Nucleation of crystals from their liquid phase

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Abstract

Liquids can be supercooled below their melting temperature T_m or pressurized above their melting pressure P_m. Many authors relate the maximum degree of supercooling—or overpressurization—to a value of the liquid–solid interfacial tension by using the standard theory of nucleation. The main goal of this review is to examine whether this relation is justified or not. We consider general arguments and two main examples: liquid helium which is simple and pure, consequently a model system, and liquid water which is complex but ubiquitous. ***To cite this article: S. Balibar, F. Caupin, C. R. Physique 7 (2006).***
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Résumé

Nucléation des cristaux à partir de leur phase liquide. Un liquide peut être surfondu en-dessous de la température d'équilibre T_m avec sa phase solide ou comprimé au-dessus de la pression d'équilibre P_m correspondante. De nombreux auteurs relient le degré de surfusion (ou de surpression) maximal d'un liquide à une valeur de la tension interfaciale liquide–solide en utilisant la théorie standard de la nucléation. Le but principal de cette revue est d'examiner dans quelle mesure cette relation est justifiée. Nous passons en revue différents arguments généraux et considérons principalement deux exemples : l'hélium liquide qui est pur et simple donc un système modèle, et l'eau qui est un liquide complexe mais omniprésent. ***Pour citer cet article : S. Balibar, F. Caupin, C. R. Physique 7 (2006).***
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1. Introduction

For simplicity, let us consider pure matter in three dimensions. The liquid–solid transition is discontinuous, that is "first order" in the Ehrenfest classification. As a consequence, there is an equilibrium line $T_m(P)$ or $P_m(T)$ in the phase diagram, the "melting line" where the liquid and solid phases can be in equilibrium with a well defined interface between them.[1] The liquid–solid interface has a free energy per unit area σ, also called the interfacial tension, which is non-zero.

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[1] The reason why it is called "melting" and not "crystallization" line is probably that supercooling liquids is much easier to observe than the reverse phenomenon, overheating of solid phases. For example, water can be supercooled down to about 232 K but ice cannot be overheated above 273 K. The reason for this asymmetry is that liquid water wets perfectly the ice–vapor interface so that, when ice warms up, the liquid water phase usually starts from the ice surface where it is already present. The wetting of solid–vapor interfaces by their liquid phase is an almost universal property.

For the transition from liquid to solid to take place, a first nucleus of the solid phase has to appear somewhere and this implies the formation of a liquid–solid interface with a non-zero area, consequently a certain cost in interfacial energy. This is, of course, the origin of an energy barrier against the nucleation of the solid from the liquid, and the reason why, for a certain time, liquids can exist in a metastable state in the region of the phase diagram where the stable state is the solid. Since, in a pure system, the temperature T and the pressure P are the two independent variables governing the thermodynamics, the metastability of liquids with respect to their solid phase can be studied not only at constant P and at $T < T_m$ (as is often the case) but equivalently at constant T and at $P > P_m$ as in recent studies of liquid helium [1].

In very pure systems where one carefully avoids nucleation on various defects, especially at walls containing the liquid, a large degree of supercooling—or overpressurization—can be achieved. For example, liquid water can be supercooled down to 232 K $= -41\,°C$ [2–4]. The main purpose of this review is to examine if a simple relation exists between the degree of supercooling and the interfacial tension σ. By doing so, we will distinguish homogeneous nucleation, an intrinsic property of the liquid, from heterogeneous nucleation which occurs on defects, walls or impurities. We will also consider the difficulties encountered when trying to improve the standard theory of nucleation which assumes that the solid–liquid interface is thin compared to the nucleus radius (see the introduction by H.J. Maris in this issue [5]). Since it looks impossible to review all measurements of the nucleation of solids from their liquid phase, we have chosen to focus on water which is complex and shows several anomalies but is ubiquitous, and on helium which is pure and simple, shows some interesting quantum properties and offers perspectives for a better understanding of solid nucleation in the future.

2. The standard theory

As explained by Landau and Lifshitz [6] and by Maris in the introductory paper of this issue [5], the standard nucleation theory considers homogeneous nucleation. It is assumed to start with a spherical nucleus of radius R whose surface energy per unit area is the same as for a macroscopic interface at the liquid–solid equilibrium, i.e. the interfacial tension σ. Let us start with a liquid at a temperature T and at a pressure $P > P_m(T)$. For a small system, the nucleation rate would depend on whether it takes place at constant volume, mass, pressure or number of particles. However, as explained by Wu et al. [7] among others, there is no difference in the thermodynamic limit, i.e. for a large system. The free energy of the nucleus writes:

$$F(R) = 4\pi R^2 \sigma - (4/3)\pi R^3 \Delta P \qquad (1)$$

where $\Delta P = (P_n - P)$, P_n being the pressure inside the nucleus. Eq. (1) shows the existence of a maximum in $F(R)$ which occurs at the critical radius

$$R_c = \frac{2\sigma}{\Delta P} \qquad (2)$$

Away from $R = R_c$, nuclei are not in mechanical equilibrium, they shrink if $R < R_c$ and they grow if $R > R_c$. The energy barrier against nucleation is

$$E = \frac{16\pi \sigma^3}{3\Delta P^2} \qquad (3)$$

The smallest energy barrier is obtained if no dissipation takes place at the interface so that the chemical potentials are the same inside and outside the nucleus [6]. This allows us to estimate P_n. A linear approximation leads to

$$\frac{P_n - P_m}{\rho_C} = \frac{P - P_m}{\rho_L} \qquad (4)$$

where ρ_C and ρ_L are respectively the solid and liquid densities. Consequently

$$\Delta P = (P - P_m)\frac{\rho_C - \rho_L}{\rho_L} \qquad (5)$$

Note that there is a density factor in the above equation, contrary to the similar equation for cavitation [5,8] where the vapor density is negligible compared to the liquid density. If one considered nucleation at a pressure P and at a

temperature T below $T_m(P)$, one could express $F(R)$ in terms of the supercooling $(T_m - T)$ by using the Clausius–Clapeyron equation and write

$$\Delta P = \rho_c \frac{L}{T}(T_m - T) \tag{6}$$

where L is the latent heat of crystallization per unit mass. However, note that the above result uses again a first order expansion which is valid when nucleation takes place close the melting line although it takes place far from it when it is homogeneous.

Finally, the standard theory writes the nucleation rate per unit volume and time as

$$\Gamma = \Gamma_0 \exp\left(-\frac{E}{k_B T}\right) \tag{7}$$

where the prefactor Γ_0 in front of the Boltzmann factor is the product of an attempt frequency Ω by a density of independent sites which is of order $1/V_c$, the inverse volume of the critical nucleus ($V_c = 4\pi R_c^3/3$).

The attempt frequency is the frequency at which the system tries to pass over the energy barrier. A rigorous calculation of it requires a kinetic theory which is difficult. In the particular case of the condensation of a vapor, Ω has been calculated by using attachment and detachment rates of atoms—or molecules—to nuclei [9]. However, in the case of crystallization, such an approach does not look rigorous enough [5]. If one neglects dissipation, Ω can be approximated by the inverse of a typical frequency in the system, for example $k_B T/h$. It is somewhat surprising to find Planck's constant h in the calculation of a classical process but $k_B T/h$ is the typical frequency of fluctuations in a system at temperature T. One could perhaps replace $k_B T/h$ by the ratio c/R_c of the sound velocity to the critical radius. Fortunately, the nucleation rate is dominated by the Arrhenius factor which varies exponentially with the departure from equilibrium ΔP, so that an error on the prefactor estimation, even by a few orders of magnitude—does not change very much the calculation of the supercooling at which the nucleation probability is of order one. For crystallization in a highly viscous liquid or a glass, where dissipation can obviously not be neglected, Turnbull and Fisher [10] have proposed that Ω equals $(Nk_B T/h)\exp(-\Phi/k_B T)$ where N is the number density of atoms or molecules in the liquid and Φ is an activation energy describing the temperature dependence of diffusion in the liquid. According to Turnbull's expression, when a liquid is cooled down, the prefactor may be very small if $(\Phi/k_B T)$ is large: instead of nucleation, one observes a glass transition, because the dynamics of the system slows down to nearly zero. However, this expression looks incorrect in limiting cases, as explained by Maris [5].

Given the nucleation rate from Eq. (7), one can calculate the probability Σ that nucleation occurs in a volume V and a time τ. A simple integration leads to the result

$$\Sigma = 1 - \exp\left[-\Gamma_0 V\tau \exp(-E/k_B T)\right] \tag{8}$$

so that, if one defines the nucleation threshold as the pressure P_c at which the crystallization probability is 0.5, one finds

$$P_c = P_m + \frac{\rho_L}{\rho_C - \rho_L}\left(\frac{16\pi\sigma^3}{3k_B T \ln(\Gamma_0 V\tau/\ln 2)}\right)^{1/2} \tag{9}$$

If, instead of a pressure threshold one estimated a temperature threshold, i.e. a maximum degree of supercooling, one could use again the Clausius–Clapeyron relation and find:

$$T = T_m - \frac{T}{\rho_C L}\left(\frac{16\pi\sigma^3}{3k_B T \ln(\Gamma_0 V\tau/\ln 2)}\right)^{1/2} \tag{10}$$

Note that, as T decreases, the nucleation barrier decreases because the departure from equilibrium increases, but the amplitude of thermal fluctuations also decreases. Close to T_m, the most important effect is the decrease of E, so that the nucleation probability increases. This is sometimes presented by chemists as a "negative activation energy" [11]. However, this is a misinterpretation; the activation energy is always positive but it decreases with the departure from T_m. Close to $T = 0$, the decrease of thermal fluctuations may force the nucleation probability to decrease. As a consequence, there is an interesting possibility that a liquid could be supercooled down to $T = 0$. This was analyzed by Maris et al. [12] in the case of liquid hydrogen because it would open the way to a study of its superfluidity. They noticed that the nucleation probability has a maximum at some intermediate temperature where
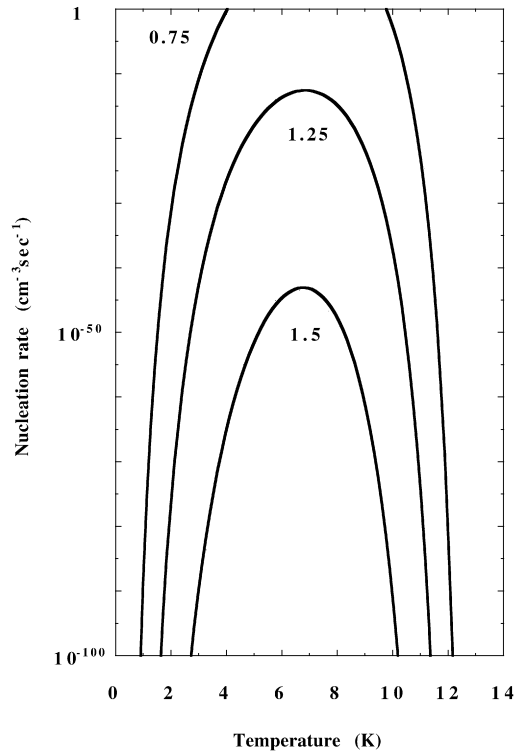
Fig. 1. As calculated by Maris [12], the nucleation rate of hydrogen crystals shows a maximum as a function of temperature. This is because, as temperature decreases, the energy difference between the solid and the crystal increases but the amplitude of thermal fluctuations decreases. The maximum rate depends on the value of the solid–liquid interfacial tension σ (from 0.75 to 1.5 erg/cm^2). If σ were large enough, it would be possible to supercool liquid hydrogen down to absolute zero, but nucleation experiments by Seidel et al. [13] showed that $\sigma = 0.87$ erg/cm^2, a small value.

the activation energy keeps decreasing with T but the decrease of thermal fluctuations becomes the dominant effect (see Fig. 1). If the surface tension σ is large enough, or the product $V\tau$ small enough, the maximum probability can be much smaller than one, in which case it appears possible to supercool a liquid down to very low temperatures.

Eq. (9) predicts that, in the limit where T tends to zero, the crystallization pressure should diverge proportionally to $T^{-1/2}$. This cannot be true because, at some temperature T^{cr} one expects a crossover to quantum nucleation to occur. The standard nucleation theory was first extended to the quantum case by Lifshitz and Kagan [14]. They found a quantum nucleation rate

$$\Gamma^Q = \Gamma_0^Q \exp\left(-\frac{135\sqrt{6}\pi^2\sigma^4\rho_L^{1/2}}{16\hbar\Delta P^{7/2}}\right) \tag{11}$$

The calculation of the quantum prefactor is very difficult. In the frame of the standard theory, the energy barrier depends on one variable only, the radius of the nucleus. In the one dimensional Kramers problem of one particle escaping from a potential well $V(x)$ showing a barrier at $x = x_b$, Γ_0^Q was shown to be proportional to the curvature $V''(x_b)$ [15–17]. Here, one would thus expect the prefactor to be proportional to $E''(R_c)$. However, as we shall see now, this might be wrong for a continuous system such as a supercooled liquid which does not depend on one variable only.

3. Objections to the standard theory

The first objection to the standard theory concerns the use of a macroscopic quantity—the interfacial tension σ—for the description of the nucleus which is usually of microscopic size. As explained by Maris [5], the typical nucleus size is 1 nm, comparable to the thickness of the liquid–solid interface. As a consequence, it is likely that the minimization

of the nucleus energy requires that the density profile and crystalline order at the nucleus surface are different from what they are at the surface of a macroscopic crystal. Even the crystalline structure inside the nucleus can be different from that of the macroscopic crystal. For example, Kelton et al. [18] have shown the influence of local icosahedral order on the nucleation barrier. Furthermore, the curvature of the nucleus surface is large while σ describes a flat surface. Finally, since neither the liquid pressure P nor the nucleus pressure P_n is equal to the melting pressure P_m, a rigorous theory should account for possible variations of the surface energy with pressure. Equivalently in terms of temperature, the nucleation temperature T is rather far from the melting temperature T_m in the case of homogeneous nucleation and a temperature variation of σ should be considered. In other words, far from equilibrium, the use of an equilibrium quantity is not justified.

A further objection to the standard theory is the possible existence of instabilities such as spinodal lines in the phase diagram where the energy barrier vanishes. The existence of a liquid–gas spinodal was shown to be essential for the understanding of cavitation, especially in liquid helium [19,20,5,8]. Speedy [21] has proposed the existence of a liquid–solid spinodal line in water near $-45\,°C$ to explain the temperature variation of thermodynamic quantities like the specific heat and the thermal expansion coefficient in supercooled water. For Helium, it has been predicted that the metastability region of the liquid phase is limited at high pressure by an instability line where phonons with a wave vector equal to the interatomic spacing become soft. In Gallium, the neutron scattering experiments by Bosio and Windsor [22] indicated the existence of a spinodal line at 150 K, about half the melting temperature $T_m = 303$ K. However, the existence of a liquid–solid spinodal limit is not demonstrated in the general case.

As explained by Maris in this issue [5], the standard theory of nucleation can be significantly improved by using density functionals. Density functional theories are examples of field theories and the description of crystalline phases requires the introduction of other parameters such as the amplitude of Fourier components of the one particle density field $\rho(r)$ [23–27]. This makes the theory even more difficult of course. Note that, even in the simpler case of cavitation [5,8], the energy depends on the configuration whose space is multidimensional. The nucleus energy is not a function of a single variable (the radius R) as assumed in the standard theory. At least the width of the density profile at the nucleus surface is important. Here, there are several profiles at the interface.

Fourier components of the one particle density field $\rho(r)$ were first used by Ramakrishnan and Yussouff [23] in their theory of freezing. Harrowell and Oxtoby [24,28] extended this method to the calculation of the nucleation barrier. Further developments have been published by Shih et al. [26] among others. Details can be found in the lectures published by Oxtoby [25] in 1991 and in the more recent review by Wu et al. [7]. Of particular interest is the discussion by Granasy et al. [27] of the dependence of the interfacial energy on the nucleus curvature radius. Very recently the density functional approach was modified by Lutsko in order to avoid the overlap of the hard cores of atoms, a possible source of errors in previous theories [29]. Both Harrowell and Lutsko found energy barriers larger than with the standard theory, as if interfacial energies were larger than at equilibrium, either because of some temperature dependence or because of some curvature dependence.

In fact, using the standard theory to predict a nucleation temperature or pressure for crystals in a metastable liquid is usually impossible for a more simple reason: the surface tension σ is not accurately known, except in ^{4}He where it was measured thanks to the existence of crystallization waves [30]. As a consequence, instead of predicting the nucleation threshold from the knowledge of σ, the study of nucleation is commonly used to measure σ. For this, one has first to make sure that nucleation is indeed homogeneous and it is not easy. Moreover, the objections to the standard theory are so strong and numerous that measuring interfacial tensions from nucleation measurements cannot be rigorous nor accurate if it is derived from standard equations; only an order of magnitude of σ can be obtained. In the next sections, we will consider mainly two examples: water and liquid helium. As we shall see, they illustrate the above difficulties.

4. Water

There has been many attempts to measure the maximum supercooling of water [31,27]. Among all of them, two different types of experiments have shown particularly large supercoolings.

The first type uses a Wilson chamber where water droplets levitate as a fog at variable temperature. The freezing of droplets is observed visually. This was done by Cwilong [2] followed by Fournier d'Albe [3]. Both of them reached $-41\,°C$. According to Mossop [32], the typical drop size in these experiments was 1 µm. Cwilong used ultrapure
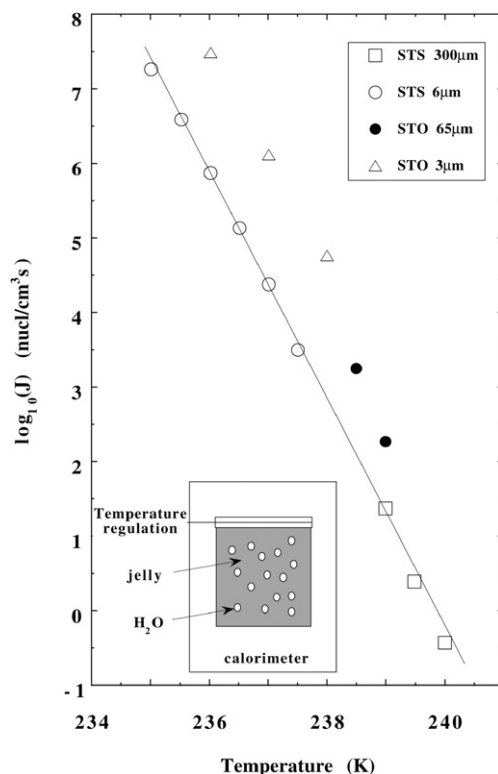
Fig. 2. Taborek [4] measured the rate of nucleation of ice in an emulsion of water droplets with petroleum jelly and two different surfactants (STS or STO). In the case of STS, the rate was found independent of droplet size, a proof of homogeneous nucleation. From the exponential temperature dependence, the standard theory of nucleation was used to extract the value of the ice/water interfacial energy.

water in clean air and found that, when using ordinary air to simulate real clouds, crystallization occurred at $-32\,°C$, indicating heterogeneous nucleation.

Taborek [4] used an emulsion of water droplets which were stabilized in an oil bath by using two different kinds of surfactants, sorbitan tristearate (STS) or sorbitan trioleate (STO). When using STO, the nucleation threshold was found to depend on the droplet size but not when using STS where a larger supercooling was also reached. Consequently, Taborek assumed that, when using STS, the oil–STS–water interface did not play any role in the nucleation of ice which was homogeneous in the bulk of the liquid. As in the fogs studied by Cwilong and by Fournier d'Albe, the division of the water sample had the great advantage that any droplet with some remnant impurity showed nucleation at smaller undercooling and could be eliminated from most of the others which were kept for the final study. When studying the homogeneous nucleation of solid-H_2, Seidel et al. also divided their liquid-H_2 sample into small droplets [13]. Taborek's measurement was based on the variation of the thermal regulation power due to the release of the latent heat of crystallization. This detection method allowed measurements of the nucleation rate over 7 orders of magnitude, in a temperature range from 240 to 235 K. He used the standard theory to extract the ice/water interfacial tension and found $0.27 < \sigma < 0.28$. A more careful analysis lead him to the conclusion that there was a slight temperature dependence, a better fit of his data being obtained with $\sigma(236\,K) = 28.3\,mJ^2$ and $d\sigma/dT = 0.1\,mJ/m^2\,K$. From this temperature dependence, he estimated $\sigma(273\,K) = 31.9\,mJ/m^2$.

In 1985, Taborek considered that his value of $\sigma(273\,K)$ was consistent with other measurements but, in our opinion, this statement deserves some comments. Hardy [33] obtained σ by measuring the shape of grain boundary grooves at the ice/water interface in a temperature gradient. Hardy found $29.1 \pm 0.8\,mJ/m^2$. Skapski et al. [34] measured the displacement of the melting temperature of ice in a tube and used the Gibbs–Thomson relation to extract the interfacial tension. They found $\sigma = 44\,mJ/m^2$, a rather different result. In 1998, Hillig [35] measured the minimum pressure which was necessary for freezing to proceed through a filter with calibrated holes. He found $\sigma = 31.7 \pm 2.7\,mJ/m^2$. The latter value is remarkably close to Taborek's result which had been obtained 13 years earlier.

In their review [27], Granasy et al. cite 7 different values of σ ranging from 25 to 44 mJ/m^2. They also present an interesting discussion of the use of nucleation data to deduce interfacial properties. After criticizing the standard theory with arguments similar to the ones above, they use a generalization of density functional theories (a "Cahn–Hilliard" theory or field theory) where the energy is expanded as a function of "*a structural order parameter m that can be interpreted as the normalized Fourier component amplitude of the dominant density waves used in expanding the free energy functional*". Thanks to particular hypotheses on coefficients in their functional, Granasy et al. could reanalyze Taborek's data and extract σ. They found a lower value for σ (0.25 mJ/m^2 at 236 K) but the same dσ/dT = 0.1 mJ/m^2, so that their extrapolation at 273 K was 27.1 ± 0.2 mJ/m^2, also lower than proposed by Taborek. Granasy et al. note that "*the comparison with independent experimental data is hardly conclusive due to the considerable scatter of the latter*". They have an interesting interpretation for the temperature variation of σ. At first sight, a positive value for dσ/dT means a negative surface entropy, and this is a surprising result. An interfacial energy being defined as a difference between two bulk free energies, the interface entropy is not necessarily positive. In fact, Granasy et al. attribute the temperature variation found in nucleation experiment to a variation of the critical radius as a function of temperature, and to a dependence of the nucleus surface energy on this radius.

We also wish to mention the measurement of Kabath et al. [11]. In their experiment, a water droplet is levitated in an electrostatic trap. Since the ice–vapor interface is known to be perfectly wet by liquid water [36], one does not expect ice to nucleate at the liquid–vapor interface but in the liquid inside the droplet. Kabath et al. have verified that their maximum degree of supercooling did not depend on the electric charge of the droplet. Since they found a smaller supercooling than Taborek, they considered that the STS molecules "inhibited" the ice nucleation. This is a surprising statement because the nucleation occurring at the lowest temperature should be the homogeneous one. The maximum degree of supercooling depends weakly on the sample volume and on the time of observation. Taborek's results extrapolate to $-41\,°C$ for 1 micron cubed samples as studied by Cwilong in his Wilson chamber.

Finally, Taborek found that σ "*is a much weaker function of temperature than most other thermodynamic parameters in the metastable region*". Such strong temperature variations are found for the specific heat C_v or the thermal expansion coefficient α and it is an important issue to understand the origin of these strong variations. Taborek showed that there was no spinodal line in the vicinity of $-45\,°C$, contrary to suggestions by Speedy [21]. If the variation of C_v and α were due to the vicinity of a second critical point, as proposed by Stanley et al. [37], there should be no effect on the solid–liquid interfacial tension because the critical point concerns a liquid–liquid transition. Taborek's results are not contradictory either to Debenedetti's hypothesis of some local minimum in the density without critical point nor spinodal line [31]. The possible existence of a critical point is an issue which is not yet settled experimentally and needs further study (see Refs. [8] and [38]).

In summary, it seems well established that liquid water can be supercooled to $-41\,°C$ where homogeneous nucleation of ice occurs. The standard nucleation theory and a more elaborate field theory have been used to deduce a certain value of the ice/water interfacial energy which is probably 30 ± 2 mJ/m^2 for a flat interface at 273 K but which may depend on both temperature and curvature. There are still numerous uncertainties in experiments and in theoretical methods of data analysis, so that no accurate conclusion can be drawn on the whole issue.

5. Liquid helium

Helium is a model system for the study of nucleation for several reasons. First of all, it is liquid at temperatures where nearly all the rest of matter is frozen so that it is easy to purify. In fact it is also superfluid below about 2 K and it flows easily through very fine filters, for example Vycor glass whose typical pore diameter is 70 Å. At such a temperature, everything is frozen and sticks to walls. The only impurity in ^{4}He is its light isotope ^{3}He whose concentration in natural helium is 10^{-7} but can be lowered below 10^{-12} by distillation. Another obvious interest of ^{4}He as a model system is that the atoms are simple with no chemical properties, only a van der Waals interaction and some quantum kinetic energy, so that the thermodynamics is very well established. For example, the equation of state has been calculated by different methods [39,40,19,41,42] which give consistent results, even at negative pressure. In particular, the spinodal limit for the liquid–gas transition is known to be at -9.5 ± 0.1 bar, in agreement with experiments by Caupin et al. [19].

At low pressure, ^{4}He remains liquid down to the absolute zero (see Fig. 3). It crystallizes above 25.3 bar in a hexagonal close packed structure. The dynamics of crystallization and melting is quantum so that it is very fast at low temperature and capillary waves can propagate at the liquid/solid interface [30]. They are named "crystallization
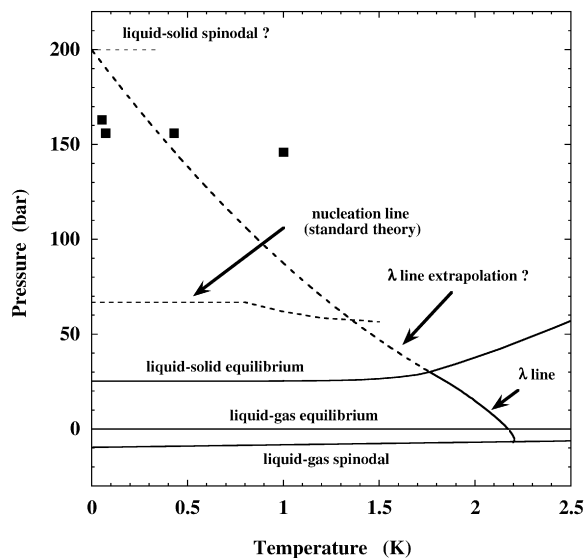
Fig. 3. The phase diagram of ^{4}He. There is no triple point where the gas, liquid and solid phases would meet. Liquid ^{4}He crystallizes above 25.3 bar at low temperature. The liquid–gas spinodal limit is at -9.5 bar at low temperature. It has been proposed that a liquid–solid spinodal exists around 200 bar. The standard nucleation theory predicts that helium crystals should nucleate at 65 bar but, according to Werner et al. [43] it is possible to overpressurize liquid helium up to 160 bar (black squares). Werner et al. also proposed that the superfluid transition (the λ line) meets the liquid–solid spinodal line at $T = 0$.
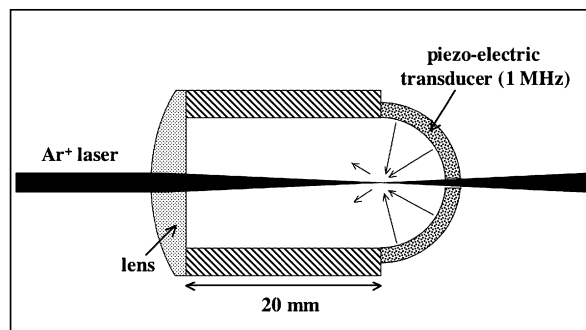

Fig. 4. The experimental setup used by Werner et al. [43] to study homogeneous nucleation. One or two hemispherical transducers are pulsed and generate acoustic waves which are focused by the geometry in the bulk liquid. In the focal region at the center, very large oscillations in pressure can be achieved. Nucleation is detected optically from the transmission of a laser beam through the center.

waves" because they involve no deformation of the crystal, only local growth and melting. Their careful study has provided an accurate value of the interfacial tension which varies from 0.16 to 0.17 mJ/m^2 as a function of orientation (see Ref. [30] and references therein). Liquid ^{4}He is much better known than any other liquid and a nearly ideal candidate for the study of crystal nucleation. We wish to summarize here our results and experiments presently in progress.

In order to isolate our sample from the influence of walls we have used the same acoustic technique which was introduced by Nissen [44], followed by Hall and Maris [45] and by our group [46,19] for the study of cavitation. A hemispherical piezoelectric transducer is pulsed at resonance in order to emit a burst of ultrasound which is focused by the geometry (see Fig. 4). At the center, the sound amplitude can be as high as 10 to 200 bar, depending on the static pressure in the cell. At a frequency $\nu = 1$ MHz, the wavelength of sound in liquid helium at P_m is 366 µm so that nucleation is observed in a volume $V \approx (\lambda/10)^3 \approx 4 \times 10^{-5}$ cm^3 during a short time of order $1/10\nu = 10^{-7}$ s [19].

In ordinary cells, crystals nucleate a few millibars only above the melting pressure, a very small overpressure [47–49]. If we estimate the activation energy for homogeneous nucleation at $P_m + 3$ mbar by using the standard theory with the known value of σ, one finds 10^{10} K, which is absurd. On ordinary walls like glass or copper, the contact angle of the liquid–solid interface is known to be 135 degrees [30] so that some cosine factors in the expression of the energy (see the articles by Maris and by Caupin in this issue [5,8]) are not sufficient to explain a reduction by so many orders of magnitude. Balibar et al. [50] proposed that nucleation takes place on particular dust particles which are known to be perfectly wet by ^{4}He crystals, such as graphite. These particles need to be larger than the critical radius for homogeneous nucleation at $P_m + 3$ mbar, which is typically 10 microns.

In a first series of experiments, Chavanne et al. [51] calibrated their sound waves by focusing them on a glass plate. As we shall see, this allowed them to study heterogeneous nucleation before progressing towards homogeneous nucleation. Chavanne et al. could show that, on their glass plate, crystals nucleated 4.3 bar above P_m (Fig. 5). This overpressure is larger than in ordinary cells by 3 orders of magnitude but still not large enough for homogeneous nucleation to take place. Indeed, if one uses the standard theory to estimate an order of magnitude of the activation
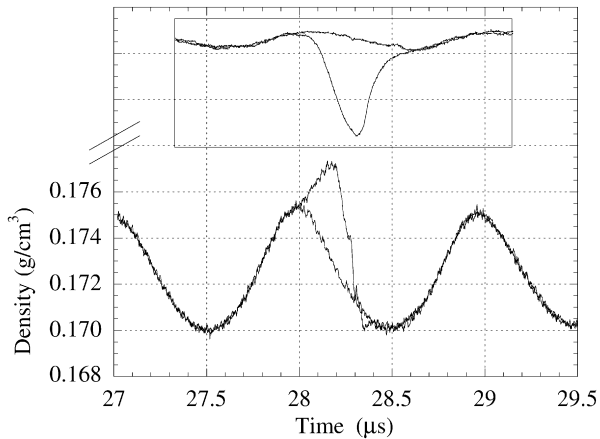
Fig. 5. The detection of crystal nucleation in the experiment by Chavanne et al. [51]. A high intensity acoustic wave is focused on a glass plate where one measures both the reflexion and the transmission of light which both depend on the local density. The light reflected at the acoustic focus shows either a modulation due to the acoustic wave only or an additional signal due to the nucleation of crystals on the glass plate. The inset in the upper part of the figure shows similar signals for the transmitted light.
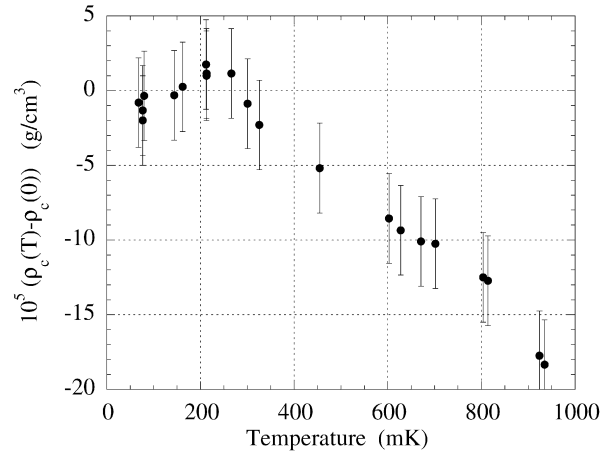

Fig. 6. The temperature dependence of the threshold pressure at which helium crystals nucleate on a glass plate [51]. At low temperature there is a quantum regime which is roughly independent of temperature. Above 300 mK, the threshold pressure decreases as expected for classical nucleation which depends on the amplitude of thermal fluctuations.

energy for homogeneous nucleation at $P_m + 4.3$ mbar, one finds 3000 K. This is much too large since nucleation was observed below 1 K. Chavanne et al. studied the nucleation probability as a function of pressure and the temperature variation of the nucleation threshold pressure. From these two sets of measurements they concluded that the activation energy was about $6k_B T$ and that the number of nucleation sites was of order 1. They concluded that nucleation was heterogeneous, taking place on one favorable defect of the glass plate where the sound wave was focused. Once more, if one supposed a flat glass surface and a crystalline nucleus with a 135 degrees contact angle on it, it would not give the right order of magnitude for the activation energy which is too small by more than 3 orders of magnitude. One has to assume that the glass wall had defects with particular shapes, and probably to calculate the effect of the van der Waals attraction by the glass in the region of this defect in order to obtain the right magnitude of the activation energy. It is likely that, given the low value of the activation energy, the nucleus which forms on the glass plate is of atomic size.

Chavanne's measurements illustrate the fundamental difficulty in the understanding of heterogeneous nucleation: one does not know the shape of the particular defect which triggers nucleation, nor its chemical composition. Finally, Chavanne's experiment showed the existence of a temperature independent regime below 300 mK (see Fig. 6) which is likely to be due to quantum nucleation. This temperature is close to the crossover temperature from a quantum to a classical regime which was predicted by several authors for homogeneous nucleation [40,52].

In a more recent series of experiments in our group, Werner et al. [43] removed the glass plate and focused the sound wave in the bulk of liquid helium. Without glass plate the calibration of the acoustic wave was difficult in Werner's experiment. The transducers are excited with a known voltage which is difficult to relate to the maximum pressure reached at the acoustic focus. For this they studied nucleation as a function of the static pressure P_{stat} in their cell. They observed nucleation of objects which they interpreted as bubbles because their nucleation pressure was an increasing function of P_{stat}. Since this function was linear, and since bubbles are known to nucleate at -9.4 bar [19], they could calibrate the wave amplitude as a function of the exciting voltage. This analysis led them to conclude that helium remained in a metastable liquid state up to 160 bar. This very large pressure was unexpected since the standard theory predicted a nucleation threshold of 65 bar from the value of σ at the liquid–solid equilibrium. As we shall see below, Werner's analysis was questioned by the later experiment by Ishiguro et al. [1] but it asked several interesting questions.

Maris and Caupin [53] proposed that the interfacial energy σ could be an increasing function of P. If the deformation of the lattice in the interface region were constant, the elastic part of σ should increase with P since the elastic

constants increase with P. If true, this could shift the nucleation threshold of crystals up to pressures much higher than 65 bar. It was also noticed that an instability could occur near 200 bar because of the possible vanishing of rotons at this pressure. In superfluid helium, there are well defined elementary excitations which are phonons. The phonon spectrum shows a minimum at a wavevector $(2\pi/a)$ where a is the average distance between nearest neighbors in the liquid. It was shown by Feynman [54] that the existence of this minimum is the consequence of a peak in the structure factor also increases which is itself a sign of local order. As P increases, the local order increases, consequently the magnitude of the peak in the structure factor, and the roton minimum energy decreases. By extrapolating a density functional introduced by Dalfovo et al. [55], Maris [56] estimated that, near 200 bar, the roton minimum should reach zero and the roton mode become soft. This is a mechanism for an instability which was first considered by Schneider and Enz [57]. It could be considered as a liquid–solid spinodal limit although it does not occur at large wavelength. A Monte Carlo calculation by Vranjes et al. [58] showed that the roton energy is still about 3 K at 250 bar so that the instability probably occurs at larger pressure. Finally, an additional question arose: what is the extrapolation of the superfluid transition line in the metastable liquid phase? The dynamics of the nucleus formation could be very different if liquid helium is a viscous normal liquid so that crossing the superfluid transition could affect the nucleation probability.

Given the above results and new questions, Ishiguro et al. [1] repeated Werner's experiment, this time with two hemispherical transducers glued together to form a sphere. By doing so, they expected to increase the maximum possible pressure they could reach. In this new geometry, they found evidence for large non-linear effects in the sound focusing which made the wave calibration extremely difficult. A careful study of the nucleation time showed that it occurred at the maximum of positive pressure swings so that the observed nucleation events had to be related to crystals, not to bubbles as claimed by Werner et al. Although Werner's geometry was different and non-linear effects clearly also different, Ishiguro's experiment introduces some doubt on Werner's analysis. Ishiguro has discovered that a large amplitude wave travelling in a very pure liquid can crystallize it on its way. This crystallization has to be due to homogeneous nucleation of crystals at high pressure but the exact pressure at which it happens needs to be carefully measured. This could be done by using light scattering inside the acoustic wave. The observation of a Brillouin line should give access to the local velocity of sound which could be converted into a local pressure with the aid of the known equation of state of helium. We thus understand that homogeneous nucleation of crystals in liquid helium is an ongoing study which is not yet completed, although promising.

6. Some other liquids

We have already mentioned Seidel's experiment on the crystallization of hydrogen. In their experiment, liquid-H_2 droplets floated in a helium gas with adjusted density. The hydrostatic equilibrium was such that liquid droplets floated at a higher level than solid droplets so that crystallization could be easily seen. They used the standard theory to deduce the liquid–solid interfacial energy σ. Unfortunately, they found that σ was not large enough for supercooling to be possible down to $T = 0$. With a slightly larger value, it could have been possible to study the superfluidity of metastable liquid H_2.

Vinet et al. [59] have reviewed the correlation between interfacial energies and crystal nucleation in metals. According to Turnbull and Cech [60], the maximum degree of supercooling ΔT is roughly equal to 0.18 T_m. However, Vinet et al. show supercooling values ranging from 0.13 to 0.50 T_m. They used nucleation experiments together with the standard theory to estimate the solid–liquid interfacial energies of metals and then examined the ratio β of the liquid–solid interfacial energy σ_{SL} to the liquid–vapor interfacial energy σ_{LV}. They found that β oscillates between 0.11 and 0.17 according to the position of elements in the periodic table.

Fokin et al. [61] has reviewed the homogeneous nucleation of crystals in silicate glasses, an issue of great practical interest. They found "dramatic discrepancies" between measured nucleation rates and rates calculated with the standard theory. They attributed these discrepancies to the bulk properties of the critical nuclei being significantly different from those of the stable phase at the macroscopic scale. One specific problem in glasses is the importance of elastic stress effects which favor the nucleation of structures which have a density close to that of the glass and are not necessarily the stable macroscopic structure. According to them, the whole issue of crystal nucleation in glasses is likely to remain "*an interesting subject for fundamental and applied research for a long time*".

7. Conclusion

This review is necessarily incomplete. The literature on this subject is extremely large. We first focused on water where nucleation studies bring important information for the standing controversies about its structure. We then considered helium which is a simpler liquid but where nucleation of crystals is not yet understood. In our opinion, both water and helium studies illustrate the fundamental difficulties in the use of nucleation experiments together with the standard nucleation theory to determine the liquid–solid interfacial tension σ. Apart from the difficult problem of avoiding heterogeneous nucleation, it is mainly because homogeneous nucleation occurs very far from equilibrium and at the atomic scale.

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