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# Metastability of the Liquid–Vapor Transition and Related Effects

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The Becker–Döring and Fisher nucleation kinetic theories of metastability of the liquid–vapor transition are outlined and compared with Temperley's theory based on equilibrium statistical mechanics, and it is claimed that the two approaches are in effect the same—a point that has been made by O. Penrose based on a different argument. The theoretical $27T_C/32$ for the limit of superheat is known to be in reasonable agreement with experiment. The tensile strengths of liquids have been measured by many methods which have appeared to be in conflict, but it is claimed that the conflicts can be resolved by invoking "rectified diffusion" of gas into a bubble performing forced oscillations in a periodic pressure field and by considering the structure of the free surface of a liquid. The transition layer almost certainly contains a region in which the velocity of sound is low. A brief account of cavitation effects is given.

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**KEY WORDS:** Liquid-phase transition; metastability, kinetic and equilibrium theories of; limit of superheat; tensile strength of liquids; cavitation.

## 1. INTRODUCTION

The metastability of the liquid–vapor and vapor–liquid transitions manifests itself in many ways: in the cloud chamber and bubble chamber, in the "bumping" when a liquid is boiled in a smooth vessel, in the possibility of superheating liquids well above their boiling point (for example, water can be heated to 270°C without explosion), and in the multitude of effects associated with "cavitation", the formation of bubbles in a liquid due to its failure under tension. For surveys see Trevena(11) and Dinham.[3]

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Metastability effects associated with the freezing transition are equally interesting (for example, water can exist in the liquid state down to −40°C, a fact which is of great importance in meteorology), but we shall not be dealing with them, because the solidification transition is much less well understood than is the vaporization transition. Water is a particularly difficult liquid because of its V-shaped molecule, hydrogen bonds, and high dipole moment, and there are six different forms of ice!

## 2. THEORIES OF THE EVAPORATION TRANSITION

There are two basic approaches to the study of the formation of drops of liquid in a supersaturated vapor or bubbles of vapor in a superheated liquid. In the kinetic approach, exemplified by the classic work of Becker and Döring, drops were assumed to be built up by the successive capture of single vapor molecules and to be removed from the system, e.g., by gravity, once they had reached a certain size, so that one could set up a differential equation that had a steady-state solution. It quickly became apparent that the predictions of theory were insensitive to the "certain size" provided that we did not take it to be zero or infinity. A very similar theory for the formation of bubbles in a liquid was developed by Fisher and others and again it turns out that it does not greatly matter what "certain size" of bubbles one takes as long as it is finite. The analytic behavior of the solutions has been studied by Penrose.(6)

As regards the second approach, Temperley was originally supposed to have discovered the statistical mechanical type of theory in a 1947 paper.(12) When it was shown to G. I. Taylor his reaction was: "I think you must be right, but I am surprised that no one has pointed this out before." In fact, someone had! Larmor made a similar suggestion in 1916.(4) If we assume a van der Waals liquid, a simple calculation shows that the "limit of superheat," the temperature for which the minimum of the van der Waals isotherm was at $P=0$, is $27T_C/32$, where $T_C$ is the critical temperature. Below this temperature the liquid should be capable of standing tension. However, he made an amusing blunder, thinking that the critical temperature of water was 365° absolute instead of centigrade! Then $27T_C/32$ would come out to be 25°C, so that Larmor wondered how sap could rise in trees in the tropics, because the sap should be incapable of standing tension at temperatures above this $27T_C/32$.

Correcting Larmor's mistake and using the accepted value of 374°C for the critical temperature of water, we arrive at 273°C for the limit of superheat corresponding closely with the observed value of 270°C. In the cited 1947 paper(12) it was shown that quite a number of liquids had limits of superheat close to this value $27T_C/32$ and the simple theory gave a value of about 500–1000 atm for the tensile strength of water, in order-of-magnitude agreement with predictions of nucleation theory.

## 3. COMPARISON OF THE TWO TYPES OF THEORY

We first show that agreement between the two types of theory is to be expected, because they are essentially the same. Recall first that the nucleation type of theory predicts "steady-state equilibrium" between drops of various sizes. Now consider the Mayer theory of the condensation of an imperfect gas. The virial equation is

$$\frac{P}{kT}=\rho-\sum_k \frac{k\beta_k \rho^{k+1}}{k+1} \tag{1}$$

where $\rho$ is the density and $\beta_k$ the $k$th irreducible cluster integral. The only configurations of the molecules that contribute to it are those in which $k+1$ or more molecules are within interaction range of at least two others. $\beta_k$ is thus not precisely the partition function of a drop of $k+1$ molecules, but is simply related to it.

We can make a theory of limit of superheat of a liquid by retaining the second and third virial coefficients in (1) and then looking for the value of temperature that makes $P=0$ and $\partial P/\partial \rho=0$, as in the 1947 theory. The fourth virial coefficient is often numerically small, but we can refine the theory by including the fourth and later coefficients.

However, we must not use the whole of the virial series, but must truncate it somewhere. This corresponds to the result of nucleation theory that we must assume that drops above a certain size are removed from the system. The reason why we must truncate the virial series is as follows: the expression (1) for the pressure arises from the following expression for pressure:

$$P=\left\langle \frac{\partial E}{\partial V} \right\rangle_{\text{average}} \tag{2}$$

where the average is over *all* microstates of the assembly. Clearly an expression such as (2) means that the pressure is a one-valued monotonic function of the density. Therefore the most general possible isotherm is as shown in Fig. 1. A flat portion and sharp corners are permissible, but a van der Waals loop would make $P$ a nonmonotonic function of $\rho$.

An isotherm exactly like ACEGH in Fig. 1 was found by Yang and Lee in their famous transformation of the Onsager model to give a model

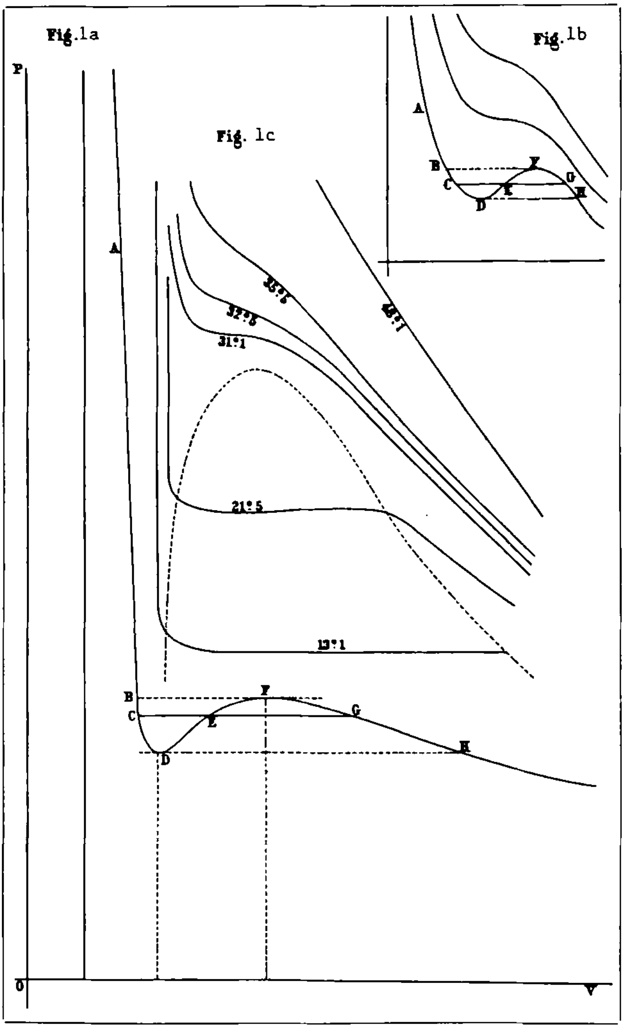

Fig. 1. Plots of isotherms from van der Waals's thesis, showing (a) van der Waals' cuves, (b) unstable isotherms according to James Thomson, and (c) experimental curves from Thomas Andrews. While van der Waals recognized that the isotherm *DEF* represents unstable states, it remained for Maxwell to show exactly where to draw the line *CEG* that represents the stable states, namely, so as to equalize the areas *CDE* and *EFG*.

of liquid vapor condensation.(5) However, truncation of the virial series restores the van der Waals loops. Some work by Domb in 1949(2) showed that the limit of metastability (i.e., the place where $dP/d\rho = 0$) was very insensitive to the precise place at which we cut off the virial series. Thus there are very close analogies between the nucleation and the equilibrium treatments, which is why we assert that they are, in effect, the same.

The situation is very similar to the so-called "Gibbs phenomenon" associated with the Fourier expansion of a step function. If we truncate the Fourier series, an initial "blip" appears and moves closer to the discontinuity very slowly as we take in more and more terms of the series, but finally disappears when we sum the whole series exactly.

## 4. COMPARISON OF PREDICTED TENSILE STRENGTHS WITH EXPERIMENT

When one of the authors took up work on underwater explosions during World War II there appeared to be complete chaos! Many experiments had been done since Berthelot's work in 1850 (in which water was heated in a sealed tube until it filled the tube, then cooling the whole till the liquid broke), but each method seemed to give a different result!

One by one, these discrepancies have been either removed or accounted for over the years and we can now say that the theoretical tensile strength of water at room temperature is about 500–1000 atm and that this value is supported by experiment. As we shall see below, one particularly stubborn discrepancy was not cleared up until 1987. A few typical experimental values are listed below.

From Berthelot tube experiments: 50–100 atm.

From underwater explosions (the pressure pulse produced by an explosion is reflected at a free surface as a tension pulse): 15 atm tension directly measured in water by pressure gauge; 40 atm tensile strength inferred from the depths at which a given size of charge no longer produced a "spray dome" at the surface.

From cavitation produced by ultrasonics or by flow of water in pipes or around propellers: 0–20 atm.

From Reynolds' centrifugal method spinning water in a J-tube: about 5 atm in original experiments, later improved to 277 atm by L. J. Briggs, who took great precautions to avoid vibrations.

From botanical measurements (e.g., the ejection of spores from ferns): 100–500 atm.

From pressure pulses produced by firing a bullet at a piston in contact with water: 10–15 atm.

For a fuller list see ref. 11.

Comparison of all these figures with one another and with the theoretical values of around 500–1000 atm for water seems bewildering. However, three factors have been found that seem to account for the discrepancies.

(a) In the first place, clear evidence has been obtained over the years by Trevena and other workers that failure of liquid in a Berthelot tube always occurs at the boundary rather than in the body of the liquid. As we shall see below, there is a reason to expect that the surface layer will be weaker than the bulk liquid.

(b) If a bubble of gas or vapor in the liquid is subjected to periodic pressure changes, it will grow and act as a collector of dissolved gas. This process has been labeled "rectified diffusion." It occurs because if a bubble makes forced oscillations, e.g., in an ultrasonic field, it spends more of its time with a radius greater than its equilibrium radius than it does with a radius less than the equilibrium value (this is because the hydrodynamic virtual mass of a spherical cavity is proportional to its volume). Consequently more dissolved gas diffuses into the bubble than out of it. This mechanism accounts for the low values of tensile strength observed in ultrasonic experiments. Clearly periodic pressure changes are also present when water flows around a propeller or through a constricted channel. The presence of vibrations probably accounted for the low values of tensile strength found in Osborne Reynolds' experiments. Briggs(1) found that much higher values could be obtained if he took precautions to eliminate vibrations.

(c) Allowing for all this, we are still confronted by the fact that the tensile strength is lower than the static value for "once-only" dynamic applications of tension such as occur if an explosion pulse is reflected at a free surface or in bullet-and-piston experiments which produce a similar pulse. This "seemed wrong." One would surely expect a higher tensile strength for a tension that lasts only a fraction of a millisecond than for a static one. The explanation of this apparent anomaly was not found until 1987, although Sedgewick and Trevena found a clue in 1976.(8)

They found that the free surface of water is *not* a perfect reflector of a pressure pulse, even when the peak pressure is so low that cavitation does not occur. Instead of being a mirror image of the pressure pulse, the peak tension is less than the peak pressure and the tension pulse is spread out. In 1987 Temperley and Trevena found(9) that such behavior would occur if there was a region of the liquid in which the effective velocity of sound was small compared with that in the bulk liquid. It is believed that water has a free surface transition layer between liquid and vapor about 3 Å thick. As the density falls off with height, we must come somewhere to the two-phase region of water, the isotherm would be nearly flat, and the assumption that the effective velocity of sound is small is reasonable. Such a two-phase region would be a prolific source of cavitation nuclei, and should therefore be weaker than the bulk liquid. (These considerations assume that we can validly use hydrodynamic concepts even when we are concerned with distances of a few Angstrom units, but our conclusions should be at least qualitatively correct.) Similar considerations probably account for the observed fact that in a Berthelot-tube type of experiment, failure always occurs at the liquid–solid interface.

Our conclusion is therefore that the tensile strength of water is 500–1000 atm and that the fact that some methods apparently give much lower values can be accounted for by the above combination of statistical mechanical and hydrodynamic considerations.

## 5. EFFECTS AFTER CAVITATION HAS OCCURRED

The best-known effect is cavitation damage to propellers and pipes. It was pointed out by Lord Rayleigh(7) that the collapse of cavitation bubbles could produce very high pressures in their neighborhood, comparable with the yieldpoints of metals. This could account for the distortions produced by cavitation, but not for cavitation erosion, the actual removal of metal. Rayleigh assumed that the cavitation bubbles would collapse as spheres, but it has been known since the war-time work of Penney and Price that the spherical shape is unstable. Work now in progress at Birmingham University by J. R. Blake and his collaborators enables one to follow the distortion of a bubble and the formation of jets, the impact of which on solids can explain cavitation erosion.

If an underwater explosion pulse is incident on a steel plate clamped at the edges rather than on a free surface, cavitation develops at the central portion of the plate, which grows a "beard" of bubbles. These eventually collapse onto the plate, increasing the damage. See Temperley.(10)

Various workers have developed "cavitation hydrodynamics," in which a cavitated liquid is regarded as an assembly of interacting bubbles. Among topics so considered are sound absorption on underwater explosion damage. For a survey see Dinham.(3)

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