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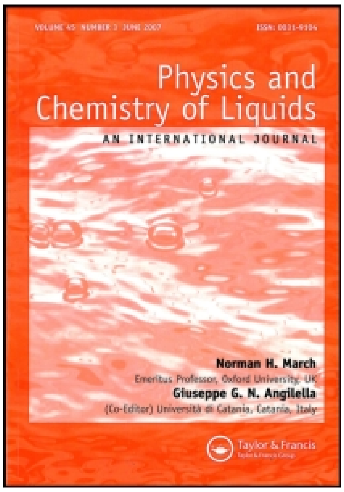

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Hard and Soft-Core Equations of State for Simple Fluids: II Characteristic Curves for Argon

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Hard and Soft-Core Equations of State for Simple Fluids

II Characteristic Curves for Argon†

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A detailed discussion is given of the geometrical properties and the physical significance of the characteristic curves of a simple fluid, with specific reference to experimental results for argon.

1 INTRODUCTION

In this second paper of this series,[1] we shall be concerned with *characteristic curves*, which are a class of loci of extrema of the compressibility factor

$$Z \equiv PV/RT \tag{1}$$

along isobars, isotherms and isochores. Characteristic curves have been introduced by Brown,[2] and used by him to test the thermodynamic consistency of experimental Joule–Thomson (Joule–Kelvin) inversion curves. We shall study characteristic curves, with specific reference to fluid argon, under the following headings:

i) Definition of characteristic curves and equations of loci;

ii) Termination temperatures and the virial expansion;

iii) Physical significance and features of geometrical interest.

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In the following paper[3] we shall examine to what extent characteristic curves may be accounted for by a hard-core type equation of state. Since the properties of characteristic curves are not generally well known, we shall find it informative and convenient to rederive and summarize some of Brown's work[2] in a notation perhaps more familiar to thermodynamicists. Certain of the more important characteristic curves are mentioned by Rowlinson in a review article.[4]

2 DEFINITION OF CHARACTERISTIC CURVES

Various characteristic curves are sketched in Figures 1, 2 and 3. We reproduce Brown's diagram in Figure 1, and "experimental" curves for argon calculated from the equation of state constructed by Gosman, McCarty and Hust[5] in Figures 2 and 3. The *zeroth order* characteristic curve, denoted by J (by Brown) is defined by the requirement

$$Z = 1, \tag{2}$$

so that along this line the ideal gas relation is numerically valid:

$$PV = RT. \tag{3}$$

Three *first order* characteristic curves, denoted A, B, C, are defined by the requirements that Z be at an extremum (i.e. maximum, minimum or point of

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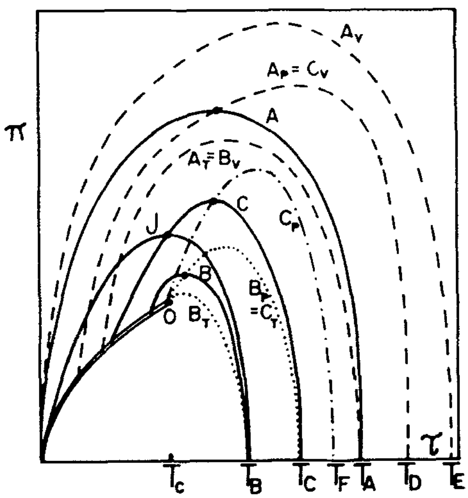

FIGURE 1 Schematic graphs of characteristic curves sketched in the $\pi \equiv \ln(P/P_c)$ vs $\tau \equiv \ln(T/T_c)$ diagram, after Brown.[2] The critical point is labelled O.

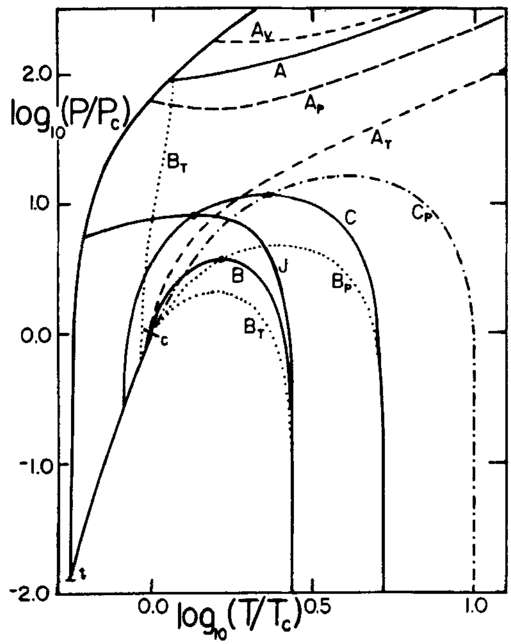

FIGURE 2 Logarithmic pressure vs temperature diagram for argon, showing characteristic curves. Critical data for argon used to scale the axes are $P_c = 48.34$ atmospheres, $\rho_c = 13.41$ mole/litre and $T_c = 150.86$ K. The vaporization and fusion curves are included.

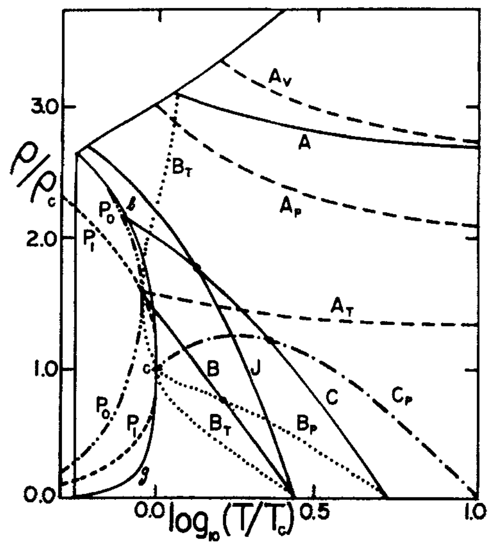

FIGURE 3 Density vs log. temperature scaled diagram for argon, showing characteristic curves. The liquid and gas (l and g) branches of the coexistence curve, and the liquid density along the fusion curve are included. The zero pressure locus is labelled P_0, and the zero isotherm slope locus, P_1.

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horizontal inflexion) along isochores, isotherms and isobars respectively:

$$A\text{, Amagat curve,}\quad \left(\frac{\partial Z}{\partial T}\right)_V = 0,\quad \text{or}\quad \left(\frac{\partial Z}{\partial P}\right)_V = 0,\quad \text{along isochores;} \tag{4a}$$

$$B\text{, Boyle curve,}\quad \left(\frac{\partial Z}{\partial P}\right)_T = 0,\quad \text{or}\quad \left(\frac{\partial Z}{\partial V}\right)_T = 0,\quad \text{along isotherms;} \tag{4b}$$

$$C\text{, Charles curve,}\quad \left(\frac{\partial Z}{\partial V}\right)_P = 0,\quad \text{or}\quad \left(\frac{\partial Z}{\partial T}\right)_P = 0,\quad \text{along isobars.} \tag{4c}$$

It is important to notice which of the three variables P, V (or ρ) and T is held *constant* in each case. Substituting for Z one may rewrite equations (4) as

$$A,\quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T}; \tag{5a}$$

$$B,\quad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}; \tag{5b}$$

$$C,\quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T}. \tag{5c}$$

If desired, one may introduce the density ρ into (5) in place of V. The Eq. (5) for A, B and C admit simple geometrical interpretations in terms of tangent conditions. For example, at any point on A the tangent to the corresponding isochore passes through the origin in the P-T diagram. Analogous properties hold for B and C in the P-ρ and V-T diagrams respectively.

Following Brown we next introduce the dimensionless quantities α, β and γ (Brown's κ):

$$\alpha = 1 + \left(\frac{\partial \ln Z}{\partial \ln T}\right)_V = \left(\frac{\partial \ln P}{\partial \ln T}\right)_V = \frac{T}{P}\left(\frac{\partial P}{\partial T}\right)_V; \tag{6a}$$

$$\beta = 1 - \left(\frac{\partial \ln Z}{\partial \ln P}\right)_T = (-)\left(\frac{\partial \ln V}{\partial \ln P}\right)_T = -\frac{P}{V}\left(\frac{\partial V}{\partial P}\right)_T; \tag{6b}$$

$$\gamma = 1 + \left(\frac{\partial \ln Z}{\partial \ln T}\right)_P = \left(\frac{\partial \ln V}{\partial \ln T}\right)_P = \frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P. \tag{6c}$$

The partial derivatives in β and γ are respectively related to the isothermal compressibility and the isobaric coefficient of thermal expansion. Clearly

$$\alpha\beta = \gamma \tag{7}$$

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and

$$\left(\frac{\partial \beta}{\partial \ln T}\right)_P = -\left(\frac{\partial \gamma}{\partial \ln P}\right)_T; \tag{8a}$$

$$\left(\frac{\partial \beta}{\partial \ln T}\right)_V = -\beta\left(\frac{\partial \alpha}{\partial \ln P}\right)_T; \tag{8b}$$

$$\left(\frac{\partial \gamma}{\partial \ln T}\right)_V = \beta\left(\frac{\partial \alpha}{\partial \ln T}\right)_P. \tag{8c}$$

Then Eq. (5) for the first order characteristic curves may be written (compare the definition of the zeroth order characteristic curve in (2))

$$\alpha = \beta = \gamma = 1. \tag{9}$$

Second order characteristic curves are now defined via derivatives of α, β and γ along isobars, isotherms and isochores. There are six independent second order curves. From the Amagat line variable α we construct

$$A_P, \quad \left(\frac{\partial \alpha}{\partial T}\right)_P = 0, \tag{10a}$$

$$A_T, \quad \left(\frac{\partial \alpha}{\partial P}\right)_T = 0, \tag{10b}$$

$$A_V, \quad \left(\frac{\partial \alpha}{\partial T}\right)_V = 0. \tag{10c}$$

From the Boyle curve variable β we construct

$$B_P, \quad \left(\frac{\partial \beta}{\partial T}\right)_P = 0, \tag{11a}$$

$$B_T, \quad \left(\frac{\partial \beta}{\partial V}\right)_T = 0, \tag{11b}$$

$$B_V, \quad \left(\frac{\partial \beta}{\partial T}\right)_V = 0, \quad (\equiv A_T). \tag{11c}$$

By (8b), the loci B_V and A_T are equivalent, and will be called A_T. Then from the Charles curve variable γ we construct

$$C_P, \quad \left(\frac{\partial \gamma}{\partial T}\right)_P = 0, \tag{12a}$$

$$C_T, \quad \left(\frac{\partial \gamma}{\partial P}\right)_T = 0, \quad (\equiv B_P) \tag{12b}$$

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$$C_V, \quad \left(\frac{\partial \gamma}{\partial T}\right)_V = 0, \quad (\equiv A_P). \tag{12c}$$

It is easy to see using (8a) that the loci C_T and B_P are equivalent, and using (8c) that the loci C_V and A_P are equivalent.

All the characteristic curves can be constructed, at least numerically, once the equation of state is supplied, with P being expressed as a function of ρ and T. The explicit combinations of partial derivatives of P required for this purpose are presented in Table I for the ten characteristic curves defined above. We have employed the equation of state for argon constructed by

TABLE I

Defining equations for characteristic curves, expressed in terms of the pressure and its density and temperature partial derivatives. The termination temperature of each locus is also quoted.

Symbol for locus	Termination temperature	Equation of characteristic curve
J	T_B	$P = \rho R T$
A	T_A	$\left(\frac{\partial P}{\partial T}\right) = \frac{P}{T}$
B	T_B	$\left(\frac{\partial P}{\partial \rho}\right) = \frac{P}{\rho}$
C	T_C	$\rho\left(\frac{\partial P}{\partial \rho}\right) = T\left(\frac{\partial P}{\partial T}\right)$
A_P	T_D	$\left(\frac{\partial P}{\partial \rho}\right)\left(\frac{\partial P}{\partial T}\right) + T\left(\frac{\partial P}{\partial \rho}\right)\left(\frac{\partial^2 P}{\partial T^2}\right) - T\left(\frac{\partial P}{\partial T}\right)\left(\frac{\partial^2 P}{\partial \rho \partial T}\right) = 0$
A_T	T_A	$\left(\frac{\partial P}{\partial \rho}\right)\left(\frac{\partial P}{\partial T}\right) - P\left(\frac{\partial^2 P}{\partial \rho \partial T}\right) = 0$
A_V	T_E	$P\left(\frac{\partial P}{\partial T}\right) + PT\left(\frac{\partial^2 P}{\partial T^2}\right) - T\left(\frac{\partial P}{\partial T}\right)^2 = 0$
B_P	T_C	$\left(\frac{\partial P}{\partial \rho}\right)\left(\frac{\partial P}{\partial T}\right) + \rho\left(\frac{\partial^2 P}{\partial \rho^2}\right)\left(\frac{\partial P}{\partial T}\right) - \rho\left(\frac{\partial P}{\partial \rho}\right)\left(\frac{\partial^2 P}{\partial \rho \partial T}\right) = 0$
B_T	T_B	$P\left(\frac{\partial P}{\partial \rho}\right) + P\rho\left(\frac{\partial^2 P}{\partial \rho^2}\right) - \rho\left(\frac{\partial P}{\partial \rho}\right)^2 = 0$
C_P	T_F	$\rho\left(\frac{\partial P}{\partial \rho}\right)^2\left[\left(\frac{\partial P}{\partial T}\right) + T\left(\frac{\partial^2 P}{\partial T^2}\right)\right] - 2\rho T\left(\frac{\partial P}{\partial \rho}\right)\left(\frac{\partial P}{\partial T}\right)\left(\frac{\partial^2 P}{\partial \rho \partial T}\right) + T\left(\frac{\partial P}{\partial T}\right)^2\left[\left(\frac{\partial P}{\partial \rho}\right) + \rho\left(\frac{\partial^2 P}{\partial \rho^2}\right)\right] = 0$

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Gosman, McCarty and Hust[5] to obtain "experimental" characteristic curves, which are displayed in the P vs T and ρ vs T diagrams in Figures 2 and 3.

3 TERMINATION TEMPERATURES AND VIRIAL EXPANSION

One observes that the ten characteristic curves terminate on the temperature axis at zero density at six distinct temperatures, which will play an important role in the theory of the second virial coefficient B to be developed in subsequent papers. By inserting a virial expansion of the form

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \cdots \tag{13}$$

into the equations for the various characteristic curves listed in Table I, and retaining only the leading order terms, which are of order ρ, one immediately finds that the termination temperatures are located by quite simple relations between the second virial coefficient B and its first and second temperature derivatives, $\dot{B}$ and $\ddot{B}$. Graphs of the second and third virial coefficients B and C for argon are presented in Figure 4.

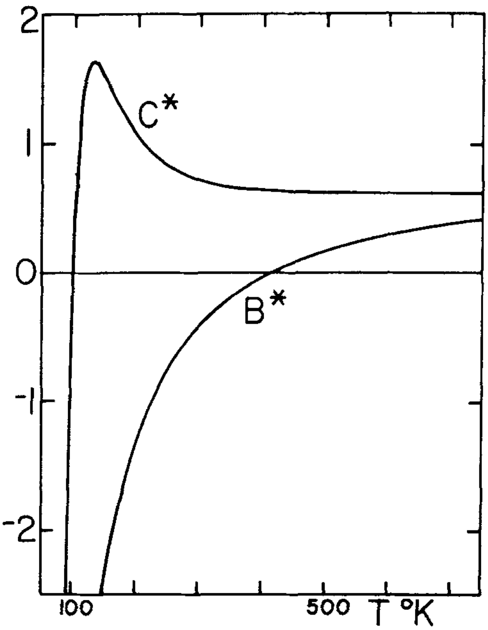

FIGURE 4 Scaled second and third virial coefficients for argon[5] versus temperature. $B^* = B/b$ and $C^* = C/b^2$, where $b = 35.70$ cm^3/mole $= 4 \times$ the volume of the molecules in a mole, and $\sigma = 3.05$ Å = molecular diameter, taken from the square well virial coefficient data of Sherwood and Prausnitz.[6] The corresponding reduced temperature $T^* = kT/\varepsilon$, with $\varepsilon/k = 93.3$ K. Over a wide range of (high) temperature, $C^* \simeq \frac{5}{8}$ = hard sphere third virial coefficient.[1]

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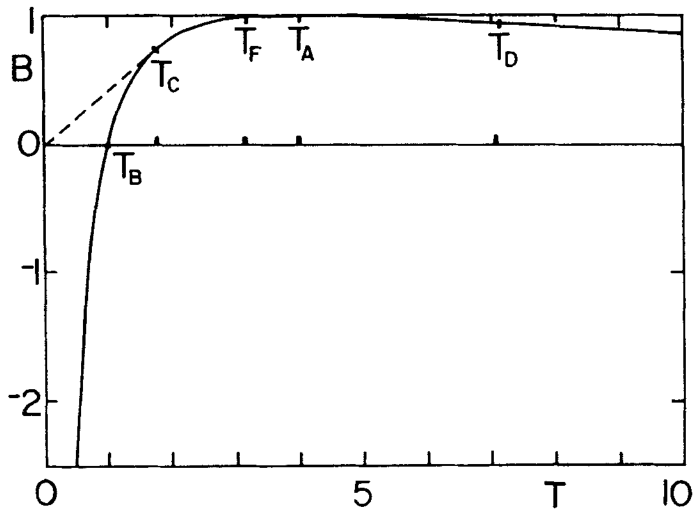

FIGURE 5 Schematic graph of second virial coefficient B vs temperature (scaled), based on the model $B = 4(T^{-1/2} - T^{-1})$, so the Boyle temperature $T_B = 1$. The termination temperatures T_B, T_C, T_F, T_A and T_D are indicated, with $T_A = 4$ and $T_E = 16$. In practice the inflexion point T_D is hard to detect.

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The zeroth order locus J and the Boyle curve B terminate at the same temperature T_B, called the Boyle temperature. For the three first order curves we have three distinct termination temperatures located as follows:

$$\text{Amagat curve } A \text{ terminates at } T_A, \text{ where } \dot{B} = 0; \tag{14a}$$

$$\text{Boyle curve } B \text{ terminates at } T_B, \text{ where } B = 0; \tag{14b}$$

$$\text{Charles curve } C \text{ terminates at } T_C, \text{ where } B = T\dot{B}. \tag{14c}$$

The expected schematic behaviour of the second virial coefficient B is illustrated in Figure 5. The Boyle temperature T_B is located by the vanishing of the second virial coefficient. The Charles temperature T_C is also the Joule–Thomson inversion temperature (see Section 7 below), and is located by the geometrical condition that the tangent at T_C passes through the origin. And T_A corresponds to the position of the maximum in the second virial coefficient, which is not often observed experimentally, first because it occurs at fairly high temperatures compared with T_B, and secondly because the graph of B vs T is rather flat over an extensive range of T above T_C.

Termination temperatures for the second order characteristic curves are located similarly, with the following results:

$$B_T \text{ terminates at } T_B, \text{ where } B = 0, \tag{15a}$$

$$B_P \text{ terminates at } T_C, \text{ where } B - T\dot{B} = 0, \tag{15b}$$

$$C_P \text{ terminates at } T_F, \text{ where } B - T\dot{B} + T^2\ddot{B} = 0, \tag{15c}$$

$$A_T \text{ terminates at } T_A, \text{ where } \dot{B} = 0, \tag{15d}$$

$$A_P \text{ terminates at } T_D, \text{ where } \ddot{B} = 0, \tag{15e}$$

$$A_V \text{ terminates at } T_E, \text{ where } \dot{B} + T\ddot{B} = 0. \tag{15f}$$

Three additional distinct termination temperatures are required for C_P, A_P and A_V. The locus A_P terminates at T_D where $\ddot{B} = 0$ and the second virial coefficient undergoes inflexion, Figure 5. T_D will be of great importance later on in connection with the locus of extrema of the constant pressure specific heat, C_p.

The termination temperatures in increasing order are

$$T_B < T_C < T_F < T_A < T_D < T_E. \tag{16}$$

We note here that for argon, only T_B, T_C and T_F can be extracted from the "experimental" second virial coefficient. Using the Gosman, McCarty and Hust equation of state, we have

$$T_B = 413.8, \quad T_C = 795.0, \quad T_F = 1{,}540, \tag{17}$$

so

$$\frac{T_C}{T_B} = 1.921, \quad \frac{T_F}{T_B} = 3.721, \quad \frac{T_F}{T_C} = 1.937. \tag{18}$$

Noting that the experimental critical temperature for argon is $T_c = 150.86\ K$, we have also

$$\frac{T_B}{T_c} = 2.743, \quad \frac{T_C}{T_c} = 5.270, \quad \frac{T_F}{T_c} = 10.21. \tag{19}$$

The appropriate shape of the characteristic curves near the temperature axis may be determined by resubstituting the virial expansion (13) in the expressions for the various loci, Table I, and retaining terms of order ρ and ρ^2 which involve the second and third virial coefficients B and C. The final slope of a locus at $\rho = 0$ can then be obtained correctly in both the ρ-T and P-T diagrams. It is of interest to compare the final slopes $(d\rho/dT)_0$ of loci which have a common termination temperature. The loci which meet the temperature axis at the Boyle temperature T_B are J, B and B_T. For small ρ

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these loci have the forms

$$J:\quad \rho \sim -\frac{B}{C}, \quad \left(\frac{d\rho}{dT}\right)_0 = -\frac{\dot{B}}{C}, \tag{20a}$$

$$B:\quad \rho \sim -\frac{B}{2C}, \quad \left(\frac{d\rho}{dT}\right)_0 = -\frac{\dot{B}}{2C}, \tag{20b}$$

$$B_T:\quad \rho \sim -\frac{B}{4C}, \quad \left(\frac{d\rho}{dT}\right)_0 = -\frac{\dot{B}}{4C}, \tag{20c}$$

where $T \leq T_B$, $B \leq 0$, $\dot{B} > 0$ and $C > 0$. One expects the third virial coefficient C to be positive for temperatures at and above the Boyle temperature. Since ρ must be positive, these loci must lie on the low temperature side of T_B, where $B \leq 0$ and $\dot{B} > 0$. These two loci C and B_P meet at the Charles temperature T_C, where

$$C:\quad \rho \sim \frac{(T\dot{B} - B)}{(2C - T\dot{C})}, \quad \left(\frac{d\rho}{dT}\right)_0 = \frac{\ddot{B}}{(2C - T\dot{C})}, \tag{21a}$$

$$B_P:\quad \rho \sim \frac{(T\dot{B} - B)}{2(2C - T\dot{C})}, \quad \left(\frac{d\rho}{dT}\right)_0 = \frac{\ddot{B}}{2(2C - T\dot{C})}, \tag{21b}$$

where $T \leq T_C$, $T\dot{B} - B \geq 0$, $\ddot{B} < 0$ and $2C - T\dot{C} > 0$. One expects the temperature derivative $\dot{C}$ of the third virial coefficient to be negative in the relevant temperature range.[6] These two loci lie on the low temperature side of T_C where $\ddot{B} < 0$. At the Amagat temperature T_A, the loci A and A_T terminate with

$$A:\quad \rho \sim -\frac{\dot{B}}{\dot{C}}, \quad \left(\frac{d\rho}{dT}\right)_0 = -\frac{\ddot{B}}{\dot{C}}, \tag{22a}$$

$$A_T:\quad \rho \sim -\frac{\dot{B}}{2\dot{C}}, \quad \left(\frac{d\rho}{dT}\right)_0 = -\frac{\ddot{B}}{2\dot{C}}, \tag{22b}$$

where $T \leq T_A$, $\dot{B} \leq 0$, $\ddot{B} < 0$ and $\dot{C} < 0$. Again, since $\dot{C} < 0$ these loci lie on the low temperature side of T_A. Various simple numerical relationships between the above final slopes are evident.

4 PHYSICAL SIGNIFICANCE OF LOCI, AND FEATURES OF INTEREST

In Sections 4 to 8 we give an account of the geometrical inter-relations between the zeroth order locus J and its three derived first order loci, A, B, and C, and between each first order locus, A, B and C, and its three derived second

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order loci. Intersections with loci of extrema along isotherms of the principal specific heats C_v and C_p will be noted. We also summarize briefly the physical significance of the loci A, B and C, which has been noted previously by Brown and Rowlinson. Novel features enter in the geometrical properties of loci in the V-T (or ρ-T) diagram, and in the observation of an extension of the locus B_T into the liquid region where it reappears effectively as a second branch in the P-T diagram.

We note that if any particular characteristic curve L has a maximum in the P-T diagram where $(dP/dT)_L = 0$, then generally at this point $(d\rho/dT)_L \neq 0$, and is negative, so $(dP/d\rho)_L = 0$, and there is also a maximum in the P-ρ diagram. Also the locus L is tangent to the corresponding isobar in the ρ-T diagram. Again, if L has a maximum in the ρ-T diagram, where $(d\rho/dT)_L = 0$, then generally at this point $(dP/dT)_L \neq 0$ and is positive, so $(dP/d\rho)_L = \infty$ and L is vertical in the P-ρ diagram. Also the locus L is tangent to the corresponding isochore in the P-T diagram.

Also at this stage, we observe that the loci A, A_P, A_V and A_T, whose termination points are associated with softening of the hard core, are generally separate from all the other loci, which are clustered in the comparatively low temperature and pressure region around the vaporization curve and the critical point. The notable exception is A_T which penetrates amongst the other loci and terminates on the vaporization curve. In addition, certain loci: B_T, B_P and C_P, actually pass through the critical point by virtue of the critical point conditions $(\partial P/\partial\rho)_T = 0$ and $(\partial^2 P/\partial\rho^2)_T = 0$.

Locus J: J is rather uninteresting. It intersects B and also B_T at its termination point on the temperature axis at the Boyle temperature T_B. J has a maximum point in the P-T diagram where it crosses C. It can in principle have a maximum point in the ρ-T diagram, where it would cross A, but in practice such a point lies beyond the fusion curve. So J loops around the critical point, with $PV < (>)\ RT$, $Z < (>)\ 1$ at points inside (outside) the loop.

5 AMAGAT LINE A

Along the Amagat line A,

$$\left(\frac{\partial Z}{\partial T}\right)_V \equiv \frac{V}{RT}\left[\left(\frac{\partial P}{\partial T}\right)_V - \frac{P}{T}\right] = 0, \tag{23}$$

and Z is a maximum along isochores. On A the tangent to an isochore in the P-T diagram passes through the origin. In the liquid region the isochores are too steep, but since one expects $(\partial^2 P/\partial T^2)_V$ to be negative, except in the liquid close to the critical point, the isochores will bend over with decreasing

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slope, and eventually a point of tangency occurs. Data for argon does not extend far enough to permit the observation of the termination point T_A, which would correspond to the temperature at the maximum in the second virial coefficient.

Since the internal energy has the volume derivative

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left[\left(\frac{\partial P}{\partial T}\right)_V - \frac{P}{T}\right], \tag{24}$$

the locus A corresponds to a minimum in the internal energy U along isotherms. From (24) one sees that A is the locus of inversion in the Joule free expansion effect,[7] in which a thermally isolated system expands without performance of external work so $dU = 0$. The subsequent temperature change can usually be read off graphs of constant U. Since

$$\left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial U}{\partial V}\right)_T \Big/ C_v, \tag{25}$$

inversion occurs on A, where graphs of constant U have vertical slope in the P-T and ρ-T diagrams. Inside the A locus loop, cooling occurs on expansion. For hard-core equations of state the RHS of (24) involves only the attractive term, which we have taken to be a/V^2, and is always positive. In this situation there is no inversion, or A locus, and only Joule cooling takes place.

The geometrical features of A are as follows. A intersects A_T ($\equiv B_V$) at its termination point T_A. If A passes through a maximum in the P-T diagram then it intersects A_P ($\equiv C_V$) at this point, and if A passes through a maximum in the ρ-T diagram before reaching the fusion curve, then it intersects A_V at this point. Also at this latter point $(\partial^2 P/\partial T^2)_V = 0$, so a locus of constant volume specific heat C_V extrema (maxima) along isotherms would pass through this maximum point on A, where also Z inflects as a function of T along isochores.

The "experimental" loci A, A_P and A_V for argon are concave (upwards) in both the P-T and ρ-T diagrams, at rather high pressures. Concavity in the ρ-T diagram implies that two intersections between A and A_V must occur before A bends down towards the temperature axis, together with an associated looping locus of C_v maxima. However, our undue extrapolation of the fitted equation of state for argon[5] into such high pressures and temperatures is more likely the cause of these particular geometrical features.

Finally we note that if A were to intersect A_T again, it would do so at a point where $(\partial^2 U/\partial V^2)_T = 0$ and the internal energy U inflects as a function of V along isotherms. The portion of the A locus beyond this point would then correspond to maxima of U along isotherms. Such behaviour does not occur for argon.

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6 BOYLE LINE B

Along the Boyle line

$$\left(\frac{\partial Z}{\partial P}\right)_T \equiv \frac{1}{RT}\left(\frac{\partial(PV)}{\partial P}\right)_T = 0, \tag{26}$$

and Z and PV are at a minimum when graphed as functions of P, or of V, along isotherms.[8] The Boyle line terminates at T_B on the temperature axis, along with J and B_T, and also the locus of inflexion points of isotherms in the P-ρ diagram, P_2, which is defined by $(\partial^2 P/\partial \rho^2)_T = 0$. For small ρ this last mentioned locus has the form $\rho \sim -B/3C$, and so lies between B and B_T. The Boyle line loops around the critical point inside J and generally terminates on the liquid branch of the coexistence curve. B passes through a maximum in the P-T diagram where it intersects the locus B_P ($\equiv C_T$). If B were to have a maximum in the ρ-T diagram, it would intersect A_T ($\equiv B_V$) there, but no such point of this type occurs for argon.

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7 CHARLES LINE C

The Charles line is better known as the Joule–Thomson inversion curve along which

$$\left(\frac{\partial Z}{\partial T}\right)_P = \frac{P}{RT}\left[\left(\frac{\partial V}{\partial T}\right)_P - \frac{V}{T}\right] = 0. \tag{27}$$

C loops around the critical point, starting at the temperature axis at T_C, where it meets B_P ($\equiv C_T$) and ending on the liquid branch of the coexistence curve. $(\partial Z/\partial T)_P > 0$ inside the loop. At the maximum point on C in the P-T diagram C intersects C_P, and Z inflects as a function of temperature along isobars, with

$$\left(\frac{\partial^2 Z}{\partial T^2}\right)_P = \frac{P}{RT}\left(\frac{\partial^2 V}{\partial T^2}\right)_P = 0. \tag{28}$$

The locus of constant pressure specific heat C_p extrema, which are maxima here, passes through the maximum point too. Z is a maximum along isobars on C between T_C and the highest point in the P-T diagram, and Z is a minimum along isobars thereafter round to the liquid side of the vaporization curve.

Since the enthalpy H has the pressure derivative

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P, \tag{29}$$

it is obvious H is a minimum along isotherms at the inversion curve. The temperature change during the Joule–Thomson isenthalpic throttling process is then described by the usual coefficient[7] (compare with RHS of (27)):

$$\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_T \Big/ \left(\frac{\partial H}{\partial T}\right)_P = \frac{T}{C_p}\left[\left(\frac{\partial V}{\partial T}\right)_P - \frac{V}{T}\right], \tag{30}$$

which is positive inside the loop of the inversion curve C, where cooling occurs on expansion. Finally one observes that C does not in practice exhibit a maximum in the ρ-T plane, but if it did intersection with A_P ($\equiv C_V$) would occur.

8 ADDITIONAL LOCI

If one extends the equation of state to the region inside the coexistence curve it is well-known that eventually the mechanical stability requirement $(\partial P/\partial\rho)_T > 0$ for positive isotherm slope breaks down. The locus P_1, on which $(\partial P/\partial\rho)_T = 0$, passes through the critical point and may easily be calculated numerically. Also the zero pressure locus, P_0, may be obtained. This locus trivially divides the ρ-T diagram into regions in which the fluid is under tension or pressure. The point of interest here is that the two loci just introduced do intersect in practice, and there is a definite maximum temperature, less than critical, up to which the liquid can sustain a tension without becoming mechanically unstable. The zero pressure locus has a vertical tangent in the ρ vs T diagram at this intersection point, which for argon occurs at 136 K, where $T/T_c = 0.901$ and $\rho/\rho_c \simeq 1.58$. Of course the usual criticisms of extending the equation of state into a metastable region apply to this discussion. The consequences of the intersection of the zero pressure locus with the mechanical stability limit locus are rather curious. Immediately from their defining equations, Table I, one observes that the loci B, B_T and A_T all pass through this intersection point. This explains why A_T descends into the comparatively low pressure and temperature region, and why B_T has a "second branch" in the liquid as noted previously. The relevant loci are illustrated in Figure 3.

9 CONCLUDING REMARKS

In this paper we have given explicit expressions for calculating ten characteristic curves and their six termination temperatures from the equation of state of fluids and the second virial coefficient respectively. By obtaining these characteristic curves for argon, we have been able to determine to what

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extent the schematic description due to Brown[2] is adequate. We find some additional features concerning multiple intersections, and an extra "branch," for B_T. Also, in practice certain curves terminate on the fusion curve (J, A, A_P, A_V and the second branch of B_T), whereas others enter the comparatively low pressure and temperature region, and end either at the critical point (B_P, B_T and C_P) or on the liquid branch of the coexistence curve (B, C, A_T and the second branch of B_T). The ability of hard-core type equations of state to account for characteristic curves is the subject of the following paper.[3] Numerical values of T_B, T_C and T_F for argon have been extracted from the second virial coefficient of Gosman *et al.*[5] The six termination temperatures will play an important role in our analysis of virial coefficients later in this series of papers.

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