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

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Received November 15, 1989

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 \(U(p) = U_0[(\rho_0/p)^{2m} - 2(\rho_0/p)^{m}]\), 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 \(a\) and \(\varepsilon\) 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 \(\text{H}_2\). Several phenomenological models have been suggested [3]. The Kihara-convex body potential finds wide applications because of its simple form and its succesful description of thermophysical properties [4, 5].

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It fits well the properties of the dilute gases [6] (a recent example is the interaction of N2–N2, 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 Ar2 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

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

(1)