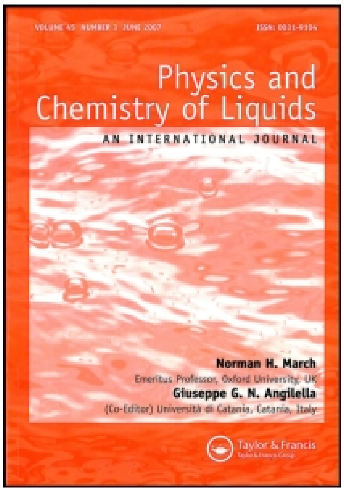

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Hard and Soft-Core Equations of State for Simple Fluids. IX. Soft-Core Equations of State and Loci of *C_p* Extrema

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Hard and Soft-Core Equations of State for Simple Fluids

IX. Soft-Core Equations of State and Loci of C_p Extrema†

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Loci of C_p extrema along isotherms are constructed for model soft-core equations of state, parameterized by an exponent $N(=3/n$, where n is the repulsive potential exponent) and a softening temperature T_s. Generally the loci exhibit two branches whose geometry depends on T_s and N. In soft-core type behaviour, a locus of C_p maxima commences at the critical point and terminates on the temperature axis at a temperature T_D where the second virial coefficient has a point of inflexion, and the second branch is located at higher pressures and temperatures. In hard-core type behaviour, a locus of C_p maxima commences at the critical point and turns into a locus of minima before crossing the fusion curve, whereas the second branch, which terminates at T_D, is generally a locus of minima lying at high pressures and temperatures. The values of T_s and N at which the geometry of the loci changes is studied in detail.

1 INTRODUCTION

It remains in this series of papers to investigate the loci of extrema along isotherms of the constant pressure specific heat C_p for soft-core equations of state. In the first papers I and II[1] we described the experimental situation for argon, and the loci of C_p extrema for hard-core equations of state. In every case examined the locus of C_p maxima commenced at the critical point, proceeded along a line almost coincident with the critical isochore, then (except for van der Waals' equation) turned into a locus of minima and terminated on the fusion curve. On the other hand, Rowlinson[2] has suggested that the locus of C_p maxima would terminate on the temperature axis, see I, Figure 1. The analysis of soft-core equations of state in this paper will reveal

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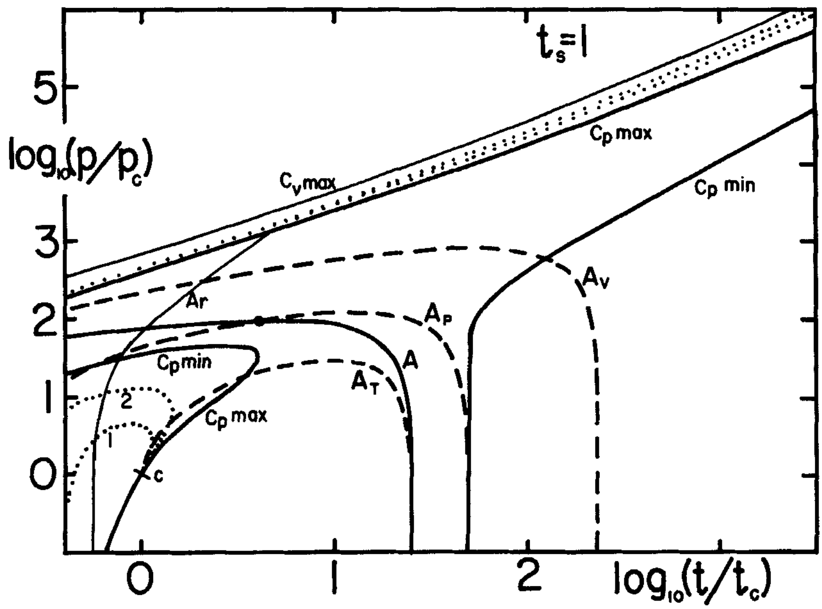

FIGURE 1 Loci of extrema of $\rho^{m-1}(\partial T/\partial\rho)_P$, $m = 1, 2, 3$, along isobars for the soft-core Frisch (F) model with $N = \frac{1}{4}$ and $t_s = 1$. For $m = 3$, these are loci of extrema of the constant pressure specific heat C_p along isotherms. Also included are the high temperature characteristic curves A, A_T, A_P and A_V, and the melting curve for argon (Ar).

how the shape of the C_p loci changes as the exponent n of the repulsive part of the intermolecular potential is varied.

In I we discussed a set of nested loci along isobars defined by

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

where the $m = 2$ locus corresponds to extrema of the isobaric coefficient of expansion along isobars, and the $m = 1$ and $m = 3$ loci correspond to the inflexion points of isobars in the T vs ρ and T vs V diagrams. From the thermodynamic identity

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \tag{2}$$

we see that the $m = 3$ isobar locus in (1) is also the locus of C_p extrema along isotherms. The right-hand side of (2) may be rewritten in terms of partial derivatives of the pressure with respect to density and temperature, (18) and II (25), which may be calculated from the equation of state. On substituting a virial expansion of PV into (2) one readily finds that the locus of

C_p extrema terminates on the temperature axis at T_D where the second virial coefficient has a point of inflexion, and that the slope of this locus depends on the third virial coefficient. In the course of our analysis, we will examine the temperature dependence of the second and third virial coefficients.

We will employ the $T_s - N$ model to soften the molecular core, as in VIII. When $T_s = 0$, the exponent $N = 3/n$ remains as a parameter. We find that as N is varied (with $T_s = 0$) the shape of the C_p loci *changes* from the "hard-core" form with termination on the fusion curve, to a "soft-core" form terminating on the temperature axis at T_D, as Rowlinson suggested.[2] This change occurs at a "critical" value of N, which we calculate numerically for the F and CS models. Moreover in the "hard-core" range of N there is a *second branch* to the C_p locus which also terminates on the temperature axis at T_D. This branch proceeds towards the very high temperature and pressure region of the phase diagram. The manner in which this second branch approaches the axis depends on the exponent N. This leads to a second "critical" value of N which we calculate and find to be independent of the precise form of the equation of state function ϕ for the F, G, T, and CS models.

When the two-parameter soft-core $T_s - N$ model is employed with both the softening temperature T_s and the exponent N as variables, the general appearance of C_p loci is qualitatively similar to the $T_s = 0$ case, except that the "critical" values of the exponent N, which determine the geometry of the loci, now depend on the softening temperature. We have traced this dependence for the F and CS models.

Our results are essentially summarized by the figures.

Many of the technical details and definitions related to the $T_s - N$ soft-core model will be found in Papers IV and VIII. In the remainder of this paper we often use scaled density, temperature and pressure variables d, t and p, as defined in VIII (3).

2 C_p LOCI FOR THE $T_s - N$ MODEL WITH $N = \frac{1}{4}$

We begin by investigating the soft-core equation of state for the Frisch (F)-model with $N = \frac{1}{4}$ ($n = 12$). The softening temperature t_s may be varied between the hard-core limit $t_s = \infty$ and the extreme soft-core limit $t_s = 0$. The loci of C_p extrema for the cases $t_s = 1$ and 0 are presented in Figures 1–4, where the density, temperature and pressure are scaled with respect to their critical values, and a logarithmic scale has been employed for temperature and pressure. (The hard-core limit case $t_s = \infty$ is in I). The characteristic curves A, A_T, A_P and A_V have been included, as have the isobar loci in (1) with $m = 1$ and 2. Clearly with $N = \frac{1}{4}$ we have "soft-core" type behaviour as suggested by Rowlinson when $t_s = 0$, and "hard-core" type behaviour when

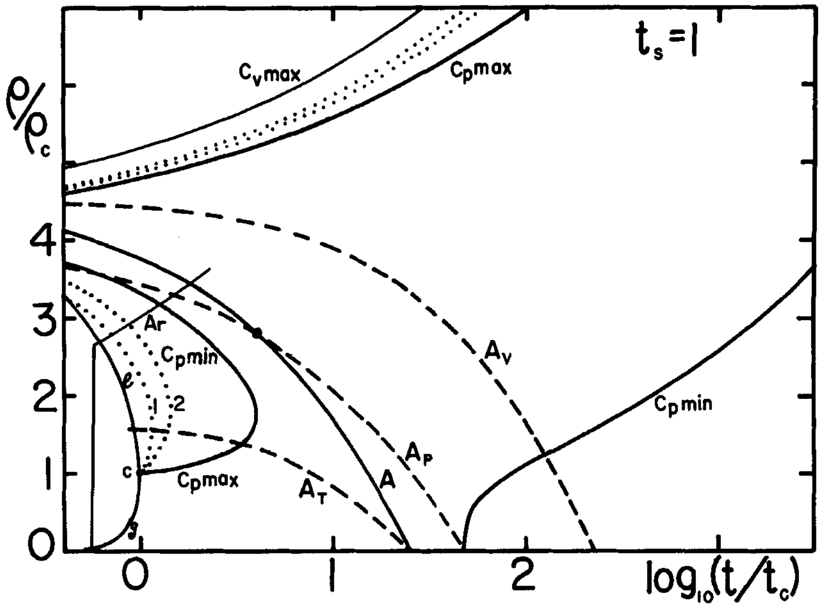

FIGURE 2 As for Figure 1.

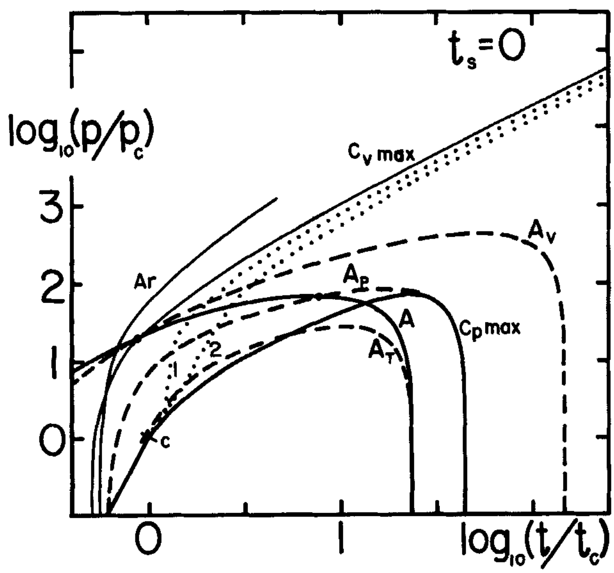

FIGURE 3 As for Figure 1, but with $t_s = 0$.

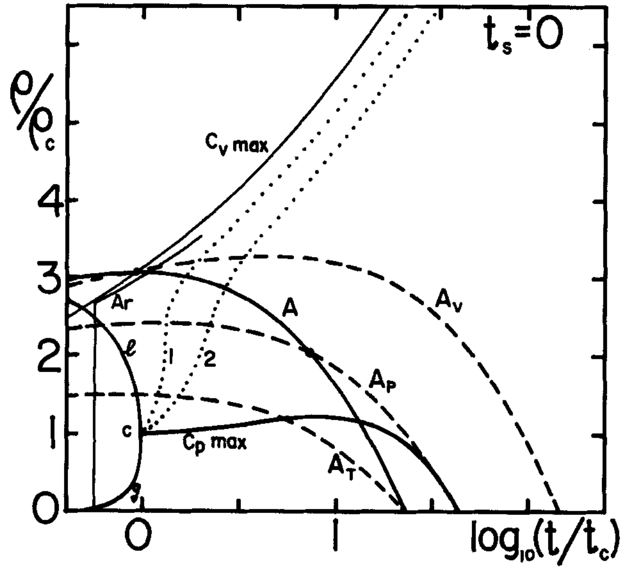

FIGURE 4 As for Figure 3.

$t_s = 1$, with a second branch of C_p minima commencing at t_D and extending into the high-temperature and high-pressure part of the phase diagram. Note the alternation of maxima and minima along the C_p loci.

To investigate the change-over in the structure of the C_p loci we repeated the calculations for additional values of t_s keeping $N = \frac{1}{4}$. The loci so obtained are presented in Figures 5 and 6. Since each set of C_p loci is indexed by a value of t_s, the loci correspond to "level-lines" of t_s. [For fixed N, t_s is regarded as a function of density and temperature, defined implicitly by the condition $(\partial C_p/\partial P)_T = 0$ via (2).] These lines exhibit a "saddle-point" structure, with the "saddle" occurring at a value of t_s between 0.01 and 0.03. A more precise calculation in Section 5 places the saddle at $t_s = 0.0174$, or $t_s/t_c = 0.0116$, with $d/d_c = 1.78$, $t/t_c = 19.4$ and $p/p_c = 151$.

Furthermore the final slopes of the loci terminating at t_D change over from negative for loci of maxima to positive for loci of minima. In a small range of t_s just above the "saddle" value, on the "hard-core" side, the final slopes of the second branches of the loci at t_D remain negative, still corresponding to C_p maxima. The second branches in this region extend out into the phase diagram and then double back towards higher temperatures and pressures. But at higher values of t_s the final slopes at t_D become positive, so the second branches then correspond entirely to minima of C_p, and proceed directly into the high temperature region. This change in the sign of the final slope

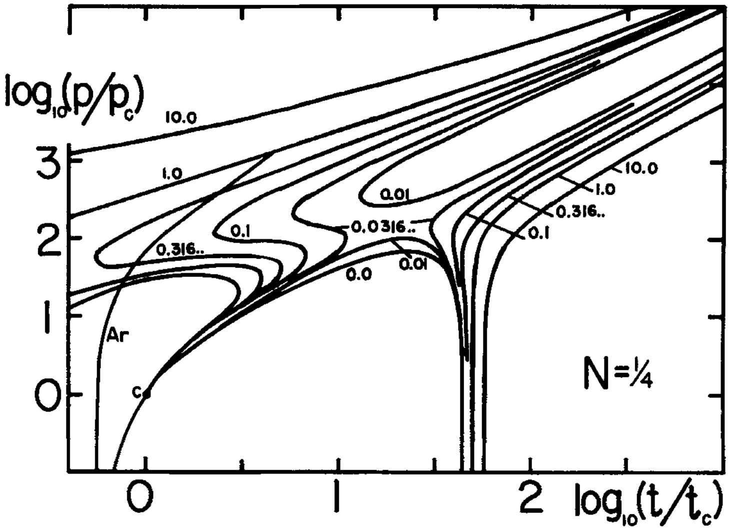

FIGURE 5 Loci of C_p extrema for the soft-core Frisch (F) model with $N = \frac{1}{4}$ and $t_s = 0.0$, 0.01, 0.0316 ..., 0.1, 0.316 ..., 1.0 and 10.0. ($10^{1/2} = 3.16$ ...)

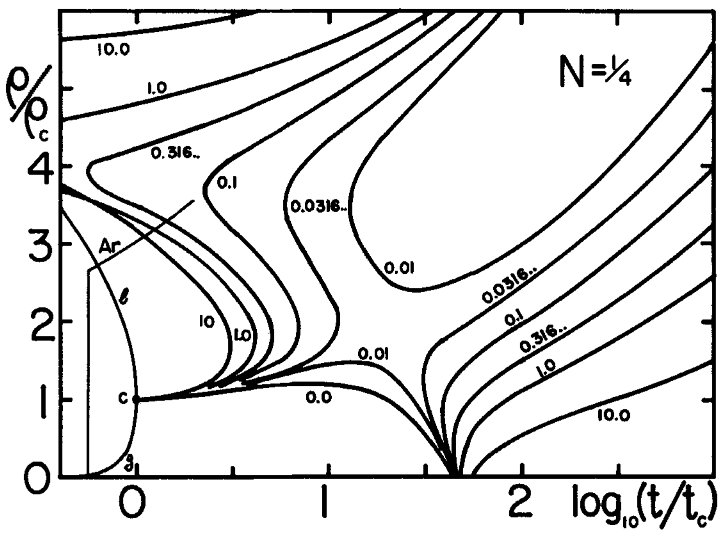

FIGURE 6 As for Figure 5.

produces another geometrical modification in the shapes of the loci, and occurs for $t_s = 1.72$, or $t_s/t_c = 2.55$, when $N = \frac{1}{4}$.

The two types of alteration in the geometrical appearance of the loci, related to the "saddle" and the "final slope," occurred here for a fixed value of N, at special values of t_s. An alternative way of viewing this problem is to regard t_s as fixed, and N as the adjustable parameter: an approach we will pursue in the next section.

3 C_p LOCI FOR THE $T_s - N$ MODEL WITH $T_s = 0$

In this limiting case of the $T_s - N$ model with $T_s = 0$, the exponent N remains as the only parameter. Noting the technical details in VIII, we again calculated loci of C_p extrema for selected values of N: $\frac{1}{12}, \frac{1}{9}, \frac{1}{6}, \frac{1}{5}$, 0.2105, 0.22, 0.24 and $\frac{1}{4}$. These loci are presented in Figures 7 and 8. Clearly the saddle-point struc-described in Section 2 is still present, and the signs of the final slopes at t_D determine whether the loci there correspond to maxima or minima of C_p. The alternation between maxima and minima takes place as before. Detailed calculation shows that the saddle-point now occurs when $N = 0.2105008$,

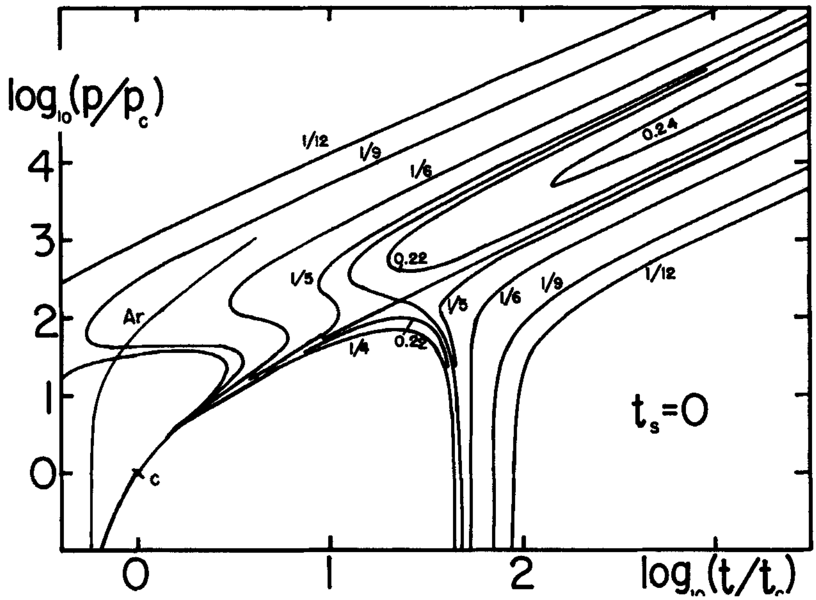

FIGURE 7 Loci of C_p extrema for the soft-core Frisch (F) model with $t_s = 0$, and $N = \frac{1}{12}, \frac{1}{9}, \frac{1}{6}, \frac{1}{5}$, 0.2105, 0.22, 0.24 and $\frac{1}{4}$. The lower portions of the loci for $N = 0.24$ and $\frac{1}{4}$ are too close to distinguish in the diagram.

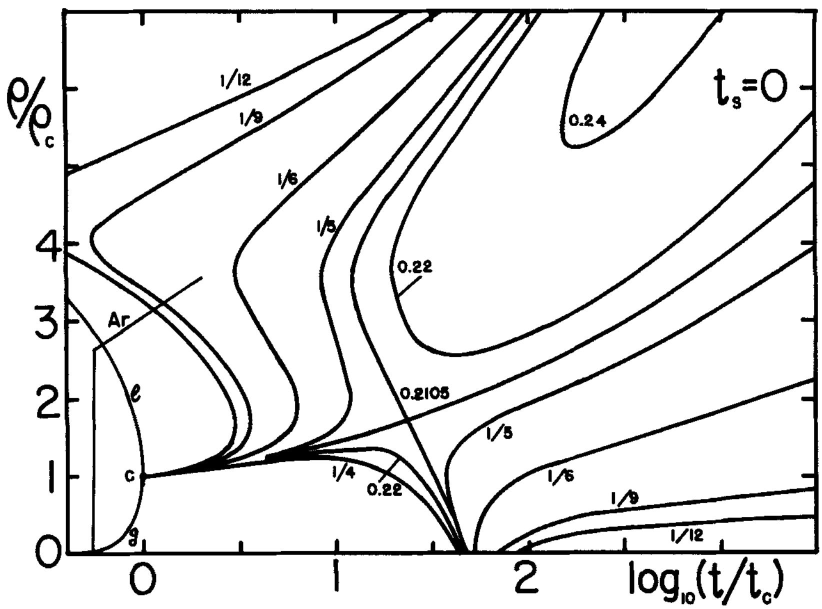

FIGURE 8 As for Figure 7.

at $d/d_c = 1.7209$, $t/t_c = 23.301$, $p/p_c = 169.38$, and the change in the sign of the final slope at t_D occurs when $N = 0.157389876$.

It is clear that a smooth increase in the value of t_s will induce a systematic shift in the position of the saddle point, and the value of N at which it occurs. There will be a similar variation in the value of N at which the final slope at t_D changes sign. We trace this behaviour in the next two sections.

4 C_p LOCI IN THE VICINITY OF THE TEMPERATURE AXIS

In order to investigate the behaviour of C_p loci in the vicinity of T_D at the temperature axis, we may employ the virial expansion of PV in powers of pressure:

$$PV = RT + B'P + C'P^2 + \cdots. \tag{3}$$

The primed "pressure" virial coefficients are related algebraically to the usual "density" virial coefficients in the expansion of

$$Z \equiv \frac{PV}{RT} = 1 + \frac{B}{V^2} + \frac{C}{V^3} + \cdots. \tag{4}$$

The inter-relations between the second and third virial coefficients are

$$B' = B,\ C' = \frac{(C - B^2)}{RT}. \tag{5}$$

One finds on substitution of (3) in (2) that the locus of C_p extrema near the temperature axis has the form

$$\ddot{B}' + \ddot{C}'P + \cdots = 0, \tag{6}$$

where $\cdot$ denotes temperature differentiation. It is clear that the locus of C_p extrema will terminate on the temperature axis where $\ddot{B} = 0$ and the second virial coefficient has a point of inflexion. This condition locates T_D(II, IV). Also the final slope of this locus on the P vs T diagram is then

$$\left(\frac{dP}{dT}\right)_0 = -\frac{\dddot{B}}{\ddot{C}'}, \tag{7}$$

where the right-hand side is evaluated at T_D. Clearly $\ddot{B} \gtrless 0$ accordingly as $T \gtrless T_D$ and $\dddot{B} > 0$ near T_D. The sign of the final slope will therefore depend on the *sign* of $\ddot{C}'$ at T_D. Accordingly we are led to investigate the temperature dependence of the third pressure virial coefficient C', which is related to the usual second and third virial coefficients as in (5).

For the hard-core equation of state models F, G, T and CS, which agree precisely with the first two exact hard-sphere expansion coefficients (I),

$$B = b_0\left(1 - \frac{1}{t}\right), \quad \text{and} \quad C = \tfrac{5}{8}b_0^2, \tag{8}$$

whence the third pressure virial coefficient is

$$C_0' = (-)\left(\frac{b_0^3}{a}\right)\left[\frac{3}{8t} - \frac{2}{t^2} + \frac{1}{t^3}\right] \tag{9}$$

(where the subscript $_0$ refers to the hard-core case). Even in the hard-core case C' has an interesting temperature dependence, Figure 9. C_0' is negative at high temperatures, and obviously has two zeros, one maximum, one minimum and two points of inflexion, Table I.

TABLE I

Feature	t
Zeros	0.558 4.775
Maximum	0.812
Minimum	9.855
Inflexion	1.072 14.928

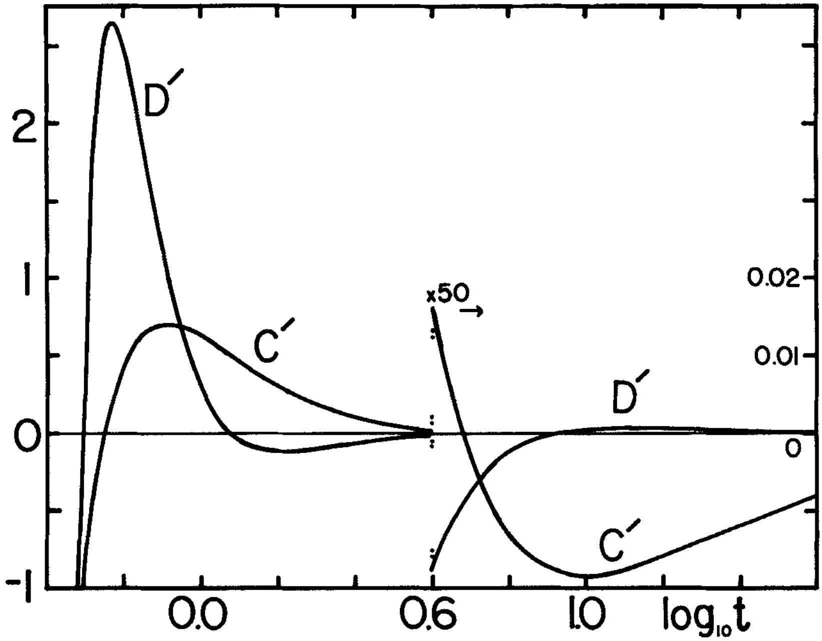

FIGURE 9 Third and fourth "pressure" virial coefficients C' and D' for the hard-sphere model. Note the magnified vertical scale for the right-hand portion of the figure.

It is the inflexion point at the higher temperature which is important for determining when $\ddot{C}'$ vanishes in (7). In the hard-core limit t_D is infinite.

In the soft-core virial coefficients we set

$$\frac{b}{b_0} = \frac{1}{[1 + (t/t_s)^N]} \equiv c, \text{ say, where } 0 < c < 1, \tag{10}$$

to obtain

$$B = b - \frac{a}{RT} = b_0\left[c - \frac{1}{t}\right], \tag{11a}$$

$$C = \tfrac{5}{8}b^2 = \tfrac{5}{8}b_0^2c^2, \tag{11b}$$

whence the third pressure virial coefficient becomes

$$C' = (-)\frac{b_0^3}{a}\left[\frac{3c^2}{8t} - \frac{2c}{t^2} + \frac{1}{t^3}\right]. \tag{12}$$

It is elementary to derive $\dot{C}'$ and $\ddot{C}'$. To obtain the "critical" value of N for which the slope of the C_p locus changes sign at t_D, we have to determine pairs of values of t_s and N for which $\ddot{C}'$ vanishes at t_D, where t_D is given implicitly by (IV (28e))

$$t_D = \frac{2[1 + (t_D/t_s)^N]^3}{\{N(t_D/t_s)^N[(1 - N) + (1 + N)(t_D/t_s)^N]\}}. \tag{13}$$

As the core is softened, t_D decreases steadily, and eventually meets the higher temperature inflexion point of C'. When t_s is finite, the temperature at which $\ddot{C}'$ vanishes also varies with N. Instead of fixing t_s and calculating N, we have preferred to select N at some value of interest (e.g. $\frac{1}{4}$) and to solve $\ddot{C}' = 0$ and (13) simultaneously for t_s and t_D. The corresponding "critical" values of t_s and N are listed with additional data in Table II, and graphed in Figure 10. Observe that the ratio t_D/t_c decreases steadily and quite slowly as N increases. The results are model independent to the extent that (12) and (13) involve only t_s, t_D and N. The choice of model becomes relevant only when the critical temperature t_c is used to scale the temperatures, VIII (10).

When $t_s = 0$, the critical value of N is 0.157389876, and is the *same* for the F, G, T and CS models since these have identical coefficients of x and x^2 in the expansion of $\phi(x)$. It is easy to show that for small t_s

$$C' \sim (-)\frac{b_0^3}{at_c^3}\left[\tfrac{3}{8}t_{c0}^2\left(\frac{t_c}{t}\right)^{1+2N} - 2t_{c0}\left(\frac{t_c}{t}\right)^{2+N} + \left(\frac{t_c}{t}\right)^3\right], \tag{14}$$

and

$$\frac{t_D}{t_c} \sim \left[\frac{2}{t_{c0}N(1 + N)}\right]^{1/(1-N)}. \tag{15}$$

TABLE II

Corresponding "critical" values of t_s and N at which $\ddot{C}' = 0$ and the slope of the C_p locus at t_D changes sign. Also tabulated are corresponding values of t_D and the ratio t_D/t_c for the soft-core F-model

N	t_s	t_D	t_D/t_c
0.157...	0	∞	54.960
0.19	$7.92E^{-3}$	72.846	52.971
0.20	0.0367	58.654	52.425
0.21	0.1159	49.854	51.906
0.23	0.5846	39.520	50.936
0.24	1.0534	36.226	50.483
0.25	1.7171	33.642	50.050
0.28	4.930	28.411	48.850
0.30	7.936	26.141	48.125
0.333...	13.755	23.495	47.027
0.4	24.860	20.357	45.160
0.5	34.471	17.888	42.941

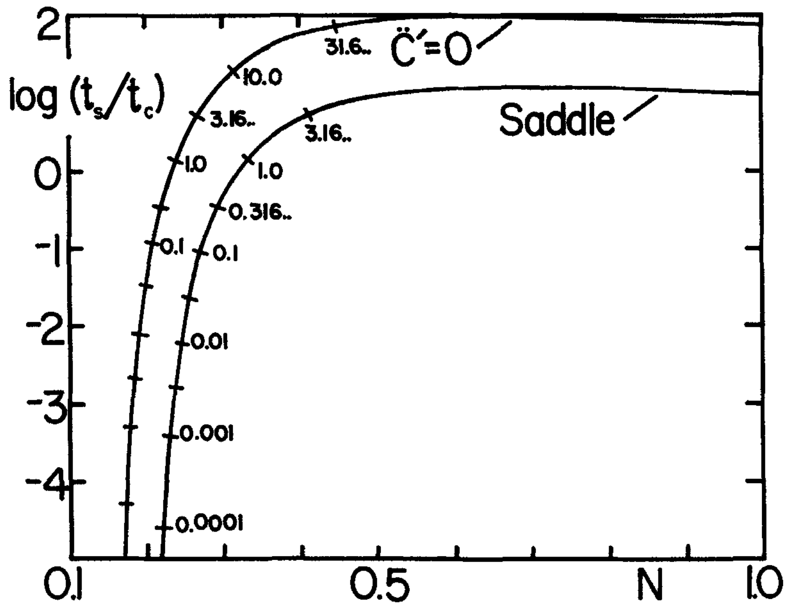

FIGURE 10 Corresponding values of t_s/t_c and N for the soft-core Frisch (F) model, at which the slope of the C_p locus changes sign at $t_D(\ddot{C}' = 0)$, and at which the saddle-point occurs.

Consequently $\ddot{C}'$ vanishes at t_D when N satisfies the cubic equation

$$8N^3 - 8N^2 - 18N + 3 = 0, \tag{16}$$

which has roots at -1.178731, 0.157390, 2.021341. The critical value of N equals the positive root in the range $0 < N < 1$.

5 THE SADDLE-POINT

The "saddle"-like geometry of the loci of C_p extrema was remarked on in Section 2, and in Section 3 for the case $T_s = 0$. In this section we trace the trajectory of the saddle-point across the phase diagram. For a fixed value of T_s, the saddle-point will correspond to a specific value of N. The saddle-point first occurs at $T_s = 0$ when $N = 0.2105008$. This special case is considered separately. For non-zero T_s, it is more convenient to fix $N(>0.2105)$ and to vary T_s. The C_p loci are then level-lines of T_s regarded as a function of density and temperature, defined implicitly through

$$\left(\frac{\partial C_p}{\partial P}\right)_T = 0, \text{ or } f(\rho, T; T_s, N) = 0, \tag{17}$$

where f is essentially the right-hand side of (1) or I(25) with $m = 3$:

$$f = \rho\left(\frac{\partial^2 P}{\partial \rho^2}\right)\left(\frac{\partial P}{\partial T}\right)^2 + 2\left(\frac{\partial P}{\partial \rho}\right)\left(\frac{\partial P}{\partial T}\right)\left[\left(\frac{\partial P}{\partial T}\right) - \rho\left(\frac{\partial^2 P}{\partial \rho\, \partial T}\right)\right] + \rho\left(\frac{\partial P}{\partial \rho}\right)^2\left(\frac{\partial^2 P}{\partial T^2}\right). \tag{18}$$

Along a C_p locus, T_s is a function of ρ and T for fixed N. Consequently along this locus

$$f(\rho, T, T_s(\rho, T), N) \equiv 0, \tag{19}$$

$$\frac{\partial f}{\partial \rho} + \frac{\partial f}{\partial T_s}\frac{\partial T_s}{\partial \rho} \equiv 0, \tag{20a}$$

$$\frac{\partial f}{\partial T} + \frac{\partial f}{\partial T_s}\frac{\partial T_s}{\partial T} \equiv 0. \tag{20b}$$

The saddle-point conditions are

$$\frac{\partial T_s}{\partial \rho} = 0, \frac{\partial T_s}{\partial T} = 0, \tag{21}$$

so the problem reduces to solving

$$\frac{\partial f}{\partial \rho} = 0, \frac{\partial f}{\partial T} = 0, \tag{22}$$

simultaneously for ρ and T, with T_s given implicitly as a function of ρ and T by (19).

[The required partial derivatives in (18) are tabulated in VIII (14). Since f in (18) is homogeneous in P, ρ and T, the extra temperature factors involving d and t (outside the square bracket terms) in VIII (14) may be cancelled out leaving a reduced form of f depending only on x and t. It is convenient to change variables from ρ and T via x and t to x and w, where

$$w \equiv u_1 = \frac{t\dot{b}}{b} = -\frac{N(t/t_s)^N}{[1 + (t/t_s)^N]}, \tag{23}$$

so

$$u_2 = \frac{t^2\ddot{b}}{b} = w(2w + N + 1), \tag{24a}$$

and

$$u_0 = \frac{1}{t_s}\left(\frac{N}{N + w}\right)\left(\frac{N + w}{-w}\right)^{1/N}. \tag{24b}$$

The transformation from ρ and T to x and w is non-singular so (17) becomes

$$f(x, w; t_s, N) \equiv 0 \tag{25}$$

and the saddle-point conditions are now

$$\frac{\partial f}{\partial x} = 0, \frac{\partial f}{\partial w} = 0. \tag{26}$$

Inspection of the manner in which the partial derivatives enter f in (25) and (18) reveals that t_s occurs only via u_0 in $(\partial p/\partial \rho)$ and $(\partial^2 p/\partial \rho^2)$, and consequently (25) is actually a quadratic equation for u_0 in terms of x and w. So u_0, and hence t_s, may be expressed explicitly in terms of x and w, and the result substituted in (26). For a chosen exponent N we then solved the saddle-point conditions (26) iteratively, by a Newton–Raphson method for two

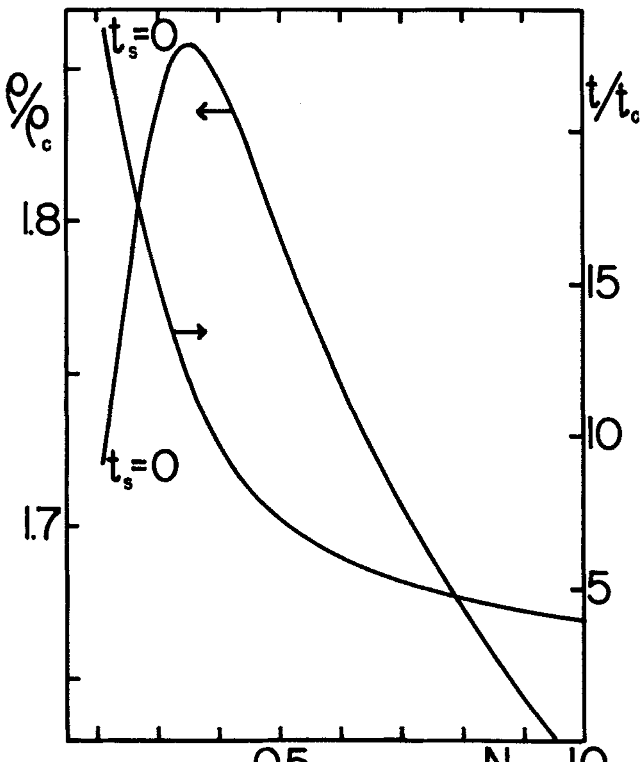

FIGURE 11 N dependence of the saddle-point values of the density and temperature (scaled by their critical values) for the soft-core Frisch (F) model.

variables, to obtain corresponding values of x and w. Thence u_0 is obtained from the solution (via the quadratic equation) of (25), and t_s from (24b). The scaled temperature t can then be extracted from w via (23), and the density follows from $d = xtu_0$.]

The solutions for the position of the saddle-point are presented graphically in Figures 10–12, which show matching values of t_s and N, and the variation of the density, temperature and pressure along the saddle-point trajectory. Soft-core type behaviour occurs in a region below the graph in the t_s vs. N diagram, Figure 10. The saddle-point has a well-defined starting point when $t_s = 0$ at $N = 0.2105$, Section 3. As t_s increases from zero, and the corresponding value of N increases too, the saddle-point moves steadily towards lower temperatures and pressures whereas the density at first increases to about $1.858\rho_c$ at $N \simeq 0.355, n = 8.45$. Only values of N less than unity are meaningful in the $t_s - N$ model. In the range $\frac{1}{2} \leq N \leq 1, t_s \simeq 10t_c$ and for the $t_s - N$ model near this parameter value the saddle-point occurs moderately close to the critical point: $\rho < 1.8\rho_c$, $t < 7t_c$ and $p < 60p_c$. The F and CS models behave in a similar manner.

The special case when $t_s = 0$ has to be treated separately since now t_s is fixed, and it is necessary to compute the value of N at the saddle-point.

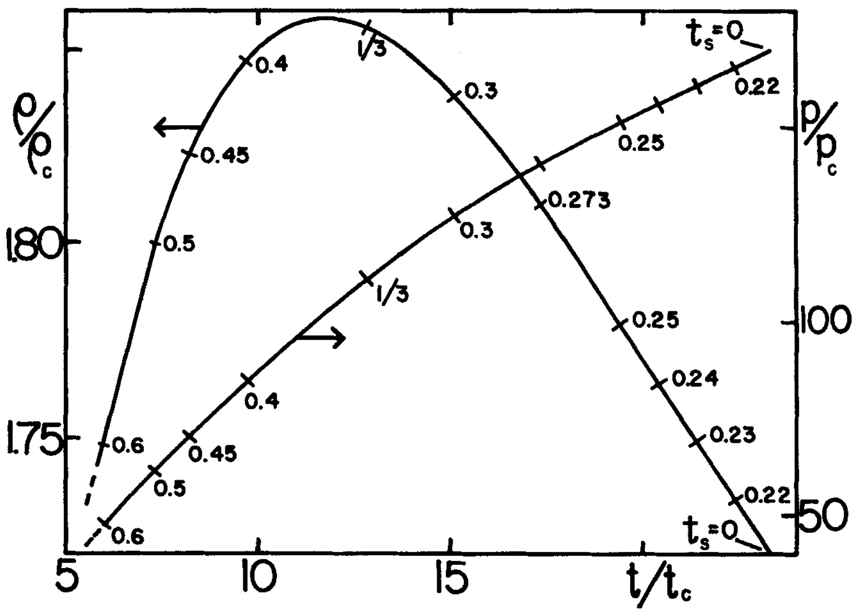

FIGURE 12 Trajectories of the saddle-point in the density versus temperature (left-hand scale) and pressure versus temperature (right-hand scale) phase diagrams, for the soft-core Frisch (F) model.

The structure of the partial derivative expressions in VIII (14) is maintained, with

$$u_1 \to -N, u_2 \to N(N+1), \tag{27}$$

but we introduce an alternative temperature variable

$$v = \lim_{t_s \to 0} u_0 = \frac{(t_c/t)^{1-N}}{t_{c0}}. \tag{28}$$

The function f now involves x, v and N, so along the C_p locus (17)

$$f(x, v; N) \equiv 0, \tag{29}$$

and the saddle point conditions become

$$\frac{\partial f}{\partial x} = 0, \frac{\partial f}{\partial v} \equiv 0. \tag{30}$$

Now N is defined as a function of x and v through (29). The new f turns out to be a quadratic in N, so N can be expressed explicitly in terms of x and v, and the result substituted in (30). The saddle-point conditions (30) are solved iteratively for corresponding values of x and v, whence N is obtained from the solution (via the quadratic equation) of (29), and t/t_c from (28). The choice of model, F or CS, determines t_{c0}, the hard-core limit (scaled) critical temperature. The density ratio d/d_c follows immediately from VIII (18): $d/d_c = (x/x_c)(t/t_c)^N$.

6 CONCLUDING REMARKS

The calculations reported in this paper have been performed for a class of soft-core equations of state constructed by substituting a somewhat arbitrary form of soft molecular core into a class of approximate hard-core equations of state which incorporate an additional van der Waals type attractive term. The question arises as to whether the qualitative behaviour revealed for these models carries over, first, to equations of state constructed by the methods of statistical mechanics from more realistic intermolecular potentials, and, second, to the observed properties of real fluid systems. The first of these problems is addressed in the next (X, final) paper of this series.

Note added in Proof (after Eqn. (16)).

The cubic Eq. in (16) can be generalized for the M-N model, in which case the second and third virial coefficients take the form

$$B = \left(\frac{b_0}{T^N}\right) - \left(\frac{a}{T^M}\right), C = \lambda\left(\frac{b_0}{T^N}\right)^2, \tag{16a}$$

where $\lambda = 5/8$ above. Then $\ddot{C}'$ vanishes at t_D when N satisfies

$$(N + 1)\left[1 - \left(\frac{N}{M}\right)\right]^2 - \lambda(2N + 1) = 0. \tag{16b}$$

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