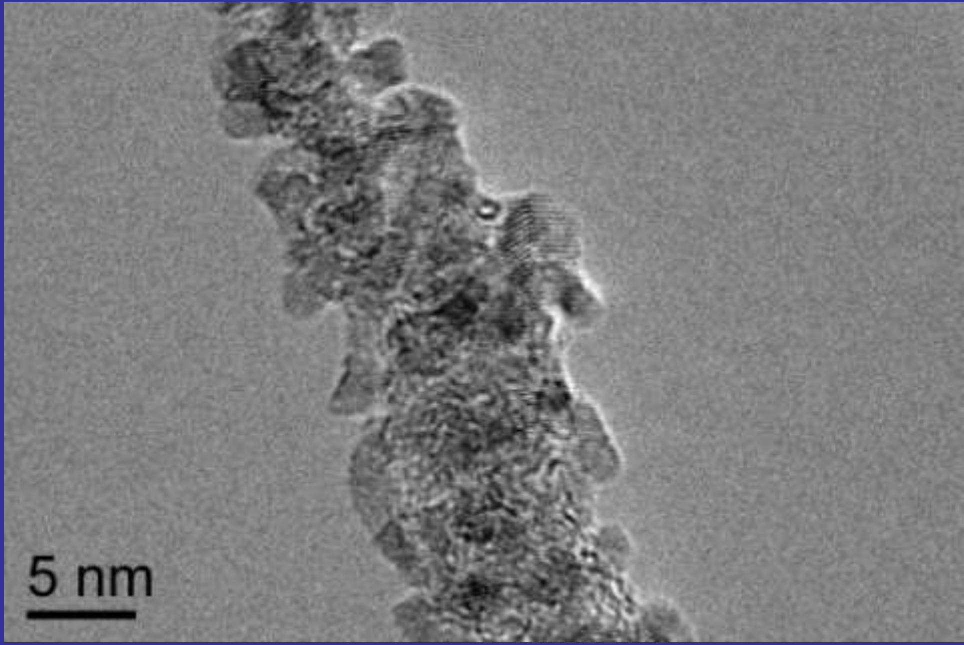


TEM images of fragments of nanowire bundles.

Nanowires of different metals display different structures: tin nanowires composed of sticked together polycrystals with crystallite sizes of 2 nm (A), indium wire are fused to each other monocrystals (B), lead nanowires unfortunately rapidly oxidized on air and only traces of consisting of oxide nanowires seen in the electron microscope (C).

Nanowire structure





Indium

Permalloy

NANO LETTERS

2009
Vol. 9, No. 4
1307-1314

Platinum Nanowires Produced by Electrospinning

Jianglan Shui and James C. M. Li*

Materials Science Program, Department of Mechanical Engineering, University of Rochester, Rochester, New York 14627

Receivec

ABSTRACT

A method of making long (cm) Pt nanowires of a few nanometers diameter from electrospinning is described. A major problem of avoiding bead formation along the nanofibers is analyzed, and the conditions under which the bead formation is minimized are investigated. Our ultimate purpose is to make free-standing fuel cell electrodes from these nanowires.

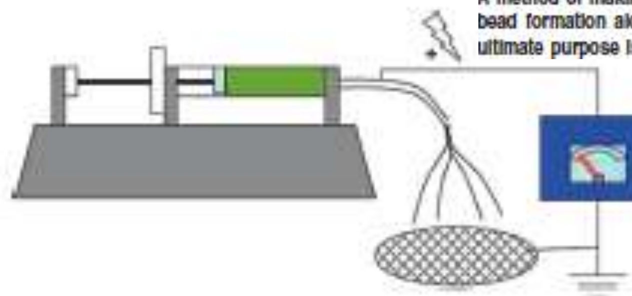
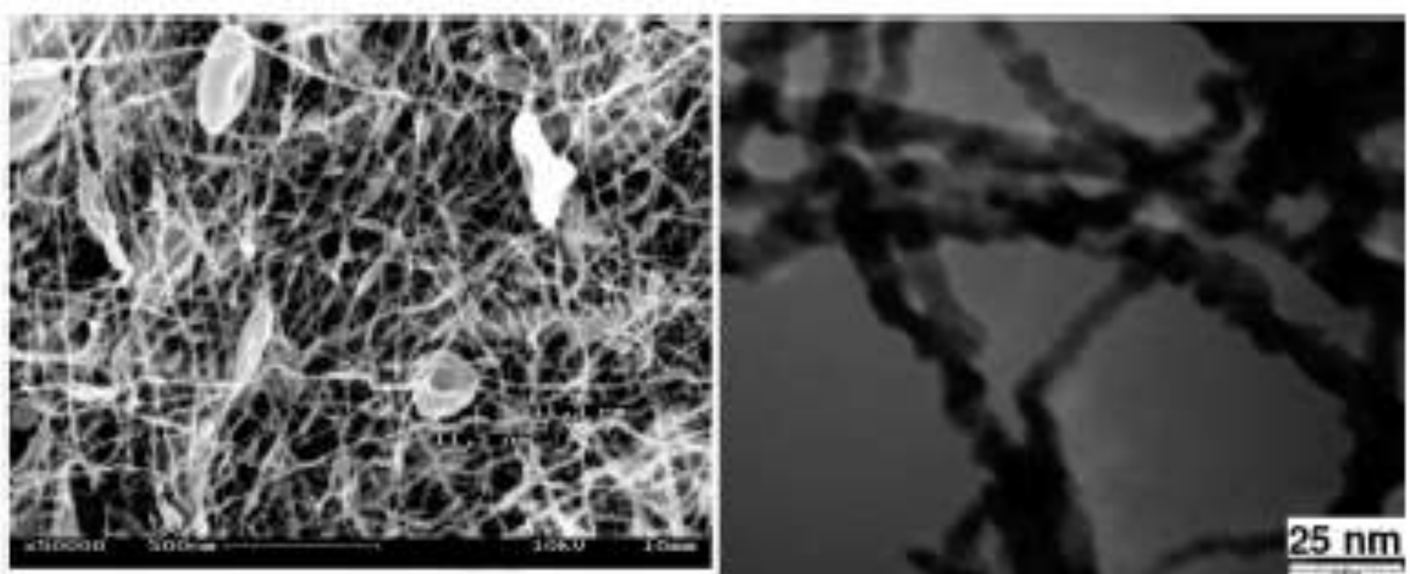
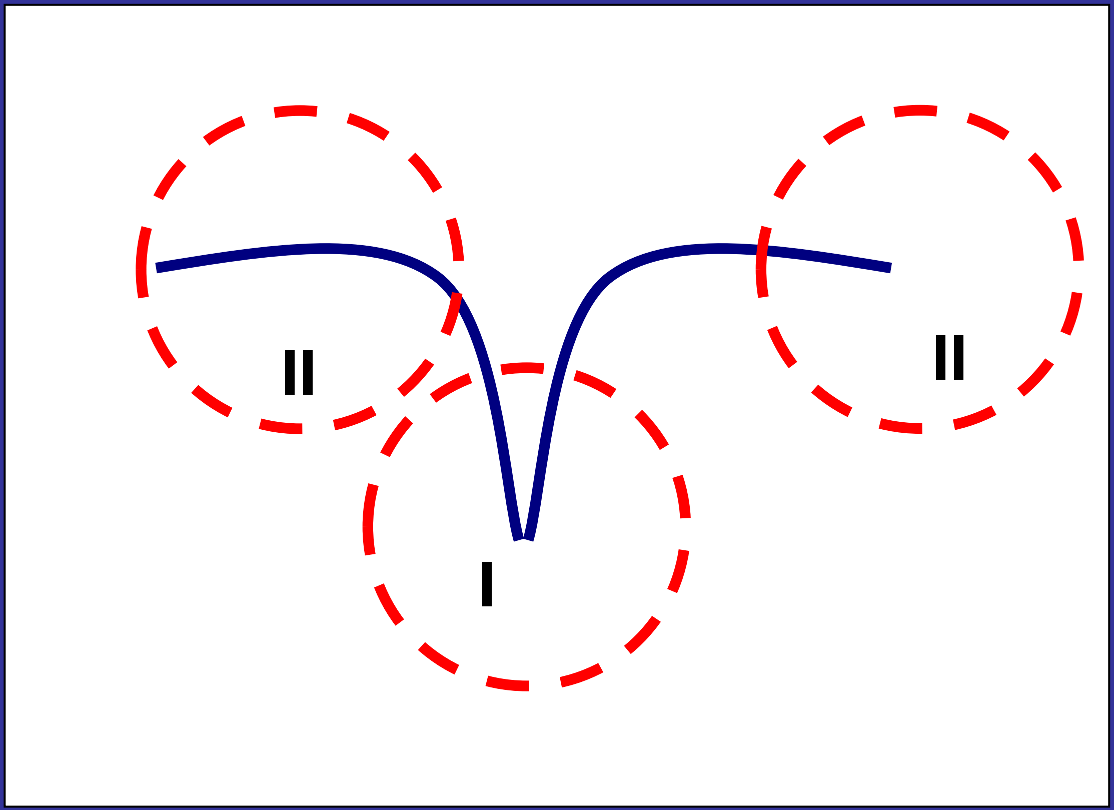


Figure 2. The setup of electrospinning used in our laboratory.



К вычислению скорости коалесценции
The vortex has a potential but there is no attractive force to it – too steep slope



Two states – one in a vortex core,

the other is in the rest volume of liquid

The pinning impurity to a vortex proceeds only at their meeting (sweeping)

Механизм конденсации металлов в сверхтекучем гелии

1. В вихрях образуются шарики радиусом несколько *нм.*
2. При малых концентрациях взвешенного в HeII металла они сталкиваются в вихрях холодными образуя нанопроволоки.
3. Лимитирующей стадией является захват атомов в вихри

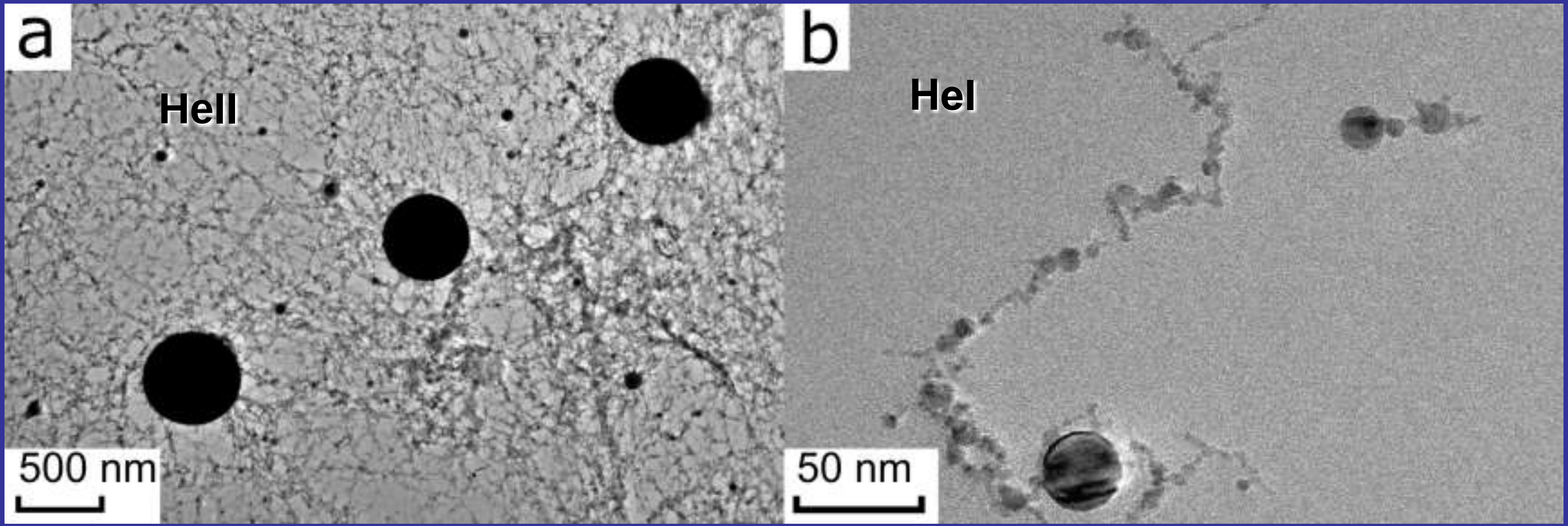
$$\frac{dn}{dt} = -\delta v N_V n = \frac{1}{\tau} n,$$

δ – диаметр вихря, v - его скорость, N_V – плотность вихрей на см^2.
Типичные значения δ = 0.2 nm, $v = 10^2$ cm/sec и $N_V = 10^5$ cm^{-2}

4. При больших концентрациях (слишком мощный лазер) частицы сталкиваются горячими образуя шары большего диаметра.
5. Шары растут до тех пор, пока не начинают взаимно отталкиваться в вихрях (получаются бусы).

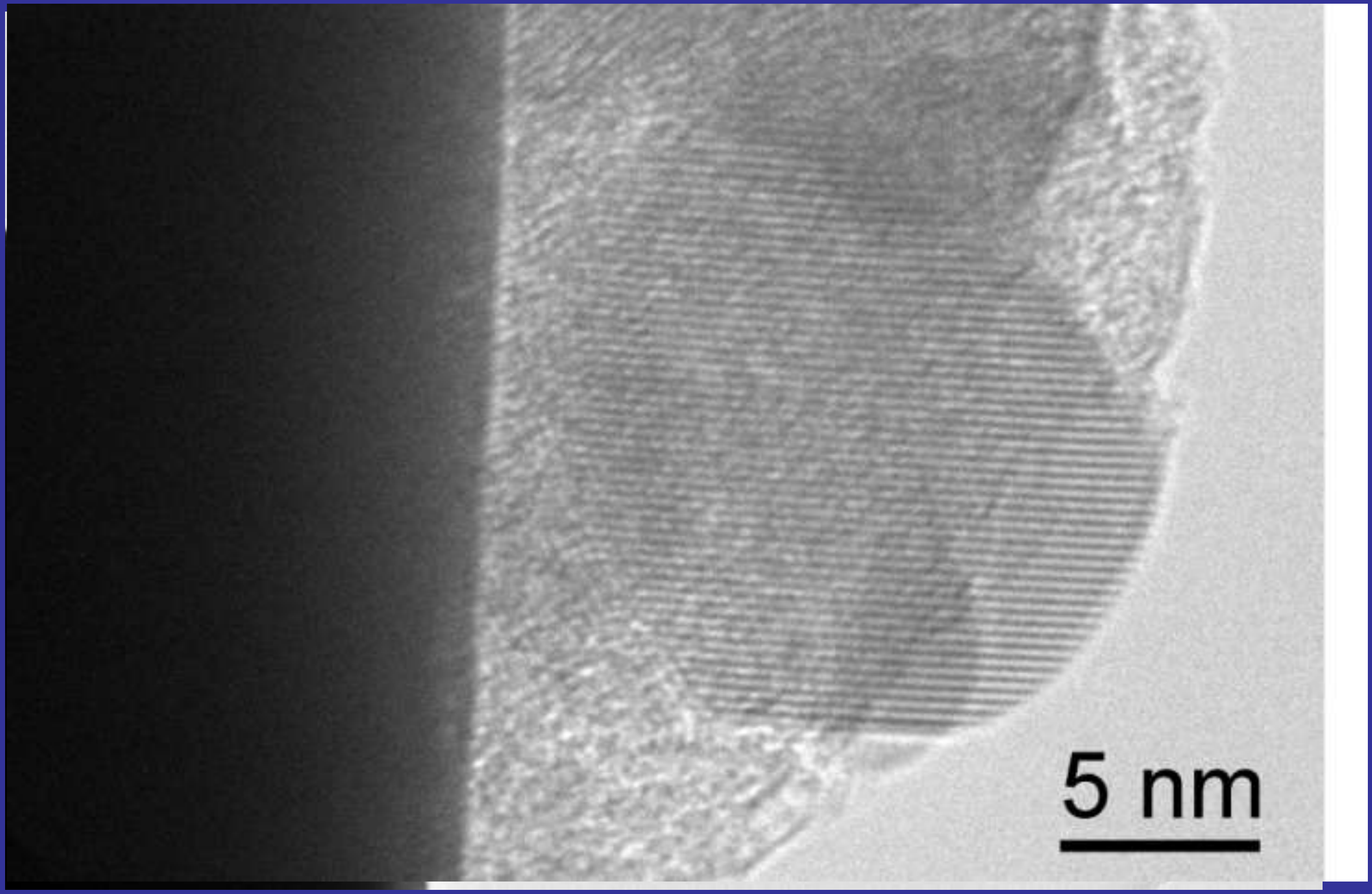
Сравнение конденсации в сверхтекучем (квантованные вихри) и нормальном гелии (обычные вихри)

Индий



В нормальном гелии (b) доза облучения лазером в 2.5 раза выше – проволочек меньше и они зигзагообразные

The metallic balls are ideal spheres



The unambiguous conclusion:
both wires and balls are formed through
molten state

In superfluid helium !!!

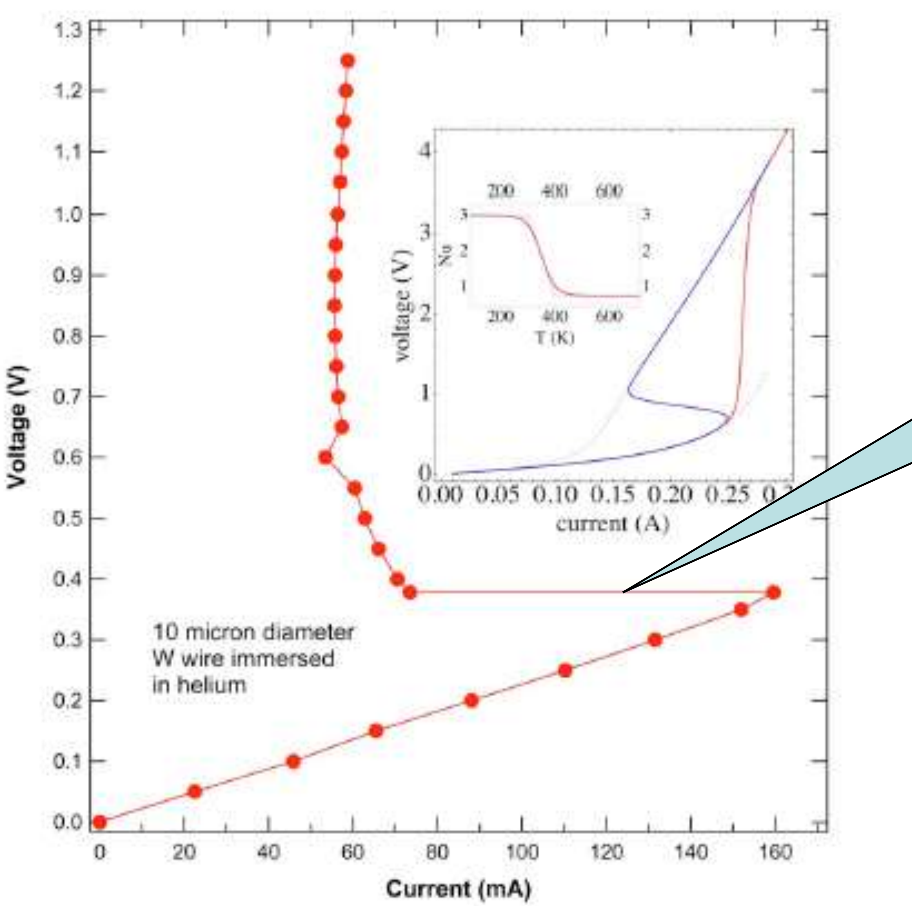
HeII “possesses thermal conductivity 200 times higher than Copper”

But for very weak heat flow – less than **10 W /cm²;**

We should remove more than **10^5 W /cm²**

Heating 10 μ tungsten wire in HeII

I.F. Silvera et al Rev. Sci. Instrum. **80**, 043901 (2009)

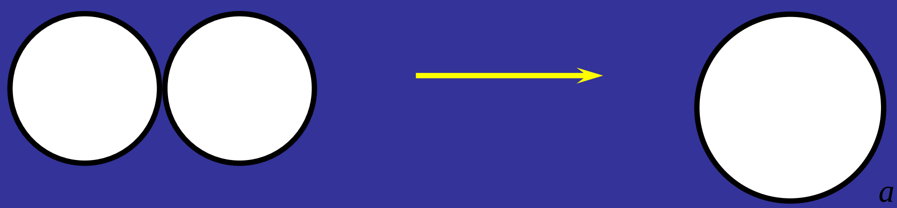


The wire temperature jump from 1.5 K to 1200 K took place at electrical power equivalent to 10 W/cm^2

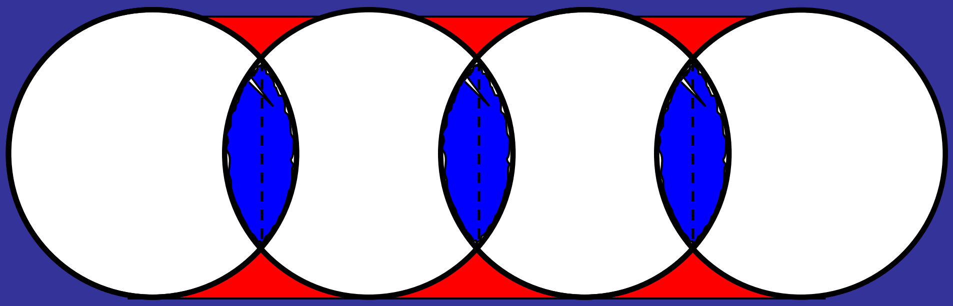
“above a certain current a vapor sheath formed around the filament, insulating it from the liquid and it would glow at temperatures up to a few thousand kelvin”

In adiabatic conditions small cold metallic clusters are known to melt at merging

Simple model for estimating limiting radius of liquid ball and wire



a – **one-layer thickness**



$$R \le R_s^{\max} \equiv 0.78\alpha a$$

$$\boxed{\alpha \equiv Q_b / (CT_m + Q_m)}$$

$$R \le R_w^{\max} \equiv \alpha a$$

Limiting sizes for premelting spheres, R_s, and wires ,R_w

	α	R_s^{max}, nm	R_w^{max}, nm
In	7.66	1.8	2.3
Ni	3.05	0.7	0.9
Sn	7.12	1.6	2.1
Pb	4.34	1.0	1.3
Cu	3.28	0.78	1.0
Au	3.49	0.78	1.0
W	3.18	0.74	0.95
H_2	0.87	-	-
H_2O	0.77	-	-

In accordance with experimental results the radius of nanowire for casting metals is more than for refractory metals.

In hydrogen and water α <1 and melting is impossible.

How large atomically smooth metallic balls can be grown in HeII?

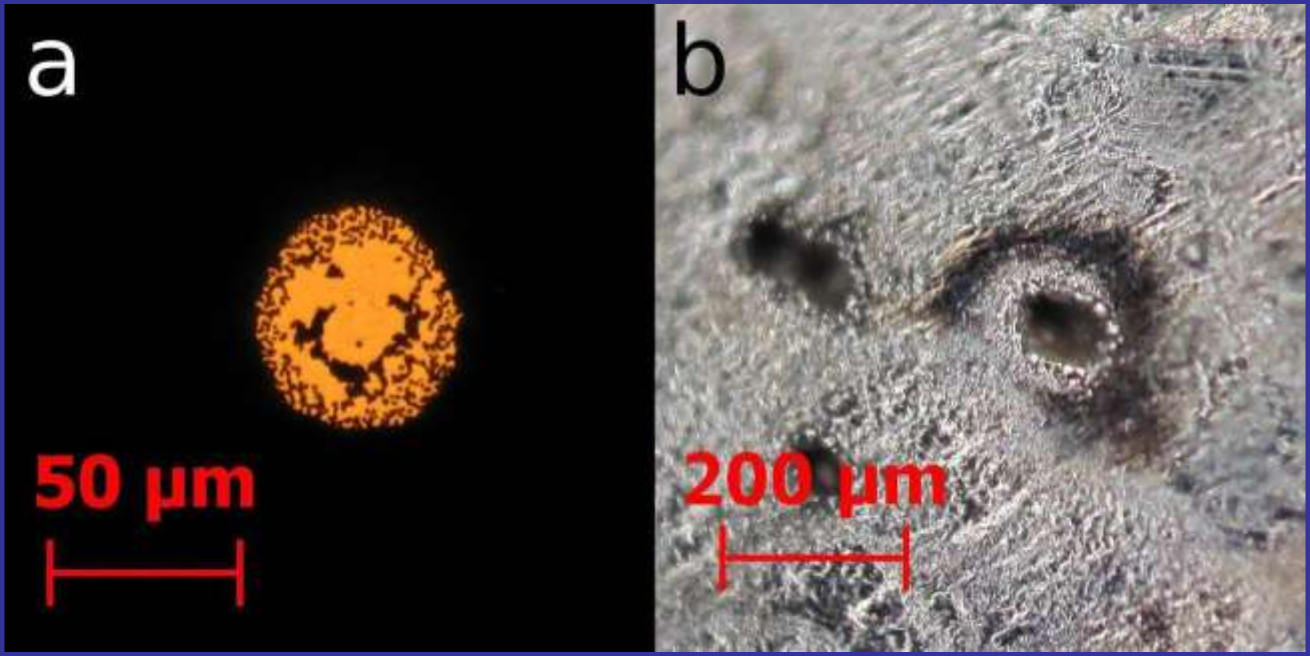
- At slow ablation rates the partners were cold. At high ablation intensities they have no time between collisions to cool down. The restrictions for size becomes softer and then disappear.

- For metals, in contrast with hydrogen, rare gases, water and most organics, the saturated vapor pressure at melting temperature is negligible and the powerful mechanism of cooling by evaporation is absent.

- The upper limit is the spheres mutual repulsion in quantized vortices. The spheres up to few μm size were grown.

Peculiarity of laser ablation of a metal into liquid helium

1. Too high density of metal in liquid → no time for cooling
2. To diminish the laser energy saving the power sufficient for overcoming ablation threshold we used thin metallic film on heat saving glass



The failure probably connected with specificity ablating into LHe:

A – for 200 nm thick Indium film – only melting and no ablation

whereas

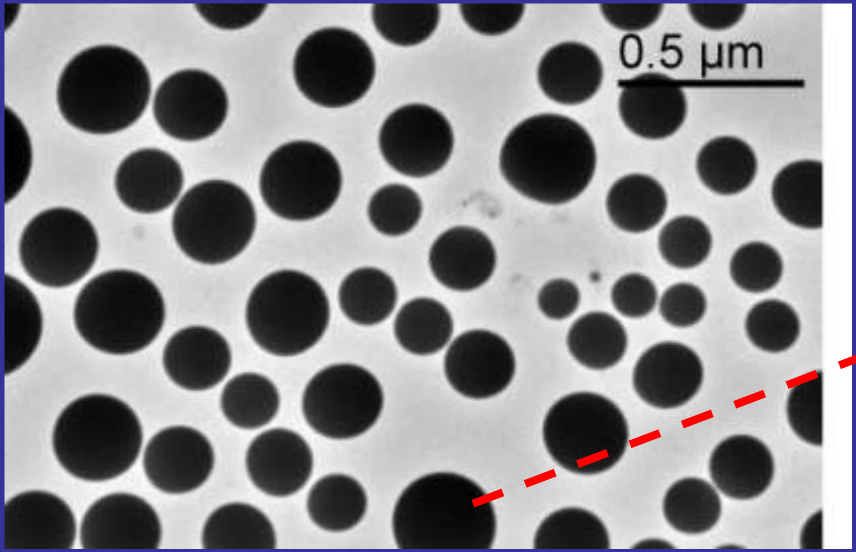
B – for 1 mm foil – intensive ablation from the crater formed

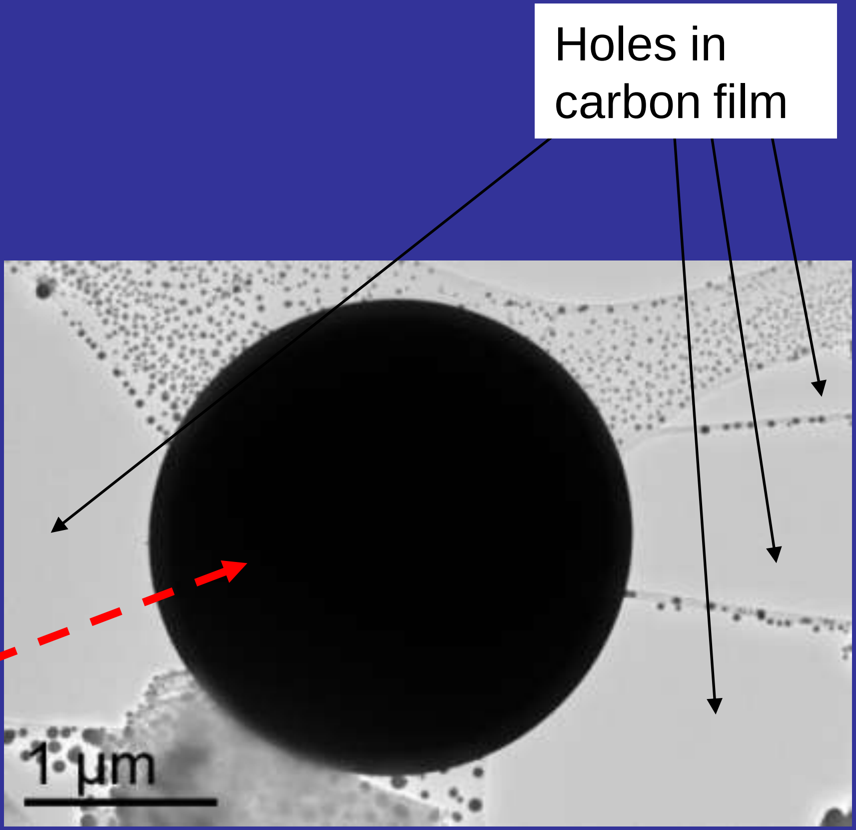
Сейчас начаты эксперименты с 400 псек лазером

This interpretation found its support in very interesting observation

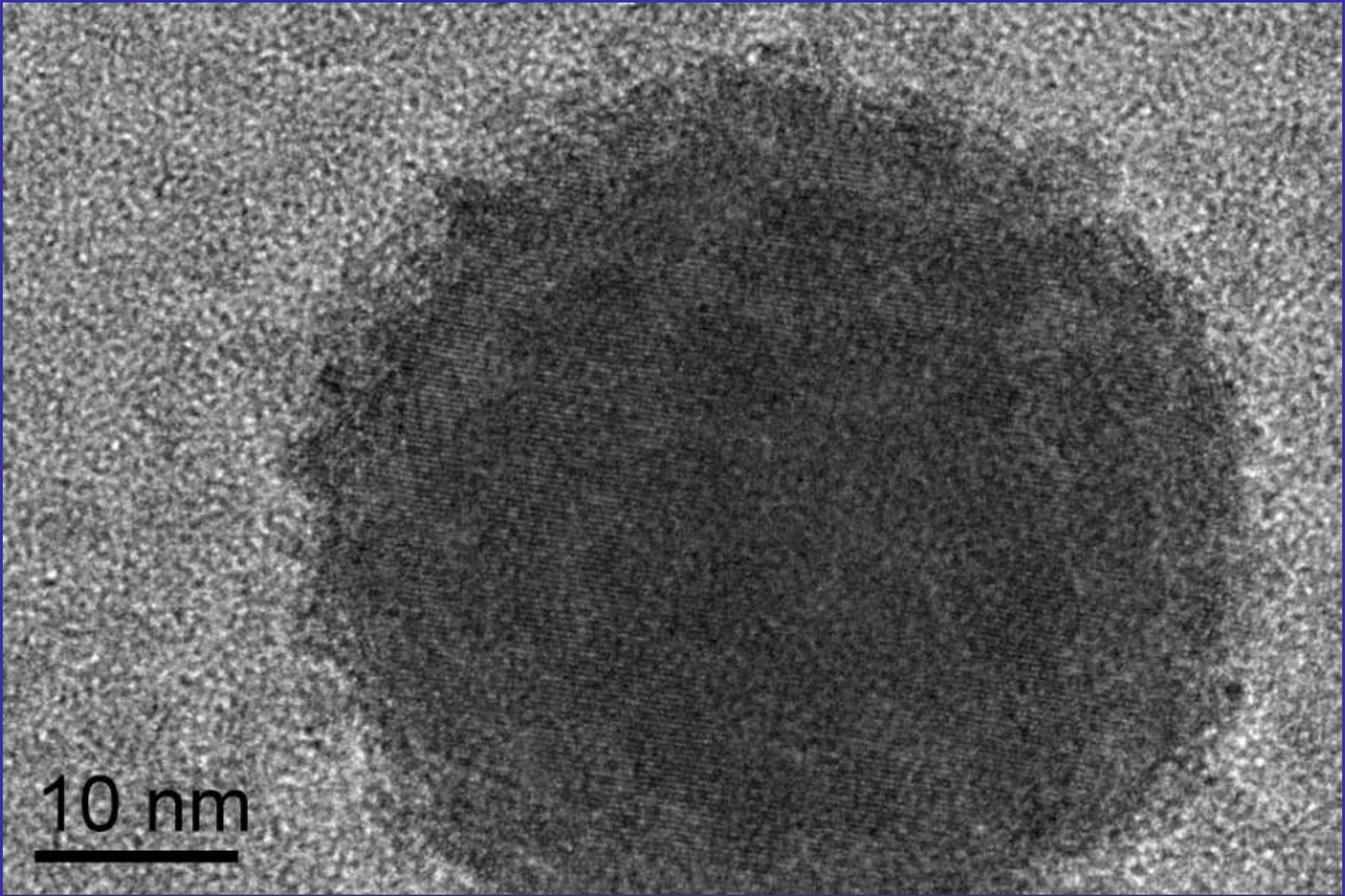
Sometime in TEM microscope (vacuum + T=300K) the ball exploded in a second after focusing electron beam on it. The negligibility of e-beam energy (ΔT_{av}= 0.2 K) was in a favor of its triggering action

Exploding ball outthrows the hundreds of small spheres



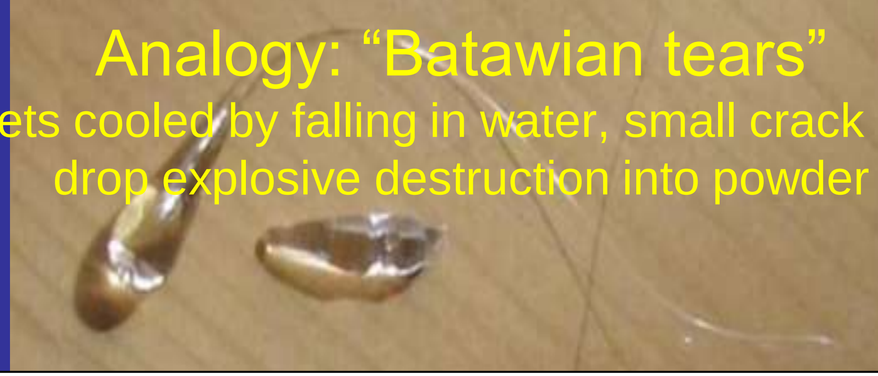


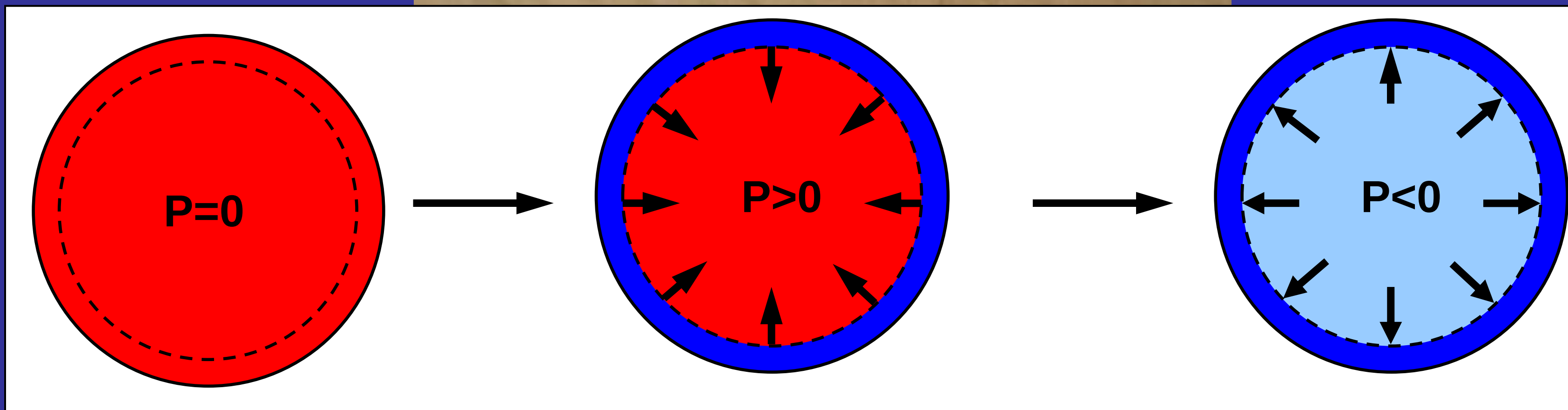
Sometime the nanoballs are definitely composed from crystals of 6 nm in diameter , interference fringes are seen



Analogy: “Batawian tears”

Glass liquid droplets cooled by falling in water, small crack led to the hardened drop explosive destruction into powder





Liquid hot drop size is higher then that of cold solid one

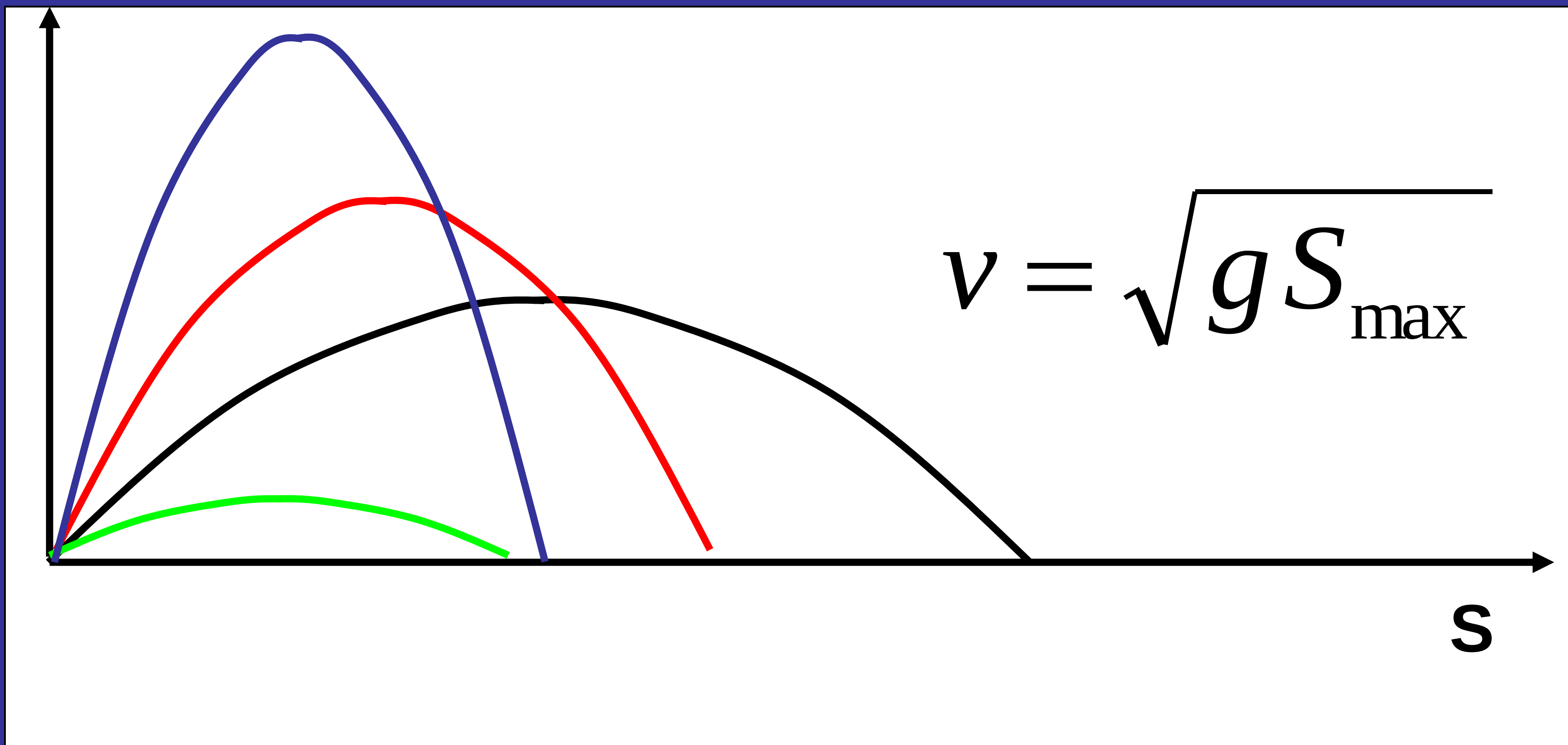
Fast cooling causes solid shell formation, which squeezed the liquid core

Further cooling leads to formatting solid core occupied the volume more then equilibrium one

The absence of dislocations and voids in micron-sized balls converts tensile metals, like indium,

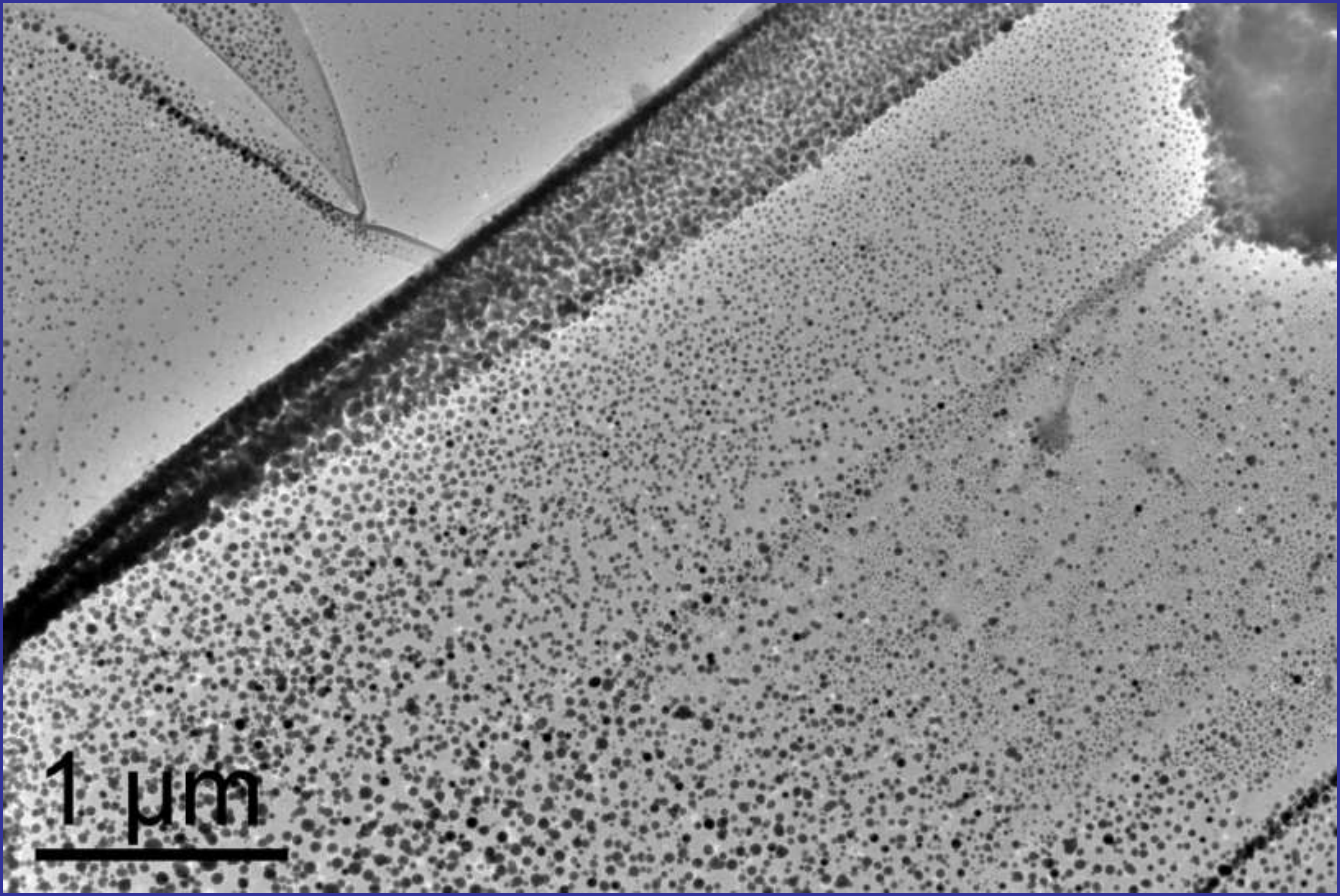
into hard elastic material as a glass

Common Batawian tears don’t explode but fall to pieces, what about our nanoballs?

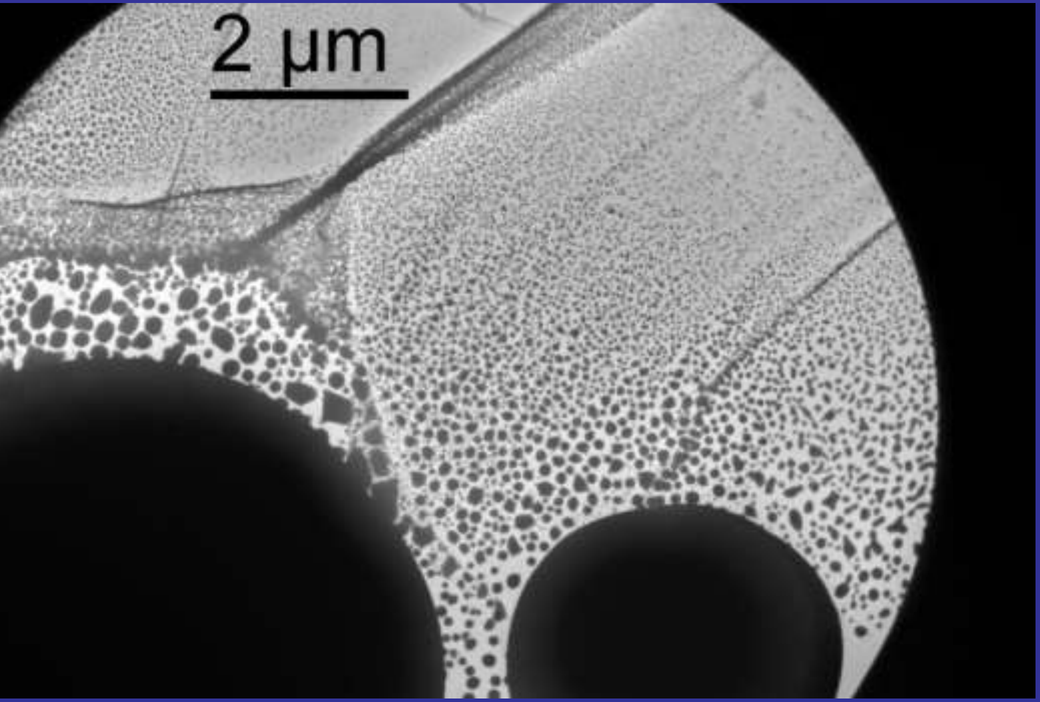


Indium ball in three months after producing

(sedimentation near ridge, low trajectories)



Wrinkled mesh makes it possible to estimate (due to shadow width) the initial velocity of secondary nanoballs



$$V_0 = \left(\frac{gls}{2h} \left(1 + \left(\frac{h(l+s)}{ls} \right)^2 \right) \right)^{1/2}$$

g - gravitational acceleration**,**

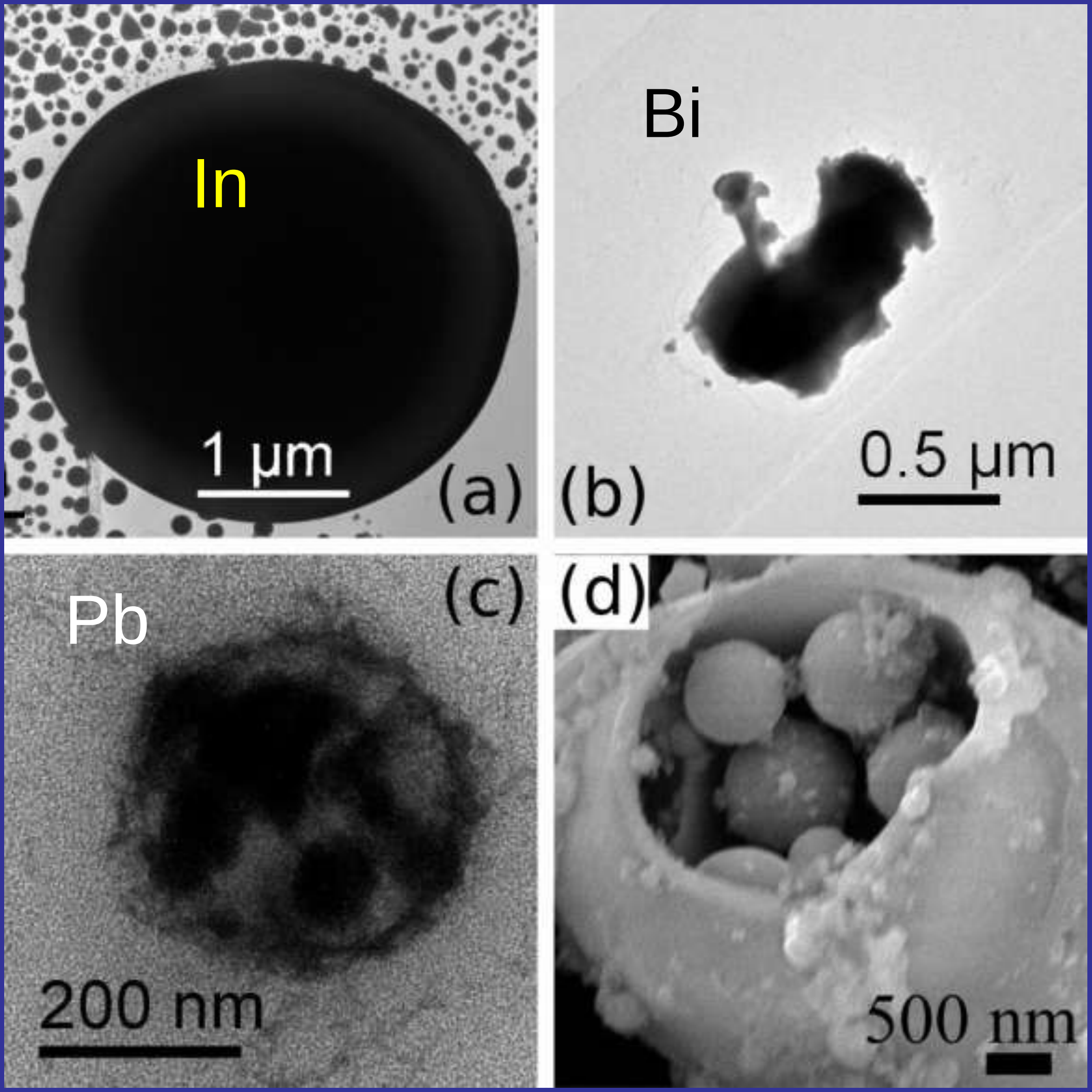
s - the distance between the wrinkle edge and the end of the shadow,

h - the height of the wrinkle,

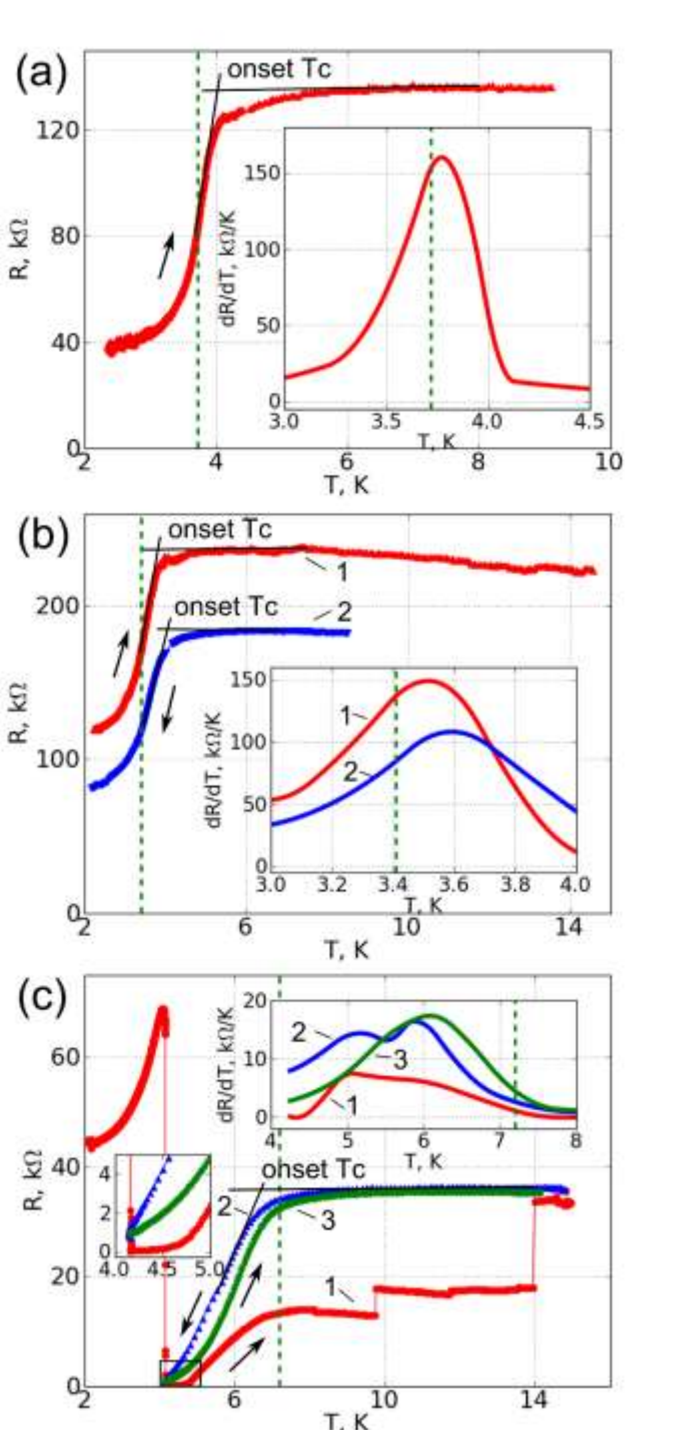
l - the distance between ball center and the wrinkle edge.

The estimate gives $V_0 \approx 3$ cm/s (!!!), corresponding to T =10^{-2} K, and suggests that, as for Prince Rupert's Drops, almost all stored elastic energy is expended the formation of new surface.

The distortion of the balls after "explosion"



TEM images of empty shells of decayed metal spheres. (a) - indium, (b) - bismuth, (c) -lead and (d) – taken from [17], the SEM photo of "hollow structure", made by laser ablation to water shown for comparison



The transition to superconducting state for the bundles of nanowires of tin (a), indium (b) and lead (c).

The "conductor-superconductor" transition in nanowire is always broadens;

onsetT_c in nanowires can be as below T_c in a bulk - (worsen superconductivity), as above it - (improving superconductivity),

but

the temperature of loss of resistance (that is necessary for applications)

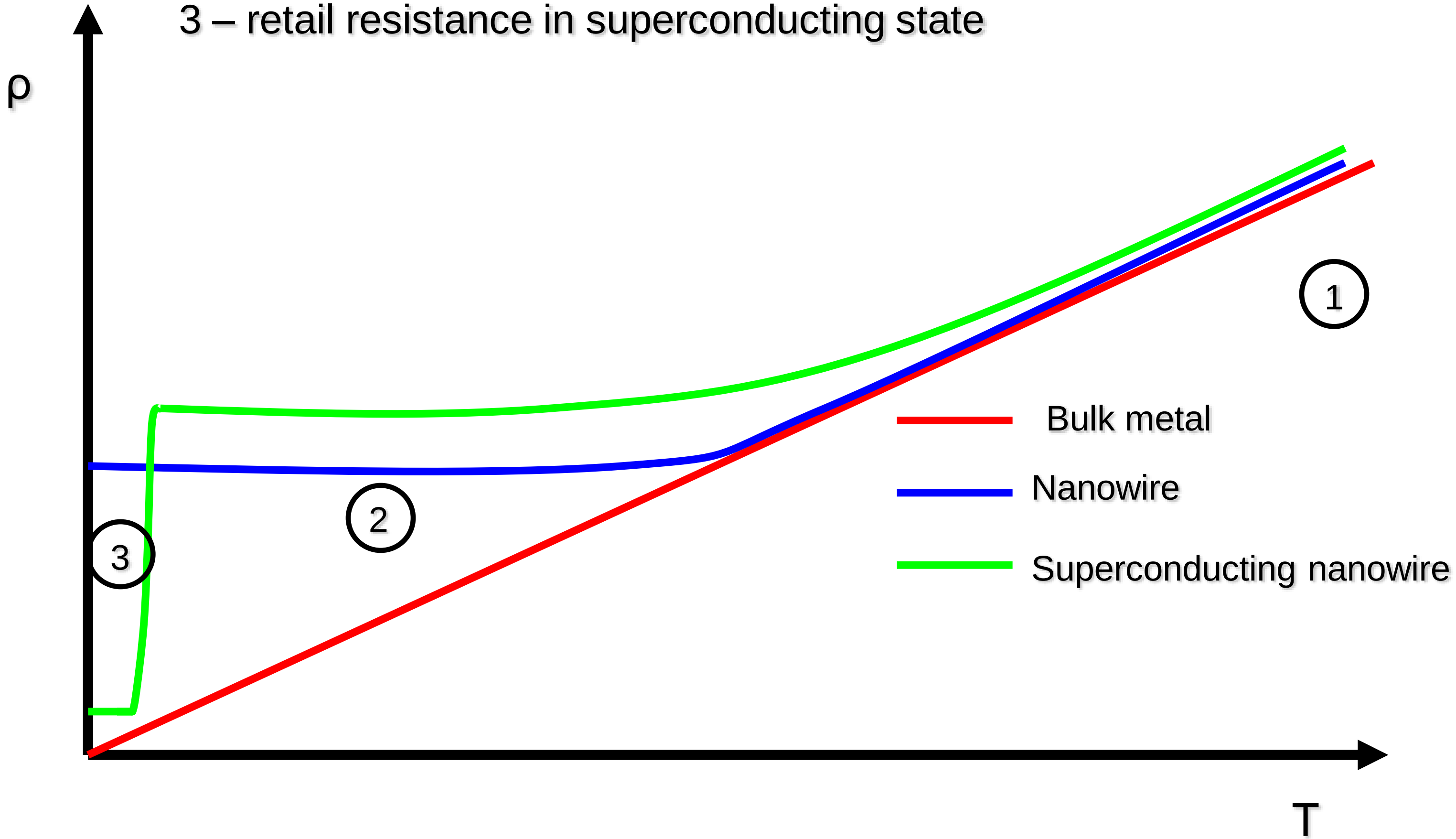
always falls down

Metal resistance *vs temperature*

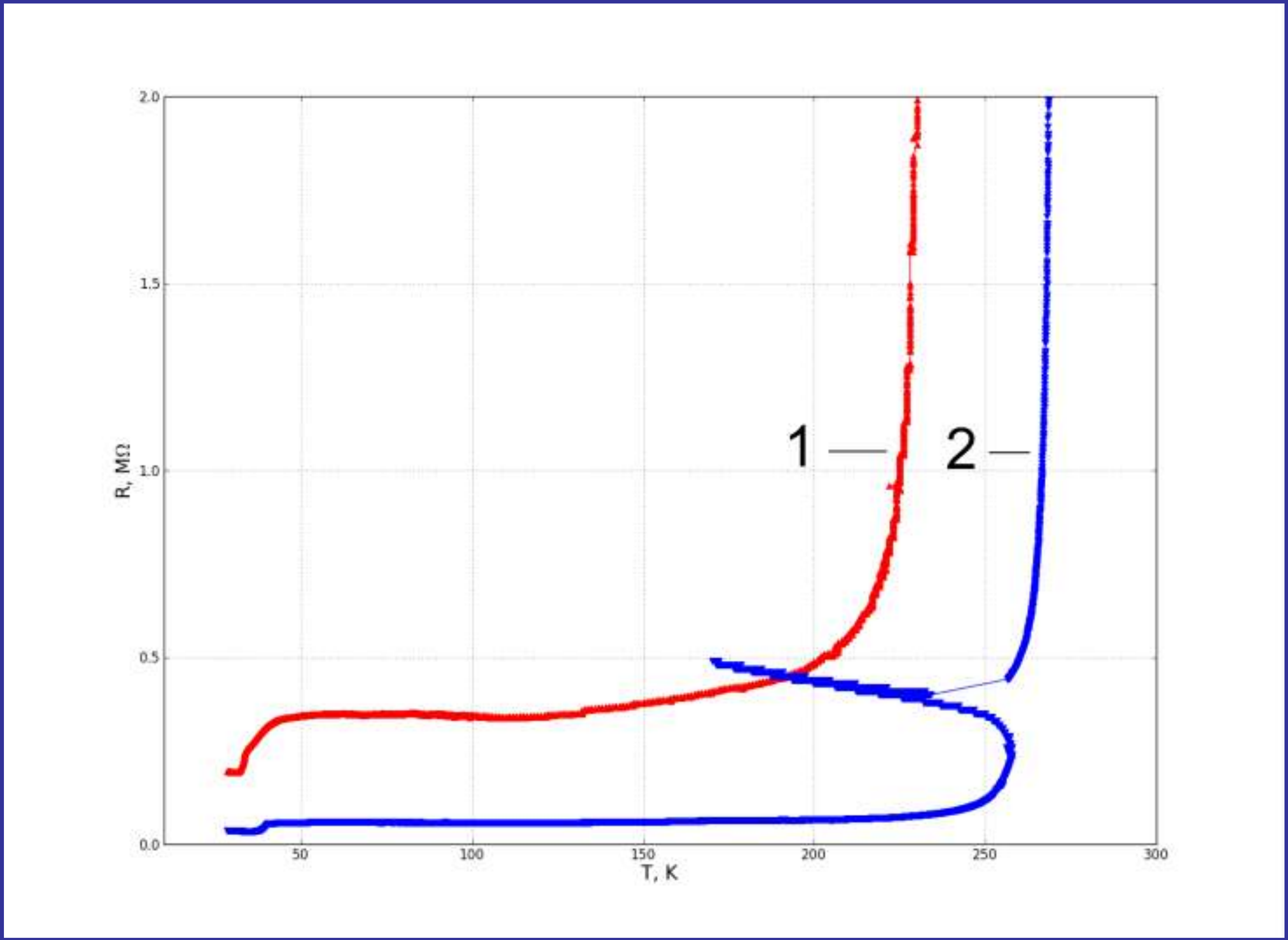
1 – electron scattering on phonons

2 – electron scattering on surface

3 – retail resistance in superconducting state



Tin nanowire bundle resistance *vs* temperature at high T

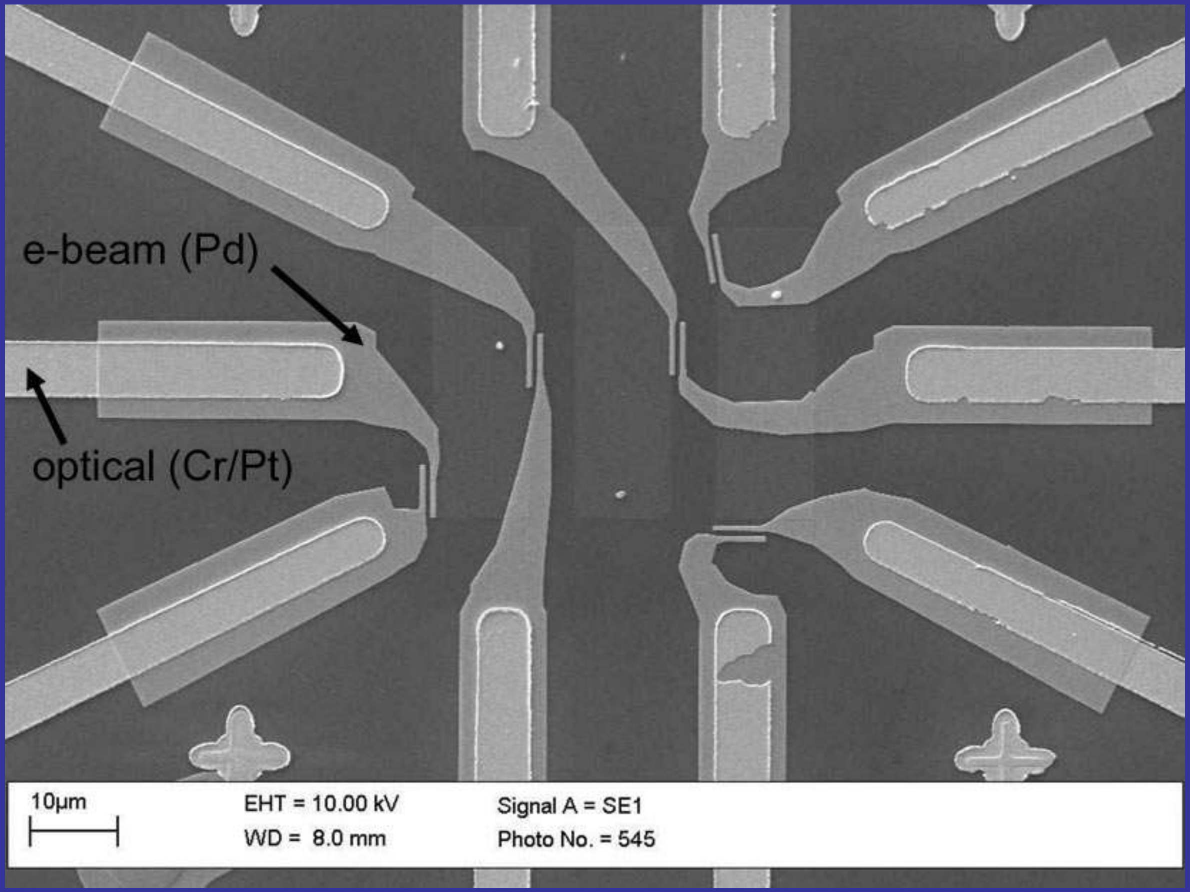


1 - R value reproducibly shows jump at T= 40K and exponential growth at T> 220K.

2 – R behavior in the case when the bundle was slowly cool down from T = 260 K to T = 170K and then slowly warm up (mystery!)

IPTM technique for separate nanowire study

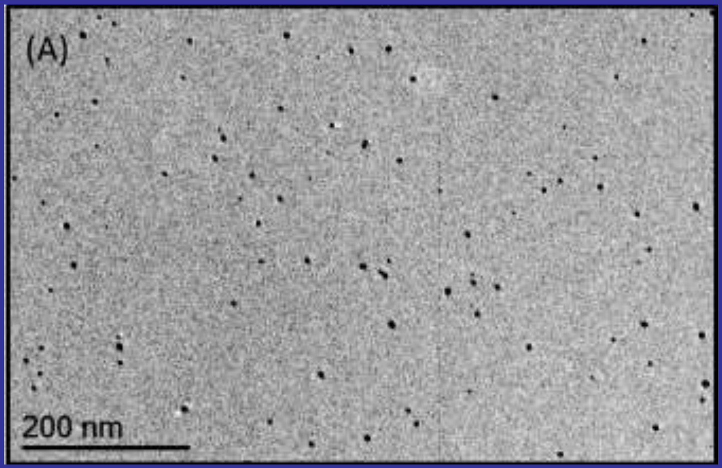
(SEM image of an area of a silicon chip with metal contact pads)

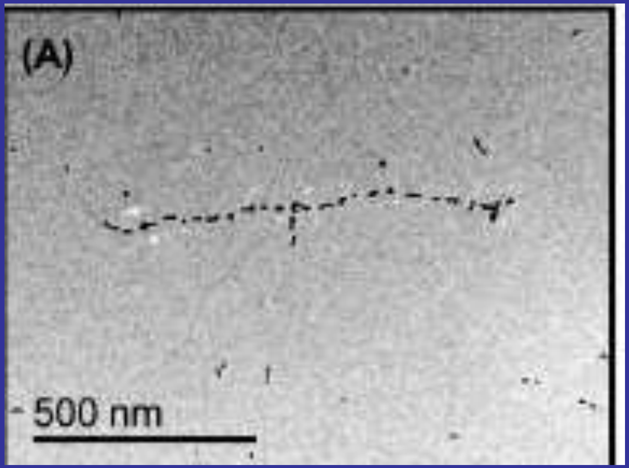


The massive contact pads made of *3 nm Cr/90nm Pt* bilayer were created on the surface of silicon chip by using photolithography method. Then the pairs of Pd electrodes with thickness of 50 nm ending by strips of 5 × 0.5 μm^2 area were made by using electron beam lithography. Electrodes were created just in places where nanowire lies.

Traces of Vortices in Superfluid Helium Droplets

L.F. Gomez, E. Loginov and A.F. Vilesov, Phys.Rev.Lett. 108, 155302 (2012)





Droplet diameter < 300nm

Droplet diameter > 300nm

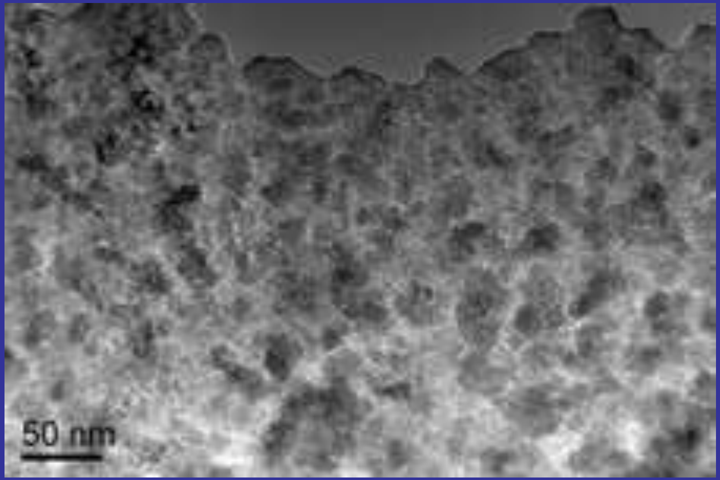
Silver atoms trapped in the superfluid ^{4}He droplets larger than 300 nm aggregated into elongated beads, whereas only spheres were observed for the smaller droplets. This fact was subscribed to appearance of quantized vortices in large droplets, the vortex formation is known to be impossible in small drops.

- Cold clusters of carbon, silicon and many other materials can not melt under fusion from thermodynamic considerations, therefore, they could not form a ball.

- For such materials the nanowires should be very thin, down to atomic chains and they aligned along the core of a quantized vortex. We still can not see them.

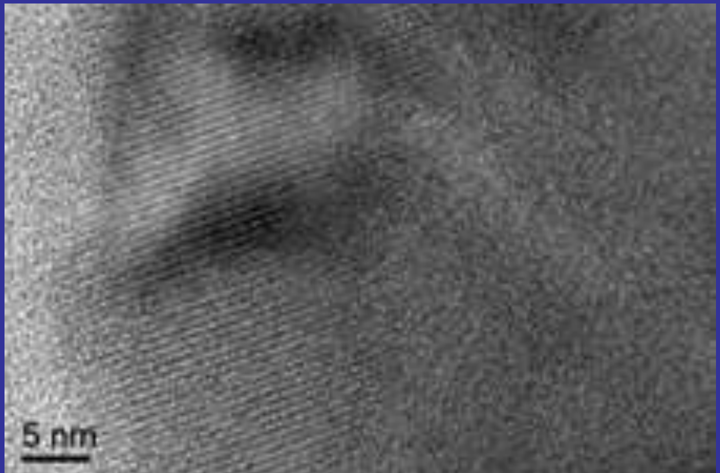
- However, provided the concentration of vaporized material, when condensation is involved neostyvshie clusters stock heat may be enough for melting, and in this case, should form the shape of the clusters are nearly spherical (for carbon - diamonds).

The products of polycrystalline graphite ablation



crystallites

Electronogram shows a lattice of partially aligned diamonds



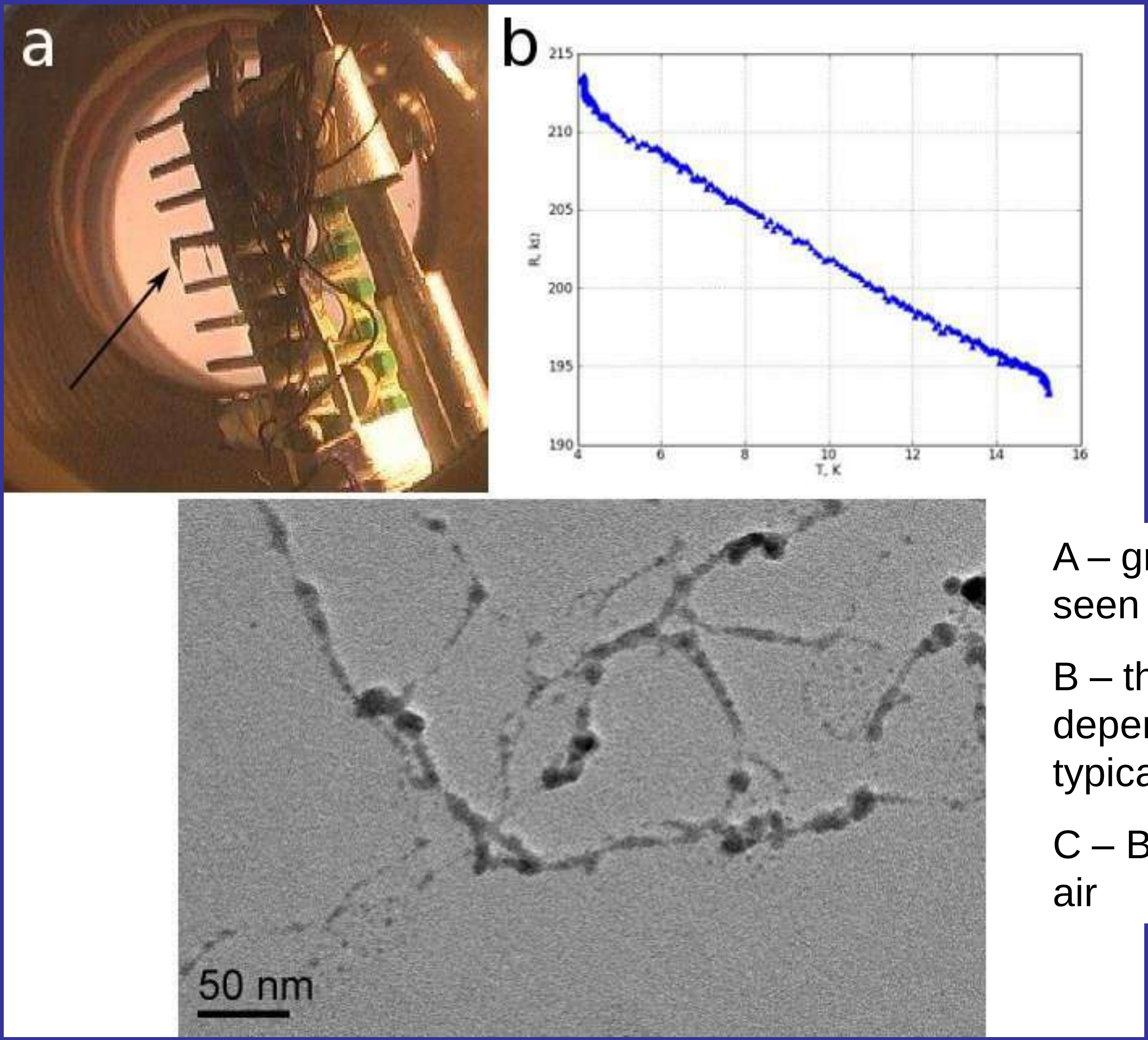
Interference spacing 6.2 A is corresponding to the length of [111] diamond spatial diagonal

Ideas for the “nonmetallic” future:

- The semiconductor deposition on the surface of s superconducting nanowires.

- Using the nanowires made of metals behaved there as semiconductors.

Bismuth behavior



A – growing nanowire bundle seen by eye;

B – the resistance dependence on T being typical for semiconductors;

C – Bi nanowires oxidized on air

The Theoretical Problems

- The calculation of the binding energy between a long chain and quantized vortex in HeII.
- The calculation of the interaction between two beads trapped into quantized vortex - a change of attraction to repulsion.
- What determines the longitudinal velocity of the particles inside the vortex.
- Could the phase transition to the superconducting state in quasi -1D objects be broaden homogeneously.

Conclusion

The role of superfluidity in the process of impurity coagulation in HeII

-is negative in the problem of HEDM creation due to fast active species condensation (via vortices) and large local overheating (by breakdown of heat transfer by second sound), and

- is positive in the problem of nanoscale component creation giving nanowires and nanofilaments as the products of coagulation catalyzing by quantized vortices.

In principle, the nano-objects maybe

- quasi-0D objects or nanoclusters,
- quasi-2D objects or nanofilms, or
- quasi-1D objects or nanowires.

There are universal approaches for the formation of nanoclusters and nanofilms:

(i) limiting the growth of particles from the initial "bricks" in a homogeneous liquid or gas by methods of colloid chemistry,

(ii) by deposition of the "bricks" on interface between the two phases.

In contrast, the growth of any wires in a liquid requires some template, restricting the product growth in transverse directions. The superfluid helium represents a unique media for that.

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Thank you for attention

D. Jin , H.J. Maris. A Study of the Motion of Particles in Superfluid Helium-4 and Interactions with Vortices, J Low Temp Phys (2011) 162: 329–339

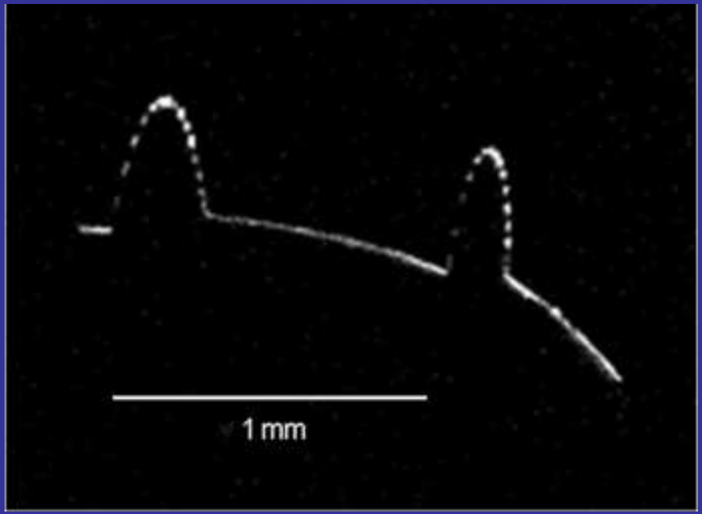
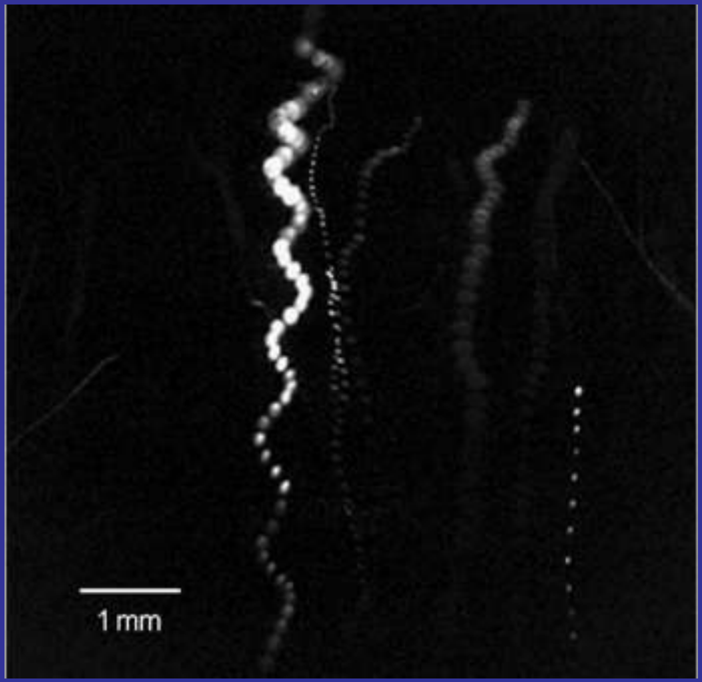


Image showing the motion of a particle moving along a vortex line and subject to impulses provided by sound. The temperature is 2.1 K and the particle is moving from *left* to *right*. The laser illuminating the cell is chopped at a frequency of 600 Hz and the sound repetition rate is 10 Hz

$$V_{\perp} = 2 \text{ см/с}$$



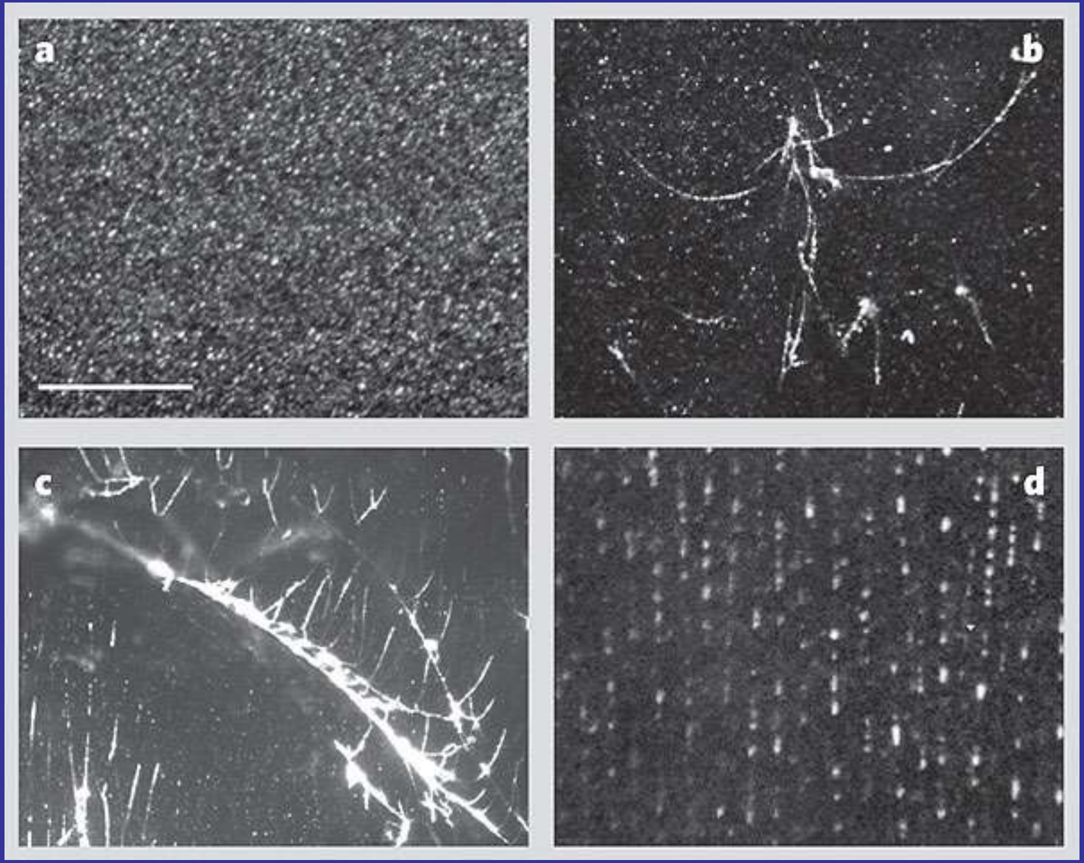
Spiral motion of a particle at 1.34 K. Image was taken with illumination pulsed at 160 Hz

$$V_{\perp} = 3 \text{ см/с}$$

Nature 441, 588 (1 June 2006) | doi:10.1038/441588a

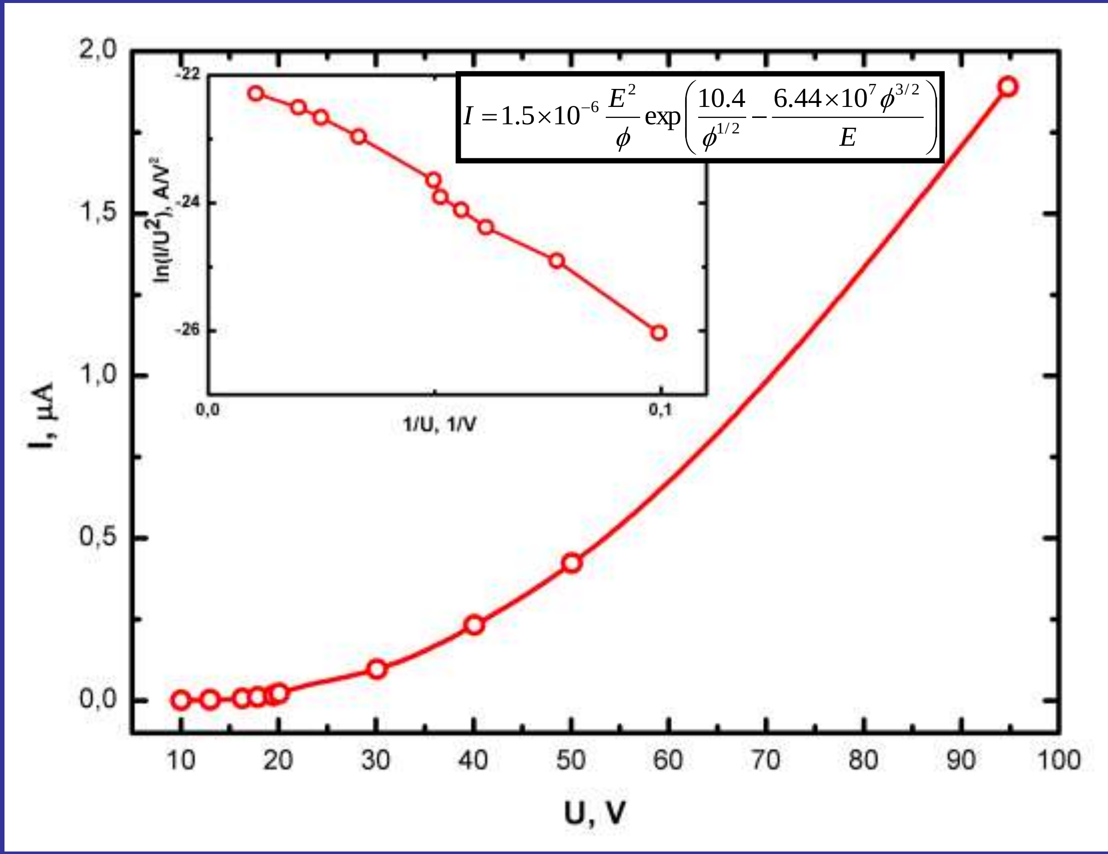
SUPERFLUID HELIUM: Visualization of quantized vortices

Gregory P. Bewley, Daniel P. Lathrop and Katepalli R. Sreenivasan



Quantized vortex cores in liquid helium.
a, just above the transition temperature, when they are uniformly dispersed;
b, c, on branching filaments at tens of millikelvin below the transition temperature; **d,** regrouping along vertical lines for steady rotation about the vertical axis.
In **b** and **c**, the particles on lines are evenly separated in small regions. Scale bar, 1mm.

Magic world of quasi 1D metals



Lead

Field-induced electron emission:

- High efficiency – µA instead of common nA
- low voltage

Large (3 mm) length of nanowire bundle - the prototype of cold cathode

E.B Gordon, A.V. Karabulin, V.I. Matyushenko, V.D. Sizov , I.I. Khodos, FNT, 36 № 7, p. 740 (2010)