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Exact Calculation of One-Dimensional Irreducible Integrals

Alan J. Liebman[1,2] and Jean-Yves Parlange[1]

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One-dimensional irreducible integrals (β_k) are computed in the form of Mayer f-function polynomials for a general interparticle potential. Obeisance to the exact specification of the irreducible integral definition produces regularities in the interaction of star graphs with the integration process. Tables of β_k for $k \leqslant 5$ and test solutions are presented.

KEY WORDS: Mayer functions; irreducible integrals; virial coefficients; statistical physics; graph theory; one-dimensional gases.

1. INTRODUCTION

The properties of nonideal classical gases have been investigated both experimentally and theoretically through the agency of the virial expansion of the state equation. The succeeding terms of this infinite power series in density represent the contributions of binary, ternary, etc., interparticle collisions to the gas pressure. Commonly, investigations are limited to the several lowest-order terms; these are sufficient to describe nonpolar gases at densities below their condensation points.

[1] Department of Engineering and Applied Science, Yale University, New Haven, Connecticut.

[2] Present address: Xerox Corporation, Rochester, New York.

The limits of experimental determination of the virial coefficients arise from the difficulty of making precise measurements at low pressure or density.[1] In particular, only the second and third virial coefficients are usually extractable. Analytic solutions for the *infinite* set of virial coefficients are available for a few special and simple forms of the intermolecular potential.[2-4] Coefficients deriving from more realistic or complex potentials (e.g., the Lennard-Jones 12–6 potential) are available as numerical solutions and are frequently limited to several lowest-order terms.[1,5-8]

A major avenue for numerical solution of virial coefficients is based upon their statistical mechanical derivation. In the late 1930's Mayer and coworkers[9] were able to derive an exact theoretical relationship between the coefficients and the molecular potential acting between particle pairs. This computation was, in essence, a very useful reordering of terms in the definition of the system's partition function. The result is that the coefficient of the $(k + 1)$th power of the density is given by

$$-KT[k/(k + 1)]\beta_k \tag{1}$$

The β_k are called "irreducible cluster integrals" and are given by

$$\beta_k = \frac{1}{k!V}\int \cdots \int \left(\sum\prod f_{ij}\right) d\tau_1 \cdots d\tau_{k+1} \tag{2}$$

The integrand consists of the sum over all products of pairs of particles such that, within each product, every particle has a minimum of two interaction connections. Between the ith and jth particles, the energy function $U_{ij}(r)$ exists and the contribution to the integrand is through a Mayer f-function:

$$f_{ij}(r) = e^{-U_{ij}(r)/KT} - 1 \tag{3}$$

where T is the temperature and K the Boltzmann constant. To evaluate (2), one has to know the allowed bondings of $k + 1$ distinguishable particles into multiply connected clusters and be able to perform the integrations over particle positions in space. This is a formidable program; in n dimensions, as the index k increases, the number of terms in the integrand increases by a value of order k^2 and the number of integrations increases as $n(k + 1)$.

In most previous computational studies *numerical* values of $f_{ij}(r)$ have been inserted into Eq. (2) with the consequent expression of each virial coefficient as a single *number*. It will be shown in this paper that there are further opportunities in the calculation of virial coefficients. The interaction of the integration process with the set of star graphs may be studied in a mathematically rigorous way. The method is independent of the particular form of $f_{ij}(r)$. Contrary to the usual practice, the f-function of (3) will be taken as the independent variable and the irreducible integrals will be expressed in the *polynomial* form $\beta_k = \beta_k(f)$. Calculations of polynomials of

f-functions for the lower-order β_k are known[10] for first-neighbor interaction in several dimensions. Unlike the present study, however, the polynomial coefficients have not been related to variations within a class of potential functions and also the infinite β_k set was not presentable.

To demonstrate the computational technique and to retain a sufficient basis for testing the result, two system conditions are admitted: The calculations are made in one dimension and discrete lattice sites are introduced. The lattice property converts the integrals of Eq. (2) to summations and the single dimension of the system simplifies the particle binding logic. No adjustments of the definition (2) are otherwise made.

The next section details the translation of the Mayer definition into computer language. Section 3 presents the programming output and the β_k for a number of test potentials. Section 4 briefly considers further usage of the technique and some of its limitations.

2. COMPUTATIONAL CONSIDERATIONS

2.1. General Plan

For both analytic and computational ease (2) is rewritten with a notation from graph theory[11–13]:

$$\beta_k = \frac{1}{k!} \sum_{x_1} \cdots \sum_{x_{k+1}} \left\{ \sum_{l} \sum_{\theta} S_{k+1,l,\theta} \left(\prod f \right)_{k+1,l,\theta} \right\} \tag{4}$$

The set of multiply connected bondings between $k + 1$ labeled particles is known as the set of star graphs[3] of $k + 1$ labeled points. The summation over l $[k + 1 \leqslant l \leqslant \frac{1}{2}k(k + 1)]$ counts stars with $k + 1$ points and differing numbers of bonds, while θ counts the number of topologically different stars that have the same values of $k + 1$ and l. The star degeneracy $S_{k+1,l,\theta}$ is an integer equal to the number of ways of relabeling the points of the $(k + 1, l, \theta)$th star such that the bonding between points is unaltered. A lattice spacing (one dimensional volume) of unity has been chosen in (4) so a spacing constant will not appear explicitly in the tabulated results.

The need for computer evaluation of Eq. (4) is seen when it is realized that the number of allowed configurations of $k + 1$ labeled points is of order $\{[(k + 1)/2]N\}^{k+1}$, where N is the force range, expressed as a number of sites. For a second neighbor range ($N = 2$) and five particles ($k = 4$), for example, there are about 3×10^3 configurations. Between the five particles a maximum of ten bonds can exist and there are ten five-point star graphs.[11] The number of operations that must be performed is therefore greater than 10^5.

[3] A star graph is a connected linear graph with no articulation points, i.e., it has no points at which all the bonds can be severed, leaving disconnected graphs.

2.2. Force Laws

The general two-particle potential for a one-dimensional lattice gas can be written as a function of separation distance r:

$$U_{ij}(r) = U_0\,\delta(r) + U_1\,\delta(r-1) + U_2\,\delta(r-2) + \cdots \tag{5}$$

where r is measured in lattice site units,

$$\delta(r-j) = \begin{cases} 1 & \text{if } r = j \\ 0 & \text{if } r \neq j \end{cases} \tag{6}$$

and the U_i are constants. The corresponding Mayer f-function is

$$f_{ij}(r) = \exp\left\{-\frac{1}{KT}\left[U_0\,\delta(r) + U_1\,\delta(r-1) + U_2\,\delta(r-2) + \cdots\right]\right\} - 1 \tag{7}$$

One form of Eq. (7) that lends itself readily to computer study is the Nth-neighbor force (N finite), for which

$$U_{ij}(r) = \begin{cases} U_0\,\delta(r) + U_1\,\delta(r-1) + \cdots + U_N\,\delta(r-N), & r \leqslant N \\ 0, & r > N \end{cases} \tag{8}$$

Such a force imposes a natural limit on the size of the cluster of $k+1$ particles through the multiple-connectedness requirement of the star graphs. The β_k for first-, second-, third-, and higher-neighbor forces are one sequence of results to be exhibited in Section 3. The second-neighbor irreducible integrals (written $\beta_k^{(2)}$), for example, will be polynomials in products of the three Mayer f-functions:

$$f_0 = e^{-U_0/KT} - 1, \qquad f_1 = e^{-U_1/KT} - 1, \qquad f_2 = e^{-U_2/KT} - 1 \tag{9}$$

A second class of potential functions are those with an infinite force range. A meaningful way must be found to limit the number of placements of particles in these cases, for the force law itself no longer sets a maximum cluster width. The chosen example of this type is the Curie–Weiss force[14]

$$U_{ij}(r) = \begin{cases} +\infty, & r = 0 \\ -U_{cw}/N, & r \neq 0 \end{cases} \tag{10}$$

which has the pair of Mayer functions f_0 and f_c:

$$f_0 = -1, \qquad f_c = e^{-U_{cw}/NKT} - 1 \tag{11}$$

Here N is the total number of particles in the system, a constant for the purposes of this computation. The β_k for the Curie–Weiss force are computed for $k+1$ particles which are allowed to be, sequentially, on $1, 2, 3, \ldots, n$ sites; $\beta_k]_n$ is the designation for the n-site system. The value of β_k in an infinitely large system will be found by taking both the limits of N and n becoming infinitely large. A further interest of the Curie–Weiss potential is

its independence of dimensionality; performing the computation in one dimension leads to a result valid in higher dimensions.

2.3. Star Graphs

The general enumeration and classification of star graphs and their degeneracies is an unsolved problem, although tabulations of stars having two through seven points are available.[6,12]

The programs written for the present study require both the degeneracy numbers and the bonding specifications for each graph in the set with $k + 1$ points. The bonding is entered into the program with an exclusion–inclusion matrix, in which the presence of a zero (or one) in the ith row and jth column relates that the jth bond is missing (or present) from the ith graph. Bonding input for the six-point graphs ($k = 5$), for example, consists of a 56×15 matrix with this method.

3. RESULTS

When finite range potentials of the form (8) with $N = 1$ and $N = 2$ are introduced, the very general polynomials shown in Appendix A are generated. A number of regularities, such as the appearance of the star degeneracies as coefficients in the first-neighbor functions, are identifiable. Greater insight may be achieved, however, if a general, physically motivated limitation is superposed on the computer evaluations. It will be appreciated that the impenetrability property—the restriction that two or more particles shall not occupy the same lattice site—is required by many physically pertinent force functions. In the present framework this condition is introduced by taking $U_0 = +\infty$ and $f_0 = -1$. Great simplification is achieved in the computer output now, for signed numbers have been introduced and the algebraic addition of graph contributions leads to term cancellations. Such N-neighbor, "hard core" integrals, $\beta_k^{(N)}$, are given in Appendix B.

The irreducible integrals for the hard core, nearest-neighbor ($N = 1$) test case are derivable analytically. This is so because the quasichemical approximation for a three-dimensional nearest-neighbor gas is an exact solution of the one-dimensional gas.[15] The pressure for this gas may be written as

$$\frac{p}{KT} = \ln \frac{1 + \gamma}{1 + \gamma - 2\rho} \tag{12}$$

where

$$\gamma^2 = 1 + 4f_1\rho(1 - \rho) \tag{13}$$

and ρ is the gas density. By expanding the derivative of the pressure and

using Mayer's relation between this derivative and the irreducible integrals,

$$\frac{1}{KT}\frac{\partial p}{\partial \rho} = 1 - \sum_{k \geq 1} k\beta_k \rho^k \tag{14}$$

it is possible to show that

$$\beta_k^{(1)} = \frac{(-1)^{k+1}}{k} \sum_{n=0}^{k} \binom{n-1}{k-n}\binom{2n}{n} f_1{}^n \tag{15}$$

Equation (15) was verified by the computer program for $k \leqslant 5$. It is also verifiable as a special case of the more general $\beta_k^{(1)}$ of Appendix A. From the computer results it was learned that the value (15) derives entirely from configurations of $k + 1$ particles on *just two sites*, despite the fact that allowed cluster widths can be as great as (the integer less than or equal to) $(k + 3)/2$. Thus, the net contribution to the nearest-neighbor virial coefficients from all particle configurations wider than the force range is zero.

The functions compiled in Appendix B reveal that many additional regularities were created by the single physical condition invoked. It is noted that all the terms in $\beta_k^{(N)}$ having only a single f-function type—the "pure" terms—are simply duplications of the first-neighbor ($N = 1$) terms given by (15). For the "mixed" f-function terms, no encompassing tangency to analytic work is available. There are suggestive trends, however. Inspection of Appendix B shows that the coefficients of $f_1{}^2 f_2{}^1$ in $\beta_k^{(2)}$ all satisfy $\binom{3}{k-2}(k + 1)$, the coefficients of $f_1{}^2 f_2{}^2$ satisfy $\binom{4}{k-3}(k + 1)$, and the coefficients of $f_1{}^3 f_2{}^1$ satisfy $4\binom{4}{k-3}(k + 1)$. A general form for $\beta_k^{(N)}$ is not derivable at once from the present tabulations, but the computer method in conjunction with graph theory may allow a step-by-step advance on the relation between force laws and virial coefficients.

A more specific, but often-studied test case is recoverable if *all* the f_i in $\beta_k^{(N)}$ are set equal to -1: this yields the irreducible integrals of a one-dimensional, hard-rod lattice gas. It is possible to show[4] that the theoretical form for hard-rod irreducible integrals is

$$\beta_k^{(N)} = -(1/k)[(N + 1)^{k+1} - N^{k+1}] \tag{16}$$

This result is obtained numerically from the functions of Appendices A and B. These can be exploited further by considering a potential which consists of an infinitely repulsive core force and a noninfinite but repulsive N-neighbor force:

$$U_{ij}(r) = \begin{cases} U_0 = +\infty, & r = 0 \\ u = \text{const} = U_1 = U_2 = \cdots = U_N, & r = 1, 2, \ldots, N \end{cases} \tag{17}$$

This potential leads to the Mayer function set:

$$f(r) = \begin{cases} -1, & r = 0 \\ e^{-|u|/KT} - 1, & r = 1, \ldots, N \end{cases} \tag{18}$$

When u is large or T is small, $|e^{-|u|/KT}| \ll 1$ and the N-neighbor form of $f(r)$ raised to any power l can be expanded as

$$f^l(r) = (-1)^l + (-1)^{l-1}\binom{l}{1}e^{-|u|/KT} + (-1)^{l-2}\binom{l}{2}e^{-2|u|/KT} + \cdots \quad (19)$$

Such a "hard and soft" repulsive force can be investigated theoretically. Its analysis involves the sums called alternating moments of the star degeneracies,[4,12] some of which are known. In Appendix C several $\beta_k^{(N)}$ are given for the "hard and soft" repulsion gas when only the first-order term in $e^{-|u|/KT}$ is kept.

The Curie–Weiss potential introduced in Section 2.2 produces the $\beta_k]_n$ of Appendix D, where n is the number of sites in the lattice. Inspection of the results for $k = 2$ and $k = 3$ leads to the supposition that the forms for arbitrary n are

$$\begin{aligned}
\beta_2]_n &= -\frac{1}{2}\left[1 + 3\binom{n-1}{1}f_c^2 - 2\binom{n-1}{2}f_c^3\right] \\
\beta_3]_n &= -\frac{1}{3}\left[1 - 3\binom{n-1}{1}f_c^2 + \left\{12\binom{n-1}{2} - 10\binom{n-1}{1}\right\}f_c^3 \cdots\right. \\
&\quad + \left\{24\binom{n-1}{2} - 9\binom{n-1}{3}\right\}f_c^4 - 18\binom{n-1}{3}f_c^5 \cdots \\
&\quad \left. - 3\binom{n-1}{3}f_c^6\right]
\end{aligned} \quad (20)$$

For the lower-order virial coefficients, (20) suggests that the strongest n dependence of the coefficients of f_c in $\beta_k]_n$ is $\binom{n-1}{k}$, which varies as n^k. For large n, $f_c^l \sim n^{-l}$, so that *all* the terms containing f_c vary at least as $1/n$. For $n \to \infty$ it is thus suggested that

$$\lim_{n\to\infty} \beta_3]_n = -\tfrac{1}{3} \quad (21)$$

Analytic studies on the Curie–Weiss system show that[2,4]

$$\lim_{n\to\infty} \beta_k]_n = -1/k \quad (22)$$

for all k. This result for the irreducible integrals of the Curie–Weiss potential is valid, of course, only in the single-phase state.

4. PROSPECTS AND LIMITATIONS

The computation point of view presented above introduces an intermediate level at which the statistical mechanical underpinning of state

equations can be attacked. In the f-function polynomial method one has less than the total abstraction of the Mayer definition to study but more than the reduction of the problem to a single number. There are indications that the application of combinatorial analysis to the computed polynomials is likely to be fruitful. The present framework also provides test cases that further tabulations of star graph properties should meet. Direct extensions to higher dimensionalities and to higher-order virial coefficients of the method are foreseeable.

At present the limitations to the f-polynomial method arise from: (i) the few star graph properties known, (ii) the increase in output term complexity, and (iii) computer resource ceilings. None of these is an intrinsic limit. The first difficulty—that we have no information on star graphs of more than seven points—impacts all virial coefficient computer studies based on the Mayer theory. In principle, stepwise tabulation to any desired star graph order should be possible. The increase in monomial term complexity follows from the expansion of the permissible f-function set and from increases in the star graph order. As the simpler polynomial coefficients are understood, the more complex will be approachable. Last, time and storage capabilities of available computers may be taxed by the large tables and large number of arithmetic manipulations that are called for by increasing graph order and polynomial length. The expansion of computer technology and availability will remove this shortcoming.

APPENDIX A. $\beta_k^{(N)}$

First Neighbor

$$\beta_2^{(1)} = \frac{1}{2!}\left[1f_0^3f_1^0 + 6f_0^1f_1^2\right]$$

$$\begin{aligned}\beta_3^{(1)} = \frac{1}{3!}\big[&1f_0^6f_1^0 + 6f_0^5f_1^0 + 3f_0^4f_1^0 + 24f_0^3f_1^2 + 36f_0^2f_1^2 \cdots \\ &+ 8f_0^3f_1^3 + 48f_0^2f_1^3 + 6f_0^2f_1^4 + 24f_0^1f_1^4 + 18f_0^0f_1^4\big]\end{aligned}$$

$$\begin{aligned}\beta_4^{(1)} = \frac{1}{4!}\big[&1f_0^{10}f_1^0 + 10f_0^9f_1^0 + 45f_0^8f_1^0 + 100f_0^7f_1^0 + 70f_0^6f_1^0 \cdots \\ &+ 12f_0^5f_1^0 + 60f_0^6f_1^2 + 360f_0^5f_1^2 + 540f_0^4f_1^2 + 240f_0^3f_1^2 \cdots \\ &+ 40f_0^6f_1^3 + 240f_0^5f_1^3 + 840f_0^4f_1^3 + 880f_0^3f_1^3 + 10f_0^6f_1^4 \cdots \\ &+ 60f_0^5f_1^4 + 450f_0^4f_1^4 + 1300f_0^3f_1^4 + 840f_0^2f_1^4 + 360f_0^1f_1^4 \cdots \\ &+ 120f_0^4f_1^5 + 600f_0^3f_1^5 + 1200f_0^2f_1^5 + 720f_0^1f_1^5 + 20f_0^4f_1^6 \cdots \\ &+ 100f_0^3f_1^6 + 240f_0^2f_1^6 + 260f_0^1f_1^6 + 100f_0^0f_1^6\big]\end{aligned}$$

$$\begin{aligned}\beta_5^{(1)} = \frac{1}{5!}\big[&1f_0^{15}f_1^0 + 15f_0^{14}f_1^0 + 105f_0^{13}f_1^0 + 455f_0^{12}f_1^0 + 1335f_0^{11}f_1^0 \cdots \\ &+ 2697f_0^{10}f_1^0 + 3535f_0^9f_1^0 + 2445f_0^8f_1^0 + 720f_0^7f_1^0 \cdots \\ &+ 60f_0^6f_1^0 + 120f_0^{10}f_1^2 + 1200f_0^9f_1^2 + 5400f_0^8f_1^2 \cdots \\ &+ 13{,}080f_0^7f_1^2 + 15{,}960f_0^6f_1^2 + 9000f_0^5f_1^2 + 1800f_0^4f_1^2 \cdots\end{aligned}$$

$$+ 120f_0^{10}f_1^3 + 1200f_0^9f_1^3 + 5400f_0^8f_1^3 + 14{,}880f_0^7f_1^3 \cdots$$
$$+ 28{,}680f_0^6f_1^3 + 30{,}960f_0^5f_1^3 + 13{,}320f_0^4f_1^3 + 60f_0^{10}f_1^4 \cdots$$
$$+ 600f_0^9f_1^4 + 2700f_0^8f_1^4 + 9000f_0^7f_1^4 + 27{,}780f_0^6f_1^4 \cdots$$
$$+ 59{,}040f_0^5f_1^4 + 60{,}060f_0^4f_1^4 + 22{,}320f_0^3f_1^4 + 5400f_0^2f_1^4 \cdots$$
$$+ 12f_0^{10}f_1^5 + 120f_0^9f_1^5 + 540f_0^8f_1^5 + 3120f_0^7f_1^5 + 17{,}940f_0^6f_1^5 \cdots$$
$$+ 56{,}664f_0^5f_1^5 + 96{,}420f_0^4f_1^5 + 77{,}040f_0^3f_1^5 + 28{,}080f_0^2f_1^5 \cdots$$
$$+ 840f_0^7f_1^6 + 8400f_0^6f_1^6 + 32{,}160f_0^5f_1^6 + 69{,}960f_0^4f_1^6 \cdots$$
$$+ 89{,}880f_0^3f_1^6 + 53{,}040f_0^2f_1^6 + 9720f_0^1f_1^6 + 1200f_0^0f_1^6 \cdots$$
$$+ 240f_0^7f_1^7 + 2640f_0^6f_1^7 + 10{,}800f_0^5f_1^7 + 26{,}880f_0^4f_1^7 \cdots$$
$$+ 43{,}680f_0^3f_1^7 + 41{,}400f_0^2f_1^7 + 19{,}440f_0^1f_1^7 + 3240f_0^0f_1^7 \cdots$$
$$+ 30f_0^7f_1^8 + 420f_0^6f_1^8 + 1890f_0^5f_1^8 + 5400f_0^4f_1^8 + 10{,}140f_0^3f_1^8 \cdots$$
$$+ 11{,}430f_0^2f_1^8 + 6900f_0^1f_1^8 + 1710f_0^0f_1^8 + 20f_0^6f_1^9 \cdots$$
$$+ 120f_0^5f_1^9 + 420f_0^4f_1^9 + 880f_0^3f_1^9 + 1020f_0^2f_1^9 \cdots$$
$$+ 600f_0^1f_1^9 + 140f_0^0f_1^9]$$

Second Neighbor

$$\beta_2^{(2)} = \beta_2^{(1)} + \frac{1}{2!}[6f_0^0f_1^2f_2^1 + 6f_0^1f_1^0f_2^2]$$

$$\beta_3^{(2)} = \beta_3^{(1)} + \frac{1}{3!}[72f_0^1f_1^2f_2^1 + 96f_0^1f_1^3f_2^1 + 12f_0^0f_1^4f_2^1 \cdots$$
$$+ 12f_0^1f_1^4f_2^1 + 36f_0^2f_1^0f_2^2 + 24f_0^3f_1^0f_2^2 + 72f_0^0f_1^2f_2^2 + 96f_0^1f_1^2f_2^2 \cdots$$
$$+ 48f_0^0f_1^3f_2^2 + 24f_0^1f_1^3f_2^2 + 48f_0^2f_1^0f_2^3 + 8f_0^3f_1^0f_2^3 + 18f_0^0f_1^0f_2^4 \cdots$$
$$+ 24f_0^1f_1^0f_2^4 + 6f_0^2f_1^0f_2^4]$$

$$\beta_4^{(2)} = \beta_4^{(1)} + \frac{1}{4!}[720f_0^2f_1^2f_2^1 + 360f_0^3f_1^2f_2^1 + 2640f_0^2f_1^3f_2^1 + 720f_0^3f_1^3f_2^1 \cdots$$
$$+ 480f_0^0f_1^4f_2^1 + 1200f_0^1f_1^4f_2^1 + 2820f_0^2f_1^4f_2^1 + 420f_0^3f_1^4f_2^1 + 720f_0^0f_1^5f_2^1 \cdots$$
$$+ 1680f_0^1f_1^5f_2^1 + 1080f_0^2f_1^5f_2^1 + 120f_0^3f_1^5f_2^1 + 140f_0^0f_1^6f_2^1 + 300f_0^1f_1^6f_2^1 \cdots$$
$$+ 180f_0^2f_1^6f_2^1 + 20f_0^3f_1^6f_2^1 + 240f_0^3f_1^0f_2^2 + 540f_0^4f_1^0f_2^2 + 360f_0^5f_1^0f_2^2 \cdots$$
$$+ 60f_0^6f_1^0f_2^2 + 1440f_0^1f_1^2f_2^2 + 3000f_0^2f_1^2f_2^2 + 1080f_0^3f_1^2f_2^2 + 3360f_0^1f_1^3f_2^2 \cdots$$
$$+ 3480f_0^2f_1^3f_2^2 + 600f_0^3f_1^3f_2^2 + 960f_0^0f_1^4f_2^2 + 3480f_0^1f_1^4f_2^2 + 1500f_0^2f_1^4f_2^2 \cdots$$
$$+ 120f_0^3f_1^4f_2^2 + 720f_0^0f_1^5f_2^2 + 1080f_0^1f_1^5f_2^2 + 360f_0^2f_1^5f_2^2 + 60f_0^0f_1^6f_2^2 \cdots$$
$$+ 120f_0^1f_1^6f_2^2 + 60f_0^2f_1^6f_2^2 + 880f_0^3f_1^0f_2^3 + 840f_0^4f_1^0f_2^3 + 240f_0^5f_1^0f_2^3 \cdots$$
$$+ 40f_0^6f_1^0f_2^3 + 720f_0^0f_1^2f_2^3 + 2160f_0^1f_1^2f_2^3 + 2040f_0^2f_1^2f_2^3 + 360f_0^3f_1^2f_2^3 \cdots$$
$$+ 1760f_0^0f_1^3f_2^3 + 2880f_0^1f_1^3f_2^3 + 1080f_0^2f_1^3f_2^3 + 200f_0^3f_1^3f_2^3 + 1000f_0^0f_1^4f_2^3 \cdots$$
$$+ 1080f_0^1f_1^4f_2^3 + 240f_0^2f_1^4f_2^3 + 40f_0^3f_1^4f_2^3 + 120f_0^0f_1^5f_2^3 + 120f_0^1f_1^5f_2^3 \cdots$$
$$+ 360f_0^1f_1^0f_2^4 + 840f_0^2f_1^0f_2^4 + 1300f_0^3f_1^0f_2^4 + 450f_0^4f_1^0f_2^4 + 60f_0^5f_1^0f_2^4 \cdots$$
$$+ 10f_0^6f_1^0f_2^4 + 600f_0^0f_1^2f_2^4 + 840f_0^1f_1^2f_2^4 + 240f_0^2f_1^2f_2^4 + 240f_0^0f_1^3f_2^4 \cdots$$
$$+ 360f_0^1f_1^3f_2^4 + 120f_0^2f_1^3f_2^4 + 30f_0^0f_1^4f_2^4 + 60f_0^1f_1^4f_2^4 + 30f_0^2f_1^4f_2^4 \cdots$$
$$+ 720f_0^1f_1^0f_2^5 + 1200f_0^2f_1^0f_2^5 + 600f_0^3f_1^0f_2^5 + 120f_0^4f_1^0f_2^5 + 100f_0^0f_1^0f_2^6 \cdots$$
$$+ 260f_0^1f_1^0f_2^6 + 240f_0^2f_1^0f_2^6 + 100f_0^3f_1^0f_2^6 + 20f_0^4f_1^0f_2^6]$$

APPENDIX B. $\beta_k^{(N)}$ FOR HARD CORE POTENTIAL

Second Neighbor ($N = 2$)

$$\beta_1^{(2)} = -(1 - 2f_1 - 2f_2)$$
$$\beta_2^{(2)} = -\tfrac{1}{2}(1 + 6f_1^2 + 6f_2^2 - 6f_1^2f_2^1)$$
$$\beta_3^{(2)} = -\tfrac{1}{3}(1 - 6f_1^2 - 6f_2^2 - 20f_1^3 - 20f_2^3 + 36f_1^2f_2^1 + 12f_1^2f_2^2 \cdots$$
$$+ 48f_1^3f_2^1 - 12f_1^3f_2^2)$$

$$\beta_4^{(2)} = -\tfrac{1}{4}(1 + 40f_1^3 + 40f_2^3 + 70f_1^4 + 70f_2^4 - 60f_1^2f_2^1 \cdots$$
$$- 80f_1^2f_2^2 - 320f_1^3f_2^1 - 40f_1^2f_2^3 + 80f_1^3f_2^2 - 280f_1^4f_2^1 \cdots$$
$$+ 40f_1^3f_2^3 + 190f_1^4f_2^2 - 20f_1^4f_2^3)$$
$$\beta_5^{(2)} = -\tfrac{1}{5}(1 - 20f_1^3 - 20f_2^3 - 210f_1^4 - 210f_2^4 - 252f_1^5 - 252f_2^5 \cdots$$
$$+ 30f_1^2f_2^1 + 180f_1^2f_2^2 + 720f_1^3f_2^1 + 300f_1^2f_2^3 - 180f_1^3f_2^2 \cdots$$
$$+ 2400f_1^4f_2^1 + 150f_1^2f_2^4 - 300f_1^3f_2^3 - 2100f_1^4f_2^2 + 1440f_1^5f_2^1 \cdots$$
$$- 150f_1^3f_2^4 - 120f_1^4f_2^3 - 1770f_1^5f_2^2 + 90f_1^4f_2^4 + 540f_1^5f_2^3 \cdots$$
$$- 30f_1^5f_2^4)$$

Third Neighbor ($N = 3$)

$$\beta_3^{(3)} = -\tfrac{1}{3}(1 - 6f_1^2 - 6f_2^2 - 6f_3^2 - 20f_1^3 - 20f_2^3 - 20f_3^3 + 36f_1^2f_2^1 \cdots$$
$$+ 12f_1^2f_2^2 - 12f_1^2f_3^2 - 12f_2^2f_3^2 + 48f_1^3f_2^1 - 12f_1^3f_2^2 + 72f_1^1f_2^1f_3^1 \cdots$$
$$+ 12f_1^1f_2^2f_3^1 + 48f_1^2f_2^1f_3^1 - 12f_1^3f_3^1 + 48f_1^1f_2^1f_3^2 - 60f_1^2f_2^2f_3^1 \cdots$$
$$- 24f_1^3f_2^1f_3^1 - 12f_1^1f_2^2f_3^2 - 12f_1^2f_2^1f_3^2 - 12f_1^3f_2^2f_3^1)$$

Fourth Neighbor ($N = 4$)

$$\beta_3^{(4)} = \beta_3^{(3)} - \tfrac{1}{3}(-6f_4^2 - 20f_4^3 + 36f_2^2f_4^1 + 48f_2^3f_4^1 - 12f_1^2f_4^2 \cdots$$
$$+ 12f_2^2f_4^2 - 12f_3^2f_4^2 - 12f_2^3f_4^2 + 72f_1^1f_3^1f_4^1 - 36f_1^2f_2^1f_4^1 \cdots$$
$$+ 48f_1^2f_3^1f_4^1 + 48f_1^1f_3^2f_4^1 - 36f_2^1f_3^2f_4^1 + 48f_1^1f_3^1f_4^2 \cdots$$
$$- 24f_1^2f_2^2f_4^1 - 12f_1^2f_3^2f_4^1 - 12f_1^2f_3^1f_4^2 - 12f_1^1f_3^2f_4^2 \cdots$$
$$- 72f_1^1f_2^1f_3^1f_4^1 - 96f_1^2f_2^1f_3^1f_4^1 - 72f_1^1f_2^2f_3^1f_4^1 \cdots$$
$$- 48f_1^1f_2^1f_3^2f_4^1 - 24f_1^2f_2^2f_3^1f_4^1 - 12f_1^2f_2^1f_3^2f_4^1)$$

APPENDIX C. $\beta_k^{(N)}$ WITH HARD CORE AND "SOFT" N-NEIGHBOR REPULSION[4]

First Neighbor ($N = 1$)

$$\beta_1^{(1)} = -(3 - 2a), \quad \beta_2^{(1)} = -\tfrac{1}{2}(7 - 12a), \quad \beta_3^{(1)} = -\tfrac{1}{3}(15 - 48a)$$
$$\beta_4^{(1)} = -\tfrac{1}{4}(31 - 160a), \quad \beta_5^{(1)} = -\tfrac{1}{5}(63 - 480a)$$

Second Neighbor ($N = 2$)

$$\beta_1^{(2)} = -(5 - 4a), \quad \beta_2^{(2)} = -\tfrac{1}{2}(19 - 42a)$$
$$\beta_3^{(2)} = -\tfrac{1}{3}(65 - 288a), \quad \beta_4^{(2)} = -\tfrac{1}{4}(211 - 1620a)$$

APPENDIX D. β_k FOR THE CURIE–WEISS POTENTIAL

$k = 2$

$$\beta_2]_1 = -\tfrac{1}{2}(1), \quad \beta_2]_2 = -\tfrac{1}{2}(1 + 3f_c^2)$$
$$\beta_2]_3 = -\tfrac{1}{2}(1 + 6f_c^2 - 2f_c^3), \quad \beta_2]_4 = -\tfrac{1}{2}(1 + 9f_c^2 - 6f_c^3)$$
$$\beta_2]_5 = -\tfrac{1}{2}(1 + 12f_c^2 - 12f_c^3), \quad \beta_2]_6 = -\tfrac{1}{2}(1 + 15f_c^2 - 20f_c^3)$$

$k = 3$

$$\beta_3]_1 = -\tfrac{1}{3}(1), \quad \beta_3]_2 = -\tfrac{1}{3}(1 - 3f_c^2 - 10f_c^3), \quad \beta_3]_3 = -\tfrac{1}{3}(1 - 6f_c^2 - 8f_c^3 + 24f_c^4)$$

[4] $a = e^{-|u|/KT}$.

$\beta_3]_4 = -\frac{1}{3}(1 - 9f_c^2 + 6f_c^3 + 63f_c^4 - 18f_c^5 - 3f_c^6)$
$\beta_3]_5 = -\frac{1}{3}(1 - 12f_c^2 + 32f_c^3 + 108f_c^4 - 72f_c^5 - 12f_c^6)$
$k = 4$
$\beta_4]_1 = -\frac{1}{4}(1), \qquad \beta_4]_2 = -\frac{1}{4}(1 + 20f_c^3 + 35f_c^4)$
$\beta_4]_3 = -\frac{1}{4}(1 + 20f_c^3 - 90f_c^4 - 180f_c^5 + 10f_c^6)$
$\beta_4]_4 = -\frac{1}{4}(1 - 315f_c^4 - 180f_c^5 + 450f_c^6 + 60f_c^7)$

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