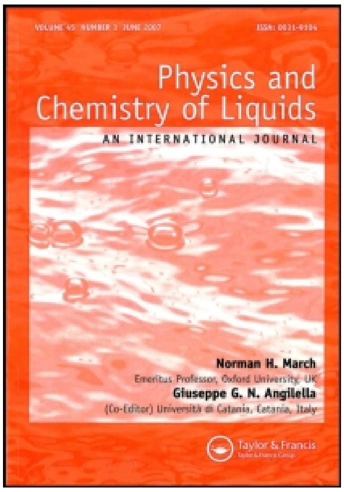

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Hard and Soft-Core Equations of State for Simple Fluids : III Characteristic Curves and Hard-core Equations of State

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Hard and Soft-Core Equations of State for Simple Fluids

III Characteristic Curves and Hard-Core Equations of State†

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Explicit formulae are presented for those characteristic curves which can be constructed for a hard-core equation of state. Excellent agreement is obtained with experimental curves for argon up to fairly high pressures (20 P_c) and temperatures (10 T_c). It is shown that only three termination temperatures are obtainable from a hard-core type second virial coefficient. The limitations of the hard-core equation of state are discussed briefly.

1 INTRODUCTION

In this paper we investigate the characteristic curves of the hard-core type equations of state for fluids:

$$P = RT\,\rho\,\phi(b\rho) - a\rho^2. \tag{1}$$

In terms of the dimensionless variables

$$x = 4y = b\rho, \tag{2a}$$

$$t = bRT/a, \tag{2b}$$

$$p = b^2P/a, \tag{2c}$$

the hard-core equation of state (1) has the very simple form

$$p = tx\phi(x) - x^2. \tag{3}$$

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Consequently it is possible to analyze the structure of the ten characteristic curves completely, and for a general function ϕ express the temperature t explicitly in terms of the density $x = b\rho$ via ϕ and its derivatives ϕ', ϕ''. Excellent qualitative and quantitative agreement is obtained between the various hard-core models F, G, T and CS described in I,[1] where the explicit forms for $\phi(x) \equiv \psi(y)$ are quoted.

The second virial coefficient for a hard-core model is a monotonic increasing function of temperature, and does not exhibit a maximum or an inflexion point. Consequently only three termination temperatures, T_B, T_C and T_F, exist, the others, T_A, T_D and T_E, being formally infinite (II).[2] Especially simple relations exist between the three finite temperatures. For all hard-core models which give the hard-sphere part of the second virial coefficient correctly, we have $T_F = 2T_C = 4T_B$. Since only three termination temperatures are finite, one would expect to be able to construct only those characteristic curves which end at T_B, T_C and T_F. The Amagat locus A, and the associated second order characteristic curves A_T, A_P and A_V, which would normally terminate at T_A, T_D and T_E, cannot now do so. In fact for hard-core models one finds that the loci A, A_P and A_V do not exist, and A_T *does occur*, but as a line of constant $x(=b\rho)$. The intersection requirements

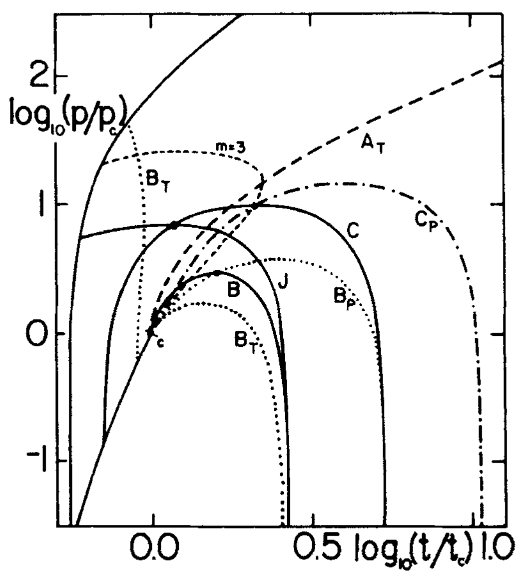

FIGURE 1 Logarithmic pressure vs temperature diagram for the F-model hard-core equation of state, displaying characteristic curves. The F-model vaporization curve and the experimental fusion curve for argon are included. The locus of C_p extrema along isotherms is labelled $m = 3$.

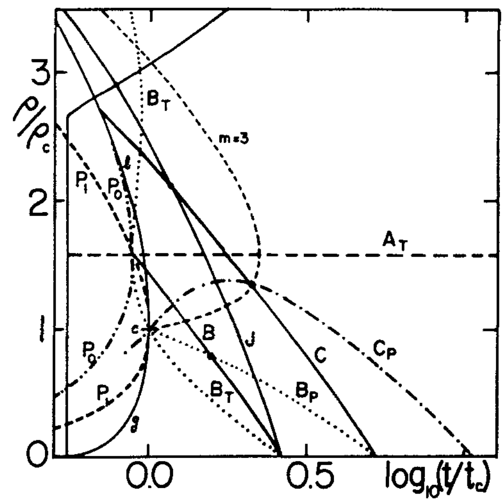

FIGURE 2 Density vs logarithm of temperature diagram for the F-model hard-core equation of state, displaying characteristic curves and the locus of C_p extrema along isotherms. The F-model liquid-gas coexistence curve and the experimental liquid density along the fusion curve for argon are included.

discussed in II are, of course, automatically satisfied by all the characteristic curves. In particular A_T passes through the multiple intersection point with B, B_T, P_0 (the zero pressure locus) and P_1 (the zero isotherm slope locus). Also, a second "branch" of B_T appears in the liquid region.

The various characteristic curves[3] are presented graphically for the F-model[4] in Figures 1 and 2. The liquid-gas coexistence curve has been calculated for the F-model, using the relevant formulae in I. We have included the experimental fusion curve for argon in Figure 1, and the corresponding liquid density graph along the fusion curve in Figure 2. We present graphs only for one model since the numerical agreement between the various hard-core models is rather close.[1] There is also remarkably good agreement between the hard-core equation of state characteristic curves and those constructed for argon in II, except of course for A, A_P and A_V.

2 TERMINATION TEMPERATURES

All the hard-core model forms for ϕ considered here have initial values at $x = 0$ for ϕ and its first two derivatives which are in exact agreement with the values obtained from the coefficients in the exact hard-sphere virial expansion (except for van der Waals' equation for which $\phi''(0) = 2$):

$$\phi(0) = 1$$
$$\phi'(0) = 1 \tag{4}$$
$$\phi''(0) = \tfrac{5}{4}$$

The scaled second virial coefficient is then for all models, including van der Waals' equation,

$$B^* \equiv B/b = 1 - 1/t \tag{5}$$

Consequently the scaled termination temperatures t_B, t_C and t_F also have the same numerical values for all models:

$$t_B = 1, \tag{6a}$$
$$t_C = 2, \tag{6b}$$
$$t_F = 4. \tag{6c}$$

We note explicitly the existence of a common ratio

$$\frac{t_C}{t_B} = \frac{t_F}{t_C} = 2, \tag{7}$$

so t_C is the geometric mean of t_B and t_F. Experimentally there appears to be a similar common ratio for argon, whose value 1.93 is slightly less than 2(II).

3 EQUATIONS OF CHARACTERISTIC CURVES

Defining relations for the required characteristic curves have been derived in II in terms of the pressure and its partial derivatives with respect to density and temperature. (Table I in II). It is an elementary matter to extract the zeroth and first order loci

$$J: \quad t = x/[\phi(x) - 1] \tag{8a}$$
$$\mathrm{B}: \quad t = 1/\phi'(x), \tag{8b}$$
$$C: \quad t = 2/\phi'(x). \tag{8c}$$

We note that the temperature on the Charles line C is double that on the Boyle line B at any given density $x(=b\rho)$.

The expressions for the second order loci B_P and B_T are

$$B_P: \quad t = 2(\phi - x\phi')/(\phi\phi' + x\phi\phi'' - x\phi'^2) \tag{9a}$$
$$B_T: \quad t = (\phi - x\phi' + x^2\phi'')/(\phi\phi' + x\phi\phi'' - x\phi'^2). \tag{9b}$$

The locus C_P is determined by a quadratic equation in t:

$$(\phi\phi' + x\phi\phi'' - x\phi'^2)t^2 - 4\phi t + 4x = 0, \tag{10}$$

so there are two parts to this locus, C_{P+}, C_{P-}, corresponding to the choice of sign of the square-root in the solution formula. These two parts join smoothly at the point where the locus has a maximum in the density vs temperature $(x - t)$ diagram, Figure 2. The loci B_P, B_T and C_P all pass through the critical point.

The equation for the locus A_T is independent of temperature, and reduces to

$$\phi = x\phi', \tag{11}$$

which can be solved numerically for x once the form for ϕ has been chosen. For the F-model $y(\equiv x/4)$ satisfies $1 - 4y - 4y^2 - 2y^3 = 0$ with solution $x = 0.816\,3785\ldots$, so $x/x_c = 1.586\,224\ldots$. For van der Waals' equation $x = \frac{1}{2}$, $x/x_c = \frac{3}{2}$; and for the G-model $x = \frac{4}{5}$, $x/x_c = 1.579\,796\ldots$. Since x is fixed, the locus A_T is an isochore in the $p - t$ diagram, and the pressure depends linearly on the temperature. Since A_T intersects the zero pressure locus P_0 inside the coexistence curve at the point where the temperature (on P_0) is at a maximum, and also mechanical stability breaks down,[2] one may use the above x-values to calculate this temperature. One finds that the liquid can sustain a tension, without becoming mechanically unstable, up to $t/t_c = 0.880$ for the F-model, 0.878 for the G-model and 0.844 for van der Waals' equation. The experimental value[2] for argon is about 0.90.

4 CONCLUDING REMARKS

We have presented explicit formulae for those characteristic curves which admit an adequate description by a hard-core type equation of state. For J, B, C, B_P, B_T and C_P, the temperature is expressed in terms of the density via the equation of state function ϕ and its derivatives. The locus A_T corresponds to an isochore, with a fixed value of the density $x(=b\rho)$. Qualitative and quantitative agreement between these theoretical loci and the experimental ones for argon is excellent over the region covered by the experimental equation of state.[2] The loci A, A_P, and A_V do not exist for a hard-core model, and the corresponding termination temperatures T_A, T_D and T_E are infinite. The associated especially simple form of the second virial coefficient is incapable of yielding all six termination temperatures. The question of how to account for the six termination temperatures by means of a more realistic expression for the second virial coefficient will be the subject of the next few papers of this series.

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