Nucleation/Nucléation

Introduction to the physics of nucleation

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Abstract

In this introductory article, I review the theory of nucleation by thermal activation and by quantum tunneling. The effect of heterogeneous nucleation at surfaces is discussed and a brief survey of experimental techniques is given. ***To cite this article: H.J. Maris, C. R. Physique 7 (2006).***
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Résumé

Introduction à la physique de la nucléation. Dans cet article introductif, je passe en revue la théorie de la nucléation par activation thermique et par effet tunnel quantique. Je discute les effets de la nucléation hétérogène aux surfaces et je propose un bref survol des techniques expérimentales utilisées. ***Pour citer cet article : H.J. Maris, C. R. Physique 7 (2006).***
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This issue contains a number of reviews all concerning different aspects of nucleation. In this introduction, I briefly summarize the basic theory of nucleation processes and then mention some selected topics of interest. Nucleation means a change in a physical or chemical system that begins within a small region, that is to say, that begins at a nucleus. The very long history of this subject has been reviewed by G.S. Kell [1] who credits Huyghens with having in 1662 performed the first experiments with metastable water under tension. A search of the literature currently finds 52 468 papers with the word nucleation in the title or the abstract. The nucleation process is important in many branches of science ranging from the decay of the false vacuum in the early universe, and to metallurgy, the physics of the atmosphere, and biology.

1. Classical nucleation theory

Let us begin with a review of the relatively simple situation of nucleation in a liquid that is in a state of tension. Let the pressure and temperature of the liquid be P and T, respectively, and let P_0 denote the pressure at which the liquid and vapor are in phase equilibrium when the temperature is T. When a small bubble of vapor is formed in the liquid, there are two contributions to the change in the energy of the system. The energy decreases because the energy

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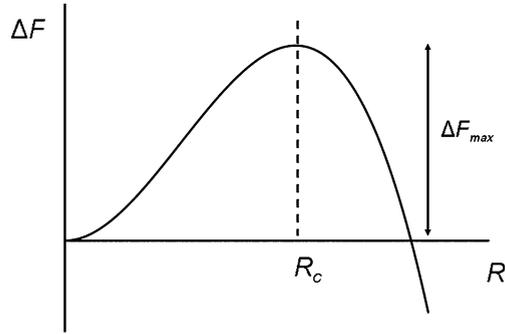
Fig. 1. Energy required to create a spherical bubble of radius R. The energy has a maximum at the critical radius R_c.

per unit volume of vapor is lower than the energy of the liquid but increases because an interface between the liquid and the vapor is created. Since the number of atoms that have changed from liquid to vapor varies as the cube of the radius R of the bubble, whereas the area of the interface goes as R^2, the total energy at first increases with increasing radius before reaching a maximum value at a critical radius R_c, and then decreasing (see Fig. 1). The critical radius can be shown to be [2]

$$R_c = \frac{2\alpha_{LV}}{\delta P} \tag{1}$$

where α_{LV} is the surface energy and $\delta P = P_0 - P$. The maximum value of the energy is

$$\Delta F_{\max} = \frac{16\pi \alpha_{LV}^3}{3(\delta P)^2} \tag{2}$$

This formula assumes that δP is small and takes the molar volume of the liquid to be negligible compared to the molar volume of the vapor [2]. The probability of nucleation of the vapor phase is then

$$\Gamma \propto \exp(-\Delta F_{\max}/kT) \propto \exp\left[-\frac{16\pi \alpha_{LV}^3}{3kT(\delta P)^2}\right] \tag{3}$$

For other phase transitions, we can write the energy of a bubble of the new phase of radius R more generally as

$$\Delta F = 4\pi R^2 \alpha - \frac{4\pi}{3} R^3 f \tag{4}$$

where α is the surface energy per unit area between the original metastable phase and the new stable phase. Then the barrier height is

$$\Delta F_{\max} = \frac{16\pi \alpha^3}{3f^2} \tag{5}$$

The free energy per unit volume f appearing in Eqs. (4) and (5) has a different form for different transitions [2]. For the nucleation of bubbles in a liquid in tension

$$f = \delta P \tag{6}$$

For nucleation of liquid droplets in over pressurized vapor

$$f = \frac{v_G}{v_L}\delta P \tag{7}$$

where v_G and v_L are the molar volumes of the gas and liquid, respectively and now $\delta P = P - P_0$. Using the Clausius–Clapeyron equation, one can also express these results in terms of the temperature δT from the phase equilibrium line, rather than in terms of δP [2]. Thus, for example, the probability of nucleation of liquid droplets in vapor that is at a temperature δT below the liquid–vapor coexistence temperature is

$$\Gamma \propto \exp\left[-\frac{16\pi \alpha_{LV}^3 v_L^2 T}{3kL^2(\delta T)^2}\right] \tag{8}$$

where L is the liquid–vapor latent heat per mole.

To be more precise, we should define the quantity Γ in the above equations to be the probability per unit time and per unit volume that nucleation of a new phase will occur. Thus, to complete the calculation of Γ it is necessary to write

$$\Gamma = \Gamma_0 \exp(-\Delta F_{\max}/kT) \tag{9}$$

and to determine the prefactor Γ_0. Then, if the metastable phase has a volume V, the probability per unit time that nucleation will occur is $V\Gamma$ and the probability that nucleation will not occur within a time τ is

$$\exp(-\Gamma V \tau) \tag{10}$$

One can consider that the prefactor is an attempt frequency per unit time multiplied by the number of places where nucleation can take place 'independently' per unit volume. As a very first approximation, it is natural to take the attempt frequency to be kT/h. For the number of possible places per unit volume, it appears reasonable to take the inverse of the volume of the critical nucleus.

The theory described above is based on the theoretical work of Gibbs [3], Volmer and Weber [4], Becker and Doring [5], and Blander and Katz [6]. There have been many attempts to improve on the simple theory just described and we give here a brief summary of some of these efforts:

(i) In the calculation just described, it is assumed that the degree of supercooling or supersaturation is small so that the difference in the free energy between the metastable phase and the stable phase is linearly proportional to the distance in the P–T plane from the coexistence curve. This is not necessarily a good approximation since, for example, the maximum degree of supercooling of a liquid can often be more than 15% of the equilibrium freezing temperature [7]. However, this limitation can be removed if an estimate can be made of the thermodynamics of the metastable phase. This estimate can be achieved either through a simple extrapolation of the thermodynamics from the temperature–pressure range within which they can be measured or can be based on some more elaborate theory.

(ii) The simple theory is based on the idealization that the critical nucleus consists of a small spherical volume of the new phase within which the thermodynamic properties are identical to those of a macroscopic volume of the new phase. This nucleus is considered to be surrounded by a sharp surface with an energy which is taken to be the area of the surface multiplied by a surface energy per unit area that has been measured in a macroscopic experiment. In general, these assumptions are unrealistic. Consider, for example, the nucleation of bubbles in a liquid that is under tension. Suppose that an experiment is performed to look for nucleation when a tension δP is applied to a volume V of liquid for a time τ. From Eq. (8), we can see that the probability is one half if

$$\Delta F_{\max} = kT \ln(\Gamma_0 V \tau / \ln 2) \tag{11}$$

A typical value of Γ_0 based on the considerations we have already given is $\sim 10^{32}\ \mathrm{cm^{-3}\,s^{-1}}$. Hence, if we take $V = 1\ \mathrm{cm^3}$ and $\tau = 1\ \mathrm{s}$, we see that $\Delta F_{\max} \approx 74kT$ and so from Eq. (2) the critical radius is

$$R_c = \left(\frac{3 \times 74kT}{4\pi \alpha_{\mathrm{LV}}}\right)^{1/2} \tag{12}$$

Now suppose that the sample is water at room temperature. Using the measured value of the surface tension in Eq. (12) gives $r_c = 10$ Å. This radius is thus only a few times the interatomic spacing. Thus, unless the degree of supersaturation or supercooling is very small, the width of the interface is comparable to the radius of the critical nucleus.

The width w of the liquid–vapor interface has been measured for a number of materials [8] and has also been calculated by Monte Carlo [9] and molecular dynamics simulations [10]. One should note that both the experimental determination and the theory of the width are complicated by thermal fluctuations in the position of the surface [11]. Thus, if the density profile of the interface is measured averaged over a large area the profile will be wider than if measured over a small area.

To overcome some of the limitations mentioned in (i) and (ii), one approach is to use a density functional scheme [12–14]. For the liquid–vapor nucleation the first step is to make an estimate of the free energy f per unit volume as

a function of the density. In the range of density in which there is a stable phase, i.e., liquid or vapor, f is taken from experiment. In the density range between the stable phases, f is estimated either by extrapolation from the values of $f(\rho)$ in the stable ranges [13], or from some theoretical model [14]. A term is then added to represent the energy associated with the rapid variation of the density in the vicinity of the interface. The simplest form for this term is

$$\lambda|\nabla\rho|^2 \tag{13}$$

where λ is a constant, although naturally a more elaborate form can be used. Thus, the total energy becomes

$$F = \int \left[f(\rho) + \lambda|\nabla\rho|^2 \right] \mathrm{d}V \tag{14}$$

The integral in this expression is to be taken over the entire volume occupied by the material. However, it is convenient to consider instead a volume of fixed dimensions that contains the region where the nucleus forms, i.e., a fixed volume but not necessarily containing a fixed number of particles. The energy can then be written as an integral over this volume

$$F = \int \left[\phi(\rho, \rho_1) + \lambda|\nabla\rho|^2 \right] \mathrm{d}V \tag{15}$$

where

$$\phi(\rho, \rho_1) = f(\rho) - f(\rho_1) - (\rho - \rho_1)\frac{\mathrm{d}f}{\mathrm{d}\rho}\bigg|_{\rho=\rho_1} \tag{16}$$

and ρ_1 is the density of the initial phase. Within this simplified model, the surface tension can be shown to be [12]

$$\alpha = 2 \int_{\rho_1}^{\rho_2} \sqrt{\lambda\phi}\,\mathrm{d}\rho \tag{17}$$

where ρ_2 is the density of the new phase. Thus the value of λ can be fixed by the requirement that Eq. (17) gives the experimental value for the surface tension. Once this is done the density profile of the critical nucleus can be found from the differential equation

$$\frac{\mathrm{d}^2\rho}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}f}{\mathrm{d}r} = \frac{1}{2\lambda}\frac{\mathrm{d}\phi}{\mathrm{d}\rho} \tag{18}$$

If a more elaborate density-functional theory is used, the calculation of the density profile of the critical nucleus is more complicated [14].

A great advantage of this approach is that it makes allowance for the rather obvious fact that, even in the absence of nucleation, there is a maximum negative pressure that a liquid can sustain. As an example, in Fig. 2 we show an estimate that has been made of the pressure as a function of density for fluid helium at 2.41 K [15]. At this temperature the saturated vapor pressure is $P_{\mathrm{SVP}} = 0.0862$ bars; this corresponds to vapor and liquid densities of $\rho_1 = 0.001838$ and $\rho_2 = 0.14526$ g cm^{-3}, respectively. As the density is decreased starting from ρ_1 the pressure decreases and reaches a maximum negative value of $P_c = -6.28$ bars at a density $\rho_c = 0.10282$ g cm^{-3}. This point is referred to as the spinodal. At the spinodal the sound velocity $v = \sqrt{\mathrm{d}P/\mathrm{d}\rho}$ becomes zero and the fluid becomes unstable against density fluctuations of long wavelength. This means that there is no barrier preventing the formation of the vapor phase. Fig. 3 shows how the energy barrier varies with pressure. The density profile of the critical nucleus is given in Fig. 4 for two selected pressures. It can be seen from these results that the 'thin wall' result for the nucleation barrier becomes increasingly inaccurate as the pressure is lowered toward the spinodal.

This simple density functional theory can be improved through the use of a more accurate expression for the energy associated with a rapid variation in the density [16]. It has also been generalized to apply to the liquid–solid transition [12,17]. In this case it is necessary to include terms involving a parameter η that describes the short range order, i.e., the formation of a periodic density variation characteristic of a crystal. The theory then becomes substantially more complicated since not only are there terms in the energy involving $|\nabla\eta|^2$ but the free energy density f is now a function of both ρ and η. Even if the function $f(\rho, \eta)$ can be estimated, it is no longer possible to determine the magnitude of both the $|\nabla\rho|^2$ and $|\nabla\eta|^2$ terms simply through their connection with the surface tension coefficient.
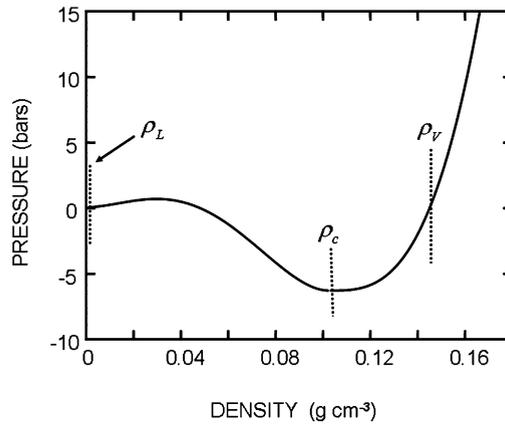
Fig. 2. The pressure of fluid helium-4 at 2.41 K as a function of the density. ρ_V and ρ_L are the densities of the vapor and liquid, respectively, when the liquid and vapor are in equilibrium at the saturated vapor pressure P_{SVP}. For densities below ρ_V and above ρ_L the experimental values of the pressure are shown. The method for estimating the pressure between ρ_V and ρ_L is described in Ref. [15]. The pressure has its largest negative value at the spinodal density ρ_c.
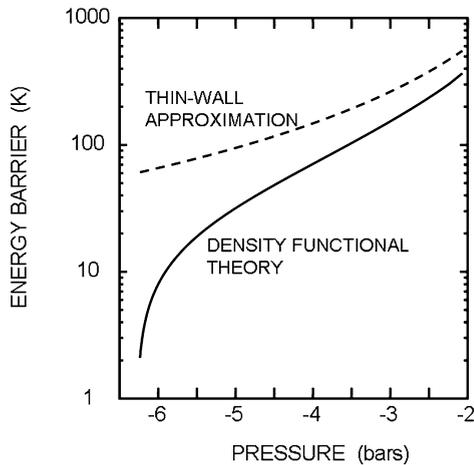
Fig. 3. The nucleation barrier for formation of a vapor bubble in liquid helium-4 at 2.41 K as a function of pressure [15]. The solid curve is calculated using a density-functional approach and the dashed curve is based on thin wall approximation.
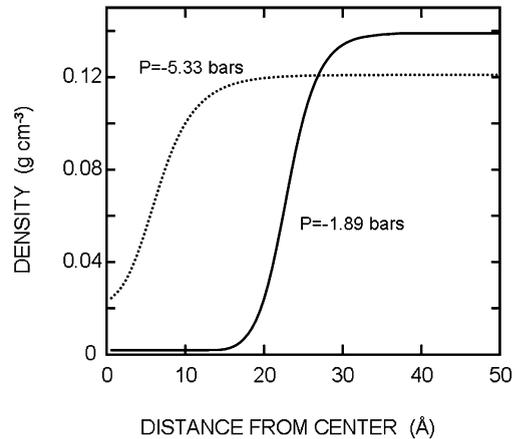
Fig. 4. Density profile of the critical nucleus as a function of the distance r from the center of the bubble [15]. These results are for helium-4 at 2.41 K.

The estimation of the prefactor Γ_0 is much harder. Fisher and Turnbull (FT) [18,19] proposed that the prefactor has the simple form

$$\Gamma_0 = \frac{nkT}{h} \exp(-\Delta f^*/kT) \tag{19}$$

where n is the total number of atoms in the liquid and Δf^* is the energy barrier that an atom has to pass over in order to move away from a bubble growing in a liquid that is under tension. Since the work of Fisher and Turnbull, there have been a large number of other papers concerning the prefactor. While it is possible to treat simplified models in a rigorous way, there is no generally applicable solution to this problem. The FT approach, and much of the more recent work, is based on the idea there always exist in the liquid small nuclei of the new phase; the number of nuclei containing i atoms decreasing with increasing i. Each nucleus loses or gains atoms one at a time and the rate at which nuclei larger than the critical size is calculated. To see the limitations of the FT formula one can consider two limiting cases. On the one hand, if we consider a system in which the energy barrier Δf^* is small compared to kT it is hard to believe that the prefactor can really be as large as nkT/h. On the other hand, it is equally hard to believe that as

Δf^* becomes very large compared to kT, the nucleation rate is zero. For such a liquid the atoms cannot jump over each other but there will still be density fluctuations due to sound modes, i.e., fluctuations which are different from the motion of a single atom. We can argue that one way to nucleate a vapor bubble is for there to be a local fluctuation of the sound modes in which the pressure becomes negative with respect to the spinodal pressure P_c and which extends over a time long enough for a bubble to grow to the size of the critical nucleus. There is certainly a finite probability of such a fluctuation occurring.

This discussion has been limited to transitions in a single component system. Phase transitions in multi-component systems, e.g., metallic alloys, are of enormous practical interest. We have also neglected the possibility that there may be more than one possible transition that can occur [20]. For example, there may be a metastable phase A, and other phases B and C. Even if phase C has lower free energy than B, the system may undergo a transition to B if the interface energy α_{AB} is significantly lower that the energy α_{AC}.

2. Quantum nucleation theory

Nucleation of a second phase can also result from quantum tunneling through the energy barrier just discussed. This process was first discussed in a classic paper by I.M. Lifshitz and Y. Kagan in 1972 (LK) [12]. When a single particle of mass m tunnels through a potential barrier $V(x)$ the tunneling rate, subject to certain conditions, is proportional to the factor

$$\exp[-2I] \tag{20}$$

where I is the WKB integral

$$I = \frac{1}{\hbar} \int_{x_1}^{x_2} \sqrt{2m[V(x) - E]} \, dx \tag{21}$$

and the integral covers the range between x_1 and x_2 in which the potential energy is greater than the total energy. To consider the probability of tunneling through the nucleation barrier, it is therefore necessary to determine what should be used as the effective mass. Before doing this, it is helpful to consider an alternative view of the tunneling process. Instead of integrating over x, we can integrate over time t and consider that at each instant of time the wave function is decaying at a rate equal to the amount by which kinetic plus potential energy exceeds E divided by $\hbar$. Thus, the total decay factor is

$$I = \frac{1}{\hbar} \int_{t_1}^{t_2} \exp\left\{-\left[\frac{1}{2}mv(t)^2 + V(t) - E\right]/\hbar\right\} dt \tag{22}$$

where t_1 and t_2 give the time range over which the particle is within the classically forbidden region with $E < V$, $v(t)$ is the velocity at time t and $V(t)$ is the value of the potential at the location of the particle at time t. The value of the integral will depend on the time-dependence of the velocity of the particle. Clearly if the velocity is very small, the transit time will be large and so I will have a large value. On the other hand, if the particle travels through the barrier fast, the range of time for the integral is short but the integrand is large. If $v(t)$ is chosen so as to minimize the value of this integral one obtains the same result as in Eq. (21). This formulation also applies in higher dimensions [21]. So, for example, consider tunneling in the potential in two dimensions with contours as shown in Fig. 5. The contour lines C_1 and C_2 show where the potential energy $V(x, y)$ equals the total energy of the particle E. There is a minimum in the potential at points A and B. The factor I for tunneling between regions A and B is given by Eq. (22) with the path in the xy-plane and the velocity $v(t)$ chosen so as to minimize the value of the integral. The path can go from any point such as P_1 on the contour C_1 to any point such as P_2 on contour C_2. In order for this to be useful, it is necessary to find a way to determine the path that minimizes the integral. It can be shown that the minimization can be achieved by the following interesting method [22,23]. Consider a classical particle that is moving under the influence of the potential $-V(x, y)$ and that starts with zero kinetic energy at some point on contour line C_1. The particle will follow a complicated trajectory which in most cases will not reach the line C_2. Only for some special positions on C_1 will the particle reach a point on C_2, and for these special positions the particle will return along the trajectory to its original
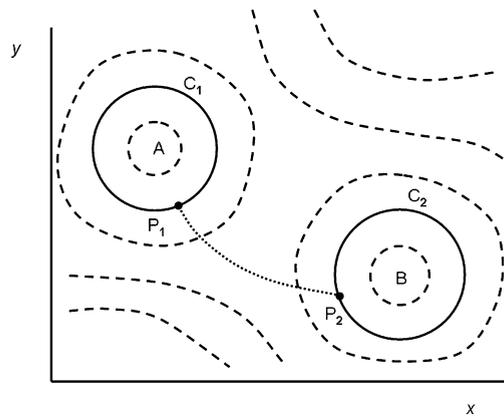
Fig. 5. Quantum tunneling in two dimensions. On the contour lines C_1 and C_2 the potential energy $V(x, y)$ is equal to the total energy E of the particle. A and B denote positions where the potential has a local minimum. The tunneling path can go from any point such as P_1 on the contour C_1 to any point such as P_2 on contour C_2.

position on C_1. It can be shown [22,23] that it is these paths together with the associated velocity $v(t)$ along the path that minimize the integral in Eq. (22). The paths are referred to as bounce trajectories.

The bounce trajectory method also applies to the tunneling of a system that is described by a continuous field rather than by the coordinate of a single particle. Consider, for example, a liquid that is described by a time-dependent density functional which gives the acceleration of the liquid at point $\vec{r}$ in the very general form

$$\frac{\partial \vec{v}(\vec{r})}{\partial t} = \int g(\vec{r} - \vec{r}')\rho(\vec{r}')\,\mathrm{d}^3\vec{r}' \tag{23}$$

The rate of change of the density will be governed by the conservation equation

$$\frac{\partial \rho}{\partial t} + \mathrm{div}(\rho \vec{v}) = 0 \tag{24}$$

To calculate I for nucleation of a bubble in liquid at negative pressure, we start with the liquid in a state of uniform density ρ_1. We then make a very small perturbation $\delta\rho(\vec{r})$ to the density in the region around the origin. Next we use Eq. (23) with a negative sign inserted on the right-hand side along with Eq. (24) to calculate how the density changes with time. Because of the addition of the negative sign, the system is unstable and so the small density perturbation grows to make a large density change with a complicated dependence on time. This calculation is then repeated for different choices of the form of the initial perturbation until a starting $\delta\rho(\vec{r})$ is found such that after some time the liquid returns to the same state of uniform density in which it began. This corresponds to the bounce trajectory already discussed.

It is difficult to find an analytical formula describing these bounce trajectories unless some simplifying assumptions can be made. If the negative pressure is small, the radius of the critical nucleus will be large. Then corrections for the finite width of the interface should be small (thin wall approximation), and so Eq. (4) should be a reasonable approximation. In this case Lifshitz and Kagan [12] show that

$$I = \frac{135\pi^2 6^{1/2} \rho_1^{1/2} \alpha^4}{32\hbar |\delta P|^{7/2}} \tag{25}$$

where ρ_1 is the density of the starting phase. Lifshitz and Kagan also consider the other limiting case in which the pressure is very close to the spinodal pressure P_c (they refer to this as the lability pressure). Their result is that as the spinodal is approached I goes to zero as

$$I \propto (P - P_c)^{1/4} \tag{26}$$

One expects that quantum tunneling will only occur when the energy barrier is small. Except in these limiting cases it is necessary to find the bounce solutions by a numerical method. This type of calculation has been carried out for quantum nucleation of bubbles in helium at negative pressures [24].

3. Computer simulations

From the above discussion, it is clear that even for classical nucleation, the predictive power of theory is somewhat limited. In addition to there being no rigorous and general theory of the prefactor, the simple thin wall approximation is valid only if the radius of the critical nucleus is sufficiently large. One further problem arises in the study of the nucleation of the solid in a supercooled liquid. For most systems the liquid–solid surface energy α_{LS} is not reliably known. In fact, in many of the early studies of the nucleation of the solid phase, a measurement of the temperature at which nucleation occurred was used to give an estimate of α_{LS}.

Given this situation, computer simulations can provide much valuable information. There have been a number of simulations that determine the liquid–solid surface energy, both for model systems in which the atoms interact via hard sphere or Lennard-Jones potentials [25] and also based on more realistic models of the interatomic potential [26]. In addition, there have been simulations of the nucleation process itself [27]. In this type of simulation, the 'experimental volume' and the run time is very small and so, for the moment at least, simulation can only provide information under conditions such that the nucleation rate is very high.

4. Heterogeneous nucleation

The discussion so far has considered the formation of a new phase in the interior of a volume of material. Nucleation can also occur at the surface of the container or at impurities within the material. Within the thin wall approximation, it is straightforward to work out the energy barrier governing classical nucleation at the surface of a flat wall. For example, consider again a liquid at negative pressure P and let the liquid–vapor, vapor–wall, and liquid–wall surface energies be α_{LV}, α_{VW} and α_{LW}, respectively. Now consider a bubble of the form shown in Fig. 6. The volume of the bubble is

$$V = \frac{1}{3}\pi R^3 (1 + \cos\theta)^2 (2 - \cos\theta) \tag{27}$$

the area of the interface between the liquid and the vapor is $2\pi R^2 (1 + \cos\theta)$, and the area of the interface between the vapor and the wall is $\pi R^2 \sin^2\theta$. Thus, the energy needed to introduce a bubble like this is

$$\Delta F = 2\pi R^2 (1 + \cos\theta)\alpha_{LV} + \pi R^2 \sin^2\theta (\alpha_{VW} - \alpha_{LW}) - \frac{1}{3}\pi R^3 (1 + \cos\theta)^2 (2 - \cos\theta)|\delta P| \tag{28}$$

If we now use the relation $\alpha_{VW} = \alpha_{LV}\cos\theta + \alpha_{LW}$, the energy can be written as

$$\Delta F = \left[4\pi R^2 \alpha_{LV} - \frac{4}{3}\pi R^3 |\delta P| \right] \frac{(1 + \cos\theta)^2 (2 - \cos\theta)}{4} \tag{29}$$

Thus, the barrier becomes

$$\Delta F_{max} = \frac{4\pi}{3}(1 + \cos\theta)^2 (2 - \cos\theta)\frac{\alpha_{LV}^3}{|\delta P|^2} \tag{30}$$

This maximum value occurs at a radius of $R = 2\alpha_{LV}/|\delta P|$, i.e., at the same radius as for nucleation in bulk. The barrier is changed by a factor of

$$\lambda = \frac{(1 + \cos\theta)^2 (2 - \cos\theta)}{4} \tag{31}$$

If the liquid completely wets the wall, then $\theta = 0$ and so $\lambda = 1$ and there is no change in the nucleation barrier. Incomplete wetting leads to a reduction in the barrier and the barrier goes to zero as $\theta \to \pi$. Experiments to test predictions of nucleation based on Eq. (31) were performed by Twomey [28] and agreement was found. In practice, unless special care is taken to keep the wall of an experimental cell clean, one has to expect that there will be some regions where the contact angle is large. Nucleation will then occur preferentially in these regions.

The barrier is further modified if the surface is not flat. The nucleation for different surface geometries can be calculated. The simplest geometry to consider is a cone (see Fig. 7). Let the semi-angle of the cone be β and assume
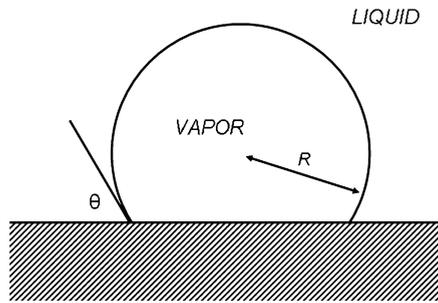
Fig. 6. A bubble of radius R formed at a flat solid wall. The contact angle is θ.
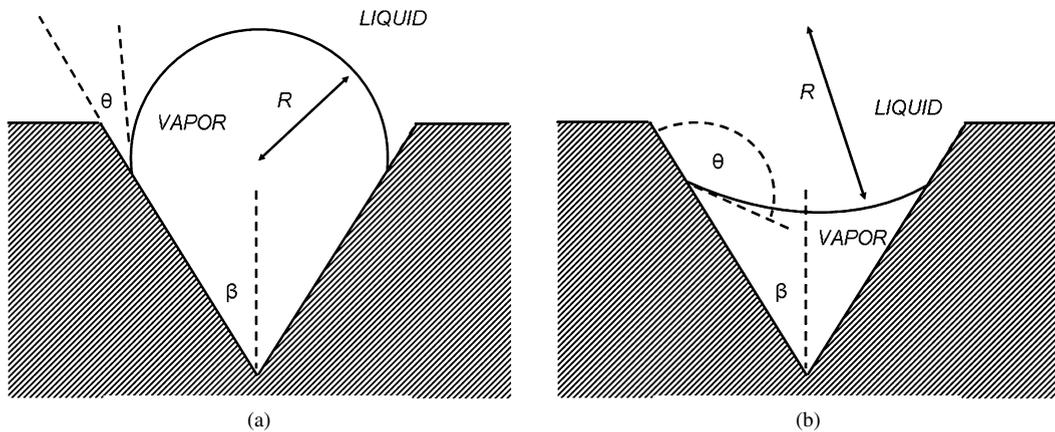
Fig. 7. A bubble of radius R formed in a cone of semi-angle β shown for (a) a small and (b) a large value of the contact angle θ.

for the moment that the interface between the liquid and vapor looks as shown in Fig. 7(a), and has a radius R. Then the energy needed to produce the vapor bubble is

$$\Delta F = \left(4\pi R^2 \alpha_{\mathrm{LV}} - \frac{4\pi}{3} R^3 |\delta P| \right) f(\theta, \beta) \tag{32}$$

where

$$f(\theta, \beta) = \frac{1}{2} - \frac{\sin(\theta - \beta)}{2} + \frac{\cos^2(\theta - \beta)\cos\theta}{4\sin\beta} \tag{33}$$

One can see from Eq. (32) that ΔF is again stationary with respect to R when $R = 2\alpha_{\mathrm{LV}}/|\delta P|$. If θ is less than $\beta + \pi/2$, $f(\theta, \beta)$ is positive and so there is a barrier of height

$$\Delta F_{\max} = \frac{16\pi \alpha_{\mathrm{LV}}^3}{3|\delta P|^2} f(\theta, \beta) \tag{34}$$

If, on the other hand, θ is greater than $\beta + \pi/2$, the interface looks as shown in Fig. 7(b). If the pressure is positive, the energy is the sum of a positive term going as R^3, and a negative term going as R^2. Hence, there is now a minimum energy when $R = 2\alpha_{\mathrm{LV}}/|\delta P|$, and the liquid does not fill the cone to the bottom. If the pressure is negative the interface moves out to the end of the cone and there may or may not be any barrier against nucleation.

5. Measurement methods

In an experiment, one would ideally like to measure the nucleation rate Γ as a function of temperature and pressure. Thus, nucleation of bubbles in a liquid can be investigated either by heating the liquid above the liquid–vapor equilibrium line in the P–T plane or by lowering the pressure. Although rather different experimental techniques would be used for these two approaches, either way the measured quantity is Γ as a function of P and T.

For a sample of volume V that is under observation for a time τ the probability that nucleation will *not* occur is

$$\exp(-\Gamma V \tau) \tag{35}$$

Hence, the probability of nucleation is

$$S = 1 - \exp(-\Gamma V \tau) \tag{36}$$

In practice, Γ varies very rapidly with changes in P or T. For classical nucleation of bubbles in a liquid under tension, for example, the thin wall approximation gives

$$\Gamma = \Gamma_0 \exp\left[-\frac{16\pi \alpha_{\mathrm{LV}}^3}{3kT(\delta P)^2} \right] \tag{37}$$

The probability of nucleation is therefore one half when

$$|\delta P| = \sqrt{\frac{16\pi \alpha_{\mathrm{LV}}^3}{3kT \ln(\Gamma_0 V \tau / \ln 2)}} \tag{38}$$

If $\Gamma_0 = 10^{30}$ cm^{-3} s^{-1}, $V = 1$ cm^3 and $\tau = 1$ s, the logarithm in this formula has the value 69.4. Then, if the volume is reduced by a factor of 10, the logarithm is only reduced to 67.1 and so the value of $|\delta P|$ is changed by less than 2%. Thus, when V and τ are macroscopic, one can consider that there is a rather well defined pressure (or temperature) at which nucleation will occur. To make this more precise one can calculate the derivative of S with respect to P at the value of δP for which S is one half. The result is that

$$P\frac{dS}{dP} = \ln\left(\frac{\Gamma_0 V \tau}{\ln 2} \right) \ln 2 = 48 \tag{39}$$

Thus, to be able to make a quantitative measurement of the variation of Γ with P or T, it is advantageous to use as wide a range of values of V and τ as possible. For example, the nucleation rate for the freezing of supercooled liquid hydrogen has been measured over a temperature range in which it changes by 7 orders of magnitude [29]. This was accomplished by studying a series of samples with different volumes.

In experimental studies of nucleation, it is extremely important to control or eliminate the possibility of heterogeneous nucleation. The first step, of course, is to make sure that the sample that is studied is highly pure. For example, sophisticated methods have been developed in order to prepare ultrapure water. Cryogenic liquids have great advantages for nucleation studies since many impurities simply freeze out on the walls of the container. For liquid helium, *all* other elements will quickly freeze out if the temperature is below about 1 K.

The sample surface is also a possible source of heterogeneous nucleation. If a macroscopic sample of material is studied while in a container, it is likely that there will be some location on the container wall at which the nucleation barrier will be less than the barrier in the bulk of the sample. This can arise because of the local geometry (e.g., a conical pit as just discussed), or a region of surface contamination where the liquid contact angle is small. There have been many attempts to eliminate heterogeneous nucleation by careful polishing of the container wall together with cleaning the surface. However, this approach is extremely difficult because only one small area of the surface needs to have the right geometry, or surface contamination, to cause problems. As a result, experimenters have looked for other methods.

As an example, consider a possible experiment that has the goal of determining the extent to which it is possible to lower the pressure in a liquid without nucleation of vapor bubbles. If the liquid sample forms one large single volume, then as soon as heterogeneous nucleation of a bubble occurs at any point, the bubble will grow until the pressure returns to the saturated vapor pressure. Thus, it is advantageous to divide the sample into a number of small volumes (sub-samples) and monitor the state of each of these as the temperature is lowered. Moreover, the smaller the sample, the lower the chance that there will be a site for heterogeneous nucleation on the wall. For example, Zheng et al. [30] have trapped water inside small inclusions (size $\sim$20 μm) in crystals and have proposed that pressures as negative as -1400 bars can be achieved before nucleation occurred.

A second possible approach is to use a wall that is made of material unlikely to cause nucleation. For example, Turnbull [31] mixed mercury with pump oil and agitated the mixture in a blender. In this way he was able to make mercury droplets with an average diameter of 3.8 μm and found that these froze in the temperature range between

−98 and −100 °C. Since the strength of the forces between mercury and an organic liquid are weak compared to the forces between mercury atoms, heterogeneous nucleation of the solid at the surface of the droplets is unlikely.

Another effective approach is to have no container for the sample. This can be achieved if the sample can be levitated in some way. The methods available include magnetic, electrostatic [32], and acoustic levitation, or experiments can be performed in space. It is also possible to achieve a form of levitation by positioning a liquid drop inside another fluid of the same density. For example, it is possible to levitate drops of liquid hydrogen in fluid helium [29]. When the temperature is above the critical point of helium (5.2 K), the density of the helium fluid can be adjusted to match the density of liquid hydrogen by varying the pressure. Apfel has shown how acoustical techniques can be used to control the position of a drop floating in an immiscible fluid [33].

One other approach for avoiding heterogeneous nucleation is described in detail in later articles in this issue. One can use a large experimental sample but make measurements on only a small part of the sample that is a long way from the container wall. A sound wave can be focused so as to make a large oscillating pressure in a small region inside the liquid, and the critical negative pressure at which vapor bubbles nucleate can be detected [34]. This approach makes it possible to study very small volumes of liquid ($V \sim 10^{-5}$ cm^3) and for short times ($\tau \sim 10^{-6}$ s). Using this technique, it has been possible to study the quantum nucleation of bubbles in superfluid helium [35].

6. Some topics of special interest

Nucleation is a very general phenomenon. Here, we mention briefly four topics of special interest.

Control of the nucleation of the water-to-ice phase transition is vital for the survival of various insects [36] and fish in polar regions [37]. Sea water freezes at −1.9 °C, whereas the blood of teleost fish has an equilibrium melting point of −0.6 °C. Thus, in order for a fish to survive, its blood must remain in a supercooled state. Even if the homogeneous nucleation [37] of ice in the blood is not a problem, the fish still has to deal with the possibility that a small ice crystal may enter its body, through the gills, for example, and then grow. Research has shown that these fish have anti-freeze proteins (AFP) which apparently adhere to the surface of any small ice crystal that enters their bloodstream and prevent it from acting as a nucleus for heterogeneous nucleation and growing in size [38]. Some insects have added subtlety in their control of nucleation and are classed as freeze tolerant or freeze avoiding [36,39]. In freeze avoiding insects AFPs are used to prevent the freezing of cells that might occur due to the growth into the insect of ice surrounding the insect and also to inhibit heterogeneous nucleation of ice inside the insect. Freeze tolerant insects, use ice nucleating agents (INAs) to induce freezing in the water outside of the cells, thereby reducing the amount of water in the cells and preventing freezing there.

We can be certain that if we apply a sufficiently large negative pressure to a liquid we will reach a point at which bubbles will form. This just follows from the fact that there is a finite strength of the interatomic forces, and so there is a spinodal at which the nucleation barrier becomes zero. But what if we cool a liquid? As we begin to lower the temperature, the probability of nucleation increases because the difference in free energy between the liquid and the solid is becoming larger (the difference is initially proportional to the supercooling δT), and so the barrier is becoming smaller. But when the temperature is sufficiently low, the free energy difference becomes constant, and the barrier no longer decreases with decreasing temperature. Since the thermal energy available to overcome the barrier is proportional to T, the nucleation rate should then begin to decrease very rapidly and the liquid would be effectively stable no matter how large the supercooling. The chance of this happening appears to be greatest for liquid hydrogen which has been supercooled from the triple point of 13.8 K down to a temperature of 10.6 K [29]. To get to lower temperatures and to explore the possibility of creating a liquid that would be stable even at very low temperatures requires the development of techniques for cooling small volumes of liquid through the temperature range in which the liquid–solid nucleation rate is high.

There is an extensive literature covering the theory of traffic flow of freeways [40]. It is believed that three distinct states can be identified, namely free flow, synchronized flow and wide moving jams. In synchronized flow there is a synchronization of the flow in adjacent lanes. A wide moving jam is a region of very slowly moving traffic that extends over a well-defined range. The transitions from free flow to synchronized flow or wide moving jams are considered to be first-order phase transitions and exhibit hysteresis. The nucleation of these transitions can occur spontaneously even on an ideal straight freeway (homogeneous nucleation) or as a result of a narrowing of the road (heterogeneous nucleation) [40,41].

There have been many reports in newspapers that in a microwave oven water can become superheated and explode unexpectedly. I had assumed that this was an idea propagated by ambitious lawyers, but it really does happen. It has been studied in several experiments [42,43] and has caused injuries [44]. When an ordinary saucepan is used to heat water, the heat enters the water at the wall and so the hottest part of the water is in a location at which heterogeneous nucleation is most likely to occur. Thus, bubbles will normally appear on the wall of the saucepan. Microwaves deposit heat uniformly throughout the water and since the heat can only escape at the surfaces, the interior of the water will be the hottest region. For very clean water, it is unlikely for heterogeneous nucleation to take place there. If there is no nucleation the water can become highly superheated and explode when a spoon is inserted and induces nucleation. Of course, the situation is complicated by the effects of convection and the presence of impurities in the water. In summary, nucleation of steam in water heated in a microwave does indeed happen, but it is rare.

Acknowledgements

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