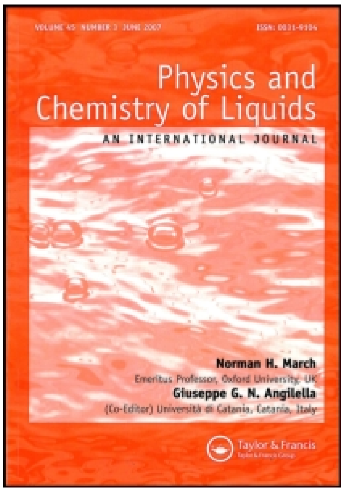

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Hard and Soft-Core Equations of State for Simple Fluids

IV. Elementary Theory of Termination Temperatures†

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An elementary theory of termination temperatures of characteristic curves is developed with the aid of two simple mathematical models. The first model contains two important constant ratios involving all six termination temperatures. The second model interpolates between the first model and the hard-core limit with the aid of a parametric softening temperature, T_s. The properties of the temperature ratios and the underlying models are discussed in detail, especially in the hard-core limit.

1 INTRODUCTION

In the preceding papers of this series[1] we introduced a set of ten characteristic curves which may be calculated from the equation of state for a simple fluid. Associated with these curves are six termination temperatures, denoted in ascending order T_B, T_C, T_F, T_A, T_D and T_E, which may be calculated from the second virial coefficient B. In order to develop an elementary theory of termination temperatures, and hence to gain some insight into the relationships between them, we shall in this paper construct two simple mathematical model expressions for the second virial coefficient. Our results and conclusions are summarized in the final section.

In order to justify the construction of artificial models, we observe that the classical expression for the second virial coefficient in which the interaction between molecules is described in terms of a two-particle scalar potential $\phi(\mathbf{r})$ is already itself a much idealized model.[2] At low temperatures cluster

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and molecule formation and other quantum effects require additional correction terms. At high temperatures a simple potential form does not adequately account for the complex high energy collision process, which again is a quantum scattering problem involving the full electron structure of the monatomic atoms comprising a simple fluid. For molecules the situation is even more complicated with the excitation of rotational and vibrational states, and the onset of dissociation at high temperatures. Eventually at very high temperatures the gas becomes ionized. We have made these rather obvious remarks in order to support our assertion that an analysis which is restricted to a classical virial coefficient potential model cannot be expected to be completely adequate, and hence we feel justified in the use of mathematical models to provide a geometrically satisfactory description of the second and third virial coefficients.

2 *M-N* MODEL: DESCRIPTION

About the simplest model we can construct to describe the second virial coefficient is the two-term expression

$$B = \frac{b'}{T^N} - \frac{a'}{T^M} \tag{1}$$

where a' and b' are positive constants, and the exponents M and N satisfy

$$M > N > 0, \tag{2}$$

so that B is large and negative at low temperatures, and small and positive at high temperatures, with a Boyle point T_B where B vanishes, and an Amagat point T_A where B has a maximum.

The high temperature behaviour chosen for B coincides with that derived by Rowlinson for systems with steep intermolecular potentials.[3] For any intermolecular potential containing a repulsive part of the inverse power form $(\sigma/r)^n$, with $n > 3$, where σ is an effective molecular diameter, one may show that at high temperatures

$$B \sim c/T^{3/n}, \tag{3}$$

where c is a constant depending on n. Hence the virial coefficient exponent N and the repulsive potential exponent n are related by

$$N = 3/n. \tag{4}$$

So if, for example, one is dealing with the popular Lennard-Jones 6,12 potential, one has $N = \frac{1}{4}$. More generally for a Lennard-Jones m,n potential, with attractive exponent $m > 3$ we have $n > m > 3$ so $N < 3/m$. For a

Lennard–Jones 6,*n* potential we must have $n > 6$, or $N < \frac{1}{2}$. In any event $n > 3$ implies $N < 1$. In the limiting case $n \to \infty$, $N \to 0$, one approaches a hard-core limit in which the repulsive part of the potential becomes an infinite barrier at $r = \sigma$. We shall keep N arbitrary in the range $0 < N < 1$.

The choice of the exponent M which determines the low temperature behaviour is more complicated. The *asymptotic* low temperature form of the second virial coefficient calculated from the classical integral expression with a Lennard–Jones type *m,n* potential, is not of a simple inverse power form,[4] V. For an equation of state with a van der Waals' type of attractive term $Ra'\rho^2$ in the pressure, one would have a second virial coefficient like

$$B = b' - a'/T, \tag{5}$$

with $N = 0$ in this hard-core case and $M = 1$. The choice $M = 2$ corresponds to the second virial coefficient of Berthelot's equation, which has been useful in physical chemistry.[5]

As we now show, we must choose $M > 1$ if we are to avoid the existence of a seventh termination temperature T_G, say, associated with the intersection of a locus of maxima or minima of the constant volume specific heat C_v with the temperature axis at zero density. For a simple fluid with no internal structure, the entire contribution to the specific heat at zero density comes from translational motion, and C_v is a constant $\frac{3}{2}$R independent of temperature. Moreover, C_v cannot be less than this value. The geometrical consequence is that no single locus of C_v extrema can intersect the temperature axis. (A pair of loci of maxima and minima could, but we consider such a possibility unlikely.) Therefore the density derivative of C_v on the temperature axis must be positive:

$$\left(\frac{\partial C_v}{\partial \rho}\right)_T = -\frac{T}{\rho^2}\left(\frac{\partial^2 P}{\partial T^2}\right)_v > 0. \tag{6}$$

Now from the virial expansion

$$Z \equiv \frac{PV}{RT} = 1 + B\rho + C\rho^2 + \cdots, \tag{7}$$

one immediately obtains at low density

$$\left(\frac{\partial C_v}{\partial \rho}\right)_T \sim -RT(2\dot{B} + T\ddot{B}). \tag{8}$$

Thus we generally require the strict inequality

$$2\dot{B} + T\ddot{B} < 0, \tag{9}$$

a condition that is automatically satisfied by the classical integral expression for the second virial coefficient,[4] VI. The theoretically non-existent termination temperature T_G associated with the C_v locus would be located by

$$2\dot{B} + T\ddot{B} = 0. \tag{10}$$

To ensure that (9) holds in our model (1) we must have $M > 1$ (see below). This criterion is useful in checking the validity, or otherwise, of various second virial coefficient expressions whether fitted to experimental data[6,7] or appearing in theoretical work.[8] Equation (10) is satisfied identically at all temperatures by the hard-core equation of state second virial coefficient (5). C_v is then a constant, $\frac{3}{2}$R, at all temperatures.

Also, in order to get the termination temperatures in the correct sequence, with T_F lying between T_C and T_A, we need $M < 1/N$ (see below). We note here (in advance) the necessity of a special extra condition to ensure $T_F < T_A$ also occurs when the second virial coefficient is derived from a potential via the classical formula,[4] VI.

So our first model assumes the form (1) with

$$0 < N < 1 \leq M < 1/N. \tag{11}$$

The model with $M = 1$ and $N = 3/n$ can also be derived as a special limiting case of the second virial coefficient for a Lennard-Jones general *m,n* potential as $m \rightarrow 3$, and the attractive portion becomes very weak,[4] V.

3 *M-N* MODEL: TERMINATION TEMPERATURES

Given the model expression (1), it is trivial to calculate the termination temperatures. From the defining expressions[1]

$$T_B\colon\ B = 0, \tag{12a}$$

$$T_C\colon\ B = T\dot{B}, \tag{12b}$$

$$T_F\colon\ B - T\dot{B} + T^2\ddot{B} = 0, \tag{12c}$$

$$T_A\colon\ \dot{B} = 0, \tag{12d}$$

$$T_D\colon\ \ddot{B} = 0, \tag{12e}$$

$$T_E\colon\ \dot{B} + T\ddot{B} = 0, \tag{12f}$$

$$T_G\colon\ 2\dot{B} + T\ddot{B} = 0, \tag{12g}$$

one quickly obtains for the $(M - N)$th power of each temperature

$$T_B^{(M-N)} = \left(\frac{a'}{b'}\right) \tag{13a}$$

$$T_C^{(M-N)} = \left(\frac{a'}{b'}\right)\left(\frac{M+1}{N+1}\right) \tag{13b}$$

$$T_F^{(M-N)} = \left(\frac{a'}{b'}\right)\left(\frac{M+1}{N+1}\right)^2 \tag{13c}$$

$$T_A^{(M-N)} = \left(\frac{a'}{b'}\right)\left(\frac{M}{N}\right) \tag{13d}$$

$$T_D^{(M-N)} = \left(\frac{a'}{b'}\right)\frac{M(M+1)}{N(N+1)} \tag{13e}$$

$$T_E^{(M-N)} = \left(\frac{a'}{b'}\right)\left(\frac{M}{N}\right)^2 \tag{13f}$$

$$T_G^{(M-N)} = \left(\frac{a'}{b'}\right)\frac{M(1-M)}{N(1-N)} \tag{13g}$$

To ensure the non-existence of T_G, we note that we must choose $M \geq 1$, so that the expression

$$2\dot{B} + T\ddot{B} = \frac{b'N(N-1)}{T^{N+1}} - \frac{a'M(M-1)}{T^{M+1}} \tag{14}$$

is negative over the entire temperature range $0 < T < \infty$. It is easy to verify that if $M > N$, then $T_B < T_C < T_A < T_D < T_E$ and $T_C < T_F < T_D$. To ensure that $T_F < T_A$ we must also require $M < 1/N$, as may be seen from comparison of (13c) with (13d).

There are three parameters: the ratio (a'/b'), and the exponents M and N. Therefore it is possible to select three independent temperatures, say T_B, T_C and T_A, and express the remaining termination temperatures in terms of these (disregarding T_G):

$$T_F = T_C^2/T_B, \tag{15a}$$

$$T_D = T_A T_C/T_B, \tag{15b}$$

$$T_E = T_A^2/T_B. \tag{15c}$$

T_C is the geometric mean of T_B and T_F, and T_A is the geometric mean of T_B and T_E. In order to establish a scale, and at the same time remove the ratio of unknown constants (a'/b'), it is appropriate to divide through by the Boyle

TABLE I

Ratios of termination temperatures for the $M - N$ model with $M = 1$

N	$n = 3/N$	$T_C/T_B = \lambda$	T_F/T_B	$T_A/T_B = \mu$	T_D/T_B	T_E/T_B	$T_A/T_C = \mu/\lambda$
1	3	1.649	2.718	2.718	4.482	7.389	1.649
3/4	4	1.706	2.910	3.160	5.392	9.989	1.853
3/5	5	1.747	3.052	3.586	6.265	12.860	2.053
1/2	6	1.778	3.160	4.000	7.111	16.000	2.250
1/3	9	1.837	3.375	5.196	9.546	27.000	2.828
1/4	12	1.871	3.502	6.350	11.882	40.317	3.393
1/5	15	1.894	3.586	7.477	14.159	55.902	3.948
1/6	18	1.909	3.646	8.586	16.394	73.716	4.497
1/7	21	1.921	3.691	9.682	18.599	93.734	5.040
1/8	24	1.930	3.725	10.767	20.782	115.933	5.579
1/9	27	1.937	3.753	11.845	22.946	140.296	6.114
1/10	30	1.943	3.775	12.915	25.096	166.810	6.647
1/11	33	1.948	3.794	13.981	27.233	195.463	7.177
1/12	36	1.952	3.810	15.041	29.360	226.244	7.706
—	—	—	—	—	—	—	—
0	∞	2.000	4.000	∞	∞	∞	∞

temperature T_B, or alternatively set $(a'/b') = 1$ in (13). Then one finds that there are just *two independent constant ratios*, involving only M and N:

$$\frac{T_C}{T_B} = \frac{T_F}{T_C} = \frac{T_D}{T_A} = \left(\frac{M+1}{N+1}\right)^{1/(M-N)} \equiv \lambda_{M,N}, \tag{16a}$$

$$\frac{T_A}{T_B} = \frac{T_D}{T_C} = \frac{T_E}{T_A} = \left(\frac{M}{N}\right)^{1/(M-N)} \equiv \mu_{M,N}. \tag{16b}$$

The ratio of these ratios is then

$$\frac{T_A}{T_C} = \frac{T_D}{T_F} = \frac{T_E}{T_D} = \left[\frac{M(N+1)}{N(M+1)}\right]^{1/(M-N)} \tag{17}$$

For fixed $M > 1$ these ratios steadily increase as N varies from 1 down to the hard-core limiting value 0. These ratios will be of great importance in our analysis of second virial coefficients in general. Table I lists these ratios for $M = 1$ and selected values of N in the range $0 < N < 1$, and the corresponding graphs are presented in Figure 1.

Certain special limiting cases are of interest. As $n \to \infty, N \to 0$ we approach the hard-core limit. The temperatures T_B, T_C and T_F remain finite, whereas T_A, T_D and T_E diverge to $+\infty$. The ratio μ then diverges too, *but* the ratio λ remains *finite*, with the limiting value

$$\lambda_{M,0} = (M+1)^{1/M}, \tag{18}$$

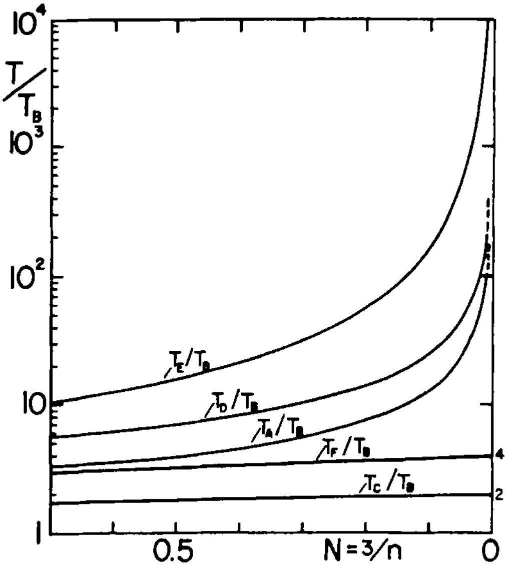

FIGURE 1 Ratios of termination temperatures plotted on a logarithmic scale versus the exponent $N = 3/n$ for the $M - N$ model with $M = 1$.

which lies between 1 and 2 since $1 < M < \infty$ ($1/N = \infty$ now). It is important to note that although T_A and T_D separately become infinite, their ratio λ remains finite.

In the most useful case $M = 1$, we have

$$\lambda_{1,N} = \left(\frac{2}{N+1}\right)^{1/(1-N)}, \qquad \mu_{1,N} = \left(\frac{1}{N}\right)^{1/(1-N)}, \tag{19}$$

which increase steadily as N varies from 1 to 0. In the hard-core limit $N = 0$, (see also (18) with $M = 1$),

$$\lambda_{1,0} = 2, \qquad \mu_{1,0} = \infty, \tag{20}$$

which is just the *same* result as we obtained for the hard-core equation of state second virial coefficient considered in III.[1] At the other extreme $N \to 1$ ($= M$), and

$$\lambda_{1,1} = e^{1/2} = 1.649\ldots, \mu_{1,1} = e = 2.718\ldots. \tag{21}$$

In general from (16), because of our restrictions on M and N, the largest possible value of λ is 2. So it is gratifying to realize that the corresponding ratios for argon are approximately equal and less than 2. Quoting from II, for argon,

$$\frac{T_C}{T_B} \approx 1.921, \qquad \frac{T_F}{T_C} \approx 1.937, \tag{22}$$

with geometric mean ~ 1.93. The corresponding ranges of exponents from Table I, where $M = 1$, are $1/9 < N < 1/7$, or $27 > n > 21$. If we try $M = 2$, say, then even in the hard-core limit, when $N = 0$, the ratio $\lambda_{2,0} = 3^{1/2}$ is too low.

4 T_s – N MODEL

Our second virial coefficient model of the preceding two sections has enabled us to examine termination temperature ratios over a range o repulsive exponents $n = 3/N$ from the hard-core limit $n = \infty$, $N = 0$ through to the other limiting case $N = 1$. ($N < 3/m$ for a Lennard–Jone m-n potential with $m > 3$). One important feature of the $M - N$ model i that it exposed the existence of two independent ratios involving the si termination temperatures. We cannot expect this special feature to carry ove to more realistic expressions for the second virial coefficient. Moreover, th hard-core is only a special limiting case. Therefore it is desirable to construc a model which will interpolate between the $M - N$ model and the hard-cor limit, while retaining the exponent N.

In our second model there is an extra parameter, a characteristic temperature T_s, which we may call the *softening temperature.* We set

$$B = b - (a/RT) \qquad \text{(23a}$$

$$= b_0/[1 + (T/T_s)^N] - (a/RT). \qquad \text{(23b}$$

The hard-core ($4\times$) molecular volume parameter b is thus softened by factor, which decreases in value at high temperatures, and represents th partial penetration of atoms on collision. b_0 denotes the hard-core value of which is effective at low temperatures. At high temperatures

$$B \sim b_0(T_s/T)^N, \qquad \text{(2}$$

and has the desired power law decay, with N related to the repulsive potenti exponent n as before. The negative term is again based on a van der Waal type attractive $a\rho^2$ contribution to the pressure. One quickly verifies th $2\dot{B} + T\ddot{B}$ is negative at all temperatures, provided $0 < N < 1$, so T_G does n exist, and the undesired C_v locus termination point is avoided.

If T_s is very large, in the limit $T_s \to \infty$ we regain a hard-core model, for any fixed value of N. On the other hand, if T_s is very small, in the limit $T_s \to 0$ we approach the $M - N$ model with $M = 1$, and

$$B \sim b_0(T_s/T)^N - (a/RT), \tag{25}$$

provided one rescales by some method, such as

i) by letting $b_0 \to \infty$ as $T_s \to 0$ so $b_0 T_s^N \to b'$, a constant, or

ii) by calculating only ratios of termination temperatures with respect to the Boyle point, for example, or

iii) by scaling with respect to a critical temperature (actually equivalent to (ii)).

We shall loosely call the limiting case $T_s \to 0$ the soft-core limit, and the limiting case $T_s \to \infty$ the hard-core limit, even though a free exponent N still remains.

It is convenient to work with the reduced temperature variable

$$t = b_0 RT/a, \tag{26}$$

so the dimensionless second virial coefficient is

$$B^* \equiv B/b_0 = 1/[1 + (t/t_s)^N] - 1/t. \tag{27}$$

Now the six termination temperatures defined as in (12a)–(12f) are given implicitly by the following expressions:

$$T_B\colon\ t_B = 1 + (t_B/t_s)^N, \tag{28a}$$

$$T_C\colon\ t_C = 2[1 + (t_C/t_s)^N]^2/[1 + (1 + N)(t_C/t_s)^N], \tag{28b}$$

$$T_F\colon\ t_F = 4[1 + (t_F/t_s)^N]^3/[1 + (2 + 2N - N^2)(t_F/t_s)^N + (1 + N)^2(t_F/t_s)^{2N}], \tag{28c}$$

$$T_A\colon\ t_A = [1 + (t_A/t_s)^N]^2/[N(t_A/t_s)^N], \tag{28d}$$

$$T_D\colon\ t_D = 2[1 + (t_D/t_s)^N]^3/\{N(t_D/t_s)^N[(1 - N) + (1 + N)(t_D/t_s)^N]\}, \tag{28e}$$

$$T_E\colon\ t_E = [1 + (t_E/t_s)^N]^3/\{N^2(t_E/t_s)^N[(t_E/t_s)^N - 1]\}. \tag{28f}$$

For a chosen value of N, one may vary t_s from 0 to ∞, and study the solution temperatures and their ratios. Logarithmic graphs of termination temperatures vs. t_s are presented in Figures 2 and 3 for the cases $N = \frac{1}{4}$ and $\frac{1}{6}$. The corresponding temperature ratios are readily obtained, and are listed in Tables II and III. As expected t_B, t_C and t_F remain finite at the hard-core $t_s \to \infty$ limit, where they approach the values 1, 2 and 4 respectively, independent of N. The ratios t_C/t_B and t_F/t_B are not now equal, but differ slightly over the entire range $0 < t_s < \infty$, while remaining finite. Also as expected

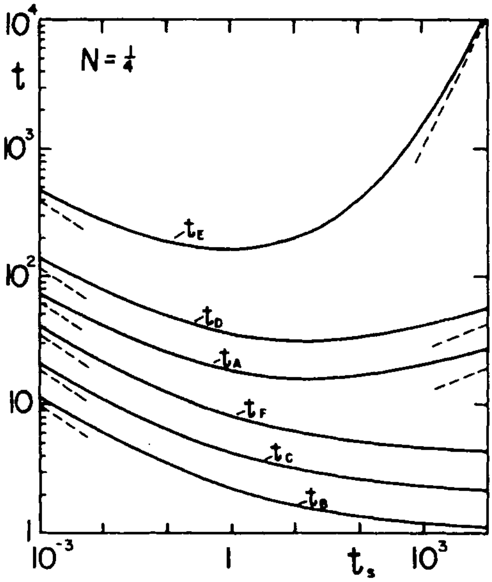

FIGURE 2 Termination temperatures $t = b_0 RT/a$ plotted versus the softening temperature t_s on logarithmic scales for the $T_s - N$ model with $N = \frac{1}{4}$. The asymptotic forms at high and low values of t_s are indicated.

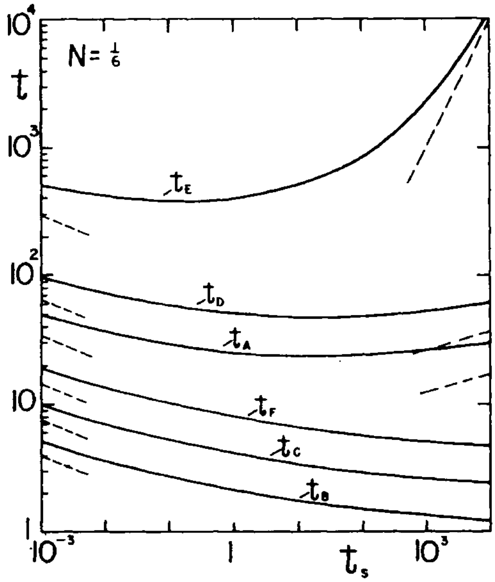

FIGURE 3 Termination temperature for the $T_s - N$ model with $N = 1/6$, as in Figure 2.

TABLE II

Ratios of termination temperatures for the $T_s - N$ model with $N = \frac{1}{4}$ for various values of $t_s = b_0 RT_s/a$

t_s	0	$\frac{1}{100}$	$\frac{1}{10}$	1	10	100	∞
t_C/t_B	1.871	1.884	1.895	1.912	1.932	1.952	2
t_F/t_B	3.502	3.549	3.592	3.657	3.737	3.816	4
t_A/t_B	6.350	6.804	7.284	8.195	9.814	12.541	∞
t_D/t_B	11.882	12.843	13.861	15.803	19.279	25.169	∞
t_E/t_B	40.317	47.264	55.609	74.930	124.811	291.400	∞
t_F/t_C	1.871	1.884	1.896	1.913	1.934	1.955	2
t_D/t_A	1.871	1.887	1.903	1.928	1.964	2.007	2.192
t_D/t_C	6.350	6.818	7.315	8.267	9.978	12.891	∞
t_E/t_A	6.350	6.946	7.634	9.144	12.717	23.235	∞

TABLE III

Ratios of termination temperatures for the $T_s - N$ model with $N = \frac{1}{6}$ for various values of $t_s = b_0 RT_s/a$

t_s	0	$\frac{1}{100}$	$\frac{1}{10}$	1	10	100	∞
t_C/t_B	1.909	1.928	1.935	1.943	1.953	1.962	2
t_F/t_B	3.646	3.717	3.745	3.779	3.815	3.852	4
t_A/t_B	8.586	10.101	10.904	12.088	13.806	16.262	∞
t_D/t_B	16.394	19.560	21.242	23.729	27.343	32.517	∞
t_E/t_B	73.716	111.049	136.947	185.809	289.747	564.383	∞
t_F/t_C	1.909	1.928	1.935	1.944	1.954	1.963	2
t_D/t_A	1.909	1.936	1.948	1.963	1.980	2.000	2.118
t_D/t_C	8.586	10.147	10.979	12.210	14.002	16.573	∞
t_E/t_A	8.586	10.994	12.560	15.371	20.987	34.706	∞

t_A, t_D and t_E become infinite as one approaches the hard-core limit $t_s \to \infty$ with N fixed:

$$t_A \sim t_s^{N/(1+N)}(1/N)^{1/(1+N)}, \tag{29a}$$

$$t_D \sim t_s^{N/(1+N)}[2/N(1-N)]^{1/(1+N)}, \tag{29b}$$

$$t_E \sim t_s. \tag{29c}$$

Consequently the ratio

$$\lambda_N \equiv T_D/T_A \sim [2/(1-N)]^{1/(1+N)} \tag{30}$$

remains finite as $t_s \to \infty$. Its value now depends on N, (cf. Eqs. (18)-(20)), and is greater than 2. λ_N lies fairly close to 2 for the values of N most likely to be useful, say $0 < N < \frac{1}{2}$. Note that the hard core limiting value is $\lambda_0 = 2$ when $N = 0$. For small t_s, when the ratios match those of the $1 - N$ model,

$$t_B \sim 1/t_s^{N/(1-N)}, \tag{31a}$$

$$t_C \sim [2/(1+N)]^{1/(1-N)}/t_s^{N/(1-N)}, \tag{31b}$$

$$t_F \sim [2/(1+N)]^{2/(1-N)}/t_s^{N/(1-N)}, \tag{31c}$$

$$t_A \sim (1/N)^{1/(1-N)}/t_s^{N/(1-N)}, \tag{31d}$$

$$t_D \sim [2/N(1+N)]^{1/(1-N)}/t_s^{N/(1-N)} \tag{31e}$$

$$t_E \sim (1/N)^{2/(1-N)}/t_s^{N/(1-N)}. \tag{31f}$$

The asymptotic forms of the termination temperatures as $t_s \to 0$ and $t_s \to \infty$ are indicated in Figures 2 and 3.

If, on the other hand, we fix t_s and vary N, one can approach the hard-core limit by letting $N \to 0$. Then one obtains, independent of t_s:

$$t_B \to 2,\ t_C \to 4,\ t_F \to 8, \tag{32a}$$

$$t_A \sim 4/N,\ t_D \sim 8/N,\ t_E \sim 8/[N^3 \ln(1/N^3)], \tag{32b}$$

and again we have a common limiting ratio

$$\frac{t_C}{t_B} \sim \frac{t_F}{t_C} \sim \frac{t_D}{t_A} \sim 2 \tag{33}$$

The chief value of the $T_s - N$ model is that it provides the freedom of an extra parameter, the softening temperature, T_s. If one compares the asymptotic behaviour of this model with that of the scaled second virial coefficient for potential models of the Lennard–Jones *m,n* type, one can actually fix the value of T_s, but unfortunately the value so obtained depends on the choice of the effective molecular diameter,[4] V. The extra parameter is more useful in that it will enable us to extend the range of investigation of characteristic curves and the locus of extrema of the constant pressure specific heat C_p, which terminates at T_D.

5 SUMMARY AND CONCLUDING REMARKS

In this paper we have presented an elementary approach to the theory of termination temperatures with the aid of two simple mathematical models which approximate the geometry of the second virial coefficient reasonably closely. The most important feature of the first model is the appearance of two independent characteristic ratios, λ and μ, interconnecting the three temperatures T_B, T_C and T_F, which remain finite in the hard-core limit, with T_A, T_D and T_E, which diverge to $+\infty$. However, the ratio $\lambda = T_D/T_A$ remains finite, and less than or equal to 2. The exponent N, describing the high temperature tail of the second virial coefficient B, is related to the exponent n of the repulsive part of the intermolecular potential by the simple relation $N = 3/n$, with $n > m > 3$, where m is the exponent of the attractive term in the potential. The requirement that no locus of C_v extrema terminate on the temperature axis leads to a restrictive condition on the derivatives of the second virial coefficient, $2\dot{B} + T\ddot{B} < 0$. The models can be made to satisfy this condition, by setting the exponent of the low temperature negative term in B equal to unity. The first model is then derivable as a limiting case of the Lennard-Jones m,n potential as $m \to 3$ for general n. The second model interpolates between the first model and the hard-core van der Waals' type limit, by means of an additional parameter, T_s, a softening temperature. In this way one may account for a range of various possible behaviour of the second virial coefficient. The properties of the termination temperatures of the more realistic Lennard-Jones m,n potential is the subject of the following paper.

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