

Second Virial Coefficients in Closed Form for a Kihara ($2m - m$)-Potential

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In the literature second virial coefficients are calculated by series expansions or by direct numerical integration. For thermodynamic quantities such as thermodynamic functions, analytical expressions are wanted. This paper gives closed formulas for the second virial coefficient for a convex-body Kihara potential of the type $U(\rho) = U_0[(\rho_0/\rho)^{2m} - 2(\rho_0/\rho)^m]$, where m can be a rational number $n > 3$. Furthermore, a number of related problems such as dielectric virial coefficients and Buckingham-Pople integrals are reduced to the same Laplace-transformation-type technique.

KEY WORDS: Kihara intermolecular potential; second virial coefficient.

1. INTRODUCTION

The second virial coefficient (SVC) is an important thermophysical quantity for the estimation and control of intermolecular potentials. Many different potentials have been developed [1]. Investigations of the intermolecular potential between diatomic and polyatomic molecules showed that a simple (14-7)-potential gives good results for the SVC, even if the molecular constants σ and ϵ did not fit well to scattering data [2].

Spherical symmetric potentials are not very well suited for the interaction of polyatomic molecules; shape, orientation, and spatial extension should be taken into account. As such ab initio calculations can be performed only for small molecules such as H_2-H_2 , several phenomenological models have been suggested [3]. The Kihara-convex body potential finds wide applications because of its simple form and its successful description of thermophysical properties [4, 5].

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- (1) It fits well the properties of the dilute gases [6] (a recent example is the interaction of N_2-N_2 , where it was better than more sophisticated models [7]).
- (2) It yields the coefficient C_6 of the van der Waals interaction of the right magnitude compared with spectroscopic measurements and quantum chemical calculations.
- (3) It resembles the Guggenheim–McGlashan potential from crystal studies [8].
- (4) It fits the interatomic potential shape for the test model Ar_2 well, though the repulsion energies are too high [9].

Up to now all calculations of the Kihara SCV were made either by numerical integration or by series expansion introduced by Lennard–Jones in 1927 [1]. The results are, therefore, given only numerically. Compact analytical expression for the SCV will be valuable. The present article aims at the following points:

- (1) to derive a closed analytical formula for the Kihara (12-6)-potential;
- (2) to generalize this approach to a $(2n-n)$ -potential, where n can be a rational number greater than 3, so that the results for the (14-7)-potential are included;
- (3) to give analytical formulas for the thermodynamic functions;
- (4) to give analytical formulas for dielectric and related second virial coefficients; and
- (5) to derive Buckingham–Pople integrals in the theory of the imperfect gas [10], including the shell model approximation.

2. CALCULATION TECHNIQUES

2.1. Sketch of the Kihara Potential

Kihara [11–13] started for polyatomic molecules with a “spherical core” potential

$$U(r) = \begin{cases} 4U_0 \left[\left(\frac{\sigma-d}{r-d} \right)^{12} - \left(\frac{\sigma-d}{r-d} \right)^6 \right], & \text{for } r > d \\ \infty, & \text{for } r \leq d \end{cases} \quad (1)$$

where

$$\begin{aligned}
 U(\sigma) &= 0 \\
 U_0 &= -\text{well depth} \\
 d &= \text{hard-core diameter}
 \end{aligned}$$

Spherical potentials are not suited for planar molecules such as benzene or long-chain hydrocarbons. Following the Isihara–Hadwiger theory of convex bodies, Kihara suggested an interaction potential of the form

$$\begin{aligned}
 U(\rho) &= \infty, \quad \text{for } \rho \leq 0 \\
 U(\rho) &= U_0 \left[\left(\frac{\rho_0}{\rho} \right)^{12} - 2 \left(\frac{\rho_0}{\rho} \right)^6 \right] \\
 U(\rho_0) &= -U_0 \equiv D_e
 \end{aligned} \tag{2}$$

where the independent distance variable ρ is no longer the distance between molecular centers but the minimum distance between convex hard cores. The body might have any shape as long as it is convex. From the known structure of a molecule it is possible to define cores adequate in size and shape; examples are the hexagon for benzene and the rod for chain molecules. While this potential takes into account nonspherical interactions in an average way, no orientation dependence of the depth of the well is usually taken into account. One counterexample is the article by Koide and Kihara [14], who calculated for the convex-body theory the potential energy curves for various orientations of diatomic molecules and CO_2 . Kihara derived the theory in various reviews [11–13, 15], so that all derivations can be omitted and one can start with the relevant formulas.

2.2. The Second Virial Coefficient for the Kihara Potential

The second virial coefficient is given as

$$B = \frac{1}{2} \int_0^\infty \{1 - \exp[-U(\rho)/kT]\} \langle S_{\text{core} + \rho + \text{core}} \rangle_{\text{AV}} d\rho + \langle V_{\text{core} + \text{core}} \rangle_{\text{AV}} \tag{3}$$

where $\langle S_{\text{core} + \rho + \text{core}} \rangle_{\text{AV}}$ is the averaged surface area of a convex body formed by the center of one molecule as it is moved around the other at a distance ρ between the impenetrable cores

$$\langle S_{\text{core} + \rho + \text{core}} \rangle_{\text{AV}} = 2[S + (4\pi)^{-1} M^2] + 4M\rho + 4\pi\rho^2 \tag{4}$$

$$\langle V_{\text{core} + \text{core}} \rangle_{\text{AV}} = 2[V + (4\pi)^{-1} MS] \tag{5}$$

where V , S , and M are the three fundamental measures of the convex body. For convenience they are given in Table I, also to illustrate the shape dependence.

For the potential a generalized Lennard-Jones form is assumed:

$$U(\rho) = \frac{C_n}{\rho^n} - \frac{C_m}{\rho^m} = U_0 \left[\frac{m}{n-m} \left(\frac{\rho_0}{\rho} \right)^n - \left(\frac{n}{n-m} \right) \left(\frac{\rho_0}{\rho} \right)^m \right] \tag{6}$$

$$C_n, C_m > 0, \quad n > m > 3 \tag{7}$$

Usually n and m are positive integers, but without loss of generality one can assume n and m as rational. One can evaluate the equations for the SVC in closed form as an infinite series of Γ functions. Convergence can, as was discussed by Mason and Spurling [4] and by Michels [16], be slow. With insertion of the fundamental measures of a convex body the SVC reads

$$2B = \int_0^\infty \{1 - \exp[-\beta U(\rho)]\} [4\pi\rho^2 + 4M\rho + 2(S + M^2/4\pi)] d\rho + 2(V + MS/4\pi) \tag{8}$$

and with the abbreviation

$$F_k = \int_0^\infty \{1 - \exp[-\beta U(\rho)]\} \rho^k d\rho \tag{9}$$

$$B = 2\pi F_2 + 2MF_1 + (S + M^2/4\pi) F_0 + (V + MS/4\pi) \tag{10}$$

Table I. Fundamental Measures for Convex Bodies^a

	V	S	M
Sphere of radius a	$4\pi a^3/3$	$4\pi a^2$	$4\pi a$
Regular tetrahedron inscribed in a unit sphere	$8\sqrt{3}/27 = 0.5132$	$8\sqrt{3}/3 = 4.6188$	$2\sqrt{6}\cos^{-1}(-1/3)$ $= 9.36015$
Regular octahedron inscribed in a unit sphere	$4/3 = 1.333$	$4\sqrt{3} = 6.9282$	$6\sqrt{2}\cos^{-1}(-1/3)$ $= 10.4450$
Perpendicular cylinder of height l , of base area f , and of base circumference c	fl	$2f + cl$	$\pi l + (\pi c/2)$
Thin plate as limit $l \rightarrow 0$	0	$2f$	$\pi c/2$
Thin rod as limit $f \rightarrow 0$; $c \rightarrow 0$	0	0	πl
Regular hexagon with side length l	0	$3\sqrt{3}l^2$	$3\pi l$

^a From Kihara [13]. As the table there is not easily available, the corresponding values are repeated here.

2.3. Analytical Integration in Closed Form

In the following text use is made of the Laplace transform-type integral [17]:

$$\begin{aligned} I[a; s; \nu] &= \int_0^{\infty} t^{\nu-1} \exp(-at^2 - st) dt \\ &= (2a)^{-\nu/2} \Gamma(\nu) \exp(s^2/8a) D_{-\nu} [s(2a)^{-1/2}] \end{aligned} \quad (11)$$

where $\Gamma(\nu)$ is the Γ function, and $D_{-\nu}[s(2a)^{-1/2}]$ the parabolic cylinder function.

This integral was used by Garrett [18] to calculate the SVC of the (12-6) Lennard-Jones potential and, independently, by Röscheisen and Witschel [19] for the partition function of an $(x^4 - x^2)$ anharmonic oscillator and by Wetzel and Witschel [20] for the SVC of the Woolley potential [21]. This is a multiparameter implicit molecular potential which gives good results for molecular constants.

$$U/U_0 = (\phi - 1)^2 - 1 \quad (12)$$

$$(r/r_0)^3 = \phi^{-1/2} \exp \left[-\sum_j 3e_j (\phi - 1)^j \right] \quad (13)$$

where $D_e = U_0$ is the dissociation energy, e_j are parameters to be adjusted to molecular spectra or to the derived Dunham or Sandeman coefficients, and r_0 is the equilibrium internuclear distance. For $e_j = 0$ it is

$$\left(\frac{r}{r_0} \right) = \phi^{-1/6}, \quad \phi = \left(\frac{r_0}{r} \right)^6 \quad (14)$$

and

$$U = U_0 \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right] \quad (15)$$

the (12-6) Lennard-Jones potential. Thus, the integration technique developed for the Woolley potential can be applied directly.

We consider

$$U(\rho) = U_0 \left[\left(\frac{\rho_0}{\rho} \right)^{2m} - 2 \left(\frac{\rho_0}{\rho} \right)^m \right] \quad (16)$$

where m can be a positive integer or a positive rational number.

Though not as general as the potential in Eq. (6), it generalizes the (12-6)-potential and includes for $\rho_0 = r_0$ and $\rho = r$ the (14-7)-potential mentioned in Section 1. The idea of taking n as rational number was for one example discussed by Kihara [12] but was not worked out in detail.

It remains to solve the integrals F_k , which is done after partial integration

$$F_k = -\frac{\beta}{k+1} \int_0^\infty \exp[-\beta U(\rho)] \left(\frac{dU}{d\rho}\right) \rho^{k+1} d\rho, \quad k \leq 2, \text{ integer} \quad (17)$$

As the algebra is straightforward, we give the final result only:

$$\begin{aligned} F_k = & -[2\beta/(k+1)] \rho_0^{k+1} U_0 \exp(\beta U_0/2) \\ & \times \left\{ (2\beta U_0)^{-[(2m-k-1)/2m]} \Gamma\left(\frac{2m-k-1}{m}\right) D_{-[(2m-k-1)/m]}[-(2\beta U_0)^{1/2}] \right. \\ & \left. - (2\beta U_0)^{-[(m-k-1)/2m]} \Gamma\left(\frac{m-k-1}{m}\right) D_{-[(m-k-1)/m]}[-(2\beta U_0)^{1/2}] \right\} \end{aligned} \quad (18)$$

Thus, this integral formula can be applied in all cases where integrals of the type F_k arise.

For completeness we give the final result for the second virial coefficient of an arbitrarily shaped Kihara potential with $m = 6$:

$$\begin{aligned} B = & -2\varepsilon\rho_0 \exp\left(\frac{\varepsilon}{2}\right) \\ & \times \left(\frac{2\pi}{3} \rho_0^2 (2\varepsilon)^{-1/4} \Gamma\left(\frac{1}{2}\right) \left\{ \frac{1}{2} (2\varepsilon)^{-1/2} D_{-3/2}[-(2\varepsilon)^{1/2}] \right. \right. \\ & \left. \left. - D_{-1/2}[-(2\varepsilon)^{1/2}] \right\} + M\rho_0 (2\varepsilon)^{-1/3} \Gamma\left(\frac{2}{3}\right) \left\{ \frac{2}{3} (2\varepsilon)^{-1/2} D_{-5/3} \right. \right. \\ & \left. \left. \times [-(2\varepsilon)^{1/2}] - D_{-2/3}[-(2\varepsilon)^{1/2}] \right\} + \left(S + \frac{M^2}{4\pi} \right) (2\varepsilon)^{-5/12} \Gamma\left(\frac{5}{6}\right) \right. \\ & \left. \times \left\{ \frac{5}{6} (2\varepsilon)^{-1/2} D_{-11/6}[-(2\varepsilon)^{1/2}] - D_{-5/6}[-(2\varepsilon)^{1/2}] \right\} \right) + \left(V + \frac{MS}{4\pi} \right) \end{aligned} \quad (19)$$

where $\varepsilon = \beta U_0$.

3. NUMERICAL EVALUATION

3.1. Parabolic Cylinder Functions

Though the result was given in a compact analytical form, a discussion of the numerical evaluation is necessary if parabolic cylinder functions are not available in the library of mathematical functions. Kihara [11] has given a very short table; longer tables have been given by Connolly and Kandalic [21].

A further advantage of the present analytical solution is the easy analytical calculation of arbitrary temperature derivatives using the well-known properties of parabolic cylinder functions. These are necessary for the evaluation of thermodynamic functions which include, in contrast to the customary calculations with the partition function for bound states, also metastable and continuum states. For example, the specific heat is written as (Ref. 3, p. 159)

$$\frac{\tilde{C}_p - \tilde{C}_p^0}{R} = - \left[\frac{B_2}{\tilde{V}} - \frac{(B - B_1)^2}{\tilde{V}^2} - \dots \right] \tag{20}$$

where $B_n = T^n(d^n B/dT^n)$, and all other symbols have their usual meaning. We recall [22]

$$U(a, x) = D_{-a-1/2}(x) \tag{21}$$

$$U'(a, x) + (x/2) U(a, x) + (a + 1/2) U(a + 1, x) = 0 \tag{22}$$

$$U'(a, x) - (x/2) U(a, x) + U(a - 1, x) = 0 \tag{23}$$

Subtraction yields

$$xU(a, x) - U(a - 1, x) + (a + 1/2) U(a + 1, x) = 0 \tag{24}$$

and straightforward application of these equations gives

$$U''(a, x) = [(x^2/4) + a] U(a, x) \tag{25}$$

For negative argument ($-x$) the analogous equations can be derived with the definition

$$V(a, x) = \pi^{-1} \Gamma[(1/2) + a] [\sin(\pi a) D_{-a-1/2}(x) + D_{-a-1/2}(-x)] \tag{26}$$

As the confluent hypergeometric series converges quickly, the following representation of $U(a, \pm x)$ may be helpful for numerical calculations:

$$\begin{aligned}
 U(a, \pm x) = & \frac{\sqrt{\pi} 2^{-1/4 - a/2} \exp(-x^2/4)}{\Gamma\left(\frac{3}{4} + \frac{1}{2}a\right)} M\left(\frac{a}{2} + \frac{1}{4}, \frac{1}{2}, \frac{x^2}{2}\right) \\
 & \mp \frac{\sqrt{\pi} 2^{-1/4 - a/2} x \exp(-x^2/4)}{\Gamma\left(\frac{1}{4} + \frac{1}{2}a\right)} M\left(\frac{a}{2} + \frac{3}{4}, \frac{3}{2}, \frac{x^2}{2}\right) \quad (27)
 \end{aligned}$$

where

$$M(a, b, z) = 1 + \frac{az}{b} + \frac{(a)_2 z^2}{(b)_2 2!} + \dots + \frac{(a)_n z^n}{(b)_n n!} + \dots \quad (28)$$

$$(a)_n = a(a+1) \cdots (a+n-1) \quad (29)$$

is Kummer's confluent hypergeometric function.

For a quick calculation one can also use the extended tables for $U(a, x)$, $V(a, x)$ given in Ref. 22. Using recursion relations and five-point Lagrange interpolation gives results of five-figure accuracy.

Epstein and Roe [23] and Michels [16] observed from the series for the (12-6)-potential that the result can be written in terms of confluent hypergeometric functions. They did not use integral transforms.

4. APPLICATIONS OF THE INTEGRAL TRANSFORM

- (1) In their monograph on the virial equation of state Mason and Spurling [4] gave many examples for the successful application of the (12-6) Kihara potential, which are not repeated here (see also Ref. 7). For illustration, we generated two short tables for Ar and Ne, (Tables II and III), which show good agreement

Table II. Second Virial Coefficient for Ar, Using a Spherical Kihara (12-6)-Potential; $\epsilon/k_B = 142.1$ K, $\sigma = 3.36 \times 10^{-10}$ m, hard-core diameter $d = 0.336 \times 10^{-10}$ m

T [K]	B	B_{exp}^a
105.5	-164.5	-167.8 \pm 1
143.16	-94.0	-94.4 \pm 1
153.16	-82.7	-82.9 \pm 1
203.16	-46.1	-46.5 \pm 1
223.16	-37.0	-37.3 \pm 1

^a From Dymond and Smith [24].

Table III. Second Virial coefficient for Ne, Using a Spherical Kihara (12-6)-Potential; $\epsilon/k_B = 39.6$ K, $\sigma = 2.74 \times 10^{-10}$ m, hard-core diameter $d = 0.105 \times 10^{-10}$ m

T (K)	B	B_{exp}^a
100	-5.8	-6.0 ± 1
200	+7.5	$+7.6 \pm 1$
300	+11.2	$+11.3 \pm 1$
400	+12.7	$+12.8 \pm 1$
600	+13.8	$+13.8 \pm 1$

a From Dymond and Smith [24].

with experimental values taken from the Dymond and Smith monograph [24]. The (12-6) Kihara potential was sufficient; an application of the general result for rational m was for the rare gases not necessary.

- (2) Pressure virial coefficients are only one example for virial expansions; the same technique can be applied also to electrical and optical properties. Expansion of the molar refraction in powers of ρ gives [25]

$$\frac{n^2 - 1}{n + 2} \rho^{-1} = A_R + B_R \rho + C_R \rho^2 \dots \quad (30)$$

where A_R , B_R , and C_R are the first, second, and third refractivity virial coefficients.

$$A_R = N\alpha^0/3\epsilon_0 \quad (31)$$

$$B_R = \frac{4\pi N^2}{3\epsilon_0} \int_0^\infty \left[\frac{1}{2} \alpha_{12}^{(0)}(r) - \alpha^{(0)} \right] \exp(-U_{12}/kT) r^2 dr \quad (32)$$

where

ϵ_0 = permittivity of free space

r = interatomic distance

$\alpha_{12}^{(0)}$ = pair polarizability

$\alpha^{(0)}$ = atomic polarizability

The integral in Eq. (32) is of the form of F_k so that Eq. (18) can be applied directly to the calculation of B_R . Even complicated

expressions for $\alpha_{12}^{(0)}(r)$ corresponding to a series expansion in terms of inverse powers of r can be included in the closed form calculation of B_R :

$$\alpha_{12}^{(0)}(r) - 2\alpha^{(0)} = 4[\alpha^{(0)}]^3 r^{-6} (4\pi\epsilon_0)^{-2} + 4[\alpha^{(0)}]^4 r^{-9} (4\pi\epsilon_0)^{-3} + \dots \quad (33)$$

- (3) Buckingham and Pople in their classical article on the statistical mechanics of imperfect polar gases defined an integral for the (12-6)-potential in the form [26]

$$\int_0^\infty r^{-k} \exp(-U/kT) r^2 dr = \frac{1}{12} r_0^{3-k} y^{-4} H_R(y) \quad (34)$$

$$U = 4U_0 \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right] \quad (35)$$

$$y = 2 \left(\frac{U_0}{kr} \right)^{1/2} \quad (36)$$

Tables for these integrals are given, in addition to those by the authors, by Gallagher and Klein [27], who calculated tables of the SVC and their first and second derivatives for the Stockmayer ($m, 6, 3$)-potential function. Recursion relations are given in the literature for the H_R which are obvious from the recursion relations for the parabolic cylinder functions. It is obvious that the integral Eq. (34) is identical to the integral Eq. (17) if $(dU/d\rho)$ is replaced by 1. Related to the spherical Kihara model is the spherical shell model, where the same integrals also are important. Spurling and DeRocco [10] compared both potentials and gave a qualitative explanation of why the Kihara potential can fit the interaction of dipolar and quadrupolar molecules even if these multipole forces are not included directly.

5. CONCLUSION

In this article analytical formulas could be derived for the second virial coefficient of the Kihara ($2m - m$)-potential using an integral transform. Furthermore, a number of related applications of the Kihara potential could also be given in closed form.

Though the solution of a one-dimensional integral with arbitrary complicated integrand has become trivial with modern computers, a closed-form solution is still important for qualitative considerations.

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