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Hard and Soft-Core Equations of State for Simple Fluids

I Hard-Core Equations of State and Loci of C_p Extrema†

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Various hard-core type equations of state for fluids are employed to describe loci of extrema of the constant pressure specific heat along isotherms, and loci of extrema of the isobaric thermal expansion coefficient along isobars. Data and formulae pertaining to the critical point and coexistence curve are presented. Comparison is made with experimental results for fluid argon.

1 INTRODUCTION

This series of papers is concerned with the thermodynamic properties of fluids which may be derived and explained by means of a suitable equation of state. The three main topics to be considered are:

- i) virial coefficients,
- ii) characteristic curves,
- iii) loci of extrema of C_p .

These topics are partially inter-related. Since our discussion in this series of papers will be somewhat detailed, the reader may wish to note that a rather brief summary has been presented elsewhere.¹

In this first paper we shall be involved with a class of equations of state which have been constructed for the purpose of describing a system of hard spheres. Some of these equations have been treated by Guggenheim,² and we shall find it useful to employ his general approach. The various equations of state will be compared numerically, and will be found to give quite similar

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numerical predictions over the ranges of density and temperature which are relevant. Specifically, we shall be interested in passing in the critical parameters, and more importantly in the loci of extrema of various thermodynamic functions. Especially we shall analyze the various predictions for the loci defined along isobars by the equations

$$\frac{\partial}{\partial \rho} \left\{ \rho^{m-1} \left(\frac{\partial T}{\partial \rho} \right)_P \right\} = 0, \quad m = 1, 2, 3, \quad (1)$$

which correspond to

$m = 1$, the locus of points of inflexion of isobars plotted in the $T - \rho$ diagram (or $\rho - T$ diagram)

$m = 2$, the locus of extrema along isobars of the isobaric coefficient of expansion

$$\alpha_P \equiv [-\rho(\partial T/\partial \rho)_P]^{-1} = (\partial V/\partial T)_P/V, \quad (2)$$

$m = 3$, the locus of points of inflexion of isobars plotted in the $T - V$ diagram, which is also the locus of extrema of C_P , the constant pressure specific heat, along *isotherms*. This equivalence follows from the thermodynamic identity

$$\left(\frac{\partial C_P}{\partial P} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P. \quad (3)$$

The behaviour of the loci in the neighbourhood of the critical point of a simple fluid has been discussed elsewhere in the context of scaling theory,³ and also some general properties of loci of extrema of thermodynamic functions are already known.⁴ The familiar prediction of van der Waals' equation that the inflexion points of isobars in the $T - V$ diagram lie along the critical isochore does not hold for real fluids. In practice all three loci of Eq. (1) curve round towards the liquid branch of the fusion curve.

In this paper we shall calculate the above isobar loci for various hard-core equations of state and compare our results with those derived from an equation of state fitted by Gosman, McCarty and Hust⁵ to experimental data for argon. We shall find that the loci derived from various hard-core equations of state do not differ significantly from each other, either qualitatively or quantitatively, except for van der Waals' equation which is inaccurate. The agreement with experimental data is quite reasonable on the qualitative side—our loci do terminate on the fusion curve(!)—but unsatisfactory from a quantitative point of view. However, the experimental data are limited to a region $T < 2T_c$ and $P < 20P_c$, which is rather restricted for proper calculation of loci, and we have been obliged to extrapolate the fitted equation of state to unreasonably high pressures and temperatures.

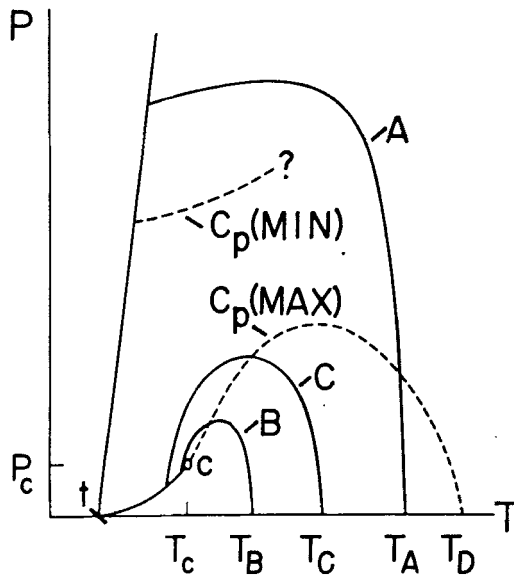


FIGURE 1 Pressure vs temperature diagram for a simple fluid, after Rowlinson,⁶ showing suggested form of loci of C_p maxima (MAX) and minima (MIN) along isotherms. The critical point c and triple point t are indicated.

In an earlier review Rowlinson⁶ has sketched the expected form of the locus of C_p extrema, and we reproduce his diagram in Figure 1. Rowlinson's locus differs qualitatively from the ones we have obtained from hard-core equations of state and from experimental data for argon, in that his locus for C_p maxima terminates on the temperature axis at zero density and pressure, rather than on the fusion curve. In this series of papers, we shall trace the origin of this qualitative discrepancy to the inability of hard-core equations of state to describe the inflexions of the second virial coefficient B as a function of temperature. We shall eventually show how by softening the hard-core that loci of C_p extrema of the hard-core type terminating on the fusion curve, and loci of the softer-core type terminating on the temperature axis, may be obtained. This is achieved by varying the "softness" of the molecular core through a combination of two parameters: a "softening" temperature T_s , and a characteristic exponent N which may be related to the repulsive exponent n of the Lennard-Jones type ($m - n$) potential. In fact $N = 3/n$.

From a more general point of view, the overall aim of this series of papers is to investigate the range of phenomenological behaviour which can, in theory, be exhibited by a simple fluid.

2 RELEVANT RANGE OF DENSITY

Following Guggenheim² we introduce the notation

L = Avogadro's number

V = molar volume

$\rho = 1/V$ = molar density

σ = molecular diameter

$b = L \frac{2\pi\sigma^3}{3} = 4 \times \text{volume of } L \text{ molecules}$

$x = 4y = b\rho$ = dimensionless density variable.

The range of the dimensionless scaled density variable x is $0 \leq x \leq x_0$, where the upper limit is determined by the requirement that the greatest possible density is achieved at geometrical close-packing, with layers of triangles stacked in face-centred-cubic or hexagonal-close-packed array. (The order of stacking is immaterial for a hard sphere system.) The values of x_0 for packing arrangements which are face-centred-cubic (fcc), body-centred-cubic (bcc) and simple-cubic (sc) are:

$$\begin{aligned} \text{fcc: } x_0 &= 4y_0 = 2\pi\sqrt{2}/3 = 2.961\,921\dots, \\ \text{bcc: } x_0 &= 4y_0 = \pi\sqrt{3}/2 = 2.720\,699\dots, \\ \text{sc: } x_0 &= 4y_0 = 2\pi/3 = 2.094\,395\dots \end{aligned} \quad (4)$$

Since the value x_c of x at the critical point of the fluid is about 0.5 for typical models, the limiting value of x_0 at close-packing is about $6x_c$. This value exceeds typical liquid densities at the triple point and along the fusion curve, which are in the range $2.5x_c$ at the triple point to $3.5x_c$ at twice the critical temperature. In practice the liquid-solid phase transition intervenes before any geometrical packing restrictions become important.

3 HARD-CORE TYPE EQUATION OF STATE

The hard-core equation of state including a van der Waals type attractive term is

$$P = RT\rho\phi(b\rho) - a\rho^2, \quad (5)$$

where a and b are constants, b being defined above in Section 2. Various forms have been suggested for $\phi(x)$. Using Guggenheim's labelling we have

for $\phi(x) \equiv \psi(y)$:

$$\begin{aligned}
 W: & (1 - 4y)^{-1}, \\
 T: & (1 + 2y + 3y^2)(1 - y)^{-2}, \\
 G: & (1 - y)^{-4} \\
 F: & (1 + y + y^2)(1 - y)^{-3} \\
 CS: & (1 + y + y^2 - y^3)(1 - y)^{-3},
 \end{aligned} \tag{6}$$

where

$W \leftrightarrow$ van der Waals' equation,

$T \leftrightarrow$ Thiele's "pressure" equation of state,⁷

$G \leftrightarrow$ Guggenheim's suggested simplified form,²

$F \leftrightarrow$ Frisch's scaled-particle equation of state,⁸ and also Thiele's "compressibility" equation of state,^{7,9}

$CS \leftrightarrow$ Carnahan and Starling's approximation to the exact hard sphere virial expansion.¹⁰

It is convenient to introduce dimensionless scaled variables as follows:

$$\begin{aligned}
 \text{scaled density,} & \quad x = 4y = b\rho, \\
 \text{scaled temperature,} & \quad t = bRT/a, \\
 \text{scaled pressure,} & \quad p = b^2P/a,
 \end{aligned} \tag{7}$$

so the scaled equation of state in dimensionless form is

$$p = tx\phi(x) - x^2. \tag{8}$$

The equation of state (8) has such a simple form that calculation of various thermodynamic functions is straightforward. Since the pressure is linear in t , the isochores are straight lines, and the constant volume specific heat C_V is constant, independent of density and temperature, and equal to its ideal gas value, $\frac{3}{2}R$ for a monatomic gas. The constant pressure specific heat C_P is then given by

$$(C_P - C_V)/R = \phi^2/[\phi + x\phi' - 2x/t]. \tag{9}$$

Guggenheim² has made a critical comparison of the equations of state for the first four entries in (6). Discarding van der Waals' equation, which is unsatisfactory both qualitatively and quantitatively, one finds that there is quite good numerical agreement between the various models T, G, F and CS , in ascending order of merit, and the exact series expansion of $\phi(x) \equiv \psi(y)$ for the hard-sphere gas. [The discrepancy between $1/\phi_F$ and $1/\phi_{CS}$ is roughly 1.2% at a density $2\rho_c$ and 2% at $2.5\rho_c$, and worsens with increasing density.

The corresponding percent discrepancies between these functions evaluated at equal values of x/x_c , where x_c is the critical value of x for the particular model, are less than 1% up to $3\rho_c$. The discrepancies between the G and CS expressions are about double those between F and CS .]

4 CRITICAL POINT DATA AND EXACT EXPANSION OF ϕ

The critical point for the hard-core equation of state is located by applying the usual conditions that the critical isotherm have a horizontal point of inflexion there. The scaled critical density is then the solution x_c of

$$\phi - x\phi' - x^2\phi'' = 0 \quad (10)$$

and the scaled critical temperature and pressure are given by

$$t = 2x/[\phi + x\phi'] \quad (11)$$

$$p = x^2[\phi - x\phi']/[\phi + x\phi']. \quad (12)$$

The critical parameters are tabulated (Table I) for the various models, together with the critical values of the compressibility factor $Z = PV/RT$, and the simplest rational algebraic factors of Eq. (10) for $y_c = x_c/4$.

TABLE I
 $\phi(x) \equiv \psi(y)$ and critical point data for various models

Model	W	T	G	F	CS
$\phi(x) = \psi(y)$ $x = 4y$	$\frac{1}{(1-4y)}$	$\frac{1+2y+3y^2}{(1-y)^2}$	$\frac{1}{(1-y)^4}$	$\frac{1+y+y^2}{(1-y)^3}$	$\frac{1+y+y^2-y^3}{(1-y)^3}$
Polynomial for y_c	$1-12y$	$1-4y-24y^2-12y^3+3y^4$	$1-6y-15y^2$	$1-7y-6y^2$	$1-5y-20y^2-4y^3+5y^4-y^5$
$x_c = 4y_c$	0.333333	0.537862	0.506395	0.514668	0.521776
$t_c = \frac{bRT_c}{a}$	0.296296	0.381623	0.373056	0.375312	0.377315
$p_c = \frac{b^2P_c}{a}$	0.037037	0.073242	0.068208	0.069510	0.070669
$Z_c = \frac{P_cV_c}{RT_c}$	0.375000	0.356826	0.361056	0.359853	0.358956

Next we make comparison between the critical point data for these models and the exact hard-sphere expansion for $\phi(x)$, the first few terms of which are¹¹

$$\begin{aligned}\phi(x) = \psi(y) &= \sum_{n=0}^{\infty} a_n y^n, \quad \text{say} \\ &= 1 + 4y + 10y^2 + (18.364\ 768\ 37\dots)y^3 \\ &\quad + (28.34 \pm 0.08)y^4 + (39.5 \pm 0.4)y^5 + (56.5 \pm 1.6)y^6 + \dots\end{aligned}\quad (13)$$

The coefficients up to a_3 are known exactly in closed form for the hard-sphere gas:

$$\begin{aligned}a_0 &= 1, \quad a_1 = 4, \quad a_2 = 10, \\ a_3 &= [438\sqrt{2} - 4131 \arccos(1/3) + 2707\pi]/70\pi\end{aligned}\quad (14)$$

Also the T , G , F and CS versions for $\phi(x)$ give the coefficients up to a_2 exactly, so the initial values, at $x = 0$, of ϕ and its slope ϕ' and curvature ϕ'' , are correct for these models. In order to estimate x_c from the exact series expansion of ϕ , we take a sequence of partial sums of ϕ and its derivatives up to some power N in y . Thus Eq. (10) for the critical density $x_c = 4y_c$ has the full expansion

$$1 - \sum_{n=1}^{\infty} (n^2 - 1)a_n y^n = 0. \quad (15)$$

For each particular value of $N \geq 2$ the smallest positive real root $y_c(N)$ of the truncated series version of Eq. (15),

$$1 - \sum_{n=1}^N (n^2 - 1)a_n y^n = 0, \quad (16)$$

provides an estimate of y_c , and the sequence of estimates $y_c(N)$ converges exponentially fast to y_c . Results for the exact expansion, and a test run on the CS model are presented in Table II. Similar sequences for the critical temperature and pressure calculated by using partial sums in (11) and (12) are also tabulated. The numerical values of the critical parameters for the various models are not so markedly different, and there is little to be gained by making extensive calculations with all the approximate forms for ϕ , or even constructing Padé approximants to the exact expansion. Instead, most of our later calculations will be for the F -model. The qualitative results will be the same for all reasonable approximations to ϕ , and we maintain the expectation that the numerical disagreements will not be too serious.

TABLE II
 Partial sum estimates of critical parameters for CS
 model and exact series expansion.

N	x_c	t_c	p_c	Z_c
Carnahan and Starling				
2	0.730297	0.422064	0.102744	0.333333
3	0.563978	0.385475	0.076123	0.350151
4	0.531823	0.378935	0.071781	0.356185
5	0.524140	0.377633	0.070895	0.358178
6	0.522304	0.377375	0.070713	0.358760
7	0.521887	0.377326	0.070677	0.358911
8	0.521798	0.377317	0.070671	0.358947
9	0.521780	0.377315	0.070669	0.358954
10	0.521776	0.377315	0.070669	0.358956
...
∞	0.521776	0.377315	0.070669	0.358956
Exact series expansion ¹¹				
2	0.730297	0.422064	0.102744	0.333333
3	0.562073	0.384939	0.075796	0.350318
4	0.530204	0.378425	0.071490	0.356306
5	0.522747	0.377156	0.070631	0.358247
6	0.520861	0.376890	0.070444	0.358846
...

5 COEXISTENCE CURVES

Since it is desirable to learn whether or not characteristic curves and other loci of interest terminate on the vaporization curve, it is necessary to locate the liquid and gas branches of the coexistence curve. The usual three requirements that the pressure, temperature and chemical potential be continuous across the vaporization curve lead to three conditions relating the gas density x_1 and the liquid density x_2 to each other and to the temperature and pressure:

$$\frac{[\phi(x_1) + \phi(x_2)](x_2 - x_1)}{(x_1 + x_2)} = \int_{x_1}^{x_2} dx \frac{\phi(x)}{x}, \quad (17)$$

$$t = \frac{(x_2^2 - x_1^2)}{[x_2 \phi(x_2) - x_1 \phi(x_1)]}, \quad (18)$$

$$p = \frac{x_1 x_2 [x_2 \phi(x_1) - x_1 \phi(x_2)]}{[x_2 \phi(x_2) - x_1 \phi(x_1)]}. \quad (19)$$

For any particular choice for ϕ , the integral in (17) is performed, if possible analytically. Then for a chosen set of values of the liquid density x_2 one calculates numerically from (17) the corresponding set of gas densities x_1 . Substitution in (18) and (19) yields the temperatures and pressures on the vaporization curve.

For the F-model, for example, the integral on the RHS of (17) is

$$\int_{y_1}^{y_2} dy \frac{(1+y+y^2)}{y(1-y)^3} = \left(\ln \left(\frac{y}{1-y} \right) + \frac{3}{2} \cdot \frac{1}{(1-y)^2} \right)_{y_1}^{y_2} \quad (20)$$

6 C_p EXTREMA ALONG ISOTHERMS AND RELATED LOCI FOR THE HARD-CORE EQUATION OF STATE

As indicated in the introduction, one of the aims of this paper is to obtain the three related loci of extrema of $\rho^{m-1}(\partial T/\partial \rho)_P$ along isobars, which are defined by Eq. (1). For the hard-core equation of state (5) or (8) one readily finds that the equations for these loci reduce to

$$t = \frac{2x[(m-2)\phi - 2x\phi']}{[(m-3)(\phi + x\phi')\phi + \phi x^2\phi'' - 2(x\phi')^2]}, \quad m = 1, 2, 3. \quad (21)$$

Along the locus of C_p extrema, with $m = 3$, a factor of x cancels and the formula for the locus simplifies slightly to

$$t = \frac{2[\phi - 2x\phi']}{x[\phi\phi'' - 2\phi'^2]}, \quad (m = 3). \quad (22)$$

Graphs of the nested loci are presented in Figures 2 and 3 for the F-model. Results for the G-model are rather similar, as expected. One observes that C_p passes through a maximum along *isotherms* at points on the portion of the locus of extrema ($m = 3$) between the critical point c and the point of *vertical tangency* in the P - T and ρ - T diagrams. Beyond this point the locus of C_p extrema along *isotherms* corresponds to minima. At the point where maxima give way to minima, C_p undergoes inflexion with $(\partial C_p/\partial P)_T = 0$ and $(\partial^2 C_p/\partial T^2)_P = 0$. There one may easily show that

$$\frac{dP}{dT} = \frac{d\rho}{dT} = \infty \quad \text{and} \quad \frac{dP}{d\rho} = \left(\frac{\partial P}{\partial \rho} \right)_T, \quad (23)$$

so the locus has vertical slope in the P - T and ρ - T diagrams, and is tangent to the corresponding isotherm in the P - ρ diagram.

The behaviour of $(-)\rho^{m-1}(\partial T/\partial \rho)_P$ along isobars can be analyzed too. For $m = 1, 2, 3$ the loci correspond to minima of these (positive) quantities along *isobars* from the critical point to the points where each locus has a

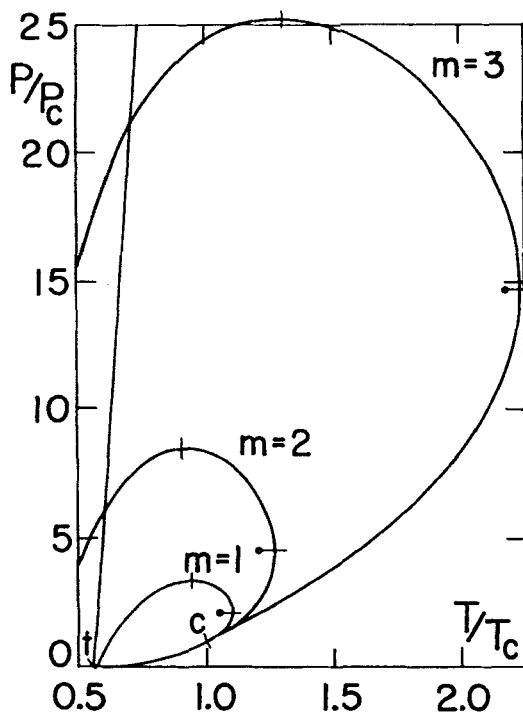


FIGURE 2 Pressure vs temperature diagram for the F-model hard-core equation of state for a simple fluid, Eqs. (5) and (6), showing loci of extrema of $\rho^{m-1}(\partial T/\partial \rho)_P$ along isobars. The locus $m = 3$ is also a locus of C_P extrema, which are maxima from the critical point c to the point of vertical tangency, and minima thereafter. The triple point t and fusion curve for argon have been inserted.

horizontal tangent in the P - T and P - ρ planes. At these places minima give way to maxima at points of inflexion where

$$\frac{dP}{dT} = \frac{dP}{d\rho} = 0 \quad \text{and} \quad \frac{dT}{d\rho} = \left(\frac{\partial T}{\partial \rho} \right)_P, \quad (24)$$

so the loci are then also tangent to the corresponding isobars. The remaining portions of the loci pertain to minima. The behaviour of the isobaric thermal expansion coefficient α_P is obtained from the case $m = 2$, so α_P has maxima along *isobars* between the critical point and inflexion point, where the locus $m = 2$ has horizontal tangency in the P - T and P - ρ diagrams, and minima thereafter. It should be noted that van der Waals' equation fails to give the change over from minima to maxima (or maxima to minima for α_P).

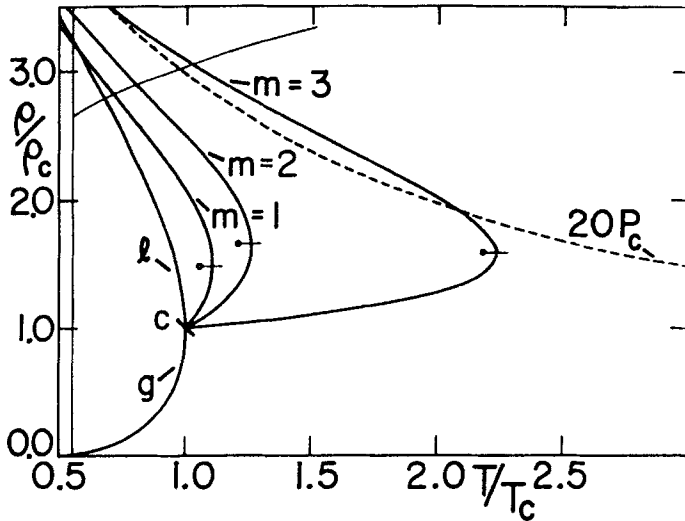


FIGURE 3 Density vs temperature diagram for the F-model, showing loci as in Figure 2. The locus $m = 3$ is a locus of C_p extrema, which are maxima from the critical point c to the point of vertical tangency, and minima thereafter. The coexistence curve has been calculated for the F-model, Eqs. (17)–(20), with liquid branch l and gas branch g . The graph of liquid density along the fusion curve for argon has been drawn. Also the $20 P_c$ isobar for the F-model has been included.

7 C_p EXTREMA AND RELATED LOCI FOR ARGON

Direct calculation of the loci of extrema of $\rho^{m-1}(\partial T/\partial \rho)_p$ is achieved via the equivalent condition

$$\begin{aligned}
 0 &= \frac{\partial}{\partial \rho} \left\{ (-) \rho^{m-1} \left(\frac{\partial T}{\partial \rho} \right)_p \right\}_p \\
 &= \frac{(\partial/\partial \rho)[\rho^{m-1}(\partial P/\partial \rho)_T]}{(\partial P/\partial T)_\rho} - \frac{2\rho^{m-1}(\partial P/\partial \rho)_T(\partial^2 P/\partial \rho \partial T)}{(\partial P/\partial T)_\rho^2} \\
 &\quad + \frac{\rho^{m-1}(\partial^2 P/\partial T^2)_\rho(\partial P/\partial \rho)_T^2}{(\partial P/\partial T)_\rho^3}.
 \end{aligned} \quad (25)$$

The various derivatives are all evaluated from the equation of state,⁵ and the results are graphed in Figures 4, 5 and 6. The qualitative agreement between the hard-core equation of state predictions and the “experimental” loci is only fair. The loci for argon lie at much higher pressures and temperatures, and exhibit a change of slope just before terminating on the fusion curve.

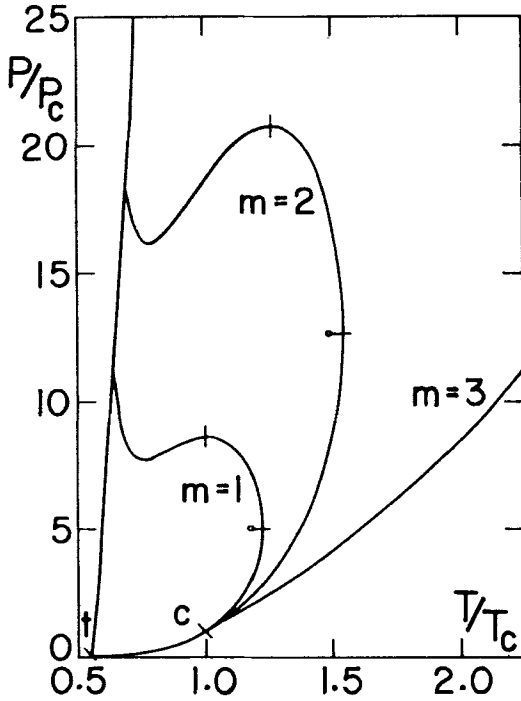


FIGURE 4 Pressure vs temperature diagram for argon,⁵ showing loci of extrema, as described for Figure 2. Critical data for argon used to scale the axes are $P_c = 48.34$ atmos., $\rho_c = 13.41$ mol/l, $T_c = 150.86$ K.

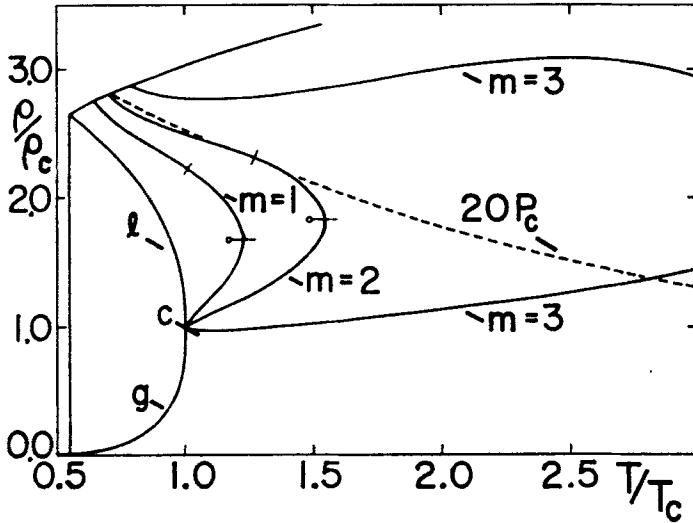


FIGURE 5 Density vs temperature diagram for argon,⁵ showing loci of extrema, as described for Figure 3. The $20 P_c$ isobar for argon has been inserted.

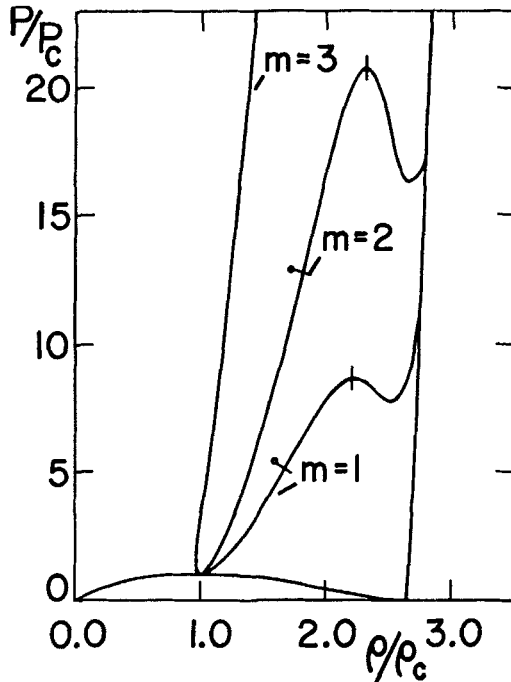


FIGURE 6 Pressure vs density diagram for argon, showing loci of extrema, as in Figures 4 and 5.

However, the region of validity of the equation of state is restricted to $T < 2T_c$ and $P < 20P_c$, so the experimental loci for C_p extrema at high pressures and temperatures are probably numerically in error. The switchbacks in the loci near the fusion curve are also of doubtful validity.

8 CONCLUDING REMARKS

In this paper we have applied hard-core type equations of state in an attempt to describe loci of extrema of C_p along isotherms, and loci of extrema of the isobaric thermal expansion coefficient α_p and related quantities along isobars. Qualitative agreement is obtained since all the loci considered are found to terminate on the fusion curve, but numerical comparisons are unsatisfactory. Various general formulae and data pertaining to the critical point and co-existence curve of the hard-core type equation of state have been presented. These will be needed in some of the later papers of this series.

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