how far can one pressurize a liquid before it crystallizes ?

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for references and files, including video sequences,

go to http://www.lps.ens.fr/~balibar/

ULTI III, Lammi, Finland, 7 jan 2004

abstract

an equivalent question:
what is the threshold for homogeneous nucleation
of crystals in a pressurized liquid phase ?

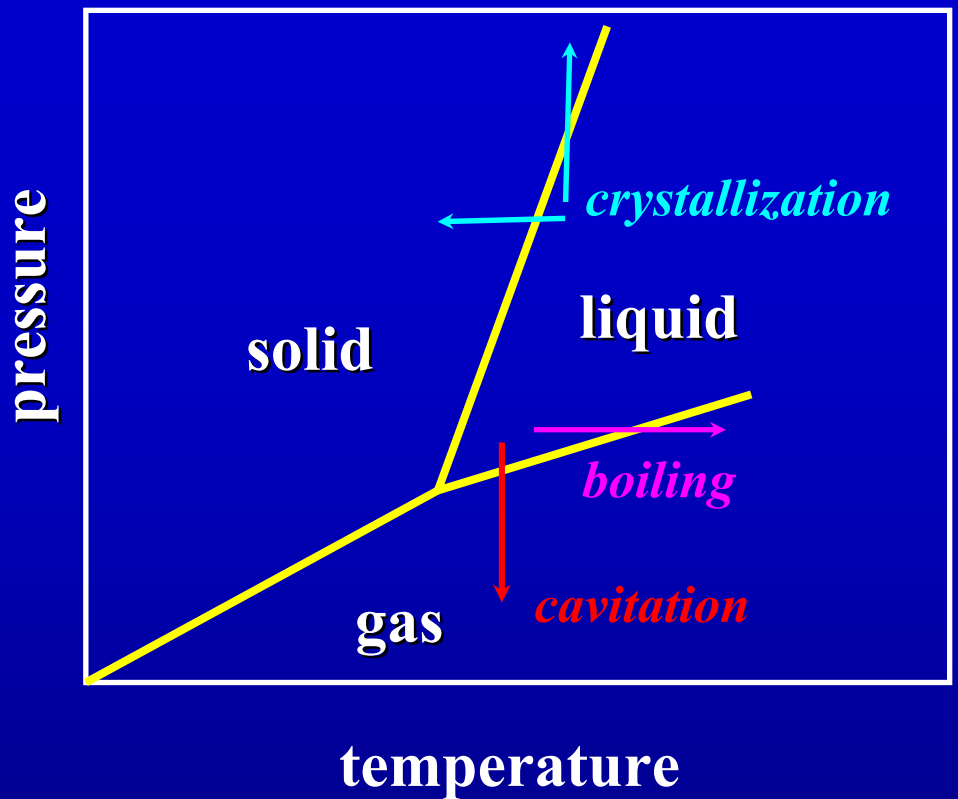
a related question :
how far can one supercool liquid water ? why - 40 °C ?

helium is pure and simple
the surface tension of solid helium is accurately known

eliminate the influence of impurities walls and defects
acoustic techniques: acoustic cavitation and acoustic crystallization

test an intrinsic stability limit of the liquid state of matter
and a few other problems related to superfluidity at high density

metastable liquids



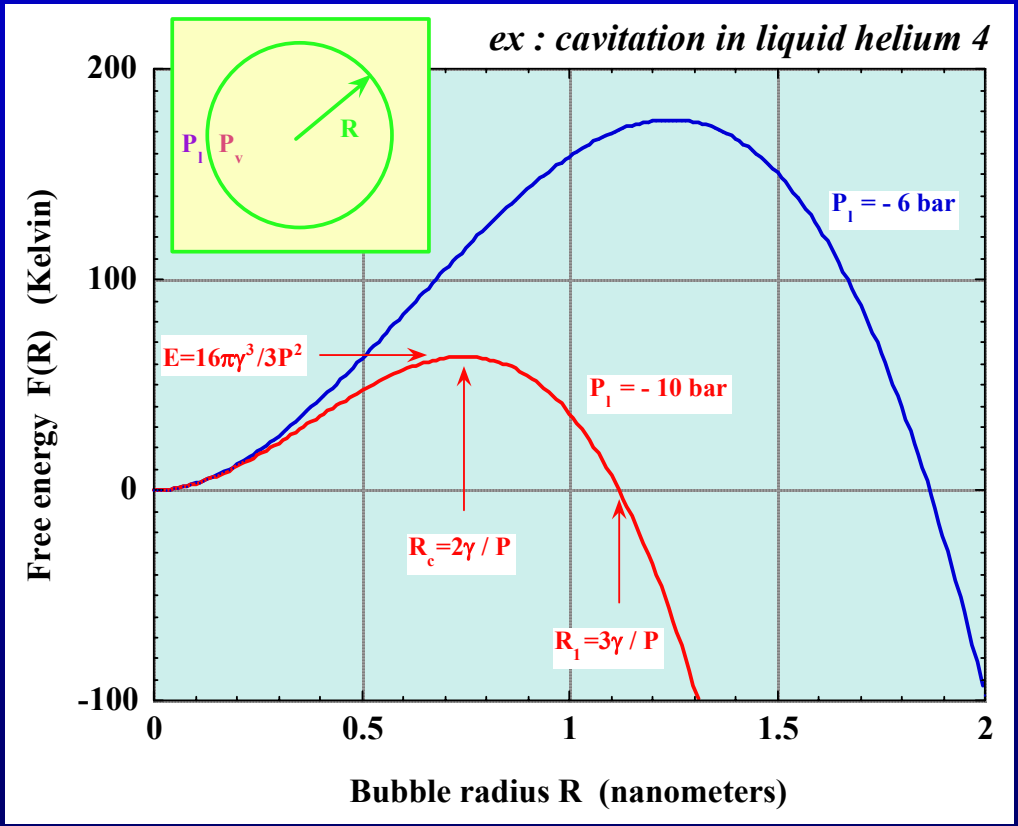
liquid-gas or liquid-solid:
first order phase transitions
⇒ metastability is possible

energy barriers against the nucleation of either the solid or the gas phase

example:
liquid water to - 40 °C or + 200°C at 1 bar, or - 1400 bar at +35 °C

the barrier against nucleation is due to the surface energy

Standard nucleation theory (Landau and Lifshitz, Stat. Phys. p553):



a spherical nucleus with radius R

and surface energy γ (the macroscopic surface tension)

$F(R) = 4\pi R^2 \gamma - 4/3\ \pi R^3 \Delta P$

ΔP : difference in free energy per unit volume between the 2 phases

Critical radius : $R_c = 2\gamma / \Delta P$

Activation energy : $E = (16\pi\gamma^3)/(3\Delta P^2)$

$R > R_c \Rightarrow$ *growth*

The critical nucleus is in unstable equilibrium

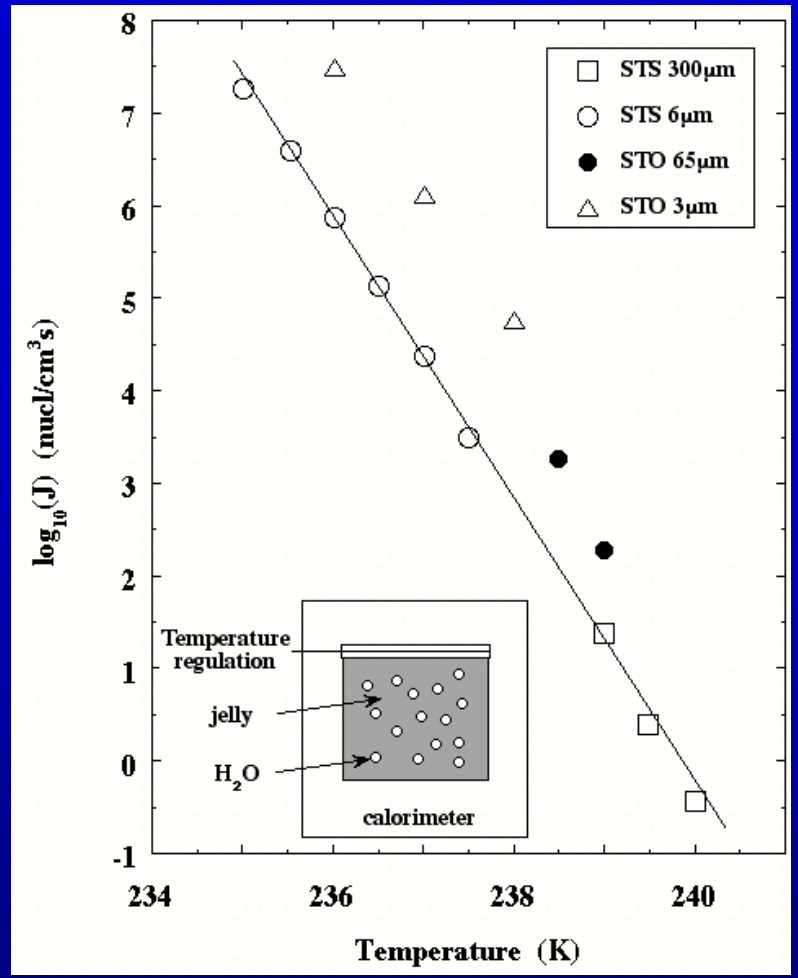
$\Rightarrow \Delta P = (1 - \rho_v/\rho_l)(P_{eq} - P)$

nucleation rate per unit time and volume : $\Gamma = \Gamma_0 \exp(-E/T)$

Γ_0 : attempt frequency x density of independent sites

supercooling water: Taborek 's experiment

(Phys. Rev. B 32, 5902, 1985)



avoid heterogeneous nucleation on defects, impurities or walls:

- divide the sample into micro-droplets

- minimize surface effects (STS not STO)

Regulate T : the heating power P increases exponentially with time

The time constant $\tau = 1/VJ$

The nucleation rate J varies exponentially with T

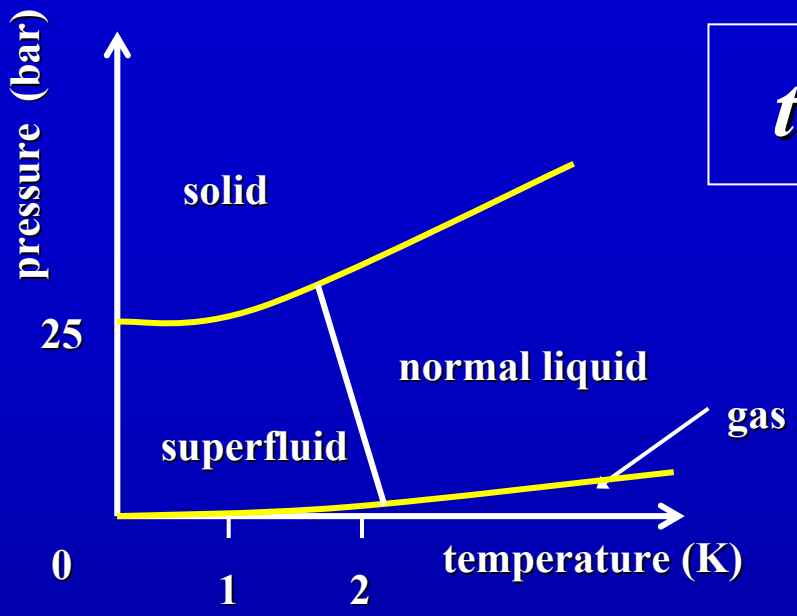
Compare with standard theory of homogeneous nucleation :

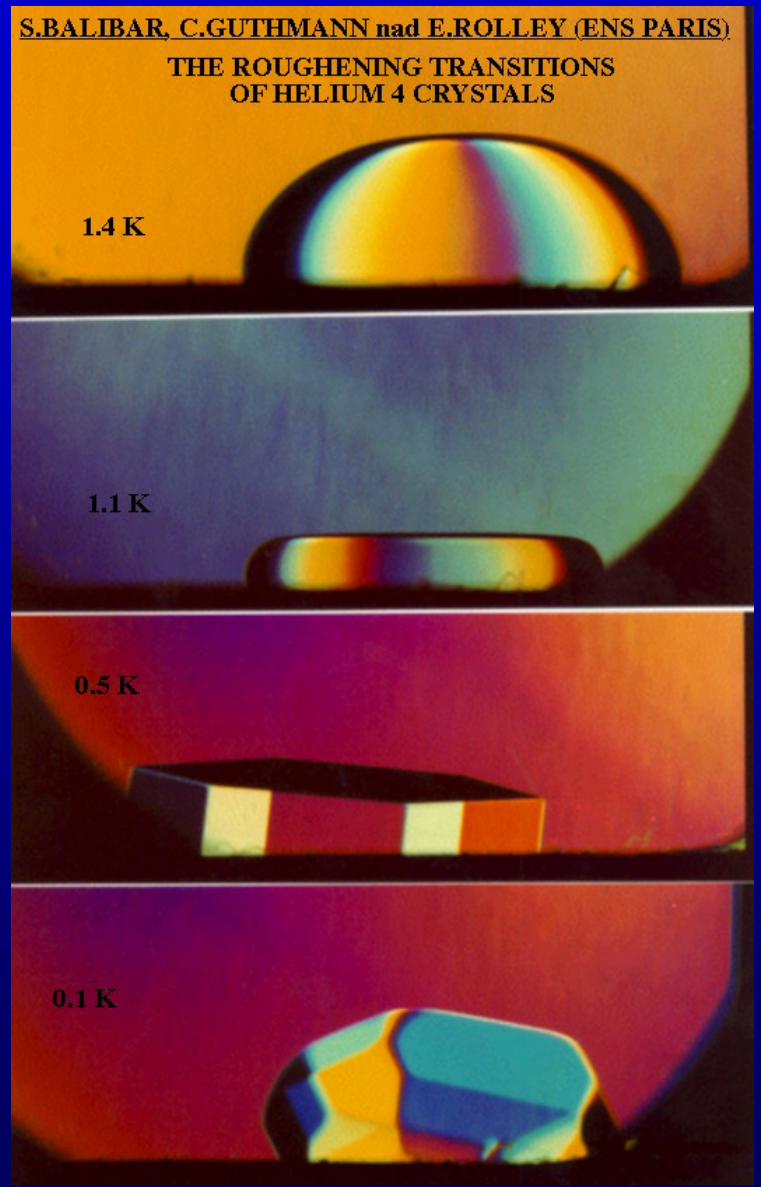
Taborek used his nucleation experiment to measure the (unknown) tension of the ice/water interface : it is 28.3 erg/cm^2 at 236 K

(see also Seidel and Maris 1986 for H_2 crystals)

the surface tension of helium 4 crystals is accurately known

the surface of helium crystals



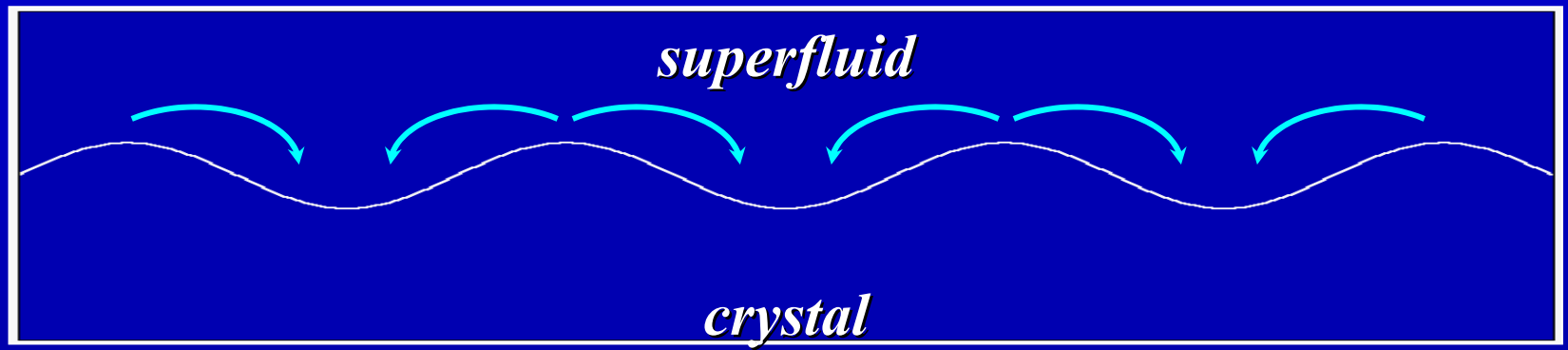


model systems
for very general properties of crystal surfaces
for ex: the roughening transitions

unusual growth dynamics of "rough" surfaces
due to quantum properties
for ex: crystallization waves

for review articles, see:
S. Balibar and P. Nozières, Sol. State Comm. 92, 19 (1994)
S. Balibar, H. Alles and A. Ya. Parshin, to be published in Rev. Mod. Phys. (2004).

crystallization waves



helium crystals can grow and melt so fast that crystallization waves propagate at their surfaces as if they were liquids.

same restoring forces :
-surface tension γ
(more precisely the "surface stiffness" γ)
- gravity g
inertia : mass flow in the liquid ($\rho_C > \rho_L$)

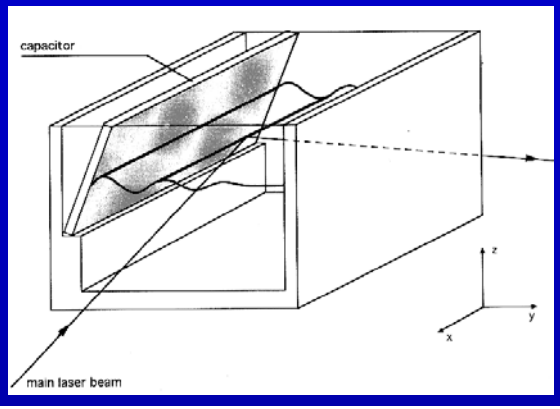
$$\omega^2 = \frac{\rho_L}{(\rho_C - \rho_L)^2}\left[\gamma q^3 + (\rho_C - \rho_L) g q\right]$$

$\Rightarrow$ *accurate measurement of the surface stiffness γ*

video waves

QuickTime™ et un
décompresseur Animation
sont requis pour visionner cette image.

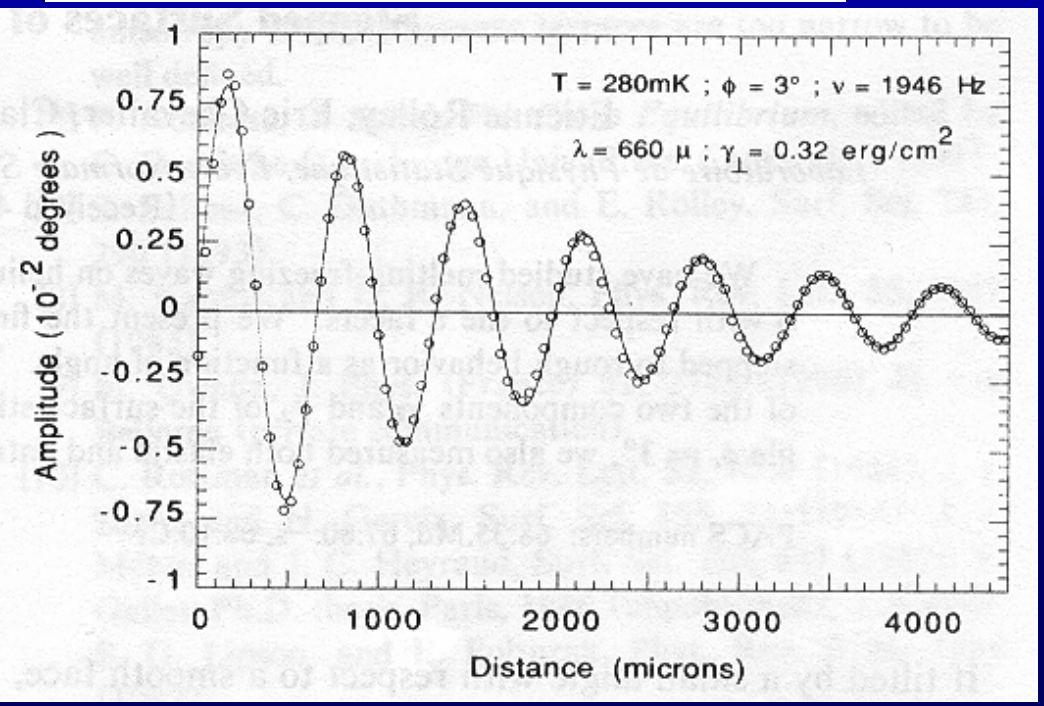
surface stiffness measurements

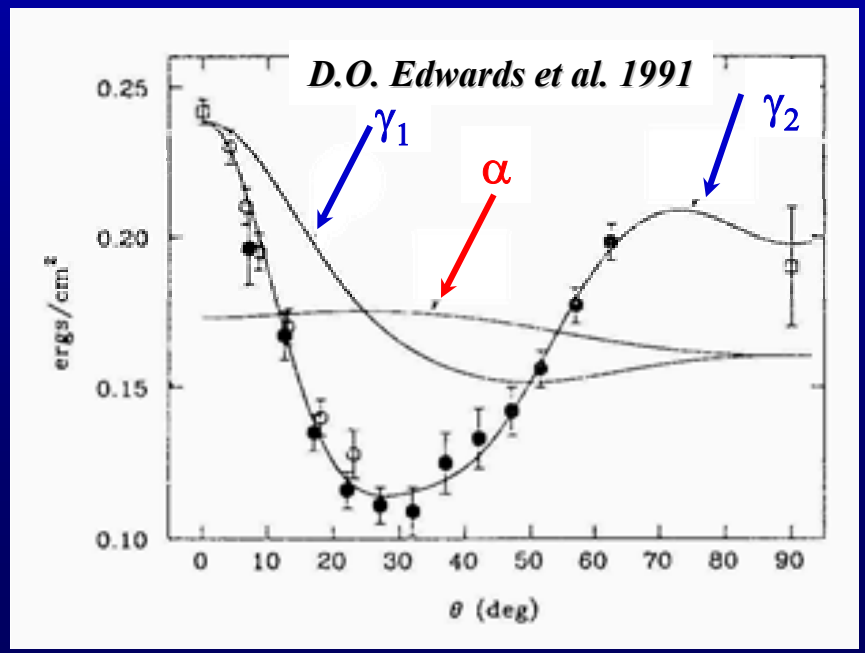


E. Rolley, S. Balibar and C. Guthmann
PRL 72, 872, 1994 and J. Low Temp. Phys. 99, 851, 1995

the surface tension α is anisotropic
the anisotropy of the surface stiffness
$\gamma = \alpha + \partial^2\alpha/\partial\theta^2$ is even larger.

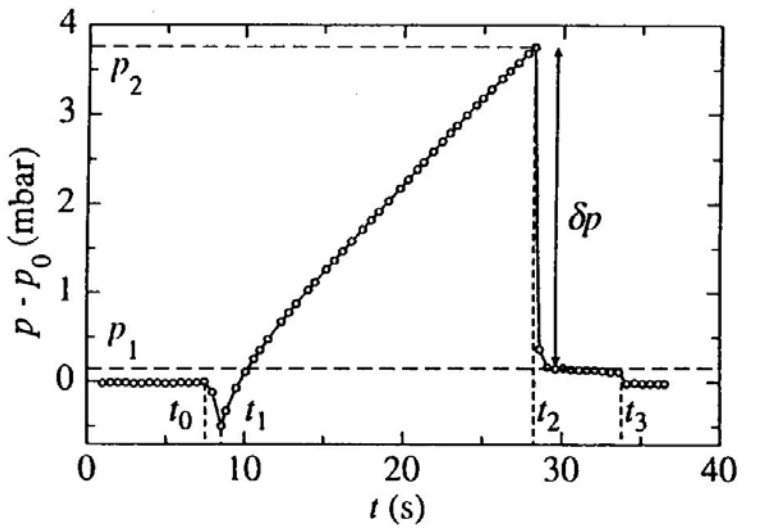
Edwards et al. (1991) from the measurements by O.A. Andreeva and K.O. Keshishev (1990) the surface tension $\alpha = 0.16$ to 0.17 erg/cm^2





nucleation of solid helium

pressurizing liquid helium in an ordinary cell:



J.P. Ruutu et al., Helsinki, 1996
consistent with other measurements by
Balibar (1980), Sasaki (1998)

heterogeneous nucleation occurs
~ 3 to 10 mbar above P_m
(Balibar 1980, Ruutu 1996, Sasaki 1998)

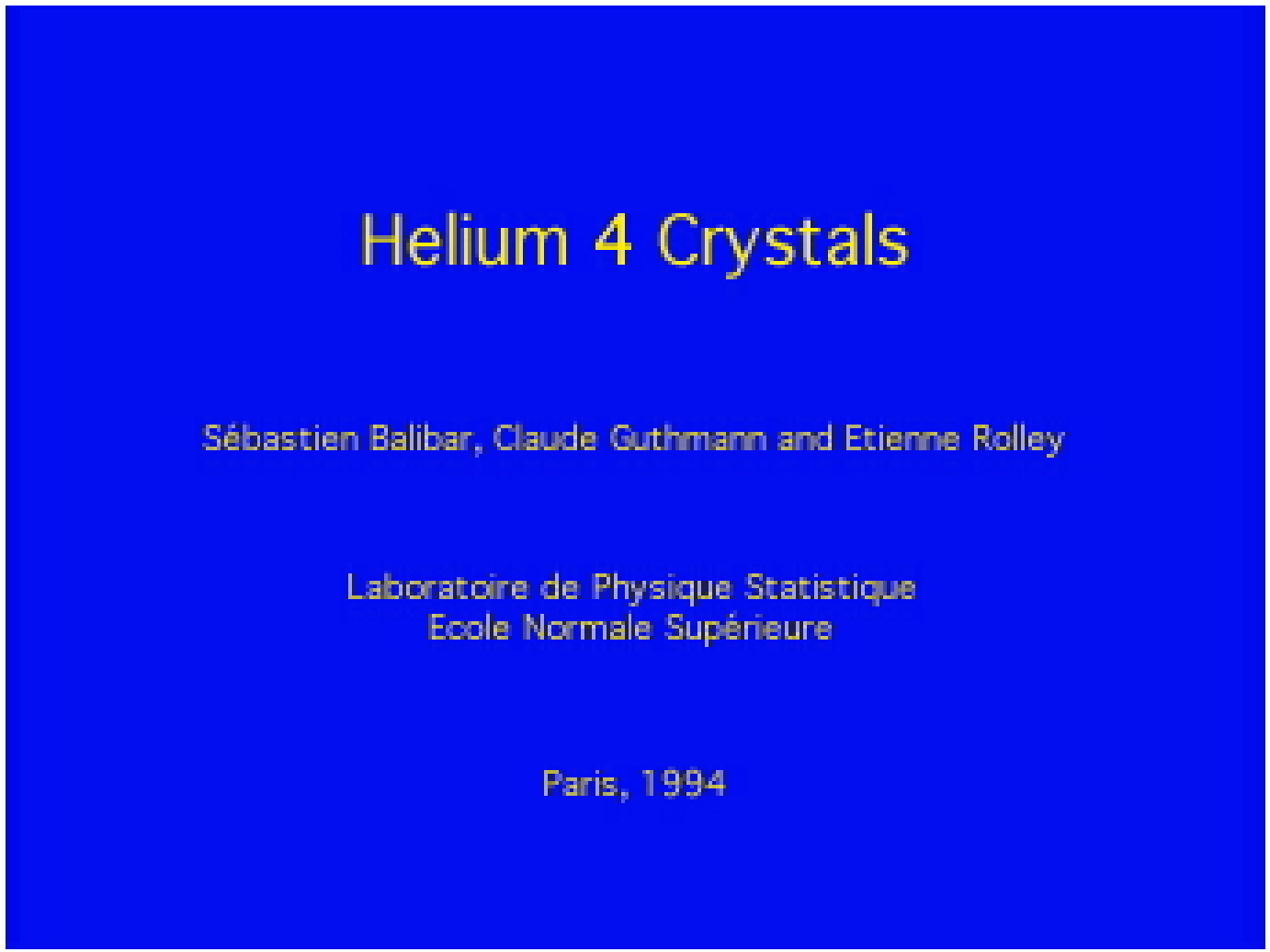
Balibar, Mizusaki and Sasaki
(J. Low Temp. Phys. 120, 293, 2000):

it cannot be homogeneous nucleation,
since $E = 16/3\ \pi\ \alpha^3/\Delta P^2 \approx 10^{10}$ K !

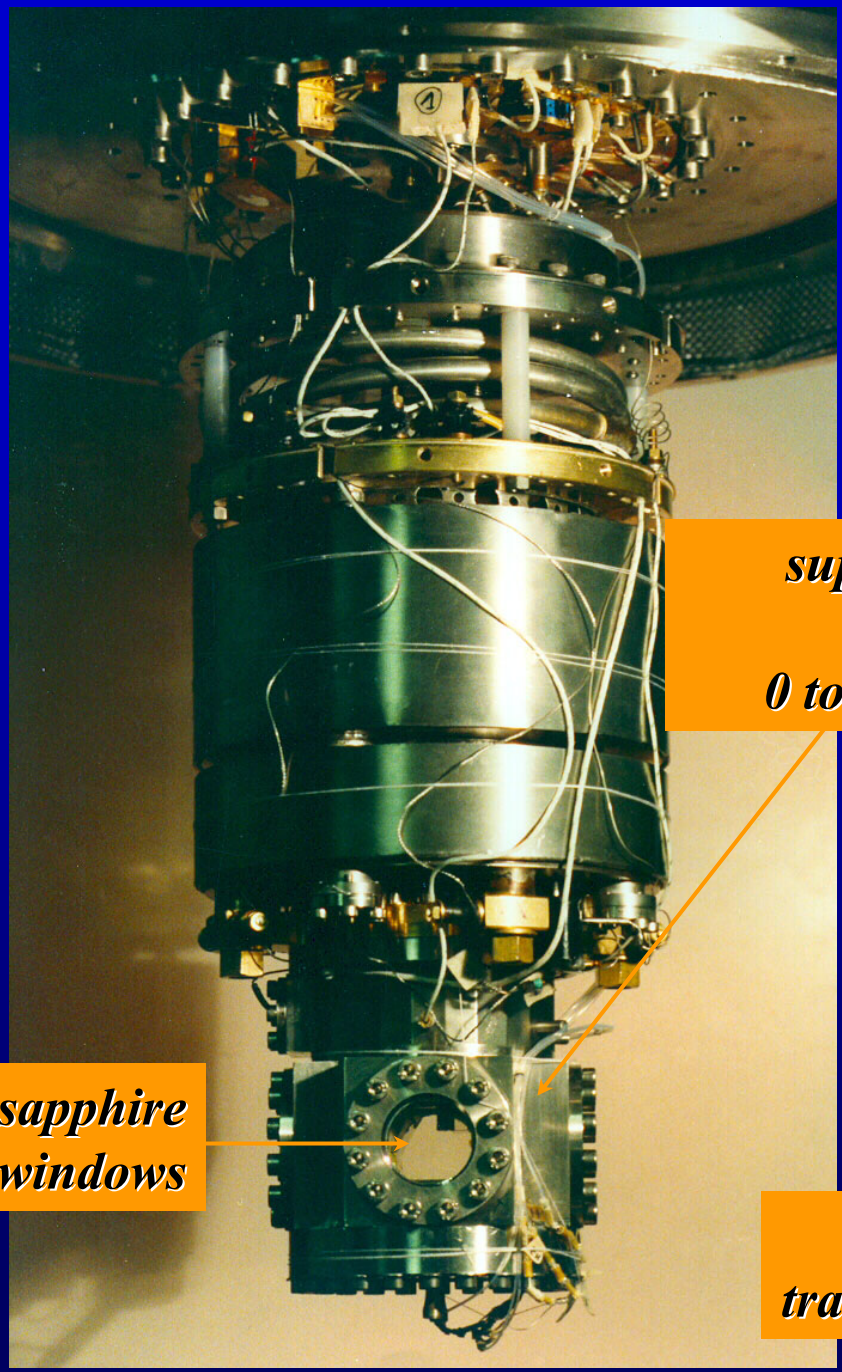
heterogeneous nucleation on favorable sites
(graphite dust particles ?)

$\Rightarrow$ acoustic crystallization : eliminate heterogeneous nucleation ?

heterogeneous nucleation with an electric field



the optical refrigerator at ENS-Paris



superfluid helium cell :
300 cm³
0 to 25 bar ; 0.02 to 1.4 K

heat exchangers

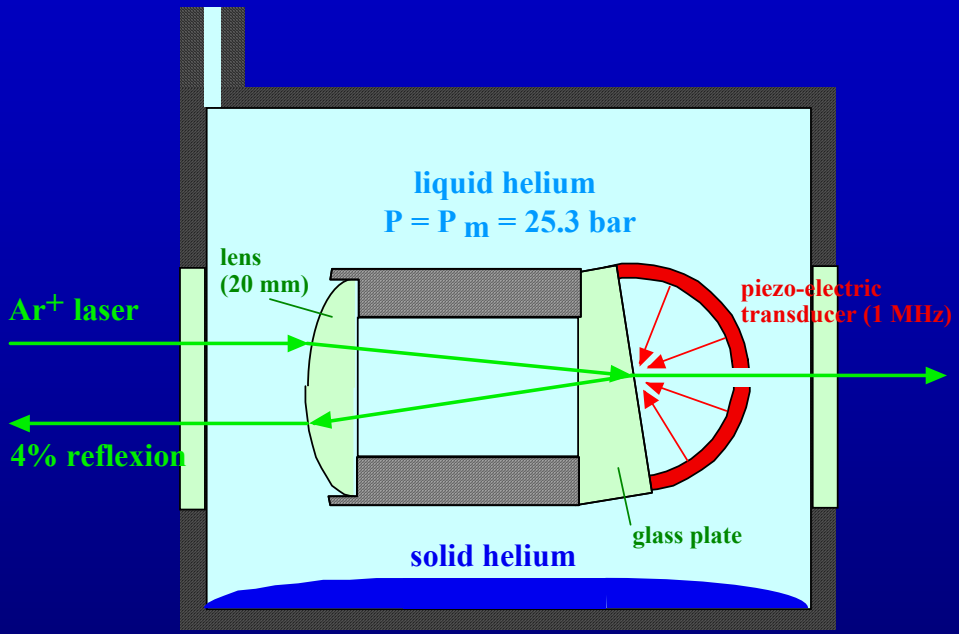
sapphire windows

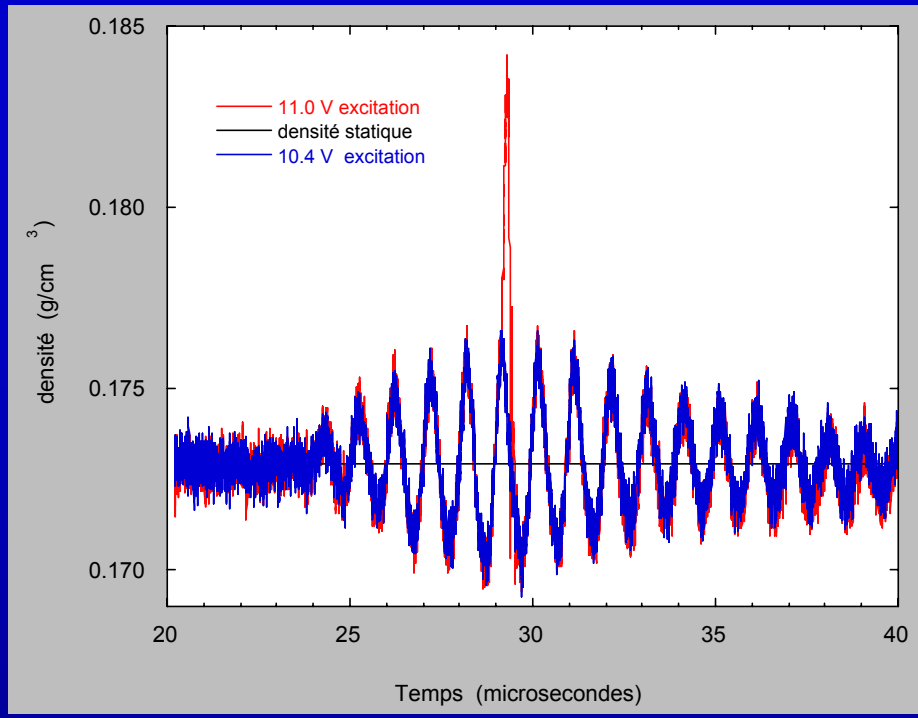
piezo-électric transducer (1 MHz)

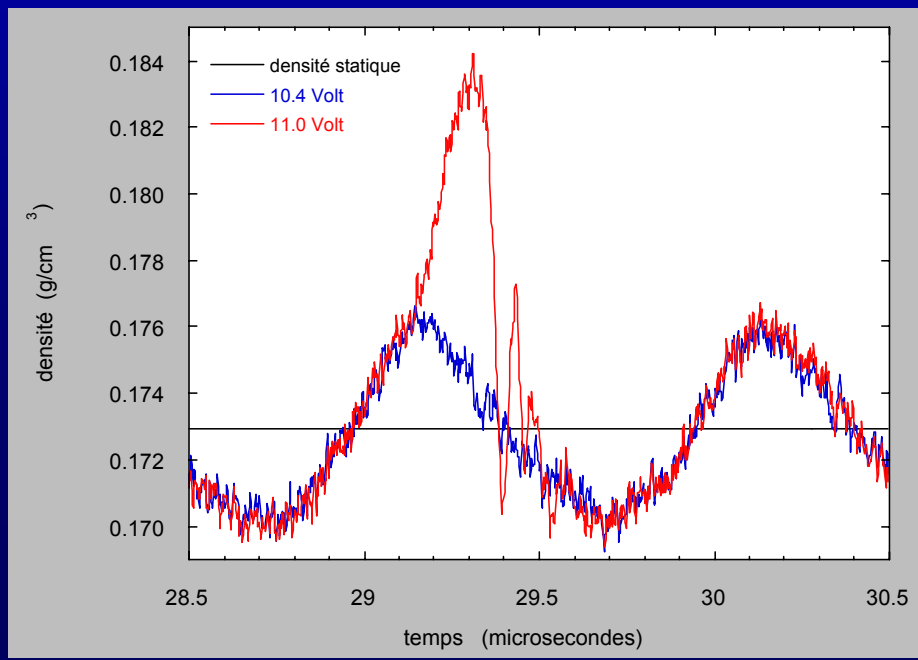
acoustic crystallization on a clean glass plate

X. Chavanne, S. Balibar and F. Caupin

Phys. Rev. Lett. 86, 5506 (2001)







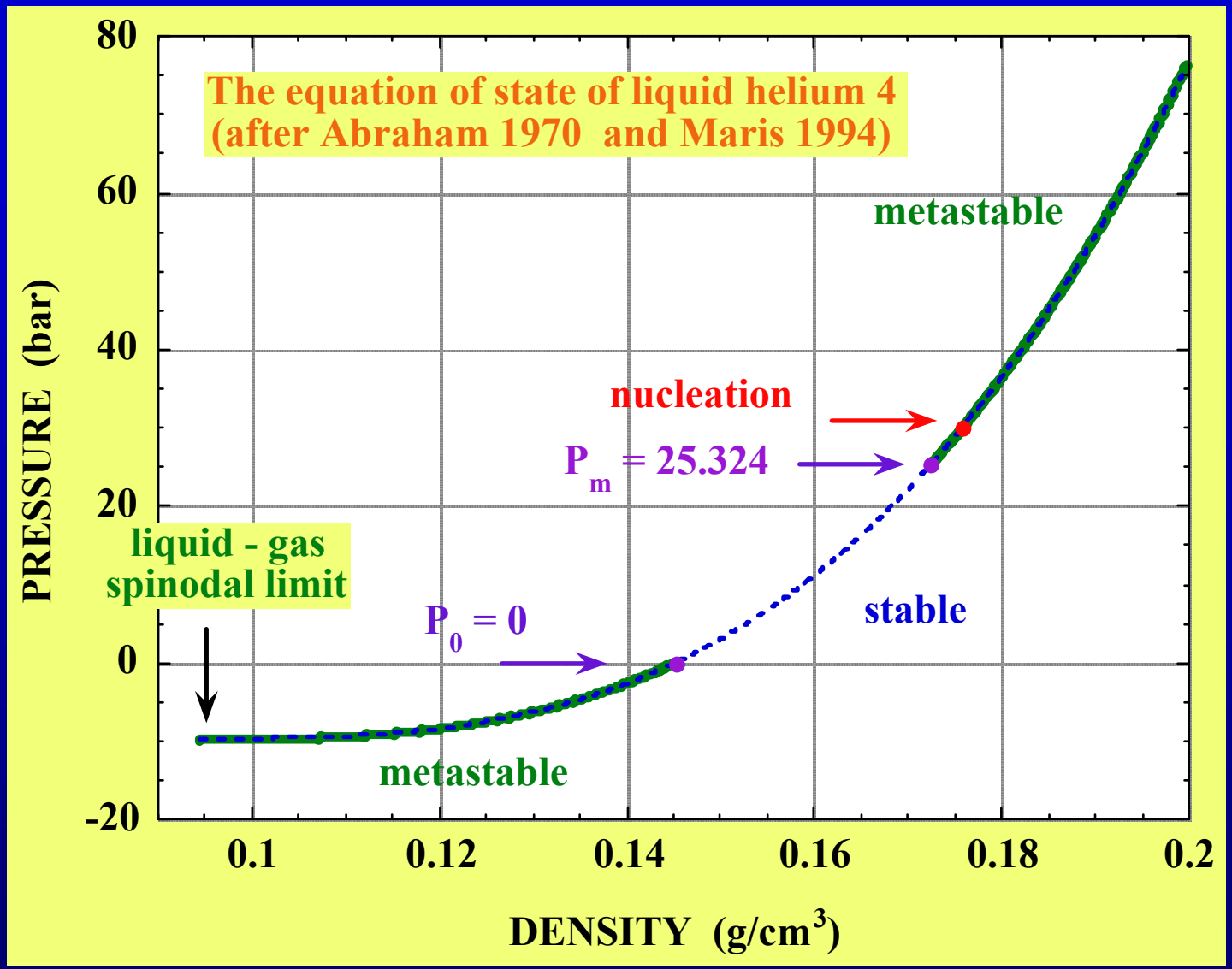
acoustic bursts (6 oscillations, rep. rate ~ 2Hz)

wave amplitude at the crystallization threshold:

± 3.1 10^{-3} g/cm³ (~2% of ρ_m),

i.e. ± 4.3 bar according to the eq. of state

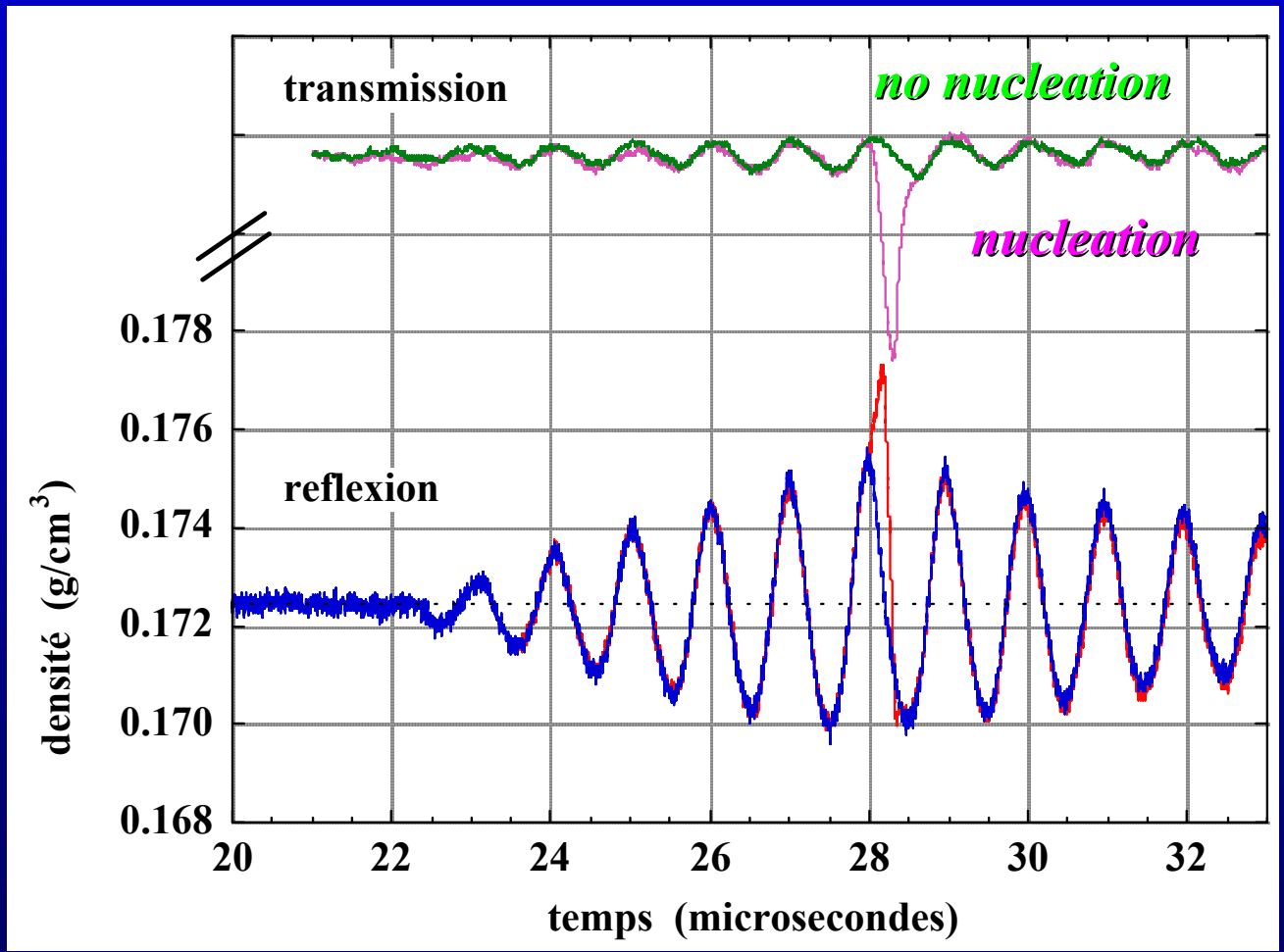
the equation of state of liquid helium 4



a rather well established cubic law (Maris 1991)

$$P - P_{sp} = a\,(\rho - \rho_{sp})^3$$

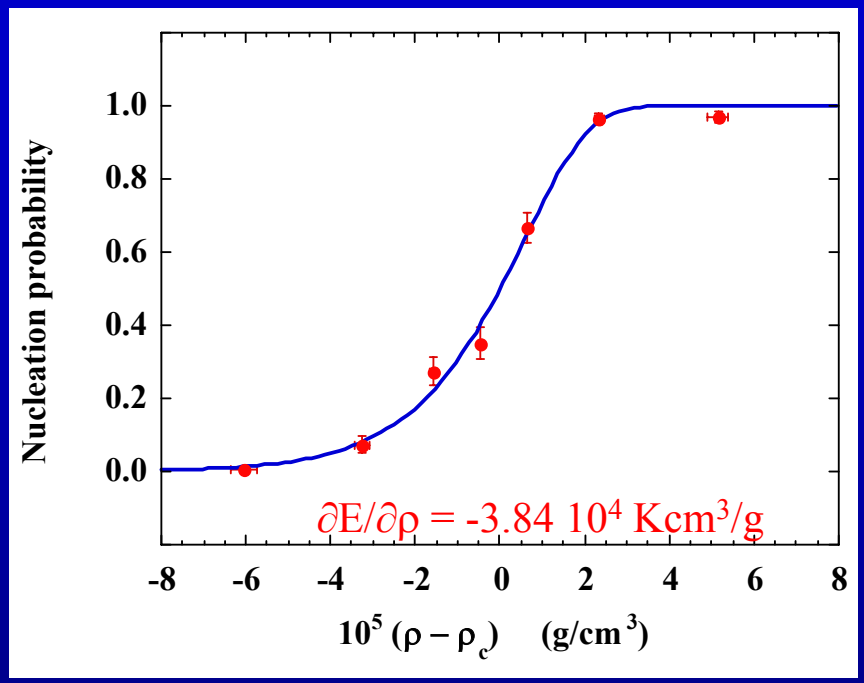
nucleation is stochastic

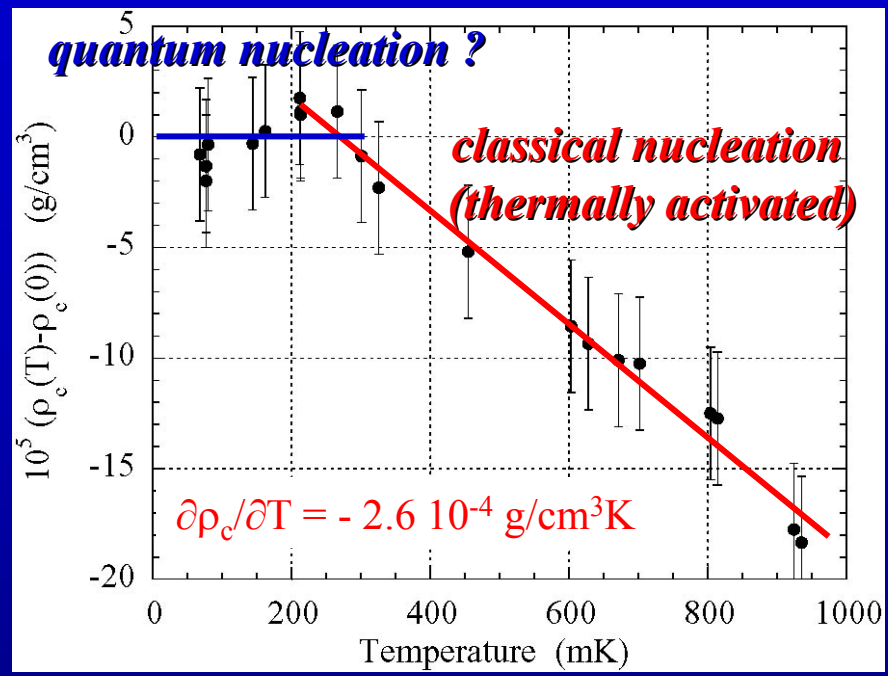


transmission signals are not averaged, so that the nucleation probability is easily obtained by counting events

a selective averaging is made on reflexion signals, in order to measure the wave amplitude at the nucleation threshold

on a clean glass plate, nucleation of solid He is still heterogeneous





the nucleation probability Σ *increases continuously from 0 to 1 in a small density interval, as expected for nucleation due to thermal or quantum fluctuations. This is the usual "asymmetric S-shape curve":*

$$\Sigma = 1 - \exp(-\Gamma_0 V \tau \exp(-E/T)) = 1 - \exp\{-\ln 2 \exp[-(1/T)(\partial E/\partial \rho)(\rho - \rho_c)]\}$$

from $\Sigma(\rho)$ *and* $\rho_c(T)$, *we obtain the activation energy* $E = T \cdot \partial E/\partial \rho \cdot \partial \rho_c(T)/\partial T = 6\,T$

$\Rightarrow$ *heterogeneous nucleation on the glass (~ 1 preferential site)*

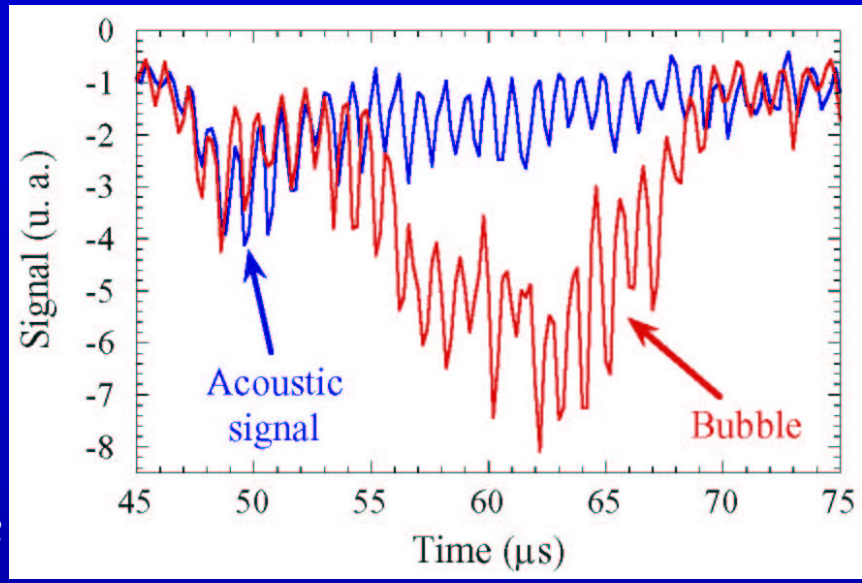
(at P_m *+ 4 bar the homogeneous nucleation barrier would be ~ 3000 K)*

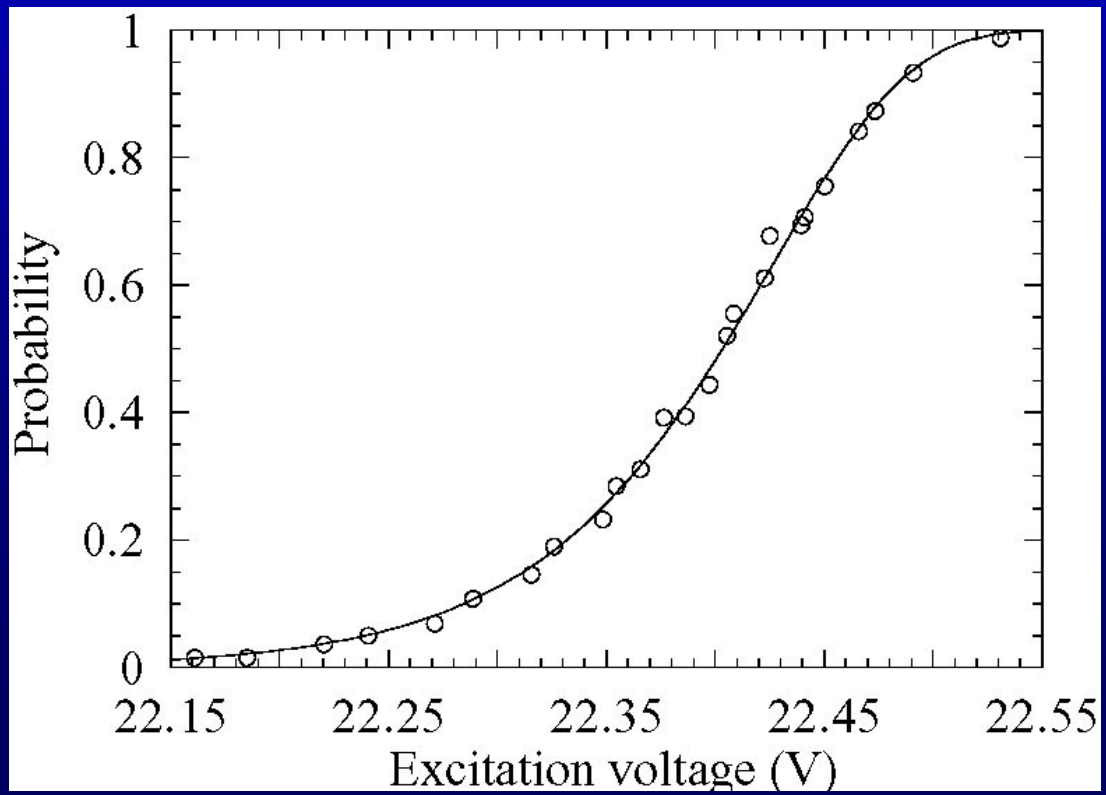
cavitation in helium 3

same "asymmetric S-shape" law for the nucleation probability:

$\Sigma = 1 - \exp(-\Gamma_0 V \tau \exp(-E/T))$

$= 1 - \exp\{-\ln 2 \exp[-(1/T)(dE/d\square)(\square - \square_0)]\}$

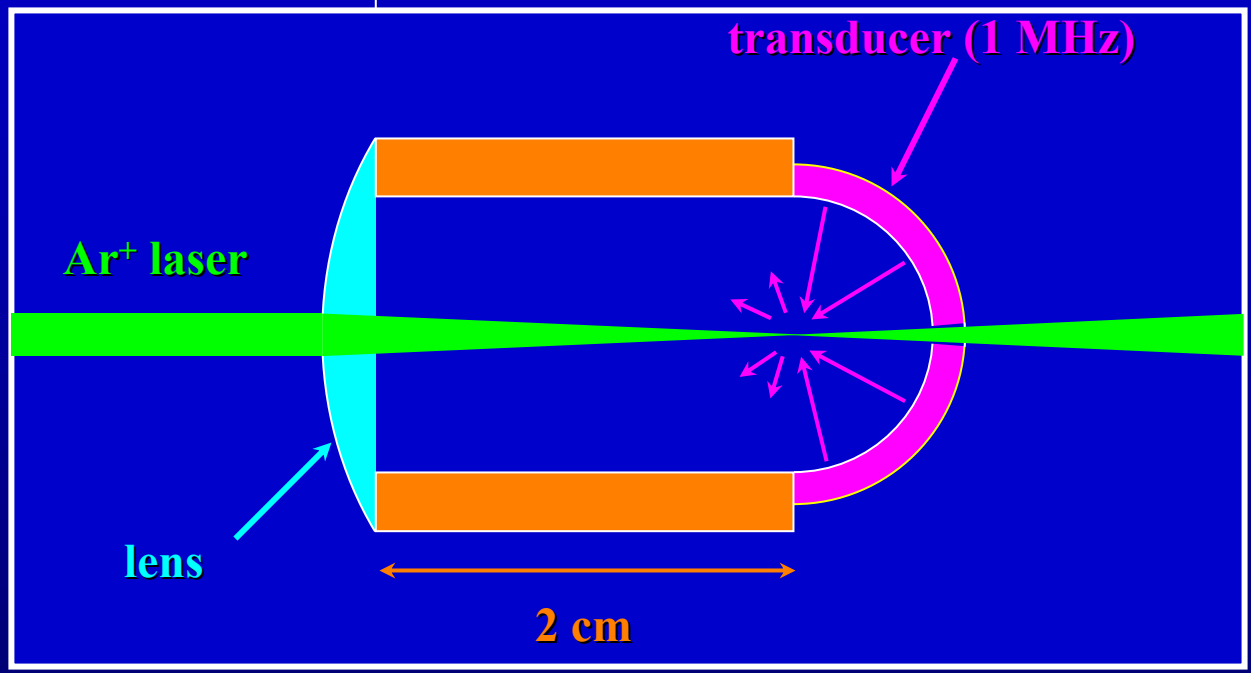




F. Caupin and S. Balibar, Phys. Rev. B 64, 064507 (2001)

search for homogeneous nucleation of solid helium with acoustic waves

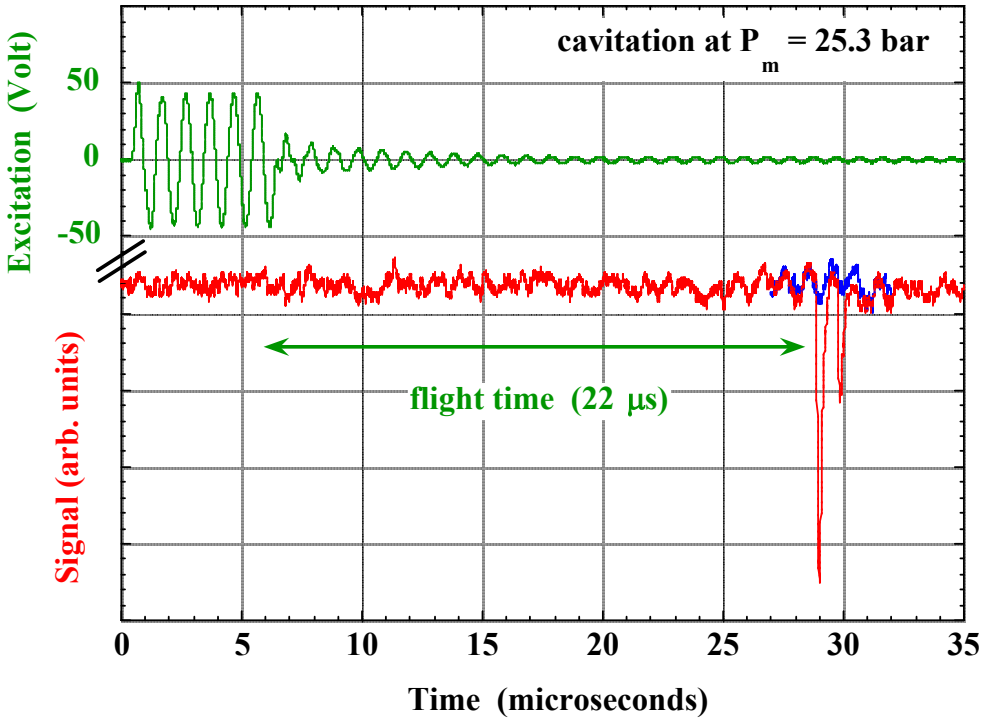
F.Werner, G. Beaume, C.Herrmann, A. Hobeika, S. Nascimbene, F. Caupin and S. Balibar (submitted to J. Low Temp. Phys. dec. 2003)

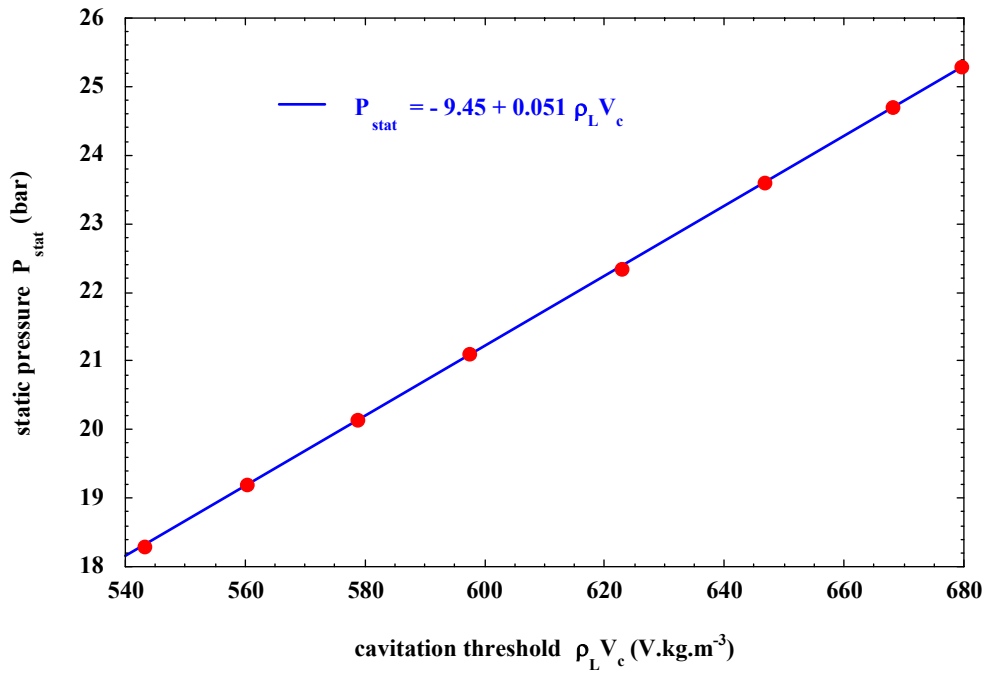


remove the glass plate

increase the amplitude of the acoustic wave

acoustic cavitation in liquid ^{4}He at high pressure





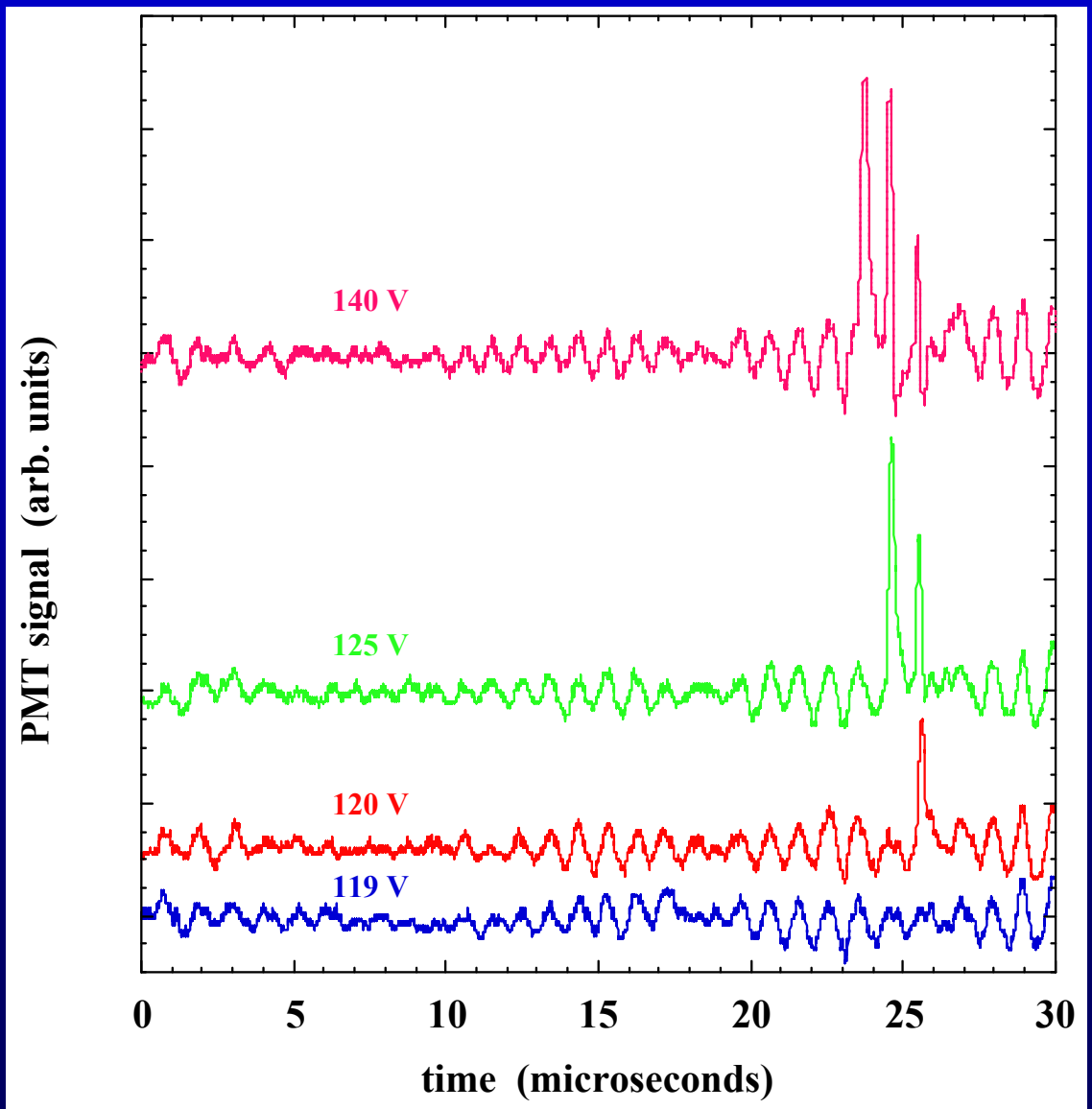
- *the cavitation threshold voltage V_c (more precisely the product $\rho_L V_c$) varies linearly with the pressure in the cell P_{stat}*
- *agreement with the linear approximation for the amplitude of the wave at the focus:*

$$\delta P \approx R\omega^2 \rho_L V$$

- *in our hemispherical geometry, non-linear efects must be small.*
- *extrapolation => cavitation occurs at -9.45 bar, in excellent agreement with theory (0.2 bar above the spinodal limit at - 9.65 bar)*

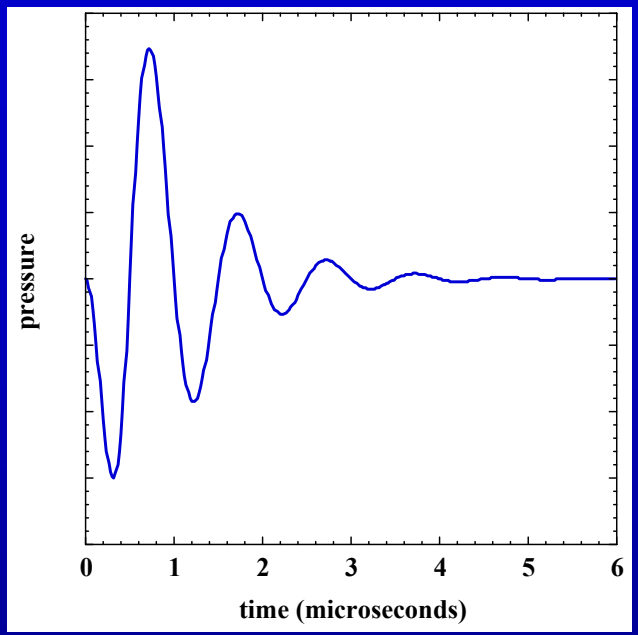
⇒ a calibration method for the wave

increasing the acoustic amplitude

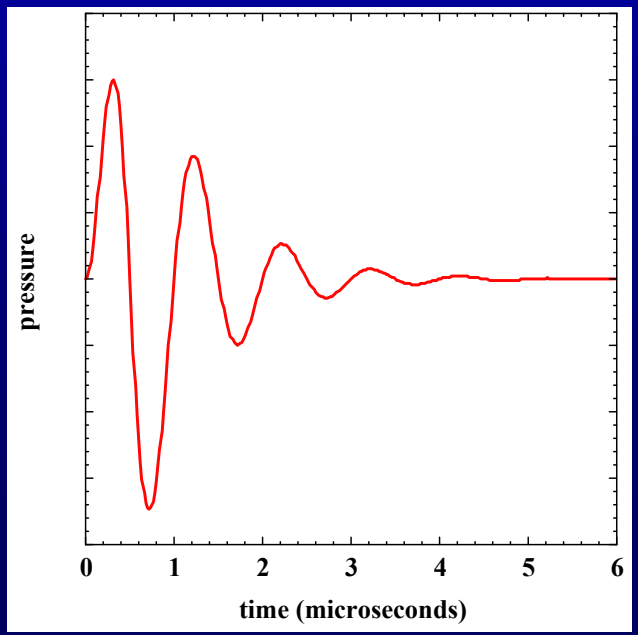


** as one increases the excitation voltage, cavitation occurs on earlier and earlier oscillations. This is due to the finite Q factor of the transducer*
(we measured Q = 53)
** here, for bursts of 3 oscillations and at 25 bar, 55 mK:*
- no cavitation at 119 V
- cavitation on third oscillation at 120 V
-on second oscillation at 125 V
- on first oscillation at 140 V

principle of the experiment

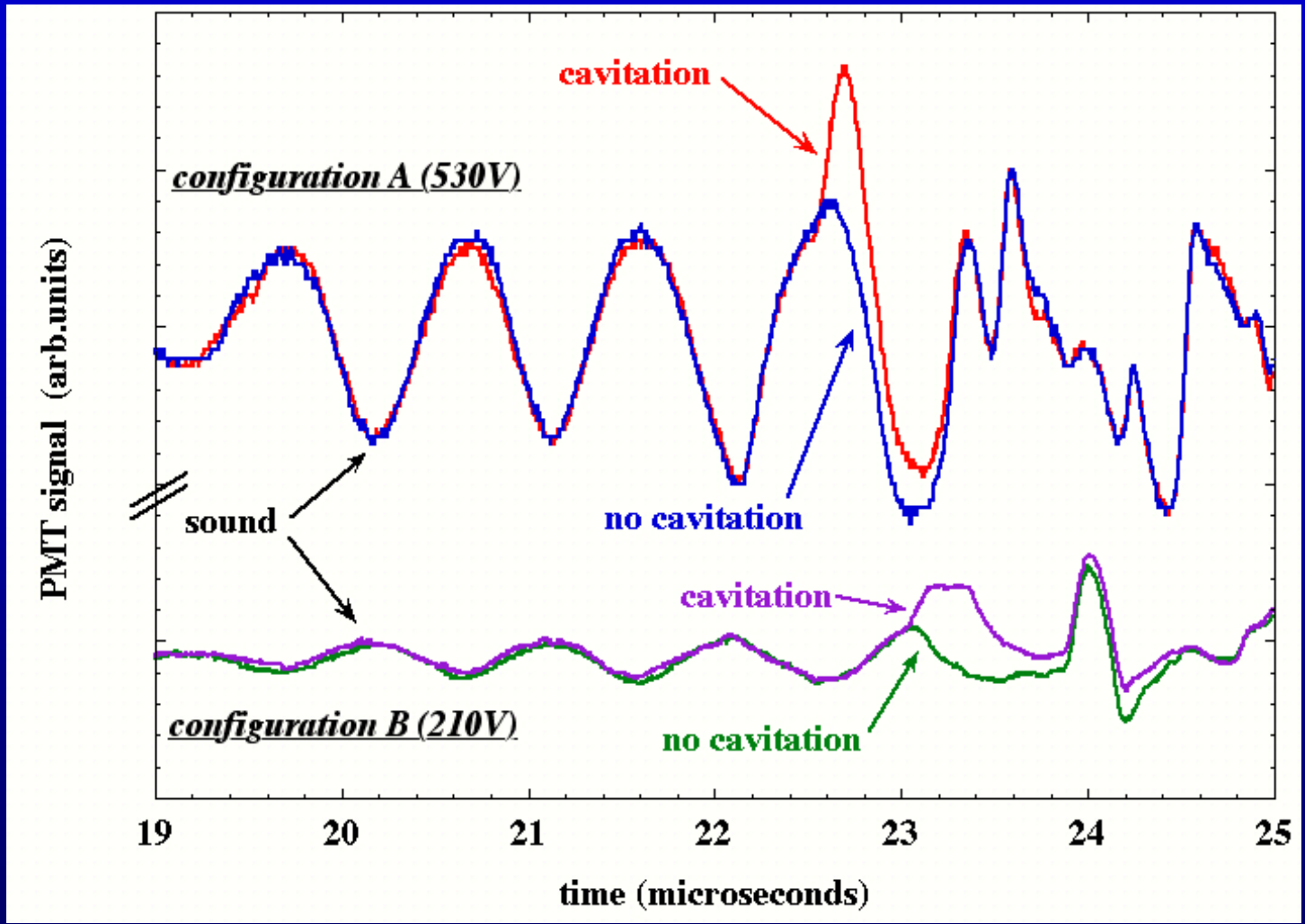


In liquid helium at 25 bar,
we emit a sound pulse, which starts with a negative pressure swing
cavitation is observed for a threshold voltage V_c,
when the pressure reaches - 9.45 bar
at the acoustic focus at time τ_{flight} + 0.25 μs.
⇒ calibration:
V_c corresponds to a 25 + 9.45 = 34.45 bar amplitude



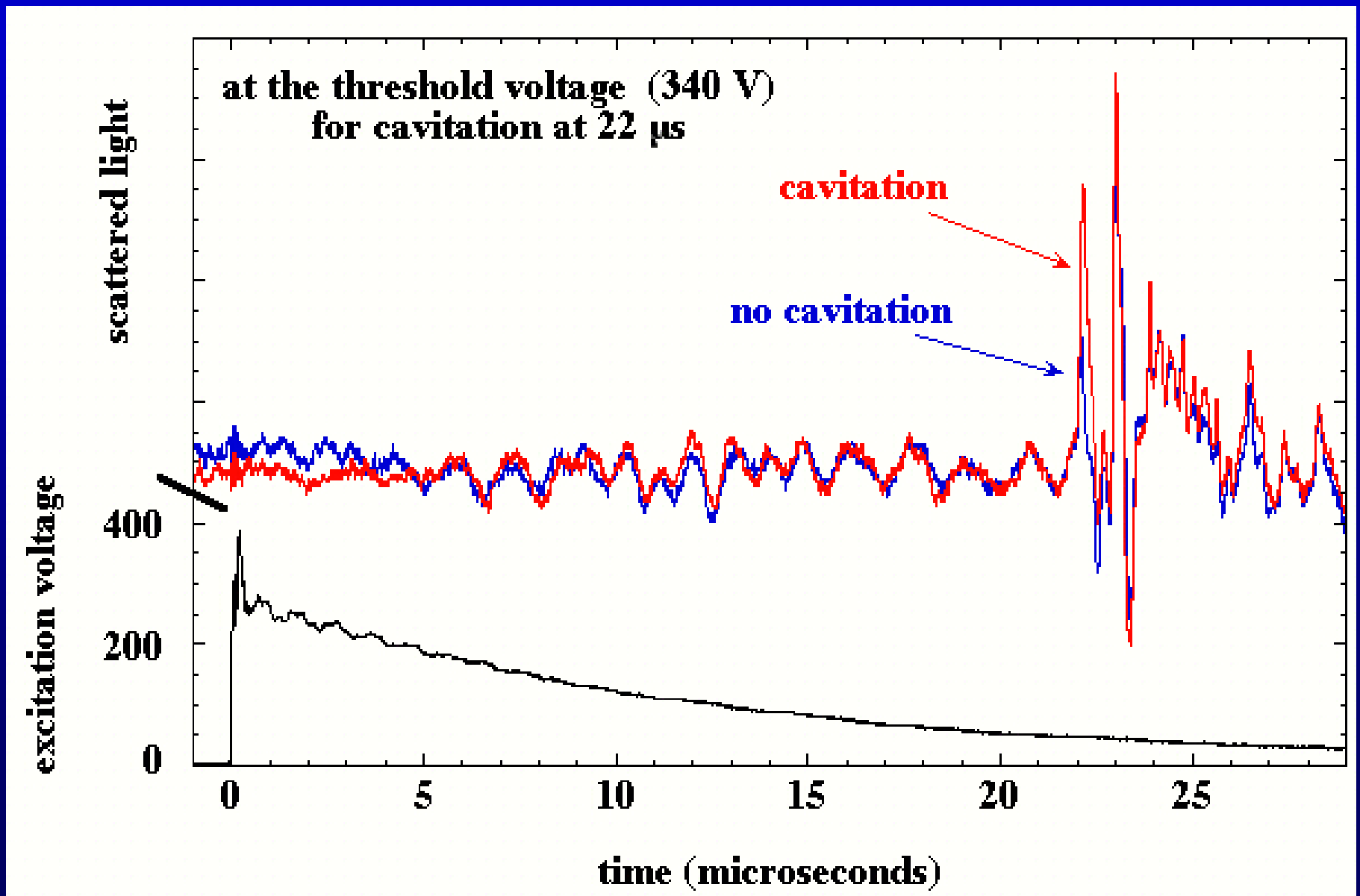
We reverse the voltage applied to the transducer.
We increase this voltage V as much as possible,
cavitation occurs at time τ_{flight} + 0.75 μs
we look for nucleation of crystals before that,
at time τ_{flight} + 0.25 μs.
A maximum positive pressure
$P_{max} = 25 + 34.45(V/V_c)$ bar
is reached at time τ_{flight} + 0.25 μs

reversing the phase in a real experiment

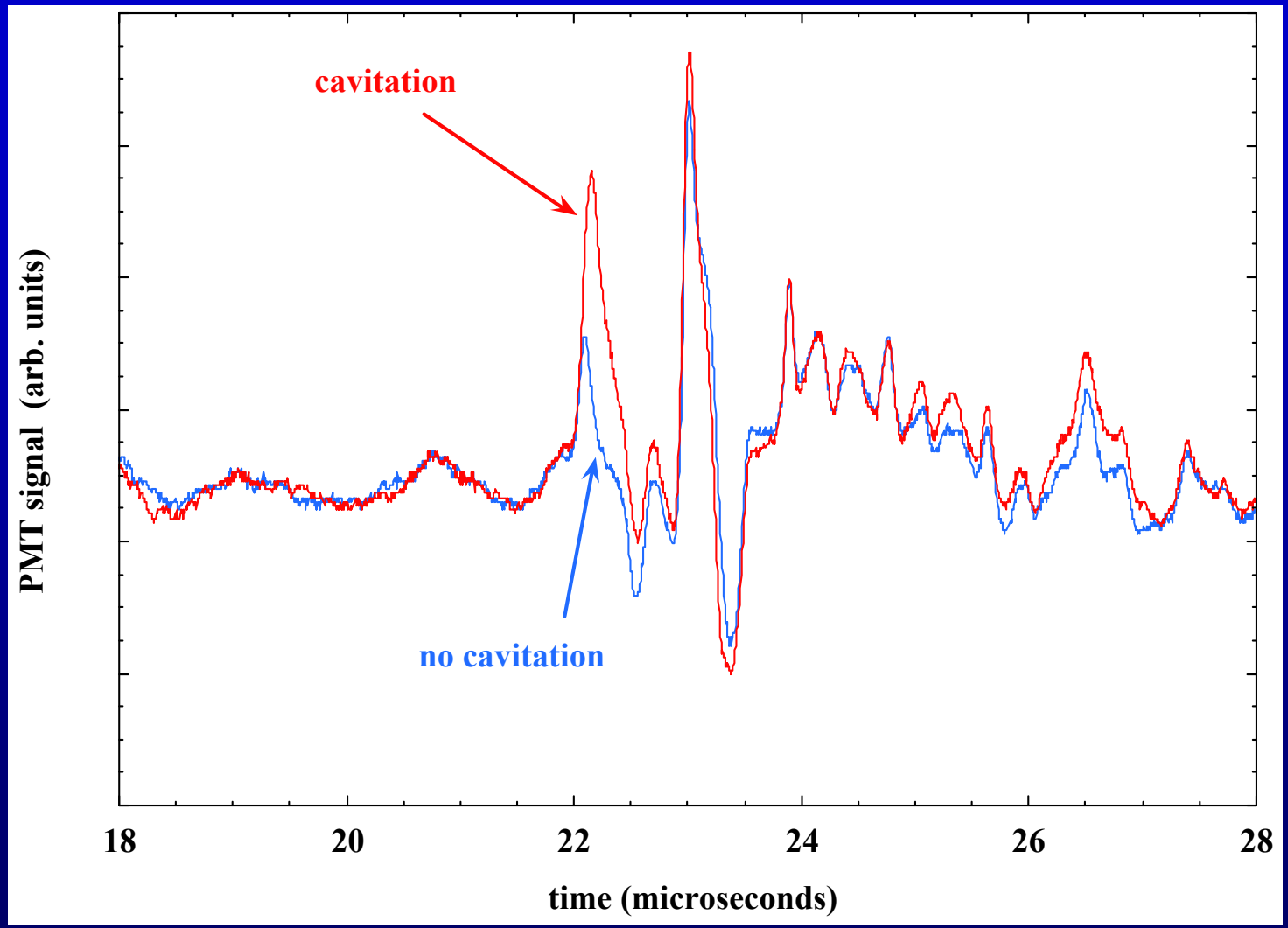


changing from configuration A to B,
the cavitation signal shifts by half a period (0.5 μs)

exciting the transducer with a simple pulse

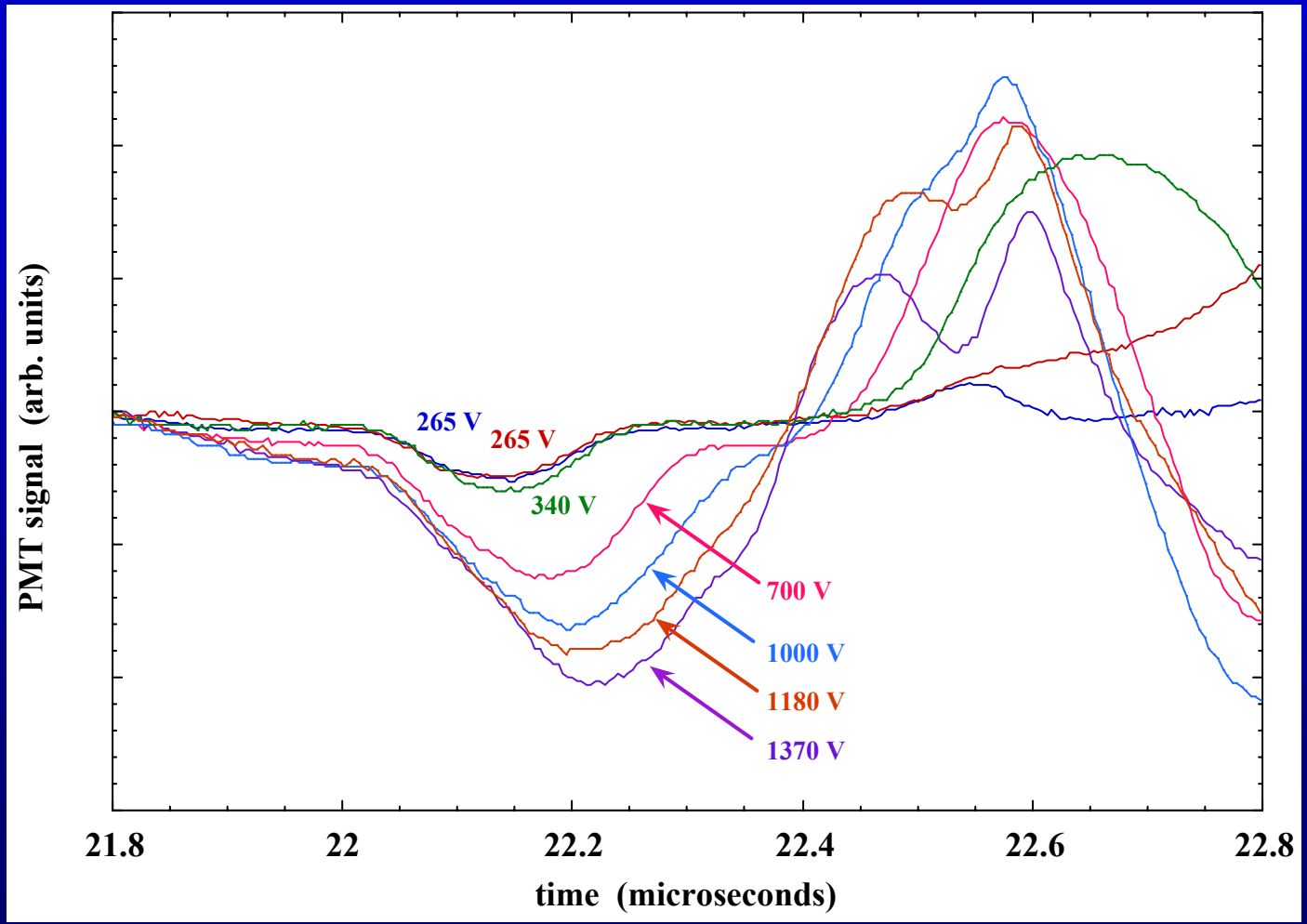


at the threshold voltage (340 V)



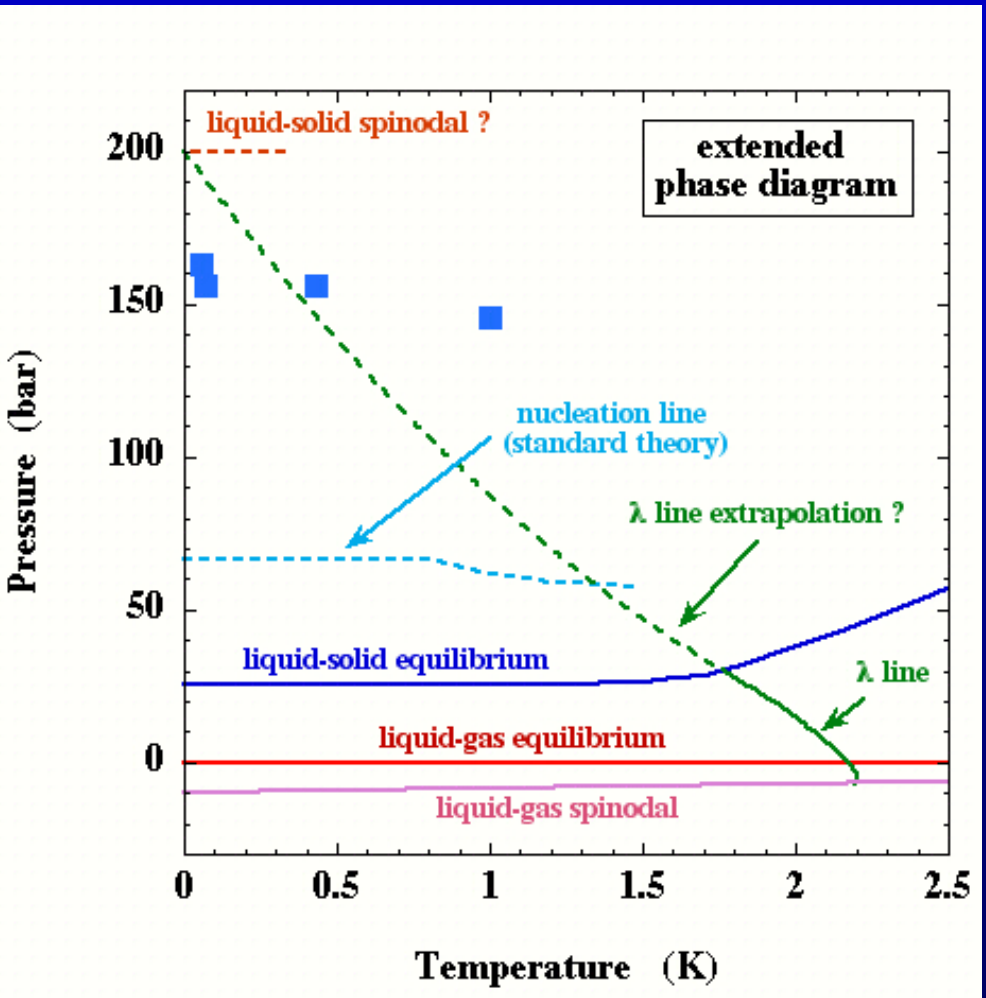
random cavitation at time 22 μs

liquid helium 4 up to 163 bar



after reversing the excitation voltage, no nucleation of crystals up to 1370 Volt.
this sound amplitude corresponds to a maximum pressure
$P_{max} = 25 + 34.45\ (1370/340) = 163$ *bar*

some comments



the standard nucleation theory fails

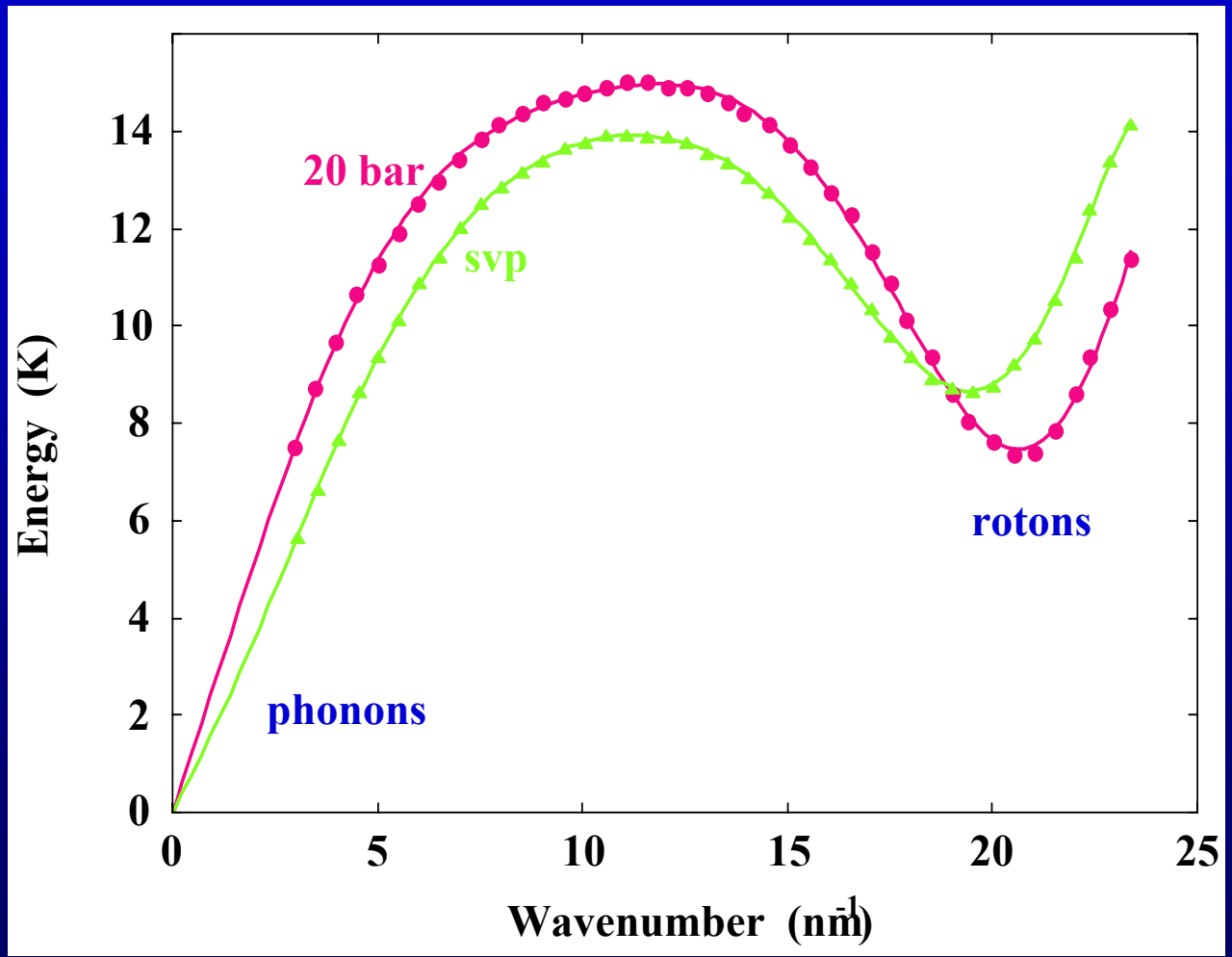
the standard theory predicts homogeneous nucleation at 65 bar.
It assumes a pressure independent surface tension, but this assumption was criticized by Maris and Caupin
(J. Low Temp. Phys. 131, 145, 2003)

superfluidity at 163 bar ?

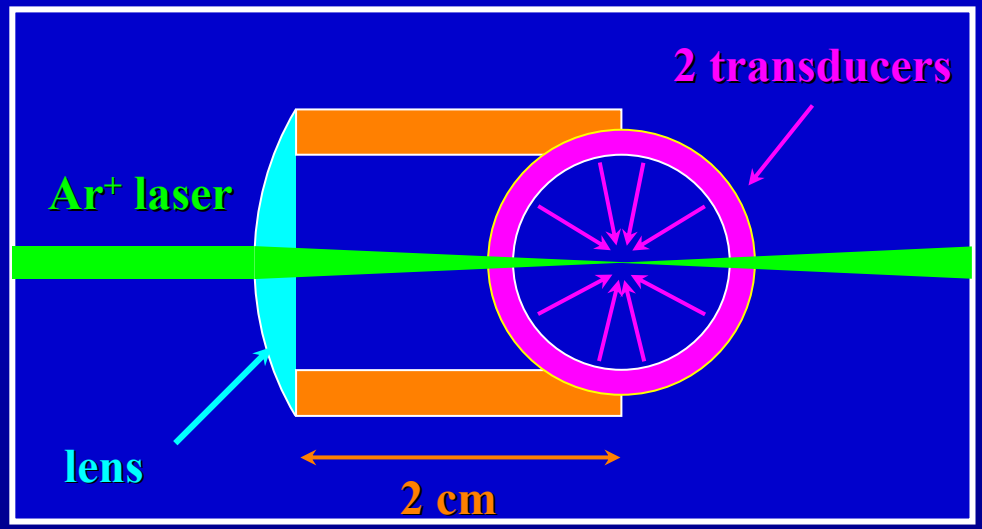
It is unlikely that crystals nucleated but were not detected, since they should grow even faster at 163 bar than at 29.6 bar, except if liquid helium is no longer superfluid ($\rho_L \sim 0.227$ gcm^{-3}, much more than $\rho_L = 0.172$ or $\rho_C = 0.191$ at 25 bar). The extrapolation of the λ line is not precisely known, but it should reach T = 0 at 200 bar, where the roton gap vanishes according to H.J. Maris, and where the liquid should become unstable (Schneider and Enz, PRL 27, 1186, 1971).

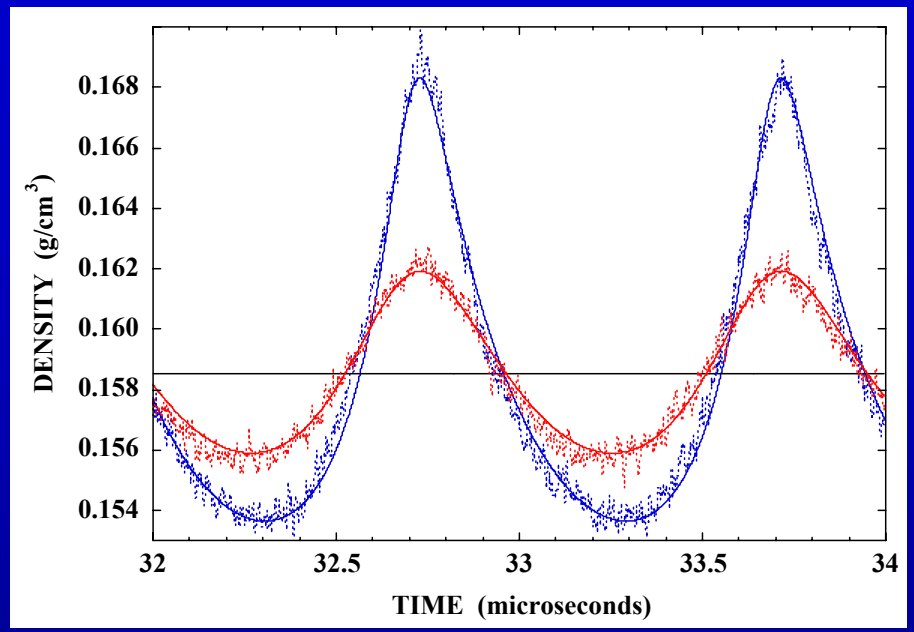
an instability at 200 bar ?

H.J. Maris noticed that, according to the density functional form of Dalfovo et al. , ***the roton gap vanishes around 200 bar where the density reaches 0.237 g/cm^3***
If true, this "soft mode" at finite wave vector could imply ***an instability towards a periodic (i.e. crystalline ?) phase***
(Schneider and Enz PRL 27, 1186, 1971)



future experiments: reach 200 bar or more





use 2 transducers (full spherical geometry)

due to non-linear effects, positive swings are larger than negative swings

easy to reach + 200 bar

difficult to calibrate the amplitude

improve numerical calculations of the sound amplitude

(see C. Appert , C. Tenaud, X. Chavanne, S. Balibar, F. Caupin, and D. d'Humières Euro. Phys. Journal B 35, 531, 2003)