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Report 4088

# SHIP RESEARCH AND DEVELOPMENT CENTER

Bethesda, Maryland 20034



A NEW, GENERAL FORMULATION FOR  
MULTIPROPERTY THERMODYNAMIC CORRELATIONS

by

Thomas S. Walton

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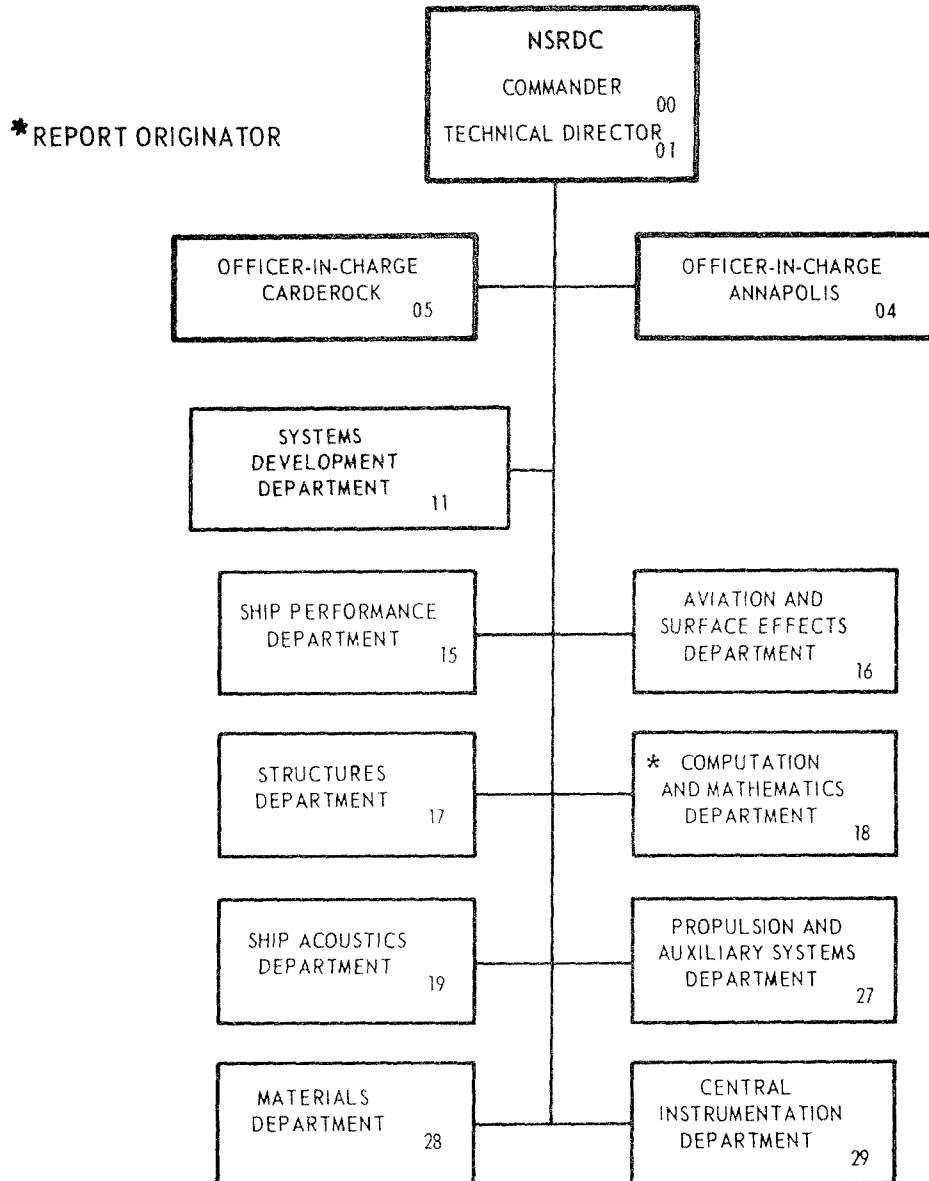
A NEW, GENERAL FORMULATION FOR MULTIPROPERTY THERMODYNAMIC CORRELATIONS

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DEPARTMENT OF THE NAVY  
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## ABSTRACT

A comprehensive equation of state based on the Helmholtz free energy has been developed for representing the thermodynamic properties of pure substances over a wide range of conditions including the region near the liquid-vapor critical point. The formulation comprises a set of terms that are regular (expandable in a Taylor series) in the vicinity of this point plus a term which becomes singular there. The latter takes account of the anomalous behavior observed when the critical state is approached, and is needed to attain a consistent, quantitative approximation to experimental data.

Both the singular and the nonsingular parts of the free energy are given in closed form as functions of density and temperature. Moreover, the expressions are designed to vary in an appropriate fashion when one or the other of the arguments approaches zero or infinity. Thus, the limiting form is in accord with Debye's  $T^3$  law for specific heats at low temperatures, while it reduces to the ideal gas law when the density is allowed to vanish. The majority of the parameters occur as coefficients of the various terms, which facilitates a least-squares determination of their values. The few that are involved in a nonlinear manner have been introduced to characterize behavior peculiar to certain regions.

The work described here augments that previously documented in Naval Ship Research and Development Center Report 3664 (May 1971). A more explicit treatment of the critical region is presented and the approximation for the singular contribution is extended to a higher order to permit better agreement with observation.

## ADMINISTRATIVE INFORMATION

The work reported here was carried out within the Advanced Software R&D Group of the Computer Sciences Division under the sponsorship of NAVSHIPS, Task Area SF53532107, Work Unit 1-1830-005.

This material was originally presented at the 74th National Meeting of the American Institute of Chemical Engineers held in New Orleans in March 1973. The format follows the guidelines prescribed for papers presented at that meeting.

## SUMMARY

A fundamental equation of state based on the Helmholtz free energy is given which permits correlation of equilibrium thermodynamic properties of simple fluids over a wide range of conditions embracing both the dispersed and condensed phases. The formulation takes account of the singularity at the critical point while exhibiting the proper asymptotic behavior for extreme values of density and temperature.

### I. INTRODUCTION

This paper deals with the mathematical representation of the thermodynamic properties of a chemically homogeneous, stable molecular substance. It is intended for applications in which a single, compact formulation yielding accurate values over a wide range of conditions is required.

There is a growing awareness that comprehensive, computer-oriented descriptions of material properties can be of great value to such tasks as engineering design and contract preparation, as well as to the quest for new knowledge. Such needs were recognized long ago in the case of water due to its nearly universal employment as the working fluid in power-generating machinery. Since 1921, under the sponsorship of what is now called the International Association for the Properties of Steam, there has been a continuing effort to reassess and improve the accuracy of available data and to extend the range of observation so that reliable tables and formulas can be compiled for designing boilers and turbines.

The incentive for undertaking the study reported here grew out of an attempt to devise an effective interpolation scheme for the data comprising the 1963 International Skeleton Table for Compressed Water and Superheated Steam. This set of values was adopted by the Sixth International Conference on the Properties of Steam (ref. 1), and a concerted effort was then made by groups in several countries to produce a suitable formulation. However, because of the great range covered by the table (from 1 to 1000

atmospheres and 0 to 800 degrees C), no single equation could be found that would satisfy the stringent tolerances prescribed by the Sixth ICPS<sup>†</sup>. An interim solution was eventually agreed upon wherein the data points were divided into six subregions, each having its own formulation, with the stipulation that they should closely conform at their common boundaries.

The representation finally adopted contained a total of 151 constants plus a large assortment of integer as well as fractional exponents (ref. 4). Such a solution leaves much to be desired, both practically and aesthetically. It became apparent that a more rational approach would have to be pursued to achieve any appreciable simplification of the situation.

## II. OBJECTIVES

The notion of the continuity of state for a given substance implies the existence of a single analytic function that will completely characterize its equilibrium thermodynamic properties (ref. 5). The problem then reduces to that of devising an accurate and concise approximation for this function. In view of the remarkably similar behavior of nearly all substances, it seemed desirable that such a formulation should expressly reflect those attributes held in common, so that it could have general application rather than be tailored to a particular substance. However, it was decided to restrict the investigation to a description of the behavior of pure substances, and thereby avoid the added complications that arise in dealing with mixtures. Logic dictates that an acceptable means of treating simple fluids should be worked out first.

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<sup>†</sup>Two of the papers presented at the Seventh ICPS in 1968 came close to satisfying the requirements (viz., reproduction of density values to better than 0.1 percent over most of the region), one by Keenan, Keyes, Hill and Moore (ref. 3) and the other by the present author (later expanded into ref. 2). Both these formulations were based on the Helmholtz function, but each suffered from the drawback that no provision had been made for the singular behavior of this function at the critical point.

A number of considerations, both practical and theoretical, entered into the step-by-step development of a comprehensive equation of state. Experimental measurements, by themselves, do not usually fulfill all the requirements of users, since observation is limited by

- 1) the availability of suitable instrumentation
- 2) the range over which measurement is feasible
- 3) the precision attainable in each region
- 4) the difficulty and cost of experimentation.

A mathematical formulation helps to mitigate some of these restrictions while providing for a variety of user needs, such as

- 1) smoothing and interpolation of data values
- 2) correlation of diverse properties
- 3) compact representation of extensive observations
- 4) evaluation of quantities not directly measurable, e.g., entropy.

Lastly, there are constraints which derive from the physical behavior of material substances. Among the phenomena that must be taken into account are

- 1) the nearly ideal behavior at low densities
- 2) the vapor pressure at low temperatures
- 3) the Joule-Thomson coefficient
- 4) the specific heat of the condensed phases
- 5) the specific-heat anomaly at the critical point
- 6) the vapor-liquid equilibrium curve.

In addition, at every point for which the substance exhibits either stable or metastable behavior, a proper formulation must satisfy the Thermodynamic Inequalities, i.e., both the isochoric specific heat and the isothermal compressibility must be positive. All in all, a general phenomenological description consistent with established theory appeared to be a reasonable goal.

### III. OVERALL APPROACH

It was concluded that the various objectives could best be achieved through the adoption of one of the canonical thermodynamic functions. All equilibrium properties can then be expressed in terms of the set of its partial derivatives with respect to two appropriate conjugate variables. The Helmholtz free energy was chosen not only because of its basic role in statistical physics but also because of its convenient attributes and regular behavior. It is the only one of the canonical functions which involves directly measurable quantities (such as pressure, volume, temperature, and energy in the form of heat or work) and which also has the property that all its first- and second-order differential coefficients are finite and continuous for all physically realizable values of the two independent variables, excluding only the critical point.

This function may be conveniently used in either of two forms:

$$f \equiv f(v, T) \quad [\text{free energy per unit mass}]$$

$$a \equiv a(\rho, T) \quad [\text{free energy per unit volume}]$$

where  $v$ ,  $\rho$ , and  $T$  stand for the specific volume, density, and absolute temperature, respectively. The relation between the two forms is simply  $a = \rho f$ . Quantities such as pressure  $p$ , isothermal compressibility  $k_T$ , specific entropy  $s$ , and specific heat at constant volume  $c_v$  are directly derivable from  $f(v, T)$ . Thus we have

$$p = -(\partial f / \partial v) \quad (1)$$

$$1/k_T = v(\partial^2 f / \partial v^2) \quad (2)$$

$$s = -(\partial f / \partial T) \quad (3)$$

$$c_v = -T(\partial^2 f / \partial T^2) \quad (4)$$

Other properties are readily obtained from various combinations of the foregoing, e.g.,

$$u = f + Ts \quad (5)$$

$$g = f + pv \quad (6)$$

$$h = u + pv = g + Ts \quad (7)$$

in which  $u$  denotes the internal energy per unit mass,  $g$ , the Gibbs function per unit mass, and  $h$ , the enthalpy per unit mass.

One of the main conclusions reached in the course of this study was that the free energy must be resolved into a singular part which predominates in the critical region plus a regular part which suffices elsewhere. This conclusion is based on experimental investigations of many different gases carried out by Voronel' and his co-workers in the Soviet Union during the 1960's. Their measurements reveal that the isochoric specific heat of pure substances becomes indefinitely large as the critical state is approached (ref. 6). No function which is analytic (i.e., expandable in a Taylor series) at the critical point can adequately represent behavior of this type. However, such a function can serve as the background onto which a properly formulated anomaly may be superimposed. We shall consider the regular part first, and then introduce an expression for the singular contribution.

#### IV. REGULAR TERMS OF THE APPROXIMATION

It will be convenient in what follows to employ nondimensional independent variables, namely,

$$\xi = \rho/\rho_c \quad [\text{reduced density}] \quad (8)$$

$$\theta = T/T_c \quad [\text{reduced temperature}] \quad (9)$$

where  $\rho_c$  and  $T_c$  stand for the critical density and temperature of the substance in question. We proceed by defining an auxiliary function of these two variables which exhibits a marked change of character in the

transition from a dispersed to a condensed state. Accordingly, we write

$$\begin{aligned}\phi(\xi, \theta) &= \frac{\xi^2}{\xi^2 + \epsilon^2 \theta^3 (\eta \xi + \zeta)} & (10) \\ &\approx \xi^2 / \epsilon^2 \theta^3 \zeta & \text{as } \xi \rightarrow 0 \text{ or } \theta \rightarrow \infty \\ &\approx 1 & \text{as } \xi \rightarrow \infty \text{ or } \theta \rightarrow 0\end{aligned}$$

and in which  $\eta(\theta) = \eta_0 (1 - e^{-\hat{\theta}/\theta})^3$  (11)

$$\zeta(\theta) = \theta^n Q_0^2 \quad (12)$$

$n$  is the number of rotational degrees of freedom of the molecule

$Q_0$  stands for the molecular partition function excluding the factors for translation and rotation

and  $\epsilon$ ,  $\eta_0$  and  $\hat{\theta}$  are adjustable constants. A significant property of  $\phi(\xi, \theta)$  is that, although its value is quite small under conditions approaching those of an ideal gas, it tends toward unity at low temperatures and/or very high densities. This feature is crucial to giving the subsequent formulation a wide scope. The function  $\eta(\theta)$  is introduced to render a better description of the Joule-Thomson coefficient as well as the second virial coefficient at low temperatures. On the other hand,  $\zeta(\theta)$  relates strictly to the behavior of the ideal gas and is assumed, in the context of this work, to be a known function. Moreover, by explicitly isolating the factor  $\theta^3$  from  $\zeta(\theta)$ , we ensure conformity with Debye's formula for the specific heat of the condensed phases at low temperatures.

The different classes of terms that contribute to the regular part of the equation for the free energy are

a) the ideal gas approximation

$$\frac{1}{2} RT \ln \phi \quad (13)$$

b) the residual entropy at absolute zero

$$R \ln \Omega_0 \quad (14)$$

c) the internal energy at absolute zero

$$RT_c \sum_{\ell=0}^m A_{\ell} \xi^{\ell} \quad (15)$$

d) the temperature-dependent, high-density corrections

$$-RT(1-\phi) \sum_{\ell=0}^m \sum_{k=0}^{\ell} B_{\ell k} \phi^k \xi^{\ell-k} \quad (16)$$

in which R is the gas constant,  $\Omega_0$  stands for the (effective) number of distinct orientations that the molecules can assume in the formation of the crystalline phase of the substance,  $A_{\ell}$  and  $B_{\ell k}$  are adjustable coefficients, and m is an index which fixes the degree of the polynomials (15) and (16). This index is set to provide as many terms as are necessary to fit the data to within the prescribed tolerances. It should be noted that none of the properties of ideal gases are in any way affected by inclusion of the various supplemental terms.

A discussion of the rationale behind the design of the above expressions, together with a detailed analysis of their asymptotic behavior, is given in reference 2. It will suffice here to indicate the limiting forms to which the proposed equation of state reduces in each of four extreme cases:

- 1) Debye's  $T^3$  law for solids (as  $T \rightarrow 0$  for constant  $\rho$ )
- 2) van der Waals' equation (as  $T \rightarrow \infty$  for constant  $\rho$ )
- 3) the ideal-gas law (as  $\rho \rightarrow 0$  for constant T)
- 4) a polynomial in density (as  $\rho \rightarrow \infty$  for constant T).

A check on the adequacy of such an equation was carried out some time ago on the basic set of values for water and steam given in the 1963 International Skeleton Tables over a grid comprising 580 combinations of pressure and temperature. Both enthalpy and PVT data were used as input to the fitting procedure. The resulting PVT approximation (with the index m equal to 5) remained generally within the assigned tolerances and was about as accurate as that obtained by Keenan et al (ref. 3).

However, the concomitant approximation for enthalpy did not prove to be as satisfactory, particularly in the area close to the critical point. The deficiencies were most evident in values calculated for the isochoric specific heat, which deviated quite significantly from experimental data taken in this region (ref. 7). This observation served as the motivation for the next stage of development.

## V. THE CRITICAL REGION

Attempts to extend analytic formulations to include the area around the critical point have generally encountered major obstacles. Either an inordinate number of terms must be used, having--for the most part--rather large numerical coefficients but nearly canceling one another (which can lead to erratic derivatives), or else the tolerances have to be greatly relaxed. An accuracy of 0.1 percent or less in fitting pressure (which is one of the least sensitive variables in the critical region) cannot be achieved without some recognition of the peculiar properties of a fluid near its critical state (see Figures 1 and 2). Careful observation has revealed striking departures from the classical behavior exemplified by an equation such as that of van der Waals (ref. 8).

The significant phenomena are: a) the greatly diminished curvature of the coexistence or vapor-liquid equilibrium curve near the critical point; b) the pronounced flatness of the pressure isotherms in the region lying just above this point; and c) the presence of an anomaly in the specific heat which, in the same region, varies approximately as

$$-c_v \sim \ln \tau = \ln(T/T_c - 1) \quad \text{for } \rho = \rho_c, T > T_c. \quad (17)$$

It has been noted by Yang and Yang (ref. 9) that the thermodynamic identity relating the specific heat, pressure, and chemical potential (or Gibbs function)

$$\rho c_v = T(\partial^2 p / \partial T^2)_v - \rho T(\partial^2 g / \partial T^2)_v \quad (18)$$

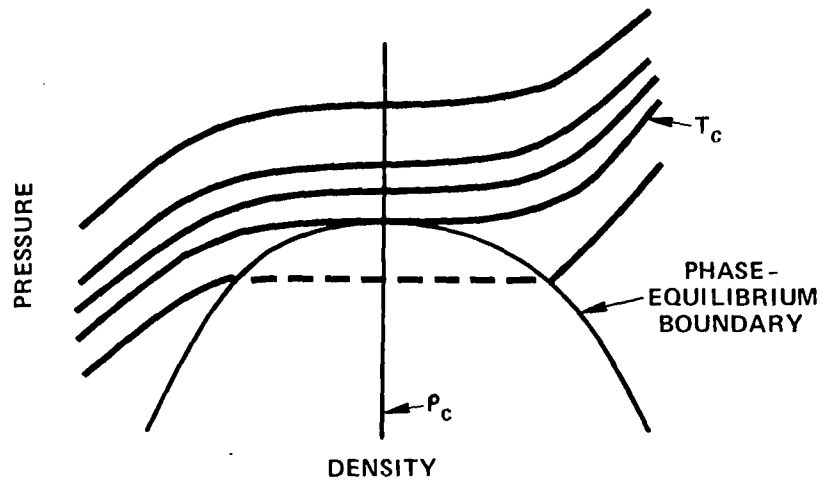


Figure 1 - Shape of Isotherms in Critical Region

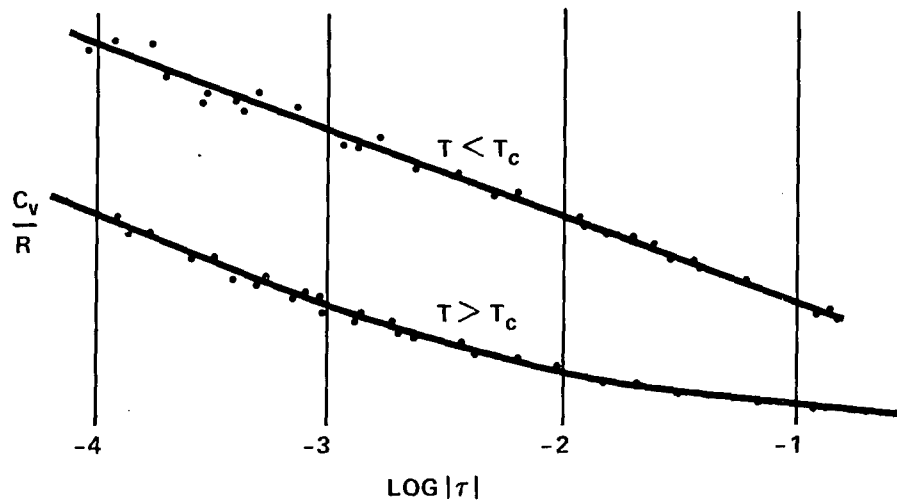


Figure 2<sup>\*</sup> - Isochoric Specific Heat Along Critical Isochore

implies that one (or both) of these second partial derivatives entails the same singularity as the specific heat.

The hypothesis that the chemical potential is analytic at the critical point has been advanced by a number of investigators on various theoretical grounds (refs. 10 and 11). Kierstead's recent measurement of the quantity  $(\partial p/\partial T)_v$  along the critical isochore of He<sup>4</sup> (ref. 12), combined with Moldover's heat-capacity data (ref. 13), strongly support this hypothesis. In fact, it appears that the quantity  $(\partial g/\partial T)_v$  is a linear function of T for  $\rho=\rho_c$  over an appreciable interval extending both above and below  $T_c$ . Such a hypothesis also has a certain appeal because it gives rise to simpler and more symmetric expressions for a number of related properties, and we will presume its validity in the following section. It then becomes natural to adopt the free energy per unit volume,  $a(\rho,T)$ , from which the chemical potential, pressure, entropy per unit volume, and heat capacity per unit volume are obtained as follows:

$$g = (\partial a/\partial \rho) \quad (19)$$

$$p = \rho g - a \quad (20)$$

$$\rho s = -(\partial a/\partial T) \quad (21)$$

$$\rho c_v = -T(\partial^2 a/\partial T^2). \quad (22)$$

## VI. THE LOCAL APPROXIMATION FOR THE ANOMALY

At this stage, it is instructive to consider an expression which can be valid only in the immediate neighborhood of the critical point--for reasons that will be made clear later. Nevertheless, a great deal may be inferred from the behavior of certain quantities derived from it in this restricted region. To simplify the notation, it is convenient to introduce as independent variables

$$\sigma = \xi - 1 \quad [\text{reduced density difference}] \quad (23)$$

$$\tau = \theta - 1 \quad [\text{reduced temperature difference}] \quad (24)$$

We then write for the singular part of the free energy

$$a^* = -RT\rho\psi^*(\sigma, \tau) \quad (25)$$

where

$$\psi^* = \frac{\alpha}{\xi} \left[ \tau^2 \ln \frac{\beta\omega}{\tau} - \frac{\beta\tau}{2} + \frac{\beta^2}{24} \right] \quad (26)$$

$$\omega = \frac{\tau}{\gamma_1 \bar{\sigma}^2 + \tau} \leq 1 \text{ if } \tau > -\gamma_1 \bar{\sigma}^2 \quad (27)$$

$$\bar{\sigma} = \sigma + \delta\tau \quad (28)$$

and  $\alpha$ ,  $\beta$ ,  $\gamma_1$  and  $\delta$  denote adjustable parameters. The magnitude or "strength" of the anomaly is measured by  $\alpha$  and its range of influence, by  $\beta$ ; while  $\gamma_1$  controls the curvature of the coexistence curve at the critical point and  $\delta$ , the slope of its diameter (defined for subcritical temperatures as the locus of the midpoints of its vapor and liquid branches).

Not only does formula (26) possess the desired type of singularity<sup>†</sup> at the critical point ( $\sigma=0, \tau=0$ ), but the argument of the logarithm also tends to infinity everywhere along the locus  $\tau = -\gamma_1 \bar{\sigma}^2$ , thus generating a continuum of singular points which curves downward from the critical point, as depicted in Figure 3. Such a locus must lie within the region of the density-temperature plane corresponding to unstable states, so that (except for the critical point) it is beyond the reach of direct experimental investigation. Its existence is implied, however, by the observation that, along isochores on either side of the critical one, the value of  $c_v$  rises at an ever increasing rate with falling temperature

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<sup>†</sup> It is shown in reference 2 that formula (26) gives rise to a logarithmic specific-heat anomaly while at the same time the quantities  $s^*$ ,  $p^*$ ,  $\partial p^*/\partial\rho$ ,  $\partial p^*/\partial T$ ,  $\partial^2 p^*/\partial\rho^2$ ,  $\partial^2 p^*/\partial\rho\partial T$  and  $\partial^3 p^*/\partial\rho^3$  all exist and remain bounded as the critical point is approached from the upper half-plane ( $\tau>0$ ). This is necessary to ensure that the formulation represents a thermodynamically stable situation along the isotherms just above the critical point.

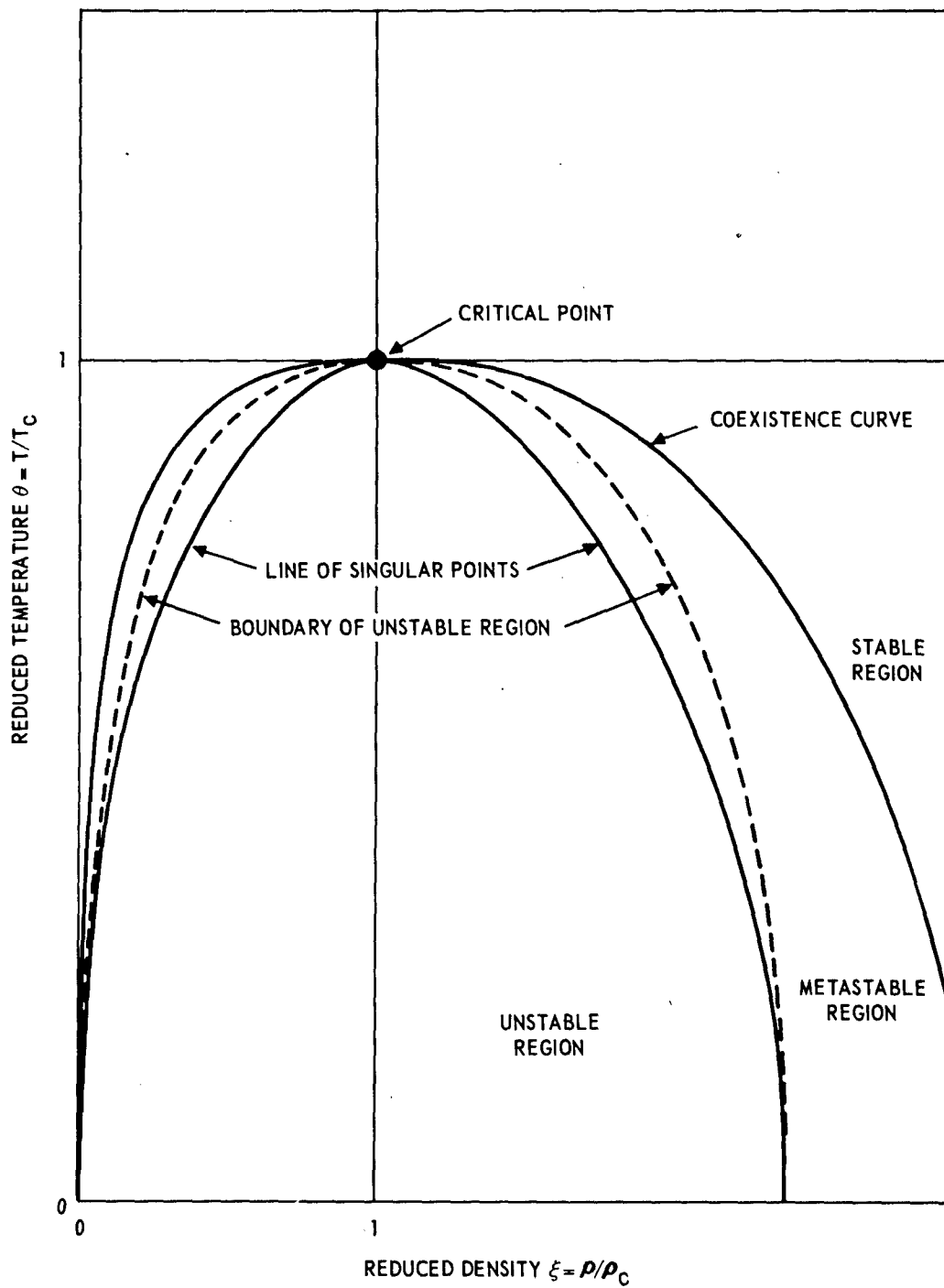


Figure 3 - State Diagram for a Typical Fluid

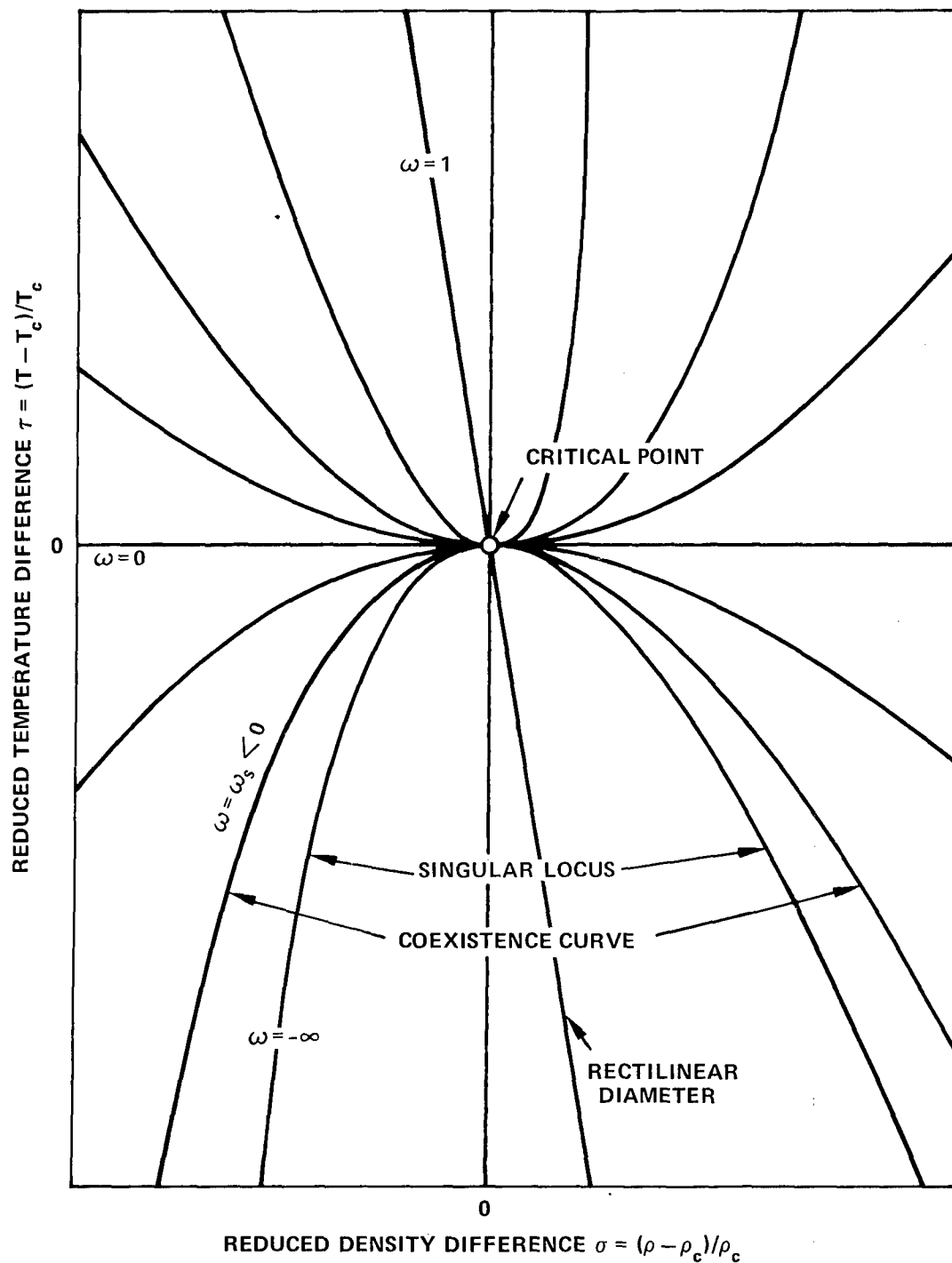


Figure 4 - Local Behavior of Contours of  $\omega$

until the coexistence curve is intersected (ref. 14). Indeed, the shape of this curve may be largely determined by the proximity of such a line of singular points.

Additional insight is gained by examining the family of trajectories generated when the quantity  $\omega$  is held constant. In particular,  $\omega$  takes on the value unity along the diameter of the coexistence curve, zero on the critical isotherm, and negative infinity along the line of singular points, as illustrated in Figure 4. It can further be shown that the coexistence curve coincides (at least in the critical region) with one of the contours of  $\omega$ . The regular part of the free energy is expanded in a Taylor series about the critical point, and to this is added the singular part given by equation (25). Then, using equation (19) to obtain  $g(\sigma, \tau)$  and invoking the condition for equilibrium of the two phases,  $g_V(\tau) = g_L(\tau)$ , we can find an expression for the value  $\omega = \omega_S$  appropriate to this curve. Moreover, as pointed out in reference 2, certain derivatives of  $\psi^*(\sigma, \tau)$  reduce to polynomials in  $\omega$ , so that their values are invariant along a trajectory for which  $\omega$  is constant. Lastly, we note that the inclusion of the term  $\delta\tau$  in the definition (28) for  $\bar{\sigma}$  allows the approximation (27) for  $\omega$  near the critical point to be carried as far as third-order terms in  $\sigma$  (since  $\tau$  is of the same order as  $\sigma^2$  there). As a result, the parabolic configuration of the trajectories is skewed so as to be symmetrical about the rectilinear diameter rather than about the critical isochore. [See reference 15 for a somewhat similar treatment of the critical region.]

## VII. REQUIREMENTS FOR GLOBAL VALIDITY

In actuality, the coexistence curve can be characterized as parabolic only over an interval extending to either side of the critical density by roughly ten percent. The curvature is so slight for most substances, however, that the corresponding drop in temperature amounts

to only about a tenth of a degree! At greater density deviations, higher-order terms have a significant effect, thus obscuring the parabolic region<sup>†</sup> whose existence has long been a matter of speculation (ref. 17).

To rectify the situation, equations (26), (27) and (28) for  $\psi^*$ ,  $\omega$  and  $\bar{\sigma}$ , respectively, must be so modified that they apply throughout the density-temperature plane while their local properties remain intact. In particular, the contours of  $\omega$  must conform to a set of constraints that ensures proper asymptotic behavior for extreme values of density and temperature. The desired effect is achieved by requiring that the numerator of the expression for  $\omega$  vanish not only at the critical temperature but also as the temperature approaches zero. It must also vanish when the density goes to zero or becomes indefinitely great. At the same time, the denominator must be given additional flexibility to permit essential nonlocal conditions to be imposed on the shape and location of the line of singular points. However, any modification has to be done in such a way that certain key features are retained: the denominator function must remain positive for all physically realizable states; the line of singular points (along which the denominator vanishes) must be concave downward with its maximum ordinate occurring at the critical point; and the conditions  $\omega = 1$  and  $\partial\omega/\partial\xi = 0$  must hold along its diameter, as before.

These considerations suggest the following generalization of equation (27)

$$\omega = q^2\theta^3(\theta^3-1)/z \quad (29)$$

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<sup>†</sup>This phenomenon can best be seen in Weber's measurements of the density of oxygen in the critical region (ref. 16). His data include six pairs of saturation densities that lie within ten percent of  $\rho_c$ , and are the most accurate available at the time of this writing.

$$\text{where } z = Ir^2 + Jr + K + (Lr + M)(\theta^3 - 1) + N(\theta^3 - 1)^2 \quad (30)$$

$$q = \frac{\bar{\sigma} + 1}{C\bar{\sigma}^2 + \bar{\sigma} + 1} = \begin{cases} 1 & \text{when } \bar{\sigma} = 0 \\ 0 & \text{when } \bar{\sigma} = -1, \infty \end{cases} \quad (31)$$

$$r = \frac{(D+1)\bar{\sigma}^2}{D\bar{\sigma}^2 + 1} = \begin{cases} 0 & \text{when } \bar{\sigma} = 0 \\ 1 & \text{when } \bar{\sigma} = -1, 1 \end{cases} \quad (32)$$

$$\bar{\sigma} = \xi v - 1 = \begin{cases} 0 & \text{when } \xi = 1/v \\ -1 & \text{when } \xi = 0 \end{cases} \quad (33)$$

and  $v = v(\theta)$  is a function of temperature (to be given later) which satisfies the condition  $v(1) = 1$ , so that  $\bar{\sigma}(\xi, 1) \equiv \sigma$ . The quantities  $C, D, I, J, K, L, M$  and  $N$  are adjustable coefficients subject to certain constraints. We assume that both  $C$  and  $D$  have nonnegative values so that the functions  $q(\bar{\sigma})$  and  $r(\bar{\sigma})$  will be free of poles on the real axis for all  $\bar{\sigma} \geq -1$ . This avoids the introduction of extraneous poles and zeroes into the definition of  $\omega$  that might adversely affect its properties.

The denominator  $z$  has the form of a general quadratic expression in the variables  $r$  and  $\theta^3 - 1$ , both of which vanish at the critical point. [Note: The quantity  $\theta^3$  is chosen here as one of the independent variables to ensure conformity with Debye's law as  $\theta \rightarrow 0$ , just as was done in Section IV with the formulation of the nonsingular part of the free energy.] To show that the linear terms of this expression suffice to characterize the region lying close to the critical point (i.e., to first-order terms in the local variables  $\bar{\sigma}^2$  and  $\tau$ ), we substitute the following approximations into equations (29) and (30):

$$\begin{aligned} q &\approx 1; & r &\approx (D+1)\bar{\sigma}^2 & |\bar{\sigma}| &\ll 1 \\ \theta^3 &\approx 1; & \theta^3 - 1 &\equiv (\theta^2 + \theta + 1)(\theta - 1) \approx 3\tau & |\tau| &\ll 1 \end{aligned} \quad (34)$$

Then, setting  $J = 3\gamma_1/(D+1)$ ,  $K = 0$  and  $M = 1$ , and neglecting the quadratic terms, we find that equation (29) reduces to equation (27).

The variable  $q$  exerts a major influence at extreme values of density: it approximates  $\xi v/C$  as  $\xi \rightarrow 0$  and  $1/C\xi v$  as  $\xi \rightarrow \infty$ . Consequently, the numerator of the expression for  $\omega$  will vary quadratically with  $\xi$  at low densities and inversely with  $\xi^2$  at very high densities, provided that  $C \neq 0$ . The maximum value of  $q(\bar{\sigma})$  occurs at  $\bar{\sigma}=0$ , although the shape is skewed with respect to this abscissa due to the presence of an odd power of  $\bar{\sigma}$  in equation (31). On the other hand, the shape of  $r(\bar{\sigma})$ , which has a minimum at  $\bar{\sigma}=0$ , is symmetrical because equation (32) involves only even powers of  $\bar{\sigma}$ . It follows that  $z$  must likewise be an even function of  $\bar{\sigma}$ .

#### VIII. THE FORM OF THE SINGULAR LOCUS

As previously noted, the vanishing of the denominator of the expression for  $\omega$  generates a line of singular points. Although the existence of such a locus has long been suspected (ref. 18, § 79), its true nature remains unknown. We propose here to assign plausible attributes to it since its specification is crucial to the development of a globally valid approximation for the anomaly. To that end, the denominator function will be subjected to certain conditions and changes of arguments.

In the  $r, \theta^3$ -plane the locus  $z=0$  is a conic section, the form of which depends upon the values of the coefficients of equation (30). Its contour is significantly altered by transformation to the  $\bar{\sigma}, \theta^3$ -plane, and finally to the  $\xi, \theta$ -plane, to produce the desired result. The rational expressions (31) and (32) have been formulated so as to make the first derivatives of both  $q$  and  $r$  equal to zero when  $\bar{\sigma} = 0$ . It is apparent from equation (33) that this condition occurs whenever  $\xi v = 1$ , that is, along the path given by

$$\xi = \xi_m(\theta) \equiv 1/v(\theta) \quad (35)$$

which corresponds to the diameter or medial axis of the curve  $z(\bar{\sigma}, \theta)=0$ . The only density-dependent variables that enter into equation (29) are

q and r. Hence, the quantity  $\partial\omega/\partial\xi = v(\partial\omega/\partial\bar{\sigma})$  will vanish everywhere on the medial axis, as required. In order that the value of  $\omega$  should be unity along the same path, we must have

$$z(0,\theta) = \theta^3(\theta^3-1) \equiv \theta^3-1 + (\theta^3-1)^2 \quad (36)$$

Comparing this with equation (30) when r is set equal to 0, we see that

$$\begin{aligned} K &= 0 \\ M &= 1 \\ N &= 1 \end{aligned} \quad (37)$$

The values of the other three coefficients remain to be determined. Two of the degrees of freedom will be used to satisfy constraints on the behavior of the singular locus as it approaches the origin in the  $\xi, \theta$ -plane. These constraints derive from the observation that the saturation density as well as the vapor pressure of pure substances decreases fairly rapidly between the critical point and the triple point. If the density is expressed as a power of the temperature, the exponent typically varies from around 6 in the upper part of the interval to considerably more than 12 near the triple point. Thus, the vapor branch of the coexistence curve approaches the temperature axis very closely at low temperatures.

It is reasonable to suppose that the line of singular points follows a somewhat similar path, descending from either side of the critical point (where it has a common tangent with the coexistence curve) to intercept the density axis at  $\xi=0$  and at a second point well beyond the critical value, as shown in Figure 3. Moreover, it will be assumed that this locus is tangent to the temperature axis at the origin and that its density coordinate varies near there as a power of  $\theta$ . We take the exponent to be 6 to make certain that the resulting path will always lie within the coexistence boundary. These requirements are satisfied by setting both z and its first partial derivative with respect to  $\theta^3$  equal to zero at the origin, which yields the relations

$$\begin{aligned} J &= 1 - I \\ L &= 1 \end{aligned} \quad (38)$$

The remaining degree of freedom will be used to accommodate to the unique behavior of the substance in question.

Let us write the coefficient I in equation (30) as  $\theta_0^3$  and replace the others with the values deduced above. The denominator function, arranged according to powers of r or  $\theta^3$ , respectively, then becomes

$$z = \theta_0^3 r^2 + (\theta^3 - \theta_0^3) r + \theta^3 (\theta^3 - 1) \quad (39a)$$

$$= \theta^6 - (1-r)\theta^3 - \theta_0^3 r(1-r) \quad (39b)$$

The intersection of the surface generated by this function with the plane  $z=0$  defines the singular locus in the  $r, \theta^3$ -coordinate system. The resulting curve will be

- a) an ellipse if  $\theta_0^3 > 1/4$ ,
- b) a parabola if  $\theta_0^3 = 1/4$ , or
- c) a hyperbola if  $\theta_0^3 < 1/4$  (but  $\neq 0$ ).

The last case degenerates into two intersecting straight lines when  $\theta_0 = 0$ .

We shift to the  $\bar{\sigma}, \theta^3$ -coordinate system via the relation

$$\bar{\sigma} = \left[ \frac{r}{1 + D(1-r)} \right]^{1/2} \quad D \geq 0 \quad (40)$$

obtained by inverting equation (32). This will always yield pairs of real roots for those points of the locus having r-coordinate values in the range 0 to 1. The constraints placed on z predetermine the occurrence of just one such arc<sup>†</sup> which (under the additional restriction  $\theta_0 > 0$ ) transforms into a

---

<sup>†</sup>In the hyperbolic case the other branch of the locus is confined to the region  $r \geq 1$ . Further, if negative values of  $\theta_0$  are disallowed, it will lie entirely within the fourth quadrant (where the temperature is negative) and can be safely ignored since it refers to a nonexistent state.

kidney-shaped contour with bilateral symmetry about the medial axis. It has a horizontal tangent at the critical point, and intercepts the density axis at the points where  $\bar{\sigma} = \pm 1$ . Extending below the axis are two lobes that unite to form an arch tangent to this line at the point where  $\bar{\sigma} = 0$ . The exact shape will, of course, depend on the parameters  $\theta_0$  and  $D$ , but regardless of the form the value of  $z$  will be negative at all points interior to the curve and positive elsewhere, so long as the aforementioned restrictions on these two quantities are observed.

Because of symmetry, the medial axis constitutes a locus of extreme values for the isothermal sections of the surface  $z(\bar{\sigma}, \theta)$ . Whether they are maxima or minima depends on the sign of the second term in equation (39a), which varies with temperature. It is evident that the curvature of the isotherms undergoes a reversal at  $\theta = \theta_0$ . Above the transition temperature, the surface is characterized by a single central trough, whereas below this value it divides into two troughs separated by a ridge which is centered along the medial axis.<sup>†</sup> The geometry of the surface in the critical region will be especially sensitive to this parameter whenever its value is near unity. (Additional analytical results are given in Appendix A.)

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<sup>†</sup> It is interesting to compare the isotherms of  $z(\bar{\sigma}, \theta)$  with results obtained by Hemmer, Kac and Uhlenbeck (ref. 19) for a one-dimensional fluid model in which the effect of both short-range (repulsive) and long-range (attractive) forces is taken into account. Through an appropriate change of variables, they develop a successive-approximation method for solving the Kac integral equation which is valid in the critical region. To zeroth order, it yields the van der Waals equation of state. The next approximation includes a term representing the first "quantum" correction, which becomes significant only as the two-phase region is approached. The solution is interpreted by analogy with that of a corresponding Schrödinger equation. The lowest eigenfunction, which is symmetric, has the form of a fourth-degree polynomial [see eq. 18 in ref. 19] and its coefficients exhibit a temperature dependence like that of equation (39a) above. In the critical region there is a smooth transition from a function with a single minimum to one with a double minimum (when the temperature falls below the critical value). It also turns out that the coexistence curve is appreciably flatter than the van der Waals theory predicts, but it still remains parabolic at the critical point.

## IX. THE EXTENDED APPROXIMATION FOR THE ANOMALY

The ground has now been laid for the proposed generalization of  $\psi^*$ , namely,

$$\psi^* = \frac{\alpha\beta^2}{\xi} \left\{ e^{-x} \left[ \frac{1}{x^2} \ln \frac{x}{1-e^{-x}} - \frac{1}{2x} + \frac{1}{24} \right] + (1-e^{-x}) \left[ \frac{1}{x_m^2} \ln \frac{x}{1-e^{-x}} - \frac{1}{2x_m} + \frac{1}{24} \right] \right\} \quad (41)$$

$$\text{in which} \quad x = 3\beta\omega/(\theta^3-1) = 3\beta q^2\theta^3/z \quad (42)$$

$$x_m = x(\xi_m, \theta) = 3\beta/(\theta^3-1) \quad (43)$$

We also furnish an explicit formula for the function  $v(\theta)$  which fixes the location of the medial axis via equation (35),

$$v = \frac{\theta^6 + 1.4}{(1-0.4\delta)(\theta^6-1) + 2.4} \quad \delta < 2.5 \quad (44)$$

The value of  $x$  given by equation (42) is such that it approaches zero under all extreme conditions of density and temperature, whereas it becomes indefinitely great along the line of singular points. It follows that the quantity  $e^{-x}$  not only vanishes at the critical point but remains negligible in the immediate vicinity as long as  $x$  is sufficiently large. Indeed, this property may be taken as demarcating the approximate extent of the critical region. Under these circumstances, only the last expression within the braces of equation (41) is of any consequence, and it reduces to the form of equation (26), as required.

Outside the critical realm, both terms of equation (41) are significant, although their respective contributions to the specific-heat anomaly vanish as  $x \rightarrow 0$ . By expanding the quantity  $\ln[x/(1-e^{-x})]$  in terms of a power series in  $x$ ,

$$\ln \frac{x}{1-e^{-x}} = \frac{1}{2}x - \frac{1}{24}x^2 + 0x^3 + \frac{1}{2880}x^4 - \dots \quad (45)$$

we can show that the first term of equation (41) varies as  $x^2$  when  $x \rightarrow 0$ , while the second one varies in accordance with the behavior of  $x/x_m$  (or  $\omega$ ) under the same conditions. Consequently, the contribution of the first term becomes negligible under all extreme conditions. The second term is also found to be negligible except when  $\theta$  becomes indefinitely great. In this particular case, its value approaches a negative constant [or 0 if  $\xi = \xi_m(\infty)$ ] with the result that  $a^*$  will ultimately increase linearly with temperature, thus contributing to the entropy but not to the specific heat. Such behavior is not only admissible but is, in fact, necessary in order to reproduce the observed character of the anomaly.

The quantities  $e^{-x}$  and  $1-e^{-x}$  that multiply the first and second terms, respectively, of equation (41) may be regarded as weighting factors which effect a transition in  $\psi^*$  from the behavior peculiar to the critical region to a form consistent with that observed elsewhere<sup>†</sup>. A special situation exists along the path  $\xi = \xi_m(\theta)$ : the two expressions enclosed in brackets become identical and the form of  $\psi^*$  is independent of the weights. Furthermore, along supercritical isotherms, the quantity  $x$  (and therefore  $\xi\psi^*$ ) attains a maximum while  $a^*$  passes through a minimum there. As a result, the singular part of the expression for the chemical potential [ $g^* = \partial a^*/\partial \rho$ ] vanishes on the medial axis.

This locus will not, in general, coincide with the diameter of the coexistence curve, although--just below the critical point--it does lie very close to the midpoints of the vapor and liquid branches, and at the critical point the two loci do have a common tangent. Equation (44) provides a means for adjusting the slope of this tangent, since  $\delta = -(d\xi_m/d\theta)_c$ . In addition, the particular form given to  $v$  has been chosen to make  $(d^2\xi_m/d\theta^2)_c = 0$ , i.e., so that the point of inflection will occur at  $\theta=1$ .

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<sup>†</sup>The introduction of such functions permits a continuous transformation from an appropriate local description to one that conforms to prescribed asymptotic conditions. This gives rise to an essential singularity (in the function-theoretic sense) at those points where the exponent goes to infinity. Such a possibility was originally noted by Zimm (ref. 20).

The section of the locus immediately below the critical point will then approximate a straight line, in conformity with the well-known law of the "rectilinear diameter." That the diameter may be so characterized is borne out by Weber's precise determination of the saturation densities of oxygen (ref. 16), which reveals no measurable curvature over an interval extending several degrees below  $T_c$ .

## X. CONCLUSION

The equation of state proposed here is intended to span the range of states from gases to very dense liquids and from low temperatures to moderately high ones. It has been formulated to exhibit correct asymptotic behavior (at least in those cases for which theory has already provided a definite answer) as one or the other of the independent variables approaches zero or infinity. This allows the flexibility provided by the adjustable constants to be devoted to the attainment of close agreement with observation in the regions where accurate measurements are available, with some degree of assurance that the approximation will not yield unreasonable values elsewhere.

Most of the parameters occur linearly (as coefficients of the various terms), thus facilitating a weighted, least-squares determination of their values. The few which are involved in a nonlinear manner have special significance. They have been introduced to characterize behavior peculiar to certain regions, and initial estimates of their values, which are needed at the outset of the fitting procedure, can usually be inferred from preliminary analysis of selected data.

Furthermore, the resulting approximation is readily differentiated to obtain expressions for such quantities as pressure, compressibility, enthalpy, entropy, specific heat, etc. Its derivatives all exist and are continuous everywhere except on the line of singular points. However, since this locus lies in a region inaccessible to observation, such

a limitation is of no practical concern apart from the critical point, where a logarithmic singularity appears in the isochoric specific heat.

Finally, we list the chief advantages that derive from adopting a formulation based on the Helmholtz function:

- 1) Permits a global correlation of empirical data in terms of a single function of density and temperature
- 2) Avoids piecewise approximation with attendant boundary matching problems
- 3) Eliminates occurrence of integrals in expressions for evaluating related properties
- 4) Ensures thermodynamic consistency of all derived quantities.

#### APPENDIX A

##### ANALYSIS OF BEHAVIOR NEAR THE CRITICAL POINT

The shape of the section  $z(\bar{\sigma}, 1)$  is of particular interest since it largely determines how both the singular locus and the coexistence curve behave near the critical point. Its local properties can be analyzed by first expanding  $r(\bar{\sigma})$  in a power series,

$$r = (D+1)\bar{\sigma}^2[1 - D\bar{\sigma}^2 + D^2\bar{\sigma}^4 - \dots] \quad (A1)$$

and then substituting the result into equation (39a) with  $\theta$  set equal

to 1. Thus, we obtain

$$z(\bar{\sigma}, 1) = 3\gamma_1 \bar{\sigma}^2 + 3\gamma_2 \bar{\sigma}^4 + \dots \quad (\text{A2})$$

where

$$3\gamma_1 \equiv \frac{1}{2} \frac{\partial^2 z}{\partial \bar{\sigma}^2}(0, 1) = (1 - \theta_0^3)(D+1) \quad (\text{A3})$$

$$3\gamma_2 \equiv \frac{1}{24} \frac{\partial^4 z}{\partial \bar{\sigma}^4}(0, 1) = [\theta_0^3(2D+1) - D](D+1) \quad (\text{A4})$$

We know on physical grounds that  $z$  can vanish on the critical isotherm only at the critical point, where a singularity appears. Elsewhere on this isotherm its value must be positive. Therefore, the first nonzero coefficient of the expansion (A2) must have a positive sign, from which we get the condition  $\gamma_1 \geq 0$ . In addition, we surmise that  $\gamma_2 \geq 0$  from the general observation that the curvature of the coexistence boundary increases rather sharply in either direction from the critical point. These two conditions, taken in conjunction with equations (A3) and (A4), respectively, imply upper and lower bounds on the permissible range of  $\theta_0$ , viz.,

$$\begin{aligned} \theta_0^3 &\leq 1 && \text{if } \gamma_1 \geq 0 \\ \theta_0^3 &\geq D/(2D+1) && \text{if } \gamma_2 \geq 0 \end{aligned} \quad (\text{A5})$$

The simultaneous solution of equations (A3) and (A4) can provide explicit formulas for  $\theta_0$  and  $D$  in terms of  $\gamma_1$  and  $\gamma_2$ . These may be written

$$\theta_0^3 = \lambda / (\lambda + 3\gamma_1) \quad (\text{A6})$$

$$D = \lambda + 3\gamma_1 - 1 \quad (\text{A7})$$

where

$$\lambda = [3\gamma_2 - 3\gamma_1(1 - 3\gamma_1)]^{1/2} = \theta_0^3(D+1) \quad (\text{A8})$$

In order that  $\lambda$  should be real, the radicand in equation (A8) must be non-negative. Hence, we have the inequality

$$\gamma_2 \geq \gamma_1(1 - 3\gamma_1) \quad (\text{A9})$$

Moreover,  $\lambda$  is taken to be the positive root because only this case can yield a value for  $D$  greater than zero. The sum of the coefficients  $\gamma_1$  and  $\gamma_2$  is also subject to an inequality. By adding equations (A3) and (A4), we find

$$\begin{aligned} 3(\gamma_1 + \gamma_2) &= [1 + (2\theta_0^3 - 1)D](D+1) \\ &= 1 + [2\theta_0^3(D+1) - D]D \geq 1 \end{aligned} \quad (\text{A10})$$

provided that  $\theta_0^3 \geq D/2(D+1)$  and  $D \geq 0$  (which do not contradict any previous assumptions). Thus, we reach the conclusion that  $\gamma_1$  and  $\gamma_2$  cannot both be small at the same time.

A power series in  $\bar{\sigma}$  may also be obtained for the line of singular points. First, we set  $z$  equal to zero in equation (39b) and solve the resultant quadratic equation for  $\theta^3$  in terms of  $r$ . This gives

$$\theta^3 = \frac{1}{2}(1-r) \pm \frac{1}{2}[(1-r)^2 + 4\theta_0^3 r(1-r)]^{1/2} \quad (\text{A11})$$

of which only the positive root can describe a locus in the first quadrant of the  $r, \theta^3$ -plane. Then, after substituting expression (A1) for  $r(\bar{\sigma})$ , we form the series expansion for  $\theta^3$  together with its cube root. The final results are

$$[\theta^3(\bar{\sigma})]_{z=0} = 1 - 3\gamma_1 \bar{\sigma}^2 - 3(\gamma_2 - \lambda\gamma_1) \bar{\sigma}^4 + \dots \quad (\text{A12})$$

$$[\theta(\bar{\sigma})]_{z=0} = 1 - \gamma_1 \bar{\sigma}^2 - (\gamma_2 - \lambda\gamma_1 + \gamma_1^2) \bar{\sigma}^4 + \dots \quad (\text{A13})$$

As expected, the coefficient of the quadratic term, which measures the downward curvature of the locus at the critical point, agrees with the local approximation considered in Section VI. It is also evident that, if  $\gamma_1$  is small, the quartic term cannot have a sizable coefficient unless  $\gamma_2$  is fairly large.

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13. ABSTRACT A comprehensive equation of state based on the Helmholtz free energy has been developed for representing the thermodynamic properties of pure substances over a wide range of conditions including the region near the liquid-vapor critical point. The formulation comprises a set of terms that are regular (expandable in a Taylor series) in the vicinity of this point plus a term which becomes singular there. The latter takes account of the anomalous behavior observed when the critical state is approached, and is needed to attain a consistent, quantitative approximation to experimental data. Both the singular and the nonsingular parts of the free energy are given in closed form as functions of density and temperature. Moreover, the expressions are designed to vary in an appropriate fashion when one or the other of the arguments approaches zero or infinity. Thus, the limiting form is in accord with Debye's $T^3$ law for specific heats at low temperatures, while it reduces to the ideal gas law when the density is allowed to vanish. The majority of the parameters occur as coefficients of the various terms, which facilitates a least-squares determination of their values. The few that are involved in a nonlinear manner have been introduced to characterize behavior peculiar to certain regions. The work described here augments that previously documented in Naval Ship Research and Development Center Report 3664 (May 1971). A more explicit treatment of the critical region is presented and the approximation for the singular contribution is extended to a higher order to permit better agreement with observation.			

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