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A systematic formulation of the virial expansion for nonadditive interaction potentials

Robert Hellmann[a)] and Eckard Bich
Institut für Chemie, Universität Rostock, Albert-Einstein-Straße 3a, D-18059 Rostock, Germany

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A new formulation of the virial expansion for a classical gas is derived without the restriction to pairwise-additive interaction potentials. Explicit expressions up to the eighth virial coefficient, suitable for numerical evaluation, are given in the form of integrals over sums of cluster diagrams. Compared with previous approaches, the number of cluster diagrams increases more moderately with increasing order of the virial coefficient. Thus, the new formulation should be particularly useful for the computation of high-order virial coefficients. © *2011 American Institute of Physics*. [doi:10.1063/1.3626524]

I. INTRODUCTION

During the 1930s intensive research was underway for a theoretically founded equation of state of an N-particle system based on statistical mechanics.[1–8] This equation of state was also supposed to explain the phenomenon of condensation.

Mayer[1] utilized the theoretical approach of Ursell[9] to derive a series expansion for the free energy, which could be used to calculate further thermodynamic functions. The derivation is based on the canonical partition function and on the assumption that the interaction potential between more than two particles can be expressed as a sum of two-particle interactions. The original series expansion was then further simplified.[3–5] A summary of these developments can be found in the books of Mayer and Goeppert-Mayer[10] and of Hill.[11]

Born[3] was the first to emphasize that the theoretically obtained coefficients β_j for the series expansion of pressure in powers of number density ρ,

$$\frac{pV_\mathrm{m}}{RT} = 1 - \sum_{j=1}^{\infty} \frac{j}{j+1}\beta_j \rho^j, \qquad \rho = \frac{N}{V} \tag{1}$$

are closely related to the virial coefficients $B_2, B_3, \ldots$ of the semi-empirical equation of state recommended by Kamerlingh Onnes and Keesom:

$$\frac{pV_\mathrm{m}}{RT} = 1 + \frac{B_2(T)}{V_\mathrm{m}} + \frac{B_3(T)}{V_\mathrm{m}^2} + \cdots. \tag{2}$$

The general expressions for the virial coefficients B_n are sums of so-called cluster integrals, which can, in principle, be calculated if the intermolecular pair potential is known.

The virial expansion cannot only be derived from the canonical partition function. Mayer[12,13] showed that a series expansion for the pressure in powers of the activity can be obtained from the grand-canonical partition function. A simpler derivation was later found by Ono.[14] The virial expansion can then be derived using the known thermodynamic relations for the average number of particles, see, for example, Ref. 11.

On the one hand, the virial expansion is an important tool for the evaluation of experimental p, ρ, T-data. The resulting virial coefficients, especially B_2, can be utilized with the aid of potential models to estimate the strength of the intermolecular interactions. On the other hand, there is the possibility to compute second and higher virial coefficients using accurate intermolecular potentials from quantum-mechanical *ab initio* calculations to predict the p, ρ, T-behavior. However, the calculation of higher virial coefficients was for a long time hindered by the huge computational costs for the calculation of the high-dimensional integrals over the configuration space. Even the calculation of B_3 for a gas of rigid non-linear molecules already requires to solve a 12-fold integral numerically, because the intermolecular potential depends not only on the distance between the molecules, but also on their mutual orientation. Only Monte Carlo methods are suitable to compute such high-dimensional integrals efficiently. Ordinary Monte Carlo integration works well for gases with short-range interaction potentials such as hard-body fluids,[15–17] but fails for long-range potentials, especially at low temperatures. An efficient importance sampling Monte Carlo procedure suitable for continuous potentials, referred to as Mayer-sampling, was recently developed by Kofke and co-workers, see, for example, Refs. 18–21 for a description of the method and applications to the virial coefficients of the Lennard-Jones fluid, alkanes, and water vapor.

Comparison between theoretically calculated and experimentally determined virial coefficients showed that nonadditive three-body interactions have to be taken into account for the calculation of B_3 to achieve good agreement.[22,23] It is to be expected that nonadditive interactions also strongly influence all higher virial coefficients. However, the method of Mayer[10] as well as the later reformulation by Ree and Hoover[24] are based on the assumption of pairwise-additive interaction potentials. So far, corrections for nonadditivity have only been derived up to B_5.[19,25,26]

In this work, we present a systematic formulation of the virial expansion for both additive and nonadditive interaction potentials in a form suitable for numerical evaluation. The derivation is based on a series expansion of the grand

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[a)] Electronic mail: robert.hellmann@uni-rostock.de.

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canonical partition function for a classical gas. Explicit expressions up to B_8 are given utilizing cluster diagrams. In the case of pairwise-additive interaction potentials, the new method gives integrands for the virial coefficients which are equal in value to the integrands from the formulations by Mayer[10] and by Ree and Hoover[24] for a given configuration of the particles. For nonadditive interaction potentials, the resulting integrands for B_3 to B_5 also recover the known nonadditivity corrections.

II. VIRIAL EXPANSION FROM THE GRAND CANONICAL PARTITION FUNCTION

Below, we present a new way of deriving the virial expansion from the grand canonical partition function. It differs from the derivation given in Ref. 11 by treating the grand canonical partition function as a product of an ideal gas part and a residual part, yielding expressions that can be adapted for practical implementation. For the sake of simplicity, the derivation is performed for pure gases composed of structureless particles without internal degrees of freedom. However, as in the case of the formulations by Mayer[10] and by Ree and Hoover,[24] the final expressions for the virial coefficients given in Sec. III are also valid for mixtures as well as for rigid molecules. In the latter case, the integrations over the positions of the particles have to be extended over their angular configurations with proper normalization of the integrals.

The grand thermodynamic potential $-pV$ as a function of the independent state variables T, V, and μ can be calculated from the microscopic properties of the system by utilizing the grand canonical partition function Ξ:

$$-pV = -k_BT \ln \Xi(T, V, \mu), \tag{3}$$

where Ξ is related to the canonical partition function for N particles, Q_N, by

$$\Xi(T, V, \mu) = 1 + \sum_{N=1}^{\infty} Q_N(T, V)\lambda^N. \tag{4}$$

Here, μ is the chemical potential, $\lambda = \exp\left(\mu/k_BT\right)$ is the absolute activity, and k_B is Boltzmann's constant. $Q_N(T, V)$ is given for a classical-mechanical system of volume V with N structureless particles of mass m by the following multidimensional integral over the momenta $\mathbf{p}$ and coordinates $\mathbf{r}$ of all particles:

$$Q_N(T, V) = \frac{1}{h^{3N}N!}\int \dots \int \exp\left(-\frac{H_N}{k_BT}\right) \times d\mathbf{p}_1 \dots d\mathbf{p}_N d\mathbf{r}_1 \dots d\mathbf{r}_N, \tag{5}$$

where h is Planck's constant, and where

$$H_N = \frac{1}{2m}\sum_{i=1}^{N} \mathbf{p}_i^2 + \phi(\mathbf{r}_1, \dots, \mathbf{r}_N) \tag{6}$$

is the classical Hamilton function. The total potential energy for all interactions between the particles, ϕ_N, may be written as a sum of pure pair potentials and, if necessary, a nonadditive contribution,

$$\phi_N = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} \phi_{ij} + \Delta\phi_N. \tag{7}$$

Integration over all momenta $\mathbf{p}$ leads to

$$Q_N = \frac{Z_N}{N!\lambda_{\text{th}}^{3N}}, \tag{8}$$

where $\lambda_{\text{th}} = h(2\pi m k_B T)^{-\frac{1}{2}}$ is the thermal wavelength. The configuration integral Z_N is given by

$$Z_N(T, V) = \int \dots \int \exp\left(-\frac{\phi_N}{k_BT}\right) d\mathbf{r}_1 \dots d\mathbf{r}_N. \tag{9}$$

Substituting Eq. (8) into Eq. (4) yields

$$\Xi(T, V, z) = 1 + \sum_{N=1}^{\infty} \frac{Z_N(T, V)}{N!} z^N, \tag{10}$$

where $z = \lambda/\lambda_{\text{th}}^3$ is the activity. For the ideal gas model, $\phi_N = 0$, we obtain

$$Z_N^{\text{id}}(T, V) = Z_1^N = V^N, \tag{11}$$

$$\Xi_{\text{id}}(T, V, z) = 1 + \sum_{N=1}^{\infty} \frac{Z_1^N}{N!} z^N = \mathrm{e}^{Vz}. \tag{12}$$

For a real gas, we now write the grand canonical partition function as a product of the ideal gas part and a residual part:

$$\Xi = \Xi_{\text{id}}\Xi_{\text{res}} = \mathrm{e}^{Vz}\Xi_{\text{res}}. \tag{13}$$

Thus, Eq. (3) may be rewritten as

$$-pV = -k_BT(Vz + \ln \Xi_{\text{res}}). \tag{14}$$

A series expansion for Ξ_{res} can be derived using the Cauchy product:

$$\Xi_{\text{res}} = \frac{\Xi}{\Xi_{\text{id}}} = \left(1 + \sum_{n=1}^{\infty} \frac{Z_n}{n!} z^n\right)\left(1 + \sum_{m=1}^{\infty} \frac{(-Z_1)^m}{m!} z^m\right) = 1 + \sum_{j=1}^{\infty} \frac{a_j}{j!} z^j = 1 + \frac{a_1}{1!}z + \frac{a_2}{2!}z^2 + \dots \tag{15}$$

with

$$a_n = (-Z_1)^n + \sum_{k=0}^{n-1} (-1)^k \binom{n}{k} Z_{n-k} Z_1^k. \tag{16}$$

It follows immediately that a_1 equals zero. Introducing

$$F_n = Z_n - Z_1^n, \tag{17}$$

and utilizing the relation $\sum_{k=0}^{n}(-1)^k\binom{n}{k} = 0$, we obtain

$$a_n = \sum_{k=0}^{n-2} (-1)^k \binom{n}{k} F_{n-k} Z_1^k, \qquad n \geq 2. \tag{18}$$

For the pressure we use the *ansatz*

$$\frac{p}{k_BT} = z + \sum_{j=2}^{\infty} \frac{b_j}{j!} z^j = z + \frac{b_2}{2!}z^2 + \frac{b_3}{3!}z^3 + \cdots, \tag{19}$$

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where b_j are so-called reducible cluster integrals. The definition of b_j given here differs from the customary definition in the literature[11] by an additional factor of $j!$.

Using Eq. (14) we can now construct a series expansion for Ξ_{res} using the reducible cluster integrals b_j:

$$\begin{aligned}\Xi_{\text{res}} &= \exp\left(V\sum_{j=2}^{\infty}\frac{b_j}{j!}z^j\right)\\ &= 1 + V\frac{b_2}{2!}z^2 + V\frac{b_3}{3!}z^3 + \left[V\frac{b_4}{4!} + \frac{V^2}{2!}\frac{b_2^2}{2!2!}\right]z^4\\ &\quad + \left[V\frac{b_5}{5!} + \frac{V^2}{2!}\frac{2b_2b_3}{2!3!}\right]z^5 + \cdots. \end{aligned} \tag{20}$$

Equating coefficients of equal powers in Eqs. (15) and (20) yields

$$V b_n = -n!\sum_{\mathbf{m}}\left[(-1)^{\sum_{j=2}^{n} m_j}\left(\sum_{j=2}^{n} m_j - 1\right)! \times \prod_{j=2}^{n}\frac{1}{m_j!}\left(\frac{a_j}{j!}\right)^{m_j}\right], \tag{21}$$

$$\sum_{j=2}^{n} j m_j = n, \qquad m_j \in \mathbb{N}_0. \tag{22}$$

The first sum in Eq. (21) extends over all possible sets $\mathbf{m} = (m_2, m_3, \ldots)$ that satisfy constraint (22). Ono[14] found a similar relationship for b_n as a function of $Z_1, \ldots, Z_n$. We have introduced Eqs. (17) and (18) as intermediate steps in order to facilitate the practical implementation, see Sec. III.

Utilizing Eqs. (3) and (19), as well as the relation for the average number of particles,

$$\bar{N} = k_B T\left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{T,V} = z\left(\frac{\partial \ln \Xi}{\partial z}\right)_{T,V},$$

a series expansion for the number density can be obtained:

$$\rho = z + \sum_{j=2}^{\infty}\frac{b_j}{(j-1)!}z^j = z + \frac{b_2}{1!}z^2 + \frac{b_3}{2!}z^3 + \cdots. \tag{23}$$

Inversion of Eq. (23) and substitution of the resulting series expansion of the activity in powers of number density into Eq. (19) leads to the virial equation of state:

$$\frac{p}{k_B T} = \rho - \sum_{j=1}^{\infty}\frac{j}{j+1}\beta_j\rho^{j+1} = \rho + \sum_{j=2}^{\infty}B_j\rho^j. \tag{24}$$

The coefficients β_j are called irreducible cluster integrals.[11] The virial coefficients B_n as functions of the reducible cluster integrals b_j (adjusted for the additional factor of $j!$ in our definition of b_j) are given by[12]

$$B_n = \frac{n-1}{n!}\sum_{\mathbf{m}}\left[(-1)^{\sum_{j=2}^{n} m_j}\left(n + \sum_{j=2}^{n} m_j - 2\right)! \times \prod_{j=2}^{n}\frac{1}{m_j!}\left(\frac{b_j}{(j-1)!}\right)^{m_j}\right], \tag{25}$$

$$\sum_{j=2}^{n}(j-1)m_j = n-1, \qquad m_j \in \mathbb{N}_0. \tag{26}$$

III. PRACTICAL IMPLEMENTATION

The derivation shown in Sec. II is not yet suitable for numerical evaluation. Like in other derivations of the virial expansion from the grand canonical partition function (see, e.g., Ref. 11) the virial coefficients B_n are ultimately expressed as sums and differences of products of configuration integrals Z_N [see Eq. (9)] and negative powers of the system volume $V = Z_1$. The configuration integrals Z_N show a strong dependence on V and will become very large if we chose a system volume that is sufficient to ensure that the virial coefficients B_n do not depend significantly on V anymore. Hence, in the expressions for the virial coefficients B_n the individual summands also become very large, whereas the total sums yield the comparably small virial coefficients B_n. This is due to a strong cancellation between the summands. The precision of the numerical integrations to obtain each Z_N would need to be extremely high, because even tiny relative errors would consequently lead to huge relative errors in the resulting virial coefficients.

In contrast, the methods of Mayer[10] and of Ree and Hoover[24] express each virial coefficient as a single multidimensional integral over all particle positions. Therefore, the problems described are avoided.

Below, we show how the derivation given in Sec. II can be modified, so that, analogously to the formulations of Mayer and of Ree and Hoover, only a single multidimensional integration needs to be performed in order to obtain the desired virial coefficient.

First of all, we define the dimensionless integrands of the quantities F_n [Eq. (17)] and a_n [Eq. (18)], as well as of the reducible cluster integrals b_n [Eqs. (21) and (22)] and of the virial coefficients B_n [Eqs. (25) and (26)]:

$$F_n = \int\cdots\int f_n d\mathbf{r}_1\ldots d\mathbf{r}_n, \tag{27}$$

$$a_n = \int\cdots\int \tilde{a}_n d\mathbf{r}_1\ldots d\mathbf{r}_n, \tag{28}$$

$$b_n = \frac{1}{V}\int\cdots\int \tilde{b}_n d\mathbf{r}_1\ldots d\mathbf{r}_n, \tag{29}$$

$$B_n = \frac{1}{V}\int\cdots\int \tilde{B}_n d\mathbf{r}_1\ldots d\mathbf{r}_n, \tag{30}$$

where

$$f_n = \exp\left(-\frac{\phi_n}{k_B T}\right) - 1 \tag{31}$$

is the n-particle Mayer function. The n-particle interaction potential ϕ_n may include nonadditive contributions, see Eq. (7). Where necessary, we will subscript the integrands in a way that allows us to assign them to a specific subgroup of a group of numbered particles. For example, the two-particle Mayer function f_2 for particles i and j would be denoted as

f_{ij}, with $f_{ij} = \exp(-\phi_{ij}/k_B T) - 1$, where ϕ_{ij} is the interaction potential between particles i and j; the $\tilde{a}_4$ function for particles i, j, k, and l would be denoted as $\tilde{a}_{ijkl}$; and so forth.

We can now utilize Eq. (18) for the a_n functions to derive expressions for the $\tilde{a}_n$ functions. For a_2 we have

$$a_2 = F_2, \tag{32}$$

and hence

$$\tilde{a}_{ij} = f_{ij}. \tag{33}$$

For $n = 3$ Eq. (18) yields

$$a_3 = F_3 - 3F_2 Z_1, \tag{34}$$

where the term $3F_2Z_1$ can be associated at the level of the integrands with the three possible ways of distributing f_2 functions among three particles. This leads to

$$\tilde{a}_{ijk} = f_{ijk} - f_{ij} - f_{ik} - f_{jk}. \tag{35}$$

Similarly,

$$a_4 = F_4 - 4F_3 Z_1 + 6F_2 Z_1^2, \tag{36}$$

$$\begin{aligned} \tilde{a}_{ijkl} = {} & f_{ijkl} - f_{ijk} - f_{ijl} - f_{ikl} - f_{jkl} \\ & + f_{ij} + f_{ik} + f_{il} + f_{jk} + f_{jl} + f_{kl}, \end{aligned} \tag{37}$$

and so on.

The $\tilde{a}_n$ functions exhibit some interesting properties. If a given set of n particles is composed of isolated clusters (i.e., the clusters do not interact with each other), and if at least one of these clusters is a single particle, $\tilde{a}_n$ will be equal to zero. On the contrary, if each of the separated clusters consists of at least two particles, the corresponding $\tilde{a}_n$ function will be non-zero in general. Here, the term "cluster" refers to a given configuration of a group of particles in which each particle interacts either directly or indirectly with all other particles.

Next, we utilize Eqs. (21) and (22) to obtain explicit expressions for the reducible cluster integrals b_n, which can thereupon be used to derive expressions for the integrands $\tilde{b}_n$. For $n = 2$ and $n = 3$ we obtain

$$Vb_2 = a_2, \qquad \tilde{b}_{ij} = \tilde{a}_{ij}, \tag{38}$$

$$Vb_3 = a_3, \qquad \tilde{b}_{ijk} = \tilde{a}_{ijk}. \tag{39}$$

For b_4 the result is

$$Vb_4 = a_4 - 3a_2^2, \tag{40}$$

where the term $3a_2^2$ may be identified with the three possible ways to separate a four-particle cluster into two two-particle clusters. We thus have

$$\tilde{b}_{ijkl} = \tilde{a}_{ijkl} - \tilde{a}_{ij}\tilde{a}_{kl} - \tilde{a}_{ik}\tilde{a}_{jl} - \tilde{a}_{il}\tilde{a}_{jk}. \tag{41}$$

The subtraction of the products of two $\tilde{a}_2$ functions from $\tilde{a}_4$ has the effect that $\tilde{b}_4$ will always become zero if the four particles are arranged as isolated clusters of any size. This holds analogously for all $\tilde{b}_n$ functions. The result for b_5 is

$$Vb_5 = a_5 - 10a_2a_3. \tag{42}$$

Here, the term $10a_2a_3$ represents the 10 ways of separating a five-particle cluster into a three-particle cluster and a two-particle cluster. Hence,

$$\begin{aligned} \tilde{b}_{ijklm} = {} & \tilde{a}_{ijklm} - \tilde{a}_{ij}\tilde{a}_{klm} - \tilde{a}_{ik}\tilde{a}_{jlm} - \tilde{a}_{il}\tilde{a}_{jkm} \\ & - \tilde{a}_{im}\tilde{a}_{jkl} - \tilde{a}_{jk}\tilde{a}_{ilm} - \tilde{a}_{jl}\tilde{a}_{ikm} - \tilde{a}_{jm}\tilde{a}_{ikl} \\ & - \tilde{a}_{kl}\tilde{a}_{ijm} - \tilde{a}_{km}\tilde{a}_{ijl} - \tilde{a}_{lm}\tilde{a}_{ijk}. \end{aligned} \tag{43}$$

For b_6 Eqs. (21) and (22) yield

$$Vb_6 = a_6 - 15a_2a_4 - 10a_3^2 + 30a_2^3, \tag{44}$$

where the individual summands can be interpreted in a similar way as before, except for the summand $30a_2^3$, which corresponds to the only 15 different ways of dividing a six-particle cluster into three two-particle clusters. However, the term $(\sum_{j=2}^{n} m_j - 1)!$ in Eq. (21) gives rise to a weighting factor of 2! for products of three a functions, 3! for products of four a functions, and so on. This should apply also to products of $\tilde{a}$ functions. To facilitate readability we give the result for the $\tilde{b}_6$ functions here only for $\tilde{b}_{123456}$ as a representative example for all possible particle combinations:

$$\begin{aligned} \tilde{b}_{123456} = {} & \tilde{a}_{123456} - \tilde{a}_{12}\tilde{a}_{3456} - \tilde{a}_{13}\tilde{a}_{2456} - \tilde{a}_{14}\tilde{a}_{2356} - \tilde{a}_{15}\tilde{a}_{2346} \\ & - \tilde{a}_{16}\tilde{a}_{2345} - \tilde{a}_{23}\tilde{a}_{1456} - \tilde{a}_{24}\tilde{a}_{1356} - \tilde{a}_{25}\tilde{a}_{1346} \\ & - \tilde{a}_{26}\tilde{a}_{1345} - \tilde{a}_{34}\tilde{a}_{1256} - \tilde{a}_{35}\tilde{a}_{1246} - \tilde{a}_{36}\tilde{a}_{1245} \\ & - \tilde{a}_{45}\tilde{a}_{1236} - \tilde{a}_{46}\tilde{a}_{1235} - \tilde{a}_{56}\tilde{a}_{1234} - \tilde{a}_{123}\tilde{a}_{456} \\ & - \tilde{a}_{124}\tilde{a}_{356} - \tilde{a}_{125}\tilde{a}_{346} - \tilde{a}_{126}\tilde{a}_{345} - \tilde{a}_{134}\tilde{a}_{256} \\ & - \tilde{a}_{135}\tilde{a}_{246} - \tilde{a}_{136}\tilde{a}_{245} - \tilde{a}_{145}\tilde{a}_{236} - \tilde{a}_{146}\tilde{a}_{235} \\ & - \tilde{a}_{156}\tilde{a}_{234} + 2!(\tilde{a}_{12}\tilde{a}_{34}\tilde{a}_{56} + \tilde{a}_{12}\tilde{a}_{35}\tilde{a}_{46} + \tilde{a}_{12}\tilde{a}_{36}\tilde{a}_{45} \\ & + \tilde{a}_{13}\tilde{a}_{24}\tilde{a}_{56} + \tilde{a}_{13}\tilde{a}_{25}\tilde{a}_{46} + \tilde{a}_{13}\tilde{a}_{26}\tilde{a}_{45} + \tilde{a}_{14}\tilde{a}_{23}\tilde{a}_{56} \\ & + \tilde{a}_{14}\tilde{a}_{25}\tilde{a}_{36} + \tilde{a}_{14}\tilde{a}_{26}\tilde{a}_{35} + \tilde{a}_{15}\tilde{a}_{23}\tilde{a}_{46} + \tilde{a}_{15}\tilde{a}_{24}\tilde{a}_{36} \\ & + \tilde{a}_{15}\tilde{a}_{26}\tilde{a}_{34} + \tilde{a}_{16}\tilde{a}_{23}\tilde{a}_{45} + \tilde{a}_{16}\tilde{a}_{24}\tilde{a}_{35} + \tilde{a}_{16}\tilde{a}_{25}\tilde{a}_{34}). \end{aligned} \tag{45}$$

For the general expression replace 1 with i, 2 with j, and so on. The results for the higher b_n and $\tilde{b}_n$ functions can be obtained similarly and only the expressions for b_7 and b_8 will be given here:

$$Vb_7 = a_7 - 21a_2a_5 - 35a_3a_4 + 210a_2^2a_3, \tag{46}$$

$$\begin{aligned} Vb_8 = {} & a_8 - 28a_6a_2 - 56a_5a_3 - 35a_4^2 + 420a_4a_2^2 \\ & + 560a_3^2a_2 - 630a_2^4. \end{aligned} \tag{47}$$

At this point, the question may arise if it would be practicable to calculate the reducible cluster integrals b_n by solving Eq. (29) with a suitable integration algorithm, e.g., the Mayer-sampling Monte Carlo method,[18] and then to use Eqs. (25) and (26) to calculate the virial coefficients. We have tested this approach for the Lennard-Jones fluid using the Mayer-sampling method and found that it only works satisfactorily up to the fourth virial coefficient, because the ratio $|b_n/B_n|$ generally increases rapidly with increasing n, resulting again in a strong cancellation between the summands in

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Eq. (25). In order to be able to compute the virial coefficients in an efficient manner, it is therefore necessary to formulate each virial coefficient B_n as a single multidimensional integral as given in Eq. (30).

We now have to find expressions for the integrands $\tilde{B}_n$ of the virial coefficients B_n by utilizing Eqs. (25) and (26). For the second virial coefficient we obtain

$$B_2 = -b_2, \qquad \tilde{B}_2 = -\tilde{b}_{12}. \tag{48}$$

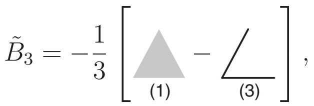
In the case of B_3 Eqs. (25) and (26) yield

$$B_3 = -\frac{1}{3}\left[b_3 - 3b_2^2\right]. \tag{49}$$

The expression for $\tilde{B}_3$ is obtained by associating the term $3b_2^2$ with the three possible combinations of two $\tilde{b}_2$ functions:

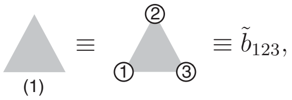
$$\tilde{B}_3 = -\frac{1}{3}\left[\tilde{b}_{123} - \tilde{b}_{12}\tilde{b}_{13} - \tilde{b}_{12}\tilde{b}_{23} - \tilde{b}_{13}\tilde{b}_{23}\right]. \tag{50}$$

Alternatively, we can devise a graphical scheme using cluster diagrams:

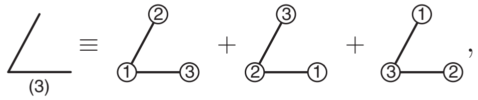


(51)

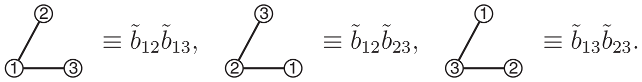
with



(52)



(53)



(54)

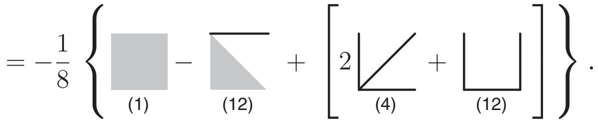
Here, each product of $\tilde{b}$ functions is represented by a labeled cluster diagram, where particle indices are represented by vertices, $\tilde{b}_2$ functions by edges, and $\tilde{b}_n$ functions for $n > 2$ by filled polygons connecting n vertices (hyperedges). We define a diagram with unlabeled vertices as the sum over all corresponding labeled diagrams that are distinguishable, the number of which is given in parentheses below each unlabeled diagram. It can be shown that generally any two $\tilde{b}$ functions that appear in a diagram may have either no common vertex or only one. In addition, the diagrams must not contain closed paths between three or more vertices that do not share a common hyperedge. Only if these two conditions are fulfilled, a product of independent integrals over each $\tilde{b}$ function may be written as an integral over a product of $\tilde{b}$ functions. It also follows that the diagrams are connected, i.e., there is always a path between any two vertices. In graph theory these diagrams are called hypertrees.

Next, we will derive an expression for $\tilde{B}_4$. From Eqs. (25) and (26) we obtain

$$B_4 = -\frac{1}{8}\left[b_4 - 12b_3b_2 + 20b_2^3\right], \tag{55}$$

where the term $12b_3b_2$ may be identified with the 12 allowed combinations of a $\tilde{b}_3$ and a $\tilde{b}_2$ function. However, the term $20b_2^3$ corresponds to only 16 allowed combinations of three $\tilde{b}_2$ functions, 12 of which are of type $\tilde{b}_{ij}\tilde{b}_{jk}\tilde{b}_{kl}$ and four of which are of type $\tilde{b}_{ij}\tilde{b}_{ik}\tilde{b}_{il}$. We could solve the problem by giving the latter a weighting factor of two. In doing so, the $\tilde{B}_4$ thus obtained will also become identical in value to the corresponding integrands of the formulations by Mayer[10] and by Ree and Hoover[24] for pairwise-additive potentials. Hence, we have

$$\begin{aligned}\tilde{B}_4 = -\frac{1}{8}\big[&\tilde{b}_{1234} - \tilde{b}_{123}\tilde{b}_{14} - \tilde{b}_{123}\tilde{b}_{24} - \tilde{b}_{123}\tilde{b}_{34} - \tilde{b}_{124}\tilde{b}_{13}\\ &- \tilde{b}_{124}\tilde{b}_{23} - \tilde{b}_{124}\tilde{b}_{34} - \tilde{b}_{134}\tilde{b}_{12} - \tilde{b}_{134}\tilde{b}_{23} - \tilde{b}_{134}\tilde{b}_{24}\\ &- \tilde{b}_{234}\tilde{b}_{12} - \tilde{b}_{234}\tilde{b}_{13} - \tilde{b}_{234}\tilde{b}_{14} + 2(\tilde{b}_{12}\tilde{b}_{13}\tilde{b}_{14}\\ &+ \tilde{b}_{12}\tilde{b}_{23}\tilde{b}_{24} + \tilde{b}_{13}\tilde{b}_{23}\tilde{b}_{34} + \tilde{b}_{14}\tilde{b}_{24}\tilde{b}_{34}) + \tilde{b}_{13}\tilde{b}_{12}\tilde{b}_{24}\\ &+ \tilde{b}_{14}\tilde{b}_{12}\tilde{b}_{23} + \tilde{b}_{12}\tilde{b}_{13}\tilde{b}_{34} + \tilde{b}_{14}\tilde{b}_{13}\tilde{b}_{23} + \tilde{b}_{12}\tilde{b}_{14}\tilde{b}_{34}\\ &+ \tilde{b}_{13}\tilde{b}_{14}\tilde{b}_{24} + \tilde{b}_{12}\tilde{b}_{23}\tilde{b}_{34} + \tilde{b}_{24}\tilde{b}_{23}\tilde{b}_{13} + \tilde{b}_{12}\tilde{b}_{24}\tilde{b}_{34}\\ &+ \tilde{b}_{23}\tilde{b}_{24}\tilde{b}_{14} + \tilde{b}_{13}\tilde{b}_{34}\tilde{b}_{24} + \tilde{b}_{23}\tilde{b}_{34}\tilde{b}_{14}\big]\end{aligned}$$



(56)

Generally, the weighting factor ω for a labeled cluster diagram as defined here is

$$\omega = \prod_{\nu=1}^{n}(\deg_\nu - 1)!, \tag{57}$$

where the product is over all n vertices of the diagram, and where $\deg_\nu$ is the degree of vertex ν, i.e., the number of $\tilde{b}$ functions in which ν appears. Since the value of ω is the same for all labeled diagrams that correspond to an unlabeled one, ω may be written in front of the unlabeled diagrams. Unfortunately, we could not prove the general validity of Eq. (57). However, this formulation for ω leads to consistency between our formulation for the integrands $\tilde{B}_n$ and Eqs. (25) and (26) for the virial coefficients B_n up to at least $n = 8$. We have also verified numerically up to $n = 6$ for pairwise-additive potentials that the resulting integrands are identical in value to the corresponding integrands by Mayer and by Ree and Hoover. For nonadditive potentials the known nonadditivity corrections for $n \leq 5$ are also recovered. Thus, it is probably safe to assume that Eq. (57) is generally valid.

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We note that the two and four unlabeled diagrams used to express $\tilde{B}_3$ and $\tilde{B}_4$, respectively, correspond in each case to all possible allowed unlabeled diagrams, i.e., there are no allowed unlabeled diagrams that do not contribute to the corresponding integrand. This applies generally to all integrands $\tilde{B}_n$.

Equations (25) and (26) yield the following expressions for B_5 to B_8:

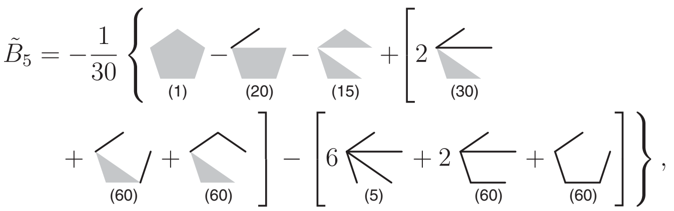
$$B_5 = -\frac{1}{30}\left[b_5 - 20b_4b_2 - 15b_3^2 + 180b_3b_2^2 - 210b_2^4\right], \quad (58)$$

$$B_6 = -\frac{1}{144}\left[b_6 - 30b_5b_2 - 60b_4b_3 + 420b_4b_2^2 + 630b_3^2b_2 - 3360b_3b_2^3 + 3024b_2^5\right], \quad (59)$$

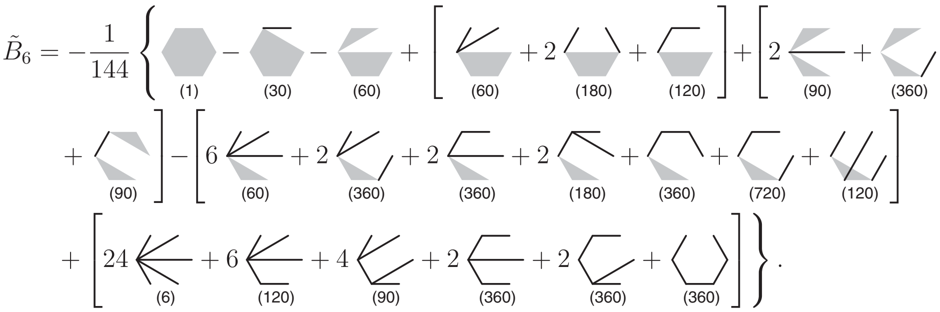
$$B_7 = -\frac{1}{840}\left[b_7 - 42b_6b_2 - 105b_5b_3 + 840b_5b_2^2 - 70b_4^2 + 3360b_4b_3b_2 - 10080b_4b_2^3 + 840b_3^3 - 22680b_3^2b_2^2 + 75600b_3b_2^4 - 55440b_2^6\right], \quad (60)$$

$$B_8 = -\frac{1}{5760}\left[b_8 - 56b_7b_2 - 168b_6b_3 + 1512b_6b_2^2 - 280b_5b_4 + 7560b_5b_3b_2 - 25200b_5b_2^3 + 5040b_4^2b_2 + 7560b_4b_3^2 - 151200b_4b_3b_2^2 + 277200b_4b_2^4 - 75600b_3^3b_2 + 831600b_3^2b_2^3 - 1995840b_3b_2^5 + 1235520b_2^7\right]. \quad (61)$$

For the integrands $\tilde{B}_5$ and $\tilde{B}_6$ the following diagrammatical representations are obtained:



(62)



(63)

The 59 and 165 unlabeled diagrams for $\tilde{B}_7$ and $\tilde{B}_8$, respectively, are given in the supplementary material.[27] We have not attempted to derive explicit expressions for still higher virial coefficients, as it seems more practicable in these cases to use computer codes in order to generate the necessary diagrams automatically when needed in numerical applications.

IV. COMPARISON WITH OTHER FORMULATIONS

We now compare the formulation of this work with the formulations by Mayer[10] and by Ree and Hoover[24] in terms of computational efficiency.

All three methods represent the virial coefficients B_n as integrals over sums of cluster diagrams with n vertices. The diagrams in the Mayer formulation are connected exclusively by two-particle Mayer functions f_{ij}, the number of which is at least n and at most $n(n-1)/2$ (fully connected). In the case of the Ree-Hoover formulation, the diagrams are always fully connected, and the vertices are connected either by f_{ij} or $\tilde{f}_{ij}$ functions, where $\tilde{f}_{ij} \equiv f_{ij} + 1$. The formulation presented in this paper uses diagrams that are less densely connected. The number of $\tilde{b}$ functions in a diagram is at most $n-1$, so that compared with the other two formulations less multiplications need to be performed in order to compute each diagram. The computation of the $\tilde{b}$ functions themselves is of course more costly in comparison with the f_{ij} and $\tilde{f}_{ij}$ functions. However, this overhead is very small relative to the computation of the whole integrand $\tilde{B}_n$.

Next, we compare the number of unlabeled diagrams. Table I shows how their number increases with increasing order of the virial coefficient for the different methods. For

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TABLE I. Number of unlabeled diagrams used to represent the virial coefficients B_n for the Mayer formulation, the Ree-Hoover formulation, and the method presented in this paper.

	Number of unlabeled diagrams		
n	Mayer	Ree and Hoover[a]	Present work
2	1	1	1
3	1	1	2
4	3	2	4
5	10	5	9
6	56	23	22
7	468	171	59
8	7123	2606	165
9	194 066	81 564	496
10	9 743 542	4 980 756	1540

[a] Numbers taken from Ref. 16.

the approach presented here, the increase is approximately exponential, whereas for the formulations by Mayer and by Ree and Hoover, the increase is much stronger. Nevertheless, up to the fifth virial coefficient the Ree-Hoover method uses the least number of diagrams and should be the most efficient overall. From the sixth virial coefficient upwards the method presented here uses the least number of diagrams. The efficiency advantage grows with increasing order of the virial coefficient. For B_8 the number of unlabeled diagrams is 16 times smaller than in the case of the Ree-Hoover approach and 43 times smaller than in the case of the Mayer formulation. As already mentioned in Sec. III, we did not derive expressions for virial coefficients beyond B_8. Yet, the number of unlabeled diagrams needed to express virial coefficients B_n for the method presented here is generally known from graph theory as the total number of unlabeled hypertrees with n vertices.[28,29] For B_{10} we would already have 1540 diagrams for the new approach, but nearly five million Ree-Hoover diagrams. Thus, we generally recommend the method presented here for the numerical evaluation of virial coefficients B_n with $n \geq 6$.

V. SUMMARY AND CONCLUSIONS

We have presented a new systematic formulation of the virial expansion for a classical gas composed of rigid particles. The resulting expressions for the virial coefficients B_n are suitable for numerical evaluation, and, in contrast to the previous approaches by Mayer[10] and by Ree and Hoover,[24] it is straightforward to account for nonadditive many-body interactions.

Up to B_5 the formulation by Ree and Hoover is computationally more efficient than the new approach. Moreover, expressions for nonadditivity corrections are already known for B_3 to B_5. However, for the new method the complexity of the integrands of the virial coefficients B_n increases more moderately with n, so that for B_6 and higher virial coefficients the formulation presented here is superior to the previous ones also in terms of computational efficiency. It should be possible to calculate virial coefficients well beyond B_{10} for simple fluids using the new formulation in combination with a suitable integration algorithm.

We have applied the new formulation in combination with the Mayer-sampling Monte Carlo method[18] to the computation of the virial coefficients of argon up to B_7 using *ab initio* two-body and nonadditive three-body potentials. The results will be published separately.[30]

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