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A matricial approach to cluster expansions†

R Aldrovandi‡ and I Monte Lima§
Instituto de Física Teórica, Rua Pamplona, 145 CEP-01405-São Paulo, SP, Brasil

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Abstract. A group structure hidden behind the usual manipulations involving cluster expansions, is brought to light through the recognition of the fundamental role played by Bell polynomials. The inversion problems are thereby reduced to matrix calculus. Simple derivations are given of the relations between cluster integrals and the virial coefficients.

1. Introduction

'If you want to find more, dig at the same place.' *Seferis.*

Since its inauguration more than fifty years ago, the subject of cluster expansions has been the cause of much work and ingenuity. Despite the fact that the fundamental relations have been found at the very beginning of its building, a continual effort has been made to clarify their meaning and simplify the calculations. Let us here only recall the insight given by graph theory (Uhlenbeck and Ford 1962) and by combinatorial and analytical methods (Widom 1954, Kilpatrick and Ford 1969, Stell 1965). Much consideration has been devoted to some particular cases such as the quantum gases, relativistic (Nieto 1970) or non-relativistic (Leonard 1968).

Our objective in this paper is to examine cluster expansions and the virial equation of state within a formalism which emphasises the purely combinatorial aspects of the question. It is subjacent to all the previous treatments involving counting problems in statistical mechanics, although, to our knowledge, it has never been presented as that. Of course, everybody knows the canonical partition functions for a gas to be polynomials in the cluster integrals, for which the grand canonical partition function is a generating function. We shall here precisely identify these polynomials as those introduced in the thirties by Bell when assessing some combinatorial problems (Riordan 1958, Comtet 1974). Besides reducing many involved manipulations to matrix calculus, the formalism of Bell polynomials has a great unifying appeal, as it embodies all the usual methods in a very simple language, being in some aspects a practical shorthand for complex variable methods. Under the guise of cycle indicators of the symmetric group, these polynomials have already been used (Aldrovandi and Teixeira Filho, 1976a, b) in order to obtain recursion relations for relativistic quantum ideal gases in the microcanonical ensemble.

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§ Fellow of the CNPq. Brasilia.

A résumé on the Bell polynomials is given in § 2. Although we have chosen specifically the topics of interest to our subject, we think they are worth exposing in detail, with some preliminary examples of their use in statistical mechanics. Section 3 is devoted to the inversion problems, tackled through the group structure which emerges from the formalism. Cluster expansions and the equation of state are then examined in § 4.

2. Bell polynomials

As we shall not be concerned with convergence problems, only formal series will be really considered here, despite our frequent use of the word 'function'. The simplest way to introduce Bell polynomials (Riordan 1958) is recalling the Faà di Bruno formula for the higher-order derivatives of a composite function. Let us take $F(t)=f[g(t)]$ and calculate its nth order derivative $F_n(0)$. In order to simplify matters we shall suppose $f(u)$ and $g(t)$ to satisfy $f(0)=0$, $g(0)=0$ and to be given by the formal series

$$f(u)=\sum_{l=1}^{\infty}\frac{f_l}{l!}u^l$$

$$g(t)=\sum_{l=1}^{\infty}\frac{g_l}{l!}t^l.$$

The variables u and t will be used as dummy variables throughout this paper. The coefficients f_l and g_l are of course the derivatives at the respective origins. For the first few orders, we obtain:

$$F_1=f_1g_1$$
$$F_2=f_1g_2+f_2g_1^2$$
$$F_3=f_1g_3+f_2(3g_1g_2)+f_3g_1^3$$
$$F_4=f_1g_4+f_2(4g_1g_3+3g_2^2)+f_3(6g_1^2g_2)+f_4g_1^4,$$

... etc. In general, we obtain:

$$F_n=\sum_{l=1}^{n}f_lB_{nl}(g_1,g_2,\ldots,g_{n-l+1}). \tag{2.1}$$

The numbers B_{nl} are polynomials in the g_i's, quite independent of $f(t)$ and its derivatives. We shall call them Bell polynomials. The F_n are sometimes called complete Bell polynomials and will be denoted by $F_n(f;g)$. They are clearly the coefficients of the formal Taylor series for $F(t)$,

$$F(t)=\sum_{n=1}^{n}\frac{t^n}{n!}F_n(f;g). \tag{2.2}$$

It will be frequently convenient to use the notation $B_{nl}[g(t)]=B_{nl}(g_1,g_2,\ldots)=B_{nl}[g_1,g_2,\ldots,g_{n-l+1}]$. As the B_{nl} are independent of $f(u)$, they can be computed by choosing any function, for instance $f(u)=\exp au-1$. In this case,

$$F(t)=\sum_{l=1}^{\infty}\frac{a^l}{l!}\left(\sum_{j=1}^{\infty}\frac{g_j}{j!}t^j\right)^l.$$

Comparison with (2.2) will then beget the multinomial theorem

$$\frac{1}{l!}\left(\sum_{j=1}^{\infty}\frac{g_j}{j!}t^j\right)^l=\sum_{n=l}^{\infty}\frac{t^n}{n!}B_{nl}[g(t)]. \tag{2.3}$$

This is the most useful expression involving Bell polynomials: from it, all their properties can be obtained. To begin with, it elucidates their meaning,

$$B_{nl}[g(t)]=\frac{1}{l!}\left[\frac{d^n}{dt^n}(g(t))^l\right]_{t=0}, \tag{2.4}$$

which can of course be read also directly from (2.1).

Their exact expression (Abramowitz and Stegun 1965) is

$$B_{nl}[g(t)]=\sum_{\{\nu_i\}}''\frac{n!}{\pi_{j=1}^{n}\nu_j!(j!)^{\nu_j}}g_1^{\nu_1}g_2^{\nu_2}\dots g_n^{\nu_n}, \tag{2.5}$$

where the double prime recalls that the summation is to be done over all the sets $\{\nu_i\}$ on non-negative integers ν_i satisfying simultaneously the two conditions

$$\sum_{j=1}^{n}\nu_j=l; \qquad \sum_{j=1}^{n}j\nu_j=n. \tag{2.6}$$

From equation (2.3) it is easily seen that

$$g_n=B_{n1}[g(t)] \tag{2.7}$$

and

$$g_1^n=B_{nn}[g(t)]. \tag{2.8}$$

Two other properties can immediately be obtained from equations (2.5) and (2.6):

$$B_{nl}(ag_1, ag_2, ag_3, \dots)=a^lB_{nl}(g_1, g_2, g_3, \dots); \tag{2.9}$$

$$B_{nl}(ag_1, a^2g_2, a^3g_3, \dots)=a^nB_{nl}(g_1, g_2, g_3, \dots). \tag{2.10}$$

As an example: the expression for the canonical partition function for a simple non-relativistic classical gas of n particles in terms of the cluster integrals b_l (Pathria 1972) is, when translated into the language of Bell polynomials, given by

$$\begin{aligned}Q_n(T,V)&=\frac{1}{n!}\sum_{l=1}^{n}\left(\frac{V}{\lambda^3}\right)^lB_{nl}(1!b_1, 2!b_2, 3!b_3, \dots)\\&=\frac{1}{n!}\sum_{l=1}^{n}B_{nl}\left(1!b_1\frac{V}{\lambda^3}, 2!b_2\frac{V}{\lambda^3}, 3!b_3\frac{V}{\lambda^3}, \dots\right),\end{aligned} \tag{2.11}$$

with λ the mean thermal wavelength. From (2.1), $Q_n(T,V)=F_n(f;g)/n!$, with $f_l=(V\lambda^{-3})^l$ so that $f(u)=\exp(V\lambda^{-3}u)-1$ and $g(t)=\sum_{l=1}^{\infty}b_lt^l$. If t is the fugacity, then $p(t)=kT\lambda^{-3}g(t)$ is the pressure, and equation (2.2) will give the grand canonical partition function $F(T,V,t)=1+\sum_{n=1}^{\infty}t^nQ_n=\exp(Vp(t)/kT)$. The numbers $\nu_1, \nu_2, \dots, \nu_j$ in (2.5) and (2.6) are here the numbers of 1-clusters, 2-clusters, ... j-clusters in the system of m particles. In particular, the only solution of equations (2.6) for $l=1$ is $\nu_n=1$, all remaining $\nu_j=0$. From the point of view of cluster diagrams, this corresponds to the case of a completely connected graph of n-particles. It contributes to $Q_n(T,V)$ a term $V\lambda^{-3}b_n$, as can be seen using (2.7). The total contribution of these connected terms to the grand canonical partition function is then $F^{(c)}=Vp(t)/kT$. In this way one gets, in a very simple way, the old result $F=\exp(F^{(c)})$ (Bloch and de Dominicis 1958).

The clumsiness of expression (2.5) is at first sight discouraging, the real trouble being the search for all the solutions of conditions (2.6) in each case. The point is, however, that these equations are really dispensable except eventually for numerical computations: all the general properties of those polynomials can be obtained from the multinomial theorem. We shall work out a few examples whose usefulness will become apparent later on, computing the polynomials B_{nl} for some functions. We shall suppose all the first coefficients to be unitary, $f_1=g_1=1$ as this will be the case with all the series we shall meet.

As a first case, let us take in (2.2) the function $f(u)=(1+u)^r-1$. The coefficients f_l will be:

$$f_l=\begin{cases}\dfrac{r!}{(r-l)!} & \text{if } r \text{ is a non-negative integer, } r\geqslant l\geqslant 0;\\[2ex] (-1)^l\dfrac{(n+l-1)!}{(n-1)!} & \text{if } r=-n,\ n=1,2,3,\ldots.\end{cases} \tag{2.12}$$

So, for instance,

$$F(t)=[1+g(t)]^{-n}-1=\sum_{l=1}^{\infty}\frac{t^l}{l!}\sum_{j=1}^{\infty}(-1)^j\frac{(n+j-1)!}{(n-1)!}B_{lj}[g(t)] \tag{2.13}$$

which allows the computation of reciprocal series of the type

$$\begin{aligned}[f(t)]^{-n}&=t^{-n}\left[1+\sum_{l=1}^{\infty}\frac{f_{l+1}}{l+1}\frac{t^l}{l!}\right]^{-n}\\ &=\frac{1}{t^n}+\sum_{l=1}^{\infty}\frac{t^{l-n}}{l!}\sum_{j=1}^{l}(-1)^j\frac{(n+j-1)!}{(n-1)!}B_{lj}\left(\frac{f_2}{2},\frac{f_3}{3},\ldots\right).\end{aligned} \tag{2.14}$$

This is not a formal series of the type we have proposed to restrict ourselves to at the beginning, as of course $f^{-n}(0)\neq 0$. In order to recover one of that kind, it is enough to consider instead

$$t^n[f(t)]^{-n}-1=\sum_{l=1}^{\infty}\frac{t^l}{l!}\sum_{j=1}^{l}(-1)^j\frac{(n+j-1)!}{(n-1)!}B_{lj}\left(\frac{f_2}{2},\frac{f_3}{3},\ldots\right).$$

From equation (2.7) we then recognise that

$$B_{l1}\left\{\frac{t^n}{[f(t)]^n}-1\right\}=\sum_{j=1}^{l}(-1)^j\frac{(n+j-1)!}{(n-1)!}B_{lj}\left(\frac{f_2}{2},\frac{f_3}{3},\ldots\right), \tag{2.15}$$

an expression which will be of use in the inversion problem.

Another case of interest is the formulation of Leibnitz rule for the derivative of the product of two functions in terms of Bell polynomials. Simply by substituting $g(t)=F(t)G(t)$ in (2.3) and comparing with the multinomial expansions for $F(t)$ and $G(t)$, one finds that

$$\left.\begin{aligned}&B_{n1}[F(t)G(t)]=l!\sum_{j=l}^{n-l}\binom{n}{j}B_{jl}[F(t)]B_{n-j,l}[G(t)] && \text{for } n\geqslant 2l;\\ &B_{nl}[F(t)G(t)]=0 \qquad \text{for } l\leqslant n<2l. &&\end{aligned}\right\} \tag{2.16}$$

This in particular says that

$$B_{n1}[F(t)G(t)] = \sum_{j=1}^{n-1} \binom{n}{j} B_{j1}[F(t)]B_{n-j,1}[G(t)]. \tag{2.17}$$

Finally, let us consider a particular case of two functions $f(u)$ and $g(t)$ which are inverse to each other in the sense that

$$f[g(t)] = t. \tag{2.18}$$

First, let $g(t) = \exp(t) - 1$. The multinomial theorem then gives

$$\frac{1}{l!}[\exp(t)-1]^l = \sum_{n=l}^{\infty} \frac{t^n}{n!} B_{nl}(1, 1, 1, \ldots). \tag{2.19a}$$

This is precisely one of the generating functions of the Stirling numbers $S_n^{(l)}$ of the second kind (Abramowitz and Stegun, 1965), usually defined by

$$x^n = \sum_{l=0}^{n} S_n^{(l)} x(x-1)\ldots(x-l+1). \tag{2.19b}$$

So, one gets

$$B_{nl}(1, 1, 1, \ldots) = S_n^{(l)}. \tag{2.20}$$

The function inverse to the one above is $f(u) = \ln(1+u)$. The multinomial theorem now reads

$$\frac{1}{l!}[\ln(1+u)]^l = \sum_{n=l}^{\infty} \frac{u^n}{n!} B_{nl}(0!, -1!, 2!, -3!, \ldots).$$

This time we have one of the generating functions for the (signless) Stirling numbers $s_n^{(l)}$ of the first kind, usually introduced through

$$x(x-1)\ldots(x-l+1) = \sum_{j=0}^{l} s_l^{(j)} x^j. \tag{2.21}$$

Consequently,

$$B_{nl}(0!, -1!, 2!, -3!, \ldots) = s_n^{(l)}. \tag{2.22}$$

Substituting (2.21) into (2.19b), or vice versa, one gets the well known fact that the matrices formed by these numbers are inverse to each other. We shall see in the next paragraph that this is not an isolated case.

3. Matrix calculus and the inversion problem

From the very expression (2.3), $n \geq l$ in B_{nl}. The Bell polynomials $B_{nl}[g(t)]$ can be considered as elements of a left-triangular infinite matrix $B[g]$. Although infinite, these matrices are most useful, as only their sections $n \times n$ are relevant to any consideration up to order n. In this case, their determinant is simply the product of the diagonal terms: from (2.8), it is $g_1^{n(n+1)/2} = 1$ in our case. As can be seen from equation (2.7), the first column of $B[g]$ is constituted precisely by the coefficients g_l. The other elements are fixed polynomials in these coefficients. These matrices are so in a one-to-one relation to the formal series.

It is a well known fact that non-singular left-triangular matrices form a group under matrix multiplication. Attention is not so frequently drawn to the fact that formal series of the type we are considering ($f(t)=\Sigma_{l=1}^{\infty}(f_l/l!)t^l$, with $f_1 \neq 0$) also form a group (Henrici 1974) under the operation of composition. We are now going to see that the latter group can be represented in the former.

Let us take the function $f[g(t)]$ in the left-hand side of equation (2.3):

$$\begin{aligned}\frac{1}{l!}\{f[g(t)]\}^l &= \frac{1}{l!}\left[\sum_{i=1}^{\infty}\frac{f_i}{i!}g^i(t)\right]^l \\ &= \sum_{n=l}^{\infty}\frac{g^n(t)}{n!}B_{nl}[f(u)] \\ &= \sum_{n=l}^{\infty}\sum_{j=n}^{\infty}\frac{t^j}{j!}B_{jn}[g(t)]B_{nl}[f(u)] \\ &= \sum_{j=l}^{\infty}\frac{t^j}{j!}\sum_{n=l}^{j}B_{jn}[g(t)]B_{nl}[f(u)].\end{aligned}$$

Hence,

$$B_{jl}\{f[g(t)]\} = \sum_{n=l}^{j}B_{jn}[g(t)]B_{nl}[f(u)],$$

or simply

$$B[f\circ g] = B[g]B[f]. \tag{3.1}$$

The matrix corresponding to the composition $f\circ g$ is the product of the matrices corresponding to each function, in the inverse order. So the composition operation between formal series corresponds to the right product of their respective matrices. A somewhat lengthier computation shows that associativity is preserved in the representation and a trivial check ensures that the identity function $g(t)=t$ is represented by the identity matrix.

These group properties allow many a manipulation involving series to be reduced to matrix calculus. We shall be particularly interested in the problem of series inversion in the sense of equation (2.18). This should not be mistaken for the search of the reciprocal series which, as can be seen from (2.14), does not in general belong to the group. Equations (2.18) and (3.1) tell us that if f and g are inverse to each other, also $g[f(t)]=t$ and $B[f]B[g]=I$, $B[g]B[f]=I$. So, the matrix of the inverse is the inverse matrix. The example involving Stirling numbers, in the previous paragraph is a particular case of this general result. Let us apply it to get the inversion of equation (2.11). There, we had

$$B[F(t)] = B[f(g(t))] = B[g(t)]B[f(u)].$$

It's simpler to consider the second line of the equation, where $f_l=1$, so that $f(u)=e^u-1$ and $g(t)=(V/\lambda^3)\Sigma_{l=1}^{\infty}b_lt^l$. Then,

$$\begin{aligned}g_n = B_{n1}[g(t)] &= \sum_{l=1}^{n}B_{nl}(F_1,F_2,\ldots)B_{l1}^{-1}[f(u)] \\ &= \sum_{l=1}^{n}B_{nl}(1!Q_1,2!Q_2,3!Q_3,\ldots)(-1)^{l-1}(l-1)!,\end{aligned}$$

because

$$B_{l1}^{-1}[\exp(u)-1]=B_{l1}[\ln(1+t)]=S_l^{(1)}=(-1)^{l-1}(l-1)!.$$

As here $g_n=n!b_nV\lambda^{-3}$,

$$b_n=\frac{\lambda^3}{V}\frac{1}{n!}\sum_{l=1}^{n}(-1)^{l-1}(l-1)!B_{nl}(1!Q_1,2!Q_2,3!Q_3,\ldots),$$

a well known result.

The general inversion problem can be handled from equation (2.1), which in this case reads simply

$$\sum_{l=1}^{n} f_lB_{nl}[g]=\delta_{n1}. \tag{3.3}$$

For $n=1$, this gives

$$f_1=1/g_1=1. \tag{3.4}$$

For $n\geqslant 2$, one can use (2.8) to write

$$f_n=-\sum_{j=1}^{n-1}B_{nj}[g]f_j \tag{3.5}$$

which is a recursion formula. Given the g_j's, all the coefficients f_n can be successively obtained in this way. This is really the usual way of inverting step-by-step a triangular matrix in numerical computations. This equation can be put into a determinantal form by applying Crammer's theorem to (3.3). The result,

$$f_n=(-1)^{n}\cdot\begin{vmatrix} B_{21} & 1 & 0 & 0 & \cdots & 0\\ B_{31} & B_{32} & 1 & 0 & \cdots & \cdot\\ \vdots & \vdots & \vdots & \vdots & & \vdots\\ B_{n-1,1} & B_{n-2,1} & \cdot & \cdot & & 1\\ B_{n1} & B_{n2} & \cdot & \cdot & & B_{n,n-1}\end{vmatrix} \tag{3.6}$$

would allow us to make contact with determinantal approaches such as Widom's (Widom 1954). It can be easily verified that (3.5) comes from the expansion of the determinant along the last row. We shall, however, find the solution of the recursion relation in a form which will prove itself very convenient for the manipulations on cluster expansions.

Our procedure will be rather devious, but it will have the advantage of being constructive and elementary. Mathematicians usually state the result and verify it afterwards, using much more than the above formalism (Henrici 1974, Riordan 1958, 1968, Comtet 1974). All calculations being highly elementary, we shall simply list the steps and results.

(i) Using (2.14) we calculate, for $n\geqslant 2, f^{-n}f'=(1/1-n)(\mathrm{d}/\mathrm{d}t)f^{1-n}$; and multiplying by t^{n+1}, we obtain

$$t^{n+1}f'f^{-n}=t+\sum_{l=1}^{\infty}\frac{t^{l+1}}{l!}\frac{l-n+1}{1-n}\sum_{j=1}^{l}(-1)^j\frac{(n+j-2)!}{(n-2)!}B_{lj}\left(\frac{f_2}{2},\frac{f_3}{3},\ldots\right);$$

(ii) From this equation we can observe that the nth coefficient is zero,

$$B_{n1}[tf't^nf^{-n}]=0;$$

(iii) This means that

$$B_{n1}[tf'(t^nf^{-n}-1)]=B_{n1}[tf't^nf^{-n}]-B_{n1}[tf']=0-nf_n,$$

this last term being immediately obtained by applying $t(\mathrm{d}/\mathrm{d}t)$ to (2.3) with $l=1$;

(iv) $B_{n1}[tf'(t^nf^{-n}-1)]$, being a matrix element corresponding to a product, is computed by using (2.17):

$$B_{n1}[tf'(t^nf^{-n}-1)]=\sum_{j=1}^{n-1}\binom{n}{j}B_{n-j,1}[t^nf^{-n}-1]B_{j1}[tf'];$$

(v) Using again $B_{j1}[tf']=jf_j$ and comparing with item (iii),

$$f_n=-\sum_{j=1}^{n-1}\binom{n-1}{j-1}B_{n-j,1}[t^nf^{-n}-1]f_j,$$

which is precisely equation (3.5) with

$$B_{nj}[g(t)]=\binom{n-1}{j-1}B_{n-j,1}[t^nf^{-n}-1]. \tag{3.7}$$

This gives the $n>j$ elements of the matrix $B[g]=B^{-1}[f]$. We have already seen that

$$B_{nn}[g(t)]=g_1^n=1. \tag{3.8}$$

By using (2.15), expression (3.7) can be written explicitly as

$$B_{nj}[g(t)]=\binom{n-1}{j-1}\sum_{l=1}^{n-j}(-1)^l\frac{(n+l-1)!}{(n-1)!}B_{n-j,l}\left(\frac{f_2}{2},\frac{f_3}{3},\ldots\right). \tag{3.9}$$

A more convenient form of equation (3.7) can be obtained by noticing that $t^nf^{-n}-1=\exp(-n\ln f/t)-1$. Then,

$$B_{n-j,1}[t^nf^n-1]=\sum_{l=1}^{n-j}B_{n-j,l}[\ln f(t)/t]B_{l1}[\exp(-nu)-1]$$
$$=\sum_{l=1}^{n-j}(-1)^ln^lB_{n-j,l}[\ln f(t)/t].$$

Collecting the results, the matrix $B[g]$ representing the function $g(t)$ inverse to a given function $f(u)$ has its elements given by

$$\left.\begin{aligned}&B_{nn}[g(t)]=1\\&B_{nj}[g(t)]=\binom{n-1}{j-1}\sum_{l=1}^{n-j}(-1)^ln^lB_{n-j,l}[\ln f(t)/t]\ .\end{aligned}\right\} \tag{3.10}$$

In particular, from (3.9) and (3.10),

$$\left.\begin{aligned}&g_n=\sum_{l=1}^{n-1}(-1)^l\frac{(n+l-1)!}{(n-1)!}B_{n-1,l}\left(\frac{f_2}{2},\frac{f_3}{3},\ldots\right)\\ \text{or}\quad&\\&g_n=\sum_{l=1}^{n-1}(-1)^ln^lB_{n-1,l}\left[\ln\frac{f(t)}{t}\right].\end{aligned}\right\} \tag{3.11}$$

These two expressions can be directly obtained from each other by observing that

(i) $B_{n-1,l}(f_2/2,f_3/3,\ldots)=B_{n-1,l}[f(t)/t-1]$;

(ii) putting $x=-n$ in (2.21) and using (2.22),

$$(-1)^l\frac{(n+l-1)!}{(n-1)!}=\sum_{j=0}^{l} B_{lj}[\ln(1+u)](-n)^j, \tag{3.12}$$

where the terms $j=0$ vanishes; a simple inversion of the summations establishes the result.

Equations (3.10) and (3.11) are really new avatars of the inversion formula of Lagrange (Comtet 1974, Whittaker and Watson 1969), which of course disregard the analytic implications of the old theorem. They give directly the nth coefficient of the inverse series in terms of the coefficients of a given series up to order n.

4. Cluster expansions and the equation of state

We can now examine, from the point of view of the formalism presented above, the questions involving cluster expansions and the virial equation of state. Let us define two formal series

$$f(z)=\frac{p\lambda^3}{kT}=\sum_{l=1}^{\infty} b_l z^l=\sum_{l=1}^{\infty}\frac{f_l}{l!}z^l \tag{4.1}$$

$$g(z)=\frac{N\lambda^3}{V}=\sum_{l=1}^{\infty} l b_l z^l=\sum_{l=1}^{\infty}\frac{g_l}{l!}z^l, \tag{4.2}$$

where the notation is hopefully obvious. The equation of state,

$$A(g)=\frac{PV}{NkT}=1+\sum_{n=1}^{\infty} a_{n+1}g^n, \tag{4.3}$$

is to be obtained by eliminating the fugacity z from the two former equations or, equivalently, by obtaining the virial coefficients a_l in terms of the cluster integrals b_j. The straightforward procedure would be to invert series (4.2), so obtaining $z(g)$ to be substituted into (4.1). As $f[z(g)]=gA(g)=\sum_{n=1}^{\infty} a_n g^n$,

$$a_n=(1/n!)F_n(f;z), \tag{4.4}$$

in the notation of equation (2.2). Then, (4.1) and (2.1) give

$$a_n=\frac{1}{n!}\sum_{l=1}^{n} l!b_l B_{nl}(z_1, z_2, z_3, \ldots). \tag{4.5}$$

The numbers z_j, coefficients of the series inverse to (4.2), can be computed directly from (3.11):

$$z_1=1;$$

$$z_n=\sum_{l=1}^{n-1}(-1)^l n^l B_{n-1,l}[\ln g(t)/t]. \tag{4.6}$$

This of course corresponds to the usual 'series-substitution' procedure given in elementary text books. The method works well for the calculation of the first few virial coefficients, but becomes increasingly impractical at higher orders. The main objective is to write a_n directly in terms of the sole b_j's, that is, to obtain Mayer's formulae. The following is a purely combinatorial approach to these formulae.

Let us begin with the simplest problem, to obtain the cluster integrals b_l in terms of the virial coefficients a_l. This is just the opposite method to the one which leads to equation (4.6): we start by obtaining the coefficients g_n in terms of the inverse series $z(g)$:

$$g_n = \sum_{l=1}^{n-1} (-1)^l n^l B_{n-1,l}[\ln z(t)/t]. \tag{4.7}$$

Here we see the fulcrum of Kahn's procedure (Kahn 1938): what is necessary is the function $\ln[z(t)/t]$. By noticing that $g(z) = z(\mathrm{d}/\mathrm{d}z)f(z) = z(\mathrm{d}g/\mathrm{d}z)[A(g) + g(\mathrm{d}A/\mathrm{d}g)]$, it is a simple matter to see that

$$\ln\frac{z(t)}{t} = \sum_{j=1}^{\infty} \frac{j+1}{j} a_{j+1} t^j. \tag{4.8}$$

As $g_n = n!nb_n$, equation (4.7) becomes

$$b_n = \frac{1}{n!} \sum_{l=1}^{n-1} (-1)^l n^{l-1} B_{n-1,l}\left(2!a_2, \frac{3!}{2}a_3, \frac{4!}{3}a_4, \ldots\right), \tag{4.9}$$

which is the relation required.

The method which leads to the inverse relation is much longer. It begins with the observation that (4.8) implies

$$\begin{aligned}\frac{(n+1)!}{n} a_{n+1} &= B_{n1}\{\ln[1 + (z(t)/t - 1)]\} \\ &= B_{nl}[z(t)/t - 1]B_{l1}[\ln(1+u)] \\ &= \sum_{l=1}^{n} (-1)^{l-1}(l-1)!B_{nl}(\tfrac{1}{2}z_2, \tfrac{1}{3}z_3, \ldots).\end{aligned} \tag{4.10}$$

In order to be able to use equations (3.9) or (3.10) to transform this expression into the desired one involving the coefficients of the series $g(t)$ inverse to $z(u)$, we have first to write $B[z(t)/t-1]$ in terms of $B[z(t)]$. This is done by applying the multinomial theorem (2.3) to the function $z(t)/t - 1$. A straightforward calculation shows that

$$B_{nl}(\tfrac{1}{2}z_2, \tfrac{1}{3}z_3, \ldots) = B_{nl}[z(t)/t - 1] = n! \sum_{j=1}^{l} \frac{(-1)^l}{(l-j)!(n+j)!} B_{n+j,j}[z(t)]. \tag{4.11}$$

Taking this result into (4.10),

$$\frac{(n+1)!}{n} a_{n+1} = n! \sum_{j=1}^{n} \frac{(-1)^{j-1}(j-1)!}{(n+j)!} \binom{n}{j} B_{n+j,j}[z(t)], \tag{4.12}$$

where use has been made of the combinatorial identity (Gradshteyn and Ryzhik 1965)

$$\sum_{l=j}^{n} \frac{(l-1)!}{(l-j)!} = (j-1)! \sum_{l=j}^{n} \binom{l-1}{l-j} = (j-1)!\binom{n}{j}.$$

It now remains to use the inversion formula (3.10), which for our case reads

$$B_{n+j,j}[z(t)] = \binom{n+j-1}{j-1} \sum_{l=1}^{n} (-1)^l (n+j)^l B_{nl} \ln[g(t)/t].$$

Substitution into (4.12) and an interchange of the summations leads to

$$\frac{n+1}{n!}a_{n+1}=\sum_{l=1}^{n}(-1)^l B_{nl}[\ln g(t)/t]\sum_{j=1}^{n}(-1)^{j-1}\binom{n}{j}(n+j)^{l-1}. \tag{4.13}$$

The result of the last summation does not seem to be widely known. It can be modified, by using (2.19) with $x=n+j$, into

$$\sum_{i=0}^{l-1}S_{l-1}^{(i)}\,i!\sum_{j=1}^{n}(-1)^{j-1}\binom{n}{j}\binom{n+j}{i}. \tag{4.14}$$

The summation involving the binomials can be shown, by the use of Klee's identity (Riordan 1968), to be $\binom{n}{i}$. It is then enough to look again at equation (2.19) to recognise in (4.14) the expression for n^{l-1}. So, finally

$$\begin{aligned}a_{n+1}&=\frac{1}{(n+1)!}\sum_{l=1}^{n}(-1)^l n^l B_{nl}[\ln g(t)/t]\\&=\frac{1}{(n+1)!}\sum_{l=1}^{n}(-1)^l n^l\sum_{j=l}^{n}B_{nj}[g(t)/t-1]B_{jl}[\ln(1+u)].\end{aligned} \tag{4.15}$$

$$\therefore\quad a_{n+1}=\frac{1}{(n+1)!}\sum_{j=1}^{n}(-1)^j\frac{(n+j-1)!}{(n-1)!}B_{nj}(2!b_2,3!b_3,4!b_4,\ldots), \tag{4.16}$$

where use has been made of equation (3.12). This is the desired inversion formula (Mayer 1942).

The final numerical expression of the equation of state is then

$$\frac{PV}{NkT}=1+\sum_{n=1}^{\infty}g^n\sum_{j=1}^{n}(-1)^j\frac{(n+j-1)!}{(n+1)!(n-1)!}B_{nj}(2!b_2,3!b_3,\ldots). \tag{4.17}$$

This form is the most convenient one for explicit calculations. For formal considerations, some other equivalent expressions, such as that obtained by directly substituting (4.15) into (4.3), may be more useful.

5. Final comments

We have shown that Bell polynomials pervade all the formalism involving cluster expansions in statistical mechanics. As matrix elements of a linear representation of the group of formal series appearing in all the usual manipulations concerning the subject, they allow for simpler versions of the main results in the field. Only time will tell whether this simplicity will breed a deeper understanding. It is our hope that, this being the common role of suitable formalisms, the above one will show itself to be of some use.

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