The fourth virial coefficient for hard spheres in even dimension

Ignacio Urrutia

Departamento de Física de la Materia Condensada, Centro Atómico Constituyentes,
CNEA, Av. Gral. Paz 1499, 1650 Pcia. de Buenos Aires, Argentina and
Instituto de Nanociencia y Nanotecnología, CONICET-CNEA, CAC.

The fourth virial coefficient is calculated exactly for a fluid of hard spheres in even dimensions. For this purpose the complete star cluster integral is expressed as the sum of two three-folded integrals only involving spherical angular coordinates. These integrals are solved analytically for any even dimension \( d \), and working with existing expressions for the other terms of the fourth cluster integral, we obtain an expression for the fourth virial coefficient \( B_4(d) \) for even \( d \). It reduces to the sum of a finite number of simple terms that increases with \( d \).

I. INTRODUCTION

An essential problem in statistical mechanics of fluids at equilibrium is how to obtain its equation of state (EOS), given the interaction potential of the particles system. This basic question has not an answer yet. However, for low density systems, one has the pressure virial series

\[
P/k_B T = \rho + \sum_{n=2}^{\infty} B_n \rho^n ,
\]

the series expansion of the EOS in powers of the density (\( \rho \) is the density, \( T \) temperature and \( k_B \) the Boltzmann constant). Here, \( B_n \) is the \( n \)-th coefficient of the series studied by Mayer and others, an integral over the position of \( n \) particles. In such coefficients, the integrand is interpreted as the double-connected or irreducible cluster where particles are connected by the Mayer \( f \) function

\[
f_{ij} = f(r_{ij}) = \exp \left[ -W(r_{ij})/k_B T \right] - 1 ,
\]

and \( W \) is the pair interaction potential between particles. The lowest order virial coefficients are

\[
B_2 = -\frac{1}{2V} \int f_{12} dr_1 dr_2 = -\frac{1}{2},
\]

\[
B_3 = -\frac{1}{3V} \int f_{12} f_{13} dr_1 dr_2 dr_3 = -\frac{1}{3} \triangle
\]

and the Mayer graph representation of the fourth cluster integral is

\[
B_4 = -\frac{1}{8} \blacksquare - \frac{3}{4} \blacksquare - \frac{3}{8} \blacksquare.
\]

Hard sphere (HS) system is a minimal model of particle-particle interaction that introduces the excluded volume expressing that the minimum distance between two particles is finite. For HS the two-body interaction potential is \( W(r_{ij}) = 0 \) if \( r_{ij} > \sigma \) and \( W(r_{ij}) = +\infty \) if \( r_{ij} < \sigma \), with \( \sigma \) the HS diameter. The origin of HS as a model of fluid could probably be traced back nearly 150 years ago from van der Waals theory. The question of found the exact EOS of the HS, the minimal model of fluid, remains up today as an open problem. The hard sphere fluid was studied not only in dimensions three and two, but also in arbitrary integer dimension \( d \). The virial expansion of the HS EOS has been studied for more than a century, but has not been solved. The more recent advances were done fifteen years ago. Clisby and McCoy obtained \( B_4 \) for even dimensions \( d = 4, 6, 8, 10, 12 \) in 2004 and Lyberg calculated \( B_4 \) for odd dimensions \( d = 5, 7, 9, 11 \) in 2005. Previously, \( B_4 \) for dimension 3 was successfully calculated by Boltzmann and van Laar in 1899. (See [6–8] for the interesting history of the calculation of \( B_4 \) in 1899, that includes the

*Electronic address: iurrutia@cnea.gov.ar
contribution of van der Waals. The complete reference to the original papers is given in Ref. [9]. For dimension 2 it was calculated independently by Rowlinson [10] and Hemmer [11] in 1964. In the present work we solve \( B_4 \) for any even dimension.

Low order virial coefficients of HS are well known, \( B_2 (d) \) is half the volume of a sphere in the \( d \) dimensional space, 

\[
B_2 = \sigma^d \frac{\pi^{d/2}}{2^\nu (d/2 + 1)}.
\]  

(6)

\( B_3 \) was calculated initially for \( d = 3 \) and \( d = 2 \) [4,12] and latter for arbitrary dimension. It reduces to 

\[
\frac{B_4}{B_2^2} = \frac{2 \sigma^{2d}}{B \left( \frac{d+1}{2}, \frac{1}{2} \right)} B_3/4 \left( \frac{d+1}{2} \cdot \frac{1}{2} \right),
\]  

(7)

where \( B(a,b) = \frac{\Gamma(a) \Gamma(b)}{\Gamma(a+b)} \) is the beta function and \( B_x(a,b) \) is the incomplete beta function, in particular \( B_{3/4} \left( \frac{d+1}{2}, \frac{1}{2} \right) = 2 \int_0^{\pi/3} \sin^d \varphi \, d\varphi \). Exact expressions for two of the three diagrams of \( B_4 \) are known, the Mayer cluster integrals \( \square \) and \( \Box \). There exist several expressions for both, Luban and Baram calculated them for arbitrary dimension [9] and found 

\[
\frac{\square}{B_2^2} = \frac{2^{d+6}d}{(d+1)^2} \frac{B(d, \frac{d+1}{2})}{B \left( \frac{d+1}{2}, \frac{1}{2} \right)} 3 F_2 \left( \frac{1}{2} \cdot 1, \frac{1}{2} \cdot 1, 2; \frac{d+3}{2} \cdot 1 \right),
\]  

(8)

where \( 3 F_2 \) is the generalized hypergeometric function. Based on the expression obtained by Luban and later modified by Joslin [9,13] we found 

\[
\frac{\Box}{B_2^2} = -\frac{2^{d+3}d}{(d+1)^2} \frac{1}{B \left( \frac{d+1}{2}, \frac{1}{2} \right)} \int_0^{\pi/2} x^{d-1} \left[ B_{1-x} \left( \frac{d+1}{2}, \frac{1}{2} \right) \right]^2 dx,
\]  

(9)

with \( B_{1-x} \left( \frac{d+1}{2}, \frac{1}{2} \right) = 2 \int_0^{\pi\cos x} \sin^d \varphi \, d\varphi \). On the opposite, no general expression is known for the complete star cluster integral \( \blacksquare \).

In the case of even dimension \( d = 2\nu \) (being \( \nu \) a positive integer) one have the following closed expressions for \( B_2 \) and \( B_3 \)

\[
B_2 = \frac{\sigma^{2\nu} \pi^\nu}{2\nu!} \quad \text{and} \quad \frac{B_3}{B_2^2} = \frac{4}{\pi} - \frac{\sqrt{3}}{\pi} \sum_{k=1}^{\nu} \frac{(k-1)!}{(2k-1)!!} \left( \frac{3}{2} \right)^{k-1}.
\]  

(10)

To evaluate \( B_4 \) for arbitrary large even dimensions \( d = 2\nu \) it is convenient to give a closed form expression for each star Mayer diagrams of four points. Joslin simplified an expression found by Luban and later modified by Joslin [9,13] we obtain [13]

\[
\frac{\blacksquare}{B_2^2} = 8 - 8 \frac{\sum_{k=1}^{\nu} (k-1)!2^{k-1}}{\pi^2 k(2k-1)!!} \left[ 4 + \frac{\nu (2\nu)! 4^k (\nu + k - 1)!}{(2\nu - 1)!! (\nu + 2k)!} \right].
\]  

(11)

To derive a closed form expression of \( \blacksquare \) for even dimension we start from Eq. (8). In the Appendix A we solve this integral using change of variables and several identities for the integral of powers of trigonometric functions taken from Ref. [14]. Here we state the result 

\[
\frac{\blacksquare}{B_2^2} = -8 \left( 1 - \frac{\sqrt{3}}{2\pi} R_0 \right)^2 + \frac{4}{\pi^2} \left[ R_1 + \frac{8(2\nu)!}{(2\nu - 1)!!} R_2 \right],
\]  

(12)

with 

\[
R_0 = \sum_{k=1}^{\nu} \frac{(k-1)!}{(2k-1)!!} \left( \frac{3}{2} \right)^{k-1}, \]

\[
R_1 = \sum_{k=1}^{\nu} \frac{(k-1)!}{(2k-1)!!} \left( \frac{3}{2} \right)^{k}, \]

\[
R_2 = \nu! \sum_{k=1}^{\nu} \frac{(k-1)!2^{k-1}}{(2k-1)!!(2\nu + k)} \left[ 4^\nu (\nu + k - 1)! \frac{3^{k+\nu}}{4^k} \sum_{j=0}^{\nu} \frac{(\nu + k + j - 1)!}{4^j} \right].
\]
Here, \( R_0, R_1 \) and \( R_2 \) are rational numbers. The Eq. (11) is an explicit form that, for a given even dimension, only involves a finite number of simple operations (sum, product, quotient).

The rest of this paper is devoted to transform the complete star integral to a triple integral for any dimension \( d \) and to solve the complete star integral to obtain \( B_4 \) for even dimension. It is organized as follows. In Sec. [II] we transform the complete star diagram and find a new expression for it in terms of two three-folded integrals. In Sec. [III] we solve each of these integrals for even dimension \( d \) and reach an explicit form of the complete star in terms of a finite sum. Some mathematical details of the calculations are relegated to the appendices. In Sec. [IV] we give the exact expression of \( B_4 \) and evaluate it for some even dimensions as large as \( d = 1000 \). Sec. [V] is devoted to some final remarks.

II. THE TRANSFORMATION OF THE COMPLETE STAR

The full star diagram of four vertex contains six \( f \)-bonds. These bonds connect each pair of vertex. For HS it takes the form \( f_{ij} = -\Theta(\sigma - r_{ij}) \), being \( \Theta(x) \) the Heaviside function, with \( \Theta(x) = 1 \) if \( x \geq 0 \) and \( \Theta(x) = 0 \) if \( x < 0 \). The symmetric form of the star integral is

\[
\Box = V^{-1} \iiint f_{12} f_{13} f_{14} f_{23} f_{24} f_{34} d\mathbf{r}_{1234},
\]

(13)

with \( d\mathbf{r}_{1234} = d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \). Here, each vertex represents a particle whose position is integrated over the complete \( d \)-dimensional euclidean space, while each line is a \( f \)-bond. The spatial translation of the rigid cluster produces a volume term that can be integrated out (also, the rigid rotations produce solid angle terms). Hence,

\[
\Box = \iiint f_{12} f_{13} f_{14} f_{23} f_{24} f_{34} d\mathbf{r}_{12} d\mathbf{r}_{13} d\mathbf{r}_{14}
\]

(14)

\[
= \sigma^{3d} B_4^d,
\]

(15)

where \( B_4^d \) is a number. Our purpose is to find the dependence of this number with \( d \). Eq. (14) could also be rewritten in different forms by adopting a different set of integrating variables, for example, by replacing \( d\mathbf{r}_{12} d\mathbf{r}_{13} d\mathbf{r}_{14} \) with \( d\mathbf{r}_{12} d\mathbf{r}_{23} d\mathbf{r}_{34} \).

In the following we present a reformulation of the full star diagram that reduces it to three-folded integrals. On one hand, we take the derivative of Eq. (15) to obtain

\[
\frac{\partial}{\partial \sigma} \Box = \frac{3d}{\sigma} \Box.
\]

(16)

On the other hand, through applying the derivative to Eq. (13) in successive steps we transform \( \Box \) by noting that \( \frac{\partial}{\partial \sigma} f_{ij} = -\delta(\sigma - r_{ij}) = -\delta_{ij} \) (with \( \delta(x) \) the Dirac delta function) which introduce the \( \delta \)-bonds (corresponding to \( \frac{\partial}{\partial \sigma} f_{ij} = f'_{ij} = \delta_{ij} \)). This is the rule to transform a \( f \)-bond to \( \delta \)-bond. This process ends with the complete star diagram written as a sum over all the \( \delta \)-simple-connected diagrams, where the non-\( \delta \)-bonds remain unmodified and each diagram includes a weight function. To draw the graphs we introduce the open-box link for the \( \delta \)-bond, when it appears formally integrated, and the bold line for the same bond once the coordinate \( r_{ij} \) is integrated on. The transformation applied to \( \Box \) results in two integrals each of them three folded.

We take the derivative of Eq. (13) giving \( \frac{\partial}{\partial \sigma} \Box = -\frac{3}{2} \iiint \delta_{12} f_{13} f_{14} f_{23} f_{24} f_{34} d\mathbf{r}_{1234} \). Once we integrate on the \( r_{12} \) degree of freedom, that fixes \( r_{12} = \sigma \) and produces the factor \( \sigma^{d-1} \), we obtain

\[
\frac{\partial}{\partial \sigma} \Box = -6 \Box,
\]

(17)

\[
= -6 \sigma^{d-1} \Box.
\]

(18)

Here, the star marks one of the vertex at the ends of the bold-bond (any of them), that was a fixed position allowing the integration. It is interesting to note that the integrated bond in \( \Box \) has no dependence on \( \sigma \). We obtain

\[
\Box = -\frac{2\sigma^d}{d} \Box.
\]

(19)
The expression at the right of Eq. (19), once the full rotational symmetry is integrated on (producing the solid angle term), is equivalent to the two center formulation of the full star [15, 16].

(Second) We take the derivative \( \frac{\partial}{\partial \sigma} \) at both sides of Eq. (19), which gives

\[
\frac{3d}{\sigma} \llbracket = \frac{d}{\sigma} \llbracket - \frac{2\sigma^d}{d} \frac{\partial}{\partial \sigma} \llbracket .
\]

(20)

The last term is

\[
\frac{\partial}{\partial \sigma} \llbracket = -2 \llbracket - 2 \llbracket - \llbracket = -\sigma^{d-1} \left( 2 \sigma \llbracket (2 - \cos \varphi) + \llbracket \right),
\]

(21)

where we used the identity

\[
(\ldots) = \llbracket \sigma \llbracket (1 - \cos \varphi).
\]

(22)

This relation is derived in the Appendix B. In Eqs. (21) and (22) \( \varphi \) corresponds to the angle between both \( \delta \)-bonds. Note that term \( 2 - \cos \varphi \) is in our notation a term \( (2 - \cos \varphi) \) inside the diagram integrand (none dependence on the angular variables can appear outside of the integral given that all angular degrees of freedom are integrated). This notation using \( (\ldots) \) will be used from here on.

Replacing Eq. (21) in Eq. (20) we obtain

\[
\llbracket = 2 \llbracket (2 - \cos \varphi) + \llbracket .
\]

(23)

(Third) We take the derivative \( \frac{\partial}{\partial \sigma} \) at both sides of Eq. (23) which gives

\[
\frac{3d}{\sigma} \llbracket = 2d \llbracket + \frac{\sigma^{2d}}{d^2} \frac{\partial}{\partial \sigma} \left( 2 \llbracket (2 - \cos \varphi) + \llbracket \right).
\]

(24)

The derivative term in Eq. (24) is

\[
\frac{\partial}{\partial \sigma} (\ldots) = -2 \llbracket (2 - \cos \varphi) - 4 \llbracket (2 - \cos \varphi) - \llbracket, - \llbracket, - 2 \llbracket,
\]

\[
= -\sigma^{d-1} \left[ 2 \llbracket (2 - \cos \varphi) + 4 \llbracket ((2 - \cos \varphi_1) (1 - \cos \varphi_2))
\]

\[
+ \llbracket \left. (1 + 2 (1 - \cos \varphi_1) + 1 - \cos \varphi_1 - \cos \varphi_2) \right] \right]
\]

Now, we replace this result in Eq. (24) to obtain

\[
\llbracket = -\frac{3d}{\sigma^3} \left[ \llbracket (4 - 2 \cos \varphi) + \llbracket (2 - \cos \varphi_1) (2 - \cos \varphi_2) - 1 \right].
\]

(25)

Here, the stars are unnecessary and thus they were not written. This expression is one of the results of the present work, once the angular variables related with rigid rotations are integrated on the remaining are two three-folded angular integrals.

III. INTEGRATION OF THE COMPLETE STAR

The star integral is thus

\[
\llbracket = A (Y + U),
\]

(26)

where

\[
A = \frac{\sigma^{3d}}{d^3} \Omega_d \Omega_{d-1} \Omega_{d-2} \text{ with } \Omega_d = \frac{d \pi^{d/2}}{\Gamma(d/2 + 1)} = \frac{2dB_2}{\sigma^d}.
\]

(27)
where \( h_1 = 4 - 2 \cos \varphi_1 \) and \( \theta_{\text{max,}I} = \min \{ \arccos \left( \frac{4 - \cos \varphi_1 \cos \varphi_2}{\sin \varphi_1 \sin \varphi_2} \right), \pi \} \). A second form for \( Y \) is obtained through a change of variable. Let be \( \psi = \tan \varphi_2 \cos \theta, \cos \theta = \sin \varphi_2 \sin \theta \) (and let rename \( \varphi = \varphi_1 \)), the Eq. (28) transforms into the simpler expression

\[
Y = 2 \int_0^{\frac{\pi}{2}} \int_0^{\frac{\theta_{\text{max,}I}}{2}} h_1 \sin (\varphi)^{d-2} \sin (\varphi_2)^{d-2} \sin (\theta)^{d-3} \, d\theta \, d\varphi_1 \, d\varphi_2, \tag{29}
\]

with \( \theta_{\text{min}} = \arccos \left( \sqrt{1 - \left( \frac{1}{2} \sec \psi \right)^2} \right) \), here the integral in \( \varphi \) is trivial. The term related with \( \boxtimes \)

\[
U = \int_0^{\frac{\pi}{2}} \int_0^{\frac{\theta_{\text{max,II}}}{2}} h_{II} \sin (\varphi)^{d-2} \sin (\varphi_2)^{d-2} \sin (\theta)^{d-3} \, d\theta \, d\varphi_1 \, d\varphi_2, \tag{30}
\]

with \( h_{II} = 4 \left[ (2 - \cos \varphi_1)(2 - \cos \varphi_2) - 1 \right] \) and \( \theta_{\text{max,II}} = \arccos \left[ \tan \frac{\varphi_1}{2} \tan \frac{\varphi_2}{2} \right] \). Here the integral in \( \theta \) gives

\[
B_{1 - (\tan \frac{\varphi_1}{2} \tan \frac{\varphi_2}{2})^2} \left( \frac{d}{2} - 1, \frac{1}{2} \right). \]

Thus, for arbitrary \( d \geq 3 \) the Eq. (26) transforms to

\[
\boxed{\int_0^{\frac{\pi}{2}} \int_0^{\frac{\theta_{\text{max,II}}}{2}} h_{II} \sin (\varphi)^{d-2} \sin (\varphi_2)^{d-2} \sin (\theta)^{d-3} \, d\theta \, d\varphi_1 \, d\varphi_2,} \tag{31}
\]

Last equation and Eqs. (26)(29)(30) are convenient for both numerical and analytical integration, even for non-integer \( d \). In the following we focus on even dimension \( d = 2m + 4 \) with \( m \) any non-negative integer, i.e, even \( d \geq 4 \). The rest of this Section is devoted to evaluate \( Y \) and \( U \).

### Integration of \( Y \) for even dimensions

We expand the binomial \( \left[ 1 - \left( \frac{\sec \psi}{2} \right)^2 \right]^{m+1} \) to obtain

\[
Y = \frac{1}{m+1} \int_0^{\frac{\pi}{2}} \int_0^{\frac{\theta_{\text{max,II}}}{2}} h_1 \sin (\varphi)^{2m+2} \left[ 1 + \sum_{n=1}^{m+1} \frac{(m+1) (-1)^n 4^{-n} \cos (\psi)^{-2n}}{\binom{m+1}{n}} \right] \, d\psi \, d\varphi. \tag{32}
\]

Next, we solve the integral in \( \psi \) variable. Let \( n \) be any positive integer, according to[19]

\[
\int \cos (x)^{-2n} \, dx = \frac{\sin x}{2n-1} \left[ \cos (x)^{-2n+1} + \sum_{k=1}^{n-1} \frac{2k \prod_{i=1}^{k} (n-i) (2n-2i-1)}{\prod_{i=1}^{n-1} (2n-2i-1)} \cos (x)^{-2n+2k+1} \right]. \tag{33}
\]

One finds

\[
\int_0^{\frac{\pi}{2}} \cos (\psi)^{-2n} \, d\psi = \frac{1}{2} B_{\cos (\frac{\varphi}{2})^2} \left( \frac{1}{2} - n, \frac{1}{2} \right) - \frac{1}{2} B_{\frac{1}{2}} \left( \frac{1}{2} - n, \frac{1}{2} \right) \tag{34}
\]

\[
= \sqrt{3} C - \frac{\sin \frac{\varphi}{2}}{2n-1} \left[ \cos \left( \frac{\varphi}{2} \right)^{-2n+1} + \sum_{k=1}^{n-1} \frac{2k \prod_{i=1}^{k} (n-i) \cos \left( \frac{\varphi}{2} \right)^{-2n+2k+1}}{\prod_{i=1}^{n-1} (2n-2i-1)} \right], \tag{35}
\]

being \( \Omega_d \) the surface area of the unit sphere in the \( d \) dimensional space (with \( \Omega_k = 1 \) if \( k < 1 \)).
here \( C = \frac{4^{n-1}}{2n-1} \left(1 + \sum_{k=1}^{n-1} \frac{2^k \prod_{i=1}^{k-1} (n-i)}{4^k \prod_{i=0}^{k-1} (2n-2i-1)} \right)\). We introduce the shortcut \( K = 4 \sum_{n=1}^{m+1} \binom{m+1}{n} (-4)^{-n} C\), i.e. \( K = \sum_{n=1}^{m+1} \binom{m+1}{n} \left(\frac{(-1)^{n-1}}{2n-1} \left[1 + \sum_{k=1}^{n-1} \frac{2^k \prod_{i=0}^{k-1} (n-i)}{4^k \prod_{i=0}^{k-1} (2n-2i-1)} \right]\right)\), to obtain,

\[
\int_0^\frac{\pi}{2} \int_{\theta_{mn}}^\frac{\pi}{2} \sin \theta \cos(\psi)^{2m+1} d\psi d\theta = \frac{2^{-1}}{m+1} \left(\sqrt{3} + \frac{\pi}{3} - \frac{\psi}{2}\right) - \frac{2^{-1}}{m+1} \sum_{n=1}^{m+1} \binom{m+1}{n} \frac{(-1)^n 4^{-n}}{2n-1} \times 
\sin \frac{\psi}{2} \left[\cos \left(\frac{\psi}{2}\right)^{-2n+1} + \sum_{k=1}^{m-1} \frac{2^k \prod_{i=1}^{k-1} (n-i)}{2n-1-2i} \cos \left(\frac{\psi}{2}\right)^{-2n+2k+1}\right].
\] (36)

To solve the integral in \( \psi \) we separate the linear term \( \sqrt{3} K + \frac{\pi}{3} - \frac{\psi}{2} \) from that involving \( \sin \frac{\psi}{2} \) and \( \cos \frac{\psi}{2} \).

\[ L = \int_0^\frac{\pi}{2} \left(\sqrt{3} K + \frac{\pi}{3} - \frac{\psi}{2}\right) (4 - 2 \cos \phi) \sin(\phi)^{2m+2} d\phi \] splits in four integrals: \( (\sqrt{3} K + \frac{\pi}{3}) \int_0^\frac{\pi}{2} \sin(\phi)^{2m+2} d\phi, -\left(\sqrt{3} K + \frac{\pi}{3}\right) \times \int_0^\frac{\pi}{2} \cos \phi \sin(\phi)^{2m+2} d\phi, -2 \int_0^\frac{\pi}{2} \phi \sin(\phi)^{2m+2} d\phi, \) and \( \int_0^\frac{\pi}{2} \phi \cos \phi \sin(\phi)^{2m+2} d\phi. \) Each of them is solved separately in Appendix [C]. The result is

\[
L = \frac{\pi^2 (2m+1)!}{3 2^{m+1}} \left(\frac{1}{2^m (m+2)} - \frac{3}{4} K + \frac{(3/4)^{m+1}}{2m+3} - Q_0 + \frac{(3/4)^{m+1}}{2m+3}\right) - \frac{2^{m+1} (m+1)!}{(2m+3) 2^{m+1}} \left[\frac{(3/4)^{m+1}}{2m+3} - Q_1 + \frac{Q_2}{(2m+3)^2}\right],
\] (37)

with

\[
K = \sum_{n=1}^{m+1} (-1)^n \binom{m+1}{n} \prod_{k=0}^{n-1} \frac{\prod_{i=1}^{k} (n-i)}{2k \prod_{i=0}^{k} (2n-2i-1)};
Q_0 = \sum_{k=0}^{m} \frac{(3/4)^{m-k}}{2^k \prod_{i=0}^{k} (2m-2i+1)};
Q_1 = \sum_{k=0}^{m} \frac{(3/4)^{m-k}}{2^k (m+k) \prod_{i=0}^{k} (m-i+1)};
Q_2 = \sum_{k=0}^{m} \frac{(3/4)^{m-k}}{2^k \prod_{i=0}^{k} (2m-2i+1)}.
\] (38)

Here \( K, Q_0, Q_1 \) and \( Q_2 \) are rational numbers. Besides, to evaluate \( L \) for a given even dimension one has to add \( \sim 2d \) terms.

Now, we focus on the integration of the term including trigonometric functions of \( \phi \). Using the shortcut \( \phi = \frac{\pi}{2} \), the terms are of the type \( \int_0^\pi 2h(\sin \phi \cos \phi)^{2m+2} \sin \phi \cos^{-2n+1} \phi d\phi \) with \( h = 2 + 4 \sin^2 \phi \). Thus, we need to solve integrals like \( \int_0^\pi \sin(\phi)^{2l+1} \phi \sin(-2n+1) \phi d\phi \).

Let us assume \( p \) and \( q \) be non-negative integers to introduce \( D \) \( (p, q) \equiv \int_0^\pi \sin(\phi)^p \cos(\phi)^q d\phi = 2^p B_p \left(\frac{p+1}{2}, \frac{q+1}{2}\right) \). Let \( n \) be any positive integer and \( q \in \mathbb{R}_{\{1, -3, ..., -2(n-1)\}} \). According to [20] we have the identity

\[
\int_0^\pi \sin(x)^{2n+1} \cos(x)^q dx = \frac{2n! (q-1)!!}{(2n+q+1)!!} \cos(u)^{q+1} \left(\sin(u)^{2n} + \sum_{k=1}^{n} \frac{2^k \prod_{i=0}^{k-1} (n-i)}{2n+q-2i-1} \sin(u)^{2n-2k}\right).
\] (39)

For \( q = 2l+1 \), with \( n \) and \( l \) positive integers, we obtain

\[
D \left(2n+1, 2l+1\right) = \frac{n!}{2(n+l+1)!} - \frac{(3/4)^{l+1}}{4^n 2(2n+l+1)} \left[1 + \sum_{k=1}^{n} \frac{4^k \prod_{i=0}^{k-1} (n-l)}{2n+q-2i-1} \sin(u)^{2n-2k}\right].
\] (40)
Let $n$ be any positive integer and $q \in \mathbb{R}_{-\{2,-4,...,-2n\}}$. According to [21] we have
\[
\int_0^u \sin(x)^{2n} \cos(x)^q \, dx = -\frac{\cos^{q+1} u}{2n+q} \left[ \sin(u)^{2n-1} + \sum_{k=1}^{n-1} \frac{\prod_{i=1}^k (2n-2i+1)}{\prod_{i=1}^k (2n+2i-2l)} \sin(u)^{2n-2k-1} \right] + \frac{(2n-1)!!q!!}{(2n+q)!!} \int_0^u \cos(x)^q \, dx ,
\] (41)
\[
\int_0^u \cos(x)^{2l} \, dx = \frac{u(2l-1)!!}{2l!!} + \frac{\sin u}{2l} \left[ \cos(u)^{2l-1} + \sum_{k=1}^{l-1} \frac{\prod_{i=1}^k (2l-2i+1)}{2^k \prod_{i=1}^k (l-i)} \cos(u)^{2l-2k-1} \right] .
\] (42)
Thus, for $q = 2l$, with $n$ and $l$ positive integers we obtain
\[
D(2n,2l) = \frac{\sqrt{3} 3^{l-1} (l-1)! (2n-1)!!}{2^{2l+n+1}(l+n)!} \left[ 1 + \sum_{k=1}^{n-1} \frac{(\frac{3}{2})^k \prod_{i=1}^k (2l-2i+1)}{\prod_{i=1}^k (l-i)} \right] + \frac{\pi (2l-1)!! (2n-1)!!}{2^{l+n}6(l+n)!} - \frac{\sqrt{3} 3^l}{2^{2l+2n+1}(l+n)!} \left[ 1 + \sum_{k=1}^{n-1} \frac{\prod_{i=1}^k (2n-2i+1)}{\prod_{i=1}^k (l+n-i)} \right] .
\] (43)
To evaluate terms like $\int_0^{\frac{\pi}{2}} 2h \sin (2\phi)^{2m+2} \sin (\phi) \cos (\phi)^{-2l+1} d\phi$ we introduce
\[
g_1(m,l) = 4^{-m-2} \int_0^{\frac{\pi}{2}} 2h \sin (2\phi)^{2m+2} \sin (\phi) \cos (\phi)^{-2l+1} d\phi = \int_0^{\frac{\pi}{2}} \left( 1 + 2 \sin (\phi)^2 \right) \sin (\phi)^{2m+3} \cos (\phi)^{2m-2l+3} d\phi = D(2m+3,2m-2l+3) + 2D(2m+5,2m-2l+3) .
\] (44)
Collecting the partial results, we find
\[
Y = \frac{L}{m+1} - \frac{M}{m+1} ,
\] (45)
with $L$ given in Eqs. [37] [38] and
\[
M = 4^2 \sum_{n=1}^{m+1} \left( \frac{m+1}{n} \right) (-1)^n 4^{m-n} \sum_{k=0}^{n-1} \frac{2^k \prod_{i=1}^k (n-i)}{\prod_{i=1}^k (2n-2i-1)} g_1(m,n-k) .
\] (46)
To evaluate $Y$ for a given large even dimension one has to add order $\sim \frac{4^3}{\pi}$ different terms.

**Integration of $U$ for even dimensions**

To solve the first integral in
\[
U \equiv \int_0^{\frac{\pi}{2}} \int_0^{\theta_{\max}} h \sin (\varphi_1)^{2m+2} \sin (\varphi_2)^{2m+2} \sin (\theta)^{2m+1} d\theta d\varphi_1 d\varphi_2 ,
\] (47)
with $h = 4[(2 - \cos \varphi_1)(2 - \cos \varphi_2) - 1]$ and $\theta_{\max} = \arccos \left[ \frac{\tan \frac{\varphi_1}{2}}{\tan \frac{\varphi_2}{2}} \right]$, we use the identity [22]
\[
\int_0^u \sin(x)^{2n+1} \, dx = \frac{2^n n!}{(2n+1)!!} - \frac{\cos u}{2n+1} \left[ \sin(u)^{2n} + \sum_{k=0}^{n-1} \frac{2^{k+1} n!}{(n-k-1)! (2n-2k-3)!!} \sin(u)^{2n-2k-2} \right] .
\] (48)
The case $m = 0$ can be solved without using Eq. (48). We introduce the shortcut $\phi_1 = \varphi_1/2$ and $\phi_2 = \varphi_2/2$ to express $\cos \theta_{\max} (\sin \theta_{\max})^{2n} = \tan \phi_1 \tan \phi_2 (1 - \tan \phi_1^2 \tan \phi_2^2)^n = \sum_{i=0}^{n} \left( \frac{n}{i} \right) (-1)^i (\tan \phi_1 \tan \phi_2)^{2i+1}$. Thus, for $m$ any positive integer we obtain,
\[
\int_0^{\theta_{\max}} \sin(\theta)^{2m+1} \, d\theta = C - \frac{1}{2m+1} \sum_{n=0}^{m} \left( \begin{array}{c} m \\ n \end{array} \right) (-1)^n (\tan \phi_1 \tan \phi_2)^{2n+1} \]
\[
- \frac{1}{2m+1} \left[ \sum_{k=0}^{m-1} \frac{2^{k+1} \prod_{i=0}^k (m-i)}{\prod_{i=0}^k (2m-2i-1)} \sum_{n=0}^{m-k-1} \left( \frac{m-k-1}{n} \right) (-1)^n (\tan \phi_1 \tan \phi_2)^{2n+1} \right] ,
\] (49)
constant term. This expression must be replaced in Eq. (47). To complete the integration in \( \varphi_1 \) and \( \varphi_2 \) for each term at the right of Eq. (49) we transform \( h \) to \( h = 16 \sin^2 \varphi_1 + 16 \sin^2 \varphi_1 \sin^2 \varphi_2 \). The complete integral of the constant term \( C \) is

\[
C \int_0^\pi \int_0^\pi h \sin (\varphi_1)^{2m+2} \sin (\varphi_2)^{2m+2} d\varphi_1 d\varphi_2 = \frac{2^{5m+10} m!}{(2m+1)!} \int_0^\pi \int_0^\pi [(\sin \varphi_1)^2 + (\sin \varphi_1 \sin \varphi_2)^2] \times (\sin \varphi_1 \cos \varphi_1 \sin \varphi_2 \cos \varphi_2)^{2m+2} d\varphi_1 d\varphi_2.
\]

(50)

It includes terms of the form \( D(2n, 2l) \) given in Eq. (43). We introduce the shortcut

\[
g_2(m) = D(2m + 4, 2m + 2) [D(2m + 4, 2m + 2) + D(2m + 2, 2m + 2)],
\]

(51)

and thus, the r.h.s of Eq. (50) reduces to

\[
\frac{2^{5m+10} m!}{(2m+1)!} g_2(m).
\]

(52)

The remaining terms in Eqs. (47), (49) contain

\[
\int_0^\pi \int_0^\pi h (\tan \varphi_1 \tan \varphi_2)^{2i+1} \sin (\varphi_1)^{2m+2} \sin (\varphi_2)^{2m+2} d\varphi_1 d\varphi_2 = \int_0^\pi \int_0^\pi (\sin \varphi_1^2 + \sin \varphi_1^2 \sin \varphi_2^2) (\tan \varphi_1 \tan \varphi_2)^{2i+1} \times (\sin \varphi_1 \cos \varphi_1 \sin \varphi_2 \cos \varphi_2)^{2m+2} d\varphi_1 d\varphi_2,
\]

(53)

which involves terms of type \( D(2n + 1, 2l + 1) \) analyzed in Eq. (40). Therefore Eq. (53) gives \( 2^{2m+10} g_3(m, i) \) with

\[
g_3(m, i) = D[2(m + i + 2) + 1, 2m - 2i + 1] \times \left[D[2(m + i + 1) + 1, 2m - 2i + 1] + D[2(m + i + 1) + 1, 2m - 2i + 1]\right],
\]

(54)

which is also a rational number.

Collecting the partial results, we obtain

\[
U = \frac{2^{5m+2} m!}{(2m+1)!} g_2(m) - \frac{2^{4m+5} m!}{2m+1} \sum_{k=0}^{m} \sum_{i=0}^{m} \frac{2^k \prod_{j=0}^{k-1} (m-j)}{\prod_{j=0}^{k-1} (2m - 2j - 1)} (-1)^i g_3(m, i).
\]

(55)

It is interesting to note that the factors \( \sqrt{3} \) and \( \pi \) originated in this expression come from \( g_2(m) \), while the second term on the right of Eq. (55) is a rational number. Moreover, all the factors \( \sqrt{3} \) and \( \pi \) appearing in \( Y \) are those explicitly written in Eq. (37). Naturally, \( A \) in Eq. (20) includes powers of \( \pi \) originated in the solid angles, in fact \( A \sim \pi^{-2} \).

IV. RESULTS

The main result we obtained, is the explicit expression of \( \frac{1}{\sqrt{2 \pi}} \) valid for even dimensions \( d > 2 \), given in Eqs. (26), (37) and (55). Once it is complemented with Eqs. (5), (10) and (11) one finds \( B_4(d) \). For even \( d = 2\nu \) (positive integer \( \nu \geq 2 \)), we derive the following form for \( B_4 \):

\[
\frac{B_4}{B_2^2} = 2 - \frac{\sqrt{3}}{\pi} a_{4,1} + \frac{1}{\pi^2} a_{4,2}.
\]

(56)

Here, \( a_{4,1} \) and \( a_{4,2} \) are positive rational numbers (we note that \( \lim_{\nu \to \infty} \frac{\sqrt{3}}{\pi} a_{4,1}(\nu) = 6 \) and \( \lim_{\nu \to \infty} \pi^{-2} a_{4,2}(\nu) = 4 \)). In fact, we verify that

\[
a_{4,1} = \frac{3}{\pi^2} \sum_{i=1}^{\nu} \frac{\nu \left( \frac{\nu}{2} \right)^i (i-1)!}{(2i-1)!!}.
\]

(57)
Unfortunately, we do not find a simple expression for \( a_{4,2} \). Instead, we obtain

\[
a_{4,2} = \left( \frac{(d-2)!}{(d-1)!} \right)^2 + \frac{9}{2} R_0^2 - 3R_1 + 3R_3 + \frac{(d-2)!}{(d-3)!} \left[ -\frac{24d}{d-1} R_2 + K \left( \frac{2^{-d} d^{4/2}}{d-1} + \frac{3}{4} Q_0 \right) + Q_1 - \frac{Q_2}{(d-1)^2} + M - \left( \frac{d}{2} - 1 \right) (U_1 + U_2) \right],
\]

(58)

with \( R_0, R_1 \) and \( R_2 \) given in Eq. (12),

\[
R_3 = \sum_{k=1}^{\nu} \frac{(k-1)!2^{k-1}}{k(2k-1)!} \left[ 4 + \frac{\nu(2\nu)!4^{k}(\nu+k-1)!}{(2\nu-1)!}(\nu+2k)! \right],
\]

(59)

\( K, Q_0, Q_1 \) and \( Q_2 \) given in Eq. (38), and

\[
M = 4^2 \sum_{n=1}^{m+1} \left( \frac{m+1}{n} \right) (-1)^n 4^{m-n} \sum_{k=0}^{n-1} \left\{ \frac{2^k \prod_{i=1}^{k} (n-i)}{\prod_{i=0}^{k} (2n-2i-1)} \times [D[2m+3, 2m-2(n-k)+3] + 2D[2m+5, 2m-2(n-k)+3]] \right\},
\]

\[
U_1 = \frac{3^{2m+2}m!}{2^{3m+2}(m+1)!} \times \left[ \frac{3m^2 + 7m + 3}{2m+3} - \sum_{k=1}^{m} \left( \frac{3}{4} \right)^k \prod_{i=1}^{k} (2m-2i+3) \prod_{k=1}^{m} (m-i+1) \right] \times \left[ \frac{(m+1)(m+2)}{2m+3} - \sum_{k=1}^{m} \left( \frac{3}{4} \right)^k \prod_{i=1}^{k} (2m-2i+3) \prod_{k=1}^{m} (m-i+1) \right] + \sum_{k=1}^{m} \left( 1 + \frac{2m-k+2}{4(2m-2k+3)} \right) \prod_{i=1}^{k} \left( m-i+1 \right) \frac{2^k \prod_{i=1}^{k} (-2i+2m+3)}{\prod_{i=1}^{k} (2m+i+2)} \right],
\]

(60)

\[
U_2 = \frac{-4^{2m+5}}{2m+1} \sum_{k=0}^{m} \left\{ \frac{2^k \prod_{j=0}^{k-1} (m-j)}{\prod_{j=0}^{k-1} (2m-2j-1)} \sum_{i=0}^{m-k} \left( \frac{m-k-i}{i} \right) (-1)^i \times \left[ D[2(m+i+2)+1, 2m-2i+1] + D[2(m+i+1)+1, 2m-2i+1] \right] \right\},
\]

where the function \( D(a, b) \) for \( a \) and \( b \) odd numbers is defined in Eq. (40).

In Table I, the exact values of \( B_4 \) for \( d \leq 50 \) are shown, there the new results correspond to even dimensions between \( d = 14 \) and \( d = 50 \). As it is usual, results are presented as the ratio \( B_4/B_2^2 \). The known values for even and odd dimensions \( d \leq 12 \) are included. Additionally, we have evaluated \( B_4 \) for each even dimension up to \( d = 200 \) and also for several higher dimensions up to \( d = 1000 \). Because their length, which increase with dimension, the obtained expressions are not given here. In the Supplementary Material, Sec. VII we give the exact value of \( B_4/B_2^2 \) for \( d = 100, 200, 300, 500 \) and 1000. Also, a computer algebra program that allows to evaluate \( B_4 \) is included.
In Table II we show some of the exactly evaluated $B_d/B_2^2$ for even dimension $50 < d < 1000$. Note that the length of the expression for the exact value increases when increasing $d$. Therefore, it becomes so long that it is inconvenient to write it here. For this reason, we only show the decimal expansion of the exact value truncated at eleven figures for $d = 60, 70, 80, 90, 100, 200, 300, 500,$ and $1000$. We also include the decimal expansion for some of the $d$ values presented in Table I. For comparison, the MonteCarlo numerical calculation of Clisyb and McCoy [17] and the high precision results of Zhang [18] (that reaches a maximum dimension of $d = 100$), are also presented. We observe, on one hand that those $B_d$ values from Ref. [17] coincide with the exact result. On the other hand, even when several $B_d$ values from Ref. [19] coincide with the exact ones, some differences appear for $d = 16, 18, 20$. Finally, the exact expression allows to evaluate $B_4$ for $d > 100$ where numerical results have not been reported.

It is known that $B_4/B_2^2$ is positive for $d \leq 7$, negative for $d > 8$, have a minimum near $d = 11$ (see Tab. I) and goes to zero when $d$ becomes arbitrary large. The value of $d$ where $B_2 = 0$ was estimated by Luban and Baram several years ago as $d_0 \approx 7.8$ and more recently as $d_0 = 7.7320(4)$ by Clisyb and McCoy, [17] who also found the minimum of $B_4/B_2^2$ at $d_1 = 10.7583(2)$. Using the new expression for $B_4$ valid for arbitrary dimension (complete star graph taken from Eq. (31)) and standard find root and find minimum routines we obtain $d_0 = 7.6558249(1)$ and $d_1 = 10.7583(2)$.

Table I: Fourth cluster integral, $B_4$, for different integer dimensions up to $d = 50$. In the third column it is shown the eleven figures decimal expansion with the corresponding bibliographic reference where the exact value was calculated for the first time.
Table II: Values of $B_4/B_2^3$ for even dimension $d > 12$. Comparison between the new exact result (conveniently truncated at eleven figures, see the text) and those obtained through Monte Carlo numerical integration.

$$d_1 = 10.67131326(3).$$ Finally, to analyze the asymptotic behavior of $B_4/B_2^3$ for large $d$ we fitted the expression

$$\frac{B_4}{B_2^3} \approx \frac{4k_1}{\sqrt{\frac{\pi d}{2}}} \left( \frac{4\sqrt{3}}{9} \right)^{d+1},$$

for even dimensions $100 \leq d \leq 200$, to obtain $k_1 = 1.683$. Indeed, a similar expression explains the asymptotic behavior of $B_3/B_2^2$ (see Ref. [3]). In Fig. 1 it is shown the asymptotic behavior of $B_4/B_2^3$ with the dimension, symbols draw the exact values for integer dimensions where $B_4/B_2^3 < 0$. In blue diamonds we plot the known values for $d = 8, 9, 10, 11$ and 12 while in red circles we plot the new results for even dimensions from $d = 14$ to $d = 200$.

V. FINAL REMARKS

We return to the properties of $B_3$ to gain some feedback on the $B_4$ form given in Eq. (62). It is known that $B_3(d) > 0$ and $\lim_{d \to \infty} B_3(d) = 0$. For even $d = 2\nu$, Eq. (9) can be written as

$$\frac{B_3}{B_2^2} = \frac{4}{3} - \frac{\sqrt{3}}{\pi} a_3,$$

where $a_3 = \sum_{k=1}^{\nu} \frac{(2k-1)(-1)^{k-1}}{(2k-1)!}$ is a positive rational and $\lim_{\nu \to \infty} \sqrt{\nu} \pi a_3(\nu) = \frac{4}{3}$ (see Tab. I in Ref. [2] for the values of $B_3$ for positive integer dimensions $d \leq 12$). It interesting to note that $a_{4,1} = \frac{9}{2} a_3$. We extrapolate Eq. (62) for $B_3$ and Eq. (56) for $B_4$ in the following conjecture:
Conjecture 1: For any even dimension, the fifth virial coefficient of hard spheres takes the form

\[
\frac{B_5}{B_2} = a_{5,0} + \frac{\sqrt{3}}{\pi} a_{5,1} + \frac{1}{\pi^2} a_{5,2} + \frac{\sqrt{3}}{\pi^3} a_{5,3},
\]

with \(a_{5,i}\) rational numbers.

In this work we introduced a transformation that, applied to the fourth vertex complete star diagram, transforms three of its \(f\)-bonds to Dirac delta bonds (\(\delta\)-bonds). The procedure allow us to obtain a new expression for the complete star diagram of \(B_4\) for HS, but could also be applied to other diagrams with vertex connected by \(f\)-bonds and similar step functions. Additionally, we analyzed the obtained expression and using extensively the Table of Integrals of Gradshteyn and Ryzhik \([14]\) for integrands involving integer powers of Sine and Cosine functions, we found an exact expression for the complete star. Finally, to obtain the exact \(B_4(d)\) for every even \(d \geq 4\), we complemented this result with expressions for the other two Mayer graphs. Further significant progress in HS virial expansion coefficients, besides to study \(B_4\) in odd dimensions, should necessary concentrate in the exact evaluation of \(B_5\) in dimensions \(d = 2\) and \(d = 3\).

VI. SUPPLEMENTARY MATERIAL

The exact expression of \(B_4(d)\) for \(d = 100, 200, 300, 500\) and \(1000\) is presented in the SupplementaryMaterial_01.txt file. Also, I include a computer algebra program that allows to evaluate \(B_4(d)\) for even dimensions in SupplementaryMaterial_02.

Appendix A: Explicit form of

To evaluate this Mayer diagram we transform Eq. (8) as

\[
\frac{\square}{B_2^2} = -2^{2\nu+6}\nu \left(\frac{(2\nu)!}{\pi(2\nu)!}\right)^2 \int_0^\frac{1}{2} x^{2\nu-1} H^2 dx,
\]

with \(H = \int_0^{\arccos x} (\sin \gamma)^{2\nu} d\gamma\), and also

\[
H = \frac{(2\nu - 1)!!}{2\nu} \arccos x - \frac{x}{2\nu \sqrt{1 - x^2}} \left[ (1 - x^2)^\nu + \sum_{k=1}^{\nu-1} \prod_{i=1}^{k} (2\nu - 2i + 1) \frac{1}{2k} \prod_{i=1}^{k} (\nu - i) (1 - x^2)^{\nu - k} \right],
\]

where we used Eq. (C1). We integrate by parts to obtain

\[
\int_0^\frac{1}{2} x^{2\nu-1} H^2 dx = \frac{x^{2\nu}}{2\nu} H^2 \bigg|_0^{\frac{1}{2}} + \int_0^\frac{1}{2} \frac{x^{2\nu}}{\nu} (1 - x^2)^{-\frac{1}{2}} H dx,
\]

where the first term on the right gives \(\frac{2^{2\nu - 2\nu^2}}{2\nu} \left\{ \frac{(2\nu - 1)!!}{\pi} \frac{\sqrt{3}}{\nu^2} \left[ (\frac{1}{4})^\nu + \sum_{k=1}^{\nu - 1} \prod_{i=1}^{k} (2\nu - 2i + 1) \frac{1}{2k} \prod_{i=1}^{k} (\nu - i) \right] \right\}^2\). To solve the remaining integral on the right of Eq. (A1) we change variable by replacing \(x = \cos y\) to obtain

\[
\int_0^\frac{1}{2} \frac{x^{2\nu}}{\nu} (1 - x^2)^{-\frac{1}{2}} H dx =
\]

\[
= \frac{1}{\nu} \int_0^\frac{\pi}{2} (\sin y \cos y)^{2\nu} \left\{ \frac{(2\nu - 1)!!}{2\nu \nu!} y - \frac{\cos y}{2\nu \sin y} \left[ (\sin y)^{2\nu} + \sum_{k=1}^{\nu - 1} \prod_{i=1}^{k} (2\nu - 2i + 1) \frac{1}{2k} \prod_{i=1}^{k} (\nu - i) \right] \right\} dy.
\]
Here, there are terms that can be written using $D(2l + 1, 2k + 1)$ analyzed in Eq. (40), and a term $\int_0^\pi y (\sin y \cos y)^{2\nu} dy = 2^{-2\nu-2} \int_0^\pi y (\sin y)^{2\nu} dy$. This last integral is solved using Eq. (C2) and gives

$$
\int_0^\pi y (\sin y)^{2\nu} dy = \frac{5\pi^2}{18} \frac{(2\nu - 1)!!}{(2\nu)!!} - \frac{\pi \sqrt{3}}{9} \left[ \left( \frac{3}{4} \right)^{\nu} + \frac{1}{2^k \prod_{i=0}^{k-1} (2\nu - 2i - 1)} \sum_{k=1}^{\nu-1} \left( \frac{3}{4} \right)^{\nu-k} \prod_{i=0}^{k-1} (2\nu - 2i - 1) \right]
$$

Thus, one finds

$$
\int_0^1 x^{2\nu-1} H^2 dx = \frac{2^{-2\nu}}{2\nu} \left\{ \frac{(2\nu - 1)!!}{(2\nu)!!} \frac{\pi \sqrt{3}}{9} \left[ \left( \frac{3}{4} \right)^{\nu} + \frac{1}{2^k \prod_{i=0}^{k-1} (2\nu - 2i - 1)} \sum_{k=1}^{\nu-1} \left( \frac{3}{4} \right)^{\nu-k} \prod_{i=0}^{k-1} (2\nu - 2i - 1) \right] \right\} 
$$

The final result is given in Eq. (11).

**Appendix B: Origin of cos φ term**

Here we derive the identity Eq. (22) showing the origin of the cos φ term. Let us start from Eqs. (17) (18)

$$
\Box = \sigma^{d-1} \Box, 
$$

we apply the derivative $\frac{\partial}{\partial \sigma}$ to both sides, to obtain

$$
- \Box - 4 \Box - \Box = (d - 1) \sigma^{d-2} \Box - \sigma^{d-1} \left( 2 \Box + 2 \Box + \Box + \Box \right),
$$

Here the dashed bond corresponds to $\delta' \sigma - r$, being $f'' = \frac{\partial f}{\partial r^2} = -\delta' \sigma - r$. Some terms on the left are readily integrated on, $\Box = \sigma^{d-1} \Box$ and $\Box = \sigma^{d-1} \Box$. For the diagram with a dashed bond we have

$$
\Box = - \int f'_{12} f_{13} f_{14} f_{23} f_{24} f_{34} (d-1) r_{12}^{d-2} dr_{12} d\Omega_{12} dr_{13} dr_{14} - \int f_{12} f_{13} f_{14} \frac{\partial f_{23}}{\partial r_{12}} f_{24} f_{34} r_{12}^{d-1} dr_{12} d\Omega_{12} dr_{13} dr_{14}
$$

$$
= - \frac{d-1}{V} \int f'_{12} f_{13} f_{14} f_{23} f_{24} f_{34} \frac{1}{r_{12}} dr_{12,3,4} - \frac{2}{V} \int f'_{12} f_{13} f_{14} \cos \phi f'_{23} f_{24} f_{34} dr_{1,2,3,4}
$$

$$
= -(d - 1) \sigma^{d-2} \Box - 2 \sigma^{d-1} \Box \langle \cos \phi \rangle
$$

We replace Eq. (B2) in Eq. (B1) to obtain

$$
\Box = \Box (1 - \cos \phi)
$$

(B3)
Appendix C: Integration of the different terms in $L$

Here we solve the split terms of $L$ (see Eq. (36)), the four integrals: $\int_0^n (\sqrt{3}K + \frac{4\pi}{3}) \sin(\varphi) d\varphi$, $-\left(\sqrt{K} + \frac{2\pi}{3}\right) \int_0^n \cos \varphi (\sin \varphi)^{2m+2} d\varphi$, $-2 \int_0^n \varphi (\sin \varphi)^{2m+2} d\varphi$, and $\int_0^n \varphi \cos (\sin \varphi)^{2m+2} d\varphi$. To solve the first one we use (23)

$$\int_0^n (\sin \varphi)^{2l} d\varphi = \frac{(2l-1)!!}{2^l l!} (\sin u)^{2l-1} - \sum_{k=1}^{l-1} \frac{\prod_{i=1}^k (2l-2i+1)}{2^l \prod_{i=1}^k (l-i)} (\sin u)^{2l-2k-1},$$  \hspace{2cm} (C1)

to obtain

$$\int_0^n (\sin \varphi)^{2m+2} d\varphi = \frac{\pi (2m+1)!!}{2^{m+1}(m+1)!} - \frac{\sqrt{3}}{8(m+1)} \left[ \left( \frac{3}{4} \right)^m + \sum_{k=1}^m \frac{\prod_{i=0}^{k-1} (2m-2i+1)}{2^k \prod_{i=0}^{k-1} (m-i)} \left( \frac{3}{4} \right)^{m-k} \right].$$

The second one is straightforward, it gives

$$\int_0^n \cos \varphi (\sin \varphi)^{2m+2} d\varphi = \frac{\sqrt{3}}{4m+6} \left( \frac{3}{4} \right)^{m+1}.$$

To solve the third one, $-2 \int_0^n \varphi (\sin \varphi)^{2m+2} d\varphi$, we apply (24)

$$\int_0^n x^l (\sin x)^n dx = \frac{u^{l-1} (\sin u)^{n-1}}{n^2} \left( \sin u - n \cos u \right) + \frac{n-1}{n} \int_0^u x^l (\sin x)^{n-2} dx - \frac{l(l-1)}{n^2} \int_0^u x^{l-2} (\sin x)^n dx,$$  \hspace{2cm} (C2)

iteratively, to obtain

$$\int_0^n x (\sin x)^{2n} dx = \frac{u^2 (2n-1)!!}{2 \left( 2^n n! \right)} + \frac{1}{4} \left[ \frac{(u)^{2n}}{n^2} + \sum_{k=1}^{n-1} \frac{\prod_{i=0}^{k-1} (2n-2i-1)}{2^k (n-k) \prod_{i=0}^{k-1} (n-i)} (u)^{2(n-k)} \right]$$

$$- \frac{u \cos u}{2 \sin u} \left[ \frac{(u^{2n}}{n} + \sum_{k=1}^{n-1} \frac{\prod_{i=0}^{k-1} (2n-2i-1)}{2^k (n-k) \prod_{i=0}^{k-1} (n-i)} (u)^{2(n-k)} \right],$$  \hspace{2cm} (C3)

and finally

$$\int_0^n \varphi (\sin \varphi)^{2m+2} d\varphi = \frac{\pi^2 (2m+1)!!}{18(2^m m!)} + \frac{1}{4} \left[ \left( \frac{3}{4} \right)^{m+1} \sum_{k=1}^{m} \frac{\prod_{i=0}^{k-1} (2m-2i+1)}{2^k (m-k+1)^2 \prod_{i=0}^{k-1} (m-i+1)} \right]$$

$$- \frac{\pi \sqrt{3}}{18} \left[ \left( \frac{3}{4} \right)^{m+1} \sum_{k=1}^{m} \frac{\prod_{i=0}^{k-1} (2m-2i+1)}{2^k (m-k+1) \prod_{i=0}^{k-1} (m-i+1)} \right].$$

To solve the fourth one we use (25)

$$\int_0^n x (\sin x)^p (\cos x)^q dx = \frac{1}{(p+q)^q} \left[ (p+q) u (\sin u)^{p+1} (\cos x)^{q-1} + (\sin u)^p (\cos x)^q \right]$$

$$- p \int_0^n (\sin x)^{p-1} (\cos x)^{q-1} dx - (q-1) (p+q) \int_0^n (\sin x)^p (\cos x)^{q-2} dx \right].$$

In particular, for $q = 1$ it reduces to

$$\int_0^n x (\sin x)^p \cos x dx = \frac{1}{(p+1)^2} \left[ (p+1) u (\sin u)^{p+1} + (\sin u)^p \cos u - p \int_0^n (\sin x)^{p-1} dx \right],$$

which gives the result

$$\int_0^n \varphi \cos \varphi (\sin \varphi)^{2m+2} d\varphi = \frac{\pi \sqrt{3} \left( \frac{3}{4} \right)^{m+1}}{6(2m+3)} + \frac{\left( \frac{3}{4} \right)^{m+1}}{2(2m+3)^2} - \frac{2(m+1)}{(2m+3)^2} \int_0^n (\sin x)^{2m+1} dx.$$
To solve the last integral we used Eq. (39) (with $q = 0$) to obtain

$$\int_0^\pi (\sin x)^{2n+1} \, dx = \frac{2^n n!}{(2n + 1)!!} - \frac{1}{2(2n + 1)} \left[ \left( \frac{3}{4} \right)^n + \sum_{k=1}^{n} \frac{2^k \prod_{i=0}^{k-1} (n - i)}{\prod_{i=0}^{k-1} (2n - 2i - 1)} \left( \frac{3}{4} \right)^{n-k} \right].$$

[1] J. D. van der Waals. *Over de Continuïteit van den Gas- en Vloeistoofstoestand (on the continuity of the gas and liquid state).* Ph. d. thesis, University of Leiden, 1873.

[2] Nathan Clisby and Barry M. McCoy. Analytic calculation of $b_4$ for hard spheres in even dimensions. *Journal of Statistical Physics*, 114(5):1343–1361, 2004.

[3] I. Lyberg. The fourth virial coefficient of a fluid of hard spheres in odd dimensions. *Journal of Statistical Physics*, 119(3):747–764, may 2005.

[4] L. Boltzmann. About the fourth virial coeff. of hs in 3d. *Versl. Gewone Vergadering Afk. Natuurk. Nederlandse Akad. Wtensch.*, 7:484, 1899.

[5] J. J. van Laar. About the fourth virial coeff. of hs in 3d. *Amsterdam Akad. Versl.*, 7:350, 1899.

[6] John H. Nairn and John E. Kilpatrick. Van der Waals, Boltzmann, and the fourth virial coefficient of hard spheres. *American Journal of Physics*, 40(4):503–515, 1972.

[7] John E. Kilpatrick. *The Computation of Virial Coefficients*, pages 39–69. John Wiley & Sons, Inc., 1971.

[8] Andrés Santos. *A Concise Course on the Theory of Classical Liquids: Basics and Selected Topics*. Lecture Notes in Physics 923. Springer International Publishing, 2016.

[9] Marshall Luban and Asher Baram. Third and fourth virial coefficients of hard hyperspheres of arbitrary dimensionality. *The Journal of Chemical Physics*, 76(6):3233–3241, 1982.

[10] J. S. Rowlinson. The virial expansion in two dimensions. *Molecular Physics*, 7(6):593–594, 1964.

[11] P. C. Hemmer. Virial coefficients for the hard-core gas in two dimensions. *The Journal of Chemical Physics*, 42(3):1116–1118, 1965.

[12] Lewi Tonks. The complete equation of state of one, two and three-dimensional gases of hard elastic spheres. *Phys. Rev.*, 50(10):955–963, Nov 1936.

[13] C. G. Joslin. Third and fourth virial coefficients of hard hyperspheres of arbitrary dimensionality. *The Journal of Chemical Physics*, 77(5):2701–2702, 1982.

[14] I.S. Gradshteyn and I.M. Ryzhik. *Table of integrals, series, and products*. Academic Press, 7th ed edition, 2007.

[15] J. de Boer. Molecular distribution and equation of state of gases. *Reports on Progress in Physics*, 12(1):305, 1949.

[16] B. R. A. Nijboer and L. van Hove. Radial distribution function of a gas of hard spheres and the superposition approximation. *Phys. Rev.*, 85(5):777–783, Mar 1952.

[17] Nathan Clisby and Barry M. McCoy. Negative virial coefficients and the dominance of loose packed diagrams for $d$-dimensional hard spheres. *Journal of Statistical Physics*, 114:1361 – 1392, 2004.

[18] Cheng Zhang and B. Montgomery Pettitt. Computation of high-order virial coefficients in high-dimensional hard-sphere fluids by mayer sampling. *Molecular Physics*, 112(9-10):1427–1447, 2014.

[19] Ref. [14], Sec. 2.519 Eq.(1), at p.156.

[20] Ref. [14], Sec. 2.512 Eq.(4), at p.152.

[21] Ref. [14], Sec. 2.512 Eqs.(1,2), at p.152.

[22] Ref. [14], Sec. 2.511 Eq.(3), at p.152.

[23] Ref. [14], Sec. 2.511 Eq.(2), at p.152.

[24] Ref. [14], Sec. 2.631 Eq.(2), at p.214.

[25] Ref. [14], Sec. 2.631 Eq.(1), at p.214.