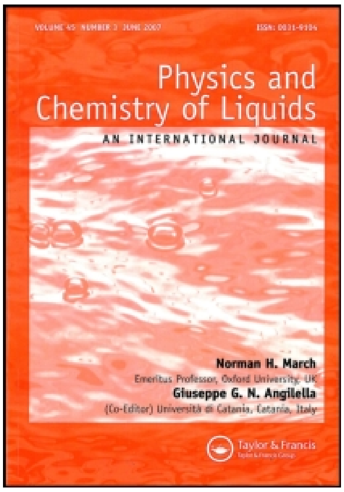

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Hard and Soft-Core Equations of State for Simple Fluids VII. Termination Temperatures for the Kihara Potential

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Hard and Soft-Core Equations of State for Simple Fluids

VII. Termination Temperatures for the Kihara Potential†

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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[1] 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 $\phi^K(r)$ by the simple recipe

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

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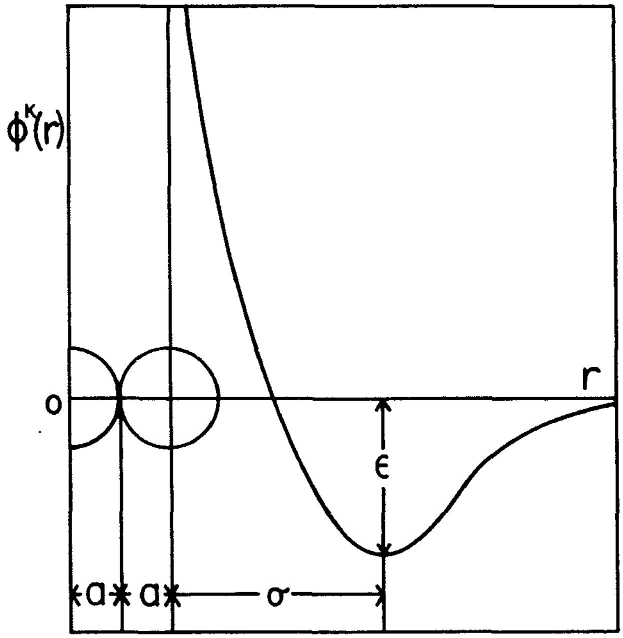

FIGURE 1 Schematic Kihara potential $\phi^K(r)$ plotted versus radial distance r. The hard-core diameter is $2a$ and the molecular diameter in the absence of a hard-core is σ.

illustrated schematically in Figure 1. In the case when ϕ 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.[2] The extra feature of the Kihara second virial coefficient is the presence of the hard-core radius a, so the Lennard-Jones molecular diameter σ, locating the minimum of the potential ϕ, 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.[1]

For selected values of a^* we will calculate the termination temperatures over the permitted range of values $m \leq n \leq \infty$ 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 m equal to 6, appropriate to the Heitler–London dispersion energy between neutral non-polar molecules. For the particular values $n = 6, 9, 12, 18, 27$ and ∞, 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 σ is the radial distance from the surface of the spherical hard-core to the point where the potential has a minimum of depth ε, Figure 1. (Kihara uses the symbol ρ_0 where we have used σ).

The classical integral formula for the second virial coefficient is

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

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:

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

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

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

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

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

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

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 $n \to m > 3$, the underlying Lennard–Jones m, n potential tends to the form

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

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

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

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.[3] 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 $n \lesssim 27$, but then increases again

TABLE I

Values of termination temperatures for the Kihara 6,n potential with $6 \leq n \leq \infty$ over a range of values of a^*. $T^* = kT/\varepsilon$

	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
T_B^*	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
	9	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
	18	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
	∞	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
T_C^*	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	2.042
	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	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
	∞	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
T_F^*	6	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
	9	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
	∞	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

TABLE I (continued)

	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_A^*	6	44.502	40.414	37.179	32.394	29.035	26.555	24.652	23.148	21.932	20.928	19.372	16.973	15.613	10.801
	9	28.798	27.009	25.526	23.216	21.500	20.179	19.131	18.280	17.576	16.984	16.045	14.544	13.660	10.295
	12	25.153	23.878	22.801	21.085	19.779	18.754	17.929	17.251	16.684	16.204	15.434	14.181	13.430	10.477
	18	23.955	22.977	22.137	20.769	19.704	18.852	18.156	17.577	17.089	16.671	15.994	14.874	14.192	11.414
	27	25.560	24.668	23.893	22.613	21.601	20.781	20.105	19.538	19.056	18.641	17.964	16.830	16.131	13.216
T_D^*	6	82.771	75.573	69.842	61.308	55.271	50.787	47.329	44.586	42.360	40.518	37.650	33.206	30.670	21.596
	9	54.663	51.462	48.800	44.628	41.513	39.101	37.181	35.617	34.320	33.227	31.488	28.695	27.042	20.684
	12	48.290	45.977	44.017	40.881	38.484	36.595	35.070	33.813	32.760	31.865	30.428	28.082	26.671	21.067
	18	46.559	44.747	43.187	40.639	38.649	37.054	35.748	34.660	33.739	32.951	31.672	29.550	28.253	22.939
	27	50.118	48.432	46.966	44.540	42.617	41.058	39.769	38.687	37.766	36.972	35.677	33.502	32.158	26.526
T_E^*	6	242.391	232.831	225.355	214.624	207.533	202.713	199.387	197.084	195.501	194.439	193.359	193.703	195.594	228.270
	9	195.963	193.596	191.932	190.090	189.567	189.869	190.702	191.878	193.273	194.806	198.076	206.268	213.592	281.988
	12	203.180	202.534	202.335	202.886	204.271	206.162	208.356	210.725	213.184	215.677	220.626	232.069	241.800	328.445
	18	251.111	251.864	252.926	255.700	259.021	262.643	266.412	270.228	274.029	277.774	285.000	301.131	314.532	432.151
	27	355.807	357.873	360.210	365.438	371.099	376.957	382.863	388.723	394.476	400.087	410.800	434.416	453.885	625.978

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^*

	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_C/T_B	6	1.844	1.853	1.861	1.872	1.879	1.884	1.887	1.888	1.888	1.888	1.884	1.870	1.853
	9	1.869	1.873	1.877	1.881	1.883	1.884	1.883	1.881	1.878	1.875	1.867	1.846	1.825
	12	1.881	1.884	1.885	1.886	1.885	1.883	1.880	1.876	1.872	1.867	1.858	1.833	1.809
	18	1.895	1.895	1.894	1.891	1.887	1.882	1.877	1.871	1.865	1.859	1.847	1.818	1.792
	27	1.904	1.902	1.900	1.894	1.888	1.881	1.874	1.867	1.859	1.852	1.839	1.807	1.780
	∞	1.923	1.917	1.911	1.899	1.887	1.876	1.865	1.855	1.845	1.836	1.818	1.780	1.749
T_F/T_B	6	3.408	3.442	3.471	3.514	3.544	3.565	3.578	3.586	3.589	3.589	3.583	3.541	3.486
	9	3.504	3.523	3.538	3.558	3.569	3.574	3.573	3.569	3.562	3.553	3.530	3.463	3.393
	12	3.557	3.567	3.574	3.582	3.582	3.577	3.569	3.558	3.545	3.531	3.501	3.420	3.343
	18	3.613	3.614	3.613	3.606	3.595	3.580	3.563	3.545	3.526	3.507	3.468	3.373	3.288
	27	3.653	3.647	3.640	3.622	3.602	3.581	3.558	3.535	3.511	3.488	3.442	3.338	3.247
	∞	3.735	3.714	3.693	3.653	3.614	3.577	3.540	3.506	3.473	3.441	3.381	3.254	3.150
T_A/T_B	6	5.242	5.556	5.862	6.451	7.015	7.556	8.077	8.579	9.064	9.533	10.424	12.428	14.168
	9	6.322	6.654	6.977	7.601	8.195	8.764	9.309	9.832	10.335	10.819	11.734	13.768	15.512
	12	7.359	7.718	8.068	8.742	9.384	9.996	10.581	11.141	11.678	12.194	13.167	15.315	17.146
	18	9.364	9.786	10.197	10.986	11.735	12.448	13.127	13.776	14.396	14.990	16.107	18.556	20.630
	27	12.271	12.791	13.297	14.268	15.187	16.060	16.890	17.681	18.435	19.156	20.509	23.460	25.944

TABLE II (continued)

	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
	9	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	6	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
	9	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	6	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
	9	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
	∞	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)

	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_A	6	1.860	1.870	1.879	1.893	1.904	1.913	1.920	1.926	1.931	1.936	1.944	1.956	1.964	1.999
	9	1.898	1.905	1.912	1.922	1.931	1.938	1.944	1.948	1.953	1.956	1.962	1.973	1.980	2.009
	12	1.920	1.926	1.930	1.939	1.946	1.951	1.956	1.960	1.964	1.967	1.972	1.980	1.986	2.011
	18	1.944	1.947	1.951	1.957	1.962	1.966	1.969	1.972	1.974	1.977	1.980	1.987	1.991	2.010
	27	1.961	1.963	1.966	1.970	1.973	1.976	1.978	1.980	1.982	1.983	1.986	1.991	1.994	2.007
	∞	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
T_D/T_C	6	5.286	5.606	5.918	6.523	7.107	7.671	8.219	8.752	9.271	9.777	10.751	13.000	15.021	
	9	6.422	6.768	7.108	7.766	8.402	9.016	9.611	10.187	10.747	11.290	12.333	14.715	16.830	
	12	7.509	7.890	8.262	8.987	9.685	10.358	11.009	11.640	12.250	12.842	13.975	16.548	18.819	
	18	9.604	10.058	10.504	11.368	12.199	13.001	13.773	14.520	15.241	15.939	17.271	20.277	22.912	
	27	12.634	13.202	13.758	14.838	15.874	16.871	17.831	18.757	19.650	20.512	22.154	25.844	29.058	
T_E/T_A	6	5.447	5.761	6.061	6.626	7.148	7.634	8.088	8.514	8.914	9.291	9.981	11.412	12.528	21.135
	9	6.805	7.168	7.519	8.188	8.817	9.409	9.968	10.497	10.997	11.470	12.345	14.182	15.636	27.390
	12	8.078	8.482	8.874	9.622	10.327	10.993	11.621	12.215	12.778	13.310	14.295	16.365	18.004	31.350
	18	10.483	10.961	11.425	12.312	13.146	13.932	14.673	15.374	16.036	16.662	17.819	20.245	22.163	37.861
	27	13.920	14.507	15.076	16.161	17.180	18.139	19.043	19.896	20.701	21.463	22.868	25.811	28.137	47.366

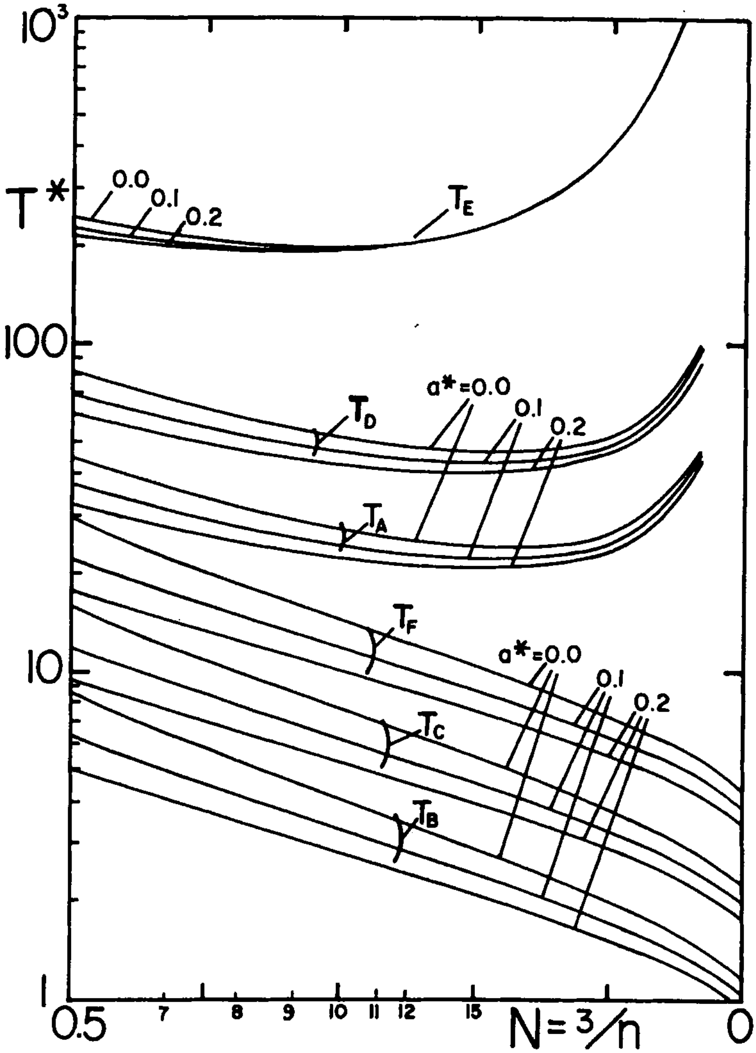

FIGURE 2 Graphs of the scaled termination temperatures T^* for the Kihara 6,n potential plotted on a logarithmic scale versus the exponent $N \equiv 3/n$ over the permitted range $0 \leq N \leq \frac{1}{2}$ for selected values of $a^* = 2a/\sigma$.

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

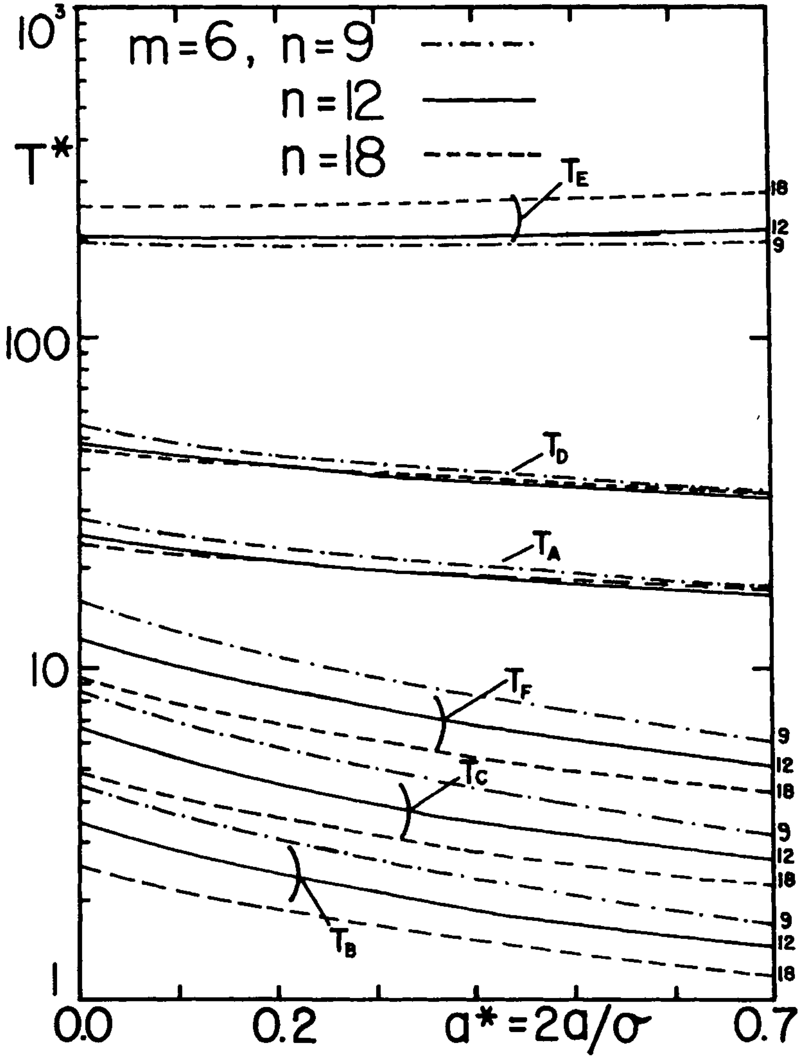

FIGURE 3 Graphs of the scaled termination temperatures T^* for the Kihara 6,n potential plotted on a logarithmic scale versus the hard-core ratio a^* over the useful range $0 \leq a^* \leq 0.7$ for selected values of the repulsive exponent n.

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 ∞, 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

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

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:

$$T_A: \dot{B} = 0, \tag{17a}$$

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

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

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

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

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

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

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).[4] In the present case it is trivial to show that the limiting coefficients in (18) are

$$c_{30} = 1, \qquad c_{20} = 3a^*, \qquad c_{10} = 3a^{*2}, \tag{19a}$$

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

so the divergent termination temperatures are related by

$$T_A^* \sim \tfrac{1}{2}T_D^* \sim T_E^* \frac{(3 + a^*)}{n(1 + a^*)} \tag{20a}$$

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

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 $n \to \infty$. Experimental values of these ratios for argon[3] 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.[5,6] The apparently greater success of the square-well potential[6] 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 hard-core diameter, so

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

[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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