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Weak lattice constants and the virial expansion for a classical gas†

H H Chen

Institute of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China

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Abstract. A new derivation of the virial expansion of the equation of state for a classical gas is given. We first show some properties of weak lattice constants. By using these properties the ordinary virial expansion for a classical gas is obtained. A method to calculate finite size corrections to the virial coefficients is discussed.

1. Introduction

The concept of graph embeddings (or lattice constants) plays an important role in the series expansion methods in statistical mechanics. Well known examples are series expansions of thermodynamic quantities of various spin systems on different lattices (Domb 1960, 1974). In the derivation of these series a major part of the work is the counting of lattice constants of graphs (up to a certain number of lines or points) on a regular lattice of infinite size. The set of weak lattice constants of connected graphs on other connected graphs (of finite size), called T-matrix by Rushbrooke (1964), plays a central role in the finite cluster method of series expansions originally suggested by Domb (1960). Due to this method the calculation of high-temperature series expansion is greatly simplified.

Another well known type of series expansions in statistical mechanics is the virial expansion of the properties of a gas (Uhlenbeck and Ford 1962). In this expansion a thermodynamic quantity, such as the pressure P, of a gas is expressed in powers of the density ρ $(=V/N)$,

$$P/k_{\mathrm{B}}T=\rho+\sum_{m=2}^{\infty}B_m(T)\rho^m, \tag{1}$$

where the coefficients B_m are sums of integrals which are represented by linear graphs. Only *stars* of m points contribute to B_m in the thermodynamic limit. Contributions from separated graphs and articulated graphs cancel exactly with high-order terms of the integrals.

There have been many different treatments of the virial expansions (Mayer and Mayer 1940, Uhlenbeck and Ford 1962, Stell 1964, Domb 1974, Wortis 1974, Aldrovandi and Monte Lima 1980). In the cluster expansion for a gas the number of terms which have the same integral represented by a linear graph is equal to the weak lattice constant of the graph on the complete graph of N points. Therefore the

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properties of weak lattice constants should be able to play important roles in the virial expansion of the equation of state for a gas. Previous studies, however, did not make explicit use of the properties of weak lattice constants. The purpose of this paper is to give a new derivation of (1) by using properties of weak lattice constants. Furthermore, previous derivations used the formalism of grand canonical ensemble. In the present work only the canonical partition function is involved.

In the thermodynamic limit $N \to \infty$, the shape and the size effects can be neglected. The coefficients B_m in (1) depend only on the temperature T. For finite N the virial coefficients depend on the size N and the shape of the system as well. Finite size corrections to the coefficients B_m can be obtained in the present approach.

In § 2 graph terminology will be described briefly. We follow the terminology of Domb (1974) closely. Some properties concerning the weak lattice constants of coloured graphs are developed. In § 3 the virial expansion, equation (1), will be derived by using theorems obtained in § 2. It is shown how the contributions from separated graphs and articulated graphs are eliminated in the limit $N \to \infty$. A prescription to determine the size dependence of B_m is described in § 4. A discussion is also given in this section.

2. Graph terminology and properties of weak lattice constants

A graph g is a collection of p points with l lines connecting certain pairs of points. A graph of p points is complete, denoted K_p, if all the $p(p-1)/2$ pairs of points are connected by lines. Two graphs are isomorphic if there is a one-to-one correspondence such that points and their connections correspond. A graph is said to be connected if there is at least one path between any two points; otherwise it is disconnected. A connected graph consists of a number n of connected components. An articulation point (or cut point) is a point whose deletion increases the number of components. A connected graph with an articulation point is called an articulated graph; otherwise it is called a star. The cyclomatic number $C(g)$ of the graph g is the number of independent cycles in the graph. For a graph with n components

$$C(g) = l - p + n. \tag{2}$$

For many applications it is important to regard the points of the graphs as being distinguishable. There are $p!$ different labellings of the points, but because of symmetry, groups of different labellings have identical connections. Among the $p!$ labelled graphs, there are only ν different kinds of labelled graphs. The number of different permutations of the points which leave the connections invariant is called the symmetry number of the graph. The symmetry number of a graph g, denoted $S(g)$, is an important quantity in the virial expansion. It is easy to see that $S(g) = p!/\nu$.

A graph is a subgraph of G when all points and lines of the graph are also points and lines of G. Any subgraph of a graph G which is isomorphic with g is said to represent a weak embedding of g on G. Different kinds of embeddings can be defined (Sykes *et al* 1966, Wortis 1974, Chen and Lee 1980). Only the weak embedding will be considered in this paper. The number of different weak embeddings of a graph g on the host graph G is called the weak lattice constant of g on G, and is usually denoted as $(g; G)$. It is sometimes abbreviated as (g) if G is not specified, and g is given pictorially. To avoid confusion we will use the notation $w(g; G)$ instead of $(g; G)$ in this paper. From a more realistic point of view $w(g; G)$ is the number of

different ways of drawing a graph g (more precisely, a graph isomorphic with g) out of the host graph G.

If $g^{(p)}$ is a graph of p points, and G is the complete graph of p points, it follows from the definition of symmetry number that

$$w(g^{(p)}; K_p) = p!/S(g^{(p)}). \tag{3}$$

It is straightforward to show that if the host graph is the complete graph of N points $(N > p)$

$$w(g^{(p)}; K_N) = N!/[(N-p)!S(g^{(p)})]. \tag{4}$$

So far we have assumed that all lines of the graphs are of the same species and each pair of points is connected by at most one line. In what follows the lines of a graph are allowed to belong to different species (conveniently represented by different types or colours of lines). A graph having different species of lines is said to be coloured; otherwise it is uncoloured (or monochromatic). A coloured graph will be denoted c_i, or $g_{i,\alpha}$ if it is obtained by colouring the uncoloured graph g_i, where the second index represents different colourings. A graph with pairs of points connected by different numbers of lines can be considered as a coloured graph. When we allow the colours in $g_{i,\alpha}$ to become the same, all $g_{i,\alpha}$ reduce to the uncoloured graph g_i.

When a graph is coloured some of its symmetric properties may disappear. Therefore coloured graphs $g_{i,\alpha}$ have symmetry numbers equal to or less than that of the uncoloured graph g_i, $S(g_{i,\alpha}) \leqslant S(g_i)$. For a coloured graph $g_{i,\alpha}$ we define the weak lattice constant $w(g_{i,\alpha}; G)$ as the number of different ways of drawing a coloured graph out of the uncoloured host graph G, such that this coloured graph is isomorphic (both the connections and the colours are significant) with $g_{i,\alpha}$. It is clear that

$$w(g_{i,\alpha}; G) = w(g_i; G)S(g_i)/S(g_{i,\alpha}). \tag{5}$$

Consider two coloured (or monochromatic) graphs c_{x_1} and c_{x_2}. If we combine c_{x_1} and c_{x_2} together, i.e. allow points in c_{x_1} to coincide with points in c_{x_2}, different coloured graphs are obtained. Coloured graphs obtained by combining c_{x_1} and c_{x_2} together are called combined graphs of c_{x_1} and c_{x_2}. Figure 1 shows an example of the combination of two graphs. Eight different combined graphs can be obtained. On the other hand, a graph can be decomposed into several graphs by cutting the points.

If the colours appearing in c_{x_1} do not appear in c_{x_2}, we define a function w of c_{x_1} and c_{x_2} as

$$w(c_{x_1}, c_{x_2}; G) \equiv \sum_i w(c_i; G), \tag{6}$$

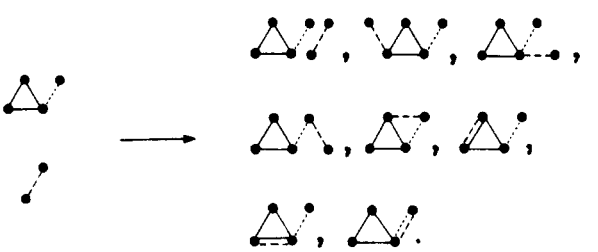

Figure 1. When the two graphs on the LHS are combined, eight different combined graphs are obtained.

where the summation goes over all combined graphs, c_i, of c_{x_1} and c_{x_2}. We have the following theorem.

Theorem 1A. For any graphs c_{x_1} and c_{x_2}, if the colours of lines appearing in c_{x_1} do not appear in c_{x_2}, then the function $w(c_{x_1}, c_{x_2}; G)$ defined by (6) satisfies the product property

$$w(c_{x_1}, c_{x_2}; G) = w(c_{x_1}; G)w(c_{x_2}; G). \tag{7}$$

Proof. Since the two graphs c_{x_1} and c_{x_2} have different colours, any combined graph can be decomposed into c_{x_1} and c_{x_2} in a unique way (i.e. we know that each line of the combined graph is either from c_{x_1} or from c_{x_2}). Therefore the total number of different ways to draw the combined graphs of c_{x_1} and c_{x_2} out of the graph G is the same as the number of ways to draw a graph c_{x_1} out of G, and then a graph c_{x_2} (independent of how c_{x_1} is drawn) out of G. This proves theorem 1A.

It is important to note that if there is no restriction on the colours of lines in c_{x_1} and c_{x_2}, a combined graph c_i may have several different ways of being decomposed into c_{x_1} and c_{x_2}. For example if the broken and dotted lines in figure 1 were indistinguishable, then the combined graph shown in figure 2 would have two different ways to be decomposed into c_{x_1} and c_{x_2}. If the number of different ways to decompose c_i into c_{x_1} and c_{x_2} is denoted by $d(c_i)$, then theorem 1A should be modified as follows.

Figure 2. If the broken and dotted lines were indistinguishable, the graph on the LHS would have two different ways to be decomposed into c_{x_1} and c_{x_2}.

Theorem 1B. For any graphs c_{x_1} and c_{x_2}, if we define

$$w(c_{x_1}, c_{x_2}; G) \equiv \sum_i d(c_i)w(c_i; G), \tag{8}$$

where the summation goes over all combined graphs of c_{x_1} and c_{x_2}, and $d(c_i)$ is the number of different ways to decompose the combined graph c_i into c_{x_1} and c_{x_2}, then

$$w(c_{x_1}, c_{x_2}; G) = w(c_{x_1}; G)w(c_{x_2}; G). \tag{9}$$

Theorem 1A is a special case of theorem 1B. For the purpose of deriving the virial expansion theorem 1A is more appropriate. Another special case of theorem 1B has been given by Sykes *et al* (1966, theorem II) in which all lines in c_{x_1} and c_{x_2} have the same colour.

It is straightforward to extend theorem 1B to the combination of several graphs.

Theorem 2. Consider n coloured graphs $c_{x_1}, c_{x_2}, \ldots, c_{x_n}$. If we define

$$w(c_{x_1}, c_{x_2}, \ldots, c_{x_n}; G) \equiv \sum_i d(c_i)w(c_i; G), \tag{10}$$

where the summation is over all combined graphs, c_i, of the n graphs, and $d(c_i)$ is the

number of different ways to decompose c_i into the n graphs, then

$$w(c_{x_1}, c_{x_2}, \ldots, c_{x_n}; G) = w(c_{x_1}; G)w(c_{x_2}; G) \ldots w(c_{x_n}; G). \tag{11}$$

The proof of theorem 2 is a straightforward extension of the case $n = 2$ (theorem 1B). We note that if any colour appearing in one graph does not appear in other graphs, then $d(c_i) = 1$. Only this special case will be considered in the derivation of the virial expansion.

For a set of n graphs there are many different ways to combine the graphs. Associated with each combination a product of the w-functions can be constructed. For example, for a set of three graphs c_i, c_j and c_k, we can combine all of them to get $w(c_i, c_j, c_k)$; we can combine two of them to construct $w(c_i, c_j)w(c_k)$, $w(c_i, c_k)w(c_j)$ or $w(c_j, c_k)w(c_i)$; or we can combine none of them to have $w(c_i)w(c_j)w(c_k)$. Here we have dropped the host graph G in $w(c; G)$ for convenience. Any of the above quantities will be called a combination of $w(c_i)$, $w(c_j)$ and $w(c_k)$. We note that the notation $w(C_p)$ stands for a graph integral in Domb (1974), and the notation $w(c_i)$ here is a weak lattice constant.

A combination which is a product of m factors of the w-functions will be called an mth-order combination (or mth-order term), and will be denoted by $W_\alpha^{(m)}(c_{x_1}, c_{x_2}, \ldots)$, with the index α representing different combinations of the same order. For instance

$$W_1^{(2)}(c_i, c_j, c_k) = w(c_i, c_j)w(c_k), \tag{12}$$

$$W_2^{(2)}(c_i, c_j, c_k) = w(c_i, c_k)w(c_j), \tag{13}$$

etc. It must be noted that the permutation of two w-functions, or the permutation of graphs in a w-function, does not generate a new combination. Although all the different combinations have different functional forms, they have exactly the same value for a given set of graphs, as a consequence of theorem 2.

In order to derive the virial expansion, equation (1), we prove the following theorem.

Theorem 3. For a set of n different graphs $c_{x_1}, c_{x_2}, \ldots, c_{x_n}$,

$$\sum_{m=1}^{n} \sum_{\alpha} (-1)^{m-1}(m-1)!\, W_\alpha^{(m)}(c_{x_1}, c_{x_2}, \ldots, c_{x_n}) = 0, \tag{14}$$

where the summations go over all different combinations $W_\alpha^{(m)}$. The n graphs are different either in colour or in structure.

Proof. It is convenient to classify the combinations of n graphs (and the associated w-functions) by the partitions of n. Consider a partition $1^{n_1}2^{n_2}3^{n_3}\ldots$, which satisfies

$$\sum_i i n_i = n, \qquad n_i = 0, 1, 2, \ldots, \tag{15}$$

and

$$\sum_i n_i = m. \tag{16}$$

This partition represents the group of combinations that n_1 graphs are not combined with others, $2n_2$ graphs are combined in pairs, and $3n_3$ graphs are combined in triples, etc.

Since all graphs are different, the number of different combinations of the n graphs represented by the partition $1^{n_1}2^{n_2}3^{n_3}\ldots$ is $n![n_1!(1!)^{n_1}n_2!(2!)^{n_2}\ldots]^{-1}$. As all combinations $W_\alpha^{(m)}$ are equal, the proof of theorem 3 is reduced to the proof of the identity

$$\sum_{\substack{\text{partition}\\ \text{of } n}} \frac{(-1)^{m-1}(m-1)!\,n!}{n_1!(1!)^{n_1}n_2!(2!)^{n_2}\ldots} = 0, \tag{17}$$

where the summation is over all partitions $1^{n_1}2^{n_2}3^{n_3}\ldots$ which satisfy (15) and m is given by (16).

Consider a function

$$f(x) = \ln(1 + a_1x + a_2x^2 + a_3x^3 + \ldots). \tag{18}$$

If we make use of the expansion

$$\ln(1+X) = X - \tfrac{1}{2}X^2 + \tfrac{1}{3}X^3 - \ldots, \tag{19}$$

$f(x)$ can be rewritten as

$$f(x) = b_1x + b_2x^2 + b_3x^3 + \ldots \tag{20}$$

where the coefficients b_n are given by

$$b_n = \sum_{\substack{\text{partition}\\ \text{of } n}} \frac{(-1)^{m-1}}{m} \frac{m!}{n_1!\,n_2!\ldots}(a_1)^{n_1}(a_2)^{n_2}\ldots. \tag{21}$$

Let $a_n = (n!)^{-1}$; the left-hand side (LHS) of (17) is equal to $n!\,b_n$. But when $a_n = (n!)^{-1}$, $f(x) = \ln e^x = x$. All coefficients b_n vanish except $b_1 = 1$. This proves equation (17) and hence theorem 3.

3. Virial expansion of a classical gas

Consider a system of N monatomic molecules contained in a volume V. The intermolecular potential between two molecules, $U(r_{ij})$, depends only on the distance r_{ij} between the particles i and j. The Hamiltonian is given by

$$H = \sum_{i=1}^{N}\left(\frac{p_i^2}{2m}\right) + \sum_{1\le i<j\le N} U(r_{ij}). \tag{22}$$

With this Hamiltonian, the partition function of the system is

$$\begin{aligned} Q_N(V,T) &= (N!\,h^{3N})^{-1}\int \exp(-H/k_BT)\,\mathrm{d}^{3N}p\,\mathrm{d}^{3N}r \\ &= (N!\,\lambda^{3N})^{-1}\int \prod_{i<j}(1+f_{ij})\,\mathrm{d}^{3N}r, \end{aligned} \tag{23}$$

where $\lambda = h/(2\pi m k_BT)^{1/2}$ is the mean thermal wavelength of the particles, the product is over all pairs of molecules, and

$$f_{ij} = \exp[-U(r_{ij})/k_BT] - 1. \tag{24}$$

Following the standard graphic expansion method (Mayer and Mayer 1940), we expand the integrand in ascending powers of the function f_{ij},

$$Q_N(V, T) = (N!\lambda^{3N})^{-1} \int \left(1 + \sum f_{ij} + \sum f_{ij} f_{kl} + \ldots\right) \mathrm{d}^{3N} r. \tag{25}$$

In this expansion, with each line representing a factor f_{ij}, a term containing l factors of f_{ij} can be represented by a labelled l-line graph. Different terms represented by isomorphic graphs will have the same contribution to Q_N. The number of different labelled graphs which are isomorphic with a graph g is nothing but the weak lattice constant of the graph g on the complete graph of N points, $w(g; K_N)$. Therefore

$$Q_N(V, T) = (N!\lambda^{3N})^{-1} \sum_g w(g; K_N) \int \prod f_{ij} \, \mathrm{d}^{3N} r, \tag{26}$$

where the summation is over all unlabelled graphs g and the product is over all lines (labelled arbitrarily) of the graph g.

All graphs in (26) are N-point graphs. They consist of connected components: isolated points, single lines, triangles, etc. For a graph of n components the integral of the graph is then a product of n integrals, one for each component of the graph. An isolated point will give a factor V. A line will contribute a factor

$$\int\int f_{ij} \, \mathrm{d}^3 r_i \, \mathrm{d}^3 r_j = V \int f_{ij} \, \mathrm{d}^3 r_j \equiv V \cdot I(\ \diagup\ ). \tag{27}$$

Similarly a triangle will give

$$\int\int\int f_{ij} f_{jk} f_{ik} \, \mathrm{d}^3 r_i \, \mathrm{d}^3 r_j \, \mathrm{d}^3 r_k = V \int\int f_{ij} f_{jk} f_{ik} \, \mathrm{d}^3 r_j \, \mathrm{d}^3 r_k \equiv V \cdot I(\ \triangle\ ). \tag{28}$$

Graph integrals $I(g)$ for other components (connected graphs) can be defined in the same way. For a connected graph of l lines and p points, the integrand is a product of l factors f_{ij} and the integration is over the coordinates of $p-1$ particles. We have assumed that the system is translationally invariant (either $N \to \infty$, or a periodic boundary condition is assumed). An arbitrary particle of the graph is fixed at the origin when we integrate over the coordinates of the other $p-1$ particles. Finally the integration over the coordinates of the 'fixed' particle gives the factor V as in (27) and (28).

For an articulated graph g, if the graph is decomposed into g_a and g_b when cut at the articulation point, then

$$I(g) = I(g_a) I(g_b). \tag{29}$$

The proof of (29) is simple. We fix the position of the articulation point and integrate Πf_{ij} over the coordinates of the other points. The integration over the coordinates of points in g_a is independent of the integration over the coordinates of points in g_b. Equation (29) follows. For a disconnected graph g consisting of the numbers n_i of connected graphs g_i, $i = 1, 2, \ldots$, we can define its graph integral as

$$I(g) = \prod_i [I(g_i)]^{n_i}. \tag{30}$$

All graph integrals are independent of V.

In what follows all points not connected by a line will be deleted from the graphs. Instead of considering all graphs to have N points (as in (26)), the graphs will have different numbers of points. The smallest component of the graphs is then a line. When the isolated points are omitted, a graph of p points and n components will contribute a term of order $V^{N-(p-n)}$ to the partition function. If g_i is the graph resulting from deleting all isolated points of an N-point graph $g_i^{(N)}$, it follows from the definition of weak embeddings that

$$w(g_i^{(N)}; K_N) = w(g_i; K_N). \tag{31}$$

Equation (26) is then rewritten as

$$Q_N = \frac{V^N}{N!\lambda^{3N}}\left(1+\sum_g V^{-(p-n)} w(g; K_N) I(g)\right) \equiv Q_0[1+X], \tag{32}$$

where the summation is over all graphs g (having no isolated points), and p and n are respectively the numbers of points and components of g. $Q_0 = V^N/(N!\lambda^{3N})$ is the partition function of the ideal classical gas of N molecules. In (32) the V-dependent part $V^{-(p-n)}$, the N-dependent part $w(g; K_N)$ and the U-dependent part $I(g)$ are separated.

Taking the logarithm of Q_N, we have

$$\ln Q_N = \ln Q_0 + X - \tfrac{1}{2}X^2 + \tfrac{1}{2}X^3 - \ldots, \tag{33}$$

where X is defined in (32). Consider a general term in X^m. The U-dependent part is a product of m factors of $I(g)$. Each factor can further be decomposed into a product of graph integrals of stars $I(s)$, through (29) and (30). If there are a number n_1 of stars s_1, a number n_2 of stars s_2, etc, when the m graphs are decomposed into stars (by cutting at all cut points), then the product of the m factors of $I(g)$ can be expressed as

$$\prod_g I(g) = [I(s_1)]^{n_1}[I(s_2)]^{n_2}\ldots. \tag{34}$$

Next consider the V-dependent part of this term. The power of V, according to (2), is equal to

$$\sum_g [p(g) - n(g)] = \sum_i n_i[l(s_i) - c(s_i)], \tag{35}$$

where $p(g)$ and $n(g)$ are respectively the numbers of points and components of the graph g. When the m graphs are decomposed into stars there are the numbers n_i of stars s_i, and $l(s_i)$ and $c(s_i)$ are the number of lines and the cyclomatic number of s_i. We note that when a graph is decomposed into stars by cutting at the cut points, the total number of lines and the total number of cycles are unchanged.

Equations (34) and (35) imply that any two terms in $\ln Q_N$, if they have the same U-dependent part, will have the same V-dependent part. The N-dependent parts, however, are different in general. When all terms having the same volume part (and hence the potential part) are grouped together, equation (33) becomes

$$\ln Q_N = \ln Q_0 + \sum_{n_1}\sum_{n_2}\sum_{n_3}\ldots C_{n_1,n_2,n_3,\ldots}\prod_i [V^{-l(s_i)+c(s_i)} I(s_i)]^{n_i}, \tag{36}$$

where each term is characterised by a set of non-negative integers $n_1, n_2, n_3, \ldots$. The

coefficients $C_{n_1,n_2,\ldots}$ depend only on N and are equal to

$$C_{n_1,n_2,\ldots} = \sum_{m=1}^{n} \frac{(-1)^{m-1}}{m} \sum_{\{g\}} \frac{m!}{m_1!\, m_2! \ldots} [w(g_1)]^{m_1} [w(g_2)]^{m_2} \ldots \tag{37}$$

where $\Sigma_{\{g\}}$ sums over all sets of graphs which contain the numbers m_i of graphs g_i such that when all graphs are decomposed into stars there are the numbers n_i of stars s_i. Here $m = \Sigma_i m_i$. The factor $(-1)^{m-1}/m$ is the coefficient of X^m in (33), and the factor $m!/(m_1!\, m_2! \ldots)$ is the number of different permutations of the m graphs in X^m.

The pressure is then obtained from $P = \partial(k_B T \ln Q_N)/\partial V$,

$$P/k_B T = \rho - \sum_{\{n\}} C_{n_1,n_2,\ldots} y\{n\} (\rho/N)^{y\{n\}+1} I\{n\}, \tag{38}$$

where the summation goes over all sets of non-negative integers $\{n\} = (n_1, n_2, \ldots)$, and

$$y\{n\} = \sum_i n_i [I(s_i) - c(s_i)] = \sum_i n_i [p(s_i) - 1], \tag{39}$$

$$I\{n\} = \prod_i [I(s_i)]^{n_i}. \tag{40}$$

Although the coefficients $C_{n_1,n_2,\ldots}$ as given by (37) are nonlinear functions of $w(g_i)$, they can be rewritten as a linear combination of weak lattice constants of connected graphs.

Consider the combinations $W_\alpha^{(m)}(c_{x_1}, c_{x_2}, \ldots, c_{x_n})$ for a set of n stars. n_1 of them are stars s_1, n_2 of them are stars s_2, etc. All stars are monochromatic, but all of them have different colours. In the combinations $W_\alpha^{(m)}$ some combined graphs will have new cycles besides the original cycles of the n stars. For illustration consider three stars; two of them are s_1 and s_1' (single lines with different colours) and one of them is s_2 (a triangle). Equation (14) for the three stars is shown in figure 3. In this figure $w(g)$ is abbreviated as (g). The first term is $3!\, W^{(3)}/3 = 2w(s_1)w(s_1')w(s_2)$. The next three terms are the expansions of $-2!\, W_1^{(2)}/2 = -w(s_1, s_1')w(s_2)$; and the following six terms are $-w(s_1, s_2)w(s_1') - w(s_1', s_2)w(s_1)$. Finally the other terms are the expansions of $W^{(1)} = w(s_1, s_1', s_2)$. The underlined terms are those having at least one new cycle.

We have the following theorem.

Theorem 4. Consider a set of n graphs, $c_{x_1}, c_{x_2}, \ldots, c_{x_n}$. n_1 of the graphs are stars s_1, n_2 of them are stars s_2, etc. Each graph is monochromatic, but all graphs have different colours. For this set of graphs the sum of terms on the LHS of (14) which do not have a new cycle (see figure 3 for illustration) is equal to $C_{n_1,n_2,\ldots}$ times $n_1!\, n_2! \ldots$.

Proof. Consider an mth-order term in $C_{n_1,n_2,\ldots}$. It has the form

$$[(-1)^{m-1}(m-1)!/m_1!\, m_2! \ldots] w(g_{y_1}) w(g_{y_2}) \ldots w(g_{y_m}),$$

where g_{y_i} are uncoloured. Among the m graphs, m_1 of them are g_1, m_2 of them are g_2, etc. When all the m graphs are decomposed into stars there are the numbers n_i of uncoloured stars s_i. If we colour out these stars on g_{y_i} according to the colours of graphs $c_{x_1}, c_{x_2}, \ldots, c_{x_n}$, we can obtain a set of terms on the LHS of (14). On the other hand, if we allow all colours to be the same, a set of terms on the LHS of (14) will reduce to $w(g_{y_1}) w(g_{y_2}) \ldots w(g_{y_m})$. This set of terms obviously does not include those having new cycles. Summing up this set of terms, and expressing weak lattice constants

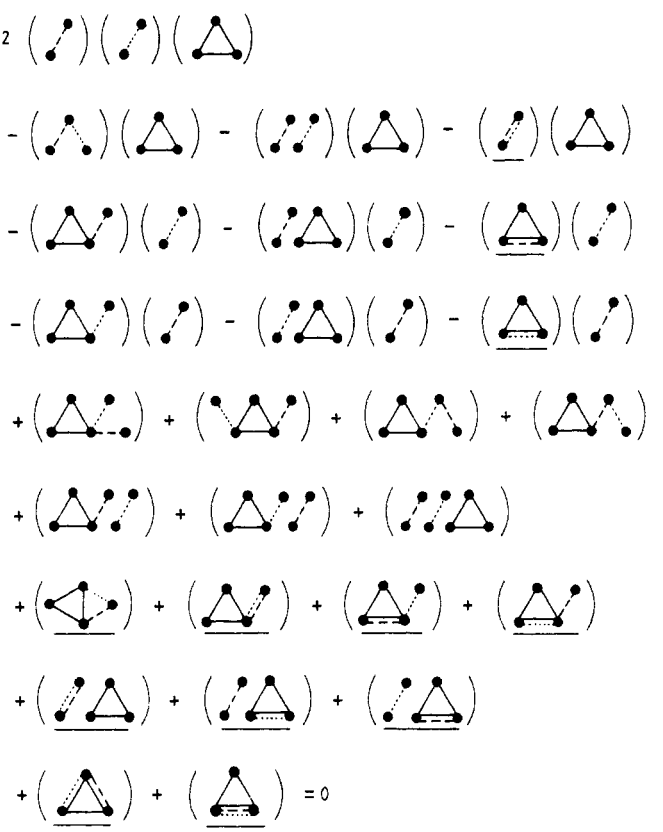

Figure 3. The explicit form of (14) for a set of three stars (two single lines and one triangle, see first term). The terms having new cycles in the graphs are underlined.

of coloured graphs in terms of weak lattice constants of uncoloured graphs (by (5)), we obtain

$$(-1)^{m-1}(m-1)!\, w(g_{y_1})w(g_{y_2})\ldots w(g_{y_m}) \times (\text{the number of different ways to}$$

$$\text{colour out } c_{x_1}, c_{x_2}, \ldots, c_{x_n} \text{ from the set of graphs } g_{y_1}, g_{y_2}, \ldots, g_{y_m}).$$

Since the colours among the stars s_1 can be exchanged, the colours among the stars s_2 can be exchanged, ..., there are $n_1!\, n_2!\, n_3! \ldots$ possible permutations of colours. Among these different colourings, some of them are simply permutations of the order of the coloured graphs of $g_{y_1}, g_{y_2}, \ldots, g_{y_m}$. The number of different permutations of the order of graphs resulting from the permutations of the colours is $m_1!\, m_2!\, m_3! \ldots$. As the order of $w(g)$ is insignificant, the total number of different colourings is equal to $(n_1!\, n_2! \ldots)/(m_1!\, m_2! \ldots)$. Therefore, the ratio of the two quantities considered above is $n_1!\, n_2! \ldots$. This ratio is the same for each term in $C_{n_1, n_2, \ldots}$ and the corresponding quantity on the LHS of (14). Theorem 4 follows.

We note that if some of the graphs $c_{x_1}, c_{x_2}, \ldots$ are not stars, theorem 4 does not hold because the method to decompose g_{y_i} into c_{x_i} is not unique.

Now consider terms on the LHS of (14) which have new cycles in the graphs. A pair of points connected by two lines is considered as a cycle (see figure 3 for illustration).

The highest-order terms with new cycles are of order $n-1$, and have the form $w(c_1')w(c_2')\ldots w(c_{n-1}')$. As all possible combinations of the w-functions are included in (14), associated with each $(n-1)$th-order term, there is a first-order term $w(c_1' \cup c_2' \cup \ldots \cup c_{n-1}')$. Here $c_1' \cup c_2' \cup \ldots \cup c_{n-1}'$ is a graph whose points and lines are respectively the collections of points and lines of c_1', c_2',... and c_{n-1}'. The term $w(c_1')w(c_2')\ldots w(c_{n-1}')$ (with coefficient $(-1)^{n-2}(n-2)!$) cancels with $w(c_1' \cup c_2' \cup \ldots \cup c_{n-1}')$ when we apply theorem 3 again to the set of $n-1$ graphs.

Each time we apply theorem 3, all possible combinations are included with proper coefficients. We then apply theorem 3 to a set of $n-2$ graphs to cancel an $(n-2)$th-order term and $w(g)$ for a disconnected graph of $n-2$ components. Repeating this process, all nonlinear terms in $w(g)$, and $w(g)$ for disconnected graphs, cancel out. What are left are linear terms in $w(g)$ for connected graphs with new cycles.

A combined graph, which is connected and has new cycles besides the cycles of the constituent stars, has the number of points

$$p < \sum_i n_i[l(s_i) - c(s_i)] + 1 = y\{n\} + 1, \tag{41}$$

since the combined graph g has $n=1$, $l = \Sigma_i n_i l(s_i)$ and $c(g) > \Sigma_i n_i c(s_i)$. This proves the following theorem.

Theorem 5. If $n_1 + n_2 + \ldots > 1$, the coefficients $C_{n_1,n_2,\ldots}$ in (36) can be expressed as *linear combinations* of weak lattice constants $w(g)$ of *connected graphs* having $p \leqslant y\{n\}$.

In all cases we have considered, $C_{n_1,n_2,\ldots}$ come out to be linear combinations of weak lattice constants of *stars* only. But, we cannot give a general proof that weak lattice constants of articulated graphs vanish.

In theorems 4 and 5 the host graph G is not specified in the weak lattice constants $w(g; G)$. These theorems are true for any G. In the virial expansion for a gas G is the complete graph of N points.

From equation (4) and theorem 5 we see that if $n_1 + n_2 + \ldots > 1$, $C_{n_1,n_2,\ldots}$ are of order $N^{\{y\}}$ or lower. These terms do not contribute to (38) in the limit $N \to \infty$. Terms contributing to (37) are those with $n_1 + n_2 + \ldots = 1$, i.e. terms represented by stars in X (equation (32)). Therefore, in the thermodynamic limit (38) becomes

$$P/k_B T = \rho - \sum_{s_i} (p_i - 1)\rho^{p_i} I(s_i)/S(s_i), \tag{42}$$

where the summation is over all stars s_i, and p_i is the number of points of s_i. $I(s_i)$ and $S(s_i)$ are respectively the graph integral and the symmetry number of s_i. Equation (42) has the same form as (1), and

$$B_m = -\sum_\alpha (m-1) I(s_\alpha^{(m)})/S(s_\alpha^{(m)}), \tag{43}$$

where the summation goes over all m-point stars $s_\alpha^{(m)}$.

4. Discussion and conclusions

In this paper we have rederived the virial expansion of the equation of state for a classical gas. This derivation is based completely on the properties of weak lattice constants of coloured graphs. We have shown how the contributions of separated

graphs, articulated graphs and the nonlinear terms (X^2, X^3, ... of (33)) cancel exactly in the thermodynamic limit $N \to \infty$.

For finite N, the equation of state is given by (38). To calculate the coefficient of ρ^m, we find all sets of stars such that for each set the number of stars n and the total number of points p satisfies $p+n=m+1$. For example, the sixth coefficient is contributed from the following sets of stars: $(s^{(6)})$, $(s^{(5)}, s^{(2)})$, $(s^{(4)}, s^{(3)})$, $(s^{(4)}, s^{(2)}, s^{(2)})$, $(s^{(3)}, s^{(3)}, s^{(2)})$, $(s^{(3)}, s^{(2)}, s^{(2)}, s^{(2)})$ and $(s^{(2)}, s^{(2)}, s^{(2)}, s^{(2)}, s^{(2)})$, where $s^{(p)}$ stands for a star of p points.

For each set of stars the U-dependent part of the coefficient is simply $\Pi_i I(s_i)$, and the size dependent part $C_{n_1,n_2,\ldots}$ is given by (37). We can calculate the coefficients $C_{n_1,n_2,\ldots}$ as functions of N directly from (37) by setting $w(g)=N!/[(N-p)!\,S(g)]$, or we can express $C_{n_1,n_2,\ldots}$ as linear combinations of weak lattice constants of connected graphs (theorem 5) before inserting equation (4) for $w(g)$.

We have calculated the N dependence of the coefficients $B_m(N)$ for the hard-sphere gas. They are

$$B_2(N)/B_2(\infty) = 1 - N^{-1},$$

$$B_3(N)/B_3(\infty) = 1 + 0.2N^{-1} - 1.2N^{-2},$$

$$B_4(N)/B_4(\infty) = 1 - 0.337N^{-1} + 7.95N^{-2} - 8.61N^{-3},$$

$$B_5(N)/B_5(\infty) = 1 + (0.035 \pm 0.03)N^{-1} - (32.7 \pm 0.2)N^{-2} + (155 \pm 1)N^{-3} - (124 \pm 1)N^{-4},$$

$$B_6(N)/B_6(\infty) = 1 + (0.07 \pm 0.35)N^{-1} + (103 \pm 5)N^{-2} - (1480 \pm 30)N^{-3} + (4110 \pm 60)N^{-4} - (2730 \pm 40)N^{-5},$$

where $B_m(\infty)$ are known from Ree and Hoover (1967), and the uncertainties in $B_5(N)$ and $B_6(N)$ are due to the uncertainties in the Monte Carlo calculation of $B_5(\infty)[=(0.1103 \pm 0.0003)B_2^4(\infty)]$ and $B_6(\infty)[=(0.0386 \pm 0.0004)B_2^5(\infty)]$. We see that for $N \simeq 10^2$ the deviations of $B_m(N)$ from $B_m(\infty)$ are about 0.3–1%, and for $N > 10^3$ the deviations are negligible.

In conclusion, we have developed some properties of the weak lattice constants of coloured graphs, and have shown a new derivation of the virial expansion for a classical gas. This derivation is straightforward and is simple if one is familiar with graph embeddings. The N dependence of the virial coefficients also follows from the new approach.

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