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## Physics and Chemistry of Liquids

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

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**To cite this Article** Stephenson, John and Leung, H. K.(1980) 'Hard and Soft-Core Equations of State for Simple Fluids VII. Termination Temperatures for the Kihara Potential', Physics and Chemistry of Liquids, 9: 2, 175 – 189 **To link to this Article: DOI:** 10.1080/00319108008084775

**URL:** http://dx.doi.org/10.1080/00319108008084775

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Phys. Chem. Liq., 1980, Vol. 9, pp. 175-190 0031-9104/80/0902-0175\$04.50/0 © 1980 Gordon and Breach Science Publishers, Inc. Printed in the U.S.A.

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

VII. Termination Temperatures for the Kihara Potential†

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(Received April 2, 1979)

The six termination temperatures associated with the ten characteristic curves of a simple fluid are calculated for the Kihara potential second virial coefficient, constructed from a Lennard-Jones m,n potential augmented by a spherical hard-core. Extreme values of the termination temperatures in both the hard-core Sutherland-type potential limit  $n \to \infty$ , and in the opposite limit  $n \to m$  are obtained. Over the useful range of values, 0 to 1, of the ratio  $a^*$  of the hard-core diameter to the molecular diameter in the absence of a hard-core, the termination temperature ratios  $T_C/T_B$ ,  $T_F/T_C$  and  $T_D/T_A$  vary only slightly, for a given value of n, with  $T_D/T_A \to 2$  in the hard-core limit  $n \to \infty$ , independent of m and  $a^*$ .

#### **1** INTRODUCTION

Kihara<sup>1</sup> has shown how to introduce a hard-core into a classical intermolecular pair potential. In the case of a spherical hard-core of radius *a* appropriate to the monatomic atoms of a simple fluid interacting via an underlying spherically symmetric scalar pair potential  $\phi(r)$ , one may construct the corresponding Kihara potential  $\phi^{\kappa}(r)$  by the simple recipe

$$\phi^{\mathbf{K}}(\mathbf{r}) = \begin{cases} \infty & r < 2a, \\ \phi(r - 2a), & r > 2a, \end{cases}$$
(1)

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

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FIGURE 1 Schematic Kihara potential  $\phi^{K}(r)$  plotted versus radial distance r. The hard-core diameter is 2a and the molecular diameter in the absence of a hard-core is  $\sigma$ .

illustrated schematically in Figure 1. In the case when  $\phi$  is the Lennard– Jones *m*, *n* potential, Kihara has obtained expressions for the classical second virial coefficient which we will use in this paper in order to study the six termination temperatures associated with the ten characteristic curves of a simple fluid. Our approach is parallel to that employed in an earlier analysis of the second virial coefficient for the Lennard–Jones *m*, *n* potential in the absence of a hard-core, in V.<sup>2</sup> The extra feature of the Kihara second virial coefficient is the presence of the hard-core radius *a*, so the Lennard–Jones molecular diameter  $\sigma$ , locating the minimum of the potential  $\phi$ , becomes increased to an effective molecular diameter ( $\sigma + 2a$ ). The useful range of the ratio

$$a^* = \frac{2a}{\sigma} \tag{2}$$

appears to be 0 to 1, based on estimates made by Kihara from the second virial coefficients of a variety of gases of spherical atoms or molecules.<sup>1</sup>

For selected values of  $a^*$  we will calculate the termination temperatures over the permitted range of values  $m \le n \le \infty$  of the repulsive exponent *n*. We pay special attention both to the hard-core limit  $n \to \infty$  when the potential is analogous to the Sutherland potential, and to the opposite limiting case  $n \to m$ . In the numerical work we set the attractive exponent mequal to 6, appropriate to the Heitler-London dispersion energy between neutral non-polar molecules. For the particular values n = 6, 9, 12, 18, 27and  $\infty$ , of the repulsive exponent, we have examined a wider range of values of  $a^*$ . The general effect of increasing  $a^*$  is to depress the termination temperatures (except  $T_E$  for larger values of  $a^*$ ), while leaving the ratios  $T_C/T_B$ ,  $T_F/T_C$ and  $T_D/T_A$  almost unchanged for a given value of n. We obtain the asymptotic forms of  $T_D$ ,  $T_A$  and  $T_E$  for large values of n, and find that the ratio  $T_D/T_A$ tends to 2 in the hard-core limit  $n \to \infty$  independent of m and  $a^*$ .

#### 2 SECOND VIRIAL COEFFICIENT FORMULAE FOR THE KIHARA POTENTIAL

The underlying intermolecular interaction is chosen to be the spherically symmetric Lennard-Jones m, n potential

$$\phi_{m,n}(r) = \frac{\varepsilon}{n-m} \left[ m \left( \frac{\sigma}{r} \right)^n - n \left( \frac{\sigma}{r} \right)^m \right], \tag{3}$$

with attractive exponent m and repulsive exponent n, with n > m > 3. The corresponding Kihara potential incorporating a hard-core of diameter 2a is constructed via (1). Now  $\sigma$  is the radial distance from the surface of the spherical hard-core to the point where the potential has a minimum of depth  $\varepsilon$ , Figure 1. (Kihara uses the symbol  $\rho_0$  where we have used  $\sigma$ ).

The classical integral formula for the second virial coefficient is

$$B = \left(\frac{b}{\sigma^3}\right) \int_0^\infty d(r^3) [1 - e^{-\phi^{\mathcal{K}}(r)/kT}], \qquad (4)$$

where

$$b = \frac{2\pi\sigma^3 L}{3} \tag{5}$$

is  $(4 \times)$  the volume of the L (Avogadro number) of molecules in a mole. Inserting (3) in (4) we obtain Kihara's formula for the second virial coefficient:

$$B = b[F_3 + 3a^*F_2 + 3a^{*2}F_1 + a^{*3}]$$
(6)

where  $a^*$  is the hard-core to molecular diameter ratio defined in (2). The temperature dependent functions  $F_s$ , s = 1, 2, 3, which we also denote by

 $F_{mn,s}$ , where we wish to indicate the dependence on m and n in the Lennard-Jones case, are defined by

$$F_{mn,s} = \int_0^\infty d(r/\sigma)^s [1 - e^{-\phi_{mn}(r)/kT}].$$
 (7)

In terms of the dimensionless temperature

$$T^* = \frac{kT}{\varepsilon} \tag{8}$$

one easily obtains, by expanding the attractive portion of the exponential in (7) and integrating term by term, the series representations

$$F_{mn,s} = -\frac{s}{n} \sum_{t=0}^{\infty} \frac{1}{t!} \Gamma\left(\frac{tm-s}{n}\right) \left(\frac{n}{m}\right)^{t} \left[\frac{m}{(n-m)T^{*}}\right]^{[(n-m)t+s]/n}$$
(9a)

$$= -\frac{s}{n} \left(\frac{p}{qT^*}\right)^{s/n} \sum_{t=0}^{\infty} \frac{\Gamma(pt-s/n)}{t! (p^p q^q T^{*q})^t},$$
(9b)

where we have introduced the convenient abbreviations

$$p = 1 - q = -\frac{m}{n} \tag{10}$$

as in V. It is clear that the required extensions of the previous calculations in V for the Lennard-Jones m, n potential will be quite easy to make: cf. V (11).

In the limit  $n \to \infty$  the Kihara potential becomes a Sutherland type potential with a hard-core of diameter  $(\sigma + 2a)$ , and an attractive inverse power tail with exponent *m*. The same limit  $n \to \infty$  may be taken in the series expansions (9) of the functions  $F_s$ . One obtains

$$F_{m\infty,s} = \left(-\frac{s}{m}\right)\sum_{t=0}^{\infty} \left[t!\left(t-\frac{s}{m}\right)T^{*t}\right]^{-1},\tag{11}$$

which may be inserted in (6). The second virial coefficient is now a monotonic increasing function of temperature, approaching the constant limiting value  $b(1 + a^*)^3$  as  $T^* \to \infty$ . (The same limiting value of *B* is attained if  $m \to \infty$  too, at any temperature). Consequently only  $T_B$ ,  $T_C$  and  $T_F$  exist in this hard-core limit, but their values still depend on  $a^*$ .

In the opposite limiting case  $n \rightarrow m > 3$ , the underlying Lennard-Jones m, n potential tends to the form

$$\phi_{mm}(r) = -\left(\frac{\sigma}{r}\right)^m \left[1 + m \ln\left(\frac{r}{\sigma}\right)\right], \qquad (12)$$

and provided m > 3 the integral formulae (7) for the functions  $F_s$  appearing in the second virial coefficient are still valid. We insert the limiting form of the

potential (12) in (7), and change the integration variable to

$$x = \left(\frac{r}{\sigma}\right)^{-m} \tag{13}$$

so the integrals for  $F_s$  become

$$F_{mm,s} = \left(\frac{s}{m}\right) \int_0^\infty dx \; x^{-1-s/m} [1 - e^{x(1-\ln x)/T^*}] \tag{14}$$

which is again a simple extension of the corresponding formula in V (25a). To derive expressions which are convenient for computation we split the integration range at x = e, and proceed as in V to obtain

$$F_{mm,s} = \left(-\frac{s}{m}\right)e^{-s/m}\left[\sum_{t=0}^{\infty}\frac{(e/T^*)^t}{(t-s/m)^{t+1}} + \int_0^1 dt \ t^{-1-s/m+e/tT^*}\right].$$
 (15)

The Kihara second virial coefficient and its temperature derivatives can be evaluated from (15) and (6) by numerical integration and summation of the series.

#### 3 TERMINATION TEMPERATURES FOR THE KIHARA POTENTIAL

The six termination temperatures  $T_B$ ,  $T_C$ ,  $T_F$ ,  $T_A$ ,  $T_D$  and  $T_E$  are defined via Eqs. (12a)-(12f) in IV.<sup>3</sup> These relations are linear and homogeneous in B and its temperature derivatives. For any chosen values of m, n and  $a^*$  with n > m > 3, one may calculate the termination temperatures numerically from the series expansion forms for B and  $F_s$  via (6) and (9). The values of the termination temperatures in the limiting cases  $n \to \infty$  and  $n \to m$  are obtained from the corresponding expressions for the limiting forms of the second virial coefficient in (11) and (15). In all the numerical work we have confined our attention to the case m = 6. Our results are presented in Tables I and II, and Figures 2 and 3, which are designed to display the variation of the termination temperatures and the ratios of interest as n and  $a^*$  are altered.

For a fixed value of *n*, the general effect of increasing  $a^*$  is to depress the values of the termination temperatures (except for  $T_E$ ) while leaving the ratios  $T_C/T_B$ ,  $T_F/T_C$  and  $T_D/T_A$  almost unchanged. The depression of  $T_B$ ,  $T_C$  and  $T_F$  is mainly due to the additional constant term  $a^{*3}$  appearing in *B*, since the defining expressions for these temperatures involve *B* itself. As  $a^* \to \infty$ ,  $T_B$ ,  $T_C$  and  $T_F$  tend to zero. The effect on  $T_A$  and  $T_D$  is moderately large in absolute terms but occurs in such a way that their ratio  $T_D/T_A$  is not greatly altered.  $T_E$  decreases initially when  $n \leq 27$ , but then increases again

| Values o | of terminati  | on temper  | ratures for  | the Kihar  | a 6, <i>n</i> pote   | ntial with  | 6 IN<br>6  | ∞ over a  | a range o  | f values o  | of a . 7*   | $= kT/\varepsilon$   |   |
|----------|---|--|--|--|--|---|--|---|--|---|---|--|---|
| n a*     | 0.0   | 0.05   | 0.1  | 0.2  | 0.3  | 0.4   | 0.5  | 0.6   | 0.7  | 0.8   | 1.0   | 1.5  | 2.0   |
| 6        | 8.490   | 7.274  | 6.342  | 5.021  | 4.139  | 3.514   | 3.052  | 2.698   | 2.420  | 2.195   | 1.858   | 1.366  | 1.102   |
| 6        | 4.555   | 4.059  | 3.659  | 3.054  | 2.624  | 2.302   | 2.055  | 1.859   | 1.701  | 1.570   | 1.367   | 1.056  | 0.881   |
| 12       | 3.418   | 3.094  | 2.826  | 2.412  | 2,108  | 1.876   | 1.694  | 1.548   | 1.429  | 1.329   | 1.172   | 0.926  | 0.783   |
| 81       | 2.558   | 2.348  | 2.171  | 1.891  | 1.679  | 1.515   | 1.383  | 1.276   | 1.187  | 1.112   | 0.993   | 0.802  | 0.688   |
| 27       | 2.083   | 1.929  | 1.797  | 1.585  | 1.422  | 1.294   | 1.190  | 1.105   | 1.034  | 0.973   | 0.876   | 0.717  | 0.622   |
| 8        | 1.171   | 1.103  | 1.044  | 0.946  | 0.867  | 0.803   | 0.751  | 0.706   | 0.668  | 0.636   | 0.582   | 0.493  | 0.436   |
| 9        | 15.659  | 13.481   | 11.801   | 9.398  | 777.7  | 6.620   | 5.758  | 5.094   | 4.569  | 4.144   | 3.502   | 2.554  | 2.042   |
| 6        | 8.512   | 7.603  | 6.866  | 5.746  | 4.941  | 4.337   | 3.869  | 3.496   | 3.194  | 2.943   | 2.553   | 1.950  | 1.607   |
| 12       | 6.431   | 5.828  | 5.327  | 4.549  | 3.974  | 3.533   | 3.185  | 2.905   | 2.674  | 2.481   | 2.177   | 1.697  | 1.417   |
| 18       | 4.848   | 4.449  | 4.112  | 3.575  | 3.168  | 2.850   | 2.595  | 2.387   | 2.214  | 2.067   | 1.834   | 1.457  | 1.233   |
| 27       | 3.967   | 3.669  | 3.414  | 3.002  | 2.685  | 2.434   | 2.230  | 2.063   | 1.922  | 1.802   | 1.610   | 1.296  | 1.107   |
| 8        | 2.251   | 2.114  | 1.995  | 1.795  | 1.637  | 1.507   | 1.400  | 1.310   | 1.233  | 1.167   | 1.059   | 0.877  | 0.763   |
| 9        | 28.937  | 25.039   | 22.013   | 17.644   | 14.669   | 12.527  | 10.920   | 9.675   | 8.685  | 7.880   | 6.657   | 4.836  | 3.841   |
| 6        | 15.963  | 14.300   | 12.943   | 10.869   | 9.364  | 8.228   | 7.343  | 6.635   | 6.057  | 5.577   | 4.827   | 3.658  | 2.988   |
| 12       | 12.157  | 11.035   | 10.101   | 8.639  | 7.550  | 6.712   | 6.048  | 5.509   | 5.065  | 4.692   | 4.103   | 3.167  | 2.618   |
| 18       | 9.243   | 8.486  | 7.844  | 6.817  | 6.036  | 5.422   | 4.928  | 4.524   | 4.186  | 3.900   | 3.443   | 2.704  | 2.262   |
| 27       | 7.609   | 7.033  | 6.540  | 5.741  | 5.124  | 4.633   | 4.235  | 3.906   | 3.629  | 3.394   | 3.015   | 2.395  | 2.019   |
| 8        | 4.373   | 4.097  | 3.856  | 3.454  | 3.134  | 2.874   | 2.658  | 2.476   | 2.321  | 2.188   | 1.970   | 1.602  | 1.374   |
|          | Values c<br>7 values c<br>9 6 6<br>12 9 6 6<br>8 12 9 7<br>8 12 9 | Values of termination $n$ a* 0.0<br>6 8.490<br>6 8.490<br>6 8.490<br>12 3.418<br>12 3.418<br>12 3.418<br>12 4.555<br>0 4.555<br>12 0.0<br>1.171<br>6 15.659<br>9 8.512<br>12 6.431<br>18 4.848<br>27 2.251<br>6 28.937<br>9 15.157<br>12 15.157<br>12 15.157<br>9 15.1563<br>12 15.157<br>9 15.1563<br>12 15.157<br>9 15.1563<br>12 15.157<br>12 15.157<br>12 15.157<br>13 | values of termination temper $n$ $a^*$ 0.0         0.05 $n$ $a^*$ 0.0         0.05           6         8.490         7.274         9           9         4.555         4.059         1.274           9         4.555         4.059         1.274           12         3.418         3.094         18         2.558         2.348           27         2.083         1.171         1.103         2.253         2.348           6         15.659         13.481         5.828         1.171         1.103           6         15.659         13.481         5.828         1.113         5.828           12         6         15.659         13.481         5.828         1.103           6         15.659         13.481         5.828         1.103         5.828           12         6.431         5.828         13.481         5.828         1.144           77         3.967         3.967         3.669         2.114         6.215.039         2.143         8.486           6         15.963         12.157         11.035         8.486         2.133         2.033 | values of termination temperatures for $n$ $a^{\bullet}$ 0.00.050.1 $n$ $a^{\bullet}$ 0.00.050.168.4907.2746.34294.5554.0593.659123.4183.0942.826182.5582.3482.171272.0831.9291.797 $\infty$ 1.1711.1031.044615.65913.48111.80198.5127.6035.826126.4315.8285.327184.8484.4494.112273.9673.6693.414 $\infty$ 2.2512.1141.995628.93725.03922.013915.96314.30012.9431212.15711.03510.101189.2438.4867.844277.6097.0336.540 $\infty$ 4.3734.0973.856 | Values of termination temperatures for the Kinar $n$ $a^{\bullet}$ 0.00.050.10.2 $6$ 8.4907.2746.3425.021 $9$ 4.5554.0593.6593.054 $12$ 3.4183.0942.8262.412 $12$ 3.4183.0942.8262.412 $12$ 3.4183.0942.8262.412 $27$ 2.0831.9291.7971.891 $27$ 2.0831.9291.7971.585 $\infty$ 1.1711.1031.0440.946 $6$ 8.5127.6036.8665.746 $9$ 8.5127.6036.8665.746 $27$ 3.9673.6693.4143.002 $\infty$ 2.2512.1141.9951.795 $27$ 3.9673.6693.4143.002 $\infty$ 2.2512.1141.9951.764 $9$ 8.53725.03922.01317.644 $9$ 9.2438.4867.8346.819 $12$ 12.15711.03510.1018.639 $12$ 12.15711.33510.1018.639 $12$ 12.15711.33510.1018.639 $12$ 7.6097.0336.5405.741 $\infty$ 4.3734.0973.8563.454 | Values of termination temperatures for the Kniata $0,n$ pote $n$ $a^{\bullet}$ 0.0         0.05         0.1         0.2         0.3 $n$ $a^{\bullet}$ 0.0         0.05         0.1         0.2         0.3           6         8.490         7.274         6.342         5.021         4.139         4.139           6         8.490         7.274         6.342         5.021         4.139         4.139           77         3.094         2.826         2.412         2.108         1.679         2.624           27         2.083         1.929         1.771         1.891         1.679         2.624           27         2.083         1.929         1.044         0.946         0.867         2.624           27         2.083         1.171         1.103         1.044         0.946         0.867           6         15.659         13.481         11.801         9.398         7.777           9         8.512         7.603         6.866         5.746         4.941           12         3.967         3.669         3.414         3.002         2.685           27         3.967         3.669 | Values of termination temperatures for the Kinara 6, <i>n</i> potential with $n$ $a^{\bullet}$ 0.0         0.05         0.1         0.2         0.3         0.4           6         8.490         7.274         6.342         5.021         4.139         3.514           9         4.555         4.059         3.659         3.054         2.624         2.302           12         3.418         3.094         2.826         2.412         2.108         1.876           12         3.418         3.094         2.826         2.412         2.108         1.876           27         2.083         1.929         1.797         1.585         1.422         1.294           27         2.083         1.929         1.797         1.679         1.515           27         2.083         1.944         0.946         0.867         0.803           6         15.659         13.481         11.801         9.397         3.533           12         6.431         5.828         5.327         4.549         3.533           12         6.431         5.828         5.327         4.549         3.533           27         3.967         3.669 | Values of termination temperatures for the Kinara 0, <i>n</i> potential with 0 $\leq n \leq $ | Values of termination temperatures for the Kinara 0, <i>n</i> potential with 0 $\leq$ <i>n</i> $\leq$ $\infty$ over <i>i n</i> $a^{\bullet}$ 0.0         0.05         0.1         0.2         0.3         0.4         0.5 $\infty$ over <i>i n</i> $a^{\bullet}$ 0.0         0.05         0.1         0.2         0.3         0.4         0.5 $\infty$ over <i>i</i> 6         8.490         7.274         6.342         5.021         4.139         3.514         3.052         2.698           9         4.555         4.059         3.659         3.054         2.624         2.302         2.055         1.876         1.548           12         3.418         3.094         2.826         2.412         2.108         1.876         1.548         1.269           27         2.083         1.929         1.797         1.8891         1.679         1.519         1.105           27         2.083         1.929         1.704         0.946         0.865         3.496         3.496         3.496           27         3.067         3.669         3.414         3.002         2.558         2.903           27         3.967         3.414         3.002         2.685 <td>values of termination temperatures for the Kinara 0, <i>n</i> potential with 0 <math>\leq</math> <i>n</i> <math>\leq</math> ∞ over a range 0<i>n</i><math>a^*</math>0.00.050.10.20.30.40.5∞ 0.60.768.4907.2746.3425.0214.1393.5143.0522.6982.42094.5554.0593.6593.0542.6242.3022.0551.8591.701123.4183.0942.8262.4122.1081.8761.6941.5481.429123.4183.0942.8262.4122.1081.8761.6941.5481.429272.0831.9291.7011.8019.9460.9460.8670.8030.7510.7060.668272.0831.9291.7011.1031.0440.9460.8670.8030.7510.7060.668615.65913.48111.8019.3987.7776.6205.7585.0944.56998.5127.6038.8665.7464.9414.3373.8693.4963.192126.4315.8285.3274.5493.9743.5333.1852.9052.674184.8484.4494.1123.5753.1682.8502.9052.674128.56316.371.5071.6091.5071.9221.922273.9673.6693.4143.0022.6852.4342.2302.0631.922<t< td=""><td>Values of termination temperatures for the Kinara 0, <i>n</i> potential with 0 <math>\leq n \leq \infty</math> over a range of values of values of termination temperatures for the Kinara 0, <i>n</i> of 0.05         0.1         0.2         0.3         0.4         0.5         0.6         0.7         0.8           <i>n</i>         a*         0.0         0.05         0.1         0.2         0.3         0.4         0.5         0.6         0.7         0.8           9         4.555         4.059         3.659         3.054         2.624         2.302         2.058         2.420         2.195           12         3.418         1.094         0.94         0.555         1.694         1.429         1.270         1.570           27         2.083         1.929         1.797         1.589         1.6679         1.515         1.333         1.229         1.112           27         2.083         1.929         1.797         1.589         1.422         1.299         1.706         1.570           27         2.033         1.044         0.946         0.865         5.746         4.941         1.909         1.105         1.034         0.975           27         2.036         3.142         2.357         4.549         3.974         3.596</td><td>Values of termination temperatures for the Kinara 6, n potential with <math>0 \le n \le \infty</math> over a range of values of a<sup>-1</sup>, 1           n         a<sup>-</sup>         0.0         0.05         0.1         0.2         0.3         0.4         0.5         0.6         0.7         0.8         1.0           9         4.555         0.1         0.2         0.3         0.4         0.5         0.1         0.8         1.0           12         3.418         3.059         3.054         3.054         2.5021         4.139         3.514         3.052         2.193         1.367         1.367           12         3.418         1.03         1.044         0.946         0.867         0.803         0.751         0.706         0.658         0.536         0.557         4.813         1.172         1.172         1.172</td><td>Values of termination temperatures for the Kinara 0, <i>n</i> potential with 0 5 <i>n</i> 5 <math>\infty</math> over a range of values of <i>a<sup>-</sup></i>, <i>I<sup>-</sup></i> = <i>K1/s</i><br/><i>n a<sup>+</sup></i> 0.0 0.05 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 1.0 1.5<br/>9 4.555 0.5 0.1 0.2 0.3 0.4 139 3.514 3.052 2.668 2.420 2.195 1.858 1.366<br/>12 3.418 3.094 2.825 2.4139 3.514 3.052 2.668 1.701 1.570 1.367 1.056<br/>18 2.558 1.929 1.797 1.585 1.422 1.294 1.190 1.105 1.034 0.973 0.876 0.717<br/><math>\infty</math> 1.171 1.103 1.044 0.946 0.867 0.803 0.751 0.706 0.668 0.636 0.582 0.493<br/>6 15.659 13.481 11.801 9.398 7.777 6.620 5.758 5.094 4.569 4.144 3.502 2.554<br/>9 8.512 7.603 6.866 5.746 4.941 4.337 3.869 3.496 3.194 2.943 2.553 1.950<br/>12 3.967 3.669 3.412 3.974 3.533 3.185 2.905 2.674 2.481 2.177 1.697<br/>27 3.967 3.669 3.412 3.974 3.533 3.185 2.905 2.674 2.481 2.177 1.697<br/>18 4.449 4.112 3.575 3.168 2.860 2.5758 5.094 4.569 4.144 3.502 2.554<br/>9 8.512 7.603 6.866 5.746 4.941 4.337 3.869 3.496 3.194 2.567 1.834 1.457<br/>27 3.967 3.669 3.414 3.002 2.688 2.599 2.674 2.481 2.177 1.697<br/>12 3.967 3.669 3.414 3.502 2.688 7.586 6.577 4.837 3.658<br/>1.507 1.400 1.310 1.233 1.167 1.059 0.877<br/>6 2.8.93 2.403 1.950 1.637 1.507 1.400 1.310 1.233 1.167 1.059 0.877<br/>6 2.8.93 2.503 2.2.013 17.644 14.669 1.2.527 10.920 9.675 8.685 7.880 6.657 4.835<br/>6 15.963 1.924 4.103 1.0101 8.639 7.550 6.712 6.048 5.596 5.577 4.827 3.658<br/>1.207 1.400 1.310 1.233 1.167 1.059 0.877<br/>8 4.244 6.186 7.880 6.657 4.827 3.658<br/>1.217 1.031 1.033 10.101 8.813 7.550 6.511 4.538 3.506 3.557 4.827 3.658<br/>1.217 1.033 1.0101 8.813 7.550 6.511 6.048 5.599 3.966 3.567 4.827 3.658<br/>1.217 1.033 1.9167 1.939 3.435<br/>1.2167 1.039 3.432 2.913 2.734 4.958 4.524 4.186 3.900 3.465 2.904 3.015 2.905 3.577 4.827 3.658<br/>1.217 7.609 7.033 6.540 5.741 5.124 4.653 4.528 3.906 3.559 3.906 3.453 2.916 3.659 2.906 3.557 4.827 3.658<br/>2.744 6.359 3.906 3.659 3.946 3.917 2.059 3.916 3.658 7.880 1.957 4.827 3.658<br/>2.759 2.908 2.663 2.663 2.663 2.663 2.665 2.577 4.827 3.658 2.944 4.958 4.916 7.055 0.877 4.827 3.658 2.908 2.577 4.827 3.558 1.577 4.827 3.558 1.577 4.828 2.958 2.94</td></t<></td> | values of termination temperatures for the Kinara 0, <i>n</i> potential with 0 $\leq$ <i>n</i> $\leq$ ∞ over a range 0 <i>n</i> $a^*$ 0.00.050.10.20.30.40.5∞ 0.60.768.4907.2746.3425.0214.1393.5143.0522.6982.42094.5554.0593.6593.0542.6242.3022.0551.8591.701123.4183.0942.8262.4122.1081.8761.6941.5481.429123.4183.0942.8262.4122.1081.8761.6941.5481.429272.0831.9291.7011.8019.9460.9460.8670.8030.7510.7060.668272.0831.9291.7011.1031.0440.9460.8670.8030.7510.7060.668615.65913.48111.8019.3987.7776.6205.7585.0944.56998.5127.6038.8665.7464.9414.3373.8693.4963.192126.4315.8285.3274.5493.9743.5333.1852.9052.674184.8484.4494.1123.5753.1682.8502.9052.674128.56316.371.5071.6091.5071.9221.922273.9673.6693.4143.0022.6852.4342.2302.0631.922 <t< td=""><td>Values of termination temperatures for the Kinara 0, <i>n</i> potential with 0 <math>\leq n \leq \infty</math> over a range of values of values of termination temperatures for the Kinara 0, <i>n</i> of 0.05         0.1         0.2         0.3         0.4         0.5         0.6         0.7         0.8           <i>n</i>         a*         0.0         0.05         0.1         0.2         0.3         0.4         0.5         0.6         0.7         0.8           9         4.555         4.059         3.659         3.054         2.624         2.302         2.058         2.420         2.195           12         3.418         1.094         0.94         0.555         1.694         1.429         1.270         1.570           27         2.083         1.929         1.797         1.589         1.6679         1.515         1.333         1.229         1.112           27         2.083         1.929         1.797         1.589         1.422         1.299         1.706         1.570           27         2.033         1.044         0.946         0.865         5.746         4.941         1.909         1.105         1.034         0.975           27         2.036         3.142         2.357         4.549         3.974         3.596</td><td>Values of termination temperatures for the Kinara 6, n potential with <math>0 \le n \le \infty</math> over a range of values of a<sup>-1</sup>, 1           n         a<sup>-</sup>         0.0         0.05         0.1         0.2         0.3         0.4         0.5         0.6         0.7         0.8         1.0           9         4.555         0.1         0.2         0.3         0.4         0.5         0.1         0.8         1.0           12         3.418         3.059         3.054         3.054         2.5021         4.139         3.514         3.052         2.193         1.367         1.367           12         3.418         1.03         1.044         0.946         0.867         0.803         0.751         0.706         0.658         0.536         0.557         4.813         1.172         1.172         1.172</td><td>Values of termination temperatures for the Kinara 0, <i>n</i> potential with 0 5 <i>n</i> 5 <math>\infty</math> over a range of values of <i>a<sup>-</sup></i>, <i>I<sup>-</sup></i> = <i>K1/s</i><br/><i>n a<sup>+</sup></i> 0.0 0.05 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 1.0 1.5<br/>9 4.555 0.5 0.1 0.2 0.3 0.4 139 3.514 3.052 2.668 2.420 2.195 1.858 1.366<br/>12 3.418 3.094 2.825 2.4139 3.514 3.052 2.668 1.701 1.570 1.367 1.056<br/>18 2.558 1.929 1.797 1.585 1.422 1.294 1.190 1.105 1.034 0.973 0.876 0.717<br/><math>\infty</math> 1.171 1.103 1.044 0.946 0.867 0.803 0.751 0.706 0.668 0.636 0.582 0.493<br/>6 15.659 13.481 11.801 9.398 7.777 6.620 5.758 5.094 4.569 4.144 3.502 2.554<br/>9 8.512 7.603 6.866 5.746 4.941 4.337 3.869 3.496 3.194 2.943 2.553 1.950<br/>12 3.967 3.669 3.412 3.974 3.533 3.185 2.905 2.674 2.481 2.177 1.697<br/>27 3.967 3.669 3.412 3.974 3.533 3.185 2.905 2.674 2.481 2.177 1.697<br/>18 4.449 4.112 3.575 3.168 2.860 2.5758 5.094 4.569 4.144 3.502 2.554<br/>9 8.512 7.603 6.866 5.746 4.941 4.337 3.869 3.496 3.194 2.567 1.834 1.457<br/>27 3.967 3.669 3.414 3.002 2.688 2.599 2.674 2.481 2.177 1.697<br/>12 3.967 3.669 3.414 3.502 2.688 7.586 6.577 4.837 3.658<br/>1.507 1.400 1.310 1.233 1.167 1.059 0.877<br/>6 2.8.93 2.403 1.950 1.637 1.507 1.400 1.310 1.233 1.167 1.059 0.877<br/>6 2.8.93 2.503 2.2.013 17.644 14.669 1.2.527 10.920 9.675 8.685 7.880 6.657 4.835<br/>6 15.963 1.924 4.103 1.0101 8.639 7.550 6.712 6.048 5.596 5.577 4.827 3.658<br/>1.207 1.400 1.310 1.233 1.167 1.059 0.877<br/>8 4.244 6.186 7.880 6.657 4.827 3.658<br/>1.217 1.031 1.033 10.101 8.813 7.550 6.511 4.538 3.506 3.557 4.827 3.658<br/>1.217 1.033 1.0101 8.813 7.550 6.511 6.048 5.599 3.966 3.567 4.827 3.658<br/>1.217 1.033 1.9167 1.939 3.435<br/>1.2167 1.039 3.432 2.913 2.734 4.958 4.524 4.186 3.900 3.465 2.904 3.015 2.905 3.577 4.827 3.658<br/>1.217 7.609 7.033 6.540 5.741 5.124 4.653 4.528 3.906 3.559 3.906 3.453 2.916 3.659 2.906 3.557 4.827 3.658<br/>2.744 6.359 3.906 3.659 3.946 3.917 2.059 3.916 3.658 7.880 1.957 4.827 3.658<br/>2.759 2.908 2.663 2.663 2.663 2.663 2.665 2.577 4.827 3.658 2.944 4.958 4.916 7.055 0.877 4.827 3.658 2.908 2.577 4.827 3.558 1.577 4.827 3.558 1.577 4.828 2.958 2.94</td></t<> | Values of termination temperatures for the Kinara 0, <i>n</i> potential with 0 $\leq n \leq \infty$ over a range of values of values of termination temperatures for the Kinara 0, <i>n</i> of 0.05         0.1         0.2         0.3         0.4         0.5         0.6         0.7         0.8 <i>n</i> a*         0.0         0.05         0.1         0.2         0.3         0.4         0.5         0.6         0.7         0.8           9         4.555         4.059         3.659         3.054         2.624         2.302         2.058         2.420         2.195           12         3.418         1.094         0.94         0.555         1.694         1.429         1.270         1.570           27         2.083         1.929         1.797         1.589         1.6679         1.515         1.333         1.229         1.112           27         2.083         1.929         1.797         1.589         1.422         1.299         1.706         1.570           27         2.033         1.044         0.946         0.865         5.746         4.941         1.909         1.105         1.034         0.975           27         2.036         3.142         2.357         4.549         3.974         3.596 | Values of termination temperatures for the Kinara 6, n potential with $0 \le n \le \infty$ over a range of values of a <sup>-1</sup> , 1           n         a <sup>-</sup> 0.0         0.05         0.1         0.2         0.3         0.4         0.5         0.6         0.7         0.8         1.0           9         4.555         0.1         0.2         0.3         0.4         0.5         0.1         0.8         1.0           12         3.418         3.059         3.054         3.054         2.5021         4.139         3.514         3.052         2.193         1.367         1.367           12         3.418         1.03         1.044         0.946         0.867         0.803         0.751         0.706         0.658         0.536         0.557         4.813         1.172         1.172         1.172 | Values of termination temperatures for the Kinara 0, <i>n</i> potential with 0 5 <i>n</i> 5 $\infty$ over a range of values of <i>a<sup>-</sup></i> , <i>I<sup>-</sup></i> = <i>K1/s</i><br><i>n a<sup>+</sup></i> 0.0 0.05 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 1.0 1.5<br>9 4.555 0.5 0.1 0.2 0.3 0.4 139 3.514 3.052 2.668 2.420 2.195 1.858 1.366<br>12 3.418 3.094 2.825 2.4139 3.514 3.052 2.668 1.701 1.570 1.367 1.056<br>18 2.558 1.929 1.797 1.585 1.422 1.294 1.190 1.105 1.034 0.973 0.876 0.717<br>$\infty$ 1.171 1.103 1.044 0.946 0.867 0.803 0.751 0.706 0.668 0.636 0.582 0.493<br>6 15.659 13.481 11.801 9.398 7.777 6.620 5.758 5.094 4.569 4.144 3.502 2.554<br>9 8.512 7.603 6.866 5.746 4.941 4.337 3.869 3.496 3.194 2.943 2.553 1.950<br>12 3.967 3.669 3.412 3.974 3.533 3.185 2.905 2.674 2.481 2.177 1.697<br>27 3.967 3.669 3.412 3.974 3.533 3.185 2.905 2.674 2.481 2.177 1.697<br>18 4.449 4.112 3.575 3.168 2.860 2.5758 5.094 4.569 4.144 3.502 2.554<br>9 8.512 7.603 6.866 5.746 4.941 4.337 3.869 3.496 3.194 2.567 1.834 1.457<br>27 3.967 3.669 3.414 3.002 2.688 2.599 2.674 2.481 2.177 1.697<br>12 3.967 3.669 3.414 3.502 2.688 7.586 6.577 4.837 3.658<br>1.507 1.400 1.310 1.233 1.167 1.059 0.877<br>6 2.8.93 2.403 1.950 1.637 1.507 1.400 1.310 1.233 1.167 1.059 0.877<br>6 2.8.93 2.503 2.2.013 17.644 14.669 1.2.527 10.920 9.675 8.685 7.880 6.657 4.835<br>6 15.963 1.924 4.103 1.0101 8.639 7.550 6.712 6.048 5.596 5.577 4.827 3.658<br>1.207 1.400 1.310 1.233 1.167 1.059 0.877<br>8 4.244 6.186 7.880 6.657 4.827 3.658<br>1.217 1.031 1.033 10.101 8.813 7.550 6.511 4.538 3.506 3.557 4.827 3.658<br>1.217 1.033 1.0101 8.813 7.550 6.511 6.048 5.599 3.966 3.567 4.827 3.658<br>1.217 1.033 1.9167 1.939 3.435<br>1.2167 1.039 3.432 2.913 2.734 4.958 4.524 4.186 3.900 3.465 2.904 3.015 2.905 3.577 4.827 3.658<br>1.217 7.609 7.033 6.540 5.741 5.124 4.653 4.528 3.906 3.559 3.906 3.453 2.916 3.659 2.906 3.557 4.827 3.658<br>2.744 6.359 3.906 3.659 3.946 3.917 2.059 3.916 3.658 7.880 1.957 4.827 3.658<br>2.759 2.908 2.663 2.663 2.663 2.663 2.665 2.577 4.827 3.658 2.944 4.958 4.916 7.055 0.877 4.827 3.658 2.908 2.577 4.827 3.558 1.577 4.827 3.558 1.577 4.828 2.958 2.94 |

TABLE I

180

| 2011       |
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| 28         |
| 08:55      |
| At:        |
| Downloaded |

TABLE I (continued)

| 8    | 0.801  | 1.596                                | 8.270   |
|------|--|--------------------------------------|---|
|      | 0.295  | 0.684                                | 1.988   |
|      | 0.477  | 1.067                                | 8.445   |
|      | 1.414  | 2.939                                | 2.151   |
|      | 3.216  | 6.526                                | 5.978   |
|      | m 9 9 9 1  | 501288<br>999999                     | 46868<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>28688<br>286888<br>286888<br>28688<br>28688<br>28688<br>28688<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>286888<br>2868888<br>2868888<br>286888<br>286888<br>286888<br>28688888<br>286888<br>286888<br>286888<br>28688888<br>286888<br>2868 |
| 2.0  | 15.61<br>13.66<br>13.63<br>13.43<br>14.19<br>14.19 | 30.67<br>27.04<br>28.25<br>32.15     | 195.59<br>213.59<br>241.80<br>314.53<br>453.88  |
| 1.5  | 16.973   | 33.206                               | 193.703   |
|      | 14.544   | 28.695                               | 206.268   |
|      | 14.181   | 28.082                               | 232.069   |
|      | 14.874   | 29.550                               | 301.131   |
|      | 16.830   | 33.502                               | 434.416   |
| 1.0  | 19.372   | 37.650                               | 193.359   |
|      | 16.045   | 31.488                               | 198.076   |
|      | 15.434   | 30.428                               | 220.626   |
|      | 15.994   | 31.672                               | 285.000   |
|      | 17.964   | 35.677                               | 410.800   |
| 0.8  | 20.928   | 40.518                               | 194.439   |
|      | 16.984   | 33.227                               | 194.806   |
|      | 16.204   | 31.865                               | 215.677   |
|      | 16.204   | 32.951                               | 277.774   |
|      | 18.641   | 36.972                               | 400.087   |
| 0.7  | 21.932   | 42.360                               | 195.501   |
|      | 17.576   | 34.320                               | 193.273   |
|      | 16.684   | 32.760                               | 213.184   |
|      | 17.089   | 33.739                               | 213.184   |
|      | 19.056   | 37.766                               | 394.476   |
| 0.6  | 23.148   | 44.586                               | 197.084   |
|      | 18.280   | 35.617                               | 191.878   |
|      | 17.251   | 33.813                               | 210.725   |
|      | 17.577   | 34.660                               | 270.228   |
|      | 19.538   | 38.687                               | 388.723   |
| 0.5  | 24.652   | 47.329                               | 199.387   |
|      | 19.131   | 37.181                               | 190.702   |
|      | 17.929   | 35.070                               | 208.356   |
|      | 18.156   | 35.748                               | 266.412   |
|      | 20.105   | 39.769                               | 382.863   |
| 0.4  | 26.555   | 50.787                               | 202.713   |
|      | 20.179   | 39.101                               | 189.869   |
|      | 18.754   | 36.595                               | 206.162   |
|      | 18.852   | 37.054                               | 262.643   |
|      | 20.781   | 41.058                               | 376.957   |
| 0.3  | 29.035   | 55.271                               | 207.533   |
|      | 21.500   | 41.513                               | 189.567   |
|      | 19.779   | 38.484                               | 204.271   |
|      | 19.704   | 38.649                               | 259.021   |
|      | 21.601   | 42.617                               | 371.099   |
| 0.2  | 32.394<br>23.216<br>21.085<br>20.769<br>22.613     | 61.308<br>44.628<br>40.639<br>44.540 | 214.624<br>190.090<br>202.886<br>255.700<br>365.438   |
| 0.1  | 37.179   | 69.842                               | 225.355   |
|      | 25.526   | 48.800                               | 191.932   |
|      | 22.801   | 44.017                               | 202.335   |
|      | 22.137   | 43.187                               | 252.926   |
|      | 23.893   | 46.966                               | 360.210   |
| 0.05 | 40.414   | 75.573                               | 232.831   |
|      | 27.009   | 51.462                               | 193.596   |
|      | 23.878   | 45.977                               | 202.534   |
|      | 22.977   | 44.747                               | 251.864   |
|      | 24.668   | 48.432                               | 357.873   |
| 0.0  | 44.502   | 82.771                               | 242.391   |
|      | 28.798   | 54.663                               | 195.963   |
|      | 25.153   | 48.290                               | 203.180   |
|      | 23.955   | 46.559                               | 251.111   |
|      | 25.560   | 50.118                               | 355.807   |
| 1 a* | 6<br>9<br>12<br>18<br>27                           | 6<br>9<br>12<br>27<br>27             | 6<br>112<br>27<br>27  |
|      | T.4*   | $T_{D}^{*}$                          | $T_{E}^{*}$   |
|      |  | 181                                  |   |

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TABLE II

Ratios of termination temperatures for the Kihara 6.n potential with  $6 \le n \le \infty$  over a range of values of  $a^*$ 

| J.   | STEPHENSON   | AND H. K. LEU   | JNG  |
|------|--|---|--|
| 2.0  | 1.853<br>1.825<br>1.809<br>1.792<br>1.780<br>1.780<br>1.749          | 3.486<br>3.393<br>3.343<br>3.343<br>3.343<br>3.247<br>3.150 | 14.168<br>15.512<br>17.146<br>20.630<br>25.944 |
| 1.5  | 1.870<br>1.846<br>1.833<br>1.833<br>1.818<br>1.807<br>1.780          | 3.541<br>3.463<br>3.463<br>3.373<br>3.373<br>3.338<br>3.254 | 12.428<br>13.768<br>15.315<br>18.556<br>23.460 |
| 1.0  | 1.884<br>1.867<br>1.858<br>1.858<br>1.847<br>1.839<br>1.818          | 3.583<br>3.530<br>3.501<br>3.468<br>3.442<br>3.381          | 10.424<br>11.734<br>13.167<br>16.107<br>20.509 |
| 0.8  | 1.888<br>1.875<br>1.867<br>1.867<br>1.859<br>1.852<br>1.852<br>1.836 | 3.589<br>3.553<br>3.531<br>3.531<br>3.441<br>3.441          | 9.533<br>10.819<br>12.194<br>14.990<br>19.156  |
| 0.7  | 1.888<br>1.878<br>1.872<br>1.872<br>1.865<br>1.859<br>1.845          | 3.589<br>3.562<br>3.545<br>3.545<br>3.511<br>3.511          | 9.064<br>10.335<br>11.678<br>14.396<br>18.435  |
| 0.6  | 1.888<br>1.881<br>1.876<br>1.871<br>1.871<br>1.871<br>1.857          | 3.586<br>3.558<br>3.558<br>3.558<br>3.535<br>3.535          | 8.579<br>9.832<br>11.141<br>13.776<br>17.681   |
| 0.5  | 1.887<br>1.883<br>1.880<br>1.877<br>1.877<br>1.874<br>1.865          | 3.578<br>3.573<br>3.569<br>3.558<br>3.558<br>3.540          | 8.077<br>9.309<br>10.581<br>13.127<br>16.890   |
| 0.4  | 1.884<br>1.884<br>1.883<br>1.883<br>1.882<br>1.881<br>1.881          | 3.565<br>3.574<br>3.577<br>3.580<br>3.581<br>3.577          | 7.556<br>8.764<br>9.996<br>12.448<br>16.060    |
| 0.3  | 1.879<br>1.883<br>1.885<br>1.885<br>1.887<br>1.888<br>1.888          | 3.544<br>3.569<br>3.582<br>3.595<br>3.602<br>3.614          | 7.015<br>8.195<br>9.384<br>11.735<br>15.187    |
| 0.2  | 1.872<br>1.881<br>1.886<br>1.891<br>1.894<br>1.894<br>1.894          | 3.514<br>3.558<br>3.582<br>3.606<br>3.622<br>3.653          | 6.451<br>7.601<br>8.742<br>10.986<br>14.268    |
| 0.1  | 1.861<br>1.877<br>1.885<br>1.894<br>1.900<br>1.911                   | 3.471<br>3.538<br>3.574<br>3.613<br>3.640<br>3.693          | 5.862<br>6.977<br>8.068<br>10.197<br>13.297    |
| 0.05 | 1.853<br>1.873<br>1.884<br>1.895<br>1.902<br>1.917                   | 3.442<br>3.523<br>3.567<br>3.614<br>3.614<br>3.714          | 5.556<br>6.654<br>7.718<br>9.786<br>12.791     |
| 0.0  | 1.844<br>1.869<br>1.881<br>1.895<br>1.904<br>1.923                   | 3.408<br>3.504<br>3.557<br>3.613<br>3.613<br>3.653<br>3.735 | 5.242<br>6.322<br>7.359<br>9.364<br>12.271     |
| n a* | 6<br>12<br>8<br>18<br>8<br>8<br>8<br>8<br>8                          | 6<br>12<br>8<br>27<br>8<br>8<br>8<br>8<br>8<br>8<br>7       | 6<br>112<br>27<br>27                           |
|      | $T_{c}/T_{B}$  | T <sub>F</sub> /T <sub>B</sub>                              | T <sub>A</sub> /T <sub>B</sub>                 |

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|               | n a* | 0.0     | 0.05    | 0.1     | 0.2     | 0.3     | 0.4     | 0.5     | 0.6     | 0.7     | 0.8     | 1.0     | 1.5     | 2.0     |
|---------------|------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| $T_D/T_B$     | 6    | 9.749   | 10.390  | 11.012  | 12.210  | 13.354  | 14.452  | 15.508  | 16.525  | 17.507  | 18.455  | 20.261  | 24.313  | 27.831  |
| i             | 6    | 12.000  | 12.678  | 13.339  | 14.611  | 15.823  | 16.983  | 18.093  | 19.158  | 20.182  | 21.166  | 23.029  | 27.163  | 30.708  |
|               | 12   | 14.128  | 14.862  | 15.576  | 16.950  | 18.257  | 19.505  | 20.696  | 21.837  | 22.930  | 23.980  | 25.960  | 30.327  | 34.049  |
|               | 18   | 18.201  | 19.058  | 19,893  | 21.496  | 23.018  | 24.466  | 25.846  | 27.163  | 28.422  | 29.628  | 31.895  | 36.865  | 41.069  |
|               | 27   | 24.060  | 25.114  | 26.138  | 28.103  | 29.964  | 31.730  | 33.410  | 35.009  | 36.536  | 37.995  | 40.731  | 46.699  | 51.720  |
| $T_{E}/T_{B}$ | 9    | 28.550  | 32,009  | 35.531  | 42.743  | 50.142  | 57.684  | 65.330  | 73.045  | 80.798  | 88.565  | 104.051 | 141.826 | 177.492 |
| i             | 6    | 43.018  | 47.694  | 52.461  | 62.233  | 72.257  | 82.465  | 92.799  | 103.209 | 113.652 | 124.093 | 144.861 | 195.253 | 242.550 |
|               | 12   | 59.445  | 65.468  | 71.598  | 84.119  | 96.909  | 109.881 | 122.962 | 136.092 | 149.220 | 162.306 | 188.224 | 250.624 | 308.690 |
|               | 18   | 98.164  | 107.272 | 116.503 | 135.252 | 154.264 | 173.418 | 192.616 | 211.779 | 230.845 | 249.763 | 287.007 | 375.672 | 457.208 |
|               | 27   | 170.814 | 185.569 | 200.468 | 230.575 | 260.917 | 291.317 | 321.637 | 351.769 | 381.629 | 411.151 | 469,000 | 605.543 | 730.000 |
| $T_F/T_C$     | 9    | 1.848   | 1.857   | 1.865   | 1.877   | 1.886   | 1.892   | 1.896   | 1.899   | 1.901   | 1.902   | 1.901   | 1.893   | 1.881   |
|               | 6    | 1.875   | 1.881   | 1.885   | 1.891   | 1.895   | 1.897   | 1.898   | 1.898   | 1.897   | 1.895   | 1.891   | 1.876   | 1.859   |
|               | 12   | 1.890   | 1.894   | 1.896   | 1.899   | 1.900   | 1.900   | 1.899   | 1.897   | 1.894   | 1.891   | 1.885   | 1.866   | 1.847   |
|               | 18   | 1.907   | 1.907   | 1.908   | 1.907   | 1.905   | 1.902   | 1.899   | 1.895   | 1.891   | 1.887   | 1.878   | 1.855   | 1.834   |
|               | 27   | 1.918   | 1.917   | 1.916   | 1.913   | 1.908   | 1.904   | 1.899   | 1.894   | 1.888   | 1.883   | 1.872   | 1.847   | 1.824   |
|               | 8    | 1.942   | 1.938   | 1.933   | 1.924   | 1.915   | 1.907   | 1.898   | 1.890   | 1.882   | 1.874   | 1.860   | 1.828   | 1.801   |

TABLE II (continued)

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|                       | n a*                                | 0.0  | 0.05  | 0.1   | 0.2  | 0.3  | 0.4   | 0.5  | 0.6  | 0.7   | 0.8  | 1.0   | 1.5   | 2.0  | 8  |
|-----------------------|-------------------------------------|--|---|---|--|--|---|--|--|---|--|---|---|--|--|
| $T_{D}/T_{A}$         | 6<br>12<br>18<br>27<br>8<br>27<br>8 | 1.860<br>1.898<br>1.920<br>1.944<br>1.961<br>2.000   | 1.870<br>1.905<br>1.926<br>1.947<br>1.947<br>1.963<br>2.000 | 1.879<br>1.912<br>1.930<br>1.951<br>1.951<br>1.966<br>2.000 | 1.893<br>1.922<br>1.939<br>1.957<br>1.957<br>1.957<br>1.957<br>2.000 | 1.904<br>1.931<br>1.946<br>1.962<br>1.973<br>2.000 | 1.913<br>1.938<br>1.951<br>1.956<br>1.966<br>1.976<br>2.000 | 1.920<br>1.944<br>1.956<br>1.969<br>1.978<br>2.000 | 1.926<br>1.948<br>1.960<br>1.972<br>1.980<br>2.000 | 1.931<br>1.953<br>1.954<br>1.974<br>1.974<br>1.982<br>2.000 | 1.936<br>1.956<br>1.977<br>1.977<br>1.983<br>2.000 | 1.944<br>1.962<br>1.972<br>1.980<br>1.986<br>1.986<br>2.000 | 1.956<br>1.973<br>1.980<br>1.987<br>1.987<br>1.991<br>2.000 | 1.964<br>1.980<br>1.986<br>1.991<br>1.991<br>2.000 | 1.999<br>2.009<br>2.011<br>2.010<br>2.010<br>2.000 |
| $T_D/T_C$             | 6<br>12<br>27<br>27                 | 5.286<br>6.422<br>7.509<br>9.604<br>12.634           | 5.606<br>6.768<br>7.890<br>10.058<br>13.202                 | 5.918<br>7.108<br>8.262<br>10.504<br>13.758                 | 6.523<br>7.766<br>8.987<br>11.368<br>14.838                          | 7.107<br>8.402<br>9.685<br>12.199<br>15.874        | 7.671<br>9.016<br>10.358<br>13.001<br>16.871                | 8.219<br>9.611<br>11.009<br>13.773<br>17.831       | 8.752<br>10.187<br>11.640<br>14.520<br>18.757      | 9.271<br>10.747<br>12.250<br>15.241<br>19.650               | 9.777<br>11.290<br>12.842<br>15.939<br>20.512      | 10.751<br>12.333<br>13.975<br>17.271<br>22.154              | 13.000<br>14.715<br>16.548<br>20.277<br>25.844              | 15.021<br>16.830<br>18.819<br>222.912<br>29.058    |  |
| $T_{\rm E}/T_{\rm A}$ | 6<br>12<br>27<br>27                 | 5.447<br>6.805<br>8.078<br>8.078<br>10.483<br>13.920 | 5.761<br>7.168<br>8.482<br>10.961<br>14.507                 | 6.061<br>7.519<br>8.874<br>11.425<br>15.076                 | 6.626<br>8.188<br>9.622<br>12.312<br>16.161                          | 7.148<br>8.817<br>10.327<br>13.146<br>17.180       | 7.634<br>9.409<br>10.993<br>13.932<br>18.139                | 8.088<br>9.968<br>11.621<br>14.673<br>19.043       | 8.514<br>10.497<br>12.215<br>15.374<br>19.896      | 8.914<br>10.997<br>12.778<br>16.036<br>20.701               | 9.291<br>11.470<br>13.310<br>16.662<br>21.463      | 9.981<br>12.345<br>14.295<br>17.819<br>22.868               | 11.412<br>14.182<br>16.365<br>20.245<br>25.811              | 12.528<br>15.636<br>18.004<br>22.163<br>28.137     | 21.135<br>27.390<br>31.350<br>37.861<br>47.366     |

TABLE II (continued)

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#### J. STEPHENSON AND H. K. LEUNG



FIGURE 2 Graphs of the scaled termination temperatures  $T^*$  for the Kihara 6,*n* potential plotted on a logarithmic scale versus the exponent  $N \equiv 3/n$  over the permitted range  $0 \le N \le \frac{1}{2}$  for selected values of  $a^* = 2a/\sigma$ .

as  $a^*$  increases. The defining formulae for  $T_A$ ,  $T_D$  and  $T_E$  involve only temperature derivatives of B, and so are not affected by the  $a^{*3}$  constant term. For large  $a^*$  the values and ratios of  $T_A$ ,  $T_D$  and  $T_E$  are determined by  $F_1$  alone, and the numerical results for  $a^* = \infty$  are entered in the final columns of Tables I and II.

Our detailed remarks on the ratios of termination temperatures are confined to the range  $0 < a^* < 1$ . For finite *n* the ratios  $T_C/T_B$  and  $T_F/T_C$ 



FIGURE 3 Graphs of the scaled termination temperatures  $T^*$  for the Kihara 6, *n* potential plotted on a logarithmic scale versus the hard-core ratio  $a^*$  over the useful range  $0 \le a^* \le 0.7$  for selected values of the repulsive exponent *n*.

initially increase slightly to weak maximum values close to 1.9 occurring at  $a^*$  values which depend on n. For n = 6 the maximum is near  $a^* \sim 1$  and moves to smaller  $a^*$  values as n increases, until  $n \approx 27$  beyond which these ratios decrease monotonically as  $a^*$  increases, while remaining greater than 1.82 and 1.86 respectively at  $a^* = 1$ . As  $a^*$  increases,  $T_A$  and  $T_D$  decrease steadily but remain finite, so that their ratio  $T_D/T_A$  increases steadily, while remaining less than 2. On the other hand,  $T_B$ ,  $T_C$  and  $T_F$  decrease relatively rapidly towards zero, so the ratios  $T_A/T_B$  and  $T_D/T_C$  increase with  $a^*$ . The initial decrease and subsequent increase in  $T_E$  are such that the ratios  $T_E/T_A$ and  $T_E/T_D$  also increase monotonically with  $a^*$ .

For a fixed value of  $a^*$  we may examine the *n* dependence of the termination temperatures and their ratios, which in graphical form, Figure 2, appears quite similar to that of the Lennard-Jones case analyzed in V with  $a^* = 0$ . For small  $a^*$  values below about 0.4,  $T_C/T_B$ ,  $T_F/T_B$  and  $T_F/T_C$  increase steadily with *n*, but when  $a^*$  is close to 0.5 these ratios pass through a maximum before decreasing towards finite limiting values as  $n \to \infty$ . Beyond  $a^* \approx 0.6$  the decrease is monotonic from n = 6 to  $n = \infty$ . The other termination temperature ratios in Table II appear to increase steadily as *n* increases from m = 6 to  $\infty$ , except for the ratio  $T_D/T_A$ , which passes through a weak maximum at very large values of  $a^*$ , and remains close to 2.

For large values of *n* we can extract the asymptotic forms of  $T_A$ ,  $T_D$  and  $T_E$  from the leading positive t = 0 terms and the leading negative t = 1 terms in the series expansion representation of *B* obtained by combining (9) with (6). To keep the working neat we write the second virial coefficient expansion in the form

$$B = a^{*3} + \sum_{s=1}^{3} \sum_{t=0}^{\infty} c_{st} (1/T^*)^{qt+s/n}, \qquad (16)$$

where the coefficients  $c_{st}$  may be identified explicitly by inspection of (9) and (6). Clearly  $c_{s0}$  are positive, and all other coefficients are negative. All the coefficients have finite limiting forms as  $n \to \infty$ , which may be extracted from (11) and (6). The divergences in  $T_A$ ,  $T_D$  and  $T_E$  arise entirely from the temperature differentiations involved in their definitions:

$$T_{\mathbf{A}}: \dot{\mathbf{B}} = 0, \tag{17a}$$

$$T_D: \ddot{B} = 0, \tag{17b}$$

$$T_E : \dot{B} + T \ddot{B} = 0. \tag{17c}$$

From (16) and (17), taking the leading terms t = 0 and t = 1 in the series, we easily find that

$$T_A^* \sim -n \frac{(\sum_{s=1}^3 c_{s1})}{(\sum_{s=1}^3 s c_{s0})},$$
 (18a)

$$T_D^* \sim -2n \frac{(\sum_{s=1}^3 c_{s1})}{(\sum_{s=1}^3 sc_{s0})},$$
 (18b)

$$T_E^* \sim -n^2 \frac{(\sum_{s=1}^3 c_{s1})}{(\sum_{s=1}^3 s^2 c_{s0})},$$
 (18c)

where the limiting forms as  $n \to \infty$  of the coefficients  $c_{s0}$  and  $c_{s1}$  must be inserted. It is now obvious that  $T_D/T_A \to 2$  as  $n \to \infty$  independent of *m* and  $a^*$ . This result is a further generalization to the Kihara potential type of second virial coefficient of the discussion leading to the same result in VI (16) and (17).<sup>4</sup> In the present case it is trivial to show that the limiting coefficients in (18) are

$$c_{30} = 1,$$
  $c_{20} = 3a^*,$   $c_{10} = 3a^{*2},$  (19a)

$$c_{31} = \frac{1}{(1 - m/3)}, \quad c_{21} = \frac{3a^*}{(1 - m/2)}, \quad c_{11} = \frac{3a^{*2}}{(1 - m)}, \quad (19b)$$

so the divergent termination temperatures are related by

$$T_{A}^{*} \sim \frac{1}{2} T_{D}^{*} \sim T_{E}^{*} \frac{(3+a^{*})}{n(1+a^{*})}$$
 (20a)

$$\sim n \left[ \frac{1}{(m-3)} + \frac{2a^*}{(m-2)} + \frac{a^{*2}}{(m-1)} \right] / (1+a^*)^2,$$
 (20b)

which reduce to the Lennard-Jones case when  $a^* = 0$ .

#### 4 CONCLUDING REMARKS

In this paper we have determined the effect on the termination temperatures and their ratios of introducing a hard-core into the Lennard-Jones m, n potential, thereby constructing the corresponding Kihara potential. For the chosen fixed value of the attractive exponent m = 6, one finds that over the entire permitted range of the repulsive exponent n and over the useful range 0 to 1 of the hard-core to molecular diameter ratio  $a^*$ , that the ratios  $T_c/T_B$ ,  $T_F/T_C$  and  $T_D/T_A$  lie within narrow bounds, with  $T_C/T_B$  and  $T_F/T_C$  not exceeding 1.905 and 1.918 respectively for values of n up to 27, and with  $T_D/T_A$ tending to 2 in the hard-core limit  $n \rightarrow \infty$ . Experimental values of these ratios for argon<sup>3</sup> are  $T_C/T_B \approx 1.921$  and  $T_F/T_C \approx 1.937$ , which considerably exceed all the entries in Table II up to n = 27. One would therefore anticipate achieving only rather limited precision in fitting experimental second virial coefficient data for argon using 6, 12 and 6, 18 Kihara and Lennard-Jones potentials.<sup>5,6</sup> The apparently greater success of the square-well potential<sup>6</sup> can be partially attributed to its ability to yield sufficiently high values of the ratios  $T_C/T_B$  and  $T_F/T_C$ , which are in better accord with the experimental values. One may refer to the entry in Table III in V with  $R^3 = 3.5$ , where R is the ratio of the outside diameter of the square-well to the molecular hardcore diameter, so

$$R \approx 1 + \frac{1}{a^*}$$
, or  $a^* \approx \frac{1}{(R-1)}$ . (21)

[The Kihara second virial coefficient in (6) approaches the square-well form at low temperatures when  $a^*$  is very large  $(R \sim 1)$ . Then one may take just the last two terms in (6) and insert the low temperature asymptotic form of  $F_1 \sim (-)e^{1/T^*}$ , to leading order (cf. V (40)). The behaviour of the termination temperatures  $T_B$ ,  $T_C$  and  $T_F$  is also similar for both models as  $a^* \to \infty$ ,  $R \to 1$ .] The experimental results for argon do not extend to the very high temperatures  $(\sim T_A)$  at which the second virial coefficient is expected to pass through a maximum, and so the necessity of using a more realistic potential and second virial coefficient does not yet become apparent. We shall study the experimental situation in more detail in another paper of this series.

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