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PHYSICS AND MATHEMATICS

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**SPECIAL HEAT TRANSFER PHENOMENA
FOR SUPERCRITICAL FLUIDS**

by

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SPECIAL HEAT TRANSFER PHENOMENA
FOR SUPERCRITICAL FLUIDS

by

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Abstract

Present-day knowledge concerning the molecular structure of supercritical fluids is briefly reviewed. It is shown that liquid-like and gas-like phases may coexist at supercritical pressures, although they may not be in equilibrium with each other. It is postulated that on the basis of the coexistence of these two phases a "boiling-like" phenomenon may provide the mechanism of heat transfer to supercritical fluids at high heat fluxes and certain other conditions.

An unusual mode of heat transfer was actually observed at supercritical pressures during tests which produced the high heat fluxes and other conditions under which such "boiling" would be expected. The tests and the various conditions are briefly described. An emission of high-frequency, high-intensity sounds usually accompanied these tests. It is shown that similar screaming sounds were heard during boiling at subcritical pressures, giving further support to the hypothesis that "boiling" may occur at supercritical pressures.

A second possible explanation for the unusual mode of heat transfer is based on boundary-layer stability considerations. At high heat fluxes large density differences exist between the bulk of the fluid and the fluid in the boundary layer near the wall. A breakdown of the boundary layer may be caused by the build-up of ripples between its low-density fluid and the high-density bulk fluid, in a manner quite similar to the breaking of ocean waves at high wind velocities.

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It is pointed out that the density variation of supercritical fluids may be used to advantage by centrifuging boundary layers. Possible schemes for centrifuging boundary layers to improve heat transfer characteristics are suggested.

Introduction

The discussion herein is concerned with fluids at pressures above their critical values. Such fluids are called supercritical fluids, although their temperatures may be higher or lower than their critical temperatures.

It is a common understanding that a supercritical fluid is a single-phase substance. For this reason, it is generally postulated that heat transfer mechanisms for supercritical fluids are similar to those that have been observed for single-phase substances such as gases^{3, 4, *}

It is one of the purposes of the present paper to point out that while a supercritical fluid is a single-phase substance under equilibrium conditions, it may not be one under nonequilibrium conditions, and that such nonequilibrium conditions do exist at certain times when thermal energy is being transferred to or from the fluid. Thus, it is postulated that two phases may coexist transiently and that under such conditions the mechanism of heat transfer may be similar to boiling.

Because of the large variations in the thermodynamic and transport properties of supercritical fluids with temperature, other heat transfer phenomena, which are not normally observed with single-phase substances, may also be encountered.

Discussions in this paper will be restricted mainly to heating, although similar considerations may also be applied to cooling of supercritical fluids.

* Superscript numerals indicate References listed at the end of this paper.

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Properties

The heat transfer characteristics of any fluid are functions of its thermodynamic and transport properties. Of particular interest for present purposes is the variation of these properties with temperature. Figure 1 shows density, specific heat, and thermal conductivity as a function of temperature for a typical supercritical fluid at a constant pressure. Several features are noteworthy.

The specific heat curve shows a pronounced peak. The temperature at which this peak occurs has been designated on the graph as "pseudo-critical temperature." This temperature is higher than the critical temperature of the fluid. The difference between the two temperatures depends on the pressure. For high pressures the temperature difference becomes larger and the magnitude of the specific-heat peak decreases.

Also shown in Figure 1 is the thermal conductivity as a function of temperature. The conductivity has a minimum value near the pseudocritical temperature. It is of special interest to note here that below this temperature, the conductivity shows a liquid-like behavior of the fluid (by decreasing with increasing temperature), while above this temperature, the conductivity varies as it would if the fluid were a gas (i. e., its conductivity increases with temperature).

This liquid-like behavior below and gas-like behavior above the pseudocritical temperature may also be discerned from the viscosity variation, which has not been shown in Figure 1, and from the density variation, which has been shown. At first the density decreases slowly with increasing temperature as it would if the fluid were a liquid. As the critical temperature region is approached, the density gradient becomes larger and reaches a maximum value at the pseudocritical temperature. The density variation then becomes less pronounced. At high temperatures the density exhibits a gas-like behavior; it follows Charles's law for perfect gases by being inversely proportional to temperature.

Further insight into the liquid-like and gas-like behavior of supercritical fluids may be gained by a review of the molecular structure

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of fluids. Figure 2, taken from Reference 15, is a two-dimensional representation of the postulated structure of the fluid states of matter in the vicinity of the critical point. The structural and numerical details refer to water. The ordinate of Figure 2 is pressure and the abscissa is temperature. The dots represent molecules. The region to the left of the solid curved line is the liquid region and that to the right of the line is the superheated-vapor or gaseous region. The solid line ends at the critical point, which has been indicated by a cross. The region above the cross is the supercritical region and the dotted line represents the loci of pseudocritical temperatures.

Of interest here is the grouping of molecules. In the liquid region molecules are grouped in cybotactic clusters, whereas in the gaseous region molecules are free to move independently of each other. The cybotactic groups decrease in size and are spaced farther apart with increasing temperatures and decreasing pressures. The transition from clusters to free molecules is sharply discontinuous below the critical pressure. Above the critical pressure, the transition from clusters (or liquid-like states) to free molecules (or gas-like states) is continuous with increasing temperature.

To decrease the size of clusters and to increase the spacing between clusters requires energy which must overcome the forces of mutual attraction between the molecules and clusters. This energy may be provided by heating the fluid.

It should be noted that these considerations regarding molecular structure are consistent with the variations of macroscopic fluid properties previously described and shown in Figure 1. For instance, the high specific heat near the pseudocritical temperature is a measure of the energy required to separate the molecules and thereby decrease the density of the fluid.

A Boiling-Like Phenomenon

From the foregoing it may be concluded that at low temperatures a supercritical fluid exists in a liquid-like state, while at temperatures

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above the pseudocritical temperature range it exists in a gas-like state. One may now begin to speculate as to the nature of heat transfer mechanisms for such a fluid.

It is clear that nothing unusual should happen if the temperature differences between the heating surface and the fluid are small. Even for moderately large temperature differences, heat transfer characteristics appear to be predictable on a quantitative basis, as has been shown in Reference 13. However, for very large temperature differences, which straddle the pseudocritical temperature region, something unusual may be expected to occur.

Consider, for instance, liquid-like water at a temperature of 400 F and a pressure of 5000 psia flowing through a nuclear reactor or an electrically heated tube whose surfaces are maintained at a temperature of 1000 F. The fluid in immediate contact with the heating surface is at 1000 F in a gas-like state. A short distance away, the bulk fluid is still in a liquid-like state at 400 F. If, by means of a transient or other disturbance, liquid-like fluid is brought into direct contact with the hot surface, a great amount of heat energy will flow from the surface into the fluid by virtue of the high conductivity of the liquid-like fluid and the large temperature difference between the surface and the fluid. One may speculate that this energy is larger than that required to separate cybotactic groups slowly into free molecules. Instead, the energy is enough to "explode" the molecule clusters. The "explosion" serves as a disturbance to bring additional cybotactic groups into contact with the 1000 F surface, resulting in similar explosions which in turn set off further disturbances. Thus, at supercritical pressures one may visualize an explosion of liquid-like molecular groups into gas-like aggregates in a manner similar to the formation of bubbles in liquids during boiling at subcritical pressures. Because of the required large temperature differences and concomitant large heat fluxes one may expect the boiling intensity to be severe under such supercritical "boiling" conditions.

An unusual mode of heat transfer, which may be explained by the aforementioned mechanism, has actually been observed experimentally at Pratt and Whitney Aircraft¹. The apparatus for the tests was the

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same as described in Reference 13. A typical test section consisted of an 8-inch length of tube with an inside diameter of 0.060 inch. Typical temperatures observed at the onset of supercritical boiling are shown in Figure 3, taken from Reference 1.

Figure 3 shows water bulk and tube-wall temperatures along the length of the electrically heated tube. The data were taken under steady-state conditions after the electric heat input had been increased first to a value corresponding to a wall heat flux of 1.12×10^6 Btu/hr-ft². The wall temperatures shown in Figure 3 under these conditions correspond to the values predicted by forced-convection heat transfer theories⁴. However, with a slight increase in heat flux to 1.16×10^6 Btu/hr-ft², the wall temperatures near the end of the tube decreased rapidly to a constant value slightly above the pseudocritical temperature. For this particular run they remained constant at approximately 860 F in the last 3 inches of tube length. The bulk water temperature increases from 600 F to 700 F in that same section of the tube. The similarity of the wall temperature profile under these conditions to profiles that are obtained at subcritical pressures with boiling occurring near the end of the tube is striking.

Other experimental evidence points towards the probability that a boiling-like phenomenon is the cause for the new heat transfer mechanism. Whenever this process occurred, it was accompanied by a loud noise, frequently described as a "whistle" or a "singing tube." Similar whistles have been heard during subcritical boiling under flow and heat flux conditions which are almost identical except for the supercritical pressures⁵. The subcritical whistles are usually heard when heat fluxes approach burnout values. Thus, film boiling, and what has more recently been called "transition boiling" by Westwater et alii^{16,17}, are the probable mechanisms of heat transfer during the subcritical tests in which whistling occurs.

The same mechanism of heat transfer, accompanied by a similar emission of high-intensity sounds, may be observed when a liquid drop is placed on a sufficiently hot horizontal surface so that the drop floats on a film of its own vapor. This phenomenon is generally known as the "Leidenfrost effect" and has more recently been investigated by Holter and Glasscock⁸.

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Another example of the whistling phenomenon is the quenching of a hot solid in a liquid. In investigating the mechanism which terminates the film boiling during quenching, Marx and Davis⁹ express the opinion that the alternate collapse and re-establishment of the vapor film produces audible notes.

On the basis of these observations one may conclude that the mechanism of heat transfer under the whistling conditions is similar for subcritical and supercritical pressures. Whether the high intensity sounds are generated by the "explosion" of cybotactic groups of molecules or not must still be proved. Harrison⁷ finds that the sound generated by a single bubble in a liquid is due to the collapse rather than the growth of the bubble. In line with this, one may speculate that the sounds during the supercritical tests were caused by the "implosion" of gas-like aggregates of molecules into liquid-like clusters, as the aggregates moved into the bulk stream, rather than by the "explosion" of the liquid-like clusters at the tube walls.

The conditions under which the tubes whistled at Pratt and Whitney Aircraft have been reported in Reference 1. Some of the more important observations may be summarized as follows:

1. At a given flow rate and inlet temperature, whistle occurs at higher heat fluxes for higher pressure levels.
2. At a given flow rate and pressure, whistle occurs at lower heat fluxes for higher inlet temperatures.
3. At a given pressure and inlet temperature, whistle occurs at higher heat fluxes for higher flow rates.
4. As heat flux is increased, whistle appears to commence when the wall temperature of a point 5 inches from the inlet of an 8-inch test section reaches a magnitude within a rather narrow range. This value varies with pressure approximately as follows: at 4000 psi it is 700 to 750 F, at 5000 psi it is 780 to 800 F, at 6500 psi it is 900 F.

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5. As heat flux is increased beyond the point of initiation of whistle, the temperature of the last three inches of an 8-inch test section remains roughly constant but increases to higher values than the value at the initiation of whistle.
6. Whistle could be produced with various lengths of test section between 8 inches and 2 inches, but the heat flux or inlet temperature had to be increased to bring it about as the tube was shortened.
7. The presence or absence of dissolved gas had no effect on whistle.
8. A system pressure increase of about 50 psi occurred at the onset of whistle.
9. The frequency of the sound varied from about 1400 cps to 2200 cps. Inlet temperature appeared to have the greatest effect on frequency. Pressure had little, if any, effect on the frequency.

Boundary-Layer Instabilities

The foregoing observations concerning an unusual mode of heat transfer strongly suggest a boiling-like mechanism. Nevertheless, it appears possible to explain some of the test results on the basis of turbulent boundary layer instabilities, leading to some sort of super-turbulence.

During all of the "singing-tube" tests, the density of the fluid in the boundary layer was much lower than the density of the bulk of the fluid. This suggests the possibility of a boundary layer breakup by the high density bulk fluid. One may perhaps visualize a wavy interface forming between the high-density, high-velocity bulk fluid and the low-density more stagnant boundary layer. With large differences in densities and velocities, the interface waves may become unstable and may actually break in a fashion similar to the breaking of surface waves of water under strong wind conditions. If this happens, the possible contact of low-

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temperature fluid with the tube wall and the increased level of turbulence will contribute greatly to increased heat transfer coefficients and lower wall temperatures.

While it would thus be possible to explain the lower wall temperatures near the end of the tubes, it would be difficult to find the source for the high intensity sounds in such an instability. It is therefore unlikely that this phenomenon was the cause for the "whistling" during the tests, although its occurrence may be expected under similar conditions.

It should be mentioned here, however, that other than boiling-type heat transfer mechanisms can generate sounds. According to Neuringer and Hudson¹¹, "The first known experiment on a singing tube containing a fine wire mesh as heat source was made by Rijke in the year 1859." The experiments by Rijke and others which followed were made with open air tubes. Various explanations have been advanced for the cause of the sounds but none appears to be completely satisfactory. At any rate, the sound intensities are low in spite of the direct communication of the heated air with the atmosphere. Thus, the oscillations responsible for this type of singing tube probably could not account for the high-intensity sounds which were heard during the supercritical-water tests.

The large property variations of supercritical fluids with temperature may also be expected to have a pronounced effect on the stability of laminar boundary layers. Thus the transition from laminar to turbulent flow should be a strong function of the heat energy which is transferred to or from a supercritical fluid. No test results are available to provide quantitative information as to the exact nature of this transition. Large flow instabilities have been observed in a closed free-convection loop¹⁴. While the major reason for these flow instabilities may be found in the large density variations, it does appear likely that the transition from laminar to turbulent flow made a significant contribution.

Other types of flow instabilities which result primarily from density variations with heat transfer have been discussed in Reference 6.

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Boundary-Layer Centrifuging

The variation of density with temperature suggests the centrifuging of boundary layers as a means for increasing heat transfer coefficients. As mentioned before, the density of the fluid in the boundary layer is less than the density of the bulk of the fluid when a supercritical fluid is being heated while flowing through a tube. If the fluid system is subjected to a centrifugal field, the denser bulk fluid will tend to replace the less dense fluid and thus break up the boundary layer. This boundary layer breakup should lead to increased heat transfer coefficients.

One method of setting up a centrifugal field is to give the fluid a spin. This may be done readily by various means, one of which consists of inserting a twisted ribbon into a straight tube. As the fluid flows along a tube with such an insert, it follows a spiral path which has a rotational component. The centrifugal field set up by the rotational component may actually be quite strong. For instance, fluid flowing with an axial velocity of 20 ft/sec through a 0.25-inch inside diameter tube with a ribbon having a pitch of one turn per inch will rotate at 14,400 rpm and will set up a rotational field which has a centrifugal acceleration of 750 g's.

Spiral or twisted ribbons have been proposed in the past as "turbulence promoters" with constant density fluids^{2,10,12}. As might be expected, test results were disappointing because with constant-density fluids the major effect of the ribbons was to increase turbulence by adding shear surfaces. The use of twisted ribbons for supercritical fluids, on the other hand, introduces strong centrifugal forces that act on the fluid particles in a direction perpendicular to the tube wall. These forces will quickly replace low-density, hot boundary-layer fluid with higher-density, cooler fluid. Thus, wall temperatures are reduced and heat transfer coefficients are increased.

The centrifuging of boundary layers in this manner is not restricted to supercritical fluids. The same methods may be applied to gases whose densities vary with temperature or to boiling liquids under very high heat fluxes.

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FIGURE I - THERMODYNAMIC AND TRANSPORT PROPERTIES OF A TYPICAL SUPERCRITICAL FLUID AT CONSTANT PRESSURE

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FIGURE 2 - MOLECULAR STRUCTURE OF WATER
(TAKEN FROM REFERENCE 15)

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FIGURE 3 - CHANGE OF HEAT TRANSFER MECHANISM
(TAKEN FROM REFERENCE 1)

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