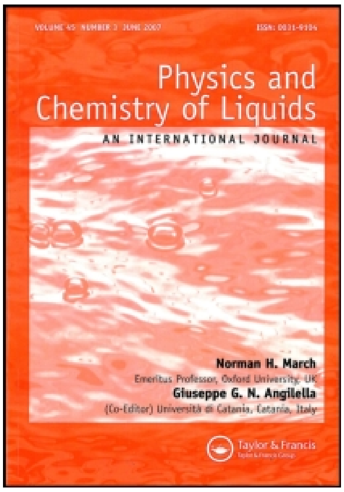

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

# Hard and Soft - Core Equations of State for Simple Fluids: V. Termination Temperatures for the Lennard - Jones m, n Potential

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**To cite this Article** Stephenson, John(1979) 'Hard and Soft - Core Equations of State for Simple Fluids: V. Termination Temperatures for the Lennard - Jones m, n Potential', Physics and Chemistry of Liquids, 9: 1, 37 — 50

**To link to this Article: DOI:** 10.1080/00319107908084765

**URL:** http://dx.doi.org/10.1080/00319107908084765

*Phys. Chem. Liq.*, 1979, Vol. 9, pp. 37-50
0031-9104/79/0901-0037$04.50/0

Printed in Holland

# Hard and Soft-Core Equations of State for Simple Fluids

## V. Termination Temperatures for the Lennard-Jones *m, n* Potential†

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(*Received September 25, 1978*)

The six termination temperatures associated with the ten characteristic curves of a simple fluid are calculated for the Lennard-Jones $m$, $n$ potential second virial coefficient with $n \geq m > 3$. The extreme values in both the hard-core Sutherland potential limit $n \to \infty$, and in the opposite limit $n \to m$ are obtained. The termination temperature ratios $T_C/T_B$, $T_F/T_C$ and $T_D/T_A$ lie within a narrow finite range, with $T_D/T_A \to 2$ in the hard-core limit, independent of $m$. The high temperature form of the second virial coefficient is derived, and used to estimate the softening temperature $T_s$. Also, some results for the square-well potential are presented.

## 1 INTRODUCTION

In this paper we discuss the Lennard-Jones $m,n$ potential and its second virial coefficient, over the permitted range of values of the repulsive term exponent $n$, $m \leq n \leq \infty$. In the hard-core limit $n \to \infty$ we obtain the Sutherland potential. From the second virial coefficient we shall calculate the six termination temperatures associated with the ten zeroth, first and second order characteristic curves of a simple fluid. Guided by our elementary theory of termination temperatures in the preceding paper IV,[1] we shall investigate the ratios of termination temperatures. We find that the ratios $T_C/T_B$, $T_F/T_C$ and $T_D/T_A$ are approximately equal for given attractive and repulsive potential exponents $m$ and $n$, and for a fixed value of $m$ lie within a quite narrow range of values, while $n$ varies from $m$ to $\infty$. In the hard-core Sutherland potential limit, we observe that $T_D/T_A \to 2$, independent of the attractive exponent $m$ ($>3$). The usual choice $m = 6$ corresponds to the Heitler-London dispersion energy. In the theory we keep $m$ general ($>3$),

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† Research supported in part by the National Research Council of Canada, Grant No. A6595.

but in most of the numerical work we set $m = 6$. We also show that the $M - N$ model in IV with $M = 1$ can be derived as a limiting case of the Lennard-Jones second virial coefficient as $m \to 3$ for any value of $n > 3$. In the case of the $m,2m$ potential, we quote the representation of the second virial coefficient $B$ in terms of confluent hypergeometric functions. It is then straightforward to obtain the asymptotic forms of $B$. At extremely high temperatures $B$ is small and positive, with the power law behaviour

$$B \sim b(T_s/T)^N, \quad \text{as } T \to \infty$$

where $N$ is related to the repulsive exponent $n$ by

$$N = 3/n.$$

This enables us for a given value of $N$ to estimate the softening temperature $T_s$ introduced in the $T_s - N$ model in IV. At very low temperatures $B$ is large and negative, and for the $m,2m$ potential asymptotically

$$B \sim (-)b2N(\pi T^*)^{1/2}e^{1/T^*}$$

where $T^* = kT/\varepsilon$ is a scaled dimensionless temperature, $\varepsilon$ being the potential well-depth.

Finally, we present some results for the square-well potential, which gives rise to a hard-core type second virial coefficient, exhibiting only three termination temperatures, $T_B$, $T_C$ and $T_F$. In a special limiting case the square-well potential can be forced to reproduce the van der Waals' second virial coefficient. For a very wide well,

$$T_C/T_B \sim T_F/T_C \sim 2.$$

## 2 THE LENNARD–JONES *m,n* POTENTIAL

The Lennard–Jones general $m,n$ potential may be written

$$\phi_{m,n}(r) = \frac{\varepsilon}{(n-m)}\left[m\left(\frac{\sigma}{r}\right)^n - n\left(\frac{\sigma}{r}\right)^m\right] \tag{1}$$

and its second virial coefficient $B$ is calculated from the classical integral formulae[2]

$$B \equiv bB^* = (b/\sigma^3)\int_0^\infty d(r^3)(1 - e^{-\phi/kT}), \tag{2a}$$

$$= (-b/\sigma^3 kT)\int_0^\infty dr r^3 \phi' e^{-\phi/kT}, \tag{2b}$$

where

$$b = \frac{2\pi}{3} L\sigma^3, \tag{3}$$

is four times the volume of the $L$ (Avogadro number) molecules in a mole, and $\sigma$ is an effective molecular diameter, chosen so the potential (1) has a minimum of depth $\varepsilon$ at a radial distance $\sigma$. The repulsive exponent $n$ and the attractive exponent $m$ are required to satisfy

$$n > m > 3, \tag{4}$$

so that the thermodynamic limit exists and the integrals appearing in $B$ (2) converge at both limits of integration. Sometimes the effective molecular diameter length parameter is chosen to be the radial distance $\sigma_0$ at which the potential vanishes. Then the length scales differ by a factor

$$\frac{\sigma_0}{\sigma} = \left(\frac{m}{n}\right)^{1/(n-m)}, \tag{5}$$

and the scaled second virial coefficient $B^*$ is modified by the cube of this factor to $B_0^* = (\sigma/\sigma_0)^3 B^*$. It is traditional to introduce "starred" dimensionless scaled variables

$$r^* = r/\sigma, \tag{6a}$$

$$T^* = kT/\varepsilon, \tag{6b}$$

$$\phi^* = \phi/\varepsilon, \tag{6c}$$

which may be substituted into equations (2a) and (2b) as desired. In terms of these scaled variables one obtains a universal curve for the scaled virial coefficient $B^*$, once $m$ and $n$ are fixed. Experimental second virial coefficients can then be fitted, after selecting $m$ and $n$, by optimizing the values of $\varepsilon$ and $\sigma$.[3]

In the limiting case $n \to \infty$, the Lennard-Jones potential (1) becomes the Sutherland hard-core potential with an infinite barrier at $r = \sigma$ and an attractive power law tail:

$$\phi_{m,\infty}(r) = \begin{cases} +\infty, r < \sigma, \\ -\varepsilon(\sigma/r)^m, r > \sigma. \end{cases} \tag{7}$$

This limit may be taken after calculation of the general second virial coefficient in the form of an inverse fractional power series.

In the opposite limit $n \to m > 3$ we still obtain a sensibly shaped potential

$$\phi_{m,m}(r) = -(\sigma/r)^m[1 + m \ln(r/\sigma)] \tag{8}$$

which has a minimum of depth $\varepsilon$ at $r = \sigma$ and vanishes at $\sigma_0 = \sigma e^{-1/m}$. In this limit one must analyze the integral form of the second virial coefficient directly, since the power series representation breaks down.

For comparison purposes it is also of interest to examine the purely repulsive inverse power potential obtained by discarding the attractive term in the Lennard-Jones potential,

$$\phi_R(r) = \varepsilon(\sigma/r)^n. \tag{9}$$

The second virial coefficient integral now yields just a single inverse fractional power law term in the temperature, which matches with the high temperature behaviour of the general *m,n* Lennard-Jones potential second virial coefficient, apart from an unimportant multiplicative factor, which is unity when $n = 2m$.

## 3 TERMINATION TEMPERATURES FOR THE LENNARD-JONES *m,n* POTENTIAL

Graphs of the scaled Lennard-Jones second virial coefficient $B^*$ versus scaled temperature $T^*$, for $m = 6$ and various values of $n$ between 6 and $\infty$, are sketched in Figure 1. To obtain an expression for $B^*$ which is convenient for computation, first make an integration variable change to

$$x = m/[(n - m)T^* r^{*n}] \tag{10}$$

in the formula (2a), then expand the attractive part of the exponential in an inverse fractional power series in $T^*$, and perform the integrations term by term. Denoting the second virial coefficient by $B^*_{m,n}$ to indicate the dependence on $m$ and $n$, the result is

$$B^*_{m,n} = \left(-\frac{3}{n}\right)\left(\frac{p}{qT^*}\right)^{3/n} \sum_{s=0}^{\infty} \frac{\Gamma(sp - 3/n)}{s!(p^p q^q T^{*q})^s} \tag{11}$$

where

$$p = 1 - q = m/n. \tag{12}$$

The first $s = 0$ term in the series is positive and all the others are negative. At high temperatures the asymptotic form of $B$ is determined by this leading positive term:

$$B^*_{m,n} \sim \left(\frac{p}{qT^*}\right)^N \Gamma(1 - N), \tag{13}$$

where we have identified the high temperature exponent as $N = 3/n$.

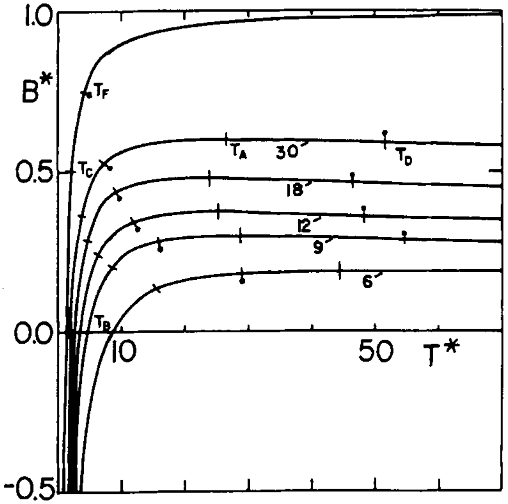

FIGURE 1 Graphs of the scaled Lennard-Jones second virial coefficient $B^* = B/b$ versus scaled temperature $T^* \equiv kT/\varepsilon$ for $m = 6$ and various values of $n$. The positions of the termination temperatures $T_B$, $T_C$, $T_F$, $T_A$ and $T_D$ are indicated.

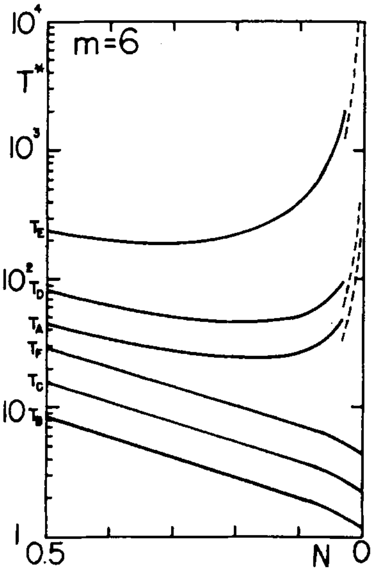

FIGURE 2 Graphs of the scaled termination temperatures $T^*$ for the Lennard-Jones 6,$n$ potential plotted on a logarithmic scale versus the exponent $N \equiv 3/n$ over the permitted range $0 \leq N \leq \frac{1}{2}$.

TABLE I

Values of termination temperatures for the Lennard-Jones 6,$n$ potential with $6 \le n \le \infty$. $T^* = kT/\varepsilon$.

| $n$ | $N = 3/n$ | $T_B^*$ | $T_C^*$ | $T_F^*$ | $T_A^*$ | $T_D^*$ | $T_E^*$ |
|---|---|---|---|---|---|---|---|
| 6 | 1/2 | 8.489967 | 15.658565 | 28.937101 | 44.50203 | 82.77130 | 242.3913 |
| 7 | 3/7 | 6.421511 | 11.908453 | 22.142081 | 36.01683 | 67.54964 | 212.8930 |
| 8 | 3/8 | 5.277899 | 9.828917 | 18.362805 | 31.49882 | 59.46897 | 200.4344 |
| 9 | 1/3 | 4.555335 | 8.511745 | 15.963015 | 28.79760 | 54.66255 | 195.9632 |
| 12 | 1/4 | 3.417928 | 6.430798 | 12.157373 | 25.15257 | 48.28984 | 203.1800 |
| 15 | 1/5 | 2.876595 | 5.435575 | 10.327955 | 24.07968 | 46.56605 | 223.8749 |
| 18 | 1/6 | 2.558081 | 4.847830 | 9.243280 | 23.95510 | 46.55854 | 251.1108 |
| 21 | 1/7 | 2.347121 | 4.457401 | 8.520447 | 24.27848 | 47.36196 | 282.7095 |
| 24 | 1/8 | 2.196433 | 4.177841 | 8.001503 | 24.84624 | 48.60744 | 317.7596 |
| 27 | 1/9 | 2.083010 | 3.966988 | 7.609227 | 25.56049 | 50.11755 | 355.8072 |
| 30 | 1/10 | 1.994295 | 3.801783 | 7.301285 | 26.36858 | 51.79680 | 396.5977 |
| 36 | 1/12 | 1.863942 | 3.558533 | 6.846815 | 28.15511 | 55.46124 | 485.8364 |
| 48 | 1/16 | 1.703997 | 3.259132 | 6.285465 | 32.06152 | 63.38388 | 692.9604 |
| 60 | 1/20 | 1.608440 | 3.079703 | 5.947850 | 36.14868 | 71.62251 | 936.4791 |
| $\infty$ | 0 | 1.170915 | 2.251248 | 4.372797 | $\infty$ | $\infty$ | $\infty$ |

At this point it is informative to insert a note on the purely repulsive inverse power potential (9). The second virial coefficient integral (2) yields exactly

$$B_R^* = \Gamma(1 - N)/T^{*N}, \tag{14}$$

confirming that the repulsive part of the potential is responsible for the high temperature form of $B$.

The six termination temperatures, $T_B$, $T_C$, $T_F$, $T_A$, $T_D$ and $T_E$ are defined via equations (12a)–(12f) in IV. These relations are linear and homogeneous in $B$ and its temperature derivatives. For any chosen values of $m$ and $n$, with $n > m > 3$, one may calculate the termination temperatures numerically from the series expansion form for $B$ in (11). Values of $T^*$ for $m = 6$ and various values of $n$ in the range $6 \le n \le \infty$ are listed in Table I, and are plotted on a logarithmic scale versus $N$ in Figure 2. Various ratios of termination temperatures are listed in Table II for $m = 6$ and the same values of $n$ as in Table I. We observe from the entries in Table II that the same termination temperature ratios which were exactly equal for the $M - N$ model in IV are still approximately equal, at least in the case when $m = 6$, for the Lennard-Jones second virial coefficient:

$$\frac{T_C}{T_B} \sim \frac{T_F}{T_C} \sim \frac{T_D}{T_A} \sim \lambda(m,n), \tag{15a}$$

$$\frac{T_A}{T_B} \sim \frac{T_D}{T_C} \sim \frac{T_E}{T_A} \sim \mu(m,n) \tag{15b}$$

TABLE II

Ratios of termination temperatures for the Lennard–Jones 6,*n* potential with $6 \leq n \leq \infty$.

| $n$ | $T_C/T_B$ | $T_F/T_B$ | $T_A/T_B$ | $T_D/T_B$ | $T_E/T_B$ | $T_F/T_C$ | $T_D/T_A$ | $T_D/T_C$ | $T_E/T_A$ |
|---|---|---|---|---|---|---|---|---|---|
| 6 | 1.844 | 3.408 | 5.242 | 9.749 | 28.55 | 1.848 | 1.860 | 5.286 | 5.447 |
| 7 | 1.854 | 3.448 | 5.609 | 10.519 | 33.15 | 1.859 | 1.876 | 5.672 | 5.911 |
| 8 | 1.862 | 3.479 | 5.968 | 11.268 | 37.98 | 1.868 | 1.888 | 6.050 | 6.363 |
| 9 | 1.869 | 3.504 | 6.322 | 12.000 | 43.02 | 1.875 | 1.898 | 6.422 | 6.805 |
| 12 | 1.881 | 3.557 | 7.359 | 14.128 | 59.45 | 1.890 | 1.920 | 7.509 | 8.078 |
| 15 | 1.890 | 3.590 | 8.371 | 16.188 | 77.83 | 1.900 | 1.934 | 8.567 | 9.297 |
| 18 | 1.895 | 3.613 | 9.364 | 18.201 | 98.16 | 1.907 | 1.944 | 9.604 | 10.483 |
| 21 | 1.899 | 3.630 | 10.344 | 20.179 | 120.45 | 1.912 | 1.951 | 10.625 | 11.644 |
| 24 | 1.902 | 3.643 | 11.312 | 22.130 | 144.67 | 1.915 | 1.956 | 11.635 | 12.789 |
| 27 | 1.904 | 3.653 | 12.271 | 24.060 | 170.81 | 1.918 | 1.961 | 12.634 | 13.920 |
| 30 | 1.906 | 3.661 | 13.222 | 25.972 | 198.87 | 1.920 | 1.964 | 13.624 | 15.041 |
| 36 | 1.909 | 3.673 | 15.105 | 29.755 | 260.65 | 1.924 | 1.970 | 15.585 | 17.256 |
| 48 | 1.913 | 3.689 | 18.815 | 37.197 | 406.67 | 1.929 | 1.977 | 19.448 | 21.613 |
| 60 | 1.915 | 3.698 | 22.474 | 44.529 | 582.23 | 1.931 | 1.981 | 23.256 | 25.906 |
| $\infty$ | 1.923 | 3.735 | $\infty$ | $\infty$ | $\infty$ | 1.942 | 2.000 | $\infty$ | $\infty$ |

Moreover these ratios increase steadily as $n$ increases from $6(=m)$ to $\infty$, or $N$ decreases from $\frac{1}{2}$ to 0. As one approaches the hard-core limit $n \rightarrow \infty$, we note that $T_C$, $T_B$ and $T_F$ remain finite, whereas $T_A$, $T_D$ and $T_E$ diverge to $+\infty$, as expected. Again, the ratio $T_D/T_A$ remain finite and approaches the value 2 in the hard-core limit. For large $n$ it is easy to show, from the two leading terms $s = 0$ and $s = 1$ in (11), which have opposite signs, that

$$T_A \sim \frac{n}{(m-3)}, \qquad T_D \sim \frac{2n}{(m-3)}, \qquad T_E \sim \frac{n^2}{3(m-3)}. \tag{16}$$

These asymptotic forms are indicated in Figure I in the case $m = 6$. So

$$T_D \sim 2T_A, \quad \text{and} \quad T_E \sim \frac{1}{3}(m-3)T_A^2 \quad \text{as} \quad n \rightarrow \infty, \tag{17}$$

with the ratio $(T_D/T_A)$ independent of $m$. The ratios denoted in (15b) by $\mu(m, \ n)$, which were observed to be approximately equal when $m = 6$, become for large $n$

$$\frac{T_A}{T_B} \sim \frac{T_D}{T_C} \sim \frac{n}{(m-3)}, \qquad \frac{T_E}{T_A} \sim \frac{n}{3}. \tag{18}$$

Allowing for the fact that in the hard-core limit $T_B$ and $T_C$ are not now exactly equal to 1 and 2 respectively, the first two ratios are asymptotically similar, and approximately equal to the third ratio $T_E/T_A$ when $m = 6$, as may be checked in Table II. More details of the hard-core limit are given in Section 4 below.

## 4 TERMINATION TEMPERATURES FOR THE SUTHERLAND POTENTIAL

In the limit $n \to \infty$ the Lennard–Jones $m,n$ potential becomes the Sutherland potential $\phi_{m,\infty}$ in (7), with a hard-core of diameter $\sigma$, and an attractive inverse power tail with exponent $m$. The same limit $n \to \infty$ may be taken in the series expansion form (11) for $B$. Thence one obtains correctly the Sutherland potential second virial coefficient

$$B^*_{m,\infty} = (-3/m) \sum_{s=0}^{\infty} [s!(s - 3/m)T^{*s}]^{-1} \tag{19a}$$

$$= \Phi(-3/m, 1 - 3/m; 1/T^*) \tag{19b}$$

where $\Phi$ is a confluent hypergeometric function. The first $s = 0$ term in (19a) is positive, and all other terms are negative. The Sutherland potential second virial coefficient is now seen to be a monotonic increasing function of temperature, approaching the constant limiting value 1 as $T^* \to \infty$. Consequently $T_B$, $T_C$ and $T_F$ exist and are finite, and their values and ratios for the case $m = 6$ are included in Tables I and II. We observe that the ratios $T_C/T_B$ and $T_F/T_C$ are approximately equal and both less than 2, as expected.

For large values of $m$ the tail of the Sutherland potential is cut off sharply. The second virial coefficient $B^*_{m,\infty}$ for large $m$ is asymptotically

$$B^*_{m,\infty} \sim 1 - (3/m)e^{1/T^*}, \; m \to \infty \tag{20}$$

which is of the square-well form, section 9 below, but in a region where the square-well parameter

$$R = (\text{well width})/(\text{molecular diameter}) \tag{21}$$

approaches 1. In (20) we may identify

$$3/m \sim R^3 - 1. \tag{22}$$

From section 9, we see that $T_B$, $T_C$ and $T_F$ now tend to zero like $1/\ln(m/3)$, and their ratios approach unity.

In the opposite limit $m \to 3$, the coefficient of the negative second term $s = 1$, diverges and

$$B^*_{m,\infty} \sim 1 - [(m/3 - 1)T^*]^{-1} + \text{finite terms involving negative powers of } T^*. \tag{23}$$

Now the termination temperatures diverge to $+\infty$ as $m \to 3$, but thei ratios $T_C/T_B$ and $T_F/T_C$ tend to 2 once more. The limit $m \to 3$ for a genera value of the repulsive exponent $n$ is considered in section 6.

## 5 TERMINATION TEMPERATURES FOR THE LENNARD–JONES POTENTIAL AS $n \to m > 3$

In this limiting case the Lennard–Jones *m,n* potential tends to the form (8), and provided $m > 3$ the integral formulae for the second virial coefficient are still valid. However, the transformation (10) now breaks down, and instead we change the integration variable from $r^*$ to

$$x = r^{*-m}, \tag{24}$$

so (2a) becomes

$$B^*_{m,m} = (3/m) \int_0^\infty dx\, x^{-1-3/m}[1 - e^{x(1-\ln x)/T^*}], \tag{25a}$$

$$= (1/T^*) \int_0^\infty dx\, x^{-3/m} \ln x e^{x(1-\ln x)/T^*}. \tag{25b}$$

By further setting $y = x/T^*$, one may use (25b) to show that at high temperatures

$$B^*_{m,m} \sim \left(\frac{\ln T^*}{T^*}\right)^{3/m} \Gamma(1 - 3/m) \tag{26}$$

[To facilitate the evaluation of $B^*_{m,m}$, one splits the range of integration at $x = e$.[4] In the portion $0 < x < e$ expand the exponential in (25a) as a power series in $(1/T^*)$, set $t = 1 - \ln x$, and integrate term by term. In the portion $e < x < \infty$ integrate the $x^{-3/m}$ term in (25a) and append the result to the series just obtained from the 0 to $e$ integration; and in the exponential term set $t = e/x$ to obtain

$$B^*_{m,m} = (-3/m)e^{-3/m}\left[\sum_{s=0}^{\infty}\left(\frac{e}{T^*}\right)^s \frac{1}{(s - 3/m)^{s+1}} + \int_0^1 dt \cdot t^{-1+3/m+e/tT^*}\right]. \tag{27}$$

An integration by parts can be employed to split this expression for $B^*_{m,m}$ into a strictly negative series and a strictly positive integral:

$$B^*_{m,m} = e^{-3/m}\left[\left(-\frac{3}{m}\right)\sum_{s=1}^{\infty}\left(\frac{e}{T^*}\right)^s \cdot \frac{1}{(s - 3/m)^{s+1}} + \frac{e}{T^*}\int_0^1 dt(1 - \ln t)t^{-2+3/m+e/tT^*}\right] \tag{28}$$

The series converges well at high $T^*$, but yields a negative contribution to $B^*_{m,m}$, which must be dominant at low $T^*$. The integrand is well behaved at low $T^*$, but yields a positive contribution to $B^*_{m,m}$, which must be dominant at high $T^*$. An asymptotic estimate of the series using Stirling's formula shows that at low temperatures

$$B^*_{m,m} \sim (-3/m)(2\pi T^*)^{1/2} e^{1/T^*}, \qquad T^* \to 0. \tag{29}$$

Now $B^*_{m,m}$ can be evaluated from (27) by numerical integration and summation of the series. We restrict our attention to the case $m = 6$. The integrand still has a nasty sharp maximum at a point $t$ located by $T = 2e(1 - \ln t)/t$, which is inside the range of integration $0 < t < 1$ when $T > 2e$.]

The values of $B^*_{m,m}$ for $m = 6$ calculated from (27) are graphed in Figure 1. One can also obtain the temperature derivatives of $B$ by differentiating under the integral sign in (27), and performing the necessary sums and integrals. Then the termination temperatures can be located numerically. For $m = 6$, the values of the six termination temperatures and their ratios are included in Tables I and II, and appear as the end points of the graphs in Figure 2 at $N = \frac{1}{2}$.

## 6 THE LIMITING CASE OF THE 3 − *n* POTENTIAL AND THE *M* − *N* MODEL

As the attractive exponent $m \to 3$ for a fixed value of the repulsive exponent $n$, one observes that the coefficient of the negative second term in (11) diverges, and

$$B^*_{m,n} \sim \left(\frac{p}{q}\right)^{3/n} \left\{ \frac{\Gamma(1 - 3/n)}{T^{3/n}} - \left[ p^p q^q \left(\frac{m}{3} - 1\right) T^* \right]^{-1} \right. \\ \left. + \text{ finite terms involving negative powers of } T^* \right\}, \tag{30}$$

which reduces to (23) in the limit $n \to \infty$. The source of the problem is that the attractive potential tail has become a sufficiently long-range inverse cube power to cause the integrals in (2) to diverge. The situation may be remedied by demanding that the attractive potential be very weak, by analogy with the weak long-range potentials used to derive van der Waals' equation.[5] In the present situation this means we just replace the divergent coefficient by a finite one and drop all the higher order negative terms in the series. $B^*$ now has the form

$$B^*_{3,n} \sim \frac{b'}{T^{3/n}} - \frac{a'}{T}, \tag{31}$$

where $a'$ and $b'$ are positive constants, which is just the $M - N$ model second virial coefficient in IV, with $M = 1$ and $N = 3/n$. So this particular case of the $M - N$ model may be derived from a potential comprising a repulsive inverse power term with exponent $n$ and a weak long-range inverse cube attractive term.

## 7 THE PARTICULAR CASE OF THE *m*,2*m* POTENTIAL

Certain simplifications in the mathematics occur when the repulsive exponent is exactly twice the attractive exponent $m$. This special case includes the popular Lennard–Jones 6,12 potential.[4] For general $m$ ($>3$) we now have $p = q = \frac{1}{2}$ in our previous formulae (11) for $B^*$. One may identify the resulting series as a combination of confluent hypergeometric functions, with $N = 3/n$ and $n = 2m$,

$$\begin{aligned} B_{m,2m} = T^{*-N}[&\Gamma(1 - N)\Phi(-N, \tfrac{1}{2}; 1/T^*) \\ &- 2N\Gamma(\tfrac{1}{2} - N)T^{*-1/2}\Phi(\tfrac{1}{2} - N, \tfrac{3}{2}; 1/T^*)]. \end{aligned} \tag{32}$$

The same results can be obtained directly from the integral form (2b). Note that if the molecular diameter $\sigma_0$ is used to scale the second virial coefficient, then $B_0^* = 2^{2N}B^*$. At low temperatures, where $B$ is large and negative, one may derive the asymptotic formula

$$B^*_{m,2m} \sim (-)2N(\pi T^*)^{1/2}e^{1/T^*}{}_2F_0(\tfrac{1}{2} + N, 1 + N; T^*). \tag{33}$$

## 8 ESTIMATES OF THE SOFTENING TEMPERATURE $T_s$

One way of describing the high temperature form of the second virial coefficient is to introduce a characteristic temperature $T_s$, so that as $T \to \infty$

$$B \equiv bB^* \sim b(T_s/T)^N \tag{34}$$

with $N = 3/n$ as before. Indeed the introduction of such a phenomenological softening temperature was a feature of the $T_s - N$ model in IV. From the asymptotic high temperature form of the Lennard–Jones second virial coefficient (13) we find that

$$T_s^* \equiv kT_s/\varepsilon = (p/q)[\Gamma(1 - N)]^{1/N}, \tag{35}$$

whence one may evaluate the softening temperature. An unavoidable defect is that the values of $T_s$ depend on whether the length scaling by an effective molecular diameter is performed using $\sigma$ at the potential minimum, or $\sigma_0$ where the potential vanishes. Using $\sigma_0$ scaling, one would have a softening temperature

$$T^*_{s0} = (\sigma/\sigma_0)^n T_s^* = (n/m)^{n/(n-m)}T_s^*, \tag{36}$$

where the extra factor can be rather large. For the 6,12 and 6,18 Lennard-Jones' potentials we have

$$n = 12, \quad T_s^* = 2.255\ldots, \quad T_{s_0}^* = 9.020\ldots, \tag{37a}$$

$$n = 18, \quad T_s^* = 1.034\ldots, \quad T_{s_0}^* = 5.374\ldots. \tag{37b}$$

If we use experimental values of $\varepsilon/k$ obtained from the second virial coefficient of fluid argon, fitted by Lennard-Jones, 6,$n$ potentials, we have[6]

$$n = 12, \quad \varepsilon/k = 112.4\ \mathrm{K}, \quad T_s = 253.5\ \mathrm{K}, \quad T_{s_0} = 1014\ \mathrm{K}, \tag{38a}$$

$$n = 18, \quad \varepsilon/k = 157.5\ \mathrm{K}, \quad T_s = 162.9\ \mathrm{K}, \quad T_{s_0} = 846\ \mathrm{K}. \tag{38b}$$

The critical temperature is 150.86 K. We conclude that although $T_s$ may be a useful parameter in the structure of the theory, its numerical values are not of any great significance.

## 9 THE SQUARE-WELL POTENTIAL

For the square-well potential

$$\phi_{sw}(r) = \begin{cases} +\infty, r < \sigma \\ -\varepsilon, \sigma < r < R\sigma \\ 0, r > R\sigma \end{cases} \tag{39}$$

where $R$ is a dimensionless parameter, $R > 1$, as in (21). Substitution of this potential in the integral expression (2a) for the second virial coefficient yields

$$B^* \equiv B/b = 1 - (R^3 - 1)(e^{\varepsilon/kT} - 1). \tag{40}$$

$B^*$ is a monotonic increasing function of temperature, approaching the limit 1 as $T^* \equiv kT/\varepsilon \to \infty$. Setting

$$\gamma = 1/(R^3 - 1) \tag{41}$$

so $0 < \gamma < \infty$, we find that the three termination temperatures which are finite, are given by

$$T_B\colon\ e^{1/T^*} = \gamma + 1, \tag{42a}$$

$$T_C\colon\ e^{1/T^*}(1 + 1/T^*) = \gamma + 1, \tag{42b}$$

$$T_F\colon\ e^{1/T^*}(1 + 3/T^* + 1/T^{*2}) = \gamma + 1. \tag{42c}$$

Clearly $T_B < T_C < T_F$. In the limit of a very wide well $R \to \infty$, the termination temperatures diverge to $+\infty$ like

$$T_B^* \sim R^3, \quad T_C^* \sim 2R^3, \quad T_F^* \sim 4R^3, \tag{43}$$

TABLE III

Values and ratios of termination temperatures for the square-well potential for various values of the well-width parameter $R$.

| $R$ | $R^3$ | $\gamma$ | $T_B^*$ | $T_C^*$ | $T_F^*$ | $T_C/T_B$ | $T_F/T_B$ | $T_F/T_C$ |
|---|---|---|---|---|---|---|---|---|
| 1.063 | 1.200 | 5.000 | 0.558 | 0.938 | 1.619 | 1.681 | 2.900 | 1.726 |
| 1.101 | 1.333 | 3.000 | 0.721 | 1.252 | 2.224 | 1.735 | 3.083 | 1.777 |
| 1.145 | 1.500 | 2.000 | 0.910 | 1.619 | 2.942 | 1.779 | 3.232 | 1.817 |
| 1.260 | 2.000 | 1.000 | 1.443 | 2.668 | 5.013 | 1.849 | 3.474 | 1.879 |
| 1.357 | 2.500 | 0.667 | 1.958 | 3.690 | 7.044 | 1.885 | 3.598 | 1.909 |
| 1.442 | 3.000 | 0.500 | 2.466 | 4.702 | 9.061 | 1.907 | 3.674 | 1.927 |
| 1.518 | 3.500 | 0.400 | 2.972 | 5.711 | 11.072 | 1.921 | 3.726 | 1.939 |
| 1.587 | 4.000 | 0.333 | 3.476 | 6.716 | 13.080 | 1.932 | 3.763 | 1.947 |
| 1.710 | 5.000 | 0.250 | 4.481 | 8.724 | 17.091 | 1.947 | 3.814 | 1.959 |
| 1.817 | 6.000 | 0.200 | 5.485 | 10.729 | 21.097 | 1.956 | 3.846 | 1.966 |
| 1.913 | 7.000 | 0.167 | 6.487 | 12.732 | 25.101 | 1.963 | 3.869 | 1.971 |
| 2.000 | 8.000 | 0.143 | 7.489 | 14.735 | 29.105 | 1.968 | 3.886 | 1.975 |
| $\infty$ | $\infty$ | 0.000 | $\infty$ | $\infty$ | $\infty$ | 2.000 | 4.000 | 2.000 |

but their ratios remain finite with limiting value

$$T_C/T_B = T_F/T_C = 2, \qquad \text{as } R \to \infty. \tag{44}$$

As $R \to 1$, and the attractive well shrinks in size, the termination temperatures tend to zero:

$$1/T_B \sim \ln \gamma, \tag{45a}$$

$$1/T_C \sim \ln \gamma - \ln \ln \gamma, \tag{45b}$$

$$1/T_F \sim \ln \gamma - 2 \ln \ln \gamma, \tag{45c}$$

and their ratios tend to unity. Numerical values of the termination temperatures and their ratios are listed in Table III for various values of the parameter $R$. One observes that the ratios $T_C/T_B$ and $T_F/T_C$ lie in the range 1 to 2, and are approximately equal.

The van der Waals' form of the second virial coefficient can be extracted as a limiting case of the square-well potential second virial coefficient. If the well-depth $\varepsilon \to 0$ and the well-width ratio $R \to \infty$, in such a way that $R^3\varepsilon/k \to c$, a constant, then

$$B \sim b(1 - c/T).$$

## CONCLUDING REMARKS

The main results of this paper concerning the Lennard-Jones, Sutherland and square-well potentials and their second virial coefficients are summarized in the Introduction. Questions involving the shape of the second virial coefficient versus temperature graph, the order of the termination temperatures, and the nonexistence of a $C_v$ locus termination temperature for a general intermolecular potential will be the subjects of the following paper, VI.

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