PHYSICAL REVIEW E **87**, 042111 (2013)

Adequacy of the virial equation of state and cluster expansion

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(Received 8 December 2012; revised manuscript received 31 March 2013; published 15 April 2013)

The limits for the accuracy of the virial expansion and the problem of its divergence have been investigated using the exact cluster expansion of the configuration integral. In the subcritical temperature regimes the virial equation of state is applicable up to the singularity point of the isothermal compressibility, i.e., to the possible beginning of the condensation process. At supercritical temperatures this equation should be applicable within the region where the cluster expansion is adequate. The problem of the virial series divergence has been found to be irrelevant to the actual behavior of the cluster expansion. Considering the Lennard-Jones fluid as well as the system of hard spheres, the inadequate behavior of the cluster expansion has been discovered in the high density regime. The major reason for this inadequacy should be the basic simplification of the cluster expansion: the integration of irreducible diagrams over the infinite limits.

DOI: 10.1103/PhysRevE.87.042111 PACS number(s): 05.20.−y, 05.70.Fh, 64.70.F−, 64.60.−i

I. INTRODUCTION

There are a number of theoretical approaches [1–4] to derive the virial equation of state (VEOS), but all of them are based on the Gibbs canonical or grand canonical ensemble in the approximation of the low density of the particle number $\rho = N/V$. One of the most rigorous approaches was presented by Mayer [4]: The configuration integral of a system with the pair additive interaction potential $U(r_{ij})$

$$Q_N = \frac{1}{N!}\int_{V^N} \exp\left[-\frac{1}{kT}\sum_{i<j} U(r_{ij})\right] d\mathbf{r}^N \tag{1}$$

may be expressed in the form of the so-called cluster expansion

$$Q_N = \frac{1}{N!}\int_{V^N} \prod_{i<j}(1+f_{ij})d\mathbf{r}^N, \tag{2}$$

where $f_{ij} = \exp(-\frac{U(r_{ij})}{kT}) - 1$ is Mayer's function.

Using the complex combinatorial methods and diagram technique at the thermodynamic limit ($N \to \infty$), Mayer derived the virial expansion for the pressure, where the virial coefficients B_{k+1}'s are related to the corresponding irreducible cluster integrals β_k's

$$B_{k+1} = -\frac{k}{k+1}\beta_k. \tag{3}$$

Each β_k is an integral of the sum of all possible products of Mayer functions for $(k+1)$ particles over their configuration phase space (but in practice the integral is over the infinite limits) which cannot be expressed in terms of any low order irreducible integrals. Unfortunately, the explicit calculation of the irreducible integrals or the corresponding virial coefficients in Eq. (3) is a complicated technical problem even for the simplest interaction potentials. At present, the maximum order of the calculated coefficients is the tenth for the hard spheres [5] and the eighth for the Lennard-Jones fluid [6,7]. Moreover, the precision of the highest order coefficients is seriously limited.

In addition to this technical problem, VEOS has also a number of theoretical limitations. The infinite virial series may diverge under some conditions and this divergence cannot correspond to the behavior of real systems.

The problem of the virial expansion divergence has been investigated in many papers [2,8–10] and some researchers [8,9] including Mayer [4] assumed the explicit relation of the divergence region to the region of condensation. In Refs. [11–13] this assumption was directly used for determining the condensation curve. There were the first 70 virial coefficients calculated approximately on the basis of the Ornstein-Zernike equation [14] and the extrapolated divergence curve of VEOS was investigated [13].

On the other hand, some studies [15,16] indicated the absence of any connection between the phase transitions and the singularity points of the virial expansion. For example, in the system of hard spheres the numerical experiments [17,18] indicated the phase transition at a density about 2/3 of the close-packing density, but the corresponding VEOS (extrapolated by Carnahan and Starling [15]) had no singularity around this point.

Apart from the convergence condition, Mayer pointed to another quantitative restriction on his derivation of VEOS [4] (in contrast to other approaches, where the qualitative criterion "low density" was used)

$$\sum_k k\beta_k\rho^k < 1. \tag{4}$$

Equation (4) limits the density more strictly in comparison to the convergence condition: at the minimum density that violates this inequality the virial series still has a finite value, i.e., the divergence may be observed only at higher densities. Despite this fact, the convergence condition is conventionally regarded (for some unknown reason) as the sole criterion of VEOS adequacy.

Today the real limits of the applicability of the virial expansion cannot be considered as strictly determined. All the simplifications and limitations used in the proofs of VEOS that are able to affect its adequacy may be listed as the following: (i) integration of the cluster and irreducible cluster integrals over the infinite limits; (ii) virial series convergence; and (iii) inequality (4).

The simplification of the pair additivity of the interaction potential could be added to this list, but there are the well-known methods to take the possible nonadditivity into account remaining within the virial expansion [19].

Therefore, the major aim of this paper is to investigate the actual influence of the simplifications and limitations enumerated above on the boundaries of the adequacy of VEOS, in particular, and on the accuracy of the cluster expansion, in general.

II. EXACT REPRESENTATION OF THE CLUSTER EXPANSION

With respect to the symmetry for the permutation of indices, the configuration integral in Eq. (2) is expressed by the so-called cluster integrals b_j

$$Q_N = V^N \sum_{\{m_j\}} \prod_{j=1}^{N} \frac{b_j^{m_j}}{m_j!}. \tag{5}$$

In turn, each cluster integral can be expressed as the sum of the products of some irreducible integrals. Different irreducible integrals of the same order k only differ from each other by their integration limits. Regarding the cluster integrals as independent of the volume (at this stage the real integration limits are replaced by the infinite limits), i.e., considering all the irreducible integrals of the kth order as absolutely identical, Mayer derived the expression for any cluster integral in terms of the irreducible ones [4]

$$b_j = j^{-2} \sum_{\{n_k\}} \prod_{k=1}^{j-1} \frac{1}{n_k!} \left(j \frac{\beta_k}{V^k} \right)^{n_k}. \tag{6}$$

Expressions (5) and (6), together with an analysis of the logarithm of activity as the power series of density and the density as the power series of activity limited by the convergence condition and inequality (4), make it possible at the thermodynamic limit to obtain the virial equation of state [4].

In Ref. [20] another approach was offered to derive an accurate expression for the cluster expansion of the configuration integral (5) based on Eq. (6) without those restrictions on the density, but still using the integration over the infinite limits

$$Q_N = V^N F^{(N)}, \tag{7}$$

where $F^{(N)}$ is the coefficient at y^N in the power expansion of the following function

$$F(y) = \left(1 - \sum_{k \geqslant 1} k \frac{\beta_k \rho^k y^k}{N^k} \right) \times \exp \left(y - \sum_{k \geqslant 1} \frac{k}{k+1} \frac{\beta_k \rho^k y^{k+1}}{N^k} + \sum_{k \geqslant 1} \frac{\beta_k \rho^k y^k}{N^{k-1}} \right). \tag{8}$$

For direct computations, Eq. (7) with respect to function (8) may be conveniently used in the following form

$$Q_N = \frac{V^N}{N!} q_N, \tag{9}$$

where

$$q_n = 1 + \sum_{i=1}^{n} (N-i) \sum_{k=1}^{i} \frac{(i-1)!}{(i-k)!} \frac{k \beta_k \rho^k}{N^k} M_{i-k},$$

and the value M_k is defined in the following recursive expression

$$M_k = M_{k-1} + \sum_{i=1}^{k} \frac{i \beta_i \rho^i}{N^{i-1}} \frac{(k-1)!}{(k-i)!} \left[M_{k-i} - \frac{(k-i)}{N} M_{k-1-i} \right],$$

while $M_0 = 1$ and $M_{k<0} = 0$.

For analysis, Eq. (7) may be treated as the polynomial in density (see the Appendix)

$$Q_N = \frac{V^N}{N!} \left(1 + \sum_{k=1}^{N} a_k \rho^k \right). \tag{10}$$

Each coefficient a_k in the term of power k is defined by the complicated sum

$$a_k = g_{N-k,k} - \sum_{i=1}^{k} \frac{i \beta_i}{N^i} g_{N-k,k-i},$$

where $g_{i,k}$ is the coefficient at x^k in the power expansion of the function

$$G_i(x) = \frac{1}{i!} \left(1 - \sum_{j \geqslant 1} \frac{j}{j+1} \frac{\beta_j x^j}{N^j} \right)^i \exp \left[N \sum_{j \geqslant 1} \frac{\beta_j x^j}{N^j} \right] = \sum_{k \geqslant 0} g_{i,k} x^k.$$

For comparison, the configuration integral that corresponds to the virial expansion has the form

$$Q_{N\to\infty} = \rho^{-N} \exp \left(N \sum_{k=1}^{\infty} \frac{\beta_k}{k+1} \rho^k \right). \tag{11}$$

It has been proved by the authors of Ref. [20], considering any finite number ($k \ll N$) of irreducible integrals at the thermodynamic limit ($N \to \infty$), that exact cluster expansion (10) and corresponding virial expansion (11) coincide in the domain limited by condition (4), but disagree fundamentally when density violates this condition. Similar results were obtained by the authors of Ref. [21] and, independently, Ref. [22] by explicit calculations (for extremely limited N, unfortunately) using Eqs. (5) and (6).

It is possible to show that Eqs. (10) and (11) differ principally in the high density regimes even considering all $(N-1)$ irreducible integrals at the thermodynamic limit. Let us represent Eq. (10) in the form

$$Q_N = \frac{N^N}{N!} \left(\frac{1}{\rho^N} + \sum_{i=1}^{N} \frac{a_{N-i}}{\rho^i} \right).$$

The logarithm of this expression at the thermodynamic limit

$$\lim_{N\to\infty} (\ln Q_N) \sim N \ln f(\rho),$$

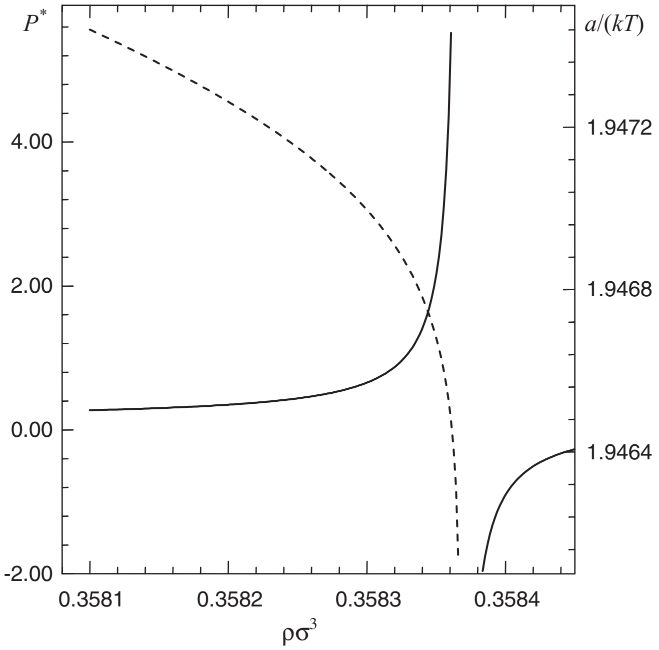

FIG. 1. The discontinuity of the Lennard-Jones fluid isotherm of Eq. (7) with the virial coefficients to the eighth order at temperature $T^* = 1.34$ ($N = 8000$). The dashed curve demonstrates the behavior of free energy a per particle.

where the function

$$f(\rho) = \lim_{N\to\infty}\left(\frac{1}{\rho^N} + \sum_{i=1}^{N}\frac{a_{N-i}}{\rho^i}\right)^{1/N} \tag{12}$$

remains finite at any arbitrarily high density. Accordingly, the pressure as the derivative of the logarithm of function (12) does not diverge at the virial series' singularities. Therefore, the divergence of the virial series (at subcriticals or supercritical temperatures) has no relation to the actual behavior of the exact cluster expansion (7) of the configuration integral.

On the other hand, this actual behavior of Eq. (7) or its representations (9) and (10) has its own specific features. For example, the configuration integral (10) may have negative values under certain conditions that correspond to the complex values of function (12) and its logarithm. Such inadequate behavior may set some serious restrictions on the applicability of the cluster expansion and should be investigated.

III. NUMERICAL INVESTIGATIONS

The behavior of the cluster expansion in comparison to the virial expansion was investigated for the Lennard-Jones fluid. The computations were based on expression (7) and VEOS, correspondingly, taking into account the first seven irreducible integrals or, in practice, the virial coefficients up to the eighth order (the last three coefficients were interpolated from the data of the authors of Refs. [6,7]). Some of the computational results are presented in Figures 1, 2, and 3. In the figures, the following symbols are used for pressure $P^* = P\sigma^3/\varepsilon$ and temperature $T^* = kT/\varepsilon$, where σ and ε are the parameters of the Lennard-Jones potential.

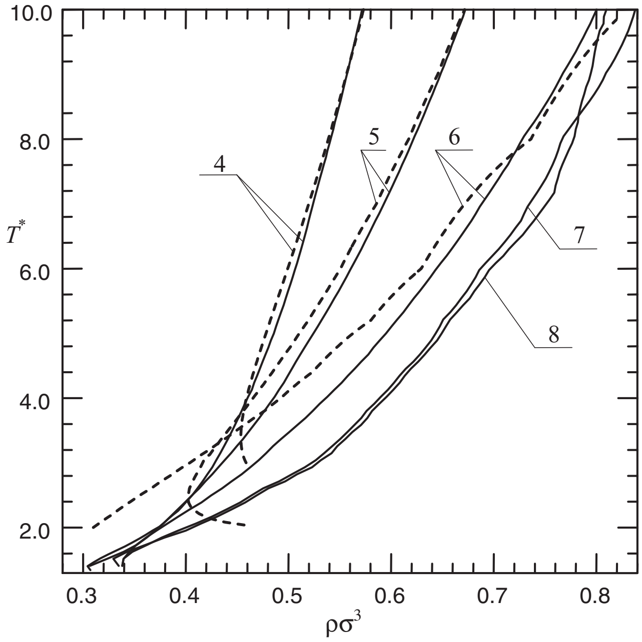

FIG. 2. Curves of the isotherm discontinuities in Eq. (7) for $N = 5 \times 10^5$. Dashed lines show the boundaries where the deviation of VEOS with n coefficiens from VEOS with $(n+1)$ coefficients reaches 3.6% ($n = 4$), 1.8% ($n = 5$), or 0.6% ($n = 6$). The numbers in the figure indicate the maximum order of virial coefficients taken into account.

At supercritical temperatures the regimes of high density were found in which the configuration integral decreases rapidly approaching zero and even negative values. There are the corresponding jumps of pressure in these regimes.

Figure 1 shows the typical essential discontinuity of the isotherm and the corresponding decrease of the Helmholtz free energy. The negative section of the isotherm at higher densities has no physical meaning and the free energy has complex values there. Similar discontinuities are observed at supercritical temperatures for any number (from 1 to 7) of the irreducible integrals used in the calculations (Fig. 2). The positions of these discontinuities are slightly different for various N. As N increases they move to higher densities, but for sufficiently large N this dependence becomes unessential. For N from 100 000 to 500 000 the difference is less than the line width in Fig. 2, and there is no reason to expect that these discontinuities may disappear at the thermodynamic limit. As it was noted in the previous section, the configuration integral in Eq. (7) may have negative (nonphysical) values at some conditions. Supercritical temperatures (the virial series is negative) and high densities (note that the cluster integrals are independent of the density) may satisfy these conditions.

At subcritical temperatures there is no discontinuity observed even for the extremely high densities ($\rho \gg 10$). In contrast, in the high density region beyond the singularity point of the isothermal compressibility ($\sum k\beta_k\rho^k = 1$), which corresponds to the boundary of condition (4), the pressure stops changing (Fig. 3). On the one hand, it may indicate the beginning of the condensation process at this point (see Refs. [20,21,24]), but on the other hand, at very high densities, which must correspond to the liquid and solid states (the points

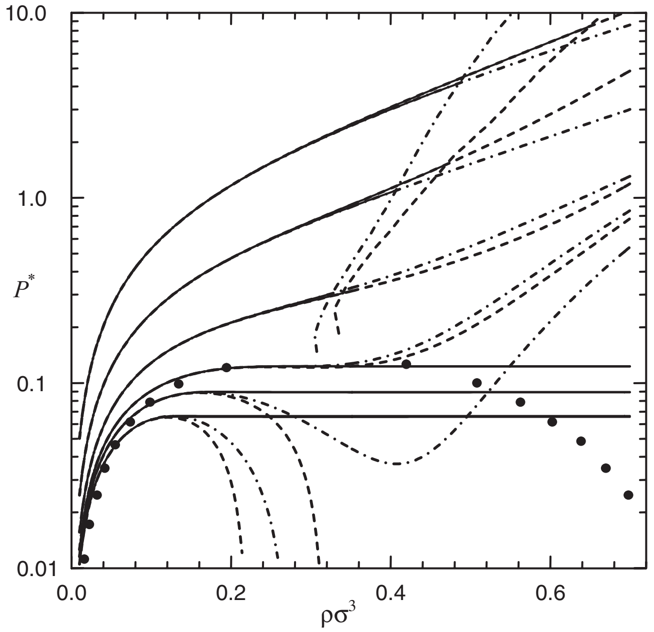

FIG. 3. Isotherms of VEOS with the first four (dot-dashed lines) and eight (dashed lines) virial coefficients of the Lennard-Jones potential for different temperatures T^* (from bottom to top: 1.1; 1.2; 1.3; 1.6; 2.5; 5.0). There are also the corresponding isotherms of Eq. (7) for $N = 10^5$ (solid lines), curves of their discontinuities (dot-dashed and dashed lines), and vapor-liquid coexistence curve (●) [23].

to the right of the coexistence curve in Fig. 3), the pressure constancy does not correspond to the real behavior of the system.

The behavior of VEOS in comparison to Eq. (7) is illustrated in Fig. 3 for both the subcritical and supercritical regions. The virial isotherms are absolutely identical to the corresponding isotherms of Eq. (7) up to the boundary of condition (4) at subcritical temperatures and to the discontinuity points described above at the supercritical region.

VEOS including any finite number of coefficients stays regular in all regimes because the divergence may only be present for infinite virial series. For VEOS with a given number of coefficients the applicability may be approximately tested by the relative deviation of the pressure when one more virial coefficient is added to the equation. The shape of the lines where this deviation reaches some considerable value (0.5–5.0%) correlates to the boundary of condition (4) at subcritical temperatures and has some correlation (possibly accidental) with the curves of the discontinuities at supercritical temperatures (Fig. 2).

Any conclusion about the inadequacy of the cluster expansion based on the example of one specific interaction potential taking into account the limited number of the irreducible integrals should not be regarded as absolutely proved. Therefore, the corresponding studies have been carried out for hard spheres considering all the possible $(N-1)$ irreducible integrals using the approximation of Carnahan and Starling [15]. Since all the integrals in this approximation are negative (there is no attraction in the potential of hard spheres) the behavior of pressure in the system of hard spheres should be similar to the behavior of the isotherms for the Lennard-Jones fluid at supercritical temperatures.

The calculations for various N really demonstrate the similar discontinuities of the pressure curves. Moreover, at $N \to \infty$ their position asymptotically approaches the density about 0.58 of the close-packing density, i.e., somewhat below the experimental phase transition point [17]. For hard spheres the pressure curve of VEOS coincides with the corresponding curve of Eq. (7) up to this discontinuity point and stays regular at higher densities not indicating any phase transition even when the density exceeds the close-packing one.

IV. CONCLUSION

The analyses as well as the numerical study based on the examples of the hard spheres and the Lennard-Jones fluid for both VEOS and the cluster expansion of the configuration integral enable to make several important conclusions.

At subcritical temperatures the region of the appropriate behavior of VEOS is limited by condition (4) at least as long as the cluster expansion itself remains adequate there.

The applicability of VEOS in the region of supercritical temperatures does not have such strong limitations. Rigorous consideration suggests that the virial equation, which was initially derived from the cluster expansion, should not be treated as absolutely adequate outside the domain of the cluster expansion accuracy. Moreover, there are some indications that the variation of the number of coefficients in VEOS leads to the significant deviations of pressure outside this domain.

The well-known problem of the virial expansion divergence is relevant to the virial representation of the cluster expansion and not to the exact cluster expansion. As to the applicability of the cluster expansion of the configuration integral, it should be limited seriously at both the subcritical and supercritical regions. At subcritical temperatures the possible beginning of the condensation process is observed (see Refs. [20,21,24]), but the pressure constancy even at very high densities is similar to some collapse of the system and has no physical meaning.

In the region of supercritical temperatures for sufficiently large but finite densities, the cluster expansion in Eq. (7) approaches zero or even negative values that cannot correspond to the actual behavior of the configuration integral in Eq. (1), in principle. The zero value of the configuration integral must correspond to the statistically unrealizable states of the system, for example, to the densities over the close-packing of hard spheres and so on. Neither the integrand nor integral (1) can be negative.

The only simplification used in the transformation of expression (1) to Eq. (7) is the infinite limits of integration, i.e., the independence of the cluster and irreducible integrals on density. This independence should be the actual reason for the inadequate behavior of the cluster expansion in Eq. (7). At low temperatures all the known integrals of higher orders are positive and it means that the attractive part of the interaction potential dominates over repulsion (independently of the density). Therefore, it is obvious that the attractive forces lead to the condensation process, but there is no repulsion to stop the possible collapse. When the volume decreases, the integration over the real limits would appropriately reduce the values of the cluster integrals and even change their sign that would make the repulsion dominant.

At supercritical temperatures the reason for the discontinuities of the isotherms is the same: In the high density regimes the effect of repulsion may only be accurate (without the jumps of pressure) if the decrease of the system volume exactly corresponds to the decrease of absolute values of cluster integrals.

Unfortunately, there was no quantitative criterion found for the inadequacy of the cluster expansion at subcritical temperatures, but the liquid branch of the experimental coexistence curve may be considered as a possible approximate boundary of this inadequacy. At supercritical temperatures, the points where the integration over the infinite limits leads to the incorrect results, i.e., the curves of discontinuities, may be determined more confidently (Fig. 2).

As a result, the line bounding the domain, where the cluster expansion may be estimated as absolutely inadequate, consists of two branches that start at the critical point and go to the higher densities: one with the increase of temperature (the discontinuity curve) and the other with its decrease (liquid branch of the coexistence curve) (Fig. 3). However, the integration over the infinite limits may influence the behavior of the system even at lower densities. It is impossible to determine the exact boundaries of the cluster expansion adequacy without accurate information about the actual dependence of the cluster integrals on density. This issue requires further research.

ACKNOWLEDGMENTS

I would like to thank David A. Kofke and his colleagues for the data on the sixth, seventh, and eighth virial coefficients of the Lennard-Jones fluid.

APPENDIX: POLYNOMIAL FORM OF THE CLUSTER EXPANSION

In the power expansion of the exponent in function (8) for both variables y and ρ

$$\left(\sum_{i\geqslant0}\frac{y^i}{i!}\right)\left(\sum_{\{l_k\}}\prod_{k\geqslant1}\frac{1}{l_k!}\left[-\frac{k}{k+1}\frac{\beta_k\rho^k y^{k+1}}{N^k}\right]^{l_k}\right)$$
$$\times\left(\sum_{\{m_k\}}\prod_{k\geqslant1}\frac{1}{m_k!}\left[\frac{\beta_k\rho^k y^k}{N^{k-1}}\right]^{n_k}\right)=\sum_{n\geqslant0}\sum_{i\geqslant0}w_{n,i}\,y^n\rho^i,$$

each coefficient $w_{n,i}$ is defined in the following expression

$$w_{n,i}=\sum_{j=0}^{n-i}\frac{1}{j!}\left(\sum_{\{l_k\}}\prod_{k\geqslant1}\frac{1}{l_k!}\left[-\frac{k}{k+1}\frac{\beta_k}{N^k}\right]^{l_k}\right)$$
$$\times\left(\sum_{\{m_k\}}\prod_{k\geqslant1}\frac{1}{m_k!}\left[\frac{\beta_k}{N^{k-1}}\right]^{n_k}\right),\qquad\text{(A1)}$$

where the sets of integers $\{l_k\}$ and $\{m_k\}$ must satisfy the equations

$$\sum_{k\geqslant1}kl_k+\sum_{k\geqslant1}km_k=i,\qquad\text{(A2)}$$
$$\sum_{k\geqslant1}(k+1)l_k+\sum_{k\geqslant1}km_k=n-j.$$

The last equation may be combined with Eq. (A2) and transformed to

$$\sum_{k\geqslant1}l_k=n-i-j.\qquad\text{(A3)}$$

On the other hand, the coefficients defined in Eq. (A1), taking into account Eqs. (A2) and (A3), are also presented in the similar power expansion of another function

$$G_i\,(x)=\frac{1}{i!}\left(1-\sum_{j\geqslant1}\frac{j}{j+1}\frac{\beta_j x^j}{N^j}\right)^i\exp\left[N\sum_{j\geqslant1}\frac{\beta_j x^j}{N^j}\right]$$
$$=\sum_{k\geqslant0}g_{i,k}x^k,$$

where $g_{i,k}=w_{k+i,k}$.

The cluster expansion of the configuration integral in Eq. (7) is related to the coefficient at y^N in the power expansion of function (8)

$$Q_N=\frac{V^N}{N!}\left(\sum_{i=0}^{N}w_{N,i}\rho^i-\sum_{k=1}^{N}k\frac{\beta_k\rho^k}{N^k}\sum_{i=0}^{N-k}w_{N-k,i}\rho^i\right)$$
$$=\frac{V^N}{N!}\left(1+\sum_{k=1}^{N}a_k\rho^k\right),$$

where

$$a_k=w_{N,k}-\sum_{i=1}^{k}\frac{i\beta_i}{N^i}w_{N-i,k-i}=g_{N-k,k}-\sum_{i=1}^{k}\frac{i\beta_i}{N^i}g_{N-k,k-i},$$

which exactly corresponds to Eq. (10).

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