Van der Waals' equation and nucleation theory

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Abstract. The assumptions and detailed predictions of Van der Waals' equation and of classical nucleation theory in relation to homogeneous condensation and cavitation are discussed. The predictions of both can be expressed in terms of reduced variables, relative to those at the critical point, and display remarkable quantitative similarity over a wide temperature range. The extent of this agreement is surprising in view of the different nature of the assumptions underlying the two theories.

Zusammenfassung. Die Voraussetzungen und detaillierten Voraussagen der Gleichung von Van der Waals, sowie die der klassischen Kernbildungstheorie werden mit Hinsicht auf homogene Kondensation und Hohlraumbildung diskutiert. Die Voraussagen beider Theorien können durch reduzierte Veränderlich bezüglich derjenigen am kritischen Punkt ausgedrückt werden, und sie weisen eine bemerkenswerte quantitative Ähnlichkeit über ein weites Temperaturintervall auf. Die Größe dieser Übereinstimmung ist in Hinsicht auf die Verschiedenheit der ben beiden Theorien zugrundeliegenden Voraussetzungen überraschend.

1. Introduction

Most students meet Van der Waals' equation in a first course in the kinetic theory of gases, where its heuristic origin is explained and its qualitative success in predicting the phase transition between vapour and liquid states is outlined. The sigmoid shape of the Van der Waals isotherms in a (p, V) plane is pointed out as giving a qualitative account of supersaturated vapour and the metastability of liquid under tension, but there the matter is usually left.

Only a few physics students enter fields such as atmospheric physics or chemical engineering, where they may make the acquaintance of the classical theory of the nucleation of phase transitions, which provides an explanation, at the molecular level, of the physical processes involved in condensation or liquid fracture.

In no cases of which we are aware do standard texts point out the surprising quantitative similarity between the predictions of Van der Waals' equation and the equations of nucleation theory. It is to remedy this omission that the present paper has been written. In doing so, we have purposely adopted a rather more sophisticated approach than would be used in a first course, but this is to avoid over-qualitative arguments.

At the outset, it should be emphasized that the discussion deals only with the behaviour of pure bulk material, so that the processes by which condensation or cavitation is initiated are homogeneous. It is possible to approach this ideal in the laboratory, but in the outside world condensation and cavitation processes are almost always heterogeneous, being initiated by the presence of solid surfaces or by suspended foreign particles. We deliberately set aside these possibilities here.

2. Van der Waals' equation

A good formal approach to deriving the behaviour of non-ideal gases is the Mayer cluster theory, in which an expansion is made in terms of the interactions between molecules grouped in clusters of 2, 3, 4, ... and so on. Such a theory could be rigorous if we were able to consider clusters of all sizes, but computational difficulties restrict what can reasonably be done. The usual result is the so-called virial expansion

$$pV = NkT\left(1 + \frac{B}{V} + \frac{C}{V^2} + \dots\right) \tag{1}$$

relating the pressure p and volume V of N molecules of the gas at temperature T. The constants $B, C, \dots$ are called the virial coefficients. The coefficient B is readily evaluated, C is more difficult, and evaluation of higher coefficients is virtually impossible. The theory therefore works well only for gases that are under rather low pressure.

Van der Waals' equation can be regarded as an extreme simplification of this approach in which only interactions between pairs of molecules are taken into account, and any cooperative effects in larger clusters are ignored. We shall not go into this derivation here, since a good account has been given by Morse [1]. Elementary derivations of the equation often use a less rigorous approach, but we wish to point out this more formal origin. The equation itself is familiar, and has the form

$$\left(p + \frac{N^2\alpha}{V^2}\right)(V - N\beta) = NkT \tag{2}$$

where α and β are constants. The term involving α represents an attraction between neighbouring molecules, and hence the effect of their pair interaction term. N/V is the number of molecules per unit volume, and hence $(N/V)^2$ is proportional to the number of pairs of molecules a specified distance apart. The term $N\beta$ is the volume that is occupied by the molecules themselves, and hence excluded from the available free volume.

The well known sigmoid isotherms of Van der Waals' equation are shown in figure 1. At temperatures above a critical value T_C the isotherms are simple, while at lower temperatures they show two stable regions, in which the compressibility $-(1/V)(\partial V/\partial p)$ is positive, separated by an unstable region. The two stable regions can be interpreted as representing gaseous and liquid phases respectively, and an appropriate joining line AE through the unstable region can be found from the requirement that the chemical potential, or molar Gibbs free energy, must be the same for liquid and gaseous phases in equilibrium, and therefore the mechanical work $\int p\,dV$ in going from A to E must be the same for the real isothermal path ACE and for the analytically

Figure 1. Isotherms predicted by the Van der Waals equation, with reduced temperature T/T_C as parameter. The inset shows the procedure for evaluating the saturation vapour pressure p_S, the position of the line AE being adjusted to make the hatched areas ABC and CDE equal.

defined path ABCDE. The hatched areas between the curve and AE must therefore balance. This requirement allows us to derive the saturation vapour pressure p_S as a function of temperature within the Van der Waals approximation. This pressure is found to vary approximately as $\exp(-\text{const}/T)$ in reasonable agreement with experiment.

It is very useful to re-express the Van der Waals equation (2) in terms of the values of the temperature T_C, pressure p_C and volume V_C at the critical point. These are given in terms of the original parameters by

$$p_C = \frac{1}{27}\frac{\alpha}{\beta^2} \qquad V_C = 3N\beta \qquad NkT_C = \frac{8}{27}\frac{\alpha}{\beta} \tag{3}$$

so that Van der Waals' equation can be written in the reduced or universal form

$$\left[\frac{p}{p_C} + 3\left(\frac{V_C}{V}\right)^2\right]\left[\frac{V}{V_C} - \frac{1}{3}\right] = \frac{8}{3}\frac{T}{T_C}. \tag{4}$$

It is these reduced isotherms that are plotted in figure 1.

The reasonable interpretation of the shape of the Van der Waals' isotherms is that they describe, at least qualitatively, the fact that a vapour can be compressed beyond its normal condensation point into a supersaturated state, and that a liquid can support a negative hydrostatic pressure without rupturing. If this interpretation is accepted, then we can readily calculate a general form for the maximum metastable supersaturation in the vapour and the maximum metastable negative pressure in the liquid by setting $\partial p/\partial V = 0$ in (4). If we write the reduced variables as

$$p_R = p/p_C \qquad V_R = V/V_C \qquad T_R = T/T_C \tag{5}$$

then differentiation of (4) gives the equation

$$\left(\frac{\partial p_R}{\partial V_R} - \frac{6}{V_R^3}\right)\left(V_R - \frac{1}{3}\right) + \left(p_R + \frac{3}{V_R^2}\right) = 0. \tag{6}$$

If we set $\partial p_R/\partial V_R = 0$ and substitute for p_R from (4), then we reach the equation

$$4T_R V_R^3 - 9V_R^2 + 6V_R - 1 = 0 \tag{7}$$

which can be solved algebraically or numerically to give the reduced volume at the two extrema of the equation. We can convert these to the related pressures p by using (6), with $\partial p_R/\partial V_R = 0$, in the form

$$\frac{p}{p_C} = \frac{3}{V_R^2} - \frac{2}{V_R^3}. \tag{8}$$

For convenience let us denote by p' the pressure at the condensation extremum D of figure 1, and by P the pressure at the cavitation extremum B. The physically significant quantities are most usefully taken not to be p' and P themselves, but rather the quantities p'/p_S, which is the limiting saturation ratio in the vapour, and $(P - p_S)/p_C$, which relates the cavitation pressure in the liquid, with respect to its saturation vapour pressure, to the pressure at the critical point.
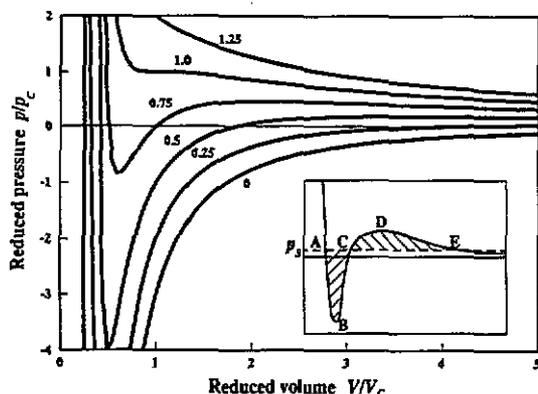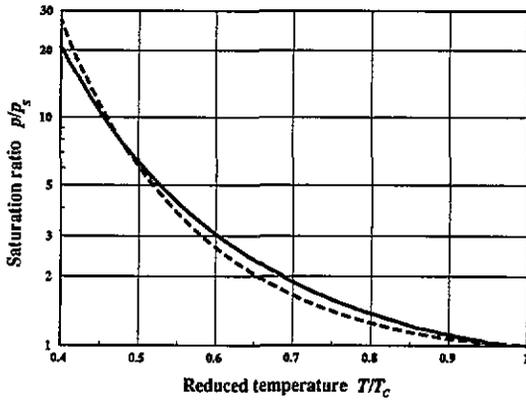
Figure 2. The supersaturation limit set by homogeneous condensation as predicted by Van der Waals' equation (full curve) and by classical nucleation theory (broken curve).

These relationships, which are universal in form, are plotted as full curves in figures 2 and 3.

3. Homogeneous nucleation of condensation

Classical nucleation theory, developed largely by Volmer and Weber [2,3], concerns itself with details of the kinetics of phase transitions and, in doing so, makes entirely different physical approximations from those adopted in deriving the Van der Waals equation. It recognises that, in a supersaturated vapour, there will be statistical fluctuations in density that can be interpreted as clusters of various sizes, and concentrates attention on those clusters that are nearly large enough to be thermodynamically metastable. Similarly, the statistical fluctuations in a liquid under negative pressure can be regarded as embryonic

Figure 3. The cavitation pressure limit as predicted by Van der Waals' equation (full curve) and by classical nucleation theory (broken curve).
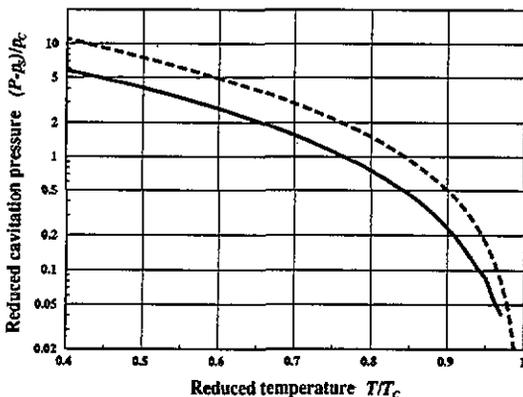
vapour bubbles, and the theory focuses on those that are nearly large enough to grow explosively. Under typical conditions, such critical clusters in either case contain some tens of molecules.

The detailed theory of nucleation behaviour considers the whole distribution of clusters of less than critical size, and calculates the equilibrium, or non-equilibrium, currents in this distribution. For our present purposes a much simpler approach suffices. Let us concentrate attention on a supersaturated vapour in the first instance, and suppose that the vapour pressure is p and the saturation vapour pressure p_S under the conditions of the experiment. Suppose that there is a spherical cluster of radius r containing $(4/3)\pi r^3 n_L$ molecules, where n_L is the number of molecules per unit volume in the liquid. Then the Gibbs free energy expended in creating such a cluster can be written

$$\Delta G(r) = \tfrac{4}{3}\pi r^3 n_L (\mu_L - \mu_V) + 4\pi r^2 \sigma \qquad (9)$$

where μ_L and μ_V are the chemical potentials (partial free energies) of molecules in bulk liquid and vapour respectively, and σ is the surface free energy per unit area, or surface tension, of the liquid. It can well be argued that σ may depend significantly upon surface curvature for such small clusters, but we omit this refinement and use its macroscopic value. We can show that the difference in chemical potential between vapour at pressure p and bulk liquid, which is in equilibrium with vapour at pressure p_S, is just

$$\mu_L - \mu_V = -kT \ln(p/p_S). \qquad (10)$$

Using (9) and (10), the free energy excess required to create a cluster of radius r, for the cases of unsaturated and supersaturated vapour, behaves as shown in figure 4. For unsaturated vapour, there is an

Figure 4. The free energy barrier ΔG for creation of an embryo droplet of radius r in a vapour, based on quasi-macroscopic classical nucleation theory. The broken curve refers to unsaturated vapour and the full curve to supersaturated vapour. ΔG^* is the nucleation barrier. A similar plot applies for nucleation of a bubble in a liquid under negative pressure.
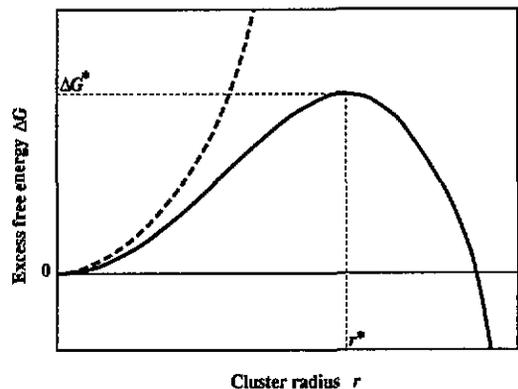
increasingly large free-energy penalty associated with the creation of large clusters, so that we expect their concentration to be small, in accord with a Boltzmann distribution

$$n(r) = n_V \exp[-\Delta G(r)/kT] \qquad (11)$$

where n_V is the number of molecules per unit volume in the vapour. If we apply the same reasoning to a supersaturated vapour, then the concentration of embryos of size r first decreases with increasing r up to a critical value r^*, after which it increases without limit. We may interpret this as the approach to condensation and suppose that, when a vapour is brought to the supersaturated state, it initially has no clusters of size greater than r^*, but that the concentration of critical clusters, $n(r^*)$, is given by (11). The rate at which condensation proceeds, by the nucleation of freely-growing droplets, is then determined by the rate at which these critical embryos can capture another molecule so that their size exceeds r^*.

Differentiating (9) with respect to r, we find for the radius of the critical clusters,

$$r^* = \frac{2\sigma}{n_L(\mu_V - \mu_L)} \qquad (12)$$

and, for the free energy barrier to nucleation of condensation,

$$\Delta G^* = \frac{16\pi\sigma^3}{3[n_L kT \ln(p/p_S)]^2}. \qquad (13)$$

The concentration of critical clusters is approximately

$$n(r^*) \approx n_V \exp(-\Delta G^*/kT). \qquad (14)$$

From kinetic theory, the number of molecules colliding with unit area of surface per unit time is $p/(2\pi mkT)^{1/2}$, where m is the mass of a molecule. The rate at which critical clusters grow to become supercritical is thus

$$J = K \exp(-\Delta G^*/kT) \qquad (15)$$

where, using (12),

$$K \sim 4\pi r^{*2} n_V \frac{p}{(2\pi mkT)^{1/2}} = \frac{pn_V}{(2\pi mkT)^{1/2}}$$

$$\times \frac{16\pi\sigma^2}{[n_L kT \ln(p/p_S)]^2}. \qquad (16)$$

For the nucleation of water vapour at room temperature, $K \sim 10^{32} \, \mathrm{m^{-3} \, s^{-1}}$, and for other liquids the magnitude is not very different, by which here we imply that it is within about a factor 10^2 in either direction.

There is clearly a conceptual weakness in the theory as outlined above. This is the assumption that, at the moment when supersaturation is established, the distribution of clusters $n(r)$, for r less than or equal to the critical size r^*, is equal to the thermodynamic equilibrium distribution, while $n(r) = 0$ for $r > r^*$. A more detailed derivation, originally put forward by

Zeldovich, considers the evolution of the cluster distribution function when the vapour pressure is suddenly increased to a value greater than saturation. The nucleation rate J is then taken as the rate at which clusters of radius $r^* + \varepsilon$ are formed, where ε corresponds to adding a single molecule to a critical cluster. The form of J is identical with that given in (15), and the numerical value of the rate constant K is modified only by a factor of order 0.1 from that given by (16). The simple treatment is therefore justified.

In examining the breakdown of supersaturation through the homogeneous nucleation of condensation —without the aid of dust particles or ions to act as condensation nuclei—we seek to find the saturation ratio p'/p_S for which the nucleation rate J becomes appreciable, say $J \sim 1 \, \mathrm{cm^{-3} \, s^{-1}} = 10^6 \, \mathrm{m^{-3} \, s^{-1}}$. Examination of (15) with the numerical value of K inserted shows that this will occur when the supersaturation has increased enough to make $\Delta G^* \approx 60 kT$. Because of the very large magnitude of the pre-exponential factor K in (15), the increase in J with saturation ratio is very sharp. We return to consider numerical values later, but note as an example that, for water vapour at room temperature, $J \approx 0.03 \, \mathrm{cm^{-3} \, s^{-1}}$ for $p/p_S = 4.2$ while, for $p/p_S = 4.6$, $J \approx 500 \, \mathrm{cm^{-3} \, s^{-1}}$. In this calculation, K occurs as the argument of a logarithm, and its exact value is not important to the final result. The theory is thus adequate to give a value of the homogeneous nucleation threshold within an uncertainty of about 10 per cent, independent of the exact definition of the nucleation rate at the threshold.

4. Homogeneous nucleation of cavitation

The theory of homogeneous nucleation of cavitation is formally very similar to that for the homogeneous nucleation of condensation, but there are some important differences. In the nucleation of condensation, the sub-critical clusters are in mechanical equilibrium with their environment, but not in thermodynamic equilibrium until the critical size r^* is reached. The vapour inside an embryo bubble in a liquid, however, is in thermodynamic equilibrium with the surrounding liquid, but not in mechanical equilibrium until the critical radius is reached.

Since the chemical potential of molecules in the bubble is the same as that of molecules in the liquid, we can evaluate the free energy $\Delta G(r)$ for the production of a bubble of radius r simply in terms of the reversible isothermal work done when the bubble is created, the external pressure remaining at the magnitude P. This gives an equation analogous to (9), namely

$$\Delta G(r) = \tfrac{4}{3}\pi r^3 (P - p_r) + 4\pi r^2 \sigma \qquad (17)$$

where p_r is the pressure of vapour in the bubble, given by (12) and (10). Using a negative radius of curvature

r for the liquid surface

$$\ln\left(\frac{p_r}{p_S}\right) = -\frac{2\sigma}{n_L kTr}.\tag{18}$$

The concentration n_V of molecules in the vapour has been neglected in comparison with that of molecules in the liquid, n_L.

At the critical bubble size r^*, we have the condition for the mechanical equilibrium of the bubble

$$p_{r^*} \equiv p^* = P + \frac{2\sigma}{r^*}.\tag{19}$$

Using this in (17) gives the free energy barrier to bubble formation

$$\Delta G^* = \tfrac{4}{3}\pi r^{*2}\sigma = \frac{16\pi\sigma^3}{3(p^* - P)^2}\tag{20}$$

which is closely analogous to (13). The critical bubble pressure p^* can be found from (19) and (18) for $r = r^*$ as the solution to

$$\ln\left(\frac{p^*}{p_S}\right) = \frac{P - p^*}{n_L kT}.\tag{21}$$

To be exact, p_S should be replaced by the saturation vapour pressure of the liquid under external pressure P, but this makes little difference and, in fact, the large value of the denominator on the right-hand side of (21) makes it an adequate approximation to take

$$p^* \approx p_S.\tag{22}$$

The kinetic treatment now goes ahead just as for the case of condensation. The concentration of critical bubbles in the liquid is

$$n(r^*) = n_L \exp(-\Delta G^*/kT)\tag{23}$$

and the nucleation rate is just the rate at which bubbles gain an extra molecule to become free-growing. In the case of boiling, this rate can be evaluated just as in the condensation case, since the vapour in the bubble is in thermodynamic equilibrium and we can examine the exchange from the vapour side of the interface. The result is thus formally the same as given by (15) except that n_L replaces n_V in the first form of (16) and increases the kinetic constant by a factor of order 10^3, making $K \sim 10^{34}\,\mathrm{m}^{-3}\mathrm{s}^{-1}$ when the Zeldovich correction is included.

In the case of cavitation, the critical bubble is too small for this approach to be valid, and we must look at bubble growth from the liquid side. In this case it can be shown [4] that the kinetic constant has the value

$$K \sim n_L \frac{kT}{h} \exp\left(\frac{-\Delta g}{kT}\right)\tag{24}$$

where h is Planck's constant and Δg is the activation energy for molecular diffusion in the liquid. Essentially kT/h is an infrared vibration frequency, characteristic of the highest excited vibration in the condensed state at temperature T, and Δg represents

a free energy barrier that must be surmounted if molecular diffusion is to take place. For most liquids, the numerical value given by (24) is not much different from that given by the vapour-side consideration.

As with homogeneous condensation, nucleation theory predicts a very sharp onset for the nucleation of bubble growth when the value of $(p^* - P)$ in (20) becomes large enough to reduce the value of ΔG^* to about $60kT$. This can occur either by super-heating, which sharply increases the saturation vapour pressure p_S and hence, by (22), the critical bubble pressure p^*, or by subjecting the liquid to large negative pressure P, as in cavitation conditions.

5. Nucleation equations in reduced form

It is instructive to attempt to rewrite the predictions of nucleation theory in universal reduced form so that they can be compared with those of the Van der Waals equation. This involves some approximations, but has a good level of accuracy.

As a first step, we rewrite the nucleation equation (15), using either (13) or (20) for ΔG^*, in the explicit form

$$\left[\ln\left(\frac{p}{p_S}\right) \text{ or } (p^* - P)\right] = \left(\frac{16\pi}{3n_L^2 \ln(K/J)}\right)^{1/2}\left(\frac{\sigma}{kT}\right)^{3/2}\tag{25}$$

where the two forms on the left side refer to condensation and bubble formation respectively.

Surface tension and surface free energy are numerically equal for liquids, though the same is not true of solids. We can therefore write

$$\sigma = E_\sigma - TS_\sigma\tag{26}$$

where E_σ is the surface energy and S_σ the surface entropy. This shows that

$$S_\sigma = -\frac{d\sigma}{dT}.\tag{27}$$

Various considerations, which we need not consider here, show that the surface entropy is positive and of order k per surface molecule, the exact value depending on the nature of the liquid (for example, whether or not it is molecularly associated and whether it is polar). The surface tension thus declines approximately linearly with increasing temperature, and vanishes at the critical temperature, where liquid and vapour states become indistinguishable. We can therefore make the reasonable approximation

$$\sigma = \sigma_0\left(1 - \frac{T}{T_c}\right)\tag{28}$$

where σ_0 is the surface free energy at $T = 0$ or, equivalently within our approximation, the surface energy E_σ.

Turning now explicitly to the case of condensation, we note that $J \sim 10^6\,\mathrm{m}^{-3}\mathrm{s}^{-1}$ for an appreciable nucleation rate, while $K \sim 10^{31}\,\mathrm{m}^{-3}\mathrm{s}^{-1}$ for nearly all liquids of interest. We can therefore use (28), together

with these data, to write (25) in the generalized form

$$\ln\left(\frac{p'}{p_S}\right) \approx 3.5 \times 10^{23} \left(\frac{\sigma_0}{n_L^{2/3} T_C}\right)^{3/2} \left(\frac{T_C}{T} - 1\right)^{3/2} \qquad (29)$$

where p' is the nucleation threshold for homogeneous condensation. We can go a little further and note that $\sigma_0/n_L^{2/3}$ measures the energy difference at 0 K between a molecule in the surface of a liquid and one in the bulk, while T_C is proportional to the binding energy of bulk liquid. We therefore expect the factor $\sigma_0/n_L^{2/3} T_C$ to have essentially the same value for all simple liquids. Indeed substitution of experimental values shows that it varies only between 2×10^{-16} and 4×10^{-16} J deg^{-1} for liquids as diverse as argon, water and mercury. Taking 3×10^{-16} J deg^{-1} as a representative value, (29) can be rewritten in the universal reduced form

$$\ln\left(\frac{p'}{p_S}\right) \approx 1.8 \left(\frac{T_C}{T} - 1\right)^{3/2}. \qquad (30)$$

Proceeding from (25) in just the same way for the case of bubble formation leads to the equation

$$\frac{p^* - P}{p_C} = \left(\frac{16\pi}{3k \ln(K/J)}\right)^{1/2} \left(\frac{\sigma_0^3}{p_C^2 T_C}\right)^{1/2} \left(\frac{T_C}{T}\right)^{1/2}$$
$$\times \left(1 - \frac{T}{T_C}\right)^{3/2}. \qquad (31)$$

Now the expression $\sigma_0^3/p_C^2 T_C$ should vary little from one material to another, since σ_0 is proportional to binding energy per unit area, and thus varies as $T_C V_C^{-2/3}$, and we expect T_C to be proportional to $p_C V_C$. Inserting typical numerical values, we find the simple reduced form

$$\frac{p^* - P}{p_C} \approx 15 \left(\frac{T_C}{T}\right)\left(\frac{T_C}{T} - 1\right)^{3/2}. \qquad (32)$$

In the case of cavitation well below the critical temperature, P is large and negative, and we can neglect p^* in comparison. More generally, it is preferable to make a better approximation and set $p^* = p_S$.

We can now display the general form of the predictions of nucleation theory for the cases of homogeneous condensation and homogeneous cavitation by plotting (30) and (32) as functions of T/T_C. This is done in figures 2 and 3, in which the predictions of nucleation theory, plotted as broken curves, are compared with those of Van der Waals' equation.

6. Discussion

Examination of figures 2 and 3 shows a remarkable degree of agreement between the shapes of the curves predicted by Van der Waals' equation and by the equations of nucleation theory. It does not appear that this quantitative agreement has been remarked

on before, though of course the general qualitative similarity of the predictions is well known. Indeed, the fact that spot comparisons of the predictions of the two theories for particular materials often show significant disagreement tends to obscure the wide extent of the agreement between them.

The derivations set out above show that the extent of this agreement is the more remarkable in that the two theories make very different initial assumptions, or at least very different truncations of the rigorous cluster expansion. The Van der Waals treatment ignores all interactions except those between pairs of molecules—not for any physical reason, but simply to allow a closed approximation to the cluster series. Nucleation theory, on the other hand, treats all clusters of less than critical size in a phenomenological manner through the introduction of a quasi-macroscopic surface free energy, and all attention is then concentrated on the very small number of clusters of critical size.

Over the temperature range plotted in figure 2, the critical saturation ratio for homogeneous condensation is in close numerical agreement for the two theories, though the predictions diverge somewhat for temperatures below $0.4T_C$. For such low temperatures, the critical clusters are so small that the quasi-macroscopic assumptions underlying nucleation theory are certainly no longer valid, while the pairwise interactions that form the basis of Van der Waals' equation are more appropriate.

The cavitation threshold curves in figure 3 are of almost exactly the same shape, and differ only by an overall factor of 2. This discrepancy is associated with choice of 'typical' values of the physical quantities to give the factor 15 in (32). Changing this factor to 7, which could readily be justified, would lead to almost exact agreement between the two theories.

It is necessary, of course, to compare the predictions of both sets of equations with experimental determinations of homogeneous condensation and cavitation thresholds. These experiments are difficult to perform because of the necessity of removing all foreign particles upon which nucleation might occur. The experimental situation is simplest in the case of water vapour condensation [5], for the condensation nuclei become captured by the droplets that they nucleate and precipitate on the floor of the chamber. Thus nucleation of water droplets from ordinary moist air at room temperature occurs initially at saturation ratios p/p_S less than 1.01, through the agency of suspended salt particles about 0.1 μm in diameter. When these have been precipitated, smaller insoluble particles are activated at progressively higher supersaturations until the true saturation limit is reached at about $p/p_S \approx 4.3$. Somewhat below this limit, condensation can be initiated by ions produced by fast charged particles, as in the Wilson cloud chamber, the critical saturation ratios for positive and negative ions being significantly different because of the structure of the water molecule.

Definitive measurements on bubble nucleation in liquids are much more difficult to perform, because nucleating particles are not removed from the liquid by the bubble formation process. All that can be done is to take the utmost care in filtering the liquid and cleaning the walls of the container. Experiments on superheating can then be performed in a simple closed container, while cavitation experiments, which require large negative pressures, can be carried out in sealed capillary tubes, filled with liquid and spun in a centrifuge. Understandably, these experiments can be relied upon only to provide a lower limit to the attainable supersaturation or cavitation pressure.

This paper is not the place to examine the experimental data in detail, and to present selected results would be to invite scepticism. A rather cursory search of the literature, however, shows that nucleation theory (without the approximations used in obtaining the reduced equations) gives a reasonably good semi-quantitative account of the measurements for supersaturation (p'/p_S from 2 to 10) and cavitation (P typically -300 bar or -30 MPa) of many materials. Where the predictions of nucleation theory differ from those of the Van der Waals equation at around room temperature, nucleation theory is generally

closer to the observations, but the remaining discrepancies are often as large as a factor 2, particularly in the case of cavitation. In most cases the metastability limit predicted by nucleation theory is greater than that observed experimentally, which suggests either a limitation in the theory or the presence of heterogeneous nuclei in the experiment. In a few carefully studied materials, such as water, the agreement between nucleation theory and experiment is surprisingly good for a variety of experimental conditions.

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