




Calculating the classical virial expansion using automated algebra

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Using schematic model potentials, we calculate exactly the virial coefficients of a classical gas up to sixth order and use them to calculate the virial expansion of basic thermodynamic quantities such as pressure, density, and compressibility. At sufficiently strong couplings, as expected, the virial expansion fails to converge. However, at least for the interactions and parameter ranges we explored, we find that Padé-Borel resummation methods are very effective in improving the convergence of the expansion.

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I. INTRODUCTION

Understanding the finite-temperature thermodynamics of interacting matter represents an important and challenging problem across many areas of physics and chemistry. Notable applications are the dynamics of neutron star mergers (where the finite-temperature equations of state of neutron matter and nuclear matter play a central role) (see, e.g., [1,2]) and ultracold atomic gases [3,4] (highly malleable systems created in many laboratories around the world). While both of those applications involve quantum matter, there are cases in chemistry and nuclear physics which are better suited for a classical description (usually at high-enough temperature that quantum effects are irrelevant or whenever those can be encoded into effective interactions) (see, e.g., [5]). Similarly, classical dynamics simulations of neutron matter at finite temperature have also been of interest [6]. This work focuses on such classical descriptions of many-particle systems at finite temperature.

At high temperatures and low densities, the virial expansion (VE) provides a rigorous approach to many-body equilibrium thermodynamics whereby each successive order N adds on the contribution of the N -body problem to the grand-canonical description. Notably, in recent years the quantum VE has attracted considerable attention, in particular in connection with ultracold atomic gases [7,8], but also as a way to characterize finite-temperature neutron star matter in dilute regimes (see, e.g., [9–11]). Similarly, as explained in Ref. [5], there is also considerable activity in this direction in the area of chemistry, where the last decade has seen renewed interest in virial equations of state. In all of these cases, novel automated algebra approaches have enabled the calculation of high-order virial coefficients, allowing for the successful application of resummation techniques (see, e.g., [12,13]).

In this work we focus on the application of the VE to a classical gas with a schematic interaction featuring a purely repulsive two-body force as well as a repulsive force with an attractive pocket at intermediate distances. Within the context of that interaction, we explore varying temperatures and coupling strengths in three spatial dimensions (although, as we explain below, our method is capable of calculating the VE in arbitrary dimensions). For this purpose, we have developed an automated algebra approach to the calculation of high-order

VE coefficients (based on the seminal work of Ref. [14]), which is now available online at [15]. For the specific form of the schematic interaction considered here, our results for the coefficients of the VE are exact (up to numerical accuracy limitations) and therefore free of statistical effects (as no stochastic estimators are used in any way).

The remainder of this paper is organized as follows. Section II presents the formalism of the VE for a gas of identical particles, first in general form and then specializing to classical statistics. Section III explains the details of our approach to calculating the virial coefficients in an automated fashion. In Sec. IV we show the schematic model interaction and corresponding results. Finally, in Sec. V we summarize, conclude, and comment on the outlook of our work.

II. FORMALISM

The VE organizes the many-body problem into a sum of N -body problems, specifically by Taylor expanding the grand-canonical partition function \mathcal{Z} in powers of the fugacity z , such that

$$\mathcal{Z} = \sum_{N=0}^{\infty} Q_N z^N, \quad (1)$$

where Q_N is the N -particle canonical partition function, $z = e^{\beta\mu}$, β is the inverse temperature, and μ is the chemical potential. The grand thermodynamic potential Ω is then given by

$$-\beta\Omega = \ln \mathcal{Z} = Q_1 \sum_{N=1}^{\infty} b_N z^N, \quad (2)$$

where b_N are the virial coefficients

$$b_1 = 1, \quad (3)$$

$$b_2 = \frac{Q_2}{Q_1} - \frac{Q_1}{2!}, \quad (4)$$

$$b_3 = \frac{Q_3}{Q_1} - b_2 Q_1 - \frac{Q_1^2}{3!}, \quad (5)$$

$$b_4 = \frac{Q_4}{Q_1} - \left(b_3 + \frac{b_2^2}{2}\right) Q_1 - b_2 \frac{Q_1^2}{2!} - \frac{Q_1^3}{4!}, \quad (6)$$

and so on. (It is useful to note that the above are also historically known as the “cluster” coefficients, and they are still referred to with that name in some areas of physics and chemistry. In the area of ultracold atoms and nuclear physics, it appears that over the last two decades, at least, the nomenclature has shifted to calling them “virial” coefficients. In other areas, the “virial” name is reserved for the series representing the pressure in powers of the density, which can be obtained from the b_N .)

In this work we focus on classical systems, but to make the connection to the quantum case explicit, it is worth noting that in that case the expansion coefficients encode both quantum as well as interaction effects. Indeed, the coefficients of *noninteracting* quantum gases are generally nonvanishing, whereas their classical counterparts are all zero beyond b_1 .

In the above expressions for b_N , the only contribution comes from the term Q_N/Q_1 ; the role of the remaining terms is to cancel out contributions from within Q_N that scale with superlinear powers of the spatial volume V . Once those cancellations are properly accounted for, the final result for b_N does not scale with the volume V . [We note that, as emphasized in Refs. [16,17], this does not mean that b_N is volume independent; the latter is only true if $N/V \ll n$, where n is the actual density of the system.] In practice, this property implies that one can focus exclusively on those terms in Q_N that are proportional to V [since Q_1 scales as V ; see Eqs. (4)–(6)]. We use this property in our calculations, as further explained below in connection with selecting the connected diagrammatic contributions.

For a classical gas of N identical particles in d spatial dimensions, the canonical partition function is

$$Q_N = \frac{1}{N! h^{dN}} \int d^N \mathbf{p} \int d^N \mathbf{r} e^{-\beta \mathcal{H}[\{\mathbf{p}\}, \{\mathbf{r}\}]}, \quad (7)$$

where

$$\mathcal{H}[\{\mathbf{p}\}, \{\mathbf{r}\}] = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i<j} v_{ij}. \quad (8)$$

Here \mathbf{p}_i represents the momentum of the i th particle, \mathbf{r}_i its position, m its mass (which will be assumed to be the same for all particles), and $v_{ij} = v(|\mathbf{r}_i - \mathbf{r}_j|)$ is the interaction potential energy that depends on the distance between particle i and particle j . We focus in this work on pairwise interactions, but generalizations to three-body forces and beyond are possible. In contrast to the quantum case, where momentum and position operators do not commute (and one must resort to Trotter-Suzuki factorizations; see, e.g., [18]), here the momenta can be integrated out, which yields

$$Q_N = \frac{1}{\lambda_T^{dN} N!} Z_N, \quad (9)$$

where $\lambda_T = \sqrt{2\pi \hbar^2 \beta / m}$ is the thermal wavelength and we define the configuration integral

$$Z_N = \int d^N \mathbf{r} \exp \left(-\beta \sum_{i<j} v_{ij} \right). \quad (10)$$

Capturing the interaction effects on the grand canonical partition function \mathcal{Z} through the b_N 's amounts to calculating

the interaction-induced change

$$\Delta Q_N = \frac{1}{\lambda_T^{dN} N!} \Delta Z_N, \quad (11)$$

where

$$\Delta Z_N = \int d^N \mathbf{r} \left[\exp \left(-\beta \sum_{i<j} v_{ij} \right) - 1 \right]. \quad (12)$$

The Δ denotes the difference between the relevant thermodynamic quantity and the value it would take in a noninteracting but otherwise equivalent system. In turn the above ΔQ_N determine the change in the virial coefficients Δb_N , which enter into the thermodynamics via

$$-\beta \Delta \Omega = \ln(\mathcal{Z}/\mathcal{Z}_0) = Q_1 \sum_{N=1}^{\infty} \Delta b_N z^N, \quad (13)$$

where

$$\Delta b_1 = 0, \quad (14)$$

$$\Delta b_2 = \frac{\Delta Q_2}{Q_1}, \quad (15)$$

$$\Delta b_3 = \frac{\Delta Q_3}{Q_1} - \Delta b_2 Q_1, \quad (16)$$

and so forth, where we have used the fact that $\Delta Q_1 = 0$, since interactions only act among at least two particles.

The formalism presented above is the standard one due to Mayer [19] and often found in textbooks (see, e.g., [20,21]), albeit not always presented in as much detail as here. The above formulas apply to any two-body interaction. Below we show how our computational method organizes the calculation of ΔZ_N to access Δb_N .

III. COMPUTATIONAL METHOD

A. Basic considerations

In order to calculate the central quantities ΔZ_N , we use Mayer's definition of the so-called f function [19] given by

$$e^{-\beta v_{ij}} = 1 + f_{ij}, \quad (17)$$

such that

$$\Delta Z_N = \int d^N \mathbf{r} \left[\prod_{i<j} (1 + f_{ij}) - 1 \right]. \quad (18)$$

The product in this equation has $\binom{N}{2}$ factors and hence $2^{\binom{N}{2}}$ individual terms. One of these terms contains no f functions (thus representing a noninteracting contribution) and is equal to unity, which will cancel out with the -1 term in the square bracket, thus leaving $2^{\binom{N}{2}} - 1$ total terms in the integrand. Letting n denote the number of f functions that appear in a given term, each integrand is a product of the form $f_{i_1 j_1} f_{i_2 j_2} \cdots f_{i_n j_n}$, where $1 \leq i_k < j_k \leq N$ and $1 \leq n \leq \binom{N}{2}$. Following the definition used in [20], we establish a bijective correspondence between the integrals in Eq. (18) and simple undirected N -particle graphs. The restriction to simple

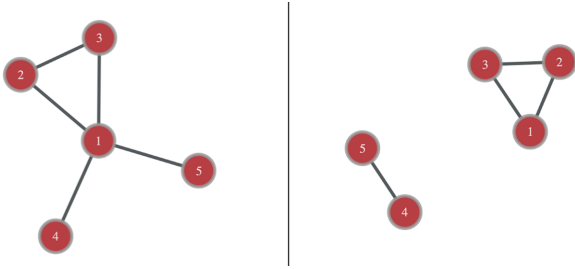


FIG. 1. The graph on the left is simply connected, so the integral Eq. (19) scales as V and hence contributes to Δb_5 . The graph on the right corresponds to an integral that scales faster than V , so it must get canceled in Eq. (18) and hence can be disregarded in computation.

graphs excludes self-loops and multiple edges, reflecting the fact that each factor f_{ij} must have distinct indices and can appear at most once in a given integrand. Let the nodes of an N -particle graph be labeled $1, 2, \dots, N$. Given an arbitrary integral term, for each factor $f_{i_k j_k}$ appearing in the integrand (which has the form $f_{i_1 j_1} f_{i_2 j_2} \dots f_{i_n j_n}$), connect an undirected edge between nodes i_k and j_k . As is well known, of all the graphs generated by the terms in the expansion, only the simply connected ones yield nonvanishing contributions to the b_N , as these correspond precisely to the terms of Q_N that scale linearly with V .

As examples, we show in Fig. 1 two contributions at order $N = 5, n = 5$, which represent the integrals

$$\int d^d \mathbf{r}_1 d^d \mathbf{r}_2 d^d \mathbf{r}_3 d^d \mathbf{r}_4 d^d \mathbf{r}_5 f_{12} f_{13} f_{14} f_{15} f_{23} \quad (19)$$

and

$$\int d^d \mathbf{r}_1 d^d \mathbf{r}_2 d^d \mathbf{r}_3 f_{12} f_{23} f_{13} \int d^d \mathbf{r}_4 d^d \mathbf{r}_5 f_{45} \quad (20)$$

on the left and right, respectively.

B. Efficient identification of contributing graphs

We are thus interested in calculating and summing the integral contributions to Eq. (18) that correspond to simply connected N -particle graphs. Assuming that all particles interact via the same pairwise potential, the result of a given integral is invariant to permutation of the indices. Expressed graphically, this means that any two isomorphic graphs will yield the same numerical value upon computation. Graph isomorphism is an equivalence relation on a set of graphs, so we can partition the set of simply connected N -particle graphs into isomorphism equivalence classes such that the integral terms in each are numerically equivalent.

We can represent this collection with a “multiset”

$$\mathcal{G}^* = \{g_1 G_1, g_2 G_2, \dots\}, \quad (21)$$

where the elements G_i represent unique isomorphism class representatives and the repetition numbers g_i represent the size of the corresponding isomorphism class. After numerically evaluating the G_i , we can form the vectors $\mathbf{g} = [g_1 \ g_2 \ \dots]^T$ and $\mathbf{G} = [G_1 \ G_2 \ \dots]^T$ and calculate Eq. (18)

via

$$\Delta Z_N = \mathbf{g}^T \mathbf{G}. \quad (22)$$

Our implementation contains the combinatorial data of \mathcal{G}^* (and hence can compute the VE coefficients) beyond the sixth order presented here. The data through order six were obtained by brute force isomorphism testing using the `graph-tools` library, which implements the VF2 algorithm of Cordella *et al.* [22]. The data for higher orders were obtained using the repository from Ref. [23] and the fact that

$$g_i = \frac{N!}{|\text{Aut}(G_i)|}, \quad (23)$$

where $|\text{Aut}(G_i)|$ is the cardinality of the automorphism class of an N -particle graph G_i .

We note that having such combinatorial data for high orders available beforehand resulted in considerable savings in terms of computation time. Fortunately, these data are universal: they do not depend on the shape of the (two-body) interaction.

C. Integral evaluation

Evaluating Eq. (22) requires us to calculate each of the dN -dimensional integrals appearing in \mathbf{G} . A completely general treatment would involve constructing the functional form of each integrand and proceeding with a broadly applicable numerical integration method like Monte Carlo. We choose instead to base our scheme on the multivariate Gaussian identity

$$\int_{-\infty}^{\infty} \exp\left(-\frac{1}{2} \mathbf{x}^T M \mathbf{x}\right) d^m \mathbf{x} = \sqrt{\frac{(2\pi)^m}{\det M}}, \quad (24)$$

where $M \in R^{m \times m}$ is a symmetric positive definite matrix and $x \in R^m$. While this identity is well known, it corresponds to an exact integration only for potentials v_{ij} that yield an integrand of this form when transformed through Eq. (17), the class of potentials for which this method is exact can emulate both a purely repulsive interaction and an interaction with an attractive pocket, as we describe below.

Additionally, this method is computationally efficient. The integrands never have to be constructed explicitly, and the results may be obtained by computing $N \times N$ determinants, even though the integration space is dN -dimensional. Indeed, computing the VE coefficients to ninth order, which requires evaluating $O(10^5)$ unique integrals, can be accomplished in seconds. Lower orders can be achieved essentially instantaneously on a modern computer, allowing one to plot smooth curves describing the evolution of the coefficients. In general, however, we note that the scaling of the computation effort needed to calculate the VE coefficients is nonpolynomial and can quickly become prohibitive at large N . Ultimately, a given N th-order calculation is limited by the number of terms that need to be evaluated, not by the computation of each term. The number of such integrals for $1 \leq N \leq 19$ can be found in Sequence A001349 of the Online Encyclopedia of Integer Sequences.

Another advantage of Eq. (24) is that it permits the use of noninteger dimensions. In our case the dimension enters

the result via $m = dN$ and the power to which we raise the eigenvalues of one block of the quadratic form represented by M . Thus, one could simply regard d as a parameter of the investigation, such that examining how the VE coefficients change with dimension would amount to the exponentiation of scalars, sidestepping the already small cost of the determinant computations.

As a final note, our current implementation offers to approximate a general integrand with one of the form in Eq. (24). We have done this to provide some degree of generality to others who may use our code, but the general case is not the focus of this paper. We restrict our attention moving forward to those potentials for which the results are exact.

IV. MODEL AND RESULTS

In this section we present our results for the pressure and density equations of state, as well as the isothermal compressibility. The approach detailed in the previous sections applies to an arbitrary two-body potential v_{ij} where, in general, the integrals that result will not have exact analytic forms (i.e., one will not be able to use the simple result valid for Gaussians, mentioned above), such that a stochastic evaluation is needed, with the concomitant statistical uncertainties. To avoid such uncertainties, in this work we use a class of schematic model potentials for which an exact evaluation is possible. Specifically, we define our two-body interaction potential v_{ij} to be such that

$$f_{ij} = Ae^{-b_1(r_i-r_j)^2} - (1+A)e^{-b_2(r_i-r_j)^2}, \quad (25)$$

where A, b_1, b_2 are constants; we will refer to this assumption as a Gaussian model. In other words, rather than fixing the shape of v_{ij} and setting the inverse temperature β , and extracting f_{ij} from them via Eq. (17), in this work we test our calculations by fixing the constants A, b_1, b_2 above, thus letting the interaction be dictated by

$$v_{ij} = -\frac{1}{\beta} \ln(1 + f_{ij}). \quad (26)$$

In a realistic application, one would instead take v_{ij} as an input and determine the temperature dependence of A, b_1, b_2 by optimization.

With f_{ij} given by Eq. (25), one may easily represent physically interesting situations such as a repulsive interaction (setting $A = 0$ or $A = -1$), as well as a repulsive two-body potential with an attractive pocket (for $A > 0$ or $A < -1$). In this work we explore both of these situations, shown schematically in Fig. 2.

A. Purely repulsive interaction

In Fig. 3 we show our results for the virial coefficients Δb_N of the purely repulsive Gaussian model (i.e., $A = -1$; see left panel of Fig. 2), as a function of the dimensionless coupling $\alpha = T/b_1$. As α grows, so do the interaction effects on the virial coefficients, as expected. In particular, we see how at large enough α , high-order coefficients tend to become larger than their lower-order counterparts; this type of behavior was found as well in the quantum case in Refs. [12,13], and it reflects the breakdown of the convergence properties of the

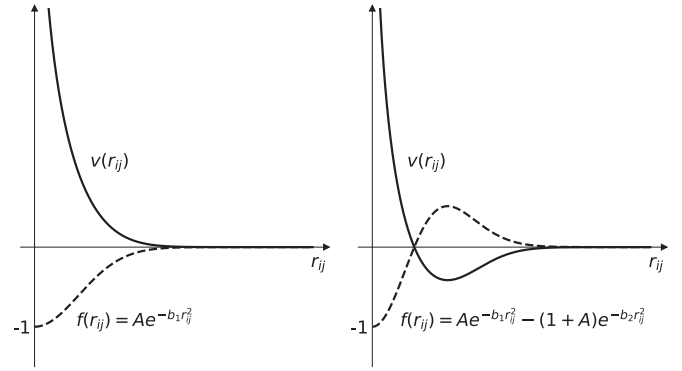


FIG. 2. Left panel: Solid line shows the potential v_{ij} as a function of $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, resulting from the Gaussian model of Eq. (25) setting $A = -1, b_1 > 0$, shown with a dashed line. Right panel: More general case corresponding to arbitrary $A > 0$ and $b_2 > b_1 > 0$ (or $A < -1$ and $b_1 > b_2 > 0$).

series. With the virial coefficients in hand, it is straightforward to evaluate the partial sums up to the available order for the pressure, density, and isothermal compressibility. They are given by

$$\frac{P}{P_0} = 1 + \sum_{N=2}^{\infty} \Delta b_N z^{N-1}, \quad (27)$$

$$\frac{n}{n_0} = 1 + \sum_{N=2}^{\infty} N \Delta b_N z^{N-1}, \quad (28)$$

and

$$\frac{\kappa}{\kappa_0} = \frac{1 + \sum_{N=2}^{\infty} N^2 \Delta b_N z^{N-1}}{\left(1 + \sum_{N=2}^{\infty} N \Delta b_N z^{N-1}\right)^2}, \quad (29)$$

where in all cases the subscript 0 indicates the noninteracting case and we have used the thermodynamic identity

$$\kappa = \frac{\beta}{n^2} \left. \frac{\partial n}{\partial(\beta\mu)} \right|_T. \quad (30)$$

It is straightforward to evaluate Eqs. (27) and (28) as partial sums, but doing so for Eq. (30) requires a bit more care. As written, Eq. (30) will include partial contributions to higher

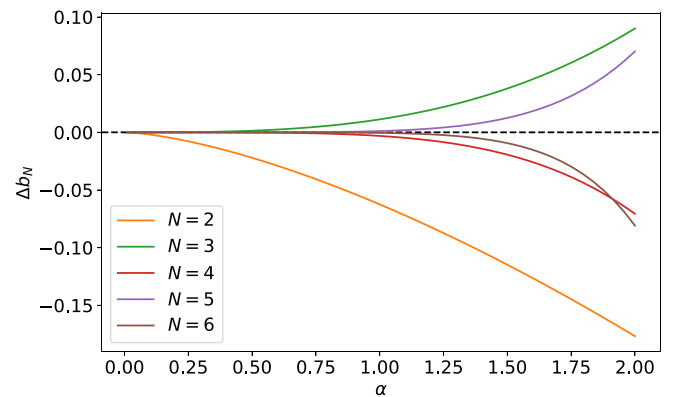


FIG. 3. Virial coefficients Δb_N for $N = 2, 3, 4, 5, 6$ for the repulsive model ($A = -1$) as a function of the dimensionless coupling $\alpha = T/b_1$.

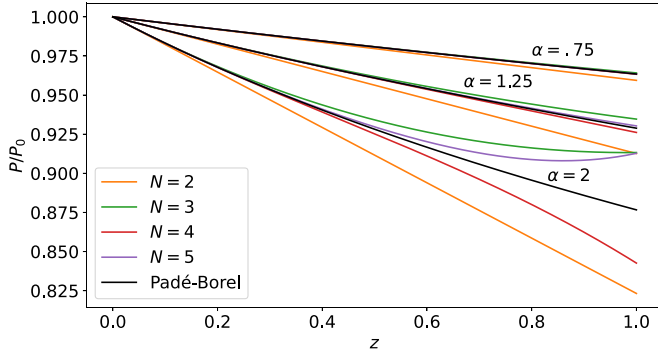


FIG. 4. Pressure P for the purely repulsive model, in units of its noninteracting counterpart P_0 , as a function of the fugacity z for three representative values of the dimensionless coupling $\alpha = T/b_1$. The colored lines show the highest value of the virial coefficient included, following the same convention as in Fig. 3. The black line shows the result of a Padé-Borel resummation, described below.

orders, making it unclear what such an expression represents [e.g., evaluating Eq. (30) with coefficients up to Δb_3 will not result in a quadratic plot, but will instead include the contributions of Δb_2 and Δb_3 to terms that are cubic and quartic in the fugacity]. Hence, to keep Eq. (30) on the same footing as Eq. (27) and Eq. (28), we rewrite it as a single power series

$$\frac{\kappa}{\kappa_0} = \sum_{N=1}^{\infty} c_N z^{N-1}, \quad (31)$$

where $c_1 = 1$ and

$$c_2 = 0, \quad (32)$$

$$c_3 = 3\Delta b_3 - 4\Delta b_2^2, \quad (33)$$

$$c_4 = 8\Delta b_4 - 24\Delta b_2\Delta b_3 + 16\Delta b_2^3, \quad (34)$$

and so on. Equation (31) truncated at c_N then represents the largest partial sum of κ/κ_0 exactly computable using VE coefficients up to order N , analogous to Eqs. (27) and (28).

Figures 4 through 7 show the above quantities for representative values of α . It is often useful to display the pressure-density equation of state, which amounts to a parametric plot that combines the information in Figs. 4 and 5. We show such a plot in Fig. 6.

1. Padé-Borel resummation of the VE

For strong enough interactions (in the sense of sufficiently large α), the partial sums of the VE show clear signs of convergence failure. To address this issue, we resort to resummation methods, specifically Padé-Borel resummation [24–26]. In this approach one replaces a given power series (in our case the VE)

$$g(z) = \sum_{n=0}^{\infty} a_n z^n, \quad (35)$$

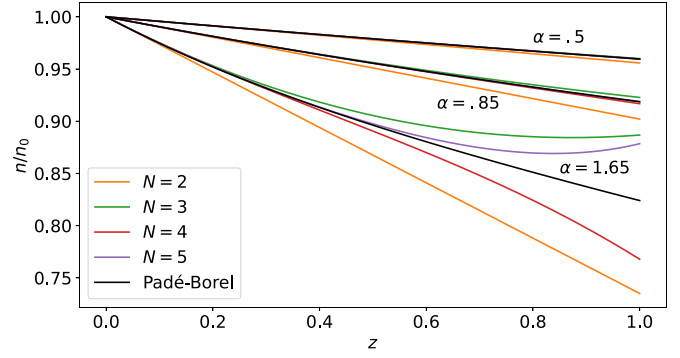


FIG. 5. Density n for the purely repulsive model, in units of its noninteracting counterpart n_0 , as a function of the fugacity z for three representative values of the dimensionless coupling $\alpha = T/b_1$. The colored lines show the highest value of the virial coefficient included, following the same convention as in Fig. 3. The black line shows the result of a Padé-Borel resummation, described below.

with its Borel transform, namely,

$$Bg(z) = \sum_{n=0}^{\infty} \frac{a_n}{n!} z^n, \quad (36)$$

whose convergence properties can be expected to be more favorable than those of the partial sums of the original function $g(z)$. We emphasize that this resummation method is simply a way to interpret the coefficients of the virial expansion. However, it does introduce a degree of arbitrariness in that it is not truly known to what extent a given Padé approximant captures the Borel transform of the series in question. Using the highest available partial sum for $Bg(z)$, a Padé approximant is used as an ansatz to fit the resulting function. These approximants take the rational form $P(z)/Q(z)$, where P and Q are polynomials. Once a proper fit is obtained (in particular one that does not display poles for real values of z , which would be unphysical), the resummed function is obtained (in fact, defined within the

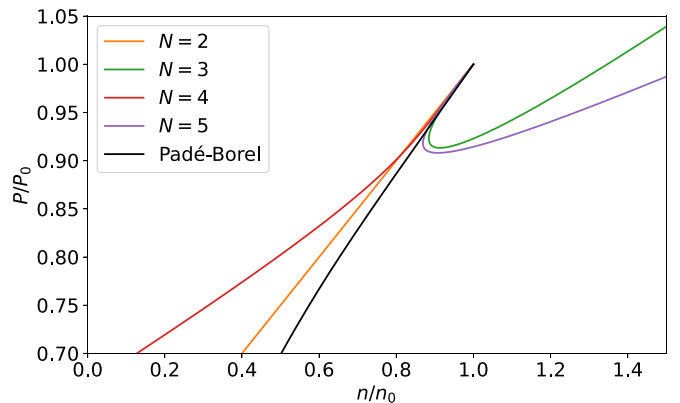


FIG. 6. Pressure-density equation of state for the purely repulsive model at $\alpha = T/b_1 = 1.25$. The colored lines show the highest value of the virial coefficient included, following the same convention as in Fig. 3. The black line shows the result of a Padé-Borel resummation, described below.

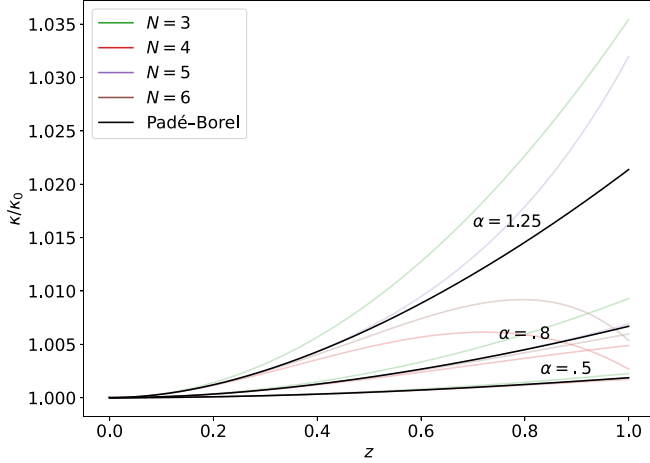


FIG. 7. Compressibility κ for the repulsive model, in units of its noninteracting counterpart κ_0 , as a function of the fugacity z . The black line shows the result of a Padé-Borel resummation.

context of the resummation method) via

$$g(z) = \int_0^\infty e^{-t} Bg(zt) dt, \quad (37)$$

which is evaluated numerically.

In each plot featuring a Padé-Borel resummation, the Padé approximant is fitted to the Borel transform of the highest partial sum displayed in the figure. Also, for all Padé approximants, $P(z)$ is linear and $Q(z)$ is quadratic. We experimented with different polynomial orders for P and Q but found that this combination behaved most reliably when performing the inverse transform of Eq. (37). The linear-quadratic approximant can replicate the Borel transforms of the pressure and density partial sums well, but the approximation quality lessens for the compressibility due to its increased curvature.

Figures 4 through 7 display the result of carrying out a Padé-Borel resummation on the series for the pressure, density, and compressibility. Our results show that this resummation approach improves the convergence properties of the VE (at least for the quantities and parameter ranges studied).

B. Repulsive interaction with attractive pocket

Encouraged by the results obtained for the purely repulsive interaction, we analyze here the more interesting case of an interaction that is repulsive at short distances but includes the more realistic feature of having an attractive pocket. The purpose of exploring this case, in the form of a toy model shown below, is to mimic the behavior of atomic and nuclear systems where the short-distance repulsion with intermediate-distance attraction is typical (as it appears, e.g., in Lennard-Jones-type potentials).

We obtain the desired shape for the interaction from Eq. (25) by setting $A = 1$ (an arbitrary illustrative choice) and varying values of $\gamma = b_2/b_1$. At $\gamma = 1$, the contribution from A disappears in Eq. (25) and one recovers the repulsive case considered in the previous section. As γ is increased beyond 1, an attractive pocket develops in the interaction (at a rate

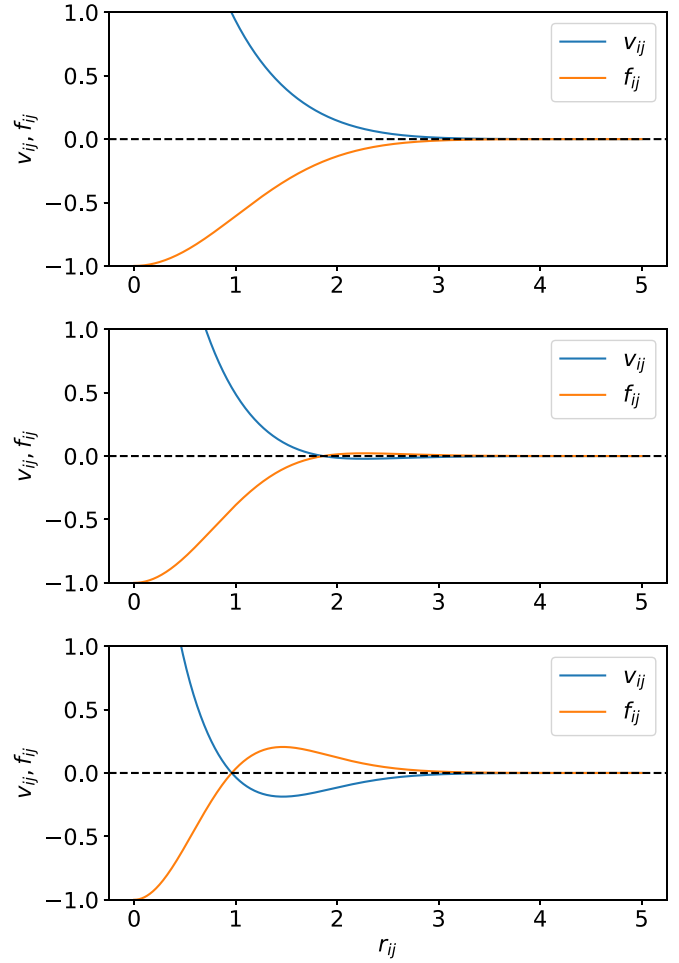


FIG. 8. Potential v_{ij} as a function of $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ (the horizontal axis is the same for all three plots), resulting from the Gaussian model of Eq. (25) setting $A = 1$ and varying the value of $\gamma = b_2/b_1$. From top to bottom, the plots show the cases of $\gamma = 1, 1.4,$ and $2.5,$ respectively.

governed by the value of A), as shown qualitatively in Fig. 2 and Fig. 8.

In Fig. 9 we show the results of our calculations for the virial coefficients as a function of γ at $\alpha = T/b_1 = 2$ (the latter being the strongest coupling considered in the previous section).

Following closely the discussion of the previous section, we show in Figs. 10 and 11 the pressure and compressibility, respectively, as functions of z , at fixed α and varying $\gamma \geq 1$, for the model with an attractive pocket. In each figure the fixed value of α used is the strongest coupling considered in the corresponding purely repulsive case (see Figs. 4 and 7). Once again, our results show that this resummation approach improves the convergence properties of the VE (at least for the quantities and parameter ranges studied).

V. CONCLUSION AND OUTLOOK

In this work we have implemented an automated algebra approach to the calculation of high-order VE coefficients Δb_N of a gas of classical particles interacting via a toy-

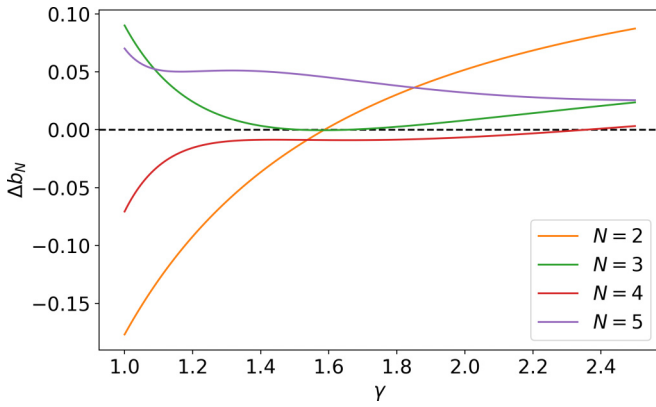


FIG. 9. Virial coefficients Δb_N for $N = 2, 3, 4, 5$ for the repulsive model with an attractive pocket ($A = 1, \alpha = 2$) as a function of the dimensionless coupling $\gamma = b_2/b_1$. At $\gamma = 1$, the model becomes the purely repulsive limit of the previous section. As γ is increased beyond 1, the attractive pocket develops, as shown in Fig. 8.

model Gaussian interaction. Using those, we calculated the pressure and density equations of state, as well as the isothermal compressibility. Additionally, we explored the convergence properties of the expansion based on the information provided by those coefficients. A more thorough study of the convergence properties of the expansion for realistic interaction potentials (considering the asymptotic behavior of the coefficients at high orders) can be found in Ref. [27].

As one of our main conclusions, we have found that resummation techniques such as Padé-Borel can extend the applicability of the VE, at least for the class of models and parameter ranges we studied. Although we present this optimistic view, our results should be taken with the proverbial grain of salt, as the analytic properties of the VE

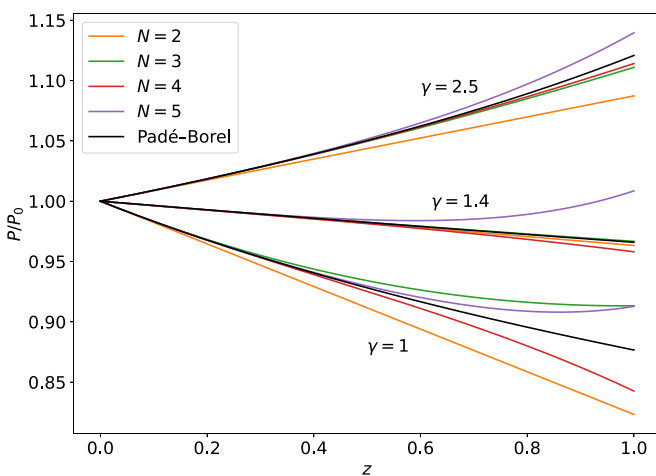


FIG. 10. Pressure P for the repulsive model with attractive pocket, in units of its noninteracting counterpart P_0 , as a function of the fugacity z , for three different values of the interaction parameter γ . Note that $\gamma = 1$ corresponds to the purely repulsive case studied in the previous section. The black line shows the result of a Padé-Borel resummation.

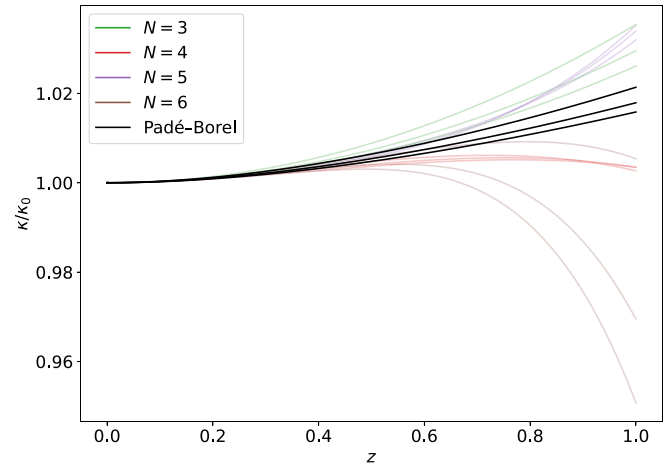


FIG. 11. Compressibility κ for the repulsive model with attractive pocket, in units of its noninteracting counterpart κ_0 , as a function of the fugacity z . The black lines show the result of a Padé-Borel resummation, from top to bottom for $\gamma = 1, 1.03, 1.05$, respectively.

are not well known for the specific family of models we considered.

The main result of this work is the creation of an automated algebra package, which can be found online as the Classical Virial Expansion Engine (CVE²); see Refs. [14] and [15] for continued developments and releases. To the best of our knowledge, this is the first project addressing this problem by implementing an approach fully based on automated algebra (without numerical integration), as presented here. Although we have used only CVE² to calculate up to b_6 in this work, the code is prepared to go beyond b_7 in its present form.

It is worth noting that the ability to evaluate b_N essentially algebraically, as advocated here, distinguishes our method from other approaches one may use to calculate this quantity. Indeed, fully numerical techniques like molecular dynamics and Monte Carlo are severely limited in their ability to calculate b_N : in one way or another they have to face cancellations that scale with powers of the volume in order to resolve the connected contributions that yield b_N ; this would be highly impractical in three dimensions beyond b_2 . In our method, the volume cancellation is implemented analytically in Eq. (24) by excluding zero eigenvalues from the computation of $\det(M)$, avoiding the issue entirely. While other methods could fit a polynomial to an equation of state, that would also be very imprecise, as it requires assuming that the higher-order coefficients are in some sense small, which is not a guarantee.

The most straightforward generalizations of our analysis, which will shed further light on the possibilities of the method, its implementation via CVE², and the properties of the VE, include extensions to multispecies systems (here we focused on identical particles of a single type), and within the latter the possibility of mass imbalance and spin polarization. Another aspect worth exploring is the dependence on spatial dimension, which is straightforward in our approach since the dimension enters analytically as a variable; in other words, within CVE², we can study classical gases

not only in three spatial dimensions (as done here) and lower integer dimensions, but also in fractional dimensions, which may be of interest from the mathematical physics perspective.

Finally, it is worth pointing out that we explored here a schematic interaction where the Mayer factor f was modeled as a single Gaussian function or a sum of two Gaussian functions. In future generalizations of this study, a higher number

of Gaussians could be used to study, for instance, more realistic interactions such as screened Coulomb potentials. We leave such investigations to future work.

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- [1] J. M. Lattimer, *Annu. Rev. Nucl. Part. Sci.* **62**, 485 (2012).
 - [2] L. Baiotti, *Prog. Part. Nucl. Phys.* **109**, 103714 (2019).
 - [3] I. Bloch, J. Dalibard, and W. Zwerger, *Rev. Mod. Phys.* **80**, 885 (2008).
 - [4] S. Giorgini, L. P. Pitaevskii, and S. Stringari, *Rev. Mod. Phys.* **80**, 1215 (2008).
 - [5] A. J. Schultz and D. A. Kofke, *J. Chem. Phys.* **157**, 190901 (2022).
 - [6] C. J. Horowitz, J. Hughto, A. Schneider, and D. K. Berry, Neutron star crust and molecular dynamics simulation, in *Neutron Star Crust*, edited by C. Bertulani and J. Piekarewicz (Nova Science Publishers, Hauppauge, NY, 2012).
 - [7] X.-J. Liu, *Phys. Rep.* **524**, 37 (2013).
 - [8] A. J. Czejdo, J. E. Drut, Y. Hou, and K. J. Morrell, *Condens. Matter* **7**, 13 (2022).
 - [9] C. Horowitz and A. Schwenk, *Nucl. Phys. A* **776**, 55 (2006).
 - [10] C. Horowitz and A. Schwenk, *Phys. Lett. B* **638**, 153 (2006).
 - [11] C. Horowitz and A. Schwenk, *Phys. Lett. B* **642**, 326 (2006).
 - [12] Y. Hou and J. E. Drut, *Phys. Rev. Lett.* **125**, 050403 (2020).
 - [13] Y. Hou and J. E. Drut, *Phys. Rev. A* **102**, 033319 (2020).
 - [14] A. M. Miller, Classical virial expansion engine (CVE²), B.Sc. (Hons) thesis, University of North Carolina, April 3rd 2023, https://cdr.lib.unc.edu/concern/honors_theses/dj52wg56j.
 - [15] A. M. Miller and J. E. Drut, Classical virial expansion engine (2023), <https://tarheels.live/cvee/>.
 - [16] D. A. Kofke, *J. Phys. Chem. B* **127**, 3690 (2023).
 - [17] M. V. Ushcats, S. Y. Ushcats, L. A. Bulavin, and V. M. Sysoev, *Phys. Rev. E* **98**, 032135 (2018).
 - [18] Y. Hou, A. J. Czejdo, J. DeChant, C. R. Shill, and J. E. Drut, *Phys. Rev. A* **100**, 063627 (2019).
 - [19] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, New York, 1940).
 - [20] K. Huang, *Statistical Mechanics*, 2nd ed. (John Wiley & Sons, New York, 1987).
 - [21] R. Pathria, *Statistical Mechanics*, International Series of Monographs in Natural Philosophy (Pergamon Press, Oxford, 1972).
 - [22] L. Cordella, P. Foggia, C. Sansone, and M. Vento, *IEEE Trans. Pattern Anal. Mach. Intell.* **26**, 1367 (2004).
 - [23] B. McKay, Combinatorial data, <http://users.cecs.anu.edu.au/~bdm/data/graphs.html>.
 - [24] M. Pindor, [arXiv:hep-th/9903151](https://arxiv.org/abs/hep-th/9903151).
 - [25] G. A. J. Baker and P. Graves-Morris, *Padé Approximants (Encyclopedia of Mathematics and its Applications, Series Number 59)* (Addison-Wesley, 1981).
 - [26] J. Gilewicz, *Approximants de Padé, Lecture Notes in Mathematics* (Springer Verlag, 1978).
 - [27] M. V. Ushcats, L. A. Bulavin, V. M. Sysoev, and S. Y. Ushcats, *Phys. Rev. E* **96**, 062115 (2017).