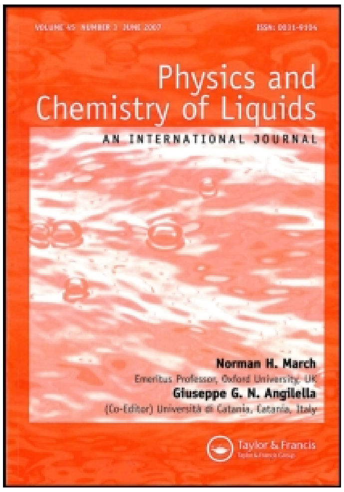

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On the Constant Pressure Specific Heat C_p of a Simple Fluid†

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Calculation of C_P from a model soft-core equation of state reveals a line in the phase diagram on which C_P is equal to its zero pressure value C_{P_0}. This line commences on the temperature axis where the second virial coefficient has a point of inflexion. At higher temperatures (and pressures) C_P falls *below* C_{P_0}. The detailed behaviour of C_P is presented via contour maps, illustrating the effects of changing the exponent $N(=3/n$, where n is the repulsive potential exponent) which parameterizes the model. For soft-core fluids at high temperatures C_P deviates only slightly from the ideal gas value over a wide range of temperature and density, in marked contrast to the behaviour of hard-core models.

1 INTRODUCTION

In order to obtain a qualitatively correct description of the constant pressure specific heat C_P of a simple fluid at high temperatures it is necessary to take into account the effective softening of the molecular hard core, or penetration of the repulsive part of the intermolecular potential.[1] Calculation of C_P, in this paper, from a model equation of state reveals a line in the phase diagram along which C_P maintains the same value as it would have at zero density: C_{P_0}. For a structureless monatomic system C_{P_0} would equal $\frac{5}{2}R$. This line commences on the temperature axis at the temperature T_D (typically 50 × Boyle temperature) at which the second virial coefficient has a point of inflexion. At higher temperatures (and pressures) C_P falls *below* its ideal gas value, whereas at lower temperatures C_P increases with pressure along isotherms. Such a behaviour has been observed (indirectly) for Helium in

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the vicinity of 200°C by Roebuck and Osterberg[2–4] using C_P values derived from the Joule–Kelvin coefficient μ:

$$\mu \equiv \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]. \tag{1}$$

The detailed behaviour of C_P described by our model may be presented compactly, and hence easily appreciated, via contour maps drawn in the density vs. temperature diagram, from which it is clear that a hard-core equation of state is inadequate at high temperatures. In the next section we provide a brief account of the model, followed in Section 3 by the calculation of C_P, and a discussion of the theoretically possible behaviour of the $C_P = C_{P_0}$ locus.

2 EQUATION OF STATE

We adopt an equation of state of the Guggenheim,[5] Longuet-Higgins, Widom[6] form

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

where a and b are van der Waals' parameters. The volume b has the constant value b_0 for a hard-core model, and is permitted to be temperature dependent for a soft-core model. The specific form of the function ϕ depends on the choice of the underlying hard-core model. In terms of scaled variables

$$x \equiv 4y = b\rho,$$

$$d = b_0\rho,$$

$$t = \frac{b_0 RT}{a},$$

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

the equation of state becomes

$$p = dt\phi(x) - d^2. \tag{4}$$

The leading terms in the exact hard-sphere expansion of $\phi(x)$ are

$$\phi(x) = 1 + x + \lambda x^2 + \cdots, \text{ with } \lambda = \frac{5}{8}. \tag{5}$$

In this paper we will use the Frisch model[1] form for $\phi(x)$, which agrees with (5) up to terms of order x^2:

$$\phi(x) = \psi(y) = \frac{1 + y + y^2}{(1 - y)^3}. \tag{6}$$

Also we choose a simple form for the temperature dependence of b:

$$b = \frac{b_0 \alpha}{t^N}, \tag{7}$$

where α is a positive constant, and the exponent N lies in the range $0 \leq N < \frac{1}{2}$, so the corresponding repulsive potential exponent $n \equiv 3/N$ exceeds 6. When $N = 0$ we retrieve the hard-core case. The resulting equation of state is then essentially a model generalization of the soft-sphere equation of state of Hoover *et al.* augmented by an attractive van der Waals ($a\rho^2$) contribution.[7] Then the second and third virial coefficients in the virial expansion

$$\frac{P}{\rho RT} \equiv \frac{p}{dt} = 1 + B\rho + C\rho^2 + \cdots \tag{8}$$

have the especially simple forms

$$B = b_0\left[\frac{\alpha}{t^N} - \frac{1}{t}\right], C = \lambda\left(\frac{b_0}{t^N}\right)^2. \tag{9}$$

Sometimes it is preferable to scale the density, temperature and pressure by their critical values. For an equation of state of the form (4) the critical parameters d_c, t_c, p_c are related to their values for the underlying hard-core case, x_c, t_{c0}, p_{c0}, by

$$d_c = x_c\left(\frac{b_0}{b_c}\right), t_c = t_{c0}\left(\frac{b_0}{b_c}\right), p_c = p_{c0}\left(\frac{b_0}{b_c}\right)^2 \tag{10}$$

where b_c is the critical value of b in (7). For the Frisch model, $x_c = 0.514668$, $t_{c0} = 0.375312$ and $p_{c0} = 0.069510$. Consequently we identify

$$\alpha = \frac{t_{c0}}{t_c^{1-N}}. \tag{11}$$

Next it is convenient to set

$$u_0 = \frac{b_0}{bt}, \quad u_1 = \frac{t\dot{b}}{b}, \quad u_2 = \frac{t^2\ddot{b}}{b}, \tag{12}$$

where $\dot{}$ denotes temperature differentiation with respect to t. For the special form of b in (7)

$$u_0 = \frac{1}{\alpha t^{1-N}} = \frac{(t_c/t)^{1-N}}{t_{c0}}, \quad u_1 = -N, u_2 = N(N + 1). \tag{13}$$

Then, for example, in terms of scaled variables

$$\begin{aligned} p &= dt[\phi - u_0 x], \\ \frac{\partial p}{\partial d} &= t[\phi + x\phi' - 2u_0 x], \\ \frac{\partial p}{\partial t} &= d[\phi + x\phi' u_1]. \end{aligned} \tag{14}$$

More detailed discussion of the equation of state (4) and an alternative derivation of the above properties has been published previously.[8]

3 SPECIFIC HEATS, C_V AND C_P

Let C_{V_0} and C_{P_0} denote the zero density values of the constant volume and constant pressure specific heats. For the special case of a structureless monatomic system we can assume

$$C_{V_0} = \frac{3}{2}R, \; C_{P_0} = \frac{5}{2}R, \tag{15}$$

independent of temperature. Now from elementary thermodynamics, at a density ρ, by integration along an isotherm at a temperature T,

$$C_V = C_{V_0} - T\int_0^\rho \left(\frac{\partial^2 P}{\partial T^2}\right)\frac{d\rho}{\rho^2} \tag{16}$$

and

$$C_P - C_V = \frac{T(\partial P/\partial T)^2}{\rho^2(\partial P/\partial \rho)} \equiv C, \text{ say.} \tag{17}$$

On substituting the equation of state (4), via (14), one obtains explicitly

$$\begin{aligned} C_V &= C_{V_0} + R[\phi(u_1^2 - 2u_1 - u_2) - u_1^2 x\phi']_0^x \\ C &= \frac{R[\phi + x\phi' u_1]^2}{[\phi + x\phi' - 2u_0 x]} \end{aligned} \tag{18}$$

where the initial values $\phi(0) = \phi'(0) = 1$ are required. It is now elementary to calculate a grid of values of C_V and C_P in the density vs. temperature diagram, and hence plot the contours which are presented in Figures 1–8. Our model attempts to describe the high temperature fluid above its critical point, over a density range which would be cut-off by the liquid branch of the fusion curve across the upper lefthand corner of each figure. (On the

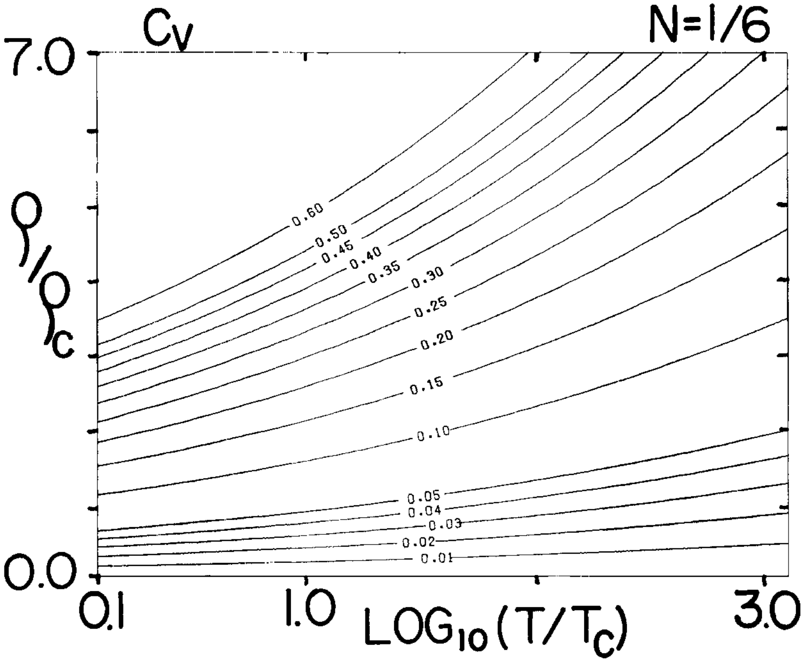

FIGURE 1 Contours of the constant volume specific heat C_V for the Frisch model with $N = 1/6$ on a scaled diagram of density vs. logarithm of temperature. ρ_c and T_c are the critical density and temperature respectively. Contours are labelled with values of $(C_V - C_{V_0})/R$.

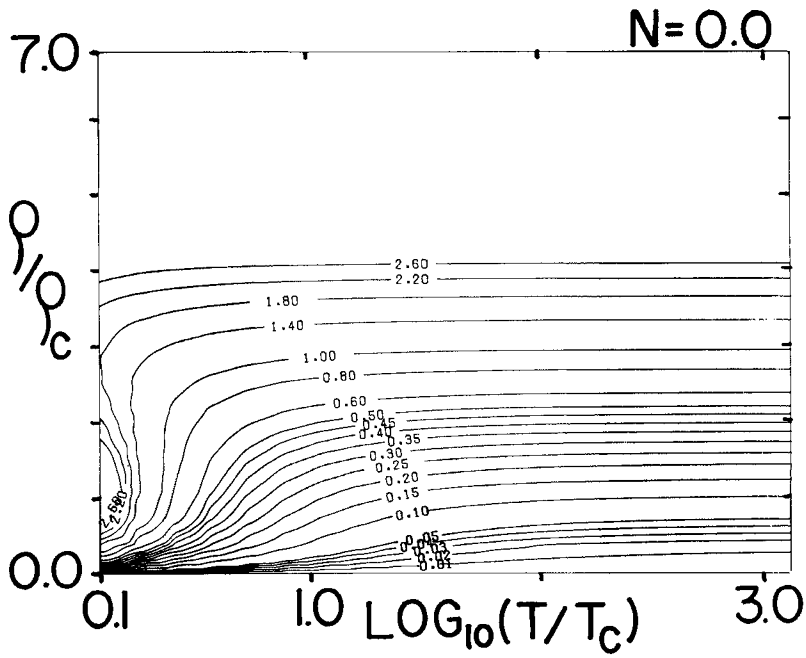

FIGURE 2 Contours of the constant pressure specific heat C_P for the hard-core Frisch model with $N = 0$, on a scaled diagram of density vs. logarithm of temperature. Contours are labelled with values of $(C_P - C_{P_0})/R$.

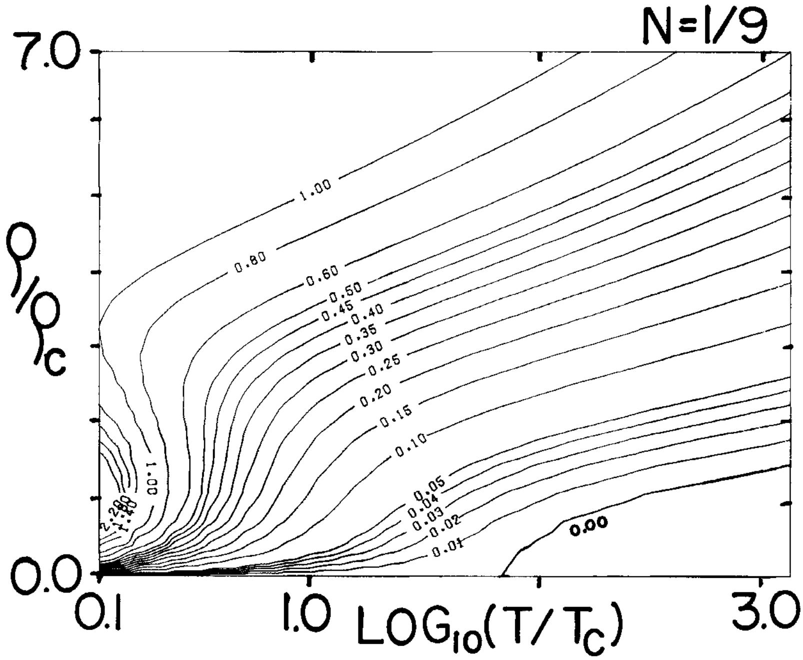

FIGURE 3 C_P contours as Figure 2, for a soft-core Frisch model with $N = 1/9$.

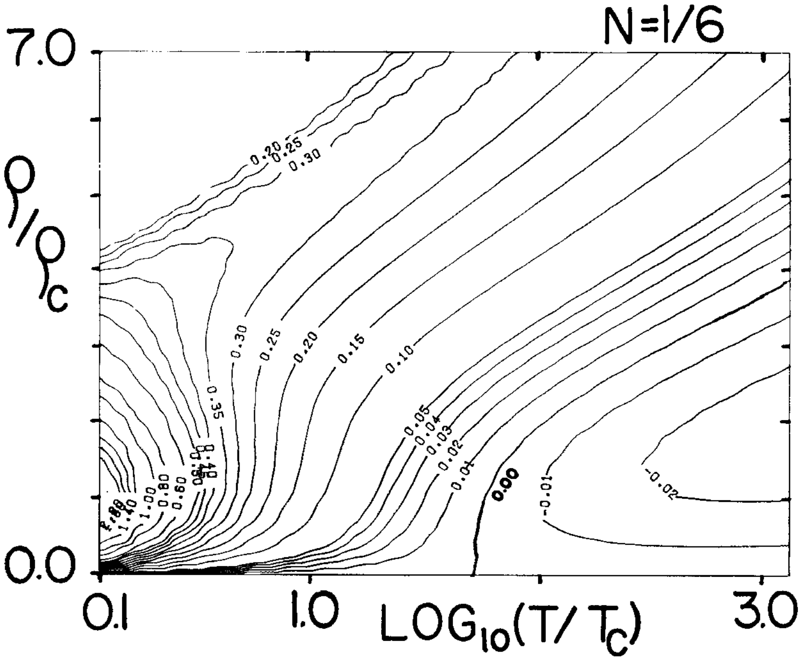

FIGURE 4 C_P contours as Figure 2, for a soft-core Frisch model with $N = 1/6$.

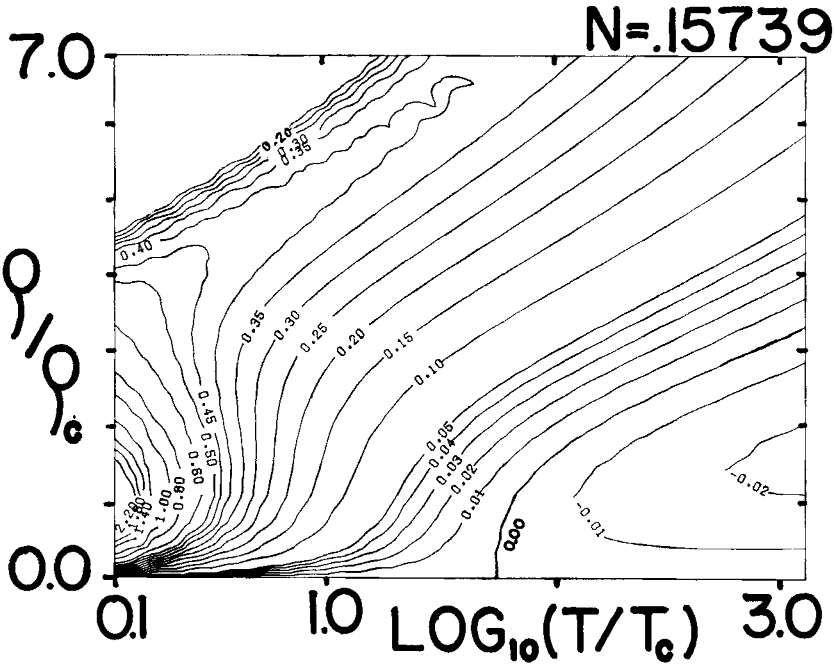

FIGURE 5 C_P contours as Figure 2, for soft-core Frisch model with $N = 0.157389\ldots$ for which the $C_P = C_{P_0}$ contour has vertical slope at the temperature axis.

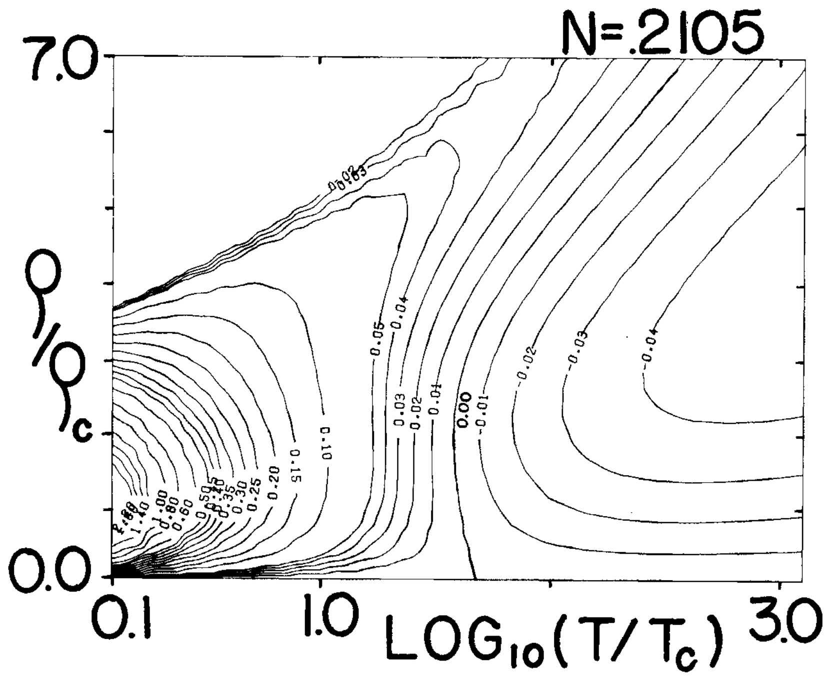

FIGURE 6 C_P contours as Figure 2, for a soft-core Frisch model with $N = 0.2105$ for which the locus of C_P extrema along isotherms is at a saddle point, as explained in Ref. 8.

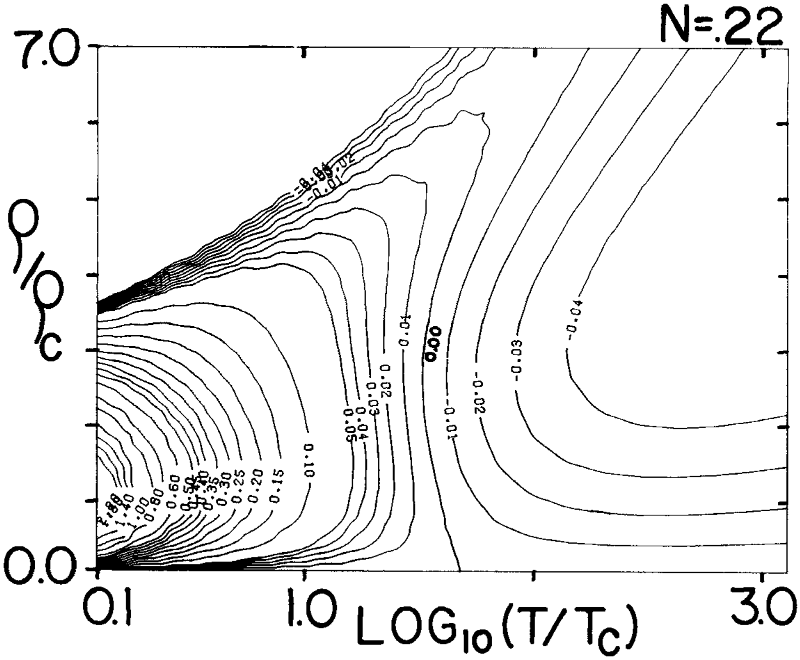

FIGURE 7 C_p contours as Figure 2, for a soft-core Frisch model with $N = 0.22$.

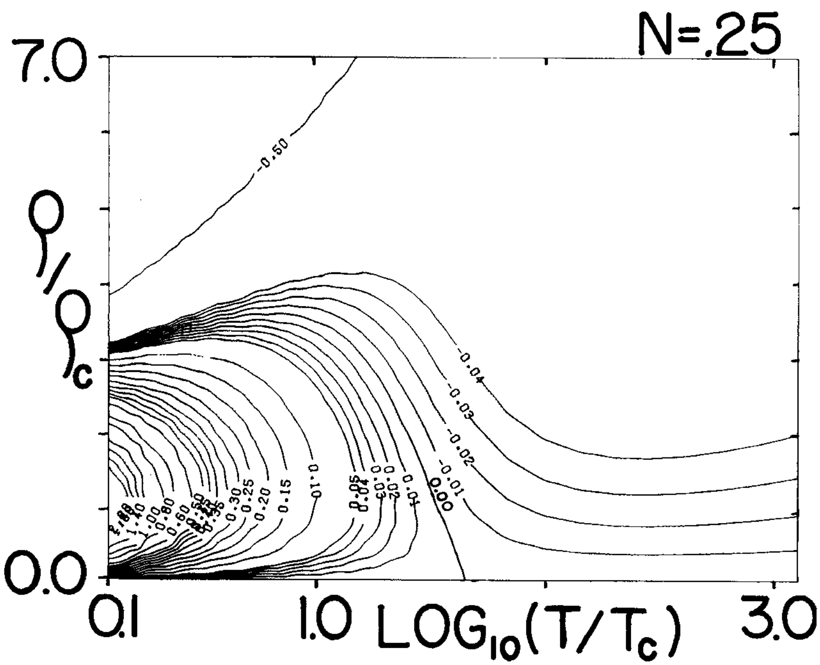

FIGURE 8 C_p contours as Figure 2, for a soft-core Frisch model with $N = 0.25$.

liquid branch of the fusion curve $\rho/\rho_c \sim 3.5$ at the critical temperature, and varies roughly like $(T/T_c)^N$ at high temperatures.)

The steady variations of C_V (Figure 1) and of C_P in the hard-core case (Figure 2) are not very exciting. However, for the soft-core models, C_P maintains its zero density value C_{P_0} along a line extending across the phase diagram, as remarked in the introduction. This line commences on the temperature axis at a temperature T_D where the second virial coefficient B has a point of inflexion, so $\ddot{B} = 0$. Expanding in powers of pressure, we have

$$PV = RT + B'P + C'P^2 + \cdots \tag{19}$$

where the primed pressure virial coefficients are algebraically related to the density virial coefficients by

$$B' = B,\ C' = \frac{C - B^2}{RT}. \tag{20}$$

Then one finds

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P = -T[\ddot{B}' + \ddot{C}'P + \cdots] \tag{21}$$

whence on integration along an isotherm at a temperature T

$$C_P = C_{P_0} - T\left[\ddot{B}'P + \frac{1}{2}\ddot{C}'P^2 + \cdots\right]. \tag{22}$$

Clearly $C_P = C_{P_0}$ on the temperature axis where $\ddot{B} = 0$. (The dot $\dot{}$ denotes $\partial/\partial T$ here). The initial slope of the line along which $C_P = C_{P_0}$ is positive for small values of N, whereas for larger soft-core values of N the initial slope is negative. The change in the sign of the initial slope occurs when $\ddot{C}' = 0$ at T_D, which is the case when N is given by the cubic equation

$$(N + 1)\left[1 - \left(\frac{N}{M}\right)^2\right] - \lambda(2N + 1) = 0 \tag{23}$$

with $M = 1$. As was remarked in a note added in proof to an earlier paper, Eq. (23) determines the special N values at which $\ddot{C}' = 0$ at T_D for any model with second and third virial coefficients of the form

$$B = \left(\frac{b'}{T^N}\right) - \left(\frac{a'}{T^M}\right), \qquad C = \lambda\left(\frac{b'}{T^N}\right)^2,$$

where

$$0 \leq N < 1 \leq M < \frac{1}{N}.$$

When $M = 1$, the relevant solution of the cubic is $N = 0.157389\ldots$ so $n \equiv 3/N = 19.0609\ldots$, and when $M = 2$ (for example, as it does in Berthelot's equation of state) the relevant solution is $N = 0.262322\ldots$, so $n = 11.4363\ldots$.

The reader may wish to compare the qualitative behaviour of C_P exhibited by contours constructed here with the discussion of loci of extrema of C_P along isotherms, published previously.[8] The special value of N remarked on above is of course the same as that at which the slope of the C_P extrema loci changes sign at T_D.

CONCLUDING REMARKS

The presentation of C_P data in the form of contours has the advantage that both the density and temperature dependence can be ascertained directly. By overlaying a grid of isobars one could examine the pressure dependence too. It is worth noting that for soft-core models at high temperature C_P deviates only slightly from the ideal gas value over a wide range of density. Consequently the neglect of the pressure dependence of C_P in, for example, the interpretation of the Joule-Kelvin coefficient obtained from isenthalpic throttling data, is to some extent justified.

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