PLENARY CONFERENCE

THE PROPERTIES AND BEHAVIOR OF SUPERHEATED LIQUIDS

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Abstract

This paper summarizes the results of recent investigations at the University of Houston into the prediction of the properties of metastable and unstable fluids. These include the p-v-T and other properties of superheated liquids, subcooled vapors, and the unstable fluid; the relation of surface tension to these properties; and the location of the spinodal lines.

Introduction

There is a growing need for better information about the properties of superheated liquids. Today's technology, presents us with a fanatical drive toward miniaturizing and intensifying thermal processes. We are driven to higher and higher heat fluxes, and this drive is accompanied by greater and greater dangers of sending liquids past their boiling points —into the metastable superheated-liquid range. Indeed, the recent accident at the Chernobyl nuclear power plant near Kiev has dramatized the dangers of operating at such elevated heat fluxes. Let us look at the kind of heat fluxes we are presently reaching for.

Gambill and Lienhard[4]* have recently adapted Schrage's[16] notion that the heat flux cannot exceed the value resulting from the latent heat associated with all of the molecules leaving a liquid-vapor interface. This sets the limiting heat flux as

$$q_{max,max} \equiv \rho_g h_{fg} \sqrt{RT/2\pi} . \tag{1}$$

The values of this upper bound, shown for three typical fluids in figure 1, are downright astronomical. For water at elevated pressure this limit suggests that one could transfer over 20 trillion Watts per square meter. Furthermore, we know that transfer occurs under driving temperature differences that are typically less than 100°C.

These numbers appear to be absurdly high; however, they are less absurd than one might think. Figure 2 shows data from many sources, for different fluids moving in a variety of forced flowboiling configurations. They reveal a suprising fact: Up to modest pressures, the heat flux can routinely be pushed to ten percent —and *just* ten percent— of this enormous upper bound. Actual heat fluxes as high as 173 MW/m² are represented here. (At higher pressures the upper bound is so high that existing systems are unable to deliver such heat fluxes to an interface. That is the reason that there are no data as high as $q_{max,\,max}/10$ on the left.)

What happens when we deal with such heat fluxes? For one thing, the liquid in contact with the heater must be brought to temperatures a hundred or so degrees above the normal boiling

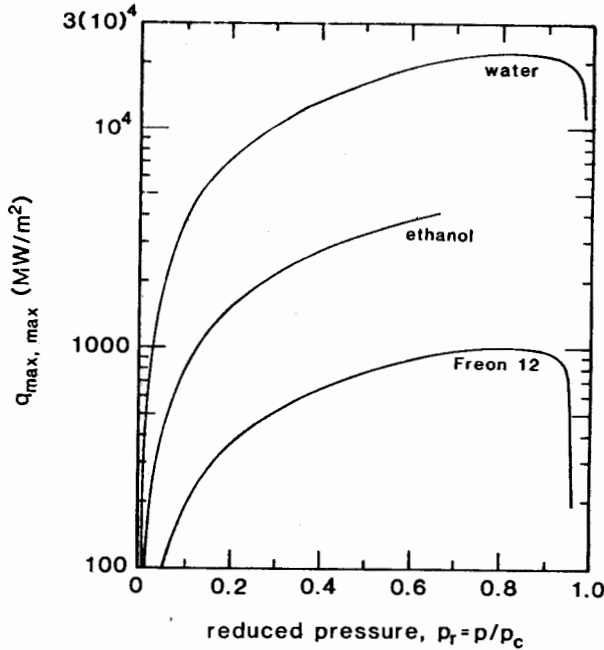* Numbers in square brackets denote entries in the *references*.

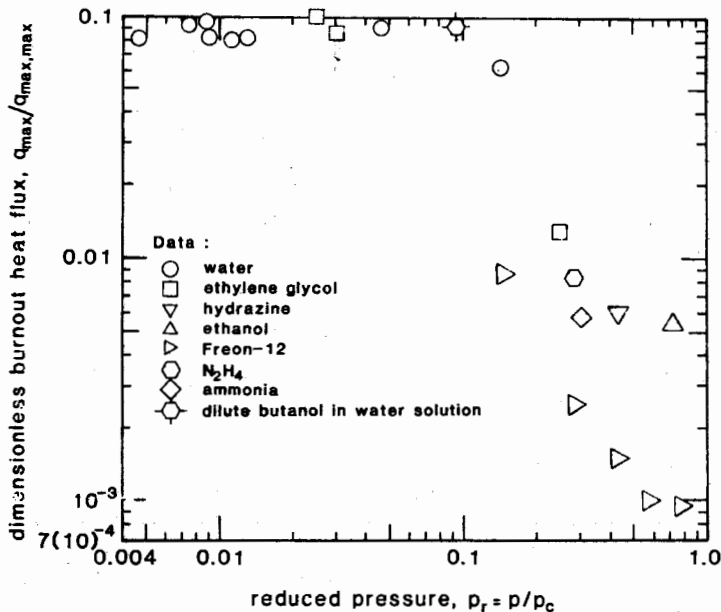Fig. 1.–   The upper bound on the peak boiling heat flux (from[4]).

Fig. 2.–   The highest observed peak boiling heat fluxes at several pressures (from[4]).

point. Furthermore, increasingly minor fluctuations in the system parameters can set off accidents that can instantly plunge liquids or vapors far into the metastable regions. The much-feared "nuclear thermohydraulic event" is an example of such an accident that we are ill-prepared to analyze

because *we have almost no knowledge of the properties of metastable liquids.* We are up against a real problem when it is necessary to predict process behavior in liquids that become superheated.

Figure 3 shows the *p-v*-T diagram for fluids in these regions showing the real isotherms of a fluid. (The reader is referred to[10,17] for more detail). We know that all states along an isotherm are *equilibrium* states. When the slope of an isotherm is positive, that equilibrium is *unstable*. When the slope is negative, the equilibrium is *stable.* When the slope is zero and the curve turns around, we define a *spinodal* point. The lines that connect these points are called the liquid and vapor *spinodal lines.*

Undergraduates are seldom even told about these isotherms and the multivalued behavior of matter. Instead, straight horizontal lines are drawn between the saturated liquid and vapor states —lines that only represent *mixtures* of saturated liquid and vapor. Doing this actually trumpets a claim to complete ignorance of the real behavior of fluids inside the saturated liquid-vapor dome.
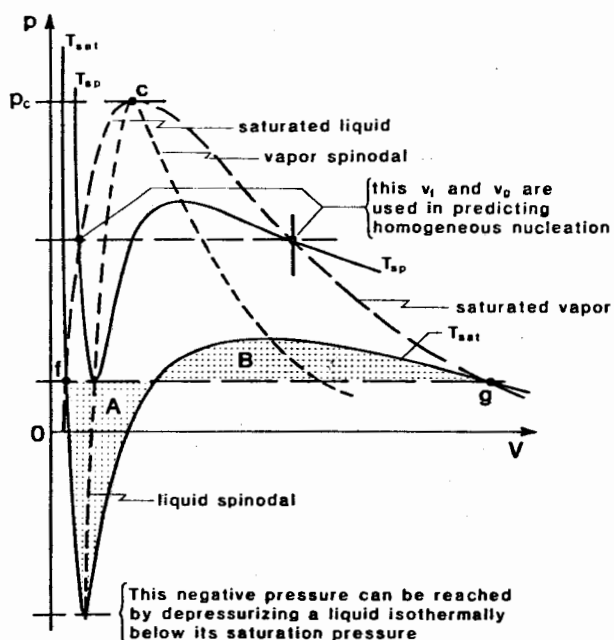

Fig. 3.– Isotherms of a real fluid.

Locating the spinodal line

Our first concern in predicting physical properties in this regime is that of locating the spinodal lines. Once they are known, we have the absolute limit beyond which a liquid can never be super-heated. For a long time, van der Waals' equation provided the only theoretical knowledge of the metastable states. Figure 3 is a three-dimensional picture of the van der Waals *p-v*-T surface with the conventional mixture regimes superposed on top of the metastable and unstable regimes.

Van der Waals wrote his equation by arguing, on the basis of molecular behavior, that there is an inherent continuity from the liquid to the vapor states[21]. An important feature of van der Waals' equation is that it can be nondimensionalized using critical data*:

* The symbols used here are common ones. They are defined in the *nomenclature* section.

$$p_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2} . \qquad (2)$$

The dimensionless van der Waals equation, in turn, suggests the Law of Corresponding States —that one should be able to write one equation of state, in reduced coordinates, that describes all substances:

$$f(p_r, \, v_r, \, T_r) = 0 . \qquad (3)$$

Today, we know that a *molecular parameter* has to be included in the Law of Corresponding States. This parameter is a second order correction[15]. The common candidates for it, are the critical compressibility, Z_c the Riedel factor, and the Pitzer acentric factor, ω. The Pitzer factor consistently, gives the best results of the three. Thus we expect to be able to write single equations of the form

$$f(p_r, \, v_r, \, T_r, \, \omega) = 0 . \qquad (4)$$

to describe either p-v-T properties, o p-v-T dependent properties, of any substance.

Figure 4 illustrates the of the Pitzer factor in a recent correlation by Dong and Lienhard[2]. These are boiling points for many liquids. Each line is for a different reduced pressure. By using the Pitzer factor as the abscissa, we get an almost perfect correlation. The solid lines show our new correlation and the dashed lines represent an older correlation that broke down at low pressures and Pitzer factors.

The important thing about this correlation, and every other such correlation that we have made, is that the van der Waals fluid correlates *right on the line.* It is a *member* of the family of real fluids[9,13]. An important corollary to such results is that the van der Waals equation should accurately describe any real fluid whose critical compressibility (or Riedel factor, or Pitzer factor) equals the van der Waals' value. So we ask: "Is there any such fluid?"

The boiling point of cesium shown on the left of figure 5 is very close to that of the van der Waals fluid, and so too is that of mercury. This is probably because the liquid metals have large hard-sphere molecules with modest attractive forces.
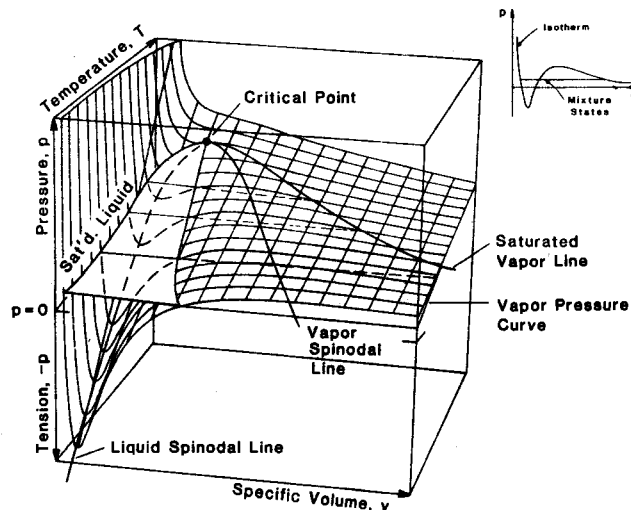

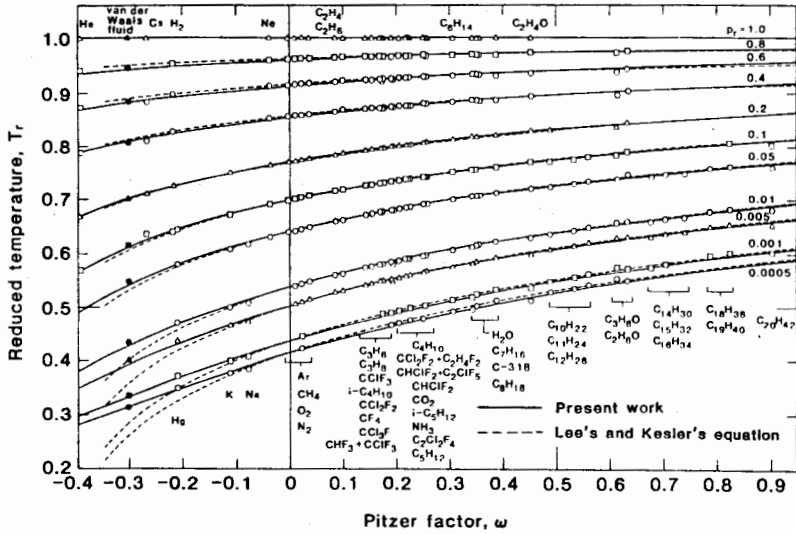Fig. 4.– Comparison of the van der Waals surface with equilibrium mixture data.

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Fig. 5.— Corresponding states correlation of the vapor-pressure curve (from[2])

The point is this: Since van der Waals' equation implies a pair of spinodal lines, and it is also the basis for the Law of Corresponding States, the real-fluid spinodal lines should therefore obey the Law of Corresponding states. If this is true, then we have a useful aid in locating the spinodal line.

Differentiation of the van der Waals' equation gives for the spinodal lines:

$$p_r = \frac{3}{v_r^2} - \frac{2}{v_r^3} \qquad (6)$$

which describes the liquid spinodal when v_r is less than 1, and the vapor spinodal when it is more than 1.

It should thus feasible to correlate the spinodal line, and that correlation should —in accordance with the Law of Corresponding states— resemble the van der Waals prediction.

It would be desirable to use *measurements* of the limit of liquid superheat to locate the spinodal line, but is that possible? Are the homogeneous nucleation limit and the spinodal line related? To bring a real liquid all the way up to the spinodal limit, there would have to be *no* disturbances or imperfections in the system. The problem is that real liquids are made of molecules which are constantly in motion. As we approach the temperature of instability, these motions provide the disturbances needed to upset the liquid stability at some temperature *less* than the spinodal temperatures.

To determine whether or not a real liquid can be brought close to the spinodal limit, we calculate the mechanical energy needed to create a minimum stable vapor bubble[6] —the bubble that will make a metastable liquid, unstable. To set the size of such a bubble, we require that it be in both static and thermal equilibrium with the surrounding superheated liquid. The result is the well-known unstable equilibrium radius, or critical radius, R_0

$$R_0 = \frac{2\sigma}{p_{sat} \text{ at } T_{superheat} - p_{sat} \text{ at } T_{ambient}}. \qquad (7)$$

Frenkel[3] used this radius to calculate the "potential barrier" to nucleation —the difference in Gibbs function between the liquid with, and without, an unstable vapor bubble in it:

$$Wk_{crit} = \frac{4}{3} \pi R_0^2 \, \sigma \, . \tag{8}$$

This barrier may also be viewed as the *critical work* needed to bring the bubble into existence. Substituting equation (7) in equation (8) and correcting the vapor pressure for the influence of curvature through surface tension, we obtain

$$Wk_{crit} = \frac{16 \pi \sigma^2}{3 \, (p_{sup} - p_{sat})^2 \, [1 - v_f/v_g]^2} \, . \tag{9}$$

We want to compare this energy with some energy that characterizes the superheated liquid[6]. Two energies are appropriate to this purpose: One is the average level of molecular vibrational energy, which is on the order of kT where T is the temperature of the superheated liquid. All the conventional theories of homogeneous nucleation are based on this energy. The other possibility is the energy required to separate two molecules from one another. This is the depth of the "potential well" of the intermolecular potential, which is on the order of $k\,T_c$.

We next define

$$j \equiv \text{probability that nucleation will occur in a given molecular collision} \tag{10}$$

The fractional increase of this probability should be proportional to the fractional decrease of the critical work:

$$\frac{dj}{j} \sim - \frac{dWk_{crit}}{kT \text{ or } kT_c} \, . \tag{11}$$

It follows that

$$j \frac{\text{nucleation events}}{\text{molecular collision}} \sim \exp \left[- \frac{Wk_{crit}}{kT \text{ or } kT_c} \right] \, . \tag{12}$$

We call the ratio of Wk_{crit} to kT (or kT_c) the Gibbs Number, Gb. Then, using $j = 1$ when $Gb = 0$, we get

$$j = e^{-Gb} \, . \tag{13}$$

Every prediction of homogeneous nucleation is some kind of a version of equation (12). One more often finds equation (13) written in terms of a nucleation rate, J, per unit volume and time:

$$J \frac{\text{nucleation events}}{\text{m}^3 - \text{sec}} = N \frac{\text{molecules}}{\text{m}^3} B \frac{\text{collisions}}{\text{sec}} e^{-Gb} \tag{14}$$

so $j \equiv J/NB$. (J runs about 39 orders of magnitude larger than j in water).

The problem we now face is that of predicting the limiting value of j —the value at which nucleation absolutely has to occur. To do this Karimi and Lienhard[6], imagined that the liquid is subdivided into regions with volumes equal to that of the smallest critical bubble. They counted

the number of collisions that can occur (per relaxation time) in this volume. If just *one* of these collisions leads to nucleation it means the simultaneous flashing of the liquid everywhere. Therefore the inverse of this maximum number of collisions is the absolute largest value that j can possibly assume. It comes out on the order of 10^{-5}. The corresponding minimum value of Gb is around 11.

Of course this limit is only an order-of-magnitude estimate, but it turns out that predictions are only affected by very large variations in j. (People who are not familiar with nucleation theory are usually startled at the idea that factors of 10 can have such a small influence.)

The other calculation Karimi and Lienhard made was to determine the temperature difference between the homogeneous nucleation point, and the spinodal point, at this limit. The result is on the order of only 1°C. When they repeated this calculation on the vapor side, they found that the two points are not even close to each other. This means that the *liquid* spinodal can be located with high accuracy using a homogeneous nucleation prediction, but that we should not even try this on the vapor side.

We next use equation (9) in the definition of Gb and the result in equation (12) and obtain:

$$\ln j = -\frac{16\pi\sigma^3}{3\,(kT \text{ or } kT_c)\,(1 - v_g/v_f)^2\,(p_{sp} - p_{sat})^2}. \tag{15}$$

We next ask what limiting homogeneous nucleation *data* exist. Skripov and his coworkers at the Urals Institute at Sverdlovsk[17,18] have pushed the limit of liquid superheat much further in the laboratory than anyone else has. Of the many techniques for creating high superheat in a liquid, the most effective has been Skripov's method of pulse heating a thin filament of wire submerged in a pure liquid. When the wire is subjected to a known electrical pulse, its temperature rises rapidly and predictably within a period of a few microseconds. As the temperature rises, a few initial instances of isolated nucleation occur, but then —at a certain temperature— a complete blanket of vapor appears on the wire. This is the point where no further temperature increase is possible in the liquid.

Skripov reached different limiting temperatures depending on the rate at which he heated the liquid; but, as the heating rate rose, the temperature approached an asymptote. The value of j calculated at that limit approached 10^{-5}. (Actually, Skripov reports some j-values that exceed 10^{-5}, but only at heating rates for which a different and less reliable experimental technique had to be used.)

Figure 6, taken from[11] shows (as open circles) those Skripov data that were available in 1974, for j values on the order of 10^{-13}. They are represented as the difference between the homogeneous nucleation temperatures, and the saturation temperature at the same pressure, as a function of reduced temperature. The homogeneous nucleation data for these twelve different liquids clearly do conform to Corresponding States correlation. Furthermore, the shape of the dashed correlating line through them is very similar in form and placement to the van der Waals spinodal line.

Notice that we have already shown *a priori* that such data should almost coincide with the spinodal line. And we know that the spinodal line has to obey the Law of Corresponding States. Therefore the fact that they do correlate provides *a posteriori* vindication for our somewhat radical claim that the limit of homogeneous nucleation can be used to locate the liquid spinodal line.

Figure 6 also includes the van der Waals *vapor* spinodal line along with the best data for droplets nucleating in subcooled vapor. Clearly, the vapor nucleation data do not conform to Corresponding States correlation at all; and that is also what we predicted would happen.

The liquid spinodal line shown in figure 6 can be quite accurately characterized by equations of the form

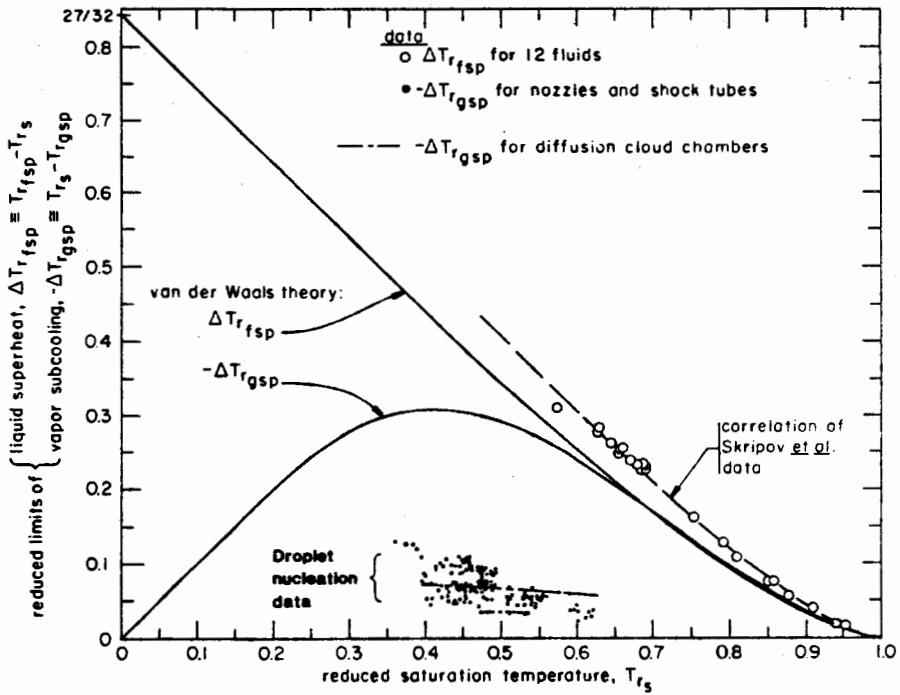$$\Delta T_r = A - T_{r,\,sat} + (1 - A)\,T_{r,\,sat}{}^B. \tag{16}$$

Fig. 6.– Correlation of extreme liquid superheating data and vapor subcooling data (from[11]).

The calculated values ΔT_r for a van der Waals fluid are well represented by equation (16) with $A = 27/32$ and $B = 5.16$. Skripov's data for liquids are well represented by $A = 0.905$ and $B = 8$. The equation for Skripov's data will give values slightly less than an accurate generalized spinodal value, because j for these data is a factor of 10^{-8} smaller than the spinodal j. In other words, we shall see shortly that the effect of an eight-order-of magnitude difference in j is minor.

All the variables in the homogeneous nucleation theory for the spinodal limit are ones that are subject to the Law of Corresponding States. That means we can also form a Corresponding States correlation for the limit of pressure undershoot[12]. This result is shown in figure 7. This correlation, of course, is for $j = 10^{-5}$.

If a particular set of physical circumstances requires us to use a different value of j, we can re-express this result in terms of the new j, thus:

$$p_{sat} = p_{sp} - \frac{4.0934}{\sqrt{-\ln(j)}} \left. \frac{\sigma^{1.5}}{\sqrt{kT_c(1 - v_f/v_g)}} \right|_{at\ T_{sp}} \tag{17}$$

This can be simplified using the correlation in figure 7 to get

$$\Delta T_r = \frac{112.82 + 224.42\ \omega}{\sqrt{-\ln(j)}} (1 - T_{r,\ sp})^{1.83}. \tag{18}$$

Of course, smaller values of j will give a homogeneous nucleation limits that lie below the spinodal line.

Finally, in figure 8, we present the Corresponding States spinodal line correlation once again in terms of temperature using $A = 0.923$ and $B = 9$ in equation (16). The result lies about 2 percent above the correlation we put through Skripov's data. This reflects the increase of j from the value of 10^{-13} (in Skripov's experiments) to $(10)^{-5}$.
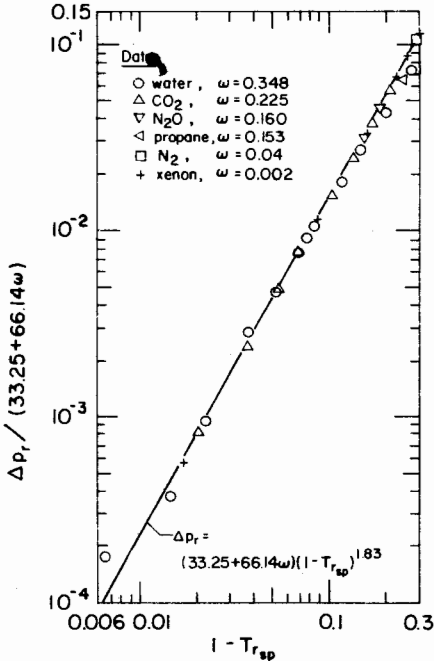

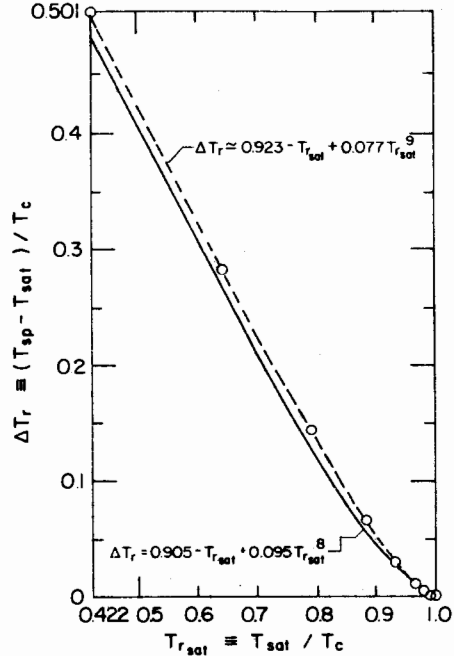Fig. 7.— Correlation of the limiting pressure under-shoot (from[12]).

Fig. 8.— Correlation of the limiting superheat (from[12]).

Thermodynamic properties of metastable and unstable fluids

We can now place the spinodal limit with reasonable accuracy, but we still cannot evaluate thermodynamic properties with any accuracy in the metastable ranges. Such data are constantly needed in boiling and two-phase heat transfer work, but measurements are very hard to come by, and little analysis has been done.

The thermodynamic properties for these regimes, are often estimated by extrapolating then linearly in temperature. This is accurate for slightly superheated liquid, but at higher superheats it leads to all kinds of trouble. (The specific heat at constant pressure approaches infinity on the spinodal lines, liquids become highly compressible at high superheat, and so forth). The next thing we have to work on is evaluating these properties.

A "fundamental" or "canonical" thermodynamic equation is one from which all equations of state can be derived. The most commonly used form is the Hemholtz function, $\Psi = \Psi(T, \rho)$, with temperature and density as independent variables. The several equations of state are obtained as the derivatives pf a fundamental equation with respect to its independent variables:

$$p = \rho 2 (\partial \Psi / \partial \rho)_T ; \quad s = -(\partial \Psi / \partial T)_\rho ; \quad \text{etc.} \tag{19}$$

Most Steam Tables are based on empirically constructed fundamental equations with, typically, over sixty constants in them[8,19,20]. Such equations make it possible to evaluate any thermodynamic property within four decimal places. But, faced with any fluid but water, we seldom have anything near such complete property information. Furthermore, such equations seldom give *any* valid information in the metastable regimes.

Karimi[7] has made the one attempt to write a fundamental valid equation for these regimes. We want to see how this is done, but first let us look at some of his results:

Figure 9 shows Karimi's p-v-T surface for water, showing the metastable and unstable portions of the isotherms. Figure 10 shows his T-s diagram for water. It shows what the real-fluid isobaric
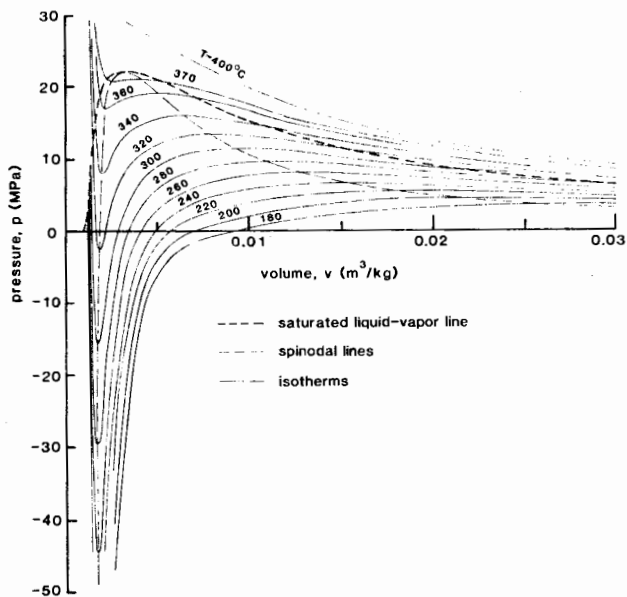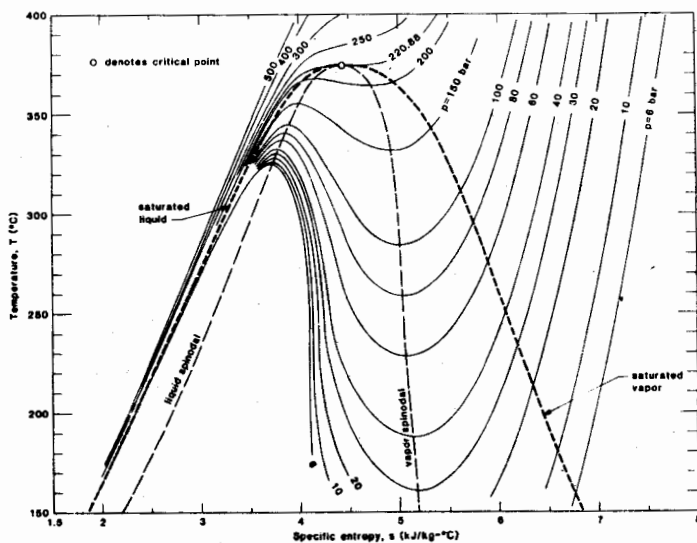

Fig. 9.– The isotherms of real water (from[7]).

Fig. 10.– The T-s diagram displaying the isobars of real water (from[7]).

lines look like in the metastable and unstable regions. The Mollier diagram shown in figure 11 looks pretty familiar until we note that the isothermal and isobaric lines now *separate* below the saturation line. (In the conventional mixture-representation, they lie on top of each other.) Finally, in figure 12, we see the less familiar pure intensive fundamental equation for water –the temperature, pressure, Gibbs-function plot.

Karimi's fundamental equation points out the potential for predicting metastable and unstable behavior. Still, he had trouble fitting the equation below 150°C, and he had to use different sets of coefficients above and below 150°C.

Karimi refit the constants of the Keenan, Keyes, Hill, and Moore (or KKHM) form of fundamental equation, which only represents stable data. Karimi extended his equation into the metastable region by imposing additional constraints.

The most important of these conditions was that it must satisfy the Gibbs-Maswell condition. This condition is based on the fact that the Gibbs functions (or chemical potentials) for the
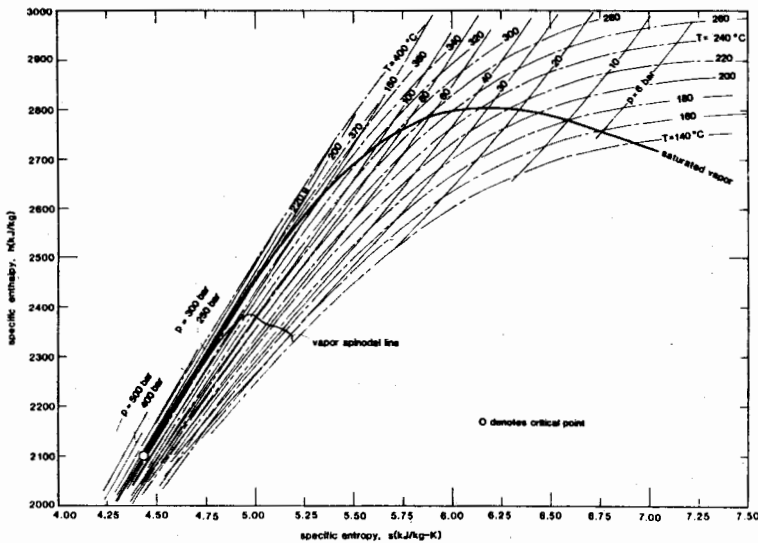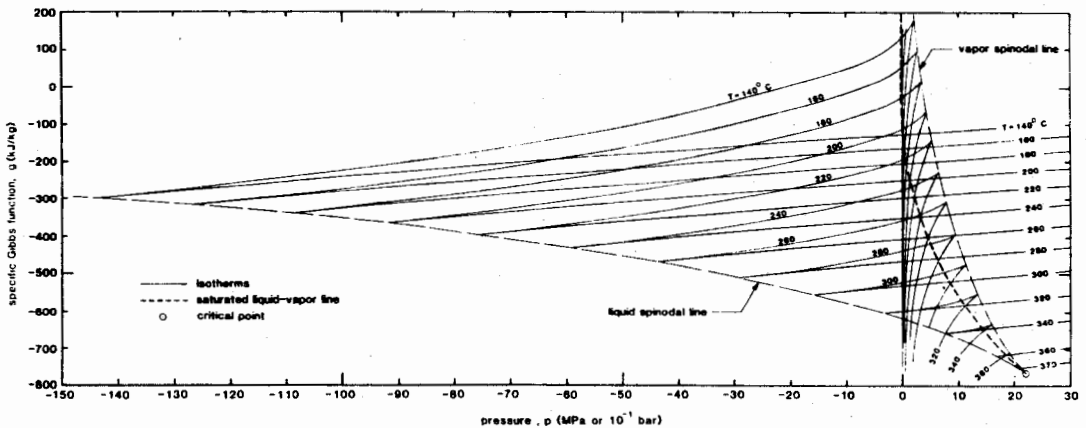

Fig. 11.– The Mollier diagram of real water (from[7]).

Fig. 12.– The purely intensive fundamental equation, $g = g\ (p,\ T)$, for water (from[7]).

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saturated liquid and vapor states must be equal. If we integrate the Gibbs function along an isotherm we find that

$$\int_f^g v\,dp = 0 \tag{20}$$

Thus Karimi forced the areas A and B, shown in figure 3, to be equal. He also made isotherms exhibit single maxima and minima; he made it match the correct spinodal limit; and so forth.

The problem was that the KKHM equation takes the form of an ideal gas expression plus a correction, and the ideal gas lead term doesn't show any features of the unstable and metastable regimes. So Karimi had to absorb all of the complexity of water in the correction term.

A student at the University of Houston, P. O. Biney, is currently using a lead term that gives pressure in a nearly cubic form in v, and which displays all of the real fluid features. That means that his correction term is now much smaller. It only has to improve the *accuracy* of the lead term —its does not have to provide all the features of real fluid behavior by itself.

One of the cubic equations being exploited for this purpose is this one, developed by Shamsundar[1],[10].

$$\frac{p}{p_{\text{sat}}} = 1 - \frac{(v - v_f)(v - v_m)(v - v_g)}{(v + b)(v + c)(v + d)} \tag{21}$$

equation (21) is just a general cubic written in a particularly useful form. The known quantities p_{sat}, v_f, and v_g; and the four free parameters, v_m, b, c, and d all vary with temperature. This means that the most straight forward use of the equation is one where we fit one isotherm at a time.

Two of the parameters can be fixed with the help of the ideal gas law limit and the Gibbs-Maxwell equal-areas condition. Then we only need two more pieces of data to fit an equation that should be quite accurate along a given isotherm. It has turned out that the isothermal compressibility of saturated liquid and one compressed liquid point give the best results. So, for a given temperature, the coefficients for the equation may be obtained using very few data. Be aware that this means fitting the coefficients of the equation *directly* (using very few data) and not *statistically*.

The temperature-by-temperature application of equation to liquid water has yielded accuracies *within the tolerance* of the IFC Skeleton Tables[12] in the subcritical range of pressures. In figure 13, (see[17]) the only other simple equation, close enough to the data to appear on the plot, is Redlich's 1975 equation[14]. Figure 14 shows a similar comparison for ethylene. Equation (21) again outclasses all other "simple" equations. Of course, the key to its success is that the coefficients are free from having to obey any predetermined dependence on temperature.

We emphasize the liquid side because liquid properties are normally so hard to predict. Equation (21) also does extremely well in predicting superheated vapor properties.

Such cubic p-v-T equations also imply liquid and vapor spinodal values. Values of the spinodal pressure implied by these curve fits are plotted in figure 15. They are compared with values predicted by equation (15) using $j = 2 \times 10^{-5}$, and based on both kT and kT_c. It is clear that the use of kT_c is far superior. The choice is not important in the region of positive pressure, and this is the only region where experiments have ever been made for large j's. At lower pressures, though, the two diverge very strongly. This makes it pretty plain that kT_c should be used in place of kT.

This exercise was repeated with many fluids in[1] and, while j varies a little from fluid to fluid, it is always on the order of 10^{-5}.

The present focus on the metastable and unstable regions is both an end in itself; and a means to a different end, at the same time. Because of the interlocking character of thermodynamic information, when we represent this region correctly we also wind up simplifying and improving p-v-T representations elsewhere.
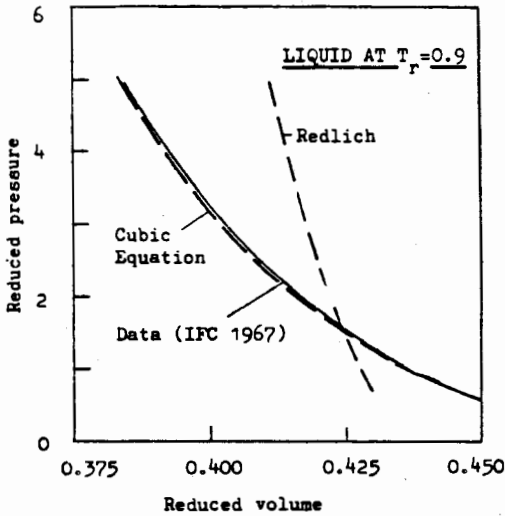
Fig. 13.– Predicted and measured isotherms of liquid water (from[10]).
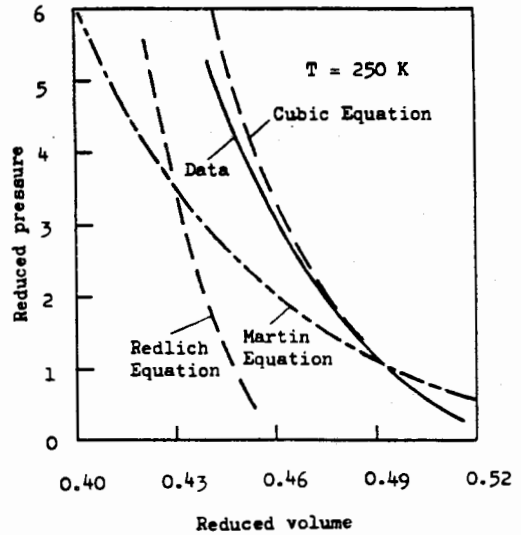
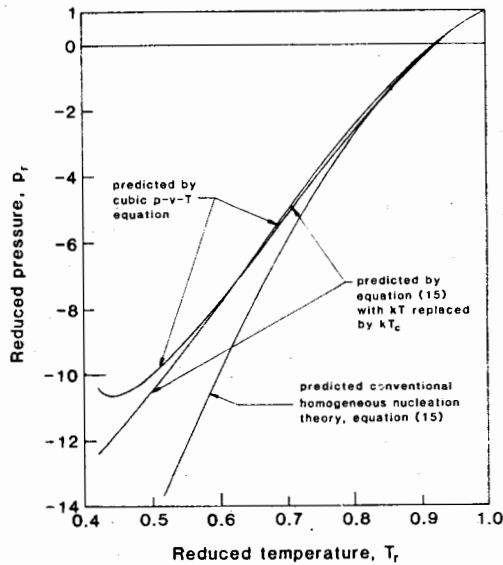Fig. 14.– Predicted and measured isotherms of liquid ethylene (from[10]).

Fig. 15.– The spinodal line for water, predicted by both homogeneous nucleation theory and the cubic equation (from[10]).

Surface tension and p-v-T data

Surface tension is intimately related to the p-v-T equation of state. In 1894 van der Waals developed the following remarkable, and completely precise, prediction of surface tension from a knowledge of the p-v-T equation of state[22]:

$$\frac{\sigma}{\sigma_0} = f(T_r) = \int_{v_{r_f}}^{v_{r_g}} \frac{1}{v_r^{5/2}} \left[p_{r\,sat}\,(v_r - v_{r,f}) - \int_{v_{r_f}}^{v_r} p_r\,dv_r \right]^{1/2} dv_r \, . \tag{22}$$

To integrate this equation we need a full knowledge of p-v-T data throughout the metastable and unstable fluid regimes. Therefore, an acid test of any p-v-T equation that purports to predict
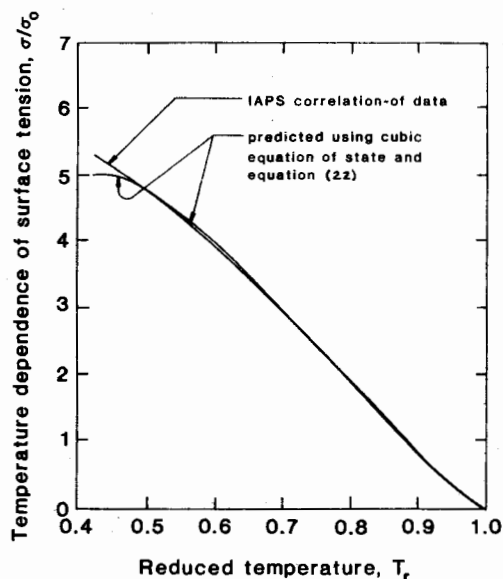

Fig. 16.– The temperature dependence of the surface tension of water: Comparison of data with the van der Waals surface tension prediction based on the cubic equation (from[10]).
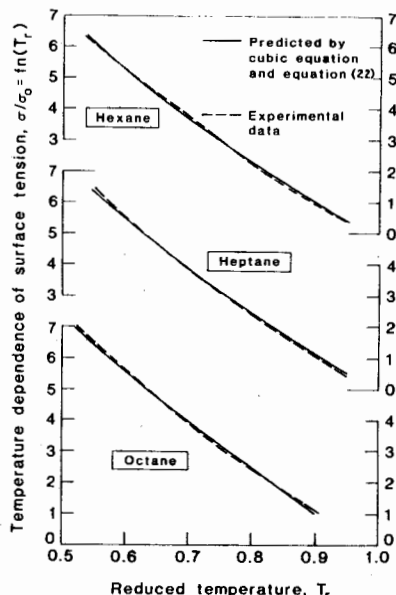
Fig. 17.– The temperature dependence of the surface tensions of hexane, heptane, and octane: Comparison of data with the van der Waals surface tension prediction based on the cubic equation (from[10]).
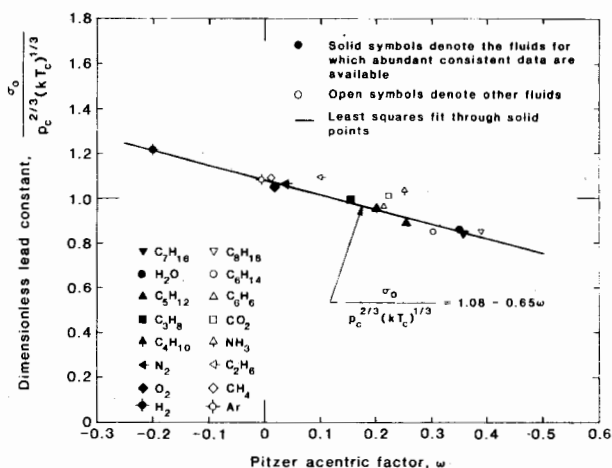

Fig. 18.– Correlation of the suraface tension lead constant for use with the van der Waals surface tension prediction (from[10]).

metastable and unstable properties is that it has to predict the correct temperature dependence of surface tension when it is used in this equation.

Figures 16 and 17 show the typical results of applying this test to water, hexane, eheptane, and octane. It is quite clear that, except at the very lowest temperatures, when we substitute the metastable and superheated properties that we have predicted in van der Waals' integral, we obtain almost perfect predictions of the temperature dependence of surface tension.

Each time this comparison is made for a fluid, we obtain the lead constant, σ_0, by comparing the prediction with actual surface tension data. These lead constants are plotted against the Pitzer factor in figure 18, using the appropriate nondimensionalization of σ. Solid symbols have been used to identify those substances for which we have high confidence in all of the relevant property data. The result is a *very* good correlation for σ_0. Using this result, p-v-T data, and the van der Waals surface tension integral it becomes possible to *predict* surface tension.

The generalized compressibility factor

We enjoy such success in interpolating physical properties with the help of cubic equations because the cubic equation has the right natural form, of course; but also because we impose the right constraints and checks. Some of the constraints —like the correct liquid and vapor volumes— are built in. Others —like the Gibbs-Maxell "equal-areas" condition and the ideal gas limit— are imposed. (By the way, it is perfectly fascinating that *none* of the fundamental equations in common use *do* satisfy the Gibbs-Maxwell condition and therefore they *cannot* give a decent representation of metastable and unstable behavior).

We have also developed several back-checks to verify, *a posteriori*, whether or not the cubic equations are accurate. The direct relation between p-v-T data and surface tension is one such check. The close relation between the spinodal line and the limit of homogeneous nucleation is another.

A third such check was developed in[5]. If we write the p-v-T equation of state in virial form

$$p = RT/v + B/v^2 + C/v^3 + \ldots \tag{23}$$

At low pressure we may drop terms on the order of v^{-3} in equation (23) when it applies to the vapor side. Then we note that on the vapor spinodal lines

$$(\partial p/\partial v)_T = - RT/v^2 - 2B/v^3 = 0 \tag{24}$$

so $B = - RTv/2$. Substituting this into equation (23) we get for the low pressure vapor spinodal line

$$Z = 1/2 . \tag{25}$$

Since all cubic equations can be cast in virial form, they satisfy this constraint automatically. But, when an entire fundamental equation is fitted, this check becomes quite important if it is not already built into the p-v-T behavior.

Finally, let us look more carefully at the compressibility factor, Z. Figure 19 is a schematic diagram from[15] which shows how the p-v-T surface maps into generalized compressibility coordinates: The various regimes of behavior are indicated on it. All of the positive pressure regimes —stable, metastable, and unstable— lie in the upper-right-hand quadrant. All of the regimes of liquid tension —metastable and unstable— lie in the lower-left-hand quadrant.

Figure 20 shows the spinodal points from the many p-v-T interpolations for a large variety of fluids, as they appear on Z coordinates. Of course, no Z-chart is valid beyond a narrow range of Pitzer factors. These data are for ω's from −0.302 up to about 0.7 or so. But the solid line re-

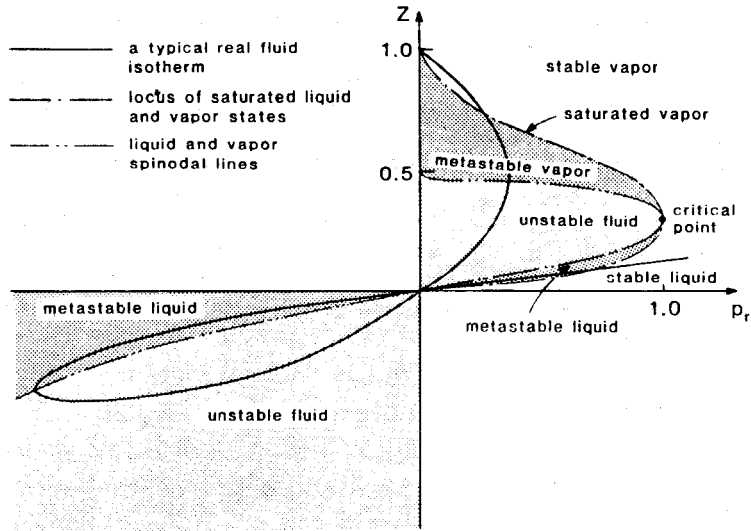Fig. 19.– The form of the complete generalized compressibility chart (from[2]).
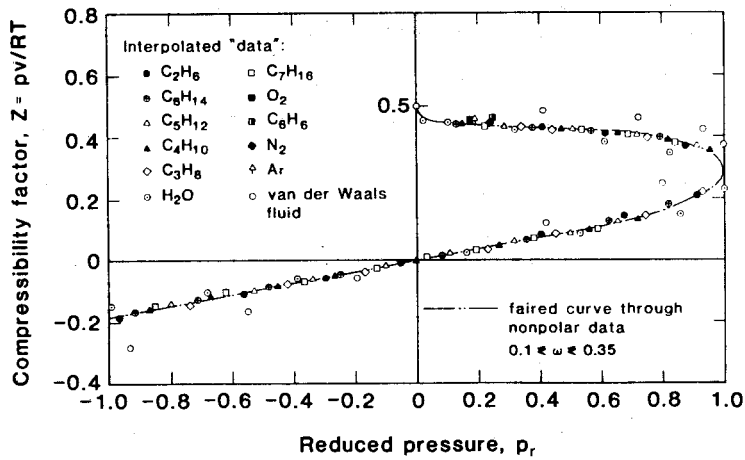

Fig. 20.– Generalized spinodal line for $0.1 > \omega > 0.35$ (from[2]).

presents data for the much smaller range between 0.1 and 0.3 within about two percent accuracy —except near the critical point. Notice, too, that the line has to extrapolate to the zero-pressure value of $Z = 1/2$.

This is also done for the isotherms in figure 21. The results are combined in figure 22 to give a generalized compressibility chart for the metastable and unstable regimes. It is valid for the common Pitzer factor range from 0.1 to 0.3 and for pressures up about nine-tenths of the critical value.
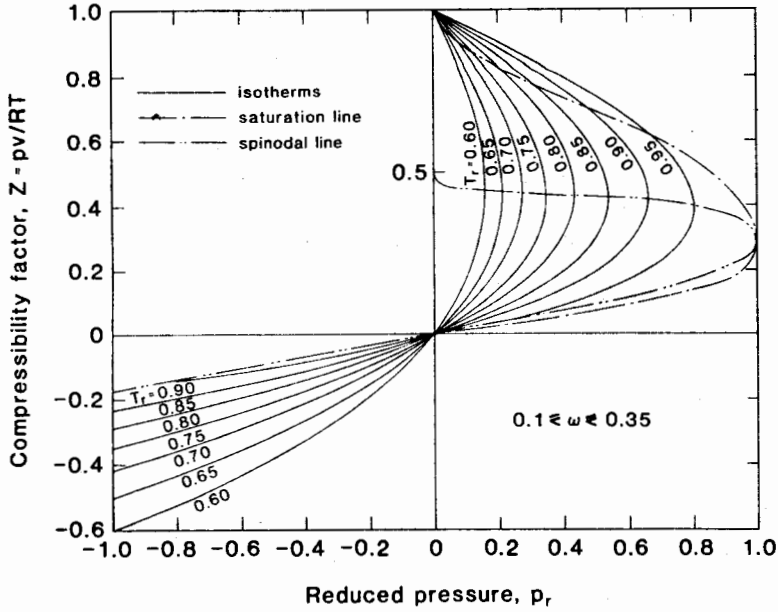
Fig. 22.-- Generalized compressibility chart for metastable and unstable fluids, for $0.1 > \omega > 0.35$ (after[2]).
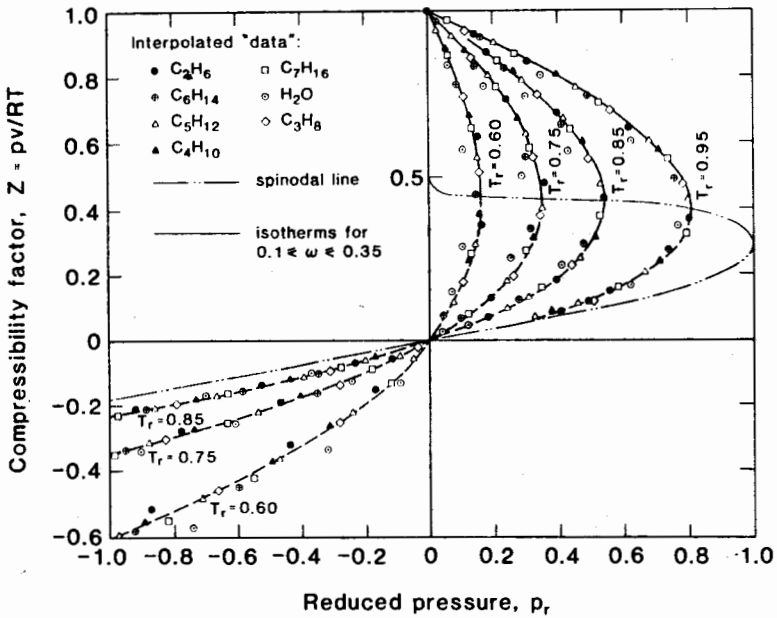

Fig. 21.- Generalized isotherms for metastable and unstable fluids, for $0.1 > \omega > 0.35$ (from[2]).

Nomenclature

B   rate of molecular collisions

B, C   arbitrary constants

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Gb   Gibbs number, $Wk_{crit}/(kT$ or $kT_c)$

g Gibbs function or chemical potential of a pure fluid

h enthalpy

h_{fg} latent heat of vaporization

j, J probability of nucleation in each molecular collision; probability of nucleation per unit volume and unit time. (See equations (10) and (14), and context)

k Boltzmann's constant

N   volumetric density of molecules in a superheated liquid

p pressure

q_{max} peak pool boiling heat flux

$q_{max, max}$
            upper bound for the peak heat flux, equation (1)

R   ideal gas constant

R_0 critical radius of an unstable nucleus, equation (7)

s entropy

T   temperature

v specific volume

Wk_{crit} potential barrier to nucleation (or minimum work required to create a critical nucleus)

Z, Z_c compressibility, pv/RT; critical compressibility, $p_c v_c/RT_c$

Greek letters

ΔT $T_{sp} - T_{sat}$

ρ density, $1/v$

σ, σ_0 surface tension, lead constant in the van der Waals surface tension prediction

Ψ Helmholtz potential function

ω Pitzer acentric factor, $-[1 + \log_{10} P_{sat} (T_r = 0.7)]$

General subscripts

c denoting a critical property

f, g denoting saturated liquid and vapor properties

m denoting the middle root of an isotherm on p-v coordinates, at P_{sat}

r denoting a reduced property —one divided by its critical value

sat   denoting a saturated state

sup   denoting a superheated liquid state

sp or

f_{sp}, g_{sp} denoting a property on a liquid spinodal line; on a vapor spinodal line

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