Exact Analytic Second Virial Coefficient for the Lennard-Jones Fluid

Byung Chan Eu

Department of Chemistry, McGill University,
801 Sherbrooke St. West, Montreal, QC H3A 2K6, Canada

(Date: September 18, 2009)

Abstract

An exact analytic form for the second virial coefficient, valid for the entire range of temperature, is presented for the Lennard-Jones fluid in this paper. It is derived by making variable transformation that gives rise to the Hamiltonian mimicking a harmonic oscillator-like dynamics. It is given in terms of parabolic cylinder functions or confluent hypergeometric functions. Exact limiting laws for the second virial coefficient in the limits of $T \to 0$ and $T \to \infty$ are also deduced for the Lennard-Jones fluid. They have the forms: $-16\sqrt{2\pi} v_0 \varepsilon \beta \left(\varepsilon \beta\right)^{3/2}$ as $T \to 0$ and $4\sqrt{2\Gamma\left(\frac{3}{4}\right)} v_0 \left(\varepsilon \beta\right)^{1/4}$ as $T \to \infty$, where $\varepsilon$ is the well depth and $v_0 = \pi \sigma^3 / 6$ with $\sigma$ denoting the size parameter of the potential, and $\beta = 1/k_B T$. 
I. INTRODUCTION

The statistical mechanical formula for the second virial coefficient can be easily computed by using a numerical method or, if temperature is sufficiently high, by a series expansion method\(^1\). As a matter of fact, a numerical table is available\(^1\) for the Lennard-Jones fluid. Therefore it does not pose a practical problem, although a low temperature expansion method is not available. Nevertheless, it would be interesting from the theoretical and pedagogical as well as aesthetic standpoints and also for the practical utility, if there were available exact analytic results for realistic interaction potential models, which are valid for the entire range of temperature. In the literature\(^2,3\), an exact analytic form for the second virial coefficient for the Lennard-Jones (LJ) fluid was obtained by using coordinate transformation in the cluster integral and reading off the integral table\(^4\) to obtain such a form. However, such transformed integrals have a deeper underlying dynamics that mimics a dynamical system obeying a harmonic oscillator potential, but reading off an integral table does not reveal the underlying dynamical structure therein. Therefore, if such a feature is made evident, one can gain a considerable insight into the dynamics of the LJ fluid\(^5\). The method employed also provides a valuable lesson on how to handle such integrals that might appear in the study of statistical mechanics of simple liquids. This method is not available elsewhere in the literature as far as this author is aware of.

In this paper, we present an exact analytic result for the second virial coefficient of the Lennard-Jones (LJ) fluid, which is obtained without using an expansion method and valid for the entire range of temperature. Exact limiting forms are also deduced therefrom as \(T \to 0\) and \(T \to \infty\). The second virial coefficient obtained is given in terms of parabolic cylinder functions or confluent hypergeometric functions, which are convergent and well defined for all values of temperature. The form presented for the second virial coefficient therefore is valid for all temperatures.

II. ANALYTIC SOLUTIONS

The second virial coefficient\(^6\) of the LJ fluid may be written in the reduced form

\[
B_2 = -12v_0 \int_0^\infty dx x^2 \left\{ \exp \left[ -4\varepsilon \beta \left( x^{-12} - x^{-6} \right) \right] - 1 \right\} \equiv -12v_0 I, \tag{1}
\]
where \( v_0 = \pi \sigma^3 / 6 \), the volume of the contact sphere of diameter \( \sigma \) (\( \sigma \) = size parameter of the LJ potential), \( \varepsilon \) is the well depth, and \( \beta = 1 / k_B T \), inverse temperature, \( k_B \) being the Boltzmann constant. The object of interest is the integral \( I \) in Eq. (1). With transformation of variables

\[
\alpha = \sqrt{\varepsilon \beta},
\]

\[
y = \frac{4 \alpha^2}{\pi^{1/2}},
\]

the integral \( I \) can be put into the form

\[
I (\alpha) = \frac{\sqrt{2 \alpha}}{12} J (\alpha),
\]

where \( J (\alpha) \) is defined by the integral

\[
J (\alpha) = \int_0^\infty dy y^{-5/4} (e^{-y} e^{2\alpha \sqrt{y}} - 1).
\]

This integral is usually evaluated either by a series expansion method or by a numerical method. Luckily, this integral is in a form readily available from the integral table in a known functional form. However, it can be analytically evaluated without using an integral table or expansion method, as will be shown below.

To achieve this aim, perform integration by parts once to obtain \( J (\alpha) \) in the form

\[
J (\alpha) = 4 \left[ \alpha B_{3/4} (\alpha) - B_{1/4} (\alpha) \right],
\]

where \( B_{1/4} \) and \( B_{3/4} \) are defined by the integrals

\[
B_{1/4} (\alpha) = \int_0^\infty dy y^{-1/4} e^{-y} e^{2\alpha \sqrt{y}},
\]

\[
B_{3/4} (\alpha) = \int_0^\infty dy y^{-3/4} e^{-y} e^{2\alpha \sqrt{y}}.
\]

These integrals are functions of parameter \( \alpha \). Differentiating these integrals with \( \alpha \), we obtain a pair of first-order differential equations

\[
\frac{dB_{1/4}}{d\alpha} = \frac{1}{2} B_{3/4} (\alpha) + 2 \alpha B_{1/4} (\alpha),
\]

\[
\frac{dB_{3/4}}{d\alpha} = 2 B_{1/4} (\alpha).
\]

This pair of differential equations can be combined to a single homogeneous second-order differential equation:

\[
\frac{d^2 \psi}{d\alpha^2} - 2 \alpha \frac{d\psi}{d\alpha} - 3 \psi = 0
\]
with the simplified notation
\[ \psi(\alpha) = B_{1/4}(\alpha). \]  
(12)

With the transformations
\[ z = \sqrt{2} \alpha \]  
(13)
and
\[ \psi(z) = e^{\frac{4}{z^2}} \phi(z) \]  
(14)
the differential equation (11) can be transformed into a standard form
\[ \frac{d^2 \phi}{dz^2} - \left( 1 + \frac{1}{4} z^2 \right) \phi(z) = 0. \]  
(15)

This is akin to the Schrödinger equation for a harmonic oscillator—of a negative eigenvalue in the present case. Therefore, it represents a particle of negative energy subjected to a parabolic potential. It, in fact, is a differential equation for parabolic cylinder functions\(^7,^8\).

Its two independent solutions, one even and the other odd function of \( z \), are:
\[ \begin{align*}
\phi_1(z) &= e^{-\frac{1}{4} z^2} M\left(\frac{3}{4}, \frac{1}{2}; \frac{1}{2} z^2\right) \\
&= e^{-\frac{1}{4} z^2} \sum_{n=0}^{\infty} \frac{\left(\frac{3}{4}\right)_n (z^2/2)^n}{(\frac{1}{2})_n n!}, \quad (16)
\end{align*} \]
\[ \begin{align*}
\phi_2(z) &= z e^{-\frac{1}{4} z^2} M\left(\frac{5}{4}, \frac{3}{2}; \frac{1}{2} z^2\right) \\
&= z e^{-\frac{1}{4} z^2} \sum_{n=0}^{\infty} \frac{\left(\frac{5}{4}\right)_n (z^2/2)^n}{(\frac{3}{2})_n n!}.
\end{align*} \]  
(17)

Here \( M(a, b, t) \) is a confluent hypergeometric function of Kummer\(^8\):
\[ M(a, b, t) = \sum_{n=0}^{\infty} \frac{(a)_n t^n}{(b)_n n!}, \]  
(18)
where
\[ (a)_0 = 1, \]
\[ (a)_n = a(a+1)(a+2)\cdots(a+n-1) \quad (n \geq 1). \]  
(19)

It is convergent for all values of \( t \). Its asymptotic form will be interest to us later: for positive real \( t \) it is given by
\[ M(a, b, t) = \frac{\Gamma(b)}{\Gamma(a)} e^t t^{a-b} \left[ \sum_{n=0}^{m-1} \frac{(b-a)_n (1-a)_n t^n}{n!} + O(t^{-m}) \right]. \]  
(20)
This formula may be used to compute the solutions for a large value of $t$ at fixed values of $a$ and $b$. The solutions $\phi_1(z)$ and $\phi_2(z)$, in fact, are parabolic cylinder functions, which are generic solutions for the Schrödinger equations for quadratic potentials. This implies that the dynamics of the LJ potential fluid closely resembles that of a harmonic (quadratic) potential.

Therefore the general solution for $\psi(z)$ is:

$$B_{1/4}(z) = \psi(z) = c_1 M\left(\frac{3}{4}, \frac{1}{2}, \frac{1}{2} z^2\right) + c_2 z M\left(\frac{5}{4}, \frac{3}{2}, \frac{1}{2} z^2\right),$$

(21)

where $c_1$ and $c_2$ are constants, which may be determined by considering the boundary conditions.

Noting that

$$\frac{d}{dt} M(a, b, t) = \frac{a}{b} M(a + 1, b + 1, t),$$

(22)

we find

$$J(\alpha) = 4 c_1 \left[ 6 \alpha^2 M\left(\frac{7}{4}, \frac{3}{2}, \alpha^2\right) - (1 + 4 \alpha^2) M\left(\frac{3}{4}, \frac{1}{2}, \alpha^2\right) \right]$$

$$+ 4 \sqrt{2} c_2 \alpha \left[ \frac{10}{3} \alpha^2 M\left(\frac{9}{4}, \frac{5}{2}, \alpha^2\right) + (1 - 4 \alpha^2) M\left(\frac{5}{4}, \frac{3}{2}, \alpha^2\right) \right],$$

(23)

The coefficients $c_1$ and $c_2$ can be determined by examining the limiting form of $J(\alpha)$ as $\alpha \to 0$ (a boundary condition). From Eq. (23)

$$J(\alpha) = 4 \left[ -c_1 + \sqrt{2} c_2 \alpha + O(\alpha^2) \right],$$

(24)

whereas direct evaluation of $J(\alpha)$ by series expansion of the factor $\exp\left(2\alpha \sqrt{y}\right)$ in Eq. (5) yields

$$J(\alpha) = -4 \Gamma\left(\frac{3}{4}\right) + 2 \Gamma\left(\frac{1}{4}\right) \alpha + O(\alpha^2),$$

(25)

where $\Gamma\left(\frac{1}{4}\right)$ and $\Gamma\left(\frac{3}{4}\right)$ are gamma functions: $\Gamma\left(\frac{1}{4}\right) = 3.62560 \cdots$ and $\Gamma\left(\frac{3}{4}\right) = 1.22541 \cdots$.

Comparing Eqs. (24) and (25), we find

$$c_1 = \Gamma\left(\frac{3}{4}\right),$$

(26)

$$c_2 = \frac{1}{2 \sqrt{2}} \Gamma\left(\frac{1}{4}\right).$$

(27)

Thus $J(\alpha)$ is now fully determined.
Putting together the results produced up to this point, we finally obtain the second virial coefficient in the form

\[-B_2/v_0\sqrt{2}(\varepsilon \beta)^{1/4} = 4\Gamma \left(\frac{3}{4}\right) \left[6\varepsilon \beta M \left(\frac{7}{4}, \frac{3}{2}, \varepsilon \beta\right) - (1 + 4\varepsilon \beta) M \left(\frac{3}{4}, \frac{1}{2}, \varepsilon \beta\right)\right]
\]
\[+ 2\Gamma \left(\frac{1}{4}\right) \sqrt{\varepsilon \beta} \left[\frac{10}{3} \varepsilon \beta M \left(\frac{9}{4}, \frac{5}{2}, \varepsilon \beta\right) + (1 - 4\varepsilon \beta) M \left(\frac{5}{4}, \frac{3}{2}, \varepsilon \beta\right)\right]. \tag{28}\]

This is the result we have set out to show for the LJ fluid. One may try to put this result into a simpler form by using the recurrence relations of Kummer’s functions, but the present form appears to be an optimum form. Rigorous limiting laws can be deduced for $B_2$ from Eq. (28).

The limiting form of $B_2$ as $T \to \infty$ or $\varepsilon \beta \to 0$ is easily deduced to be

\[B_2 = 4\sqrt{2}\Gamma \left(\frac{3}{4}\right) v_0 (\varepsilon \beta)^{1/4} [1 + O(\varepsilon \beta)]. \tag{29}\]

Thus $B_2 \to +0$ as $T \to \infty$. This means that there is a high temperature regime where $B_2$ is positive, and as $T \to \infty$, it vanishes on the positive side according to the law indicated.

On the other hand, the limiting form of $B_2$ as $T \to 0$ or $\varepsilon \beta \to \infty$ is deduced from the asymptotic forms of the confluent hypergeometric functions given in Eq. (20). We find

\[B_2(T) = -16\sqrt{2\pi} v_0 e^{\varepsilon \beta} (\varepsilon \beta)^{\frac{3}{2}} \left[1 + \frac{19}{16\varepsilon \beta} + \frac{105}{512 (\varepsilon \beta)^2} + \cdots \right]. \tag{30}\]

This limiting law shows that $B_2(T)$ tends to negative infinity according to the formula indicated and is negative below a certain point in $T$.

These limiting laws for $B_2$ are not easily deducible from Eq. (11) or Eq. (5) or the series expansion forms thereof, but they are simple to deduce if the exact analytic solution presented is made use of.

From the limiting behaviors (29) and (30) we can conclude there must exist a point in $T$ at which $B_2(T)$ crosses the $T$ axis (i.e., becomes zero), that is, the Boyle temperature $T_B = \beta_B^{-1}/k_B$ is defined, as usual, by

\[B_2(T_B) = 0. \tag{31}\]

According to the analytic result obtained, the Boyle point is determined from a real root of the equation

\[0 = 4\Gamma \left(\frac{3}{4}\right) \left[6\varepsilon \beta_B M \left(\frac{7}{4}, \frac{3}{2}, \varepsilon \beta_B\right) - (1 + 4\varepsilon \beta_B) M \left(\frac{3}{4}, \frac{1}{2}, \varepsilon \beta_B\right)\right]
\]
\[+ 2\Gamma \left(\frac{1}{4}\right) \sqrt{\varepsilon \beta_B} \left[\frac{10}{3} \varepsilon \beta_B M \left(\frac{9}{4}, \frac{5}{2}, \varepsilon \beta_B\right) + (1 - 4\varepsilon \beta_B) M \left(\frac{5}{4}, \frac{3}{2}, \varepsilon \beta_B\right)\right]. \tag{32}\]
Its numerical solution yields

\[ T_B^* = (\varepsilon \beta_B)^{-1} = 3.41793, \tag{33} \]

which should be compared with the literature value \( T_B^* = 3.42 \). This value is practically attained with the truncation of \( M(a, b, \varepsilon \beta_B) \) at \( n = 3 \).

In conclusion, we have presented an exact analytic second virial coefficient of the LJ fluids, which are valid for the entire temperature range, and its asymptotic behaviors (limiting laws) as \( T \to 0 \) or \( T \to \infty \). In view of the agreement of the Boyle temperature with the literature value deduced from the table for the second virial coefficient, it seems to be unnecessary to tabulate the numerical values of the second virial coefficients; it is rather trivial to do so. The utility of the result obtained is self-evident for some deductions one can make about thermodynamic properties of the LJ fluid. Compared to the method that simply reads off the integral table upon variable transformation in the integral for \( B_2 \), the present method provides considerable insights into the dynamics of the LJ liquid.

Finally, it is useful to note that the present exact analytic result for the second virial coefficient owes its existence to the mathematically favorable combination of the exponents 12 and 6 of the potential that produces the closed form for the differential equation for \( B_{1/4}(\alpha) \), Eq. (11). For other potential models consisting of repulsive and attractive branches with different exponents we do not obtain a closed differential equation, but a open hierarchy of first-order differential equations for integrals making up \( J(\alpha) \). The case of exponents (9, 6), namely, the LJ (9, 6) potential, produces a closed inhomogeneous second order differential equation, but its solutions do not seem to be simple and clean.

The present work was supported in part by the grants from the Natural Sciences and Engineering Research Council of Canada.

\begin{enumerate}
\item J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, \textit{Molecular Theory of Gases and Liquids} (Wiley, New York, 1954), p. 163.
\item A. J. M. Garrett, J. Math. A: Math. Gen. 13, 379 (1980).
\item M. L. Glasser, Phys. Lett. A 300, 381 (2002).
\item I. S. Gradshteyn and I. M. Ryzhik, \textit{Tables of Integrals, Series and Products}, 4th ed. (Academic, London, 1965).
\end{enumerate}
See B. C. Eu and H. Guerin, Can. J. Phys. 49, 486 (1971) in which the Schrödinger equation for the LJ (10,6) and (12,6) potentials are shown solvable analytically at zero energy in terms of a confluent hypergeometric function. At non-zero energy a perturbation method is applicable to compute the energy eigenvalue in a form reminiscent of the eigenvalues of an anharmonic oscillator.

T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956).

A. Erdelyi, ed., *Higher Transcendental Functions* (H. Bateman Manuscript Project) (McGraw-Hill, New York, 1953), Vols. 1 and 2.

M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (NBS, Washington, D.C., 1964).