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Estimates of General Mayer Graphs. I: Construction of Upper Bounds for a Given Graph by Means of Sets of Subgraphs

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A large number of physical quantities (thermodynamic and correlation functions, scattering amplitudes, intermolecular potentials, etc. . . .) can be expressed as sums of an infinite number of multiple integrals of the following type:

$$\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n) = \int \prod f_L(\mathbf{x}_i, \mathbf{x}_j)\, d\mathbf{x}_{n+1} \cdots d\mathbf{x}_{n+k}$$

These are called Mayer graphs in statistical mechanics, Feynman graphs in quantum field theory, and multicenter integrals in quantum chemistry. We call them n-graphs here. In a preceding note [*Physics Letters* **62A**:295 (1977)], we have proposed a new estimation method which provides upper bounds for arbitrary n-graphs. This article is devoted to developing in detail the foundations of this method. As a first application, we prove that all virial coefficients of polar systems are finite. More generally, we show on some examples that our estimation method can give *finite* upper bounds for n-graphs occurring in the perturbative developments of thermodynamic functions of neutral, polar, and ionized gases and of Green's functions of Euclidean quantum field theories (thus improving Weinberg's theorem), as also in variational approximations of intermolecular potentials. Our estimation method is based on the Hölder inequality which is an improvement over the mean value estimation method, employed by Riddell, Uhlenbeck, and Groeneveld, except for the hard-sphere gas, where both methods coincide. The method is applied so far only to individual graphs and not to thermodynamic functions.

KEY WORDS: Upper bound; subgraph; covering; Hölder's inequality.

1. INTRODUCTION

This paper is the first in a series devoted to the construction of estimates (upper bounds, in this paper) for arbitrary n-graphs. An n-graph is a

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multiple integral whose integrand is a product of 2-body functions:

$$\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n) = \int \prod f_L(\mathbf{x}_i, \mathbf{x}_j)\, d\mathbf{x}_{n+1} \cdots d\mathbf{x}_{n+k} \tag{1.1}$$

(A more precise definition is given in Section 2.1.)

The importance of n-graphs comes from the fact that a great number of physical quantities can be expressed as sums of an infinite number of n-graphs. This is the case for thermodynamic and transport properties of classical[1] and quantum[2] systems, for amplitudes of scattering processes,[3] for energy levels of atoms and molecules,[4] for atomic and intermolecular potentials,[5] etc. . . . . In classical statistical mechanics, n-graphs are usually called Mayer graphs (or integrals) with n root-points. In quantum field theory, they are usually called Feynman graphs (or integrals, or amplitudes) in coordinate space and, in quantum chemistry, multicenter integrals. Of course, all these quantities, and in particular thermodynamic functions, can be studied without ever making use of n-graphs (see for example Ruelle's book[6]). However, n-graphs enable us to take into account a considerable wealth of numerical information. For example, approximate integral equations for the radial distribution function $g(r)$ and perturbative developments with a nonideal reference gas are known to provide accurate values for thermodynamic functions of fluids at almost any density and temperature (see, for example, Ref. 7 and references therein). This very important and highly nontrivial information can be readily expressed in terms of n-graphs, whereas it does not seem possible to incorporate it in the other more modern approaches.

We have been led to search for estimates of arbitrary n-graphs in connection with the study of thermodynamic properties of dense plasmas. These systems are of considerable importance, in particular in view of applications to controlled thermonuclear fusion.[8] But their experimental study is extremely difficult and measurements are scarce and relatively inaccurate, so that it is desirable to try to obtain information on their thermodynamic properties which should be quantitative and at the same time as rigorous as possible. In fact, this would also be interesting even for systems such as polar gases and dense neutral systems, although their thermodynamic functions are known very accurately from experiment and numerical simulations. Indeed, the various approximate theories that are used to compute these functions, as for example integral equations for $g(r)$ or perturbative developments with a nonideal reference gas, are based on uncontrolled approximations since they are obtained (after suitable resummations) by dropping the n-graphs that one does not know to compute. Therefore, their validity lies much more on their excellent agreement with computer simulations than on a sound theoretical basis. On the other hand, the rigorous results that have been proved for dense neutral systems are

mainly qualitative, since they consist in proofs of existence (for thermodynamic functions, phase transitions, etc. . . .) or in very general functional properties (such as positivity, continuity, convexity, etc. . . .)[6] which provide hardly any information on the numerical value of thermodynamic functions. For polar gases, no rigorous results have been proved, up to now, not even the existence of thermodynamic functions. In quantum chemistry, a similar situation prevails: rigorous results give only proofs of existence (or nonexistence) for bound states and for Møller wave operators, or general functional properties such as analyticity in coupling constants,[9] while numerical results are obtained by approximating variationally the wave functions, or by truncating their developments on various types of complete sets. In quantum field theory, the situation is even worse, since rigorous results have been proved only for some simple (low-dimensional) models,[10] while one has to cope with the infrared and ultraviolet divergences to obtain quantitative results for realistic models.[3]

To improve the situation, one can try to look for accurate estimates for those n-graphs that cannot be computed, rather than just to drop them, as was the approach of J. Groeneveld.[12] Unfortunately, in most practical situations, this is quite insufficient to obtain rigorous and quantitative results. This is particularly clear in quantum field theory and in the study of thermodynamic properties of plasmas, since most high-order n-graphs are divergent.[3,11] This is still true even for simpler systems such as neutral fluids, where all n-graphs are finite, because one must further resum together those n-graphs that cancel approximately each other.[12] However, one can hope that accurate estimates for any n-graphs could permit us to make a first step towards rigorous and quantitative results, by indicating which n-graphs contribute significantly to the quantities of interest and which do not, and by clarifying the mechanism of cancellations that occur.

On a more practical point of view, this could provide reasonable indications on the domain of validity of the various approximate theories through estimates of the first few neglected terms. This could also save large amounts of computer time by permitting us to know which n-graphs are negligible without having to compute them, or by indicating which is the best approximate theory for a given system, without having to perform costly numerical simulations. In quantum chemistry, this could help in choosing good test functions including explicit dependence on interelectronic distances, and thus improve our physical knowledge of molecular structure and interatomic or intermolecular potentials by reducing considerably the number of contributing n-graphs[13] (when making use of the configuration interaction method,[4] there are usually a very large number of n-graphs that contribute significantly, typically 10^4 to 10^6, so that it is impossible to give them a precise physical meaning).

It has been remarked by Riddell and Uhlenbeck[14] and used exten-

sively by Groeneveld[12] that one can obtain simple upper bounds for any given n-graph by dropping a certain number of lines until one obtains a "computable" n-graph (see Section 2.4). Unfortunately, this estimation method gives finite bounds for neutral gases only. In this article, we propose constructing upper bounds from an *ensemble* of computable subgraphs, so that no line is dropped now (see the introduction to Section 3). These bounds have two noticeable properties that will be investigated in detail in later articles. The first property is that they are *finite* for a large number of n-graphs that occur in statistical mechanics, in quantum field theory, and in quantum chemistry. This is the case for neutral, polar, and ionized gases, for Euclidean fields of massive scalar particles in self-interaction or interacting with particles of zero mass, and even for molecular integrals where some f_L's grow to infinity as r^m at large distances. The second noticeable property of our upper bounds is that they have a *correct order of magnitude* for a large number of the n-graphs described above. This is probably the most important point about our estimation method since it was not at all obvious a priori that an upper bound has a correct order of magnitude, in the absence of any computation of a lower bound, whereas this is a necessary condition for an estimation method to be useful in the study of dense systems.

In Sections 2.1 and 2.2, we give a precise definition of n-graphs and recall their graphical representation. Then, we describe various forms under which n-graphs can appear. In the last section, we describe the mean value estimation method.[12] In Sections 3.1 and 3.2, we give first the expression of our upper bounds in its most general form. Then, in Section 3.3, we work out in some detail a few examples of application, to illustrate how to obtain bounds by our method, and to show off some of their properties. This section can be read almost independently from the rest of the article, except for some definitions. In Section 3.4, we show that the mean value bounds can be regarded as a particular case of ours, and that one can always find by our method bounds which are strictly smaller than the mean value ones, except for the hard-sphere gas. In Section 3.5, we construct some particular types of bounds, which we call canonical. As an application, we prove that the virial coefficients of polar systems are finite.

2. GENERALITIES

2.1. Definition of n Graphs

n-graphs are multiple integrals of the following type:

$$\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda) = \int_{\Lambda^k} \prod_{L \in \mathring{\Gamma}} f_L(\mathbf{x}_i, \mathbf{x}_j)\, d\mathbf{x}_{n+1} \cdots d\mathbf{x}_{n+k} \qquad (2.1)$$

In (2.1), Γ is a graph[15] with $n + k$ points and l simple lines $L = (i, j)$ joining the points i and j $(i \neq j)$. Γ is called the associated graph of the n-graph $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$. The set of lines of Γ is denoted by $\mathfrak{L}\Gamma$, and its set of points by $\mathfrak{P}\Gamma$. The k points over which the integrations are performed are called field-points, and the n others are called root-points. In all the following, the numbers of root-points, field-points, and lines of any graph will be denoted, respectively, by n, k, and l.

In the case where it is necessary to indicate explicitly that Γ has n root-points, we say that Γ is an n-rooted graph. If no confusion is possible between the graph theoretical concept and the multiple integral (2.1), Γ will also be called simply an n-graph. On the other hand, when we speak of an n-graph with a topological property (for example connected, irreducible, etc. . . .) it means an n-graph $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ whose associated graph Γ has the given topological property.

$\mathbf{x}_i$ represents the coordinates required to fix the spatial location, and in some cases also the orientation, of particle i. More precisely, $\mathbf{x}_i = \mathbf{r}_i$ or $\mathbf{x}_i = (\mathbf{r}_i, \omega_i)$, where $\mathbf{r}_i$ is the vector to the center of particle i from the origin of a laboratory coordinate system S, and ω_i is the rotation which is necessary to make the coordinate system S_i, attached to particle i, coincide with S.[16]

The functions $f_L(\mathbf{x}_i, \mathbf{x}_j)$ are supposed to depend only on the relative coordinates of particles i and j, that is, they are invariant by any translation and rotation of the system composed of the two particles as a whole.

Furthermore, the functions f_L are assumed to be at least locally integrable. But, apart from these restrictions, the f_L's can be arbitrary. In particular, they can be *all different*. The product over the functions f_L in (2.1) runs over all lines L of Γ. For convenience, the functions f_L themselves will very often be called lines. For example, we will speak of the Debye–Hückel line e^{-r}/r, instead of the Debye–Hückel function.

Λ is a d-dimensional domain, where the particles are free to move (and, as the case may be, to rotate). We will usually assume $d = 3$, in the applications, but most of our considerations are independent of the dimensionality. When the domain of integration Λ is infinite (i.e., is the whole space), it is denoted by Λ_∞. In such a case, the symbol Λ will be omitted altogether. For example, we will usually write $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n)$ instead of $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda_\infty)$.

The symbol

$$\int_{\Lambda^k} d\mathbf{x}_{n+1} \ldots d\mathbf{x}_{n+k}$$

represents an integration over the k variables $\mathbf{x}_{n+1}, \ldots, \mathbf{x}_{n+k}$. Therefore, (2.1) is a dk- or $2dk$-dimensional integral, according to whether $\mathbf{x}_i = \mathbf{r}_i$, or $\mathbf{x}_i = (\mathbf{r}_i, \omega_i)$. One-dimensional integrals will always be specified by the limits of integration. For example, $\int_0^\infty f(r)\,dr$ is one-dimensional whereas $\int f(\mathbf{x})\,d\mathbf{x}$

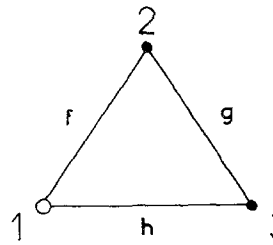
is three- or six-dimensional, in the usual space. Note that most of our results to be discussed are equally valid for lattice systems, although they will always be formulated for continuous systems. Many of them are also valid if we replace Lebesgue's measure $d\mathbf{x}_{n+1} \ldots d\mathbf{x}_{n+k}$ by any positive measure $d\mu$[17] (i.e., $\int f d\mu \geqslant 0$ for any positive f), because our estimates are obtained by means of inequalities insensitive to such an exchange. We can have, for example, $d\mu = p(\mathbf{x}_1, \ldots, \mathbf{x}_{n+k})\, d\mathbf{x}_{n+1} \ldots d\mathbf{x}_{n+k}$ where p is a positive function, involving Boltzmann factors of an external potential, distribution functions, absolute values of correlation functions, etc. . . . .

In so far as we are interested only in finding estimates of one single n-graph at a time, we will generally assume that $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ cannot be further simplified by means of certain theorems of factorization of n-graphs.[18]

2.2. Graphical Representation of n Graphs

The usual way of writing integrals such as (2.1) is very cumbersome, when the product is made explicit. It is well known that Mayer's way of writing such integrals, by means of graphs, is much more elegant and compact.[19,20] We describe it in this section.

2.2.1. Representation of n Graphs with Arbitrary Lines. If the functions f_L are allowed to be all different, the n-graph $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ must be, in general, represented by a weighted graph,[20] i.e., a graph where, to each line L, is associated a weight f_L. Pictorially, the weight f_L is written near the line L. For example, one has



$$= \int_{\Lambda^2} f(\mathbf{x}_1, \mathbf{x}_2) g(\mathbf{x}_2, \mathbf{x}_3) h(\mathbf{x}_3, \mathbf{x}_1)\, d\mathbf{x}_2\, d\mathbf{x}_3 \quad (2.2)$$

Here, the root-point and the field-points have been represented, as usual, as white and black circles, respectively.[20] The function $f(\mathbf{x}_1, \mathbf{x}_2)$ is represented by a line joining points 1 and 2, together with the weight f.

Usually, in the literature, different functions are represented by different types of lines (see, for example, Refs. 21 and 22), for example wiggly or dotted lines, etc. . . . . We will sometimes use this convention, when there are only two or three types of functions in the integrand of an n-graph.

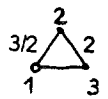
It must be noted that making use of Mayer's notation presupposes that the partial integrations over the field-points can be performed in any order, and thus that the conditions of applicability of Fubini's theorem[17] are fulfilled. If these conditions are not satisfied, Mayer's notation becomes ambiguous. Such an ambiguity can happen in the case of polar systems, because the Mayer function of these systems is not absolutely integrable in an infinite domain. In this case, an integral such as (2.1) cannot, in general, be defined directly for an infinite domain, but one has to indicate precisely *how* the domain is going to infinity. For certain n-graphs, however, and in particular for irreducible n-graphs, this is unnecessary, as will be shown in Section 3.5.

2.2.2. Representation of n Graphs with Lines f^{α_L}. A very important class of n-graphs, in our work, consists in n-graphs where all the functions f_L are equal to a power of the same (nonnegative) function f:

$$f_L = f^{\alpha_L}, \qquad \alpha_L \text{ real positive} \tag{2.3}$$

Actually, the bounds that we obtain in Section 3, for any n-graph with identical Mayer lines f, are products of such n-graphs.

In this case, the weight of line L will be simply written α_L, instead of f^{α_L}. Furthermore, when the weight α_L is equal to 1, it will be omitted (this enables one to recover the usual Mayer convention,[1,18] if all the α_L's are equal to 1). This gives, for example,



$$= \int f_{12}^{3/2} f_{23}^{2} f_{31}\, d\mathbf{x}_2\, d\mathbf{x}_3 \tag{2.4}$$

where we have set $f_{ij} = f(\mathbf{x}_i, \mathbf{x}_j)$.

In the case where all the α_L's are integers, an n-graph with lines $f^{\alpha_L}(\mathbf{x}_i, \mathbf{x}_j)$ is usually represented as a graph with α_L lines in parallel joining points i and j.[22] We will sometimes use this representation,[23] when it is more convenient than the preceding one. But it must be noted that the representation of n-graphs with functions f^{α_L} by means of weighted graphs is more general, because it allows us to represent n-graphs with lines f^{α_L} where α_L is noninteger.

Finally, we would like to draw attention to the trivial but very useful fact that the integrand of an n-graph is an $(n + k)$-graph. This enables us to represent the integrand of any n-graph by means of the preceding conventions, as the n-graph itself. For example, the integrand of the 1-graph $K_4(\mathbf{x}_1)$, defined by

$$K_4(\mathbf{x}_1) = \int_{\Lambda_\infty^3} f_{12} f_{13} f_{14} f_{23} f_{24} f_{34}\, d\mathbf{x}_2\, d\mathbf{x}_3\, d\mathbf{x}_4 \tag{2.5}$$

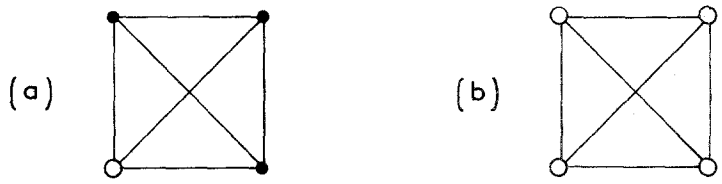


Fig. 1. Graphical representation of: (a) the 1-graph $K_4(\mathbf{x}_1)$, defined by Eq. (2.5); (b) the 4-graph $K_4(\mathbf{x}_1, \ldots, \mathbf{x}_4)$, defined by Eq. (2.6).

is the 4-graph

$$K_4(\mathbf{x}_1, \ldots, \mathbf{x}_4) = f_{12}f_{13}f_{14}f_{23}f_{24}f_{34} \tag{2.6}$$

and these are represented graphically as indicated in Fig. 1 above.

There is another way proposed by Feynman to represent n-graphs (see, for example, Ref. 24) that is slightly different from the Mayer one. Root-points are usually omitted, so that lines which would join a field-point to a root-point in the Mayer representation, are now linked only to one point in the Feynman representation. Such lines are said to be external. In Fig. 2b, we have represented with the Mayer convention one of the Feynman graphs of second order[24] represented in Fig. 2a.

2.3. Various Possible Forms for n Graphs

Very often one has to deal with quantities that do not look like n-graphs, but that can nevertheless be recast into the form (2.1). These quantities can thus be bounded by means of our estimation method, once this transformation has been performed.

In the study of *nonuniform* systems of particles and in *quantum chemistry*, one has (or can have) to deal with multiple integrals of the following type[20,25,5]:

$$\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda) = \int_{\Lambda^k} \prod_{i \in \mathfrak{P}\Gamma} \rho_i(\mathbf{x}_i) \prod_{L \in \mathfrak{L}\Gamma} f_L(\mathbf{x}_i, \mathbf{x}_j)\, d\mathbf{x}_{n+1} \ldots d\mathbf{x}_{n+k} \tag{2.7}$$

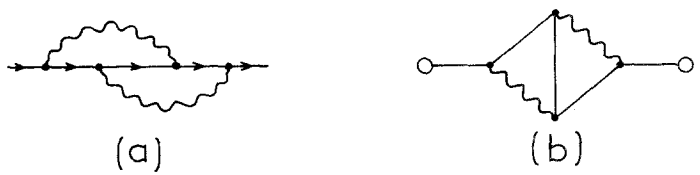


Fig. 2. The Feynman integral of second order, represented in (a) by means of the Feynman convention,[24] is represented alternatively in (b) by means of the Mayer convention.[1, 19]

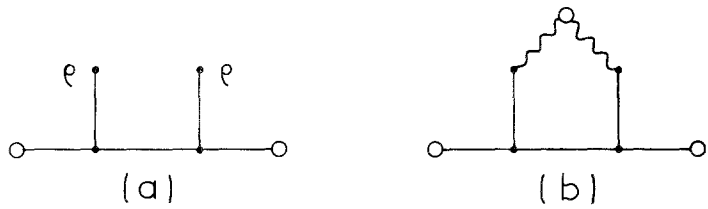


Fig. 3. The 2-graph of nonuniform system, represented in (a) by means of a 2-rooted graph with weighted points, is represented alternatively in (b) by means of a 3-rooted graph, as it can also be considered as a 3-graph. The wiggly line represents the function $\rho(\mathbf{x})$.

We will call these, for convenience, n-graphs of nonuniform systems. Equation (2.7) can be represented by the n-rooted graph Γ, where each line L has the weight f_L and each point i has the weight ρ_i. It is not difficult to see that (2.7) can also be represented as an $(n+1)$-graph of a uniform system, provided the domain Λ is infinite. One has just to add a point 0 and lines $f_L(x_0, x_i) = \rho_i(x_i)$, as illustrated in Fig. 3.

Feynman graphs in momentum space also can be cast into the form of n-graphs. They are defined as

$$\Gamma(\mathbf{q}_1, \ldots, \mathbf{q}_n) = \int \prod_{L \in \mathfrak{L}\Gamma} f_L(k_L)\, d\mathbf{k}_1 \ldots d\mathbf{k}_m \tag{2.8}$$

where m is the number of independent loops of Γ and $\mathbf{k}_L$ is the flow of momentum through line L. The k_L's satisfy the law of conservation of momentum at each point. We have[26]

$$\Gamma(\mathbf{q}_1, \ldots, \mathbf{q}_n) = (2\pi)^{d(m+n-1)} \int \exp\left(i \sum_{j=2}^{n} \mathbf{q}_j \cdot \mathbf{r}_{1j} \right) \prod_{L \in \mathfrak{L}\Gamma} f_L(r_{ij})\, d\mathbf{r}_2 \ldots d\mathbf{r}_n \tag{2.9}$$

with

$$f_L(r_{ij}) = (2\pi)^{-d} \int f_L(k_L) \exp(i\mathbf{k}_L \cdot \mathbf{r}_{ij})\, d\mathbf{k}_L \tag{2.10}$$

and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. Therefore, $\Gamma(\mathbf{q}_1, \ldots, \mathbf{q}_n)$ can be viewed as the 1-graph $\tilde{\Gamma}(r_1)$ obtained from $\Gamma(\mathbf{r}_1, \ldots, \mathbf{r}_n)$ by adding $(n-1)$ lines $f_j(\mathbf{r}_{1j}) = \exp(i\mathbf{q}_j \cdot \mathbf{r}_{1j})$ between root-points 1 and j ($j = 2, \ldots, n$). This provides us also with an alternative way of representing Feynman graphs in momentum space. For example, the Feynman graph of Fig. 4a has been represented as a 1-graph in Fig. 4b.

In theories of liquids[7] and of ionized systems (see, for example, Refs. 28 and 21), one can meet n-graphs with multiple lines. However, it is not necessary to make use of graphs of the latter type, because we have

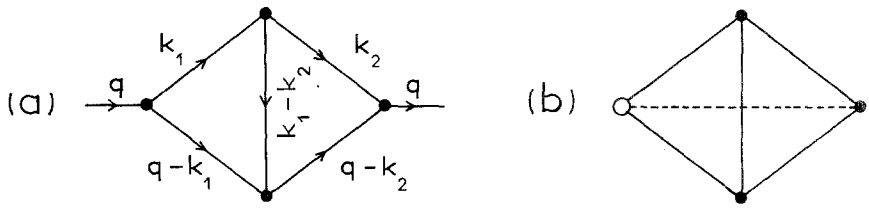


Fig. 4. (a) Standard representation of the Feynman graph in momentum space $\epsilon(q) = \int d\mathbf{k}_1 d\mathbf{k}_2 \{(k_1^2 + m^2)(k_2^2 + m^2)[(\mathbf{k}_1 - \mathbf{k}_2)^2 + m^2][(\mathbf{q} - \mathbf{k}_1)^2 + m^2][(\mathbf{q} - \mathbf{k}_2)^2 + m^2]\}^{-1}$. (b) Alternative representation of $\epsilon(q)$, as a 1-graph. The full lines represent the function $f(r) = e^{-mr}/4\pi r$ [or, respectively, $mK_1(mr)/4\pi^2 r$] for a three-dimensional (respectively, four-dimensional) space, and the wiggly line represents the function $\exp(i\mathbf{q} \cdot \mathbf{r})$.

assumed that the functions f_L can be *all different*. An n-graph with multiple lines can be put into the form (2.1) simply by replacing the set of lines $L_1, \ldots, L_m$ joining a given pair of points by one single line, and assigning to the latter the function $f_{L_1} \ldots f_{L_m}$.

2.4. The Mean Value Estimation Method

It has been remarked by Riddell and Uhlenbeck,[14] and used systematically by Groeneveld,[12b] that one can obtain simple upper bounds for any given n-graph $\Gamma(x_1, \ldots, x_n; \Lambda)$ by deleting a certain number of lines until one obtains an n-graph $\gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ that can be computed. By applying the theorem of the means,[29] one obtains then the upper bound

$$|\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)| \leqslant \prod_{L \in \mathfrak{L}(\Gamma - \gamma)} M_L(\Lambda) \int_{\Lambda^k} \prod_{L \in \mathfrak{L}\gamma} |f_L(\mathbf{x}_i, \mathbf{x}_j)| \, d\mathbf{x}_{n+1} \ldots d\mathbf{x}_{n+k} \tag{2.11}$$

with

$$M_L(\Lambda) = \sup_{\mathbf{x}_i, \mathbf{x}_j \in \Lambda} |f_L(\mathbf{x}_i, \mathbf{x}_j)| \tag{2.12}$$

The upper bound (2.11) will be called a mean value bound.

If Γ is a 1-rooted graph, and γ is chosen to be a spanning tree T of Γ (which is always possible[30]), the upper bound (2.11) takes the following very simple form[12b]:

$$|\Gamma(\mathbf{x}_1; \Lambda)| \leqslant \prod_{L \in \mathfrak{L}(\Gamma - T)} \sup |f_L(\mathbf{x})| \prod_{L \in \mathfrak{L}T} \int |f_L(\mathbf{x})| \, d\mathbf{x} \tag{2.13}$$

A spanning tree of a graph Γ is a subgraph that is a tree and that contains all the points of Γ. The upper bound (2.13) has been used by Groeneveld[12b] (for nonnegative potentials) and Penrose[31] (for potentials with a hard core) to prove that the Mayer series are absolutely convergent at small

activities. A more sophisticated version of (2.13) was used by Ruelle (Ref. 6, Chap. 4) to generalize these results.

More generally, it can be proved that any n-rooted graph contains at least one spanning n-tree τ,[32] and the theorem of the means gives the following upper bound:

$$|\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)| \leqslant \prod_{L \in \mathfrak{L}(\Gamma - \tau)} \sup |f_L(\mathbf{x})| \prod_{L \in \mathfrak{L}_\tau} \int |f_L(\mathbf{x})| \, d\mathbf{x} \quad (2.14)$$

This is the extension of (2.13) to an arbitrary n-graph. Equation (2.14) will be called *the* mean value bound (associated to the spanning n-tree τ) for $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$. Note that, if all the f_L's are identical, (2.14) takes the same value for all possible spanning n-trees and one can thus omit any reference to τ.

For n-graphs occurring in statistical mechanics, the mean value bound (2.14) is *finite* for systems whose interaction potential $\varphi(x)$ is bounded below (so that $\exp[-\beta\varphi(x)]$ and $|f(x)|$, with $f(x) = \exp[-\beta\varphi(x)] - 1$, are bounded) and decays sufficiently rapidly at large distances (so that $\int |f(\mathbf{x})| \, d\mathbf{x} < +\infty$). But for polar and ionized systems, as also for most n-graphs occurring in quantum field theory and in quantum chemistry, the mean value bound (2.14) is *infinite*. For polar systems and for the primitive model of ionic solutions, $\int |f(\mathbf{x})| \, d\mathbf{x}$ is infinite because $|f(\mathbf{x})|$ decays at large distances like, respectively, r^{-3} and r^{-1}. For the Debye–Hückel and the Abe–Meeron models of ionized gases[11a,33] [i.e., for lines $f_L(r) = b(r)$ or $B(r)$, with $b(r) = -\epsilon e^{-r}/r$ and $B(r) = e^{b(r)} - 1 - b(r)$], the preceding difficulty disappears because the Debye screening length is incorporated into the f_L's, so that they decay exponentially. But another difficulty arises in the case of plasmas, because the f_L's grow now to infinity as r^{-1} at small distances and the factor $\sup |f_L(\mathbf{x})|$ is infinite and, as a consequence, (2.14) is. The same type of problem occurs in Euclidean quantum field theory, because one has $f_L(r) = e^{-mr}/4\pi r$ in three dimensions, which grows to infinity as r^{-1} at small distances, while in four dimensions $r^{-1}K_1(mr)$ grows to infinity as r^{-2}. The situation is even worse if the particle has zero mass because $f_L(r)$ is equal to $(4\pi r)^{-1}$ in three dimensions, and to $(2\pi r)^{-2}$ in four dimensions, so that the difficulties arise at the same time from short and long distances. Both types of difficulties arise also for the multicenter integrals (such as exchange integrals[34]) that contain a line $f_L(r) = r^{-1}$.

3. DESCRIPTION OF OUR ESTIMATION METHOD

We have seen in the preceding section that the mean value bounds are infinite for all n-graphs that we are interested in, except for n-graphs of neutral systems.

The underlying reason is that these bounds make use of only *one* subgraph of Γ, which does not convey a sufficient amount of information about the topological structure of Γ (unless the subgraph is almost as complicated as Γ itself, which must be excluded if one wants to obtain a computable upper bound). For example, the bound (2.14) is obtained by means of only one spanning n-tree of Γ. In other terms, one makes use only of the fact that Γ is connected, whereas the numerical value of n-graphs usually depends strongly on their topological structure.[2]

As it is known that the knowledge of the subgraphs of a given graph largely determines its topological structure,[36] we are led to ask ourselves whether it is possible, loosely speaking, to obtain an accurate estimate of a given n-graph $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ by making use of a *set* of subgraphs of Γ instead of only one. On the other hand, it is known that it may be unnecessary to know the complete topological structure of Γ to obtain an accurate estimate of $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$. For example, in the case of the Gaussian gas, the exact value of a 1-graph is determined only by the number of its spanning subtrees.[1] Therefore, one can expect to obtain relatively accurate upper bounds by means of *simple* subgraphs only (i.e., subgraphs whose associated n-graphs are computable).

However, it must be noted that an increase in accuracy can be obtained only to the prejudice of generality. This means, as concerns the choice of subgraphs, that one single set of subgraphs cannot, in general, give an upper bound accurate for any distance $\mathbf{x}_{ij}$ between the root-points, but only in a certain range of distances. Therefore, an accurate bound will be obtained, in general, only as the lower envelope over different sets of subgraphs.[37]

Throughout this section, $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ is any given n-graph. The subgraphs γ_i of Γ, which are used to obtain estimates of $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$, are considered as fixed parameters unless stated otherwise.

3.1. Some Preliminary Conventions

The integrand of a given n-graph $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ is defined in (2.1), as a product of factors $f_L(\mathbf{x}_i, \mathbf{x}_j)$. These are allowed to change sign, for different values of the variables $\mathbf{x}_i$ and $\mathbf{x}_j$.

But our estimation method applies only to n-graphs whose integrands are products of nonnegative functions. Therefore, we will not estimate $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ directly, but rather the n-graph obtained from

[2] See, for example, Ref. 35a, where a large number of 1- and 2-graphs of the Gaussian gas are computed; Ref. 35b; and Ref. 35c, where 1- and 2-graphs of the Lennard-Jones gas are computed.

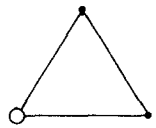
$\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ by replacing the f_L's by their absolute values. This new n-graph will be denoted by $|\Gamma|(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$:

$$|\Gamma|(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda) = \int_{\Lambda^k} \prod_{L \in \mathfrak{L}\Gamma} |f_L(\mathbf{x}_i, \mathbf{x}_j)| \, d\mathbf{x}_{n+1} \ldots d\mathbf{x}_{n+k} \tag{3.1}$$

The n-graph $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ which we are interested in and the quantity which is really estimated, namely, $|\Gamma|(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ are related by the inequality

$$|\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)| \leqslant |\Gamma|(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda) \tag{3.2}$$

When no confusion is possible, however, we will usually keep the same notation $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ to denote the right-hand side of (3.1), even if the f_L's are not positive everywhere. Moreover, in the graphical representation of n-graphs, we will usually make no distinction between the functions f and $|f|$, and will represent these by the same line. But it must be borne in mind that an inequality such as



(3.3)

really means

$$\left| \int f(\mathbf{x}_{12}) f(\mathbf{x}_{23}) f(\mathbf{x}_{31}) \, d\mathbf{x}_2 \, d\mathbf{x}_3 \right| \leqslant \left[\int |f(\mathbf{x})|^{3/2} \, d\mathbf{x} \right]^2 \tag{3.4}$$

In the statement of theorems, no mention will be made of the intermediate n-graph $|\Gamma|(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$, for reasons of simplicity, and the absolute value signs, for the f_L's, will be omitted in the proofs.

3.2. Formulation of the Method

To obtain an estimate of a given n-graph $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$, not computable by the usual methods, we look for computable upper bounds. To find upper bounds, we proceed in three steps:

(S1) The graph Γ is decomposed into a union of c line-subgraphs γ_i:

$$\Gamma = \bigcup_{i=1}^{c} \gamma_i \tag{3.5}$$

(S2) The integrand of $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ is decomposed into a product of c factors, determined by the γ_i's:

$$\prod_{L \in \mathfrak{L}\Gamma} f_L = \prod_{i=1}^{c} \left(\prod_{L \in \mathfrak{L}\gamma_i} f_L^{z_{iL}} \right) \tag{3.6}$$

(S3) Hölder's inequality[29] is applied to the preceding product, to decouple the factors:

$$\int \prod_{i=1}^{c} F_i \leqslant \prod_{i=1}^{c} \left(\int F_i^{y_i^{-1}} \right)^{y_i} \tag{3.7}$$

The numbers z_{iL} and y_i will be defined more precisely in Theorem 3.1 below.

Definition 3.1. A set of subgraphs of Γ satisfying the condition (3.5) will be called a covering of Γ.

We recall that (3.5) means

$$\mathcal{P}\Gamma = \bigcup_i \mathcal{P}\gamma_i \tag{3.5a}$$

$$\mathcal{L}\Gamma = \bigcup_i \mathcal{L}\gamma_i \tag{3.5b}$$

where $\mathcal{P}\Gamma$ and $\mathcal{L}\Gamma$ denote, respectively, the sets of points and lines of Γ. As the γ_i's are assumed to be line-subgraphs (i.e., $\mathcal{P}\gamma_i = \mathcal{P}\Gamma$, $\forall i$), the first condition is trivially satisfied, and condition (3.5) can be replaced simply by (3.5b).

By applying the three steps S1–S3 to $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$, we obtain the following theorem:

Theorem 3.1. Let $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ be a given n-graph. To each covering of Γ by c line-subgraphs γ_i, one can associate the following infinite set of upper bounds:

$$|\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)| \leqslant \prod_{i=1}^{c} \left[\int_{\Lambda^k} \prod_{L \in \mathcal{L}\gamma_i} |f_L|^{z_{iL} y_i^{-1}} d\mathbf{x}_{n+1} \ldots d\mathbf{x}_{n+k} \right]^{y_i} \tag{3.8}$$

where the z_{iL} and y_i are nonnegative real numbers whose sum over i is equal to unity:

$$\sum_{i=1}^{c} z_{iL} = 1, \qquad \forall L \in \mathcal{L}\Gamma \tag{3.9a}$$

$$z_{iL} \geqslant 0 \qquad \text{if } L \in \mathcal{L}\gamma_i \tag{3.9b}$$

$$z_{iL} = 0 \qquad \text{if } L \notin \mathcal{L}\gamma_i \tag{3.9c}$$

$$\sum_{i=1}^{c} y_i = 1 \tag{3.10a}$$

$$y_i \geqslant 0 \tag{3.10b}$$

Proof. To obtain (3.8), we have first to find a covering of Γ (step S1), i.e., a set of line-subgraphs satisfying condition (3.5b). For any given graph, there always exists at least one covering (take $\gamma_1 = \Gamma$) but there are usually a large number of different ones. Let us choose one of them.

In a second step, we have to associate a function F_i to each subgraph γ_i, in such a manner that the product of all the F_i's gives back the integrand of Γ. To this end let us associate, to each line L of γ_i, a part of the function f_L, i.e., $f_L^{z_{iL}}$, where z_{iL} is any real number. Thus, to the subgraph γ_i, we associate in this manner the factor $F_i = \prod_{L \in \mathfrak{L}\gamma_i} f_L^{z_{iL}}$. If we set $z_{iL} = 0$ when the line L of Γ does not belong to γ_i, this factor F_i can be written as

$$F_i = \prod_{L \in \mathfrak{L}\Gamma} f_L^{z_{iL}}$$

Then, if we impose moreover the condition that the F_i's have a product equal to the integrand of Γ, we must have the identity

$$\prod_{i=1}^{c} \prod_{L \in \mathfrak{L}\Gamma} f_L^{z_{iL}} = \prod_{L \in \mathfrak{L}\Gamma} \prod_{i=1}^{c} f_L^{z_{iL}} \equiv \prod_{L \in \mathfrak{L}\Gamma} f_L \tag{3.11}$$

and thus the z_{iL} must satisfy the constraints (3.9a).

Inequality (3.8) is then obtained by applying Hölder's inequality to the product of the c factors of the left-hand side of (3.11). As this inequality is valid for any set of positive numbers satisfying the constraint (3.10a) we see that there is an infinity of y_i satisfying this constraint. Therefore, our estimation method gives us an infinite number of different upper bounds, for the fixed n-graph $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$, and for each covering of Γ.

Up to now, we have only imposed the condition that the z_{iL} to be real numbers satisfying the conditions (3.9a) and (3.9c). We will nevertheless assume from now on, in this article, that all the z_{iL} are nonnegative. The reason is that, when f_L decays to zero at large distances, one usually wants that $f_L^{z_{iL}}$ decays also to zero, because this is a necessary condition for this latter function to be integrable in an infinite volume. Therefore, one has to assume $z_{iL} \geqslant 0$, in this case. Furthermore, when f_L does not decay to zero at large distances, the only L^p norm which is finite in an infinite volume is the sup norm, i.e., $p = \infty$. This implies that one must have $z_{iL} y_i^{-1} = +\infty$, and thus one still has $z_{iL} \geqslant 0$ because $y_i \geqslant 0$.

Nevertheless, one can be led, in some problems, to release the restriction $z_{iL} \geqslant 0$, $\forall L$. This is in particular the case if we want to control the volume dependence of n-graphs with Coulomb lines $C(r) = \exp(-L/r) - 1$.[38]

It is not forbidden that one or several γ_i be identical to Γ. This can enable one, for example, to bound n-graphs of realistic neutral systems by means of n-graphs of the hard-sphere gas, as will be shown elsewhere.

Hölder's inequality, which is a generalization of the well-known Cauchy–Schwartz inequality, is usually written as[29]

$$\int F_1 F_2 \cdots F_m \, d\mu \leqslant \left(\int F_1^{p_1} d\mu \right)^{1/p_1} \cdot \left(\int F_2^{p_2} d\mu \right)^{1/p_2} \cdots \left(\int F_m^{p_m} d\mu \right)^{1/p_m} \tag{3.7a}$$

for any set of positive numbers $p_1, p_2, \ldots, p_m$ satisfying the condition $\sum_i p_i^{-1} = 1$, any nonnegative functions $F_1, F_2, \ldots, F_m$, and any positive measure $d\mu$. Here we have used it with $p_i = y_i^{-1}$ for the constraint (3.10a) to be linear in the variables y_i.

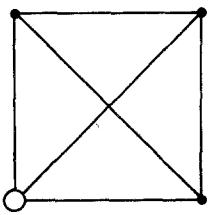
The n-graph $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ being fixed, the mean value estimation method associates, to a given subgraph of Γ, a unique upper bound, given by (2.11). Here, to a given covering of Γ, we associate an infinite number of upper bounds, given by (3.8). Therefore, an important problem which arises now, and which did not arise with the mean value method, is to find [for the fixed n-graph $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ and a given covering of Γ] the best upper bound of type (3.8). In other words, one has to minimize the right-hand side of (3.8) over the variables y_i and z_{iL}, subject to the constraints (3.9) and (3.10). All these constraints are linear (this is why we have used y_i in preference to the more usual p_i). On the other hand, the right-hand side of (3.8) (called the objective function) is usually a nonlinear function of the variables y_i and z_{iL}. Therefore, the problem of finding the best upper bound of type (3.8) can be viewed as a nonlinear programming problem, with a nonlinear objective function and linear constraints.[39] This problem can be solved, at least in principle, by iterative techniques.[39] Note, however, that the best upper bound is obtained only after an infinite number of steps. It will be shown elsewhere[37] that, in some cases, it is possible to reduce the nonlinear programming problem into a linear one (i.e., one has to minimize a linear function), that can be solved in a finite number of steps by the simplex algorithm.[40]

3.3. Examples of Application

Before going on any further with general considerations, we are first going to illustrate our procedure with three examples. We first consider the 1-graph $K_4(\mathbf{x}_1)$, which occurs in the fourth virial coefficient of the pressure.[1] $K_4(\mathbf{x}_1)$ is defined by the equality

$$K_4(\mathbf{x}_1) = \int_{\Lambda_\infty^3} f_{12} f_{13} f_{14} f_{23} f_{24} f_{34} \, d\mathbf{x}_2 \, d\mathbf{x}_3 \, d\mathbf{x}_4 \tag{3.12a}$$

Pictorially, this is written as

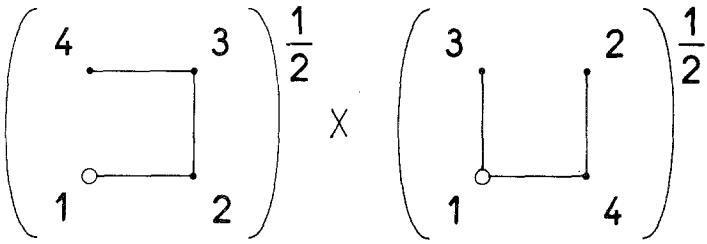
$K_4(\mathbf{x}_1) =$  (3.12b)

We will make use of two different coverings of K_4 (see Definition 3.1 in Section 3.2). The first one is a set of spanning trees (for a definition, cf. Section 2.4), and the second one a set of spanning cycles (a cycle is a connected graph where all points are of degree 2). Finally, we will study some 2-graphs that occur in quantum chemistry and in quantum field theory.

3.3.1. Upper Bound for $K_4(\mathbf{x}_1)$ by Means of Spanning Trees. If we rewrite the integrand of $K_4(\mathbf{x}_1)$ as the product of the two functions $F = f_{12}f_{23}f_{34}$ and $G = f_{24}f_{41}f_{13}$, and apply the Cauchy–Schwartz inequality to the product FG, we find

$$|K_4(\mathbf{x}_1)| \leqslant \left(\int f_{12}^2 f_{23}^2 f_{34}^2 \, d\mathbf{x}_2 \, d\mathbf{x}_3 \, d\mathbf{x}_4\right)^{1/2} \times \left(\int f_{24}^2 f_{41}^2 f_{13}^2 \, d\mathbf{x}_2 \, d\mathbf{x}_3 \, d\mathbf{x}_4\right)^{1/2} \tag{3.13}$$

Pictorially, the right-hand side of (3.13) reads

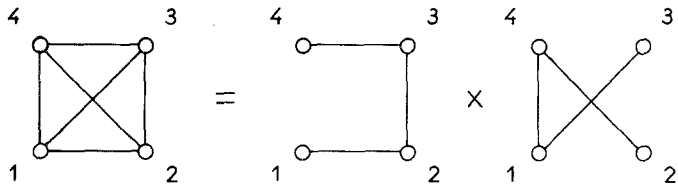


(3.14)

where a line represents the function $f^2(\mathbf{x})$. We see that the two graphs of (3.14) are spanning trees. Therefore, (3.13) can be simplified to give

$$|K_4(\mathbf{x}_1)| \leqslant \left[\int |f(\mathbf{x})|^2 \, d\mathbf{x}\right]^3 = \overline{T_4} \tag{3.15}$$

Before discussing the properties of this upper bound, let us first analyze the way it has been obtained. The essential step is the factorization of the integrand into the product FG. It is particularly useful to view the functions F and G as 4-graphs, and to rewrite this factorization pictorially, by making use of the graphical representation of 4-graphs:



(3.16)

This shows clearly that the factorization of the integrand of $K_4(\mathbf{x}_1)$ into the product FG can be obtained by first choosing a covering of K_4 by two trees,

and then regrouping the factors f_{ij} of the integrand in a way consistent with the covering.

The upper bound $\overline{T_4}$ that we have obtained in (3.15) is very simple, as simple as the mean value bound (2.13), which is

$$|K_4(\mathbf{x}_1)| \leqslant M^3\Big(\int |f(\mathbf{x})|\, d\mathbf{x}\Big)^3 = M^3 T_4 \tag{3.17}$$

One can see immediately, on this example, the main advantages of our estimation method over the mean value one. First, the two important types of thermodynamic systems which cannot be treated by the mean value method, namely, the polar systems (because of long-range behavior) and the Debye–Hückel system (because of short-range behavior) can be studied by our method, because $K_4(\mathbf{x}_1)$ is now bounded by a finite quantity. For the Debye–Hückel model of plasmas, one has $f(r) = e^{-r}/r$ (in appropriate unit of length), and thus $\overline{T_4} = [4\pi \int_0^\infty r^2 (e^{-r}/r)^2\, dr]^3 = 8\pi^3$. The exact value is $K_4(\mathbf{x}_1) \sim 0.188 \times 8\pi^3$ and hence, our upper bound $\overline{T_4}$ overestimates the exact value by a factor 5.3. For polar systems the new lines f^2 decay like r^{-6}, and thus they are integrable in an infinite volume.

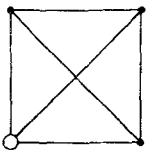
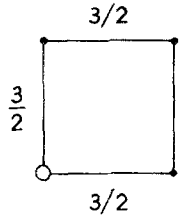
Note that the Debye–Hückel line e^{-r}/r can also be interpreted as the propagator of a scalar particle of unit mass in three dimensions (see Section 2.3). $\overline{T_4}$ gives thus for the particular 1-graph $K_4(\mathbf{x}_1)$ an improvement over the Weinberg theorem,[41] which tells us only that $K_4(\mathbf{x}_1)$ is finite because its superficial divergence $d(K_4) = 3d - 12$ is negative for $d = 3$ (as also the superficial divergence of all its subgraphs). On the contrary, $\overline{T_4}$ is infinite for a four-dimensional Euclidean scalar field, because $\overline{T_4} = \{\int_0^\infty r^3 [r^{-1} K_1(r)]^2\, dr\}^3$ diverges logarithmically at small distances. This is consistent with the Weinberg theorem, since $d(K_4)$ is equal to zero for $d = 4$, indicating actually a logarithmic divergence for $K_4(\mathbf{x}_1)$. The possibility of improving the Weinberg theorem for arbitrary n-graphs will be investigated in later articles.

Let us now turn to the case of neutral gases, for which the mean value bounds are finite. For the Gaussian gas, one has $\overline{T_4} = 4.42 \times 10^{-2}$ and $M^3 T_4 = T_4 = 1$. As the exact value is $K_4(\mathbf{x}_1) = 1.55 \times 10^{-2}$, we see that our bound $\overline{T_4}$ overestimates K_4 by a factor of 2.83 whereas the mean value bound T_4 overestimates K_4 by a factor of 64. More generally, for most neutral systems, $\overline{T_4}$ is an improvement over the mean value bound $M^3 T_4$. The only important exception is the hard sphere gas, where the bounds $M^3 T_4$ and $\overline{T_4}$ coincide. This can be seen by integrating the inequality

$$f_{12}^2 f_{13}^2 f_{14}^2 \leqslant M^3 f_{12} f_{13} f_{14} \tag{3.18}$$

We obtain a strict inequality, $\overline{T_4} < M^3 T_4$, for any $f(\mathbf{x})$ except if $|f(\mathbf{x})| = M$ for any $\mathbf{x}$ such that $f(\mathbf{x}) \neq 0$.

3.3.2. Upper Bound for $K_4(\mathbf{x}_1)$ by Means of Spanning Cycles. We have seen that the three steps of our estimation method arise quite naturally, in the preceding example. We are now going to see in detail how our estimation method works, in a more complicated case. We want to prove the inequality

$K_4 =$  $\leqslant$ 

$\approx \overline{C_4}$ (3.19)

Note that we have by our conventions

$$\overline{C_4} = \int f_{12}^{3/2} f_{23}^{3/2} f_{34}^{3/2} f_{41}^{3/2} \, d\mathbf{x}_2 \, d\mathbf{x}_3 \, d\mathbf{x}_4 \tag{3.20}$$

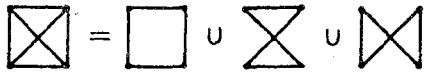
Therefore, (3.19) gives a very simple upper bound because, for $f(r)$ radially symmetric, $\overline{C_4}$ can be recast into the form[42]

$$\overline{C_4} = \frac{1}{2\pi^2} \int_0^\infty [\, g(k) \,]^4 k^2 \, dk \tag{3.21a}$$

with

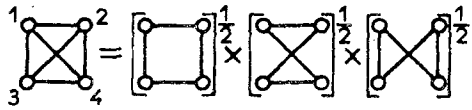
$$g(k) = 4\pi \int_0^\infty |f(r)|^{3/2} (r/k) \sin kr \, dr \tag{3.21b}$$

The first step to obtain (3.19) consists in finding a covering of the graph associated to K_4. A simple one is the following:



(3.22)

Then, in a second step, we associate to this covering a factorization of the integrand of K_4. The constraints (3.9) can be satisfied by taking $x_{iL} = \frac{1}{2}$. As the integrand of $K_4(\mathbf{x}_1)$ is identical to the 4-graph $K_4(\mathbf{x}_1, \ldots, \mathbf{x}_4)$, it can be represented in the following way:



(3.23a)

This is simply a pictorial way of writing the identity

$$f_{12}f_{13}f_{14}f_{23}f_{24}f_{34} = F_1F_2F_3 \tag{3.23b}$$

with

$$F_1 = (f_{12}f_{23}f_{34}f_{41})^{1/2}$$

$$F_2 = (f_{13}f_{32}f_{24}f_{41})^{1/2}$$

$$F_3 = (f_{12}f_{24}f_{43}f_{31})^{1/2}$$

The last step S3 consists in applying Hölder's inequality to the product of the right-hand side of (3.23). If we choose $y_1 = y_2 = y_3 = \frac{1}{3}$, we obtain

$$K_4(\mathbf{x}_1) = \int F_1F_2F_3\,d\mu \leqslant \left(\int F_1^3\,d\mu\right)^{1/3}\left(\int F_2^3\,d\mu\right)^{1/3}\left(\int F_3^3\,d\mu\right)^{1/3} \tag{3.24}$$

where we have set $d\mu = d\mathbf{x}_2\,d\mathbf{x}_3\,d\mathbf{x}_4$. By noticing that the three integrals in the right-hand side are equal, we get

$$|K_4(\mathbf{x}_1)| \leqslant \int f_{12}^{3/2}f_{23}^{3/2}f_{34}^{3/2}f_{41}^{3/2}\,d\mathbf{x}_2\,d\mathbf{x}_3\,d\mathbf{x}_4 \tag{3.25}$$

which is precisely (3.19).

Our upper bound $\overline{C_4}$ is obtained by making use of spanning cycles as line-subgraphs. Note that we can also obtain a mean value bound by taking a spanning cycle as subgraph γ (see Section 2.4). We find

$$|K_4(\mathbf{x}_1)| \leqslant M^2\int_{\Lambda_\infty^3} f_{12}f_{23}f_{34}f_{41}\,d\mathbf{x}_2\,d\mathbf{x}_3\,d\mathbf{x}_4 = M^2C_4 \tag{3.26}$$

with $M = \sup_{\mathbf{x}}|f(\mathbf{x})|$, as usual.

For the Debye–Hückel system (and, also, for a self-interacting Euclidean three-dimensional scalar field), the mean value upper bound M^2C_4 is still infinite, as M^3T_4 was, because $M = +\infty$, whereas our upper bound $\overline{C_4}$ is equal to (see Appendix A):

$$\overline{C_4} = 32\pi^4\int_0^\infty \left\{\frac{\left[(3/2)^2 + y^2\right]^{1/2} - 3/2}{(3/2)^2 + y^2}\right\}\frac{dy}{y^2} = \frac{64\pi^4}{27}(16 - 5\pi) \tag{3.27}$$

This bound overestimates K_4 by 45%, and thus is an improvement over $\overline{T_4}$. For the four-dimensional Euclidean scalar field, $\overline{C_4}$ is of course infinite since the 1-graph K_4 itself is infinite.

For a polar gas, the mean value upper bound M^2C_4 is finite, as will be shown in Section 3.5.3., whereas M^3T_4 was infinite. However, in this case, our upper bound $\overline{C_4}$ is an improvement over the mean value bound M^2C_4.

This can be seen by integrating the inequality

$$f_{12}^{3/2} f_{23}^{3/2} f_{34}^{3/2} f_{41}^{3/2} \leqslant M^2 f_{12} f_{23} f_{34} f_{41} \tag{3.28}$$

For neutral systems, for example for a Lennard–Jones gas, $\overline{C_4}$ is still an improvement over $M^2 C_4$ for the same reason as above. The only exception is the hard-sphere gas. For the Gaussian gas, one finds $\overline{C_4} = 2.02 \times 10^{-2}$ and $C_4 = 12.5 \times 10^{-2}$. As the exact result is $K_4 = 1.56 \times 10^{-2}$, we see that our bound $\overline{C_4}$ overestimates K_4 by 29%, whereas the mean value bound C_4 overestimates K_4 by 800%.

We could have covered the graph K_4 with two cycles only, for example with the first two cycles of the right-hand side of (3.22). We have used the covering (3.2) because it enables us to find the best upper bound for $K_4(\mathbf{x}_1)$, among the infinite set of upper bounds of type (3.8) that can be obtained by making use of spanning cycles as subgraphs, as will be shown in a subsequent article. The reason why one can obtain the best upper bound with (3.22) is that each line of K_4 belongs to the same number of subgraphs, more precisely to two cycles. We say that the covering (3.22) of K_4 is uniform.

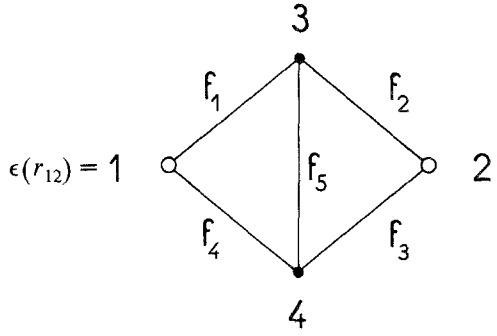
We have seen, in two particular cases (the Debye–Hückel system and the Gaussian gas), that our bound $\overline{C_4}$, obtained by means of spanning cycles, is an improvement over $\overline{T_4}$, which is obtained by means of spanning trees. We prove in Corollary 3.5 below that this result holds true for any system. In other words, one has $\overline{C_4} < \overline{T_4}$ for any line $f(\mathbf{x})$.

As the 1-graph K_4 can be estimated (computed) with a high accuracy by the usual methods,[35b] our estimates $\overline{T_4}$ and $\overline{C_4}$ are not very useful by themselves. Their usefulness comes rather from the fact that they enable us to evaluate the accuracy of our estimation method for "uncomputable" n-graphs by extrapolation. Indeed, as $\overline{T_4}$ and $\overline{C_4}$ have a correct order of magnitude for the Debye–Hückel, Gaussian, and Lennard–Jones[43] systems, this can reasonably be expected to hold true for a certain number of n-graphs, more complicated than K_4, and completely out of range of present-day computers (for example, K_6 or K_7). This information is all the more important as, very often, we are unable to find lower bounds sufficiently accurate to ensure that the order of magnitude of our bounds is actually correct. Therefore, the extrapolated accuracy is the only information available.

3.3.3. Upper Bounds for 2-Graphs Occurring in Quantum Chemistry and Quantum Field Theory. The second example we are going to study is the 2-graph $\epsilon(r_{12})$, defined by

$$\epsilon(r_{12}) = \int f_1(r_{13}) f_2(r_{32}) f_3(r_{24}) f_4(r_{41}) f_5(r_{34})\, d\mathbf{r}_3\, d\mathbf{r}_4 \tag{3.29a}$$

for various types of lines f_i. This 2-graph is represented graphically as



(3.29b)

Several bounds have been given for this 2-graph in Ref. 37, Fig. 2. We reproduce two of them in Fig. 5 below, together with the coverings they come from.

Let us first assume that $f_1 = f_2 = f_3 = f_4 = e^{-r}$ and $f_5 = r^{-1}$ (see Fig. 5b), and let us call $\epsilon_1(r_{12})$ the corresponding 2-graph. $\epsilon_1(r_{12})$ is called an exchange integral, in quantum chemistry,[5,34] and represents a contribution to the potential of interaction of two hydrogen atoms in their ground states, in the Born–Oppenheimer and LCAO–MO (linear combination of atomic orbitals–molecular orbitals) approximations.[5] The root-points 1 and 2 represent the two nuclei, and the field-points the two electrons. The two bounds given in Fig. 5 are finite. Let us call them $A_1(r_{12})$ (Fig. 5d) and $B_1(r_{12})$ (Fig. 5e), respectively. The first one is equal (up to a constant

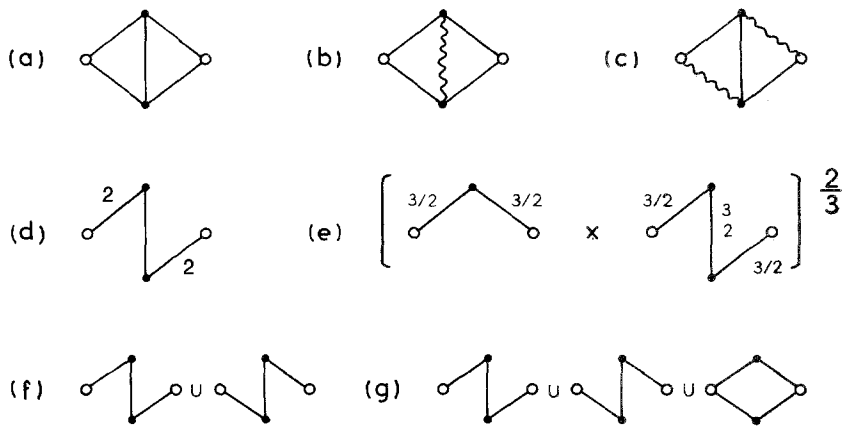


Fig. 5. The 2-graph (a) is bounded by the 2-graphs (d) and (e). These bounds are obtained, respectively, from the coverings (f) and (g). For 2-graphs whose lines are not all identical, such as (b) and (c), the bounds (d) and (e) must be modified suitably.

numerical factor) to a Coulomb repulsion integral, and thus can be computed analytically.[3] We have

$$\epsilon_1(r_{12}) \leqslant A_1(r_{12}) \tag{3.30a}$$

with

$$A_1(r) = \frac{\pi^2}{r}\left[1 - \left(1 + \frac{11}{8}r + \frac{3}{4}r^2 + \frac{1}{6}r^3\right)e^{-2r}\right] \tag{3.30b}$$

Note that one can obtain a *finite* mean value bound by deleting the lines f_1 and f_3 in (3.29). By setting $\mathbf{r}_i = 2\mathbf{R}_i$ in this bound, we obtain

$$\epsilon_1(r_{12}) \leqslant 2^5 A_1(r_{12}/2) \tag{3.30c}$$

However, (3.30c) is much less accurate than (3.30a), as can be seen in Table I below. The second bound $B_1(r_{12})$ is also finite, as can be seen from Eq. (B.4) in Appendix B.

Let us now assume that the full and wiggly lines of Fig. 5b represent the propagators of two interacting Euclidean scalar fields, whose masses are equal, respectively, to unity and to zero, and let us call $\epsilon_2(r_{12})$ [respectively, $\epsilon_3(r_{12})$] the corresponding 2-graph for a three-dimensional space (respectively, four-dimensional). For $\epsilon_2(r_{12})$, the two bounds $A_2(r_{12})$ and $B_2(r_{12})$ represented by the graphs (d) and (e) of Fig. 5, are *finite*. This can be seen immediately on the simplified expressions given in Appendix B, Eqs. (B.2) and (B.5). For $\epsilon_3(r_{12})$, the bound $A_3(r_{12})$ is infinite but $B_3(r_{12})$ is *finite*. This can be seen most simply by means of the double inequality $e^{-r}/r < K_1(r) < r^{-1}$ (see Appendix C) and of the Riesz composition formula,[48] which can be written as

$$\int r_{13}^{-\alpha} r_{32}^{-\beta}\, d\mathbf{r}_3 = k_{\alpha\beta} r_{12}^{d-(\alpha+\beta)} \tag{3.31a}$$

Table I. Comparison of the Exact Value of the Exchange Integral $\epsilon_1(r_{12})$ to Its Bounds (3.30b) and (3.30c), for Various Values of r_{12}.[a]

r_{12}	0	1	1.5	2	2.5	3
$\pi^{-2}\epsilon_1(r_{12})$	0.625	0.437	0.297	0.184	0.106	0.059
$\pi^{-2}A_1(r_{12})$	0.625	0.555	0.490	0.426	0.368	0.320
$\pi^{-2}2^5 A_1(\frac{1}{2}r_{12})$	20	19.4	18.6	17.7	16.7	15.7

[a] The exact values are taken from Hirschfelder et al., Ref. 34, p. 1106. We have restricted ourselves to $r_{12} \leqslant 3$ because the bound (3.30b) [and, *a fortiori*, (3.30c)] is accurate only at small distances.[37]

[3] See Ref. 44; the Coulomb repulsion integral is denoted as $[1S_a \mid 1S_b]$ in this article. One has $A_1(r) = \pi^2 \times [1S_a \mid 1S_b]$.

where

$$k_{\alpha\beta} = \pi^{d/2} \frac{\Gamma(\frac{1}{2}(d-\alpha))\Gamma(\frac{1}{2}(d-\beta))\Gamma(\frac{1}{2}(\alpha+\beta-d))}{\Gamma(\frac{1}{2}\alpha)\Gamma(\frac{1}{2}\beta)\Gamma(d-\frac{1}{2}(\alpha+\beta))} \tag{3.31b}$$

provided

$$0 < \alpha < d, \qquad 0 < \beta < d, \quad \text{and} \quad d < \alpha + \beta < 2d \tag{3.31c}$$

For $A_3(r)$, the inequality $e^{-r}/r < K_1(r)$ gives

$$\int \frac{e^{-2r_{13}}}{r_{13}^4} \frac{1}{r_{34}^2} \frac{e^{-2r_{42}}}{r_{42}^4} d\mathbf{r}_3 d\mathbf{r}_4 < A_3(r_{12}) \tag{3.32}$$

and $A_3(r_{12})$ is infinite since the left-hand side is.

The second inequality $K_1(r) < r^{-1}$ gives

$$B_3(r_{12}) < \left(\int r_{13}^{-3} r_{34}^{-3} r_{42}^{-3} d\mathbf{r}_3 d\mathbf{r}_4 \times \int r_{13}^{-3} r_{32}^{-3} d\mathbf{r}_3 \right)^{2/3} \tag{3.33}$$

By making use of (3.31), we find

$$B_3(r_{12}) < k_{33}^{4/3} k_{32}^{2/3} r_{12}^{-2} = \pi^4 r_{12}^{-2} \tag{3.34}$$

This shows that the upper bound $B_3(r)$ is finite everywhere, except perhaps at small distances. From inequality $e^{-r}/r < K_1(r)$ and from homogeneity considerations (take $\mathbf{R}_i = r_{12}^{-1}\mathbf{r}_i$ as new variables), we can see that the 2-graph $\epsilon_3(r_{12})$ itself diverges as r^{-2} at small distances. This result shows that the upper bound $B_3(r)$ diverges at small distances, not because our estimation method is insufficiently accurate, but because the 2-graph itself diverges. Furthermore, combined to (3.34), this result shows that our estimation method is in fact sufficiently accurate to give exactly the degree of the divergence.

Note that $\pi^4 r_{12}^{-2}$ is also an upper bound for the 2-graph of Fig. 5c, which represents a massive particle emitting and absorbing successively two massless particles, as also for all the 2-graphs obtained in substituting either $r^{-1}K_1(r)$ or r^{-2} to each f_i in $\epsilon(r_{12})$ [and in particular for the 2-graph (a), where all lines are equal to r^{-2}].

3.4. Comparison of Our Estimation Method to the One of Groeneveld Based on the Mean Value Theorem

3.4.1. The Mean Value Estimation Method, as a Particular Case of Our Estimation Method. In the preceding section, we have checked on *particular* examples that our estimation method can give better bounds than the mean value one. We are now going to show that, for *any* given n-graph, our estimation method can give bounds at least as good as the

mean value one, because this latter estimation method can be viewed as a particular case of ours.

To prove this, let us cover Γ with the line-subgraphs γ and $\Gamma - \gamma$ [where γ is the same line-subgraph which is used in (2.14)]. Equation (3.8) gives, for any finite domain Λ and any y_1 and y_2,

$$\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda) \leqslant \left[\int_{\Lambda^k} \prod_{L \in \mathfrak{L}(\Gamma - \gamma)} f_L^{y_1^{-1}} d\mathbf{x}_{n+1} \cdots d\mathbf{x}_{n+k} \right]^{y_1} \times \left[\int_{\Lambda^k} \prod_{L \in \mathfrak{L}\gamma} f_L^{y_2^{-1}} d\mathbf{x}_{n+1} \cdots d\mathbf{x}_{n+k} \right]^{y_2} \tag{3.35}$$

Both integrals, in the right-hand side of (3.35), are finite for any y_1 and y_2 if all the f_L's are assumed to be bounded in Λ. Therefore, if we let y_2 go to 1 (and thus y_1 go to 0), the second factor of the right-hand side of (3.35) goes to $\gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$. The first one goes[29] to $\lim_{y_1 \to 0} V^{my_1} \times \sup \prod f_L = \prod \sup f_L$, where m denotes the number of components of $\Gamma - \gamma$ which do not contain any root-point, and where the product runs over all lines of $\mathfrak{L}(\Gamma - \gamma)$. Therefore, one recovers effectively (2.14), in the limit $y_1 \to 0$. Note that, in the case where the domain is infinite, one cannot recover directly (2.14) from (3.8). One must first go back to a finite volume, make use of (3.35), and then let Λ go to infinity in both sides of (3.35).

In conclusion, we have shown that the best of our bounds of type (3.8), over the x_{iL} and y_i, is at least as good as (2.14), for any given n-graph.

If some f_L's don't decay to zero at large distances, for example if they are equal to a Boltzmann factor $\exp(-\beta\varphi)$, the sup norm, $\|f\|_\infty$, is the only L^p norm, $\|f\|_p$, which is finite when the domain Λ is infinite. Therefore, in this case, we can in a first step apply the mean value estimation method to $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$, to get rid of these f_L. The graph γ, which occurs in (2.14), is made out of all the lines L whose associated functions f_L decay to zero at large distances (we do not require these functions to be absolutely integrable because, as we show in Section 3.5, an n-graph can be absolutely integrable even if all the f_L's individually are *not* absolutely integrable). Then, in a second step, one can apply our estimation method to $\gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$. The results of this section show that we can equivalently perform both steps together, provided we choose γ_1 to be $\Gamma - \gamma$, and $\gamma_2, \ldots, \gamma_c$ to be a covering of γ, and provided moreover that the limit $y_1 \to 0$ is taken before the limit $\Lambda \to \Lambda_\infty$.

3.4.2. A Sufficient Condition for Our Bounds to be Strictly Smaller than the Mean Value Ones. In Section 3.4.1, we have shown that our estimation method can give, for any n-graph, upper bounds at least as good as those of the mean value type. In Section 3.3 we have also obtained, for the particular 1-graph $K_4(\mathbf{x}_1)$, bounds of type (3.8) which were

strictly smaller than the bounds of mean value type for almost all systems. We are now going to generalize this latter result to any n-graph.

Of course, we must compare what is comparable. This means that our bound (3.8) cannot be, in general, compared to the mean value bound (2.14) if the subgraph γ used in (2.14) is different from the subgraphs $\gamma_1, \gamma_2, \ldots, \gamma_c$ used in (3.8). We cannot either compare these two bounds, even if γ is identical to one of the γ_i's, say $\gamma = \gamma_1$.

On the other hand, our bound (3.8) can be compared to a certain mean of the bounds of mean value type, B_i, obtained by substituting to γ, in (2.14), successively $\gamma_1, \gamma_2, \ldots, \gamma_c$:

$$B_i = \prod_{L \in \mathfrak{L}(\Gamma - \gamma_i)} M_L \int_{\Lambda^k} \prod_{L \in \mathfrak{L}\gamma_i} f_L \, d\mathbf{x}_{n+1} \cdots d\mathbf{x}_{n+k} \tag{3.36}$$

Let us denote by $\overline{B_i}$ the quantity in brackets, in the right-hand side of (3.8):

$$\overline{B_i} = \int_{\Lambda^k} \prod_{L \in \mathfrak{L}\gamma_i} f_L^{z_{iL} y_i^{-1}} \, d\mathbf{x}_{n+1} \cdots d\mathbf{x}_{n+k} \tag{3.37}$$

We are going to prove the following corollary.

Corollary 3.2. Let us assume that $z_{iL} y_i^{-1} \geqslant 1$ for any i and L, and that at least one $z_{iL} y_i^{-1}$ is strictly larger than 1. One has, for any set of functions f_L,

$$\prod_{i=1}^{c} (\overline{B_i})^{y_i} \leqslant \prod_{i=1}^{c} (B_i)^{y_i} \tag{3.38}$$

If moreover the f_L's are piecewise continuous, a sufficient condition for the strict inequality to hold true is that each f_L vanishes only at a finite number of points. A sufficient condition for the equality to hold true is that all functions f_L, such that $z_{iL} y_i^{-1} > 1$ for some i, are proportional to a characteristic set function:

$$f_L(\mathbf{x}) = M_L \chi_L(\mathbf{x}) \tag{3.39}$$

with

$$\chi_L^2(\mathbf{x}) = \chi_L(\mathbf{x}) \qquad \text{for any } \mathbf{x} \tag{3.40}$$

Proof. As all $z_{iL} y_i^{-1}$ are assumed to be larger than or equal to 1, we have

$$f_L^{z_{iL} y_i^{-1}}(\mathbf{x}) \leqslant M_L^{(z_{iL} y_i^{-1} - 1)} f_L(\mathbf{x}) \tag{3.41}$$

There is equality if $z_{iL} y_i^{-1} = 1$. When $z_{iL} y_i^{-1} > 1$, there can be equality between the two members of (3.41) if and only if one has either $f_L(\mathbf{x}) = M_L$

or $f_L(\mathbf{x}) = 0$. This means that $M_L^{-1} f_L(\mathbf{x})$ is equal to 0 or 1 for any $\mathbf{x}$, and hence is a characteristic set function (M_L is nonnull, because otherwise, $f_L(\mathbf{x})$ would be identical to zero for any $\mathbf{x}$).

From (3.41), we find

$$\overline{B_i} \leqslant \left(\prod_{L \in \mathfrak{L}\gamma_i} M_L^{(z_{iL} y_i^{-1} - 1)} \prod_{L \in \mathfrak{L}(\Gamma - \gamma_i)} M_L^{-1} \right) \times B_i \tag{3.42}$$

As we have $z_{iL} = 0$ if $L \in \mathfrak{L}(\Gamma - \gamma_i)$ [because of condition (3.9c)], we can replace M_L^{-1} by $M_L^{z_{iL} y_i^{-1} - 1}$ in the second product inside the brackets.

Therefore, (3.42) can be rewritten as

$$\overline{B_i} \leqslant \left[\prod_{L \in \mathfrak{L}\Gamma} M_L^{(z_{iL} y_i^{-1} - 1)} \right] B_i \tag{3.43}$$

By raising both members of (3.43) to the power y_i, and making the product over all values of i, we find

$$\prod_{i=1}^{c} (\overline{B_i})^{y_i} \leqslant \left[\prod_{i=1}^{c} \prod_{L \in \mathfrak{L}\Gamma} M_L^{(z_{iL} - y_i)} \right] \times \prod_{i=1}^{c} (B_i)^{y_i} \tag{3.44}$$

By inverting the order of the products inside the brackets, and noticing that we have $\sum_{i=1}^{c} (z_{iL} - y_i) = 0$ because of (3.9a) and (3.10a), we obtain finally the inequality (3.38).

For the strict inequality to hold true in (3.38), it is necessary and sufficient that there is a strict inequality in (3.41) for one B_i (provided one has $B_i \neq 0$ for any i). Let us then choose i such that $z_{iL} y_i^{-1} > 1$ for some L. As the integrands of B_i and $\overline{B_i}$ are products of piecewise continuous functions, the equality can hold true in (3.42) if and only if the integrands are equal everywhere, except on a set of measure zero:

$$\prod_{L \in \mathfrak{L}\gamma_i} f_L^{z_{iL} y_i^{-1}} = \prod_{L \in \mathfrak{L}\gamma_i} M_L^{(z_{iL} y_i^{-1} - 1)} f_L \tag{3.45}$$

If the f_L's are supposed not to vanish except at a finite number of points, (3.45) can be satisfied only if $f_L(\mathbf{x}) = M_L$, for any $\mathbf{x}$ (except at the points where f_L vanishes, where L is the line such that $z_{iL} y_i^{-1} > 1$). If we exclude this trivial case, where some f_L would be constant almost everywhere, we see that (3.45) cannot be satisfied. Therefore, the strict inequality holds true in (3.38).

Finally, if all the functions f_L, such that $z_{iL} y_i^{-1} > 1$ for some i are characteristic set functions, we see immediately that (3.45) is satisfied for any i, and thus the equality holds true in (3.38).

If the f_L's are equal either to the Mayer function of a given potential $\varphi(\mathbf{x})$, or to the Boltzmann factor $\exp[-\beta\varphi(x)]$, there is a strict inequality in (3.38), in particular for the Lennard–Jones and soft-sphere potentials. On the other hand, both members of (3.38) are equal, for the hard-sphere

potential. They are also equal if all the functions f_L are equal to the Mayer function $f(\mathbf{x})$ of a given potential $\varphi(\mathbf{x})$, constant in a certain domain of interparticles distances, $\varphi(\mathbf{x}) = \epsilon$, and null elsewhere. Note that ϵ must be positive, for such a system to have finite thermodynamic functions.[6] Finally, the equality holds true also for a square well potential if all the f_L are equal to the Mayer function f, and if moreover the reduced temperature T^* is equal to 1.44 [i.e., $(\ln 2)^{-1}$].

From the discussion just following inequality (3.41) one would be tempted to say that both sides of (3.38) are equal if and only if all functions f_L such that $x_{iL} y_i^{-1} > 1$ for some i, are proportional to a characteristic set function. This is nevertheless false, as can be seen in the following example. Ree and Hoover[49] have exhibited an infinite set of 1-graphs, the integrands of which are products of characteristic set functions $\chi_L(r)$, these products being identical to zero, $\prod_L \chi_L = 0$. Therefore, if we multiply each χ_L by an arbitrary positive function g_L, we have a set of 1-graphs, whose integrands $\prod_L (g_L \chi_L)$ are still identical to zero, but whose lines $f_L = g_L \chi_L$ are *not* characteristic functions. Let us now choose one of these graphs, say Γ_1. We can construct a graph Γ which contains Γ_1 as subgraph, and extract from Γ a covering by two line-subgraphs γ_1 and γ_2, where γ_1 contains Γ_1. By making use of Corollary 3.3 below, we obtain a set of $\overline{B_i}$ with all $x_{iL} y_i^{-1}$ larger than or equal to 1. But, as the integrands of B_1 and $\overline{B_1}$ contain a factor $\prod_L \chi_L \equiv 0$, we see that both sides of (3.38) are *equal* (to zero), although the lines $f_L = g_L \chi_L$ of Γ are *not* characteristic set functions.

3.5. The Canonical Upper Bounds

In the preceding section, we have shown that our estimation method can improve the mean value one, provided certain conditions are fulfilled. Here, we are going to associate, to each covering of Γ, a particular upper bound which satisfies these conditions. As an application, we prove that the virial coefficients of polar systems are finite (this cannot be proved by the mean value method).

3.5.1. Definition of the Canonical Upper Bounds. To each covering of Γ, one can associate a particular upper bound, by taking all the y_i to be equal:

$$y_1 = y_2 = \cdots = y_c = c^{-1} \tag{3.46a}$$

and by attributing the same piece of f_L to each of the subgraphs which contain the line L:

$$z_{iL} = X_L^{-1} \qquad \text{if} \quad z_{iL} \neq 0 \tag{3.46b}$$

where X_L is equal to the number of subgraphs which contain the line L. This gives the following corollary:

Corollary 3.3. Let $\gamma_1, \gamma_2, \ldots, \gamma_c$ be a covering of Γ. To this covering, one can associate the following upper bound:

$$|\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)| \leqslant \prod_{i=1}^{c} \left[\int_{\Lambda^k} \prod_{L \in \mathcal{L}\gamma_i} |f_L|^{cX_L^{-1}} d\mathbf{x}_{n+1} \ldots d\mathbf{x}_{n+k} \right]^{c^{-1}} \tag{3.47}$$

with

$$cX_L^{-1} \geqslant 1 \qquad \forall L \tag{3.48}$$

Equation (3.47) will be called *the canonical upper bound* (*associated to the given covering*). Moreover, if at least one γ_i is a proper subgraph of Γ, there is at least one line L_0 such that

$$cX_{L_0} > 1 \tag{3.49}$$

Proof. The upper bound (3.47) is obtained by substituting (3.46a) and (3.46b) into (3.8). As we have clearly $X_L \leqslant c$ from the definition of X_L, inequality (3.48) follows. Finally, if at least one γ_i, say γ_1, is a proper subgraph of Γ, there is at least one line of Γ, say L_0, which does not belong to γ_1. Therefore, we have $X_{L_0} < c$, which gives (3.49).

The bound (3.47) is interesting because of its great simplicity, of course, but also because it can be expected to be a good bound for small distances $\mathbf{x}_{ij}$ between the root-points. This point will be made clearer in later articles. For the time being, let us just say that (3.47) gives even the *best* upper bound [over the set of x_{iL} and y_i subject to the constraints (3.9) and (3.10)] that one can obtain by making use of n-trees as subgraphs, provided the covering of Γ by the n-trees $\gamma_1, \gamma_2, \ldots, \gamma_c$ is uniform.[37] Finally, (3.47) is also interesting because of its application to polar systems, as we are going to see.

3.5.2. A Particular Canonical Upper Bound for Irreducible n-Graphs

Corollary 3.4. Let $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$ be an irreducible n-graph with l lines, and $\gamma_1, \gamma_2, \ldots, \gamma_l$ the set of subgraphs of Γ with $(l-1)$ lines, obtained by deleting successively each line of Γ. The canonical upper bound associated to this covering is

$$|\Gamma(\mathbf{x}_1 \ldots \mathbf{x}_n; \Lambda)| \leqslant \prod_{i=1}^{l} \left[\int_{\Lambda^k} \prod_{L \in \mathcal{L}\gamma_i} |f_L|^{l/(l-1)} d\mathbf{x}_{n+1} \ldots d\mathbf{x}_{n+k} \right]^{1/l} \tag{3.50}$$

Corollary 3.5. The 1-cycle $C_{f_1,\ldots,f_m}(\mathbf{x}_1;\Lambda)$ and the 2-chain $C_{f_1,\ldots,f_m}(\mathbf{x}_1,\mathbf{x}_2;\Lambda)$, formed out of m lines $f_1,\ldots,f_m$, are bounded by

$$\prod_{i=1}^{m}\left(\int|f_i(\mathbf{x})|^{m/(m-1)}\,d\mathbf{x}\right)^{(m-1)/m} \tag{3.51}$$

In the particular case where all the f_i are identical and Λ is infinite, the 1-cycle is independent of $\mathbf{x}_1$, and it has been denoted C_m in this case. We have

$$C_m \leqslant \left(\int|f|^{m/(m-1)}\right)^{m-1} \tag{3.52}$$

By replacing f by $f^{3/2}$ in both members of (3.52) and taking $m=4$, we obtain $\overline{C_4}<\overline{T_4}$ for any f, as was announced in Section 4.3.2. More generally, inequality (3.52) can be used to compare bounds obtained by means of cycles, to bounds obtained by means of trees, for any given n-graph.

The upper bound (3.52) can be put into the form

$$C_m \leqslant \left(\int|f|^{l/k}\right)^{k} \tag{3.53}$$

where l is the number of lines of the graph, and k its number of field-points. It will be shown elsewhere[37] that this formula holds true for any n-graph $\Gamma(\mathbf{x}_1,\ldots,\mathbf{x}_n;\Lambda)$ provided a certain condition on Γ is satisfied.

3.5.3. Application of the Canonical Upper Bounds to Polar Systems.

Corollary 3.6. Any irreducible n-graph, the lines of which are all equal to the Mayer function of a given potential $\varphi(\mathbf{x})$, satisfies the inequality

$$|\Gamma(\mathbf{x}_1,\ldots,\mathbf{x}_n;\Lambda)| \leqslant M^{l[1-k/(l-1)]}\left(\int|f|^{l/(l-1)}\right)^{k} \tag{3.54}$$

with

$$M=\sup_{\mathbf{x}}|f(\mathbf{x})| \tag{3.55}$$

For a polar system, the upper bound (3.54) is finite, and thus the virial coefficients are finite too.

Proof. In irreducible 1-graphs, each field point is linked to the root-point by at least two point-disjoint chains (i.e., chains without points in common). In irreducible n-graphs ($n \geqslant 2$), each field-point is linked to at least two root-points by such chains. Thus, in both cases, the deletion of one line gives an n-rooted graph which is connected. By deleting successively each line of Γ, we get a set of l connected n-rooted subgraphs γ_i

which cover Γ. Therefore, the mean value bound for the quantity in brackets, in the right-hand side of (3.50), is equal to

$$(M_l)^{l-1-k}\left(\int |f|^{l/(l-1)}\right)^k$$

with $M_l = \sup |f|^{l/(l-1)}$. Equation (3.54) is then a consequence of the identity $\sup(|f|^{l/(l-1)}) = (\sup |f|)^{l/(l-1)}$.

For a polar system, $|f(\mathbf{x})|^{l/(l-1)}$ decays at large distances like $r^{-(3+\alpha)}$, with $\alpha = 3/(l-1)$, and thus is integrable in an infinite volume. This shows that the upper bound (3.54) is finite, whereas the mean value upper bound (2.14) was infinite because $\int |f(\mathbf{x})|\, d\mathbf{x} = +\infty$.

We have shown that irreducible n-graphs are absolutely convergent in Λ_∞ for polar systems. But for some models of ionized systems, where the lines decay like r^{-1}, this is no more true and one can encounter irreducible n-graphs which are not absolutely convergent in an infinite volume. This is the case, for example, for all 1-graphs such that $l \leqslant 3k$. But, on the other hand, one can also encounter n-graphs which are absolutely integrable in an infinite volume, provided one has $l > 3k$.[38]

Corollary 3.6 can be generalized to the case where the functions f_L are different, provided that there exists an irreducible n-rooted subgraph γ having the following two properties: (i) The functions $|f_L|^{l/(l-1)}$ are absolutely integrable in an infinite domain, for any L belonging to $\mathfrak{L}\gamma$. (ii) The functions $|f_L(\mathbf{x})|$ are bounded for any $\mathbf{x}$, and for any L. To prove this, we bound $\Gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$, in a first step, by means of $\gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$, by making use of (2.14). Then, we apply Corollary 3.4 to $\gamma(\mathbf{x}_1, \ldots, \mathbf{x}_n; \Lambda)$. Finally, we proceed along the lines of Corollary 3.6.

It is important to note, however, that if one wants to extend to polar systems the results which have been proved by Groeneveld and Penrose in the case of neutral systems,[12b,30] one cannot use the preceding generalization because the 1-graphs which one has to bound have only a tree of Mayer lines.[30] Therefore, one must proceed along different lines.

From Corollary 3.6, we see that any *connected* n-graph which does not contain any block of field-points reduced to a single line, is absolutely integrable in Λ_∞. On the contrary, a connected n-graph which contains a block of field-points reduced to a line, is *not* absolutely integrable in Λ_∞, because one has $\int |f|\, d\mathbf{x} = +\infty$. We have thus obtained a necessary and sufficient condition for any connected n-graph to be absolutely integrable in Λ_∞. This could be useful to investigate the convergence properties of Mayer series, in the case of polar systems.

As was noted in Section 2.2.1, Corollary 3.6 implies that irreducible n-graphs of polar systems can be represented unambiguously by means of graphs, without specifying how the domain Λ goes to infinity.

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APPENDIX A

In this appendix, we compute the upper bound $\overline{C_4}$ of the 1-graph K_4, for the Debye–Hückel system. We have

$$\overline{C_4} = 32\pi^4\left[I(\infty) - I(0)\right] \tag{A.1}$$

with

$$I(y) = \int \left[\frac{(\alpha^2 + y^2)^{1/2} - \alpha}{\alpha^2 + y^2} \right]^2 \frac{dy}{y^2} \tag{A.2}$$

and $\alpha = 3/2$. This integral is convergent. To compute it, we can perform the square. We have then to compute three indefinite integrals. We find

$$\begin{aligned} I(y) = & -\alpha^{-2}y^{-1} - (\alpha^2 + y^2)^{-1}y^{-1} \\ & + 2\alpha^{-3}\left[(\alpha^2 + y^2)^{1/2}y^{-1} + y(\alpha^2 + y^2)^{-1/2}\right] \\ & - \tfrac{3}{2}\alpha^{-2}y(\alpha^2 + y^2)^{-1} - \tfrac{5}{2}\alpha^{-3}\arctan(y/\alpha) \end{aligned} \tag{A.3}$$

The first three terms have no limit individually, as y goes to zero, but their sum is asymptotically equal to $2\alpha^{-4}y$. We have thus $I(0) = 0$. Finally, we obtain immediately $I(\infty) = \alpha^{-3}(4 - \frac{5}{4}\pi)$, and hence (3.27).

APPENDIX B

In this appendix, we reexpress the bounds appearing in section 3.3.3 as one-dimensional integrals. We have

$$A_2(r_{12}) = \int \frac{e^{-2r_{13}}}{r_{13}^2} \frac{1}{r_{34}} \frac{e^{-2r_{42}}}{r_{42}^2} \, d\mathbf{r}_3 \, d\mathbf{r}_4 \tag{B.1}$$

Since the Fourier transforms of the functions $r^{-2}e^{-2r}$ and r^{-1} are equal,[46] respectively to $4\pi k^{-1}\arctan(k/2)$ and $4\pi k^{-2}$, we find

$$A_2(r_{12}) = \frac{32\pi}{r} \int_0^\infty \left(\frac{1}{k} \arctan \frac{k}{2} \right)^2 \frac{\sin kr}{k} \, dk \tag{B.2}$$

This integral exists, since it is absolutely convergent for small values of k (the integrand goes to $r/4$) and semiconvergent for large values of k, thanks to the second theorem of the means[47] [the function $k^{-1}(k^{-1}\arctan k/2)^2$ decreases monotonically, and $|\int_{k_0}^{\infty} \sin kr\, dk| < \infty$].

The bounds $B_1(r_{12})$ and $B_2(r_{12})$ are equal to

$$B_i(r_{12}) = \left[\int f_i(r_{13}) r_{34}^{-3/2} f_i(r_{42})\, d\mathbf{r}_3\, d\mathbf{r}_4 \int f_i(r_{13}) f_i(r_{32})\, d\mathbf{r}_3 \right]^{2/3} \tag{B.3}$$

with $f_1(r) = e^{-3r/2}$ and $f_2(r) = r^{-3/2}e^{-3r/2}$. The Fourier transforms of $f_1(r)$, $f_2(r)$ and $r^{-3/2}$ are equal,[46] respectively, to $12\pi(\alpha^2 + k^2)^2$, $(2\pi)^{3/2}k^{-1} \times [\alpha^2 + k^2]^{-1/2} \times [(\alpha^2 + k^2)^{1/2} - \alpha]^{1/2}$ and $(2\pi)^{3/2}k^{-\alpha}$, with $\alpha = 3/2$. Therefore, we obtain

$$B_1(r) = \left[\frac{32(2\pi)^{5/2}}{3r} e^{-3/2r} \left(\frac{3}{4} r^2 + \frac{3}{2} r + 1 \right) \int^{\infty} \frac{1}{\sqrt{k}\left(\frac{9}{4} + k^2\right)^4} \sin kr\, dk \right]^{2/3} \tag{B.4}$$

$$B_2(r) = \left[\frac{4(2\pi)^{7/2}}{r^2} \int_0^{\infty} \frac{(\alpha^2 + k^2)^{1/2} - \alpha}{k(\alpha^2 + k^2)} \sin kr\, dk \right.$$
$$\left. \times \int_0^{\infty} \frac{(\alpha^2 + k^2)^{1/2} - \alpha}{k^{5/2}(\alpha^2 + k^2)} \sin kr\, dk \right]^{2/3} \tag{B.5}$$

Both integrals in the right-hand side of (B.5) are absolutely convergent at large distances, as also at small distances since $\lim_{k\to 0} k^{-2}[(\alpha^2 + k^2)^{1/2} - \alpha] = (2\alpha)^{-1}$.

APPENDIX C

We want to prove the inequality

$$e^{-r}/r < K_1(r) < 1/r \tag{C.1}$$

To prove this, we use the following integral representation of $K_1(r)$[45]:

$$K_1(r) = \int_0^{\infty} e^{-rcht} \operatorname{cht}\, dt \tag{C.2}$$

From the inequality $sht < cht$, we obtain the double inequality

$$\int_0^{\infty} e^{-rcht} \operatorname{sht}\, dt < K_1(r) < \int_0^{\infty} e^{-rsht} \operatorname{cht}\, dt \tag{C.3}$$

As cht grows monotonically from 1 to ∞ and sht from 0 to ∞, as t grows

from 0 to ∞, (C.4) can be rewritten as

$$\int_1^\infty e^{-ru}\,du < K_1(r) < \int_0^\infty e^{-ru}\,du \tag{C.4}$$

whence inequality (C.1)

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