Nucleation of Hydrogen Droplets in Supercooling Condition in Droplet Formation Chamber[*]

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Abstract：Because of the existence of supercooling in a droplet formation chamber，the hydrogen micro-spheres are still in liquid phase even though their temperature is lower than the triple-point temperature. This may cause the droplets to shatter in the vacuum injection capillary. Based on the knowledge about supercooling of liquid hydrogen，we have done a thermodynamic simulation of the droplets in the droplet formation chamber，and theoretically suggested the optimal working conditions under which the droplets will most properly nucleate to solid pellets. The suggested working conditions are that the helium-gas pressure and the hydrogen vapor pressure in the droplet formation chamber are kept as low as possible，and the droplet formation chamber should be no-less than 6 cm in the length.

Key words：pellet target；hydrogen droplet；supercooling；nucleation

CLC number：TL594   **Document code**：A

1 Introduction

Pellet target is one kind of effective internal target in the storage ring. In principle，the frozen micro-spheres (as we called pellets) are injected into the storage ring and interact with the circulating ion beam perpendicularly in the reaction chamber on the premise that the whole procedure doesn't affect the vacuum of storage ring obviously[1−2]. Compared with other internal targets，pellet target has many distinct merits such as high luminosity comparable to that of an external target and nearly 4π detectable space. As a result，the pellet target is chosen to be one of the most important internal targets in the Main Ring of Cooling Storage Ring (CSRm) at Lanzhou，China. At present，there is only one pellet target facility in use in the world which is located in Jülich，Germany.

The hydrogen pellet target is the most commonly used internal target[3]. Typically，the temperature of the glass nozzle is set to be a little higher than the triple-point temperature of hydrogen. A pure liquid hydrogen jet，ejecting through a glass nozzle with a 12 μm inner diameter，is broken up into uniformly sized and spaced droplets by means of acoustical excitation applied on the nozzle，as depicted in Fig. 1. The pressure inside the droplet formation chamber (DFC) is kept much lower than the triple-point pressure of hydrogen so that the hydrogen droplets could cool down to a temperature lower than its triple-point temperature rapidly by evaporation cooling. Normally，the liquid hydrogen should freeze at the triple-point temperature of 13.96 K，but the experimental observation revealed that the micro-spheres were still

kept in liquid phase at the end of the DFC. Obviously, a phenomenon called supercooling is inevitably encountered in this super clean environment of the DFC. It has been theoretically and experimentally proven that the hydrogen droplets are fragile because of their low surface tension and thus easily destroyed by the turbulent gas flow in the vacuum injection capillary while solid pellet would survive the vacuum injection better. So it's strongly recommended that the hydrogen droplets should nucleate to pellets as soon as possible in the DFC.
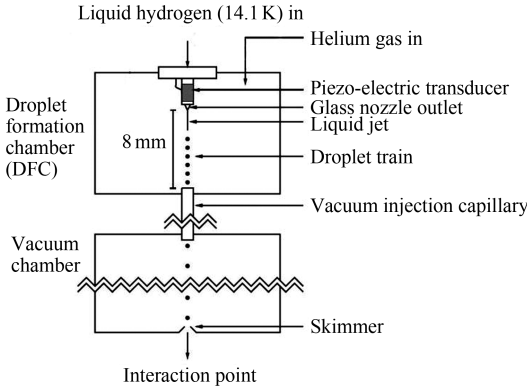

Fig. 1   A schematic picture of the pellet target.

In this paper, we will investigate the thermodynamic behavior of the droplets in the DFC, and seek the optimal working conditions of the pellet target which are beneficial to the nucleation of hydrogen droplets in the DFC.

2 The Droplet Behavior in the DFC in Standard Working Conditions

In the DFC, the ambient gas is actually a mixture of helium gas and the evaporated hydrogen gas. Due to the convective flow, the mass transfer for the droplet in the DFC can be expressed as[4]

$$\dot{m} = -4\pi a^2 \kappa_{\rm m} \frac{M_{\rm H}}{R} \left(\frac{P_{\rm sat}(T_S)}{T_S} - \frac{P_\infty}{T_\infty} \right) , \quad (1)$$

where $\dot{m}$ is the mass loss rate by evaporation, a is the droplet radius, R is the universal gas constant, $\kappa_{\rm m}$ is the mass transfer coefficient and $M_{\rm H}$, P and T are the molecular weight, the pressure and the

temperature of the hydrogen vapor, respectively. The subscript S denotes the droplet surface, and the subscript ∞ denotes the place far away from the droplet surface. $P_{\rm sat}(T_S)$ is the saturated vapor pressure of hydrogen at the droplet surface temperature T_S.

Because of the finite conductivity inside the droplet, the droplet should be divided into many isothermal layers. The interfacial heat balance at the droplet surface can be expressed as[5−6]

$$\rho_{\rm L} C_{\rm L} \frac{\partial T_{\rm L}}{\partial t} = \frac{\kappa_{\rm L}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T_{\rm L}}{\partial r} \right) , \quad 0 \leqslant r \leqslant a(t) (2)$$

where $\rho_{\rm L}$, and $C_{\rm L}$ are the density and the heat capacity of the droplet, respectively. The following boundary conditions should satisfy

$$\frac{\partial T_{\rm L}}{\partial r}(0, t) = 0 , \quad (3)$$

$$T_{\rm L}(a, t) = T_S(t) . \quad (4)$$

The energy balance equation for a given isothermal layer inside the droplet is given by Refs. [5—6]

$$\kappa_{\rm L} \frac{\partial T_{\rm L}}{\partial r} \Big|_{r=a} = \frac{\dot{m}}{4\pi a^2} h_{\rm fg} + h_{\rm c}(T_\infty - T_S) , \quad (5)$$

where $\kappa_{\rm L}$ is the thermal conductivity of the droplet, and $T_{\rm L}$ is the droplet temperature at the radial position r and time t. $h_{\rm fg}$ is the latent heat of vaporization of liquid hydrogen, and $h_{\rm c}$ is the convective heat transfer coefficient. The mass transfer coefficient $\kappa_{\rm m}$ and the convective heat transfer coefficient $h_{\rm c}$ can be calculated according to the empirical equations given by Renksizbulut et al[5].

The typical working parameters of the pellet target are as follows: (1) Hydrogen droplet temperature: 14.1 K; (2) Droplet diameter: 38 μm; (3) Droplet velocity: 21.4 m/s; (4) The length of the DFC: 8 mm; (5) Surrounding gas temperature: 15 K; (6) Helium (background gas) pressure: 1500 Pa; (7) Hydrogen vapor pressure: 8×10² Pa, so the total pressure in the DFC is 2300 Pa.

Based on above thermodynamic equations，the thermodynamic simulations in supercooling condition are performed，and the result is shown in Fig. 2. The calculations show that when the elapsed time is longer than 2 ms，a dynamic equilibrium temperature of about 10.8 K is found to be the lowest temperature that the droplet can approach in the DFC. As for the commonly used 8 mm long droplet chamber，the surface and center temperatures of the droplet are about 11.07 and 12.45 K，respectively[7].
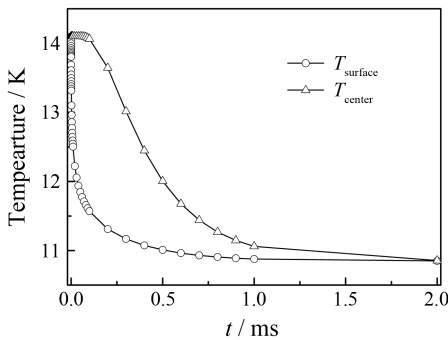

Fig. 2 Temperature variations with the time，where $T_{surface}$ and T_{center} denote the temperature at surface and center of the droplet，respectively.

3　Knowledge about Supercooling of Liquid Hydrogen

In order to find out under what conditions the supercooled hydrogen droplets will nucleate to solid pellets，we need to get a clear understanding of the nucleation process. The transformation of a supercooled liquid to a solid takes place by the growth of crystals. It follows that when a solid begins to form，it must at first take the form of extremely small crystals. The free energy $\delta F(R)$ required to form a small solid sphere of radius in the liquid is[8]

$$\delta F(R) = 4\pi R^2 \alpha_{LS} - \frac{4}{3}\pi R^3 n_s (f_1 - f_s)，\quad (6)$$

where α_{LS} is the surface energy between the liquid and solid，n_s is the number density in the solid phase，and f_1 and f_s are the free energies per molecule in the liquid and solid phases. Because of the surface energy，δF is positive for small R and has a maximum value of

$$\delta F_0 = \frac{16\pi}{3} \frac{\alpha_{LS}^3}{n_s^2 (f_1 - f_s)^2}，\quad (7)$$

which occurs when

$$R_0 = \frac{2\alpha_{LS}}{n_s (f_1 - f_s)}。\quad (8)$$

For $R > R_0$ the solid tends to grow without limit because this decreases the free energy of the system. Thus，the criterion that determines whether a liquid at a particular temperature will nucleate is therefore the relationship between the size of the largest cluster and the critical size. If a sphere with $R > R_0$ is produced by a thermal fluctuation，the supercooled liquid will make a transition to the solid phase. The probability of this happing per unit time per unit volume，namely the nucleation rate，is given by

$$\Gamma_T = \frac{n_L k_B T}{h} \exp\left(\frac{-\phi_{LS}}{k_B T}\right) \exp\left(\frac{-\delta F_0}{k_B T}\right)，\quad (9)$$

where n_L is the number density in the liquid phase，and ϕ_{LS} is the activation energy for diffusion of atoms across the liquid-solid interface. The form of the expression for Γ_T indicates that the nucleation rate is only determined by temperature if all the other quantities are known. It should be noted that equation (9) holds when the effect of vapor pressure is ignored. This is a reasonable approximation for liquid hydrogen at low temperatures when it is in equilibrium with its vapor pressure[8]. In addition，the diameter of the droplet (38 μm) is big enough that the surface effect can also be neglected.

G. M. Seidel et al. have measured the nucleation rate of supercooled liquid hydrogen at an applied helium pressure of 15×10^5 Pa，and the result is shown in Fig. 3(curve A)[9]. Based on this data，theoretical rates for classical nucleation of hydrogen at zero pressure was calculated and also shown in Fig. 3(curve B). As for the pellet target，the helium pressure in the DFC is only 1500 Pa，so the nucleation rate will be more close to that at zero

pressure.

Besides，the nucleation rate Γ is defined as $\Gamma = 1/(V\tau)$，where V is the droplet volume and τ is the lifetime of droplet before freezing. For a 38 μm droplet，its volume is 2.873×10^{-8} cm^3. If the lifetime of the droplet is as short as 1 ms，the needed nucleation rate will be as large as 3.48×10^{11} cm^{-3}/s. It will correspond to a transition temperature of 10.16 and 9.4 K in curve A and B，respectively.

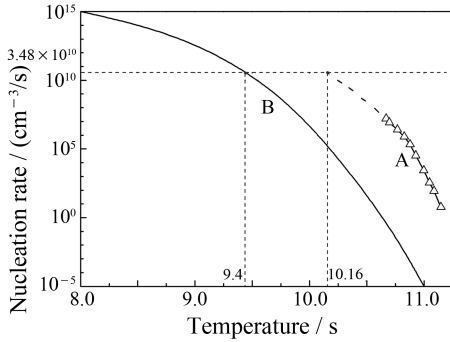
Fig. 3　The nucleation rates of liquid hydrogen. All dates are taken from Ref.[9].

As stated previously，the nucleation of the supercooled hydrogen droplets is just sensitive to their temperature under suitable assumptions. If the droplet temperature reaches a lower value，the higher nucleation rate that corresponds to it will make the droplets freeze in a shorter time. Then we'll make some thermodynamic simulations to see how the droplet temperature changes with the working parameters，and try to find out whether the droplets can nucleate in the DFC.

4　Thermodynamic Simulations at Different Working Parameters

The working parameters of the hydrogen droplets in the DFC are mainly the droplet size，droplet speed，hydrogen vapor pressure，helium pressure，and the temperature of the background gas. As a result of the simulations，we find that the droplet size and speed have little influence on the droplet temperature and thus don't discuss them here.

4.1　The influence of the background gas temperature on the droplet temperature in supercooling condition

Normally，cooled helium gas is used as background gas inside the DFC. Considering the cooling mechanism of the cold head，the temperature of the helium gas is usually higher than that of the initial hydrogen droplet(14.1 K). On this premise，we change the temperature of the background gas while all the other conditions keep unchanged. The results of the calculations are shown in Fig. 4.
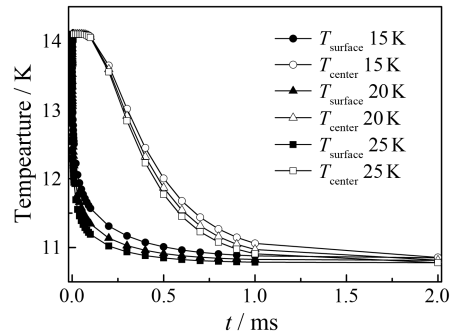

Fig. 4　The droplet temperature evolutions at different background gas temperatures.

We can see that the equilibrium temperature of the droplet decreases with the increase of the background gas temperature，but it's quite limited. No matter the temperature is set to 15，20 or 25 K，the final equilibrium temperature of the droplet is always around 10.8 K.

Since changing the background gas temperature is nearly not beneficial to the cooling of hydrogen droplets，we intend to keep it as low as possible for the following reason：The higher the temperature of the background gas，the greater the mass loss. Take 50 K for example，the droplets will loss 80% of their initial mass in 2 ms. It's possible for the droplets to disappear prior to the vacuum injection. Normally，a temperature around 15 K is suitable for this situation.

4.2　The influence of the background gas pressure on the droplet temperature in supercooling condition

During the operation of pellet target，the flow of helium is manually regulated by the total DFC

pressure. Now we only change the helium gas pressure while keep the temperature of background gas at 15 K and hydrogen vapor pressure at 800 Pa unchanged. As shown in Fig. 5，we can easily find that the equilibrium temperature of the droplet decreases obviously as the background gas pressure decreases. The droplet will reach an equilibrium temperature of 11. 06 K at a pressure of 3000 Pa，and 10. 77 K at 1000 Pa.

Now that the lower background gas pressure is beneficial for the droplets to reach a lower temperature，can we switch off the helium gas? The answer is no. In the real experimental situations，when the pressure of the background gas is lower than 1000 Pa，we find the nozzle is much easier to be frozen，and thus hinder the stable generation of the droplets. Therefore，it's suggested to set the helium gas pressure at 1000 Pa and no more less.
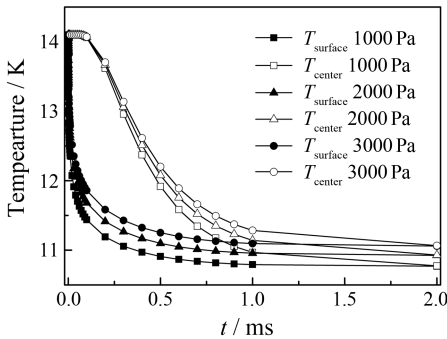

Fig. 5 The droplet temperature evolutions at different background gas pressures.

4.3 The influence of the hydrogen vapor pressure in background gas on the droplet temperature in supercooling conditions

As mentioned above，the ambient gas in the DFC is actually a mixture of helium gas and hydrogen vapor. It was found that when the helium supply was shut off temporarily and the generation of droplets was still fortunately operated in the DFC，the ambient gas was only the hydrogen vapor because the residual gas was not pumped off instantaneously. The hydrogen vapor pressure would arrive at the homeostasis with the coaction of the

droplet evaporation and exhaust of vacuum injection capillary. The pressure of this residual gas was measured to be 800 Pa and it could be treated as the partial pressure of hydrogen vapor in the real experimental runs.

If we find some methods to change the partial pressure of hydrogen vapor，such as changing the inner diameter of the injection capillary，what's the evolution of droplet temperature? In the simulations，we only change the pressure of hydrogen vapor while keep the temperature of background gas at 15 K and the helium gas pressure at 1000 Pa. The calculation results are shown in Fig. 6. It's found that the equilibrium temperature of the droplets changes with the hydrogen vapor pressure synchronously. The smaller the hydrogen vapor pressure，the lower the droplets equilibrium temperature. It is noteworthy that the droplet equilibrium temperature will reach to 9. 5 K at 100 Pa.
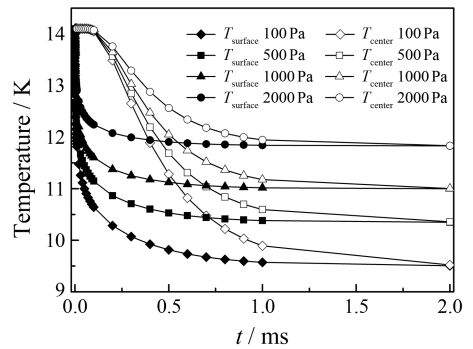

Fig. 6 The droplet temperature evolutions at different vapor pressures.

According to experimental Liquid-Vapor equation for H_2[10]，we know that the saturated vapor pressure of liquid hydrogen has a direct relationship with its temperature. When the hydrogen droplets are injected into the DFC，ambient vapor pressure lower than their saturated vapor pressure leads to the process of gasification and drop of temperature. Once the hydrogen droplets arrive at the dynamic equilibrium，they can't be cooled any more and will maintain a constant temperature. In this condition the value of ambient vapor pressure is basically equal to that of the saturated vapor pressure corresponding to current temperature.

That is to say, the liquid hydrogen is in equilibrium with its vapor pressure in the DFC. Neglecting the effect of pressure, we can speculate that the droplets at a temperature of 9.5 K will possibly nucleate within 1ms if curve B in Fig. 3 was correct.

5　Summary and Conclusions

Because of existence of the supercooling, the hydrogen droplets can't freeze prior to vacuum injection. This phenomenon has influenced the survival of the droplet in the capillary and the angular divergence at the end of the capillary. We have analyzed all the factors that may affect the droplet temperature, and concluded that the hydrogen vapor pressure in the DFC is the most prominent one. In order to make the supercooled droplets nucleate in the DFC, the optimal working conditions suggested by theoretic calculation are as follows: the pressure of the helium gas should be as low as possible, so is the pressure of the hydrogen vapor, and the length of the DFC must be extended properly such as 6 cm to make the droplet have enough time to cool down and nucleate. The values of these parameters should be determined experimentally.

The theory about equation (9) was developed for classical fluids, and it is not clear how it should be modified for quantum systems. It assumes that a nucleus grows or shrinks as a result of the random addition or subtraction of individual atoms. Collective motions of the type that are important in quantum fluids are not considered. Lifshitz and Kagan considered the collective motion and discussed the nucleation by thermal fluctuations in quantum fluids[8]. The results for the quantum nucleation rate tells us that the nucleation rate is highest and keep constant at low temperatures ($T < 3$ K). At higher temperatures, the free energy barrier increases and the tunneling rate decreases very rapidly. In the range of 9.5—10.8 K given by the thermodynamic simulation, the quantum effect has little effect on the nucleation rate. Therefore it's a reasonable approximation for the hydrogen droplets under current experimental conditions to be treated as one kind of classical fluids.

References:

[1]　Ekstrom C. Nucl Instr and Meth, 1995, **A362**: 1.

[2]　Ekstrom C, Fridén C J, Jansson A, et al. Nucl Instr and Meth, 1996, **A371**: 572.

[3]　Trostell B. Nucl Instr and Meth, 1995, **A362**: 41.

[4]　Renksizbulut M, Nafziger R, Li X. Chem Eng Sci, 1991, **46**(9): 2351.

[5]　Devarakonda V, Ray A K. Aerosol Science, 2003, **34**: 837.

[6]　Law C K. Prog Energy Combust Sci, 1982, **8**: 171.

[7]　Li Zhankui, Xu Hushan, Zhang Xueying. Science in China Ser, 2005, **G48**(5): 529.

[8]　Maris H J, Seidel G M, Huber T E. J Low Temp Phys, 1983, **G51**: 471.

[9]　Seidel G M, Maris H J, Williams F I B, et al. Phys Rev Lett, 1986, **56**: 2380.

[10]　Souers P C. Cryogenic Hydrogen Date Pertinent to Magnetic Fusion Energy. LLNL Report, UCRL-52628, 1979, 11.

液滴室内的氢液滴超冷条件下的结晶[*]

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摘　要：液滴室内超冷现象的存在使得氢微球在自身温度低于其三相点温度的情况下依然处于液态。这可

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能导致液滴在真空注入过程中发生碎裂。结合液氢的超冷知识，对液滴室内的氢液滴进行了热力学模拟，理论上提出了利于氢液滴尽快冷却成固体小丸的最佳实验条件，即保持液滴室内氦背景气体和氢蒸汽的压强尽可能低，并将液滴室长度延长到 6 cm 以上。

关键词：小丸靶；氢液滴；超冷；结晶