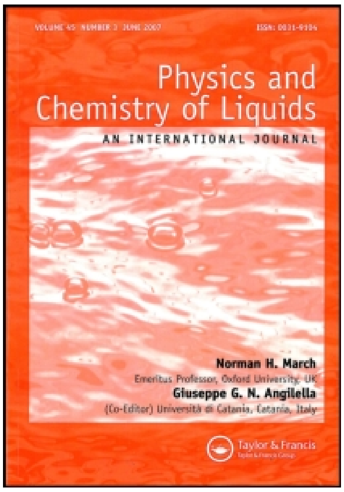

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Hard and Soft-Core Equations of State for Simple Fluids. VIII. Soft-Core Equations of State and Characteristic Curves

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Hard and Soft-Core Equations of State for Simple Fluids

VIII. Soft-Core Equations of State and Characteristic Curves†

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A class of soft-core equations of state is constructed by introducing a temperature dependent molecular volume parameter into hard-core equations of state. Characteristic curves are calculated numerically for a soft-core version of the Frisch model, parameterized by a "softening temperature" T_s, and a repulsive potential exponent n. The entire range of behaviour from the extreme hard-core ($T_s = \infty$) to soft-core ($T_s = 0$) limit is investigated.

1 INTRODUCTION

In this paper we return to the problem of describing the characteristic curves of a simple fluid. In two previous papers (II and III of this series)[1] we showed that hard-core equations of state are capable of describing the characteristic curves of argon in the comparatively low temperature and pressure region surrounding the critical point: $T \lesssim 10T_c$, $P \lesssim 20P_c$. At higher temperatures soft-core effects become apparent through the temperature dependence of the second and higher virial coefficients. In particular the second virial coefficient locates the termination temperatures T_A, T_D and T_E of the second order characteristic curves A_T, A_P and A_V associated with the Amagat line A. (II) These characteristic curves make a wide sweep

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around the critical point generally at rather high temperatures and pressures, and, with the exception of A_T, intersect the fusion curve. This behaviour is not accounted for by a hard-core equation of state (III).

In the next section we discuss how to soften the core and how to introduce this soft-core into a hard-core equation of state, thereby constructing the corresponding soft-core equation of state. The remainder of the paper contains technical details concerning the calculation and scaling of the critical constants and termination temperatures (Section 3), the calculation of the characteristic curves (Section 4), the construction of the coexistence curve (Section 5), and the selection of a "cut-off" criterion at high densities (Section 6). The $T_s = 0$ limit is considered in some detail. However in Section 7 we discuss the desirability of placing a lower bound on the softening temperature T_s, so that the critical density remains less than the largest permitted zero-point density.

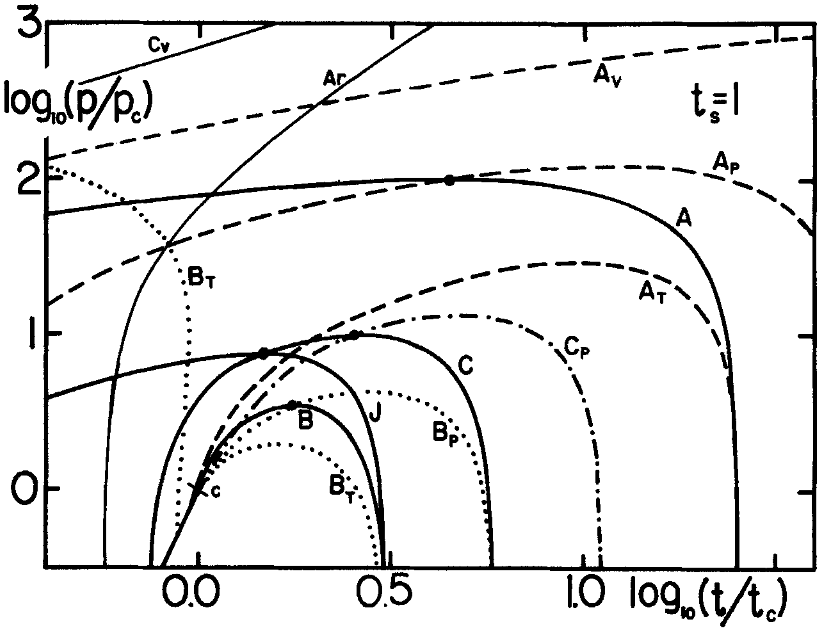

FIGURE 1 Characteristic curves for the soft-core Frisch (F) model with $N = \frac{1}{4}$ and $t_s = 1$. The argon melting curve (Ar) has been included.

Our results are essentially summarized in Figures 1–4, which display the characteristic curves for the soft-core Frisch model[3] with $N = \frac{1}{4}(n = 12)$ for various values of T_s, including zero.

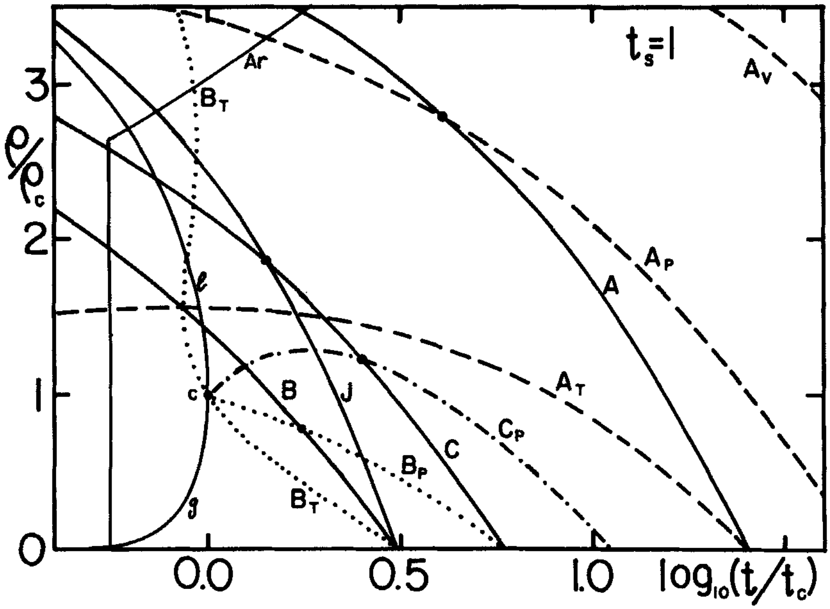

FIGURE 2 As for Figure 1.

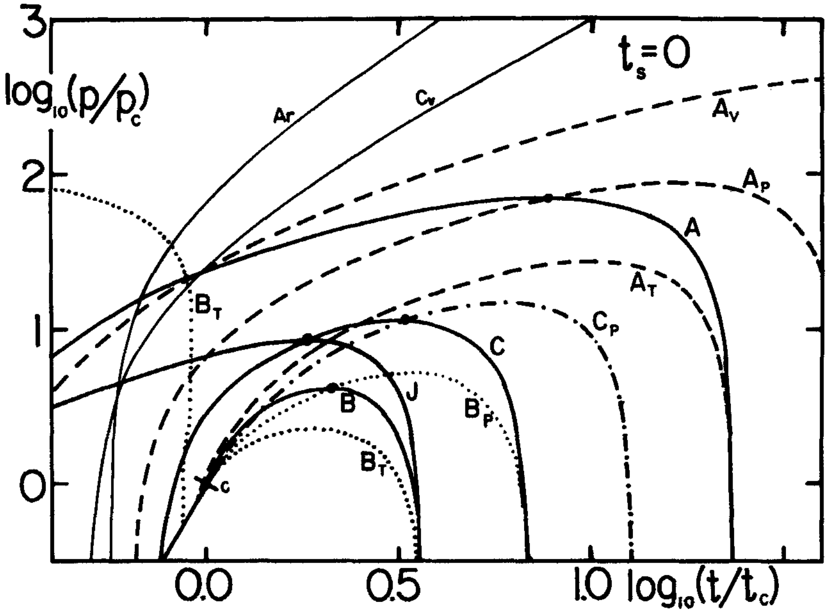

FIGURE 3 As for Figure 1, but with $t_s = 0$.

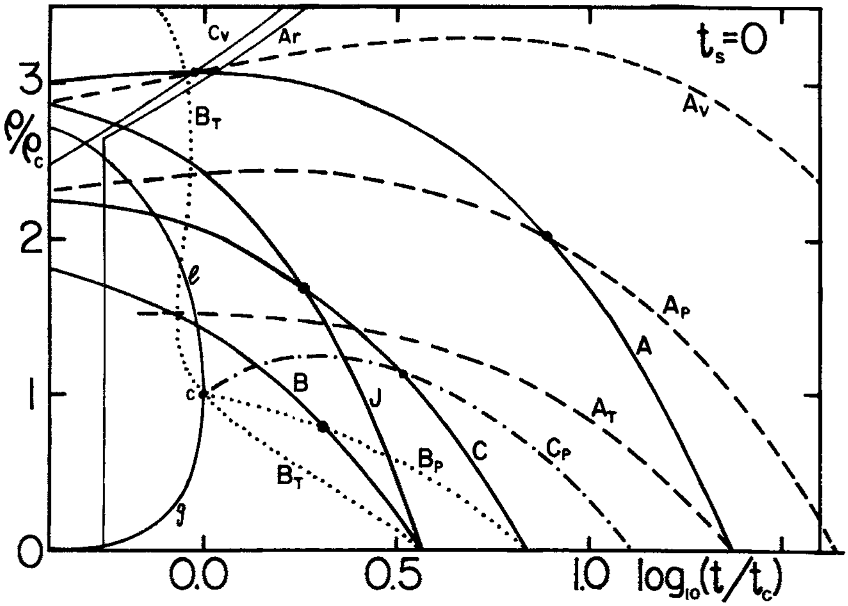

FIGURE 4 As for Figure 3.

2 SOFT-CORE EQUATIONS OF STATE

The question arises as to how to introduce a soft-core. It would be desirable to employ the equation of state for a fluid with a reasonably realistic intermolecular potential, such as the Lennard-Jones $m - n$ potential, for example. Such equations of state can be constructed for fixed values of the exponents m and n, e.g. $m = 6$, $n = 12$, and will be studied in a subsequent paper. However it is our purpose here to investigate the entire range of possible behaviour of a simple fluid between extreme hard and soft-core limits. Se we have preferred to adopt a model expression, as in IV, for the molecular volume parameter b which will describe the softening of the core at high temperatures. We set

$$b = \frac{b_0}{[1 + (T/T_s)^N]}, \tag{1}$$

where b_0 is the hard-core value of b at zero temperature. This provides *two* parameters: the exponent N which can be related to the exponent n of the repulsive part of the intermolecular potential ($N = 3/n$); and the softening temperature T_s, which may be varied in the range 0 to ∞. This is just the $T_s - N$ model studied in IV, where the termination temperatures were calculated for a range of values of T_s and N. In this paper we shall first fix N and vary T_s between the hard-core limit $T_s = \infty$ and the soft-core limit $T_s = 0$. We shall choose $N = \frac{1}{4}$, corresponding to a repulsive exponent $n = 12$. Qualitatively similar results for the characteristic curves are obtained for other choices of N. We shall also investigate the soft-core limit in some detail, since it is important for analysis of the loci of C_p extrema in the next paper of this series.

One way of introducing a soft-core molecular volume into an equation of state would be to replace the second virial coefficient by a more realistic temperature dependent expression, such as the classical second virial coefficient for a Lennard–Jones potential, leaving all higher virial coefficients unchanged. Instead we have chosen to insert the soft-core form (1) for the molecular volume parameter b into *every* virial coefficient by substitution in the hard-core equation of state variable

$$x = b\rho. \tag{2}$$

This retains the technical simplicity of the hard-core equation of state calculations, in I and III, while introducing a reasonable high-temperature behaviour in all the virial coefficients. This substitution has the disadvantage that the critical value of the compressibility factor $Z \equiv (PV/RT)$ is unchanged (Section 3 (13) below), and also necessitates the introduction of a "cut-off" into the phase diagram at high densities (Section 6). The dimensionless density, temperature and pressure variables are now

$$d = b_0\rho, \tag{3a}$$

$$t = \frac{b_0 RT}{a}, \tag{3b}$$

$$p = \frac{b_0^2 P}{a}, \tag{3c}$$

and the equation of state

$$P = RT\rho\phi(b\rho) - a\rho^2 \tag{4}$$

becomes

$$p = dt\phi(x) - d^2. \tag{5}$$

The second virial coefficient is now

$$\begin{aligned} B &= b - \frac{a}{RT} \\ &= b_0\left\{\frac{1}{[1 + (t/t_s)^N]} - \frac{1}{t}\right\} \end{aligned} \tag{6}$$

as in the $T_s - N$ model in IV (27).

The selection of the underlying hard-core model is made through the function $\phi(x)$, for which various suggestions were summarized and discussed in I. Most of the calculations reported in this paper will be for the Frisch model (F) with

$$\phi(x) = \psi(y) = \frac{1 + y + y^2}{(1 - y)^3}, \text{ where } x = 4y. \tag{7}$$

Qualitatively similar results are obtained for the other models considered in I. Figures 1–4 display the characteristic curves for the soft-core Frisch model with $N = \frac{1}{4}$ and $t_s = 1$ and 0. The pressure, density and temperature are scaled by their critical values, and a logarithmic scale has been used for the pressure and temperature.

3 CRITICAL POINT CONSTANTS

The critical point for the soft-core equation of state is located by applying the usual conditions that the critical isotherm have a horizontal point of inflexion there. Since the required derivatives are at constant temperature, the form of the equations for ρ_c, T_c and P_c are the same as in the hard-core case, except that b is replaced by its soft-core from (1). The critical value of the parameter $x(=b\rho)$ is the solution of

$$\phi - x\phi' - x^2\phi'' = 0 \tag{8}$$

just as in the hard-core case. The critical density, temperature and pressure are now given by

$$b\rho_c = x_c, \tag{9a}$$

$$\frac{bRT_c}{a} = \frac{2x}{[\phi + x\phi']}, \ (= t_{c0}, \text{ say}) \tag{9b}$$

$$\frac{b^2 P_c}{a} = \frac{x^2[\phi - x\phi']}{[\phi + x\phi']}, \ (= p_{c0}, \text{ say}) \tag{9c}$$

where x takes its critical value x_c on the right-hand side. It is convenient to denote the scaled critical temperature and pressure for the underlying hard-core model by t_{c0} and p_{c0}, as in (9b) and (9c). Then the scaled critical density, temperature and pressure for the soft-core model become

$$t_c = t_{c0}\left(\frac{b_0}{b}\right) = t_{c0}\left[1 + \left(\frac{t_c}{t_s}\right)^N\right], \tag{10}$$

$$d_c = x_c\left(\frac{b_0}{b}\right), p_c = p_{c0}\left(\frac{b_0}{b}\right)^2, \tag{11}$$

or in ratio form

$$\frac{d_c}{x_c} = \frac{t_c}{t_{c0}}, \qquad \frac{p_c}{p_{c0}} = \left(\frac{t_c}{t_{c0}}\right)^2. \tag{12}$$

Clearly the value of the compressibility factor Z in our soft-core model is unchanged from the hard-core value, which depends on the choice of the function ϕ. We have from (10) and (11)

$$Z_c = \frac{p_c}{d_c t_c} = \frac{p_{c0}}{x_c t_{c0}}. \tag{13}$$

The calculation of the critical constants proceeds by choosing values for N and t_s, solving (10) numerically for t_c, and substituting in (11) or (12). The values of x_c, t_{c0} and p_{c0} are known from the underlying hard-core model. Actually the solution of (10) for t_c/t_{c0} and the ratios in (12) are independent of the choice of model for ϕ. Numerical values of these ratios are presented in Table I for a range of values of t_s/t_{c0}. For large t_s, $t_c/t_{c0} \sim 1$, and for small t_s, $t_c/t_{c0} \sim (t_{c0}/t_s)^{N/(1-N)}$. For small t_s the asymptotic form of t_c is similar to that of the characteristic temperatures in IV (31), so in the soft-core limit their ratios remain finite. [In the soft-core limit it therefore becomes essential to scale the density, temperature and pressure by their critical values, Section 4]. Some numerical values of the critical temperature t_c

TABLE I

Ratios of critical parameters t_c, d_c and p_c for the soft-core T_s-Nmodel with $N = \frac{1}{4}$ to the critical parameters t_{c0}, x_c, p_{c0} for the corresponding hard-core model. These ratios are independent of the choice of hard-core model (F, CS, etc.). For a selected value of t_s/t_{c0}, the ratio t_c/t_{c0} is calculated from Eq. (10), and and then $d_c/x_c = t_c/t_{c0}$, and $p_c/p_{c0} = (t_c/t_{c0})^2$.

$\log_{10} t_s/t_{c0}$	$\log_{10} t_s/t_c$	$t_c/t_{c0} = d_c/x_c$	p_c/p_{c0}
3.0	2.9261	1.1856	1.4055
2.0	1.8728	1.3402	1.7963
1.5	1.3345	1.4638	2.1428
1.0	0.7862	1.6360	2.6764
0.5	0.2263	1.8778	3.5263
0.0	−0.3465	2.2207	4.9317
−0.5	−0.9332	2.7112	7.3503
−1.0	−1.5338	3.4179	11.6821
−1.5	−2.1477	4.4428	19.7387
−2.0	−2.7735	5.9360	35.2358

TABLE II

Numerical values of the critical temperature t_c and the logarithms of ratios of characteristic temperatures to t_c for the soft-core Frisch (F) model with $N = \frac{1}{4}$ for various values of t_s

t_s	t_c	$\log_{10}\left(\frac{t_B}{t_c}\right)$	$\log_{10}\left(\frac{t_C}{t_c}\right)$	$\log_{10}\left(\frac{t_F}{t_c}\right)$	$\log_{10}\left(\frac{t_A}{t_c}\right)$	$\log_{10}\left(\frac{t_D}{t_c}\right)$	$\log_{10}\left(\frac{t_E}{t_c}\right)$
∞	0.3753	0.4256	0.7266	1.0277	∞	∞	∞
100	0.4738	0.4516	0.7422	1.0332	1.5499	1.8525	2.9161
10	0.5577	0.4674	0.7534	1.0399	1.4592	1.7525	2.5636
1	0.7212	0.4885	0.7699	1.0516	1.4020	1.6872	2.3631
$\frac{1}{10}$	1.0511	0.5121	0.7897	1.0675	1.3745	1.6539	2.2573
$\frac{1}{100}$	1.7380	0.5334	0.8085	1.0836	1.3662	1.6421	2.2080
0	∞	0.5675	0.8396	1.1118	1.3702	1.6424	2.1730

and the corresponding (logarithms of) ratios of characteristic temperatures to t_c are presented in Table II for the case $N = \frac{1}{4}$, and $t_c = \infty$, 100, 10, 1, $\frac{1}{10}$, $\frac{1}{100}$ and 0.

4 CHARACTERISTIC CURVES

The definitions and equations determining characteristic curves are available in II. It is necessary to calculate first- and second-order partial derivatives of the pressure with respect to density and temperature. It is trivial to show that in terms of scaled variables

$$p = dt[\phi - u_0 x], \tag{14a}$$

$$\frac{\partial p}{\partial d} = t[\phi + x\phi' - 2u_0 x], \tag{14b}$$

$$\frac{\partial p}{\partial t} = d[\phi + x\phi' u_1], \tag{14c}$$

$$\frac{\partial^2 p}{\partial d^2} = \frac{t}{d}[2x\phi' + x^2\phi'' - 2u_0 x], \tag{14d}$$

$$\frac{\partial^2 p}{\partial d\,\partial t} = [\phi + x\phi' + 2x\phi' u_1 + x^2\phi'' u_1], \tag{14e}$$

$$\frac{\partial^2 p}{\partial t^2} = \frac{d}{t}[2x\phi' u_1 + x^2\phi'' u_1^2 + x\phi' u_2], \tag{14f}$$

where

$$u_0 = \frac{[1 + (t/t_s)^N]}{t},$$
$$u_1 = \frac{t\dot{b}}{b}, u_2 = \frac{t^2\ddot{b}}{b}, \tag{15}$$

and · denotes temperature differentiation ($\partial/\partial t$) with respect to t.

The defining equations for the zeroth and first order characteristic curves remain simple in the soft-core case.

$$J: (\phi - 1)/x = \frac{[1 + (t/t_s)^N]}{t}, \tag{16a}$$

$$A: \phi' = \frac{[1 + (t/t_s)^N]^2}{Nt(t/t_s)^N} \tag{16b}$$

$$B: \phi' = \frac{[1 + (t/t_s)^N]}{t}, \tag{16c}$$

$$C: \phi' = \frac{2[1 + (t/t_s)^N]^2}{t[1 + (1 + N)(t/t_s)^N]}. \tag{16d}$$

It is easier to work directly with the general defining equations II (Table I) and the derivative expressions in (14) above. Since the defining equations are (dimensionally) homogeneous in P, ρ and T it is clear that the resulting equations for the various characteristic curves turn out to involve implicit relations between x and t, such as for J, A, B and C in (16). As a straightforward numerical procedure, for chosen values of N and t_s one selects the temperature ratio t/t_c, evaluates x by iteration and hence d/d_c (from $d = x[1 + (t/t_s)^N] = xtu_0$), and p/p_c by substitution in the equation of state (5) or (14a).

Graphs of the characteristic curves are presented in Figures 1–4 in both the density vs. temperature and pressure vs. temperature digrams. A logarithmic scale has been employed for pressure and temperature. The features of these figures are broadly as expected from earlier work in II and III. The characteristic curves associated with A are now obtained with finite termination temperatures.

The calculation of characteristic curves has been extended to the limit $t_s = 0$, in which case the structure of the defining equations and the partial pressure derivatives remains unchanged. In fact there is a certain amount of simplification since now

$$u_0 \rightarrow \frac{(t_c/t)^{1-N}}{t_{c0}}, u_1 \rightarrow -N, u_2 \rightarrow N(N + 1). \tag{17}$$

Again one chooses N, selects t/t_c and iterates numerically to obtain x. Then

$$\frac{d}{d_c} = \frac{x}{x_c}\left(\frac{t}{t_c}\right)^N, \tag{18}$$

$$\frac{p}{p_c} = \frac{x_c}{p_{c0}} \cdot \frac{d}{d_c}\left[\left(\frac{t}{t_{c0}}\right) t_{c0}\,\phi(x) - x_c\left(\frac{d}{d_c}\right)\right]. \tag{19}$$

The second virial coefficient rescales to

$$\frac{Bt_c}{b_0} = t_{c0}\left(\frac{t_c}{t}\right)^N - \left(\frac{t_c}{t}\right), \tag{20}$$

which is just the soft-core form discussed in IV under the $M - N$ model with $M = 1$.

5 COEXISTENCE CURVE

General formulae for determining the coexistence curve for the underlying hard-core equation of state were given in I, and we quote these here for ease of reference:

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

$$\frac{bRT}{a} = \frac{(x_2^2 - x_1^2)}{[x_2\phi(x_2) - x_1\phi(x_1)]}, \; (= t_0,\ \text{say}), \tag*{I(18)}$$

$$\frac{b^2P}{a} = \frac{x_1x_2[x_2\phi(x_1) - x_1\phi(x_2)]}{[x_2\phi(x_2) - x_1\phi(x_1)]}, \; (= p_0,\ \text{say}). \tag*{I(19)}$$

From I(17) one obtains a table of corresponding values of the gas density x_1 and the liquid density x_2 in the hard-core case, and hence from I(18), (19) the temperature t_0 and pressure p_0 on the vaporization curve, where the subscript $_0$ refers to the hard-core case in which $b = b_0$. Once t_0 is known, the temperature t for the soft-core case is obtained by solving numerically the implicit relation

$$t = t_0\left[1 + \left(\frac{t}{t_s}\right)^N\right] \tag{21}$$

obtained by inserting (1) and (3b) in the left-hand side of I(18) above. The pressure p follows similarly from I(19):

$$p = p_0\left(\frac{t}{t_0}\right)^2. \tag{22}$$

These soft-core coexistence curves have been included in Figures 1–4.

6 CUT-OFF CRITERIA

In practice the high density portion of the phase-diagram of a fluid terminates at the liquid branch of the fusion curve. This is fortunate because the soft-core model constructed by modifying the molecular volume parameter b in $x(=b\rho)$ has some undesirable properties at high densities, or more precisely at large values of x. One consequence is that the coexistence curves are distorted from their expected shape in the high-density low-temperature region. Further, the necessity of some kind of "cut-off" arises since as $y = \frac{1}{4}x \rightarrow 1$ (in the F, G, T and CS models), the derivative $\partial p/\partial t$ becomes large and negative. (u_1 and $\dot{b}$ in (14c) are negative and ϕ' diverges more strongly than ϕ as $y \rightarrow 1$). This implies that $\partial p/\partial t$ and also $\partial^2 p/\partial t^2$ and $\partial^2 p/\partial d\partial t$ must vanish along certain loci in the density vs. temperature diagram, and that the isotherms intersect each other in some region. These are not generally expected properties of real fluids, although $\partial p/\partial t$ can be negative for water. Moreover the constant volume specific heat C_v calculated for the soft-core model can fall below its ideal gas value C_{v0} at large x, which is clearly unacceptable. Rather arbitrarily we have adopted the "safe" cut-off $\partial^2 p/\partial t^2 = 0$, along which locus C_v passes through a maximum along isotherms.

Perhaps it is worth noting that the loci $\partial^2 p/\partial t^2 = 0$ and $\partial^2 p/\partial d\partial t = 0$ are quite close together in the phase diagram, as are the lines on which $\partial p/\partial t = 0$ and C_v equals its ideal gas value C_{v0}. (C_v cut-off). Moreover at "low" temperatures (less than t_s for the van der Waals equation, irrespective of N) the $\partial p/\partial t = 0$ locus can lie in the physical region where $C_v > C_{v0}$. It is clear from the thermodynamic identity

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V, \tag{23}$$

with $\partial^2 p/\partial t^2$ being negative at low densities, that the $\partial^2 p/\partial t^2 = 0$ cut-off occurs at lower densities than the C_v cut-off. General expressions can be derived for the various "cut-off" criteria lines mentioned above, but these are not of sufficient interest to merit further discussion.

7 RANGE OF VALUES OF t_s

Another kind of "cut-off" can be established at low temperatures by insisting that the zero-point density be greater than some arbitrarily prescribed value, such as the critical density (say). This places a lower bound on the acceptable range of values of the softening temperature t_s. The critical density

$$d_c \equiv b_0 \rho_c = x_c\left[1 + \left(\frac{t_c}{t_s}\right)^N\right], \left(= \frac{x_c t_c}{t_{c0}}\right), \tag{24}$$

varies in value from x_c in the hard-core limit to arbitrarily large values for small softening temperatures t_s. On the other hand, at zero temperature the (scaled dimensionless) density d equals x, and the maximum permitted value of x is 4 for the F, G, T and CS models, at which value the pressure is infinite. Alternatively we may wish to restrict x to a maximum value x_m determined by the close-packed hexagonal value ≈ 3, or the simple-cubic packing value ≈ 2, as in I(4). And again we might wish to keep the density less than the fluid-solid transition value determined by molecular dynamics, in which case $\rho < 0.67 \times$ close-packing (*hcp*) density, or $x_m < 0.67 \times 2.962 \approx 2$, so $x_m/x_c \approx 4$.

If we require $d_c \leq x_m$ then

$$x_m \geq x_c\left[1 + \left(\frac{t_c}{t_s}\right)^N\right] = \frac{x_c t_c}{t_{c0}}, \tag{25}$$

which limits the size of t_c/t_{c0}. Now from (10), we obtain corresponding limits on the ratios t_s/t_c and t_s/t_{c0}:

$$\begin{aligned} \frac{t_s}{t_c} &= \frac{1}{[(t_c/t_{c0}) - 1]^{1/N}} \geq \frac{1}{[(x_m/x_c - 1]^{1/N}}, \\ \frac{t_s}{t_{c0}} &= \frac{(t_c/t_{c0})}{[(t_c/t_{c0}) - 1]^{1/N}} \geq \frac{(x_m/x_c)}{[(x_m/x_c) - 1]^{1/N}}. \end{aligned} \tag{26}$$

The numerical restrictions on t_s for the various choices of x_m mentioned above, with $x_c = \frac{1}{2}$ (approximately for the F, G and CS models) and $N = \frac{1}{4}$ are presented in Table III. In the van der Waals model $x_m = 1$, and $x_c = \frac{1}{3}$, so $x_m/x_c = 3$. However, if one accepts the fusion curve as a natural cut-off, then the above restrictions on t_s are no longer relevant in practice.

TABLE III

Restrictions on the softening temperature t_s when the critical density d_c is kept less than a prescribed maximum value x_m, for the case $N = \frac{1}{4}$. [See Section 7, Eqs. (24), (25) and 26)].

x_m	x_c	x_m/x_c	t_s/t_c	t_s/t_{c0}
4	$\frac{1}{2}$	8	$4.16E^{-4}$	$3.33E^{-3}$
3	$\frac{1}{2}$	6	$1.60E^{-3}$	$9.60E^{-3}$
2	$\frac{1}{2}$	4	$\frac{1}{81}$	$\frac{4}{81}$
1	$\frac{1}{3}$	3	$\frac{1}{16}$	$\frac{3}{16}$

CONCLUDING REMARKS

We have partially achieved one of the original aims of this series of papers: to model the characteristic curves of a simple fluid by softening the molecular core at high temperatures. We plan to extend our analysis to more realistic equations of state. The characteristic curves obtained do have the expected overall shape (II), which is qualitatively similar for all *finite* values of the softening temperature t_s, even down to the extreme soft-core limit $t_s = 0$. No surprises occur, even for other possible values of N, in contrast to the more exotic behaviour of the loci of C_p extrema, which are the subject of the following paper.

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