

Properties of the n -Body Correlation Functions near the Liquid–Gas Critical Point. Correlation Inequalities

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We investigate the behavior of the many-body correlation functions in the vicinity of the gas–liquid critical point. We use the framework of the liquid state theory and, accordingly, no reference to an effective Landau–Ginzburg Hamiltonian is made. The critical condition is introduced by means of the equation of state. From the Baxter equation relating the many-body correlation functions $h(n)$ and $h(n+1)$, we find that the integrals of all the $h(n)$ diverge at the critical point. Then we present strong arguments and this leads to GKS-like inequalities, under some limiting conditions: the interparticle distances must be large and the thermodynamic state of the system must be close to the critical point. In order to get these inequalities, an upper bound for $h(n)$ is obtained. Particular attention must be paid to the fact that the usual asymptotic approximations of the liquid state theory are no longer valid.

KEY WORDS: Critical phenomena; many-body correlation functions; correlation inequalities.

1. INTRODUCTION

The usual way to describe the structure of a one-component fluid, according to liquid state theory, is to use the set of n -body distribution functions $\rho^{(n)}(1, 2, \dots, n)$ which gives the probability of finding the n molecules labeled $(1, 2, \dots, n)$ in a given state, characterized by their position and their orientation.⁽¹⁾ Hereafter, we shall consider only the case of spherical molecules, interacting via two-body pairwise additive potential, and only the positions of the molecules are involved. The n -body distribution functions are related to the correlation functions, which can be separated into two types: the

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total, $h^{(n)}$, and the direct, $c^{(n)}$, correlation functions. The functions $h^{(n)} = h(1, \dots, n)$ are defined as functional derivatives of the grand potential Ξ with respect to the activities $z(i)$,⁽¹⁾

$$\rho(1) \cdots \rho(n) h^{(n)} = z(1) \cdots z(n) [\delta^n \text{Ln } \Xi / \delta z(1) \cdots \delta z(n)]$$

and the functions $c^{(n)} = c(1, \dots, n)$ are defined as functional derivatives of A_{exc} , which is the excess part of the intrinsic free energy A : $A_{\text{exc}} \equiv -\beta^{-1} c[\rho] = A - A_{\text{ideal}}$, with respect to the densities $\rho(i)$,⁽¹⁾

$$\begin{aligned} c^{(n)} &= -\beta [\delta^n A_{\text{exc}} / \delta \rho(1) \cdots \delta \rho(n)] \\ &= \delta^n c[\rho] / \delta \rho(1) \cdots \delta \rho(n) \end{aligned}$$

For our analysis we give an alternative and equivalent definition in terms of a graph representation⁽¹⁾: $h^{(n)}$ is the sum of all simple diagrams free of articulation points with n white circles, ρ black circles, and f bonds, where f is the Mayer functions; $c^{(n)}$ is the sum of all simple diagrams with n white circles, ρ black circles, and f bonds and which are free of nodal points.

However, in the vicinity of the critical point, other theories have been developed; it is generally well accepted that a suitable theory is the standard Φ^4 theory (or the Ising model) where a Landau-Ginzburg type of Hamiltonian is involved.⁽²⁻⁶⁾ It is of course understood that the Φ^4 theory is adapted to reproduce the critical behavior only asymptotically close to the critical point; the usefulness of such a model appears then to be limited, besides the understanding of the critical phenomena in general, to the determination of the critical exponents. In any case, the structure of a liquid cannot be investigated in such a framework since the correlations concern a field, ϕ , the physical meaning of which is not so clear (see, for instance, work dealing with the so-called "revised scaling theory"⁽⁷⁾). It is then clear that all the properties of the Ising model cannot be applied at the critical point in liquids; as an example, one has the well-known GKS inequalities,⁽⁸⁻¹⁰⁾ which are inequalities between the n -body correlation functions satisfied by the Ising model for each thermodynamic state and for all interparticle distances. Clearly this cannot be true for liquids, but both in the very close vicinity of the critical point and for very large interparticle distances (comparable to the correlation length). The problem then remains to know whether such correlation inequalities are satisfied by the actual correlation functions in the vicinity of the liquid-gas critical point and this is the purpose of this work.

We investigate the behavior of the usual n -body correlation functions of the liquid state theory in order to determine if they satisfy inequalities similar to the GKS inequalities. However, since we do not start from an

effective Hamiltonian (as in a Landau-Ginzburg type of approach) we have to state from the beginning a phenomenological critical equation of state and the behavior of the two-body total correlation function, the integral of which is related to the isothermal compressibility,⁽¹⁾ which diverges at the critical point.^(2, 3, 11) This amounts to assuming both the existence of the critical point and that the critical exponents δ and η are known. Then we use the integral equations first derived in ref. 24, in the form given by Baxter⁽¹²⁾; these are exact relations between the n -body and $(n+1)$ -body correlation functions. In addition, we use the n -body Ornstein-Zernike equation, which show that the n -body total correlation function can be expanded in a *finite* number of Mayer diagrams, involving the $h^{(2)}$ total correlation function, and the direct correlation functions, $c^{(p)}$, with $3 \leq p \leq n$.

In Section 2, by using the Baxter relations, we determine the behavior, in terms of the density, of the integrals of the correlation functions on the critical isotherm. Moreover we show that the leading contribution to the integrals of the total correlation functions $h^{(n)}$ is due to the region of space where all the interparticle distances are of the order of the correlation length, generalizing the behavior of the two-body total correlation function, the weak decrease of which is responsible for the divergence of its integral at the critical point (C.P.). In Section 3 we analyze the form taken by the correlation functions in the algebraic regime. In Section 4 we obtain an upper bound for the total correlation function, when all the interparticle distances are large, but where two length scales are involved. We analyze a diagrammatic expansion of $h^{(n)}$ in terms of a finite number of Mayer diagrams, built up from $h^{(2)}$ bonds and some $c^{(p)}$ functions with $3 \leq p \leq n$. Notice that we could have used the formalism of the generating functional⁽²⁴⁾; this would lead to a simpler derivation of the n -body Ornstein-Zernike equation of Section 4.1. However, an important cancellation of the sum of a set of graphs is obtained; this cancellation is necessary to recover the correct "dimension" of the integrals of the functions $h^{(n)}$. This property justifies *a posteriori* our choice for the $h^{(n)}$ and the $c^{(n)}$ functions, instead of using the alternative generating functional formalism, since overall it would not simplify or clarify the presentation of our work.

In Section 5 we discuss our results, and finally we conclude briefly in Section 6.

2. INTEGRALS OF THE CORRELATION FUNCTIONS

In this section we focus on the Baxter relations,⁽¹²⁾ which are exact and satisfied in the whole thermodynamic space. We study their consequences, in the vicinity of the critical point (C.P.), for the integrals of the

correlation functions. This is done in two steps. In Section 2.1 we start from the Baxter relations and we perform the integrations over the space variables, which leads to a hierarchy between the integrals of the n -body correlation functions; then in Section 2.2. we introduce the critical equation of state on the critical isotherm and we get the desired relations.

2.1. Exact Relations Between the Integrals of the Correlation Functions

Starting from the canonical ensemble, Baxter⁽¹²⁾ established that the n - and $(n+1)$ -body total correlation functions $h^{(n)}$ and $h^{(n+1)}$ are related according to

$$\int h^{(n+1)} d[n+1] = (\partial h^{(n)}/\partial \rho)_T \left\{ 1 + \rho \int h(1, 2) d[2] \right\} + n h^{(n)} \int h(1, 2) d[2] \quad (1)$$

where $h(1, 2)$ is the two-body total correlation function and ρ is the number density. To each of these functions, depending on the space coordinates of the molecules, we associate the integrals

$$H^{(n)} = \int h(1, 2, \dots, n) d[1] \dots d[n-1] \quad (2)$$

performed over the coordinates of $(n-1)$ molecules; due to the translational invariance, $H^{(n)}$ depends only on the thermodynamic state, which can be characterized, for instance, by ρ and T . From Eqs. (1) and (2), we get

$$H^{(n+1)}(\rho, T) = [1 + \rho H^{(2)}(\rho, T)] [\partial H^{(n)}(\rho, T)/\partial \rho]_T + n H^{(2)}(\rho, T) H^{(n)}(\rho, T) \quad (3)$$

Since $H^{(2)}(\rho, T)$ is related to the isothermal compressibility χ_T by⁽¹⁾

$$\rho^2 \chi_T / \beta = (\rho/\beta)(\partial \rho / \partial P)_T = (\partial \rho / \partial \beta \mu)_T = \rho [1 + \rho H^{(2)}(\rho, T)] \quad (4)$$

where P is the pressure, μ the chemical potential, and $\beta^{-1} = kT$, the knowledge of the behavior of $\chi_T(\rho, T)$ allows one to get some information on the whole set of integrals $H^{(n)}(\rho, T)$.

The distribution functions $g^{(n)} = \rho^{(n)}(1, 2, \dots, n)/\rho^n$ can be expanded in terms of products of correlation functions $h^{(m)}$, with $m \leq n$, according to

$$g(1, 2, \dots, n) = 1 + \sum_Q \left\{ \prod [h(i_1, i_2, \dots, i_m)] \right\} \tag{5}$$

where the sum runs over all the partitions Q of the set $(1, 2, \dots, n)$ in distinct and nonoverlapping subsets (i_1, i_2, \dots, i_m) with $1 \leq m \leq n$, $i_p \in (1, 2, \dots, n)$, and the product runs over all the subsets of the partition under consideration; when the subset includes only one point, the corresponding h function is set equal to 1. From Eqs. (1) and (5) we obtain, after some tedious manipulations,⁽¹³⁾

$$\begin{aligned} [1 + \rho H^{(2)}(\rho, T)](\partial g^{(n)}/\partial \rho)_T + n H^{(2)}(\rho, T) g^{(n)} \\ = \int [g^{(n+1)} - g^{(n)}] d[n+1] \end{aligned} \tag{6}$$

or equivalently the well-known relation⁽¹⁴⁾

$$[(\partial \rho^{(n)}/\partial \beta \mu)_T - n \rho^{(n)}] = \int [\rho^{(n+1)} - \rho \rho^{(n)}] d[n+1] \tag{7}$$

Between the direct correlation functions $c^{(n)}$ we have the relation

$$(\partial c^{(n)}/\partial \rho)_T = \int c^{(n+1)} d[n+1] \tag{8}$$

which leads for the integrals

$$C^{(n)} = \int c^{(n)} d[1] \dots d[n-1] \tag{9}$$

to

$$[\partial C^{(n)}(\rho, T)/\partial \rho]_T = C^{(n+1)}(\rho, T) \tag{10}$$

2.2. Properties of the Integrals of the Correlation Functions near the Critical Point

We consider the vicinity of the critical point, along the critical isotherm, and we examine the form then taken by Eqs. (3) and (10); however, we emphasize that we focus only on the leading terms of each quantity considered. In the following, A_c will denote the value taken by the

quantity A at the critical point. We state a critical equation of state in the form^(2, 3, 11)

$$(P - P_c) = (\rho - \rho_c)^\delta + \dots \quad (11)$$

where the dots represent the correction to the dominant contribution to $(P - P_c)$. The exponent δ is greater than or equal to 3 because the thermodynamic stability imposes that the compressibility takes only positive values and as a result $(\partial^2 P / \partial \rho^2)_T$ vanishes, while $(\partial^3 P / \partial \rho^3)_T$ takes a finite value at the critical point, where χ^{-1} and thus $(\partial P / \partial \rho)_T$ vanish.⁽¹¹⁾ From Eqs. (4) and (11) we get, by neglecting 1 compared with $H^{(2)}$,

$$\rho_c H^{(2)}(\rho, T) = A_c (\Delta \rho)^{(1-\delta)} \quad (12)$$

Here A_c is a dimensionless amplitude, positive because χ_T is positive, and $\Delta \rho$ is the reduced deviation in density $(\rho - \rho_c) / \rho_c$; $\Delta \rho$ is positive throughout this work, without any loss of generality. Indeed, because we deal with the critical isotherm, we only consider here the fluid region where the exponents are continuously defined and therefore no difference between the case $\Delta \rho \geq 0$ and $\Delta \rho \leq 0$ is to be expected. At this point we assume also that the two-body total correlation function $h^{(2)}$ takes its standard form,⁽¹⁵⁾ namely

$$h^{(2)}(r_{12}) = B \exp(-r_{12}/\xi) (r_{12})^{-(d-2+\eta)} \quad (13)$$

where B is a constant and ξ is the correlation length. Then, from Eq. (12) we get the behavior of the correlation length in terms of $\Delta \rho$, namely

$$\xi = \Delta \rho^{(1-\delta)/(2-\eta)} \quad (14)$$

Moreover, from the arguments given in ref. 2, the deviation of the total free energy from its value at the critical point is localized in a volume ξ^d and therefore the deviation of the free energy per unit volume is $f_v = f_c \xi^{-d}$. Then, from $(\partial P / \partial \rho)_T = \rho (\partial^2 f_v / \partial \rho^2)_T$ and from Eq. (11) we obtain $\xi = \Delta \rho^{-(\delta+1)/d}$. From these two expressions of ξ we deduce the well-known relation $\delta = (d+2-\eta)/(d-2+\eta)$ and an alternative relation between ξ and $\Delta \rho$,

$$\xi = \Delta \rho^{-2/(d-2+\eta)} = \Delta \rho^{-1/d_\phi} \quad (15)$$

where we have introduced $d_\phi = (d-2+\eta)/2$. We note that d_ϕ coincides with the so-called anomalous dimension of the field used in the field-theoretic approach to critical phenomena.⁽³⁾

Now we examine the hierarchy of integrals $H^{(n)}$; we start from Eq. (3), and since $H^{(2)}$ diverges when we approach the critical point, we can drop

1 compared to $\rho H^{(2)}$ in the first factor of the r.h.s. Moreover, for the same reason, the whole set of $H^{(n)}$ is expected to present a singular behavior in terms of $\Delta\rho$ and accordingly the second term of the r.h.s. of Eq. (3) can be neglected when one focuses on the leading term of $H^{(n)}$. Therefore we get $H^{(n+1)}$ from $H^{(n)}$ by using

$$H^{(n+1)} = \rho H^{(2)}(\partial H^{(n)}/\partial\rho) \tag{16}$$

and from Eq. (12) we get

$$H^{(n)} = A(n) \Delta\rho^{x_n} \tag{17a}$$

with

$$x_n = 1 - (n - 1) \delta \tag{17b}$$

$$A(2) = A_c > 0 \tag{17c}$$

$$A(n) = (-1)^n [A_c^{(n-1)} |x_2 x_3 \cdots x_{n-1}|] \tag{17d}$$

Hence, only from thermodynamics, we can conclude the following: (i) All the integrals $H^{(n)}$ diverge at the C.P. We can associate this divergence with the weak decrease of the functions $h^{(n)}$ with respect to the distances r_{ij} . (ii) The behavior of $H^{(n)}$ is only determined by the specific (A_c, ρ_c) and universal (δ) parameters which characterize $H^{(2)}$. (iii) The sign of the $H^{(n)}$ is alternating. Notice that the last point, in contrast to the first two, is not *a priori* expected. It is interesting to relate the integral $H^{(n)}$ to $H^{(2)}$. We find

$$H^{(n)} = (-1)^n (B/A_c) |x_2 x_3 \cdots x_{n-1}| (H^{(2)})^{(n-1)} (\Delta\rho)^{(2-n)} \tag{18}$$

where B is a constant. Thus, we see that $H^{(n)}$ cannot be reduced to a product of $H^{(2)}$; in particular, we can deduce from (18) that the popular superposition approximation^(1, 16) for $h^{(n)}$ does not work. According to this approximation $g^{(n)}$ is simply a product of $g^{(2)}$, hence $h^{(n)}$ is a product of $h^{(2)}$ bonds connecting the different root points, with neither field points nor convolutions. In the case of $h^{(n)}$ the minimum number of bonds required to connect the n root points is $(n - 1)$. Accordingly, if we calculate $H^{(n)}$ in the superposition approximation, we get a first contribution $(H^{(2)})^{(n-1)}$, and the other contributions are negligible compared to this first one. Furthermore, the factor $(\Delta\rho)^{(2-n)}$ in (18) shows that $h^{(n)}$ is a longer range function than the corresponding result in the superposition approximation.

Concerning the direct correlation functions, the integrals $C^{(n)}$ have already been obtained in ref. 17; with the result

$$\begin{aligned} \rho^{n-1} C^{(n)} &= (-1)^n (n - 2)! - C_c \xi^{-(2-\eta)(\delta-n+1)/(\delta-1)} \\ &= (-1)^n (n - 2)! - C_c \xi^{(n-1)d - nd\phi} \end{aligned} \tag{19}$$

where the magnitude of the volume integration is explicit, i.e., $\xi^{(n-1)d}$, and $d'_\phi = d - d_\phi$. In contrast to $H^{(n)}$, which diverges at the C.P. whatever the value of n , $C^{(n)}$ is finite if $n \leq \delta + 1$. For these values of n , $C^{(n)}$, which is a pure number, $(-)^n (n-2)!$, at the C.P., results from both the long-range and the short-range contributions of $c^{(n)}$. The relative importance of these two terms may depend on the specificity of the system under consideration. For these values of n the deviation relative to the critical value of $C^{(n)}$, given by $C_c \xi^{(n-1)d - nd'_\phi}$, is small and positive. This singular part of $C^{(n)}$ can result from the algebraic behavior of $c^{(n)}$. Indeed, from the two-body Ornstein-Zernike equation,^(1,18) which reads, in Fourier space,

$$c^{(2)}(k) = h^{(2)}(k) / [1 + h^{(2)}(k)] \tag{20}$$

and from the long-range contribution to $h^{(2)}$, given by (13), we can deduce the long-range part of $c^{(2)}$, and this allows one to explain the dependence of $C^{(2)}$ with respect to ξ . However, since the correction to the critical value is small, we cannot deduce that the singular part results only from the long-range behavior of $c^{(2)}$. For instance, we cannot rule out the presence in $c^{(2)}$ of a short-range contribution presenting a nonanalytic amplitude, in the form $f(r_{12}) \Delta \rho^{(\delta-1)}$, leading for the integral $C^{(2)}$ to the same behavior with respect to ξ . If this occurs for $c^{(2)}$, which means simply that the long-range behavior is coupled to the short-range one, this is necessarily also the case for the other $c^{(n)}$ because of the Baxter relations, Eq. (8). Notice that $h^{(2)}$ can also exhibit a similar small nonanalytic amplitude, but since $H^{(2)}$ diverges at the C.P., this effect can only be a correction to the leading behavior of $H^{(2)}$.

When $n \geq \delta + 1$, $C^{(n)}$ diverges at the C.P. and its sign is alternating. In this case, the singular part of $C^{(n)}$ can be related to the weak decrease of the function $c^{(n)}$ as is the case for $h^{(n)}$.

Now we examine the case of the integral of $h^{(n)}(1, 2, \dots, n)$ when the distance between two particles, say 1 and 2, of the set $(1, 2, \dots, n)$ cannot exceed λ , with $\sigma < \lambda \ll \xi$ (σ is a molecular length scale). This will give us some information concerning the part of $h^{(n)}$ which is responsible for the leading contribution to the integral $H^{(n)}$. We start from the Baxter equation, Eq. (1),

$$\int h^{(n)} d[n] = H^{(2)} [(\rho \partial h^{(n-1)} / \partial \rho)_T + (n-1) h^{(n-1)}] \tag{21a}$$

$$= [H^{(2)} \partial + (n-1) H^{(2)}] h^{(n-1)} \tag{21b}$$

where ∂f is a shortened notation for $\rho(\partial f / \partial \rho)_T$. Then we integrate over the

coordinates of particle $(n - 1)$ and we use once again Eq. (21b) at order $(n - 2)$:

$$\int h^{(n)} d[n] d[n - 1] = \{ [H^{(2)}\partial + (n - 1) H^{(2)}] [H^{(2)}\partial + (n - 2) H^{(2)}] \} h^{(n-2)} \quad (22)$$

and we follow this procedure until the r.h.s. includes only the two-body total correlation function $h^{(2)}(1, 2)$. We thus obtain

$$\int h^{(n)}(1, 2, 3, \dots, n) d[n] d[n - 1] \dots d[3] = \left\{ \prod_{i=2, (n-1)} [H^{(2)}\partial + iH^{(2)}] \right\} h^{(2)}(1, 2) \quad (23)$$

Finally, we get

$$H_\lambda^{(n)} = \int_\lambda d[2] \int h^{(n)}(1, 2, 3, \dots, n) d[n] d[n - 1] \dots d[3] = \left\{ \prod_{i=2, (n-1)} [H^{(2)}\partial + iH^{(2)}] \right\} \left(\int_\lambda d[2] h^{(2)}(1, 2) \right) \quad (24)$$

where $\int_\lambda d[2] = \int (r_{12} < \lambda) dr_{12}$. The order of magnitude of the leading term (i.e., its dependence with respect to $\Delta\rho$) in Eq. (24) is determined as follows. First, each multiplication by $H^{(2)}$ brings a factor $\xi^{d-2d\phi}$. Second, $(H^{(2)}\partial)f$ leads to $\approx H^{(2)}f$ if the function f is regular and nonzero at the C.P. and to $\approx (1/\Delta\rho) H^{(2)}f$ if the function f is singular, where a function is called "singular" if it presents a nonanalytic power-law dependence with respect to $\Delta\rho$. In any case the first term of $[H^{(2)}\partial + iH^{(2)}]$ is greater than or comparable to the second one and therefore the leading term of $H_\lambda^{(n)}$ is determined from

$$H_\lambda^{(n)} = \{ [H^{(2)}\partial]^{(n-2)} \} H_\lambda^{(2)} \quad (25)$$

From Eq. (13), we have

$$\partial H_\lambda^{(2)} = (1/\xi)(\partial\xi) \int_\lambda h^{(2)}(r)(r/\xi) dr + (1/B)(\partial B) H_\lambda^{(2)} \quad (26a)$$

$$|\partial H_\lambda^{(2)}| \leq (1/\Delta\rho)(\lambda/\xi) |H_\lambda^{(2)}| + |(1/B)(\partial B) H_\lambda^{(2)}| \quad (26b)$$

and we expect $(1/B)(\partial B) \approx 1$. The inequality (26b) is obtained by considering that for small values of λ , for instance, $\lambda \approx \sigma$, the first term on the r.h.s. of (26a) is negligible as a consequence of (15), the second term, which is the regular contribution to $\partial H_\lambda^{(2)}$ being the dominant one. In contrast, the first term is dominant for large values of λ , where the monotonous behavior of $h^{(2)}$ for large r is sufficient to yield an upper bound for the integral by simply replacing (r/ξ) by its largest value (λ/ξ) . Equation (26b) tells us that $(\partial H_\lambda^{(2)})/H_\lambda^{(2)}$ is smaller than or equal (when $\lambda = \xi$) to $(\partial H^{(2)})/H^{(2)}$ and we deduce from Eq. (25)

$$\begin{aligned} H_\lambda^{(n)} &= \{ [H^{(2)}\partial]^{(n-3)} \} (H^{(2)}\partial(H_\lambda^{(2)})) \\ &\approx (H^{(2)})^{(n-3)} (\partial^{(n-3)} H^{(2)}) (\partial H_\lambda^{(2)}) \\ &\approx (H^{(2)})^{(n-2)} (1/\Delta\rho)^{(n-3)} (\partial H_\lambda^{(2)}) \end{aligned} \tag{27a}$$

The third line in Eq. (27a) is obtained by using $(\partial^{(n-3)} H^{(2)}) = H^{(2)}(1/\Delta\rho)^{(n-3)}$. Equation (27a) is transformed according to

$$\begin{aligned} H_\lambda^{(n)} &\approx (H^{(2)})^{(n-1)} (1/\Delta\rho)^{(n-2)} [H_\lambda^{(2)}/H^{(2)}] [\Delta\rho(\partial H_\lambda^{(2)})/H_\lambda^{(2)}] \\ &= H^{(n)} [H_\lambda^{(2)}/H^{(2)}] [(\partial H^{(2)})/H^{(2)}]^{-1} [(\partial H_\lambda^{(2)})/H_\lambda^{(2)}] \end{aligned} \tag{27b}$$

where we have replaced $(\Delta\rho)$ by $[(\partial H^{(2)})/H^{(2)}]^{-1}$. We then use the fact that the divergence of $H^{(2)}$ is due to the weak decrease of $h^{(2)}$ when $r_{12} \rightarrow \infty$; this together with Eq. (26) leads us to introduce an exponent $x(\lambda)$, according to

$$\begin{aligned} \partial H_\lambda^{(2)}/H_\lambda^{(2)} &\approx (1/\Delta\rho)(\lambda/\xi) + 1 \approx \Delta\rho^{-1} [(\lambda/\xi) + \Delta\rho] \\ &= [(\partial H^{(2)})/H^{(2)}] [\Delta\rho^{x(\lambda)}] \end{aligned}$$

with

$$x(\lambda) = \inf\{ 1, [1 - \text{Ln}(\lambda/\sigma)/\text{Ln}(\xi/\sigma)]/d_\phi \} \tag{28}$$

where Eq. (15) has been used. Obviously, $x(\lambda) \geq 0$ and $x(\xi) = 0$. Moreover, when λ is comparable to the molecular length σ , the regular contribution to $[\partial H_\lambda^{(2)}/H_\lambda^{(2)}]$ warrants that $x(\sigma) = 1$. From Eqs. (27), (28) we get

$$H_\lambda^{(n)} \approx H^{(n)} [H_\lambda^{(2)}/H^{(2)}] \xi^{-x(\lambda) d_\phi} = H^{(n)} [H_\lambda^{(2)}/H^{(2)}] \Delta\rho^{-x(\lambda)} \tag{29}$$

When $\lambda \approx \sigma$, the integral of $h^{(2)}$ is a constant with respect to ξ and we get the result

$$H_\sigma^{(n)} \approx H^{(n)} [1/H^{(2)}] \xi^{-x(\sigma) d_\phi} \approx H^{(n)} \xi^{-d + [2 - x(\sigma)] d_\phi} \tag{30}$$

Since $(-d + 2d_\phi) < 0$ and $x(\lambda < \xi) > 0$, in any case we have $H_\sigma^{(n)} \ll H^{(n)}$ and this result may be generalized to the case where more than one distance is kept of the order of σ in the integral. The important point is that we demonstrate the intuitive result that first the leading contribution to the integral $H^{(n)}$ comes from the part of the space where all the distances are of order ξ , which is a generalization of the explanation for the divergence of $H^{(2)}$ at the critical point, and second that $H_\sigma^{(n)} \approx H^{(n-1)}$, since $x(\sigma) = 1$.

Notice that the preceding result cannot be generalized to the $C^{(n)}$, because Eq. (28) cannot be stated for $c^{(2)}$ and the second equality of (30) has no equivalent for the direct correlation function, since its integral $C^{(2)}$ is finite at the critical point.

3. FORM OF THE CORRELATION FUNCTIONS NEAR THE CRITICAL POINT

In this section, we consider the form of $h^{(n)}$ and $c^{(n)}$ in the vicinity of the C.P., by using the results of the preceding section. The expressions of $h^{(n)}$ and $c^{(n)}$ depend on $3n - 6$ independent distances among the $n(n - 1)/2$ distinct ones. We consider a partition of the configuration space V^n into V_σ^n , $V_{\sigma\xi}^n$, and V_ξ^n defined as follows: in V_σ^n all the distances between the particles are bounded by the molecular length σ ; in $V_{\sigma\xi}^n$ at least one distance is of order σ and at least one distance is of order ξ ; while in V_ξ^n all the distances are of order ξ . To this partition we associate a splitting of the correlation functions into $f_\sigma^{(n)}$, $f_{\sigma\xi}^{(n)}$, and $f_\xi^{(n)}$, where $f = c$ or h . This splitting is defined in such a way that $f^{(n)} = f_\sigma^{(n)} + f_{\sigma\xi}^{(n)} + f_\xi^{(n)}$ and $f_a^{(n)}(\{r_{ij}\}) = 0$ if $\{r_{ij}\} \notin V_a^n$. Obviously, one can imagine a simple form for $f^{(n)}$ only in the region where the universal behavior may hold, namely in V_ξ^n . Thus, we investigate the form of $c_\xi^{(n)}$ and $h_\xi^{(n)}$, on the basis of what is done for the long-range part of $h^{(2)}$,⁽¹⁵⁾ and by using the arguments developed by Cardy.⁽¹⁹⁾ However, in order to do that, we have to be sure that the effect of $f_\xi^{(n)}$ is actually dominant in the critical behavior. Given the results of the preceding section [see, for instance, Eq. (30)], we can conclude that this is indeed the case for $h^{(n)}$, and therefore we can analyze separately $h_\xi^{(n)}$.

3.1. Total Correlation Function $h^{(n)}$

We separate $h_\xi^{(n)}$ into three different factors, playing different roles:

$$h_\xi^{(n)}(\{r_{ij}\}) = \sum \left[\prod (r_{ij})^{z(n;i,j)} \right]^{-1} \phi^{(n)}(\{r_{ij}/\xi\}) F(\{r_{ij}/r_{lk}\}) \quad (31a)$$

The first factor is the inverse of a product of a set of distances; different sets are involved and we consider a sum of such products symmetric with

respect to the permutations of particles; the second factor is a cutoff function, playing the role of the factor $\exp(-r_{12}/\xi)$ in $h^{(2)}$; the third factor, according to ref. 19, is a dimensionless function F depending on products of the ratio of distances $\{r_{ij}/r_{ik}\}$. Furthermore, by definition, $h_\xi^{(n)}$ vanishes when at least one distance becomes comparable to σ , which means that it includes a product $\prod [\phi_0(r_{ij}/\sigma)]$, not made explicit in (31), where $\phi_0(x < 1) = 0$. Since we deal here with the actual correlation functions, and not with a perturbation scheme including at a given stage the so-called ultraviolet divergences,⁽²⁻⁶⁾ the short-distance cutoff function ϕ_0 does not need to be treated explicitly and can be dropped in our analysis. The unknown function F describes the “angular” structure of $h^{(n)}$: it is likely to play a crucial role in situations where two length scales, say λ_1 and λ_2 , must occur in the set $\{r_{ij}\}$, with $\sigma \ll \lambda_1 \ll \lambda_2 \leq \xi$. Its properties can be obtained in some cases under the hypothesis of conformal invariance;^(19, 20) for instance, $F = 1$ for the three-body correlation function and for the four-body case the argument of F is a cross ratio of the distances.

The important point at this stage is that the product $[\prod (r_{ij})^{z(n;i,j)}]^{-1}$ and the function F do not play the same role: $[\prod (r_{ij})^{z(n;i,j)}]^{-1}$ has a dimension, while F is dimensionless. Therefore, in a dilation of all the distances which leaves the angles unchanged, the function F is invariant and the behavior of $h_\xi^{(n)}$ is determined by $[\prod (r_{ij})^{z(n;i,j)}]^{-1}$. Now, from the discussion of Section 2.2 we know that the leading part of the integral $H^{(n)}$ is due to $h_\xi^{(n)}$ and we thus have

$$\begin{aligned}
 H^{(n)} &= \int h_\xi^{(n)}(\{r_{ij}\}) d[1] \cdots d[n-1] \\
 &= \xi^{(n-1)d - \sum z(n;i,j)} \int \sum \left[\prod (r_{ij}^*)^{z(n;i,j)} \right]^{-1} d[1^*] \cdots d[(n-1)^*] \quad (32)
 \end{aligned}$$

where $r^* = r/\xi$ and $d[i^*] = d[r/\xi]$. From Eqs. (17) we get the sum of the exponents involved in $[\prod (r_{ij})^{z(n;i,j)}]^{-1}$, or the “dimension” of $h_\xi^{(n)}$:

$$\sum [z(n; i, j)] = nd_\phi \quad (33)$$

3.2. Direct Correlation Function $c^{(n)}$

It is tempting to treat the direct correlation functions $c^{(n)}$ in the same way. Writing

$$c_\xi^{(n)}(\{r_{ij}\}) = \sum \left[\prod (r_{ij})^{z(n;i,j)} \right]^{-1} \Psi^{(n)}(\{r_{ij}/\xi\}) K(\{r_{ij}/r_{ik}\}) \quad (31b)$$

one can see that instead of (33) we obtain

$$\sum [z'(n; i, j)] = nd'_\phi \tag{34}$$

As mentioned in Section 2.2, we have two contributions to $C^{(n)}$:

$$C^{(n)} = (-1)(n-2)! + (C_c/\rho^{n-1}) \xi^{(n-1)d-nd'_\phi}$$

The first term is dimensionless and represents the leading contribution to $C^{(n)}$ when $n > \delta + 1$. It is *a priori* not possible to state whether the short- or long-range part of $c^{(n)}$ contributes most and to which of these terms. However, in the case of $c^{(2)}$ (or even $c^{(3)}$ if one adds the hypothesis of conformal invariance; see Appendix B), we know the behavior for large distances $r \gg \sigma$:

$$c^{(2)}(r) \approx (1/r)^{2d'_\phi}$$

When integrated over a volume where this expression holds, for instance, outside a sphere of several molecular diameters σ , such as $R \geq N\sigma$ with $N \gg 1$, we see that this long-range part cannot give the leading $(-1)^n (n-2)!$ ($n=2$) contribution, which then can only come from the short-range part. We extend this analysis to all $c^{(n)}$, arguing that all $c^{(n)}$ are decreasing functions and that the dimensionless part is essentially related to the short-range part of the functions. Therefore, we redefine the $c^{(n)}$ by separating it into a short-range, $c_\sigma^{(n)}$, contribution and a long-range, $c_\xi^{(n)}$, contribution, such that the integral of $c_\sigma^{(n)}$ yields the nondimensional constant contribution. As we are concerned with the long-range behavior, we write

$$c_\sigma^{(n)}(1, 2, \dots, n) = [(-1)^n (n-2)!/\rho^{(n-1)}] \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta(\mathbf{r}_1 - \mathbf{r}_3) \cdots \delta(\mathbf{r}_1 - \mathbf{r}_n) \tag{35a}$$

and we define the long-range contribution $c_\xi^{(n)}$, which can contain both length scales σ and ξ , such that $c_\xi^{(n)} = (c^{(n)} - c_\sigma^{(n)})$ and

$$\int c_\xi^{(n)} d[1] \cdots d[n-1] = -(C_c/\rho^{n-1}) \xi^{(n-1)d-nd'_\phi} \tag{35b}$$

4. DETERMINATION OF AN UPPER BOUND FOR $h^{(n)}$

In order to find an upper bound for $h^{(n)}$, which is to be understood as $h_\xi^{(n)}$, we use the n -body version of the Ornstein-Zernike (OZ) equation from which $h^{(n)}$ can be rigorously expressed via a finite set of integral equations involving $h^{(2)}$ and the functions $c^{(m)}$, with $3 \leq m \leq n$. The n -body OZ

equation can be represented by an expansion in Mayer diagrams; it is then nothing else than the analysis of $h^{(n)}$ in terms of nodal points. This expansion involves only a finite number of diagrams, and thus avoids any problem of convergence of infinite series. In the following, we investigate the structure of these graphs, in order to find the leading contribution of the sum when all the distances between particles are large, and then to deduce an upper bound for $h^{(n)}$.

4.1. Recursive Construction of the N -Body Ornstein-Zernike Equation

In order to establish the n -body Ornstein-Zernike equation we proceed in a recursive way, showing how we can get $h^{(n)}$ from $h^{(n-1)}$. In $h^{(n-1)}$, we isolate three different diagrammatic structures.

First, we consider the set of graphs in which there is no field point and only $n-1$ root points, some $h^{(2)}$ bonds, and no subgraph forming a loop: these are tree graphs. To create a new root point, we add an extra $h^{(2)}$ bond at one of the $n-1$ vertices, and we then generate a part of $h^{(n)}$ which is still a tree (see Fig. 1a).

Second, we have the part of $h^{(n-1)}$ which is free of nodal points: by definition this coincides with $c^{(n-1)}$. From this we generate either a new graph without a nodal point, i.e., $c^{(n)}$ or a graph with one nodal point by adding to $c^{(n-1)}$ a $c^{(3)}$ function (see Fig. 1b).

Finally we consider in $h^{(n-1)}$ the graphs including field points, some $c^{(m)}$ functions, and some $h^{(2)}$ bonds. The rules from which the graphs are constructed are the following: the function $c^{(2)}$ is absent because $h^{(2)}$ and $c^{(2)}$ cannot be put in series,⁽²¹⁾ and so $m \geq 3$; two $h^{(2)}$ bond cannot be connected in series,⁽²¹⁾ namely just by a field point; as can be seen from pictorial arguments, we must have $m \leq n$. The introduction of a new root point can be done in only three different ways. First, from a root point of $h^{(n-1)}$ we may add an $h^{(2)}$ bond terminated by the new root point. Second, from a $c^{(m)}$ we have two possibilities: (i) we can generate $c^{(m+1)}$, which contains the new root point, or (ii) from $c^{(m+1)}$ we add an $h^{(2)}$ bond terminated by the new root point. Third, we can split an $h^{(2)}$ bond introducing a new $h^{(2)}$ directly or via a three-body direct correlation function $c^{(3)}$ (see Fig. 1c).

Therefore, starting from the OZ equation for $h^{(3)}$, which is explicitly known, we can construct the equation relative to $h^{(n)}$ and the important point is that it can be represented by a finite number of graphs $G(n)$; in the set of graphs $\{G(n)\}$ each element contains some $h^{(2)}$ bonds and a given number of $c^{(m)}$, with $3 \leq m \leq n$.

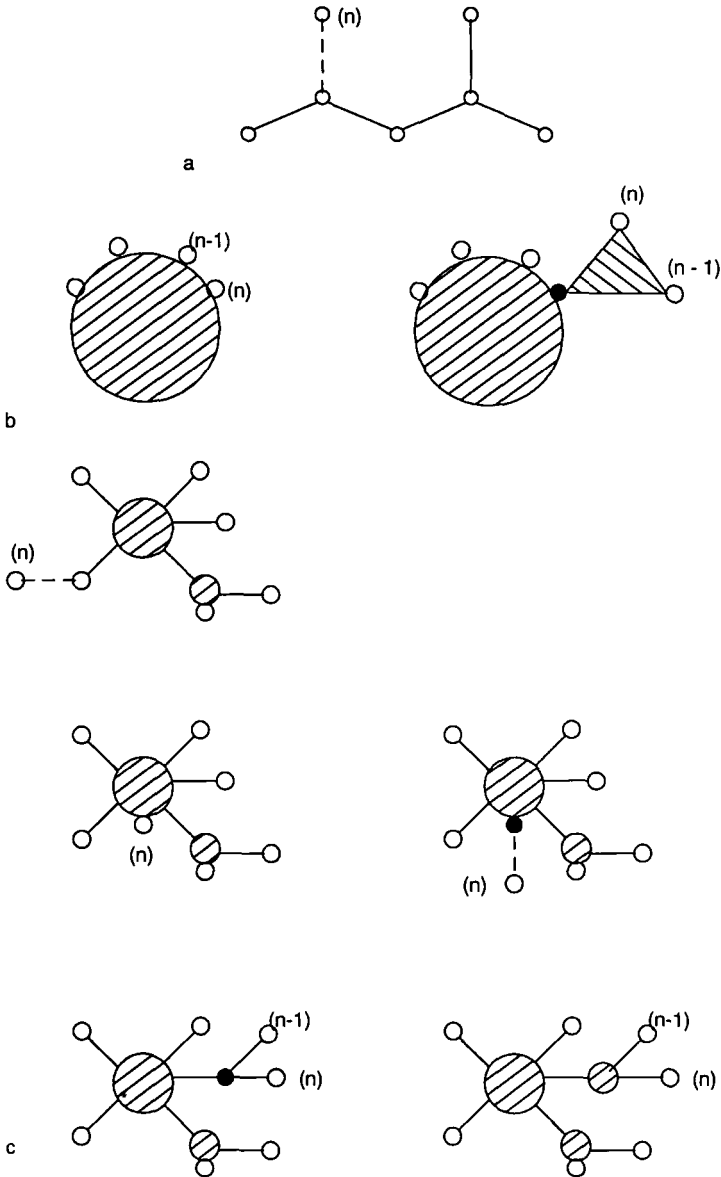


Fig. 1. Recursive construction of the n -body Ornstein-Zernike equation.

We first eliminate the graphs of the first two cases in the preceding analysis since, once integrated over the root points, they lead to a smaller dimension than that of $H^{(n)}$. Similarly, we can eliminate the graphs where a point of a $c^{(m)}$ function is a root point; indeed let us consider such a graph, $G(1, 2, \dots, n)$, the root point belonging to a $c^{(m)}$ function being, say r_1 ; the expansion of $h^{(n)}$ includes also the graph

$$G_2(1, 2, \dots, n) = \int G(1', 2, \dots, n) h^{(2)}(1, 1') d[1']$$

whose dimension is higher than that of G because of the $h^{(2)}$ bond. Therefore, in the following the graphs that we consider include some $c^{(m)}$ functions, at least two $h^{(2)}$ bonds, and some field points, and each root point ends an $h^{(2)}$ bond. It is convenient to define a node as follows: this will

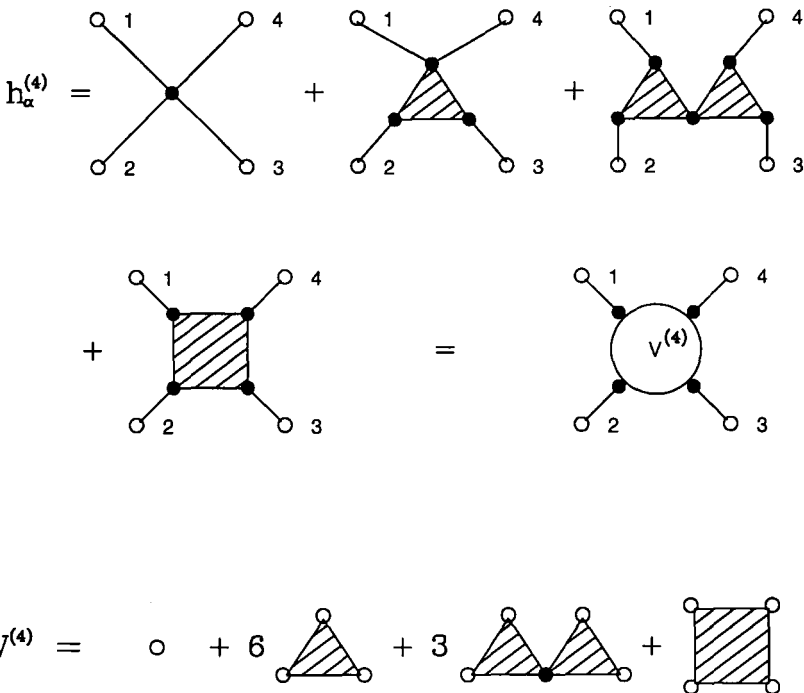


Fig. 2. Illustration, from a particular contribution to $h^{(4)}$, of the definition of the nodes $V^{(p)}$. Here, we consider $V^{(4)}$. The permutations of the second and of the third graphs of the first line are not made explicit; they are responsible for the factors 6 and 3 in the expansion of $V^{(4)}$. The hatched subgraphs are $c^{(p)}$ functions and the lines are $h^{(2)}$ bonds.

denote the sum of the subgraphs of $h^{(n)}$ including only some $c^{(m)}$ functions directly connected together through field points and characterized by the number of external $h^{(2)}$ bonds connecting the node to the whole graph. A node with p external bonds will be denoted by $V^{(p)}$. With this definition, we see that a node $V^{(p)}$ is built up by a set of graphs, denoted $V^{(\alpha,p)}$, each $V^{(\alpha,p)}$ being characterized by a number p_α of external points, with $p_\alpha \leq p$. The simplest component of $V^{(p)}$ is a point at which, in the whole diagram of $h^{(n)}$, start $ph^{(2)}$ bonds; this component will be denoted the “1” component of $V^{(p)}$. We can obviously define the $V^{(\alpha,p)}$ in such a way that they all present exactly p external points, by using appropriate δ functions, and in the following we denote by $W^{(\alpha,p)}$ this definition of the components $V^{(\alpha,p)}$. It is easy to see that the graphs we consider for $h^{(n)}$, are free of loops of $h^{(2)}$ bonds and nodes $V^{(p)}$ since such a loop is a part of a $c^{(m)}$ function, with $m > p$, as it is a graph at least doubly connected. Thus we are left with graphs including some field points, at least two $h^{(2)}$ bonds, and nodes $V^{(p)}$, with $3 \leq p \leq n$. As an example, $V^{(4)}$ is shown in Fig. 2.

4.2. Cancellation of Constants Related to the Short-Range Part of $c^{(m)}$

In this section we show that the sum of the graphs of $h^{(n)}$ in which only the component $c_\sigma^{(m)}$ of each function $c^{(m)}$, involved in the nodes $V^{(p)}$ is taken into account vanishes. We denote by $V_\sigma^{(p)}$ the contribution to $V^{(p)}$ calculated by using only the components $c_\sigma^{(m)}$ of $c^{(m)}$. We replace all the $c^{(m)}$ by their short-range part, $c_\sigma^{(m)}$, defined in (35); the nodes $V_\sigma^{(p)}$ are thus also constants times a product of δ functions; let $\{1, 2, \dots, p\}$ be the points of the node $V_\sigma^{(p)}$, we have

$$V_\sigma^{(p)} = b^{(p)} \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta(\mathbf{r}_1 - \mathbf{r}_3) \cdots \delta(\mathbf{r}_1 - \mathbf{r}_p) \tag{36}$$

and we just have to show that all the $b^{(p)}$ vanish. At first sight, we calculate the first three terms of the set, namely $b^{(3)}$, $b^{(4)}$, and $b^{(5)}$. The important point is that these are labeled graphs; moreover, the convolutions involved are easily calculated since the $c_\sigma^{(m)}$ functions, once integrated over $m - 1$ coordinates, are constants $C^{(m)}$, leading to a very simple factorization and finally the field points are weighted by the density ρ . We get

$$b^{(3)} = 1 + \rho^2 C_\sigma^{(3)} \tag{37a}$$

$$b^{(4)} = 1 + \rho^3 C_\sigma^{(4)} + 6\rho^2 C_\sigma^{(3)} + 3\rho^4 C_\sigma^{(3)} C_\sigma^{(3)} \tag{37b}$$

$$b^{(5)} = 1 + \rho^4 C_\sigma^{(5)} + 10\rho^3 C_\sigma^{(4)} + 10\rho^5 C_\sigma^{(4)} C_\sigma^{(3)} + 25\rho^2 C_\sigma^{(3)} + 45\rho^4 C_\sigma^{(3)} C_\sigma^{(3)} + 15\rho^6 C_\sigma^{(3)} C_\sigma^{(3)} C_\sigma^{(3)} \tag{37c}$$

From Eq. (19), we obtain $b^{(3)} = b^{(4)} = b^{(5)} = 0$. We use the Baxter relations on the hierarchy of the $c^{(p)}$, Eq. (8), and we define, for convenience, the operator $\partial[\cdot]$ by

$$\partial f = \partial(\rho f) / \partial \rho$$

By using (8) we obtain

$$b^{(4)} = \partial[b^{(3)}] + 3C_\sigma^{(3)}b^{(3)} \quad (38a)$$

$$b^{(5)} = \partial[b^{(4)}] + 4\rho^2 C_\sigma^{(3)}b^{(4)} + 3b^{(3)}\rho^2 C_\sigma^{(3)}b^{(3)} \quad (38b)$$

These equations suggest that there is a recurrence relation between the $b^{(p)}$. This is obtained by decomposing the procedure allowing us to generate $V_\sigma^{(p)}$ from $V_\sigma^{(p-1)}$.

The first step is to take into account all the possibilities to add a new external bond to $V_\sigma^{(p-1)}$, without introducing a convolution. We have to consider two types of transformations: the first one changes the topology by generating a new external point changing a $c^{(m-1)}$ into a $c^{(m)}$ and the other one consists in adding the new external $h^{(2)}$ bond on an existing external point or on a nodal point between two $c^{(m)}$ functions in the graph $V_\sigma^{(p-1)}$ which is left unchanged. This first step is exactly performed by the action of the operator $\partial[\cdot]$ [the derivative with respect to ρ of the integrals $b^{(p)}$ correspond to a functional derivative with respect to $\rho(\mathbf{r})$ of the Mayer diagrams⁽¹⁾]. In this first step one pattern is left out, which is the case where the new p th $h^{(2)}$ bond is attached as a unique bond to a point of a $c^{(3)}$ function, while if this $h^{(2)}$ is not alone, the corresponding graph is accounted for with the operator $\partial[\cdot]$ acting on an external point of an existing $c^{(3)}$ function of $V_\sigma^{(p-1)}$. Now when this bond is alone the peculiarity of $c^{(3)}$ is that it can be generated only by the derivative of a $c^{(2)}$ function and this one, unlike the other $c^{(m)}$ functions with $m \geq 3$, does not exist in the n -body OZ equation: thus the above-mentioned graphs are not generated by the $\partial[\cdot]$ operator. The second and third steps consist precisely in introducing the new $h^{(2)}$ bond via a $c^{(3)}$ function.

In the second step we consider the introduction of a $c^{(3)}$ function on an external point of $V_\sigma^{(p-1)}$, which we refer to as a j point on which $k(j)$ points are connected. The result of this is a $c^{(3)}(j, j_1, p)$ function, where on the p point we have the p th $h^{(2)}$ bond, on the point j_1 we choose in this second step to have only one $h^{(2)}$ bond, and on the point j we have the convolution with the rest of the original diagram. This operation is done on each external point of the graph and each time we select a single external

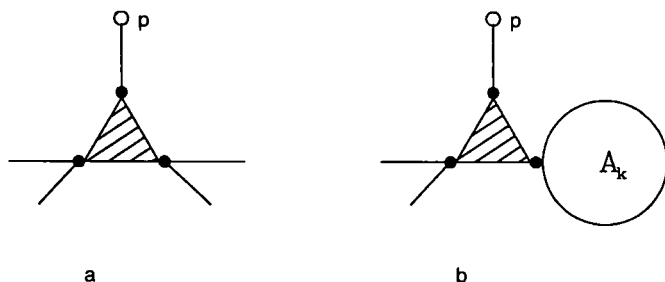


Fig. 3. Examples of graphs which cannot be obtained by the two first steps (made explicit in the text) of the procedure generating $V^{(p)}$ from $V^{(p-1)}$. The hatched subgraphs are $c^{(p)}$ functions and the lines are $h^{(2)}$ bonds.

bong among the $k(j)$ ones to be attached on j_1 . The number on external bonds being $p - 1$, for each graph of $V_{\sigma}^{(p-1)}$, we have in $b^{(n)}$ a term

$$(n - 1) \rho^2 C^{(3)} b^{(n-1)} \tag{39}$$

However, in the construction of $b^{(p)}$, we have to consider more complex situations where more than one $h^{(2)}$ bond or even a combination of $h^{(2)}$ and $c^{(m)}$ functions is attached to j_1 . Examples of graphs not generated by steps 1 and 2 are given in Fig. 3.

In the third step, we consider the case where the $c^{(3)}$ function is introduced on a j convolution point of $V_{\sigma}^{(p-1)}$; in this respect an external point with $k(j) \geq 2$ is also a convolution point with the use of adequate δ functions. The transformation corresponding to this third step can be formally represented by

$$A_{k_1}^* A_{k_2} \rightarrow A_{k_1}^* \rho^2 C^{(3)} * A_{k_2} \tag{40}$$

The A_{k_i} graphs are labeled according to the number of $h^{(2)}$ external bonds attached to them: k_i is the number of external bonds of A_{k_i} plus one, the nodal point connecting A_{k_1} and A_{k_2} . We thus have the constraint $k_1 + k_2 = p - 1$ and $k_1, k_2 \geq 2$ (the case k_1 or $k_2 = 1$ has been accounted for in step 2). Rather than discussing each diagram in $V_{\sigma}^{(p-1)}$ and constructing all possible combinations, let us observe that for the graph A_{k_1} , the remaining $\rho^2 C^{(3)} * A_{k_2}$ part is simply a label. For a given $\rho^2 C^{(3)} * A_{k_2}$, the possible choice of A_{k_1} graphs is equivalent to the problem of attaching $k_1 + 1$ labels to a graph, which is nothing else than $V_{\sigma}^{(k_1+1)}$. The contribution of these graphs is simply $b^{(k_1+1)}$ and symmetrically for A_{k_2} ; therefore (40) is summed up into

$$b^{(k_1+1)} * \rho^2 C^{(3)} * b^{(k_2+1)} \tag{41}$$

Considering all sets constituted with $k_1 h^{(2)}$ bonds drawn from the set of $p - 1$ external bonds, we have the permutation factor

$$C_{k_1}^{p-1} \equiv [(p-1)(p-2) \cdots (p-k_1)]/[k_1!(p-1)!]$$

and an overall 1/2 factor to account for the symmetry between A_{k_1} and A_{k_2} . We thus have in $b^{(p)}$ the term

$$(1/2) \sum_{\{k_1=2, p-3\}} C_{k_1}^{p-1} [b^{(k_1+1)} \rho^2 C^{(3)} b^{(p-k_1-2)}] \tag{42}$$

We can finally check, first, that all graphs of $b^{(p)}$ for all possible ways of introducing a new p th bond are accounted for via the $\partial[\cdot]$ operator or via the introduction of a $c^{(3)}$ function; second, that no graph is counted twice, because the three steps above define different graph specifications. We can therefore write

$$b^{(p)} = \partial[b^{(p-1)}] + (p-1) \rho^2 C_{\sigma}^{(3)} b^{(p-1)} + (1/2) \sum_{\{k_1=2, p-3\}} C_{k_1}^{p-1} [b^{(k_1+1)} \rho^2 C^{(3)} b^{(p-k_1-2)}] \tag{43}$$

which is the desired result. Indeed, starting from the recurrence hypothesis according to which $b^{(p)} = 0$ if $p \leq p_0$, we get $b^{(p)} = 0$ whatever the value of p ; since the recurrence hypothesis is indeed satisfied for $p \leq 5$, we get the announced result, namely

$$b^{(p)} = 0, \quad \forall p \tag{44}$$

Thus, the fully localized part of the nodes $V^{(p)}$ does not contribute to the expansion of $h^{(n)}$ and we have to deal with “dimensioned” nodes. Now, we shall take into account only the leading part of these nodes, which we christen $V_1^{(p)}$, and this is obtained as the contribution to $V^{(p)}$ leading to the greater dimension for the corresponding diagram of $h^{(n)}$. According to this scheme, one finds

$$V_1^{(p)} = c_{\xi}^{(p)} + \dots \tag{45}$$

where the dots denote the nonleading terms, which can be disregarded in the present analysis, and $c_{\xi}^{(p)} = (c^{(p)} - c_{\sigma}^{(p)})$ is “dimensioned” part of $c^{(p)}$, defined by Eq. (35b). At this stage, the leading contribution of the long-range part of $h^{(n)}$ is obtained from the sum of graphs including some field points, some $h^{(2)}$ bonds, and some $c_{\xi}^{(p)}$ functions, playing the role of p -point

nodes. We emphasize that this cancellation is of crucial importance, since without this cancellation some graphs of $h^{(n)}$ would have a higher dimension than $h^{(n)}$.

4.3. Reduced Diagrammatic Expansion for $h_1^{(n)}$

In order to find an upper bond for $h^{(n)}$, we have to classify the graphs involved in the expansion we have obtained for the leading contribution $h_1^{(n)}$ of the long-range part $h_\xi^{(n)}$ of $h^{(n)}$ ($h_\xi^{(n)} = h_1^{(n)} + \dots$). The diagrammatic expansion obtained in Section 4.2. is a sum, say S_1 , of a finite number of graphs; each of these graphs is characterized by the number of $h^{(2)}$ bonds, the number of nodes of each type $V_1^{(p)}$, and the topology of the graph, i.e., the location of the nodes with respect to the root points $(1, 2, \dots, n)$. Now, for a given combination of the orders p of the nodes, say $\{p\} = (p_1, p_2, \dots, p_N)$ for a graph including N nodes, we consider the sum of all the corresponding graphs, which we christen $S_{\{p\}}$. In Fig. 4 we display an example of the representation of a contribution to $h^{(5)}$ in terms of $S_{\{p\}}$. We focus on the graphs presenting the largest range. Our criterion to determine the dominating graph is based on the fact that $h^{(2)}$ is the most delocalized bond. As a result the number of $h^{(2)}$ bonds is fixed once the combination $\{p\}$ is given and the dependence with respect to ξ of the integral over the $n-1$ coordinates of the $S_{\{p\}}$ is independent of the combination $\{p\}$ and coincides with that of the integral of S_1 . In other words, all the graphs $S_{\{p\}}$ when integrated over the $n-1$ coordinates have the same dimension. In the following, for the sake of simplicity, the dimension of a graph having n root points will denote the dimension of its integral over $n-1$ coordinates.

We now have to find a criterion allowing us to classify different graphs. This is not a simple task in general since the result of a graph $G_1(n)$ and the comparison between two graphs $G_1(n)$ and $G_2(n)$ depends on the configuration of the n root points; for $h_\xi^{(n)}$ this is a consequence of the function F of Eq. (31). Nevertheless we can avoid this problem in the case where all the distances r_{ij} are of the same order: then the dimension of the graph is indicative of its value in terms of ξ or in other words we can relate directly the range of the graph and its dimension [the function F of Eq. (31) does not play any role in this case since all its arguments are of order 1]. Thus, for a configuration of the n points where only one length scale is involved, i.e., when all the distances are of the same order, we can already estimate $h_1^{(n)}$ as one of the sums $S_{\{p\}}$ entering in S_1 . Then we can take the simplest one, namely S_3 , where the only node involved is $V_1^{(3)} = c_1^{(3)}$. This is illustrated in Fig. 4. The graphs of S_3 are very simple to analyze and this is done in Appendix A.

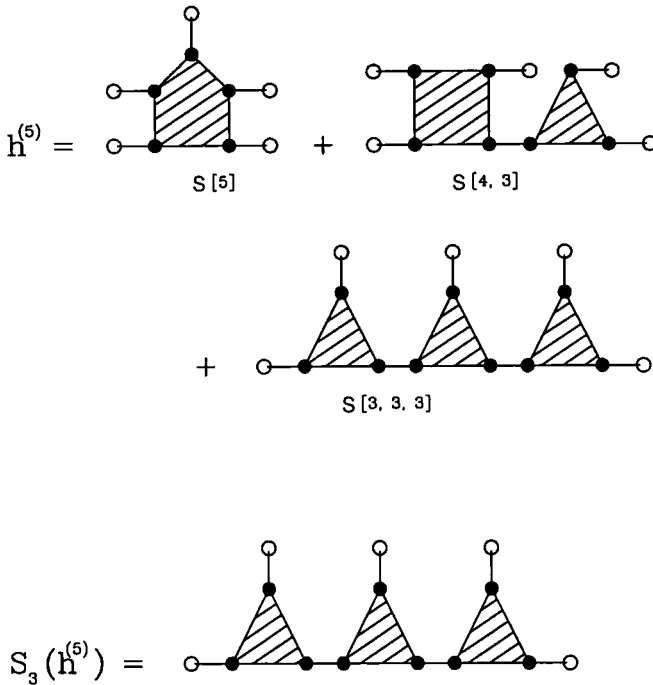


Fig. 4. Decomposition of a contribution to $h^{(5)}$ (as an example) in terms of the functions $S_{\{p\}}$ defined in the text. Each graph must be understood as a sum which makes the result symmetrical with respect to permutations of the particles $(1, 2, \dots, n)$. The corresponding S_3 representation referred to in the text is also shown. The hatched subgraphs are nodes $V^{(p)}$.

We consider the case where two length scales are involved in the configuration of the n points $(1, 2, \dots, n)$. These are denoted by α and λ , and we shall consider only the case where we have $\sigma \ll \alpha \ll \lambda \leq \zeta$, which means that both α and λ can be compared to ζ , α/ζ takes a very small value, while λ/ζ may be of order 1 and in any case $\sigma/\zeta \rightarrow 0$. We separate the n points into m groups i of $m(i)$ points located in a volume α^d , centered at \mathbf{R}_i ; the coordinates of the points in the group i are $\mathbf{r}_k = \mathbf{R}_i + \mathbf{r}_{ik}$, with $|\mathbf{r}_{ik}| \leq \alpha$, and the distance between different groups is $\mathbf{R}_i \approx \lambda$. Here, \mathbf{R}_i is not one of the root points of the graph, and it serves only to locate the group.

Then our task consists in determining the graphs where the nodes connect as less as possible the root points separated by the large length λ . Moreover, as we have already mentioned, we take into account only the graphs where the root points are connected to the graph through an $h^{(2)}$ bond and not directly on a node. Two rules will be important in the following for the estimations of graphs and these are deduced below.

First let us consider a node $V_1^{(p)}$ to which $p - 1$ root points located in the same volume α^d centered on \mathbf{R}_1 are connected through $h^{(2)}$ bonds; this node is connected to the rest of the graph by an $h^{(2)}$ bond via its p th external point (which is a field point). We claim that the main contribution to the integral corresponding to this field point is obtained when the integral is performed in the volume α^d centered on \mathbf{R}_1 . In other words, we consider that the field point, say p , is located in the vicinity of the $p - 1$ fixed root points. In the same way, we consider that this holds also when the node under consideration is connected to one (or more) root point of the group i and to another node $V_1^{(p')}$ connected to at least $p - 2$ root points of the same group i (see Fig. 5). This claim is justified by the fact that the nodes $V_1^{(p)}$ are $c_1^{(p)}$ functions which are at least doubly connected. We focus on the graph illustrated in Fig. 5a and we examine its dependence with respect to the large length scale λ . Because of the $h^{(2)}$ bonds connecting the root points labeled 1, 2, ..., which are separated by the small length α , to the j_i field points of the node, we can assume that the node is localized in the sense that the integral over the j_i points can be performed only in the volume α^d centered on \mathbf{R}_1 . The integral corresponding to p localized in the vicinity of \mathbf{R}_1 is $I_1 \approx h^{(2)}(\lambda) f(\alpha)$, where $f(\alpha)$ is a function depending only on the length α . To estimate the integral corresponding to the point p outside the volume α^d centered on \mathbf{R}_1 we take advantage of the fact that the function $c_1^{(p)}$ is at least doubly connected. If the integral is performed for p in the vicinity of \mathbf{R}_2 we obtain $f_2(\alpha) h^{(2)}(\alpha) \lambda^{-2z}$, where the exponent $2z$ describes the double bond. A simple dimensional analysis leads to $z = d'_\phi$, while in any case $z \geq d_\phi$, and this gives us $\approx f_2(\alpha) h^{(2)}(\alpha) \lambda^{-4d_\phi} \ll f_2(\alpha) h^{(2)}(\alpha) h^{(2)}(\lambda)$. When the integral is performed in the whole space, excepted the vicinity of both \mathbf{R}_1 and \mathbf{R}_2 , we describe the double bond of the function $c_1^{(p)}$ by replacing $c_1^{(p)}$ by

$$G = \int_\alpha d[j_1] d[j_2] \int_\xi d[k_1] d[k_2] c_1^{(p+1)}(1, \dots, p-1, j_1, j_2) \times h^{(2)}(j_1, k_1) h^{(2)}(j_2, k_2) c_1^{(3)}(k_1, k_2, p) \tag{46a}$$

The reason for this is that if we consider the graph G_0

$$G_0 = \int_\alpha d[j_1] d[j_2] \int_\xi d[k_1] d[k_2] c_1^{(p+1)}(1, \dots, p-1, j_1, j_2) \times h^{(2)}(j_1, k_1) h^{(2)}(j_2, k_2) c_1^{(3)}(k_1, k_2, p) \tag{46b}$$

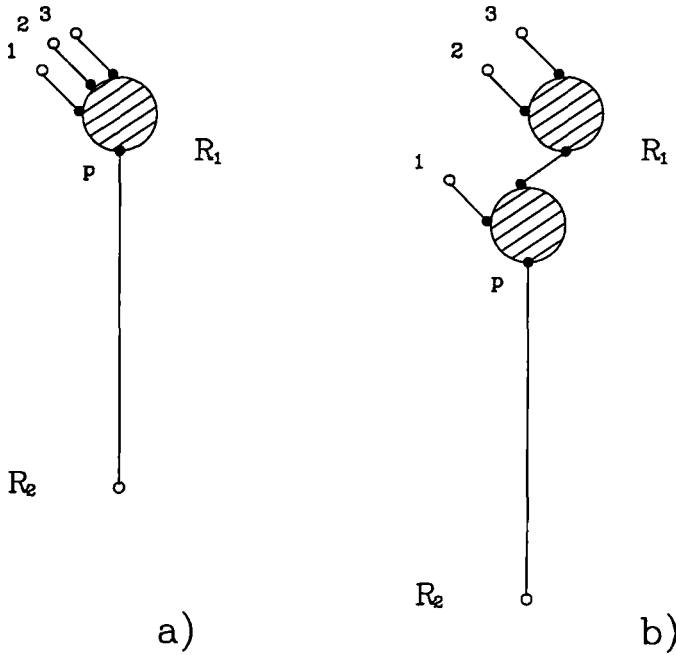


Fig. 5. Examples of configurations for the connection of a group i , including the points labeled $(1, 2, 3)$, located at \mathbf{R}_1 to a point \mathbf{R}_2 ; $R_{12} \approx \lambda$ and $r_{ij} \approx \alpha$ for $(i, j) \in (1, 2, 3)$, with $\alpha/\lambda \ll 1$. The hatched subgraphs are nodes $V^{(p)}$.

where the double bond is represented by the two $h^{(2)}$ functions, then the graph G_1 obtained from G_0 by taking the function $\delta(k_1, k_2, p)$ instead of the function $c^{(3)}$ is also to be taken into account. Adding G_0 to G_1 , the short range cancellation $1 + \rho^2 C^{(3)} = \rho^2 C_1^{(3)}$ justifies the use of $c_1^{(3)}$ in G , in cases where this estimation of $c_1^{(p)}$ is used in a graph where a long-range function is connected to the point p . The Graph we focus on is then estimated from its dimension: we determine the integral over \mathbf{R}_2 and we get $f_3(\alpha)(\xi^{-d_\phi}) H^{(2)}$. This dimensional estimation is an upper bound, as it does not take into account the constraint due to j_1 and j_2 close to one another. This is illustrated in the framework of the conformal invariance hypothesis presented in Appendix B: in this case the estimation gives a term $(\alpha/\xi)^{d-3d_\phi} \xi^{-d_\phi}$ (Appendix B.3), which is indeed smaller than the previous estimation ξ^{-d_ϕ} . Therefore the contribution related to G is equal to or smaller than the dimensional estimation which satisfies $f_3(\alpha)(\xi^{-d_\phi}) H^{(2)} \ll f(\alpha) H^{(2)} = \int I_1 d\mathbf{R}_2$. Now, the fact that j_1 and j_2 are integrated in a volume α^d is not a restriction. If these points are far from \mathbf{R}_1 and \mathbf{R}_2 , the argument used with the point p can also be applied to the points j_1 and j_2 . We can conclude then that I_1 , which is related to the field points of a node

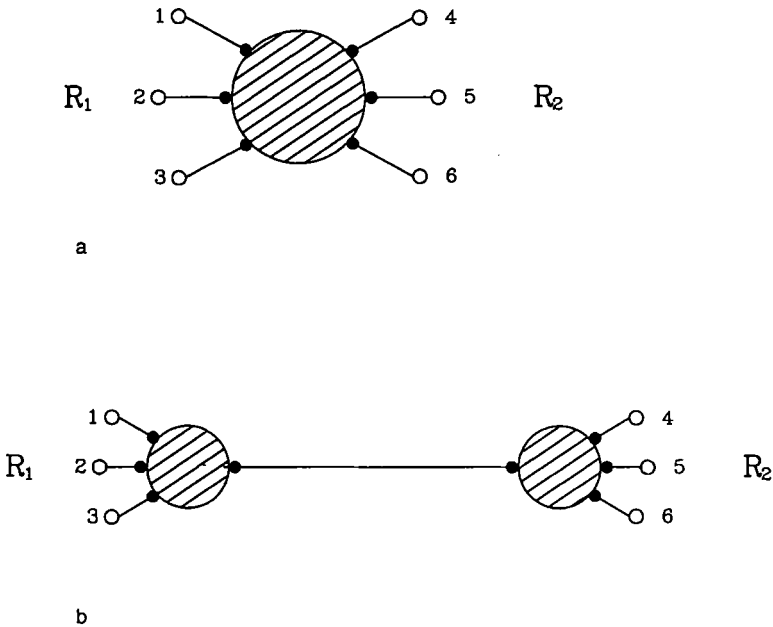


Fig. 6. Two different configurations to connect two groups located respectively at \mathbf{R}_1 and \mathbf{R}_2 with $R_{12} \approx \lambda$ and $r_{ij} \approx \alpha$ for either $(ij) \in (1, 2, 3)$ or $(ij) \in (4, 5, 6)$, with $\alpha/\lambda \ll 1$. The hatched subgraphs are nodes $V^{(6)}$. (a) The node $V^{(6)}$ is shared between the two groups; (b) the $h^{(2)}$ bond only is concerned with the long distance λ when the integrals corresponding to the field points are performed in localized volumes centered on the corresponding groups.

integrated over the volume α^d centered on each group, is indeed the leading contribution to the graph.

The second rule is that a node is not shared by two different groups, located say at \mathbf{R}_1 and \mathbf{R}_2 . We consider the graph of Fig. 6a. We have

$$G = \int h^{(2)}(i_1, i'_1) \cdots h^{(2)}(i_{k_1}, i'_{k_1}) c_1^{(p)}(i'_1, \dots, j'_{k_2}) h^{(2)}(j'_1, j_1) \cdots h^{(2)}(j'_{k_2}, j_{k_2}) \tag{47a}$$

where $p = k_1 + k_2$. Because of the k_1 $h^{(2)}$ bonds in the first group and of the k_2 $h^{(2)}$ bonds in the second group, the integrals over the field $\{i'_m\}$ are performed in the vicinity of \mathbf{R}_1 and those over the field points $\{j'_m\}$ are performed in the vicinity of \mathbf{R}_2 . Since $c_1^{(p)}$ is at least doubly connected, the graph G is majored by $f_1(\alpha)(h^{(2)}(\lambda))^2 f_2(\alpha)$. Then G is negligible compared to the graph G_1 , shown in Fig. 6b,

$$G_1 = \int h^{(2)}(i_1, i'_1) \cdots h^{(2)}(i_{k_1}, i'_{k_1}) c_1^{(k_1+1)}(i'_1, \dots, t_1) \times h^{(2)}(t_1, t_2) c_1^{(k_2+1)}(i'_1, \dots, t_2) h^{(2)}(j'_1, j_1) \cdots h^{(2)}(j'_{k_2}, j_{k_2}) \tag{47b}$$

including one node in each group, and which is estimated as $G_1 \approx f_1(\alpha) h^{(2)}(\lambda) f_2(\alpha)$. Let us point out that the previous rules are illustrated in Appendix A, under the conformal invariance assumption and for the S_3 representation.

In the following we define for convenience a t-point (trailer point) as follows: (i) An external point of a node connected to at least two root points separated by α ; or an external point of a node connected to one (or more) root point of a group and to another node which is also connected to a root point of the same group through an $h^{(2)}$ bond; (ii) not directly connected through an $h^{(2)}$ bond to a root point, or to a node connected to a root point of the preceding group. It is in fact a nodal point separating a group of points from the rest of the graph (see p point in Fig. 5).

We first examine the case of a configuration including only two groups, of $m(1)$ and $m(2)$; points respectively. Following our criterion, we consider the graph where one t-point of one group is connected to one t-point of the other group by an $h^{(2)}$ bond. We have two subgraphs, say G_1 and G_2 , connected together by an $h^{(2)}$ bond via the t-points (see Fig. 6b). Given the preceding arguments, one can convince oneself that the main contribution to the graph is obtained when the integral over the field points of G_1 (respectively G_2) are performed in the volume α^d centered on \mathbf{R}_1 (respectively \mathbf{R}_2). Therefore we estimate the whole graph by replacing the $h^{(2)}$ bond by a constant equal to $h^{(2)}(R_{12} = \lambda)$; the subgraphs G_1 and G_2 are functions where only the scale α is involved and they can be estimated according to their dimension (we recall that it is the dimension of the integral). This is easily obtained since G_1 (and G_2) can be decomposed in a combination of sums $S_{\{p\}}$ simply amputated of one $h^{(2)}$ bond; since the dimension of $S_{\{p\}}$ does not depend on the combination $\{p\}$, we can use the estimation of G_1 (and G_2) obtained from S_3 , which we denote by $S_3[G_1]$. In other words, when we deal with a configuration characterized by two groups, we can estimate $h_1^{(n)}$ by

$$\begin{aligned}
 h_1^{(n)} &\approx S_3[G_2(\alpha)] * h^{(2)}(\lambda) * S_3[G_1(\alpha)] \\
 &\approx h^{(2)}(\lambda) K(\alpha)
 \end{aligned}
 \tag{48}$$

where $K(\alpha)$ is a finite function depending only on the length scale α .

We now consider the general case of a configuration including any number of groups of localized points. As we have seen, we consider only the graphs where no node connected to root points via $h^{(2)}$ bonds is shared between different groups. We can then consider different possibilities. First we have the case of graphs, which we refer to as G_0 , in which a root point belonging to group i is connected only to a node located in the vicinity of group j ($i \neq j$): such a graph can be disregarded since we can consider a

similar graph from the point of view of the topology where the root point under consideration is connected to a node belonging to its own group; the value of this second graph is that of the first one times $[h^{(2)}(\alpha)/h^{(2)}(\lambda)] \gg 1$. Then we have to consider the graphs which can be written as a convolution of subgraph G_i , describing the groups i , with some $h^{(2)}$ bonds. Indeed, each root point of a group i is connected to a node $V_1^{(p)}$; given the graph G_0 has been eliminated, each path relating two root points of i goes through a node which appears then to be connected to at least two root points which are close to each other: the node under consideration is then "localized" in the vicinity of group i . We recall that the node is localized in the sense that the main contribution to the integrals over the corresponding field points is obtained when the integrals are performed in the volume α^d centered on \mathbf{R}_i . Now, it is easy to convince oneself that the subgraph we thus define, G_i , presents the structure of a combination of $S_{\{p\}}$ terms, where each graph entering $S_{\{p\}}$ is amputated of one $h^{(2)}$ bond. We introduce now a recurrence hypothesis: let us suppose that for a configuration including $m \leq m_0$ groups the part of the graph which connects the subgraphs G_i is $h_1^{(m)}$. We add a group described by the subgraph G_{m_0+1} to a configuration including m_0 groups: this new group can be connected simply to one of the other ones by an $h^{(2)}$ bond, or we can change the preceding $h^{(m_0)}$ in $h^{(m_0+1)}$. Therefore we have to choose between $[h^{(2)}(\lambda) h^{(m_0)}(\lambda)]$ and $h^{(m_0+1)}(\lambda)$: since the superposition approximation leads to an underestimation of $h^{(m)}(\lambda)$, and since our recurrence hypothesis is satisfied for $m_0 = 2$, we conclude that it is satisfied for all values of m .

Then we get

$$h_1^{(n)} = h_1^{(m)}(\lambda) * \{G_{\{i\}}(\alpha)\} \quad (49)$$

Then, the value of $h_1^{(n)}$ can be estimated in terms of α and λ ; for this we write $h_1^{(n)}$ in the form

$$h_1^{(n)} = h_1^{(m)} \prod_{i=1, m} \{Y_{p(i)}(\alpha)\} \quad (50)$$

where $Y_{p(i)}(\alpha)$ is the order of magnitude of the graph G_i including $p(i)$ root points. Since G_i involves only the length scale α , we can determine $Y_{p(i)}(\alpha)$ from the dimension of the graph G_i . This is done easily by using the S_3 representation of G_i . With the arguments developed above, we see that all the integral over the field points entering in the definition of G_i can be performed in a volume α^d centered on \mathbf{R}_i ; the dimension of G_i is then obtained from the value of the integral of G_i over $p(i) - 1$ of the $p(i)$ root points, performed in the volume α^d (the t-point is a field point) and then in order to get Y we divide the result by $\alpha^{(p(i)-1)d}$. We see that α is the only relevant

length scale and we can determine the dimension of the involved integrals by using α instead of ξ as in Section 2. The dimension of G_i is then that of $h^{(p(i)+1)}$ divided by that of $h^{(2)}$, since G_i is a graph of $h^{(p+1)}$ (p root points plus the t-point) amputated of one $h^{(2)}$ bond. We get

$$\begin{aligned} Y_{p(i)}(\alpha) &= [H^{(p(i)+1)}(\alpha)][H^{(2)}(\alpha)]^{-1} [\alpha^{(p(i)-1)d}]^{-1} \\ &= C[\alpha^{-(p(i)-1)d}] \end{aligned} \quad (51)$$

Finally, we get the following estimation for $h_1^{(n)}$ in the case of a configuration of the n points which separates into m groups a distance λ apart one from each other:

$$\begin{aligned} h_1^{(n)}[m] &\approx h_1^{(m)}(\lambda) f_{(n,m)}(\alpha) = h_1^{(m)}(\lambda) \prod_{i=1,m} [\alpha^{-(p(i)-1)d}] \\ &= h_1^{(m)}(\lambda) [\alpha^{-(n-m)d}] \end{aligned} \quad (52)$$

where we have introduced the function $f_{(n,m)}(\alpha)$ for convenience in the following. We emphasize that α holds for the dimensionless distance (α/σ), which means that $h^{(2)}(r)$ is of order 1 only for molecular distances; as a result, when $n \neq m$, since we are interested in very large distances, the function introduced in (52) is always very small compared to 1. Let us denote r_{\max} the largest distance in the set $\{r_{ij}\}$. Therefore we find that, when $n > 2$, $h_1^{(n)}$ is either comparable to $h^{(2)}(r_{\max})$ times a function very small compared to unity when there are only two groups, or very small compared to $h^{(2)}(r_{\max})$ when there are more than two groups.

4. DISCUSSION

The main result of this work, which we now analyze, is given by Eq. (52). It provides an estimation of the total correlation function when all the distances are large, namely in the "algebraic" regime of $h^{(n)}$, and when up to two length scales are involved. Because of this last point, it is a first attempt to go beyond the dimensional analysis.

Now we exploit this result in order first to derive an equivalent of the GKS⁽⁸⁻¹⁰⁾ inequality, which reads in our case

$$[g^{(n+1)} - g^{(n)}] \geq 0 \quad (53)$$

Following Eq. (5), the difference $[g^{(n+1)} - g^{(n)}]$ can be written as

$$\begin{aligned} [g^{(n+1)} - g^{(n)}] &= \sum_{i=1,n} [h^{(2)}(i, n+1)] + h^{(n+1)} \\ &\quad + \sum_Q \left\{ \prod [h^{(p)}(i_1, i_2, \dots, i_p)] \right\} \end{aligned} \quad (54)$$

where the sum $\sum_{Q'}$ runs over all the partitions Q' of the set $(1, 2, \dots, n + 1)$ in distinct and nonoverlapping subsets (i_1, i_2, \dots, i_p) , which cannot be obtained from the set $(1, 2, \dots, n)$, and because we have isolated both $h^{(n+1)}$ and the sum of the $h^{(2)}$ terms, the products in (54) include at least two factors $[h^{(p_1)}h^{(p_2)}]$ with $p_1, p_2 \geq 2$. Moreover, at least one of the subsets involved in each partition Q' includes the point $(n + 1)$ because none of the partitions Q' can be deduced from the set $(1, 2, \dots, n)$.

Now we get an upper bound for $\prod [h^{(p)}(i_1, i_2, \dots, i_p)]$. By using Eq. (52), we know that the leading terms of the sum $\sum_{Q'}$ corresponds to the sum of the products $[h^{(2)}(r_{ij}) h^{(2)}(r_{mk})]$ where $n + 1$ is one of the points (i, j, m, k) ; therefore the last term of (54) is majored according to

$$\left\{ \sum_{p'} \prod [h^{(p)}(i_1, i_2, \dots, i_p)] \right\} \leq Ch^{(2)}(r_{\min}) \sum_{i=1, n} [h^{(2)}(i, n + 1)] \quad (55)$$

where C is a constant, and r_{\min} is the smallest distance between particles of the set $(1, 2, \dots, n + 1)$, which, in any case, is at least equal to α . Then, from (52) we know that $h^{(n+1)}$ is small compared to $h^{(2)}(r_{\max})$ since $n + 1 \geq 3$. As a result, we get

$$[g^{(n+1)} - g^{(n)}] = \sum_{i=1, n} [h^{(2)}(i, n + 1)] + \dots \quad (56)$$

for any configuration of the $n + 1$ points, involving up to two length scales if all the distance are very large compared to the molecular length α . Finally, because of the positive sign of the compressibility and because we expect a monotonous behavior for $h^{(2)}(r \geq \sigma)$,⁽¹⁵⁾ we have $h^{(2)}(r \geq \alpha) > 0$ and we conclude from (56)

$$[g^{(n+1)} - g^{(n)}] > 0 \quad (57)$$

It remains to determine the range of validity of (57); in other words, we have to specify what is a "large" distance or equivalently what is the minimum value of α . We emphasize that our analysis, especially the estimation given in Eq. (51), relies upon the argument that we can estimate the value (in the sense of its range) of a graph $G(1, 2, \dots, p)$ from its dimension when only one length scale is involved in the distances r_{ij} , $i, j = 1, p$. This is used for subgraphs of $h^{(p)}$ and we thus have to verify that we deal with a range of distances where the correct dimensional behavior of integrals of $h^{(p)}$ is reached. We start from Eq. (21) and we see that we can deduce two regimes according on whether the first or the second term dominates. In the framework of the algebraic regime of $h^{(p)}$, Eq. (31a), we have

$$\rho \partial(h^{(n-1)})/\partial \rho \approx h^{(n-1)} \sum_{(i, j)} (r_{ij}/\xi)(\sigma/\xi)^{-d_d} \quad (58)$$

If this term dominates, in the l.h.s. of (21), we get

$$\int h^{(n)} d[n] \approx [(\xi/\sigma)^{d-d_\phi}] h^{(n-1)} \sum_{(i,j)} (r_{ij}/\xi) \tag{59a}$$

which is easily seen to be in agreement with the dimensional behavior of the integral over $n - 1$ coordinates of $h^{(n)}$. This means that in this case, the behavior of $h^{(n)}$ with respect to a dilatation of all the distances corresponds to its dimension. On the other hand, if the second term dominates, then we get

$$\int h^{(n)} d[n] \approx [(\xi/\sigma)^{d-2d_\phi}] h^{(n-1)} \tag{59b}$$

and in contrast to the preceding case, this integral is not in agreement with the dimension of $h^{(n)}$, which means that the integral of $h^{(n)}$ on the $n - 1$ coordinates performed in this range of distances is not indicative of the result for the integral performed in a volume ξ^d , and that the behavior of $h^{(n)}$ with respect to a dilatation of all the distances cannot be obtained from its dimension. Clearly, then, (51) is no longer satisfied. Therefore our criterion is that the distances are such that the derivative given by (56) is much larger than $h^{(n-1)}$ and thus α satisfies

$$\alpha/\xi \geq (\sigma/\xi)^{d_\phi} \tag{60}$$

Notice that the second region, as can be seen from (59b), corresponds to the range of validity of the superposition approximation: $n - 1$ particles are in a “small” volume centered on \mathbf{r}_0 and the main contribution to the integral over the n th one is obtained for large r_{0n} distances where $h^{(n)} \approx h^{(2)}(r_{0n}) h^{(n-1)}(1, 2, \dots, n - 1)$. The volume in which the $n - 1$ particles are enclosed must be smaller than $[\xi(\sigma/\xi)^{d_\phi}]^d$.

Finally, if we assume that the conformal invariance is satisfied by $h^{(3)}$, then, given the corresponding result for $h^{(3)}$ (see Appendix B), namely that it is a monotonous function of all the distances, and because $H^{(3)} < 0$ we get the equivalent of the GHS inequality, which reads

$$h^{(3)}(1, 2, 3) < 0 \tag{61}$$

5. CONCLUSION

In conclusion, we emphasize the following points. First, the present work takes place neither within framework of renormalization group theory^(2, 3, 22, 23) nor within the renormalization theory of the field-theoretic

approach to critical phenomena.^(4,5) Indeed, our purpose is not to provide a way to deduce the critical behavior of fluids. Conversely, we have assumed the existence of a critical point and our starting point is on the one hand the phenomenological equation of state of the critical isotherm characterized by the critical exponent δ and on the other hand the asymptotic form of the two-body correlation function and the associated Fisher critical exponent, η . The values δ and η are assumed to be known. The purpose of this work was then to deduce the behavior of the n -body total correlation functions, which are both actual physical quantities (and not correlation functions deduced from an effective Landau-like Hamiltonian) and the usual tools for liquid-state physics. We emphasize that the correlations we deal with correspond to the spatial fluctuations of the actual density and therefore have a clear physical meaning.

Concerning the GKS inequalities, the difference from the Ising model (or the ϕ^4) theory is the following. The GKS inequalities are neither satisfied in all space nor for each thermodynamic state, as is the case for the Ising model, but only for large distances and in the close vicinity of the critical point. Moreover, they do not result from a simple convexity condition as is the case in the Ising model. Therefore a careful analysis of the correlation functions must be performed *after* the critical equation of state has been stated. This analysis leads us to the estimation of the total n -body correlation function, Eq. (52), which can be considered as the important result of this work, the GKS inequalities being then a consequence of this estimation. Moreover, we had to consider two length scales in the distances involved in the set of points $\{r_{ij}\}$ and we found the minimum length scale for the GKS inequalities to be satisfied. This appears to be an attempt to go beyond the regime where the usual dimensional analysis is valid.

APPENDIX A

In this appendix we analyze the representation of some graphs using only the node $V^{(3)}$, which is, moreover, replaced by its leading contribution, $c_1^{(3)}$. This is what we called in the text the " S_3 " representation. As an example, we have the graphs of $h_\xi^{(n)}$, where all the root points end $h^{(2)}$ bonds, which are connected to the $c_1^{(3)}$ function. An example is the S_3 representation of $h^{(5)}$ shown in Fig. 4. It is easy to see that the graphs of the S_3 representation of $h_\xi^{(n)}$ include exactly $n-2$ functions $c_1^{(3)}$ and $2n-3$ functions $h^{(2)}$; in other words, these graphs can be built up using the function $s^{(3)}$, defined as the convolution of a $c_1^{(3)}$ function with two $h^{(2)}$ bonds, as displayed in Fig. 7, and a supernumerary $h^{(2)}$ bond. One can check that the dimension of the S_3 representation of $h^{(n)}$ (which is the dependence with respect to ξ of the integral of $h^{(n)}$ over $n-1$ coordinates) is the same

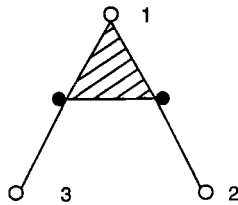


Fig. 7. Representation of the $s^{(3)}$ function. The hatched subgraph is a $c^{(3)}$ function and the lines are $h^{(2)}$ bonds.

as that of $h^{(n)}$. Moreover it is important to notice that one constructs the S_3 representation of $h^{(n)}$ whatever the value of n ; this is not the case if we consider, for instance, the S_4 representation where the use of only the node $V^{(4)}$ is not sufficient to describe $h^{(n)}$ for odd n . From the particular topology of the S_3 representation of $h^{(n)}$, we can easily deduce that of the graphs characterizing the groups of localized points, denoted G_i in Section 3. Indeed, a group i including $p(i)$ points localized in a volume α^d centered on \mathbf{R}_i is characterized by a graph G_i of $h^{p(i)+1}$ amputated of one $h^{(2)}$ bond; the S_3 representation of G_i , denoted by $S_3(G_i)$, is therefore built up from $s^{(3)}$ functions only (this is shown in Fig. 8. The properties of this S_3 representation are similar to those of the S_3 representation of $h^{(n)}$: the dimension is conserved, and it can be constructed for each value of $p(i)$. Notice that when we deal with a group i of localized points $\{k_1, k_2, \dots, k_{p(i)}\}$ of the set $\{1, 2, \dots, n\}$ we consider only one length scale, α , and then the dimension of the graph G_i is meaningful. Furthermore, from Appendix B, knowledge of the three-body correlations and related integrals is sufficient to show that this is indeed so. Finally, let us consider the S_3 representation of $h^{(n)}$ for a

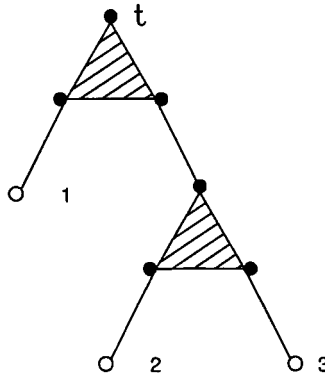


Fig. 8. Example in the S_3 representation of a graph G_i defined in section 3. G_i is connected to the rest of the graph via the unique "trailer" point t . The hatched subgraph is a $c^{(3)}$ function and the lines are $h^{(2)}$ bonds.

set of points separated into p groups. When the graphs G_i of the groups are removed, the remaining graph which connects the groups together, say K_p , includes the above-mentioned supernumerary $h^{(2)}$ bond since this is not used in the subgraphs G_i . Then we recover in this particular case the fact that the subgraph depending on the largest length scale, and connecting the groups together, K_p , is nothing else than a graph of $h^{(p)}$ in the S_3 representation, since K_p is built up from $s^{(3)}$ functions and a supernumerary $h^{(2)}$ bond.

APPENDIX B. THREE-BODY FUNCTIONS ACCORDING TO CONFORMAL INVARIANCE

B1. Expressions of $h^{(3)}$ and $c^{(3)}$

We first deduce the three-body correlation functions $c^{(3)}$ and $h^{(3)}$ using the conformal invariance hypothesis. This hypothesis is very likely to be satisfied since at the C.P. our system fulfils the necessary conditions given, for instance, by Cardy⁽¹⁹⁾: scale invariance, translational invariance, rotational invariance, and short-range interactions. The important property that we use is that three arbitrary points $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3$ can be mapped by a conformal transformation into three preassigned points $\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}'_3$. Then the explicit spatial dependence of a correlation function $f_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ satisfying the conformal invariance is totally determined by the rescaling factors of the transformation since $f_3(\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}'_3)$ is the same for any initial set $(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ and is thus a constant. Then, from refs. 19 and 20 we have

$$f_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = F_3[(r_{12})^{x_1+x_2-x_3} (r_{23})^{x_2+x_3-x_1} (r_{13})^{x_3+x_1-x_2}]^{-1} \quad (\text{B1})$$

where the x_i are the scaling exponents. In our case, $f_3 = c^{(3)}$ or $h^{(3)}$ is totally symmetric with respect to the permutations of the points and accordingly $x_1 = x_2 = x_3 = x$. Then we get the value of x from the transformation law of f_3 through a global dilatation (corresponding to the global scale invariance) which is obtained from the dependence of the integral $H^{(3)}$ (or $C^{(3)}$) with respect to x . We get $x = d_\phi$ for $h^{(3)}$ and $x = d'_\phi$ for $c^{(3)}$ and the final result is

$$h^{(3)} = H_3(r_{12}r_{13}r_{23})^{-d_\phi}, \quad c^{(3)} = C_3(r_{12}r_{13}r_{23})^{-d'_\phi} \quad (\text{B2})$$

We emphasize that the important result here is that the function F_3 is simply a dimensionless constant, which is then taken equal to 1. It is worth mentioning that this result can be obtained at least for the function $h^{(3)}$, from the Baxter equation relating the integral of $h^{(3)}$ over \mathbf{r}_3 to $h^{(2)}$, Eq. (1),

by exploiting the divergence of the integral at the C.P. without referring to the hypothesis of conformal invariance. We see therefore that this hypothesis is in agreement with the existence of the Baxter equation.

B2. Expression of $s^{(3)}$

The S_3 representation of a graph, where only the node $V^{(3)}$ is involved, necessitates two elements: the function $h^{(2)}$ and the function $s^{(3)}$, which is a convolution of a $c^{(3)}$ function with two $h^{(2)}$ bonds (see Appendix A). Here we analyze this function $s^{(3)}$ in the framework of conformal invariance. We consider the function $s(1, 2, 3)$ such that the point labeled 1 is the root point connected to the function $c^{(3)}$ (see Fig. 7). In order to deduce the function $s^{(3)}$ we cannot use the preceding route, since this function is not totally symmetric with respect to the permutation of the points, and we must consider the behavior of the function $s(1, 2, 3)$ with respect to a conformal transformation by using its integral form and then by imposing that $s(1, 2, 3)$ is invariant.

We consider a special transformation characterized by an infinitesimal vector α . The component l of the vector \mathbf{r} , r_l , is transformed into the component r'_l of the vector \mathbf{r}' according to

$$r'_l = r_l + \alpha_l r^2 - 2(\alpha \cdot \mathbf{r}) r_l \tag{B3a}$$

At order α , the distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ transforms according to

$$r'_{ij} = r_{ij}(1 - \alpha(r_i + r_j)) \tag{B3b}$$

and the Jacobian of the transformation is

$$d\mathbf{r}' = (1 - 2(\alpha \cdot \mathbf{r}))^d d\mathbf{r} = (1 - 2d(\alpha \cdot \mathbf{r}) + O(\alpha^2)) d\mathbf{r} \tag{B3c}$$

The function s is given by

$$s(1, 2, 3) = \int c(r_{1i}, r_{1j}, r_{ij}) h(r_{i2}) h(r_{j3}) d\mathbf{r}_i d\mathbf{r}_j$$

and thus we get

$$\begin{aligned} s(1', 2', 3') &= s(1, 2, 3) + \int c(r_{1i}, r_{1j}, r_{ij}) h(r_{i2}) h(r_{j3}) \\ &\quad \times (-2d\alpha \cdot (\mathbf{r}_i + \mathbf{r}_j)) d\mathbf{r}_i d\mathbf{r}_j \\ &\quad + \int [\delta c(r_{1i}, r_{1j}, r_{ij}) h(r_{i2}) h(r_{j3}) \\ &\quad + c(r_{1i}, r_{1j}, r_{ij}) \delta h(r_{i2}) h(r_{j3}) + h(r_{i2}) \delta h(r_{j3})] d\mathbf{r}_i d\mathbf{r}_j \tag{B4} \end{aligned}$$

where $\delta f(r_{ij})$ means $[f(r'_{ij}) - f(r_{ij})]$; we have

$$[f(r'_{ij}) - f(r_{ij})] = (\partial f(r_{ij})/\partial r_{ij}) \delta r_{ij} = r_{ij}(\partial f(r_{ij})/\partial r_{ij})(-\alpha \cdot (\mathbf{r}_i + \mathbf{r}_j)) \quad (\text{B5})$$

where we have used (B3b). From (B3b), and by using the form of $h^{(2)}$ and of $c^{(3)}$, Eq. (B2), we get

$$\begin{aligned} \delta s(1, 2, 3) &= s(1, 2, 3)[d'_\phi \alpha \cdot (\mathbf{r}_1 + \mathbf{r}_2) + d'_\phi \alpha \cdot (\mathbf{r}_1 + \mathbf{r}_3) \\ &\quad + (2d_\phi - d'_\phi) \alpha \cdot (\mathbf{r}_3 + \mathbf{r}_2)] \\ &= -s(1, 2, 3)[-d'_\phi \alpha \cdot (\mathbf{r}_1 + \mathbf{r}_2) - d'_\phi \alpha \cdot (\mathbf{r}_1 + \mathbf{r}_3) \\ &\quad + (d - 3d_\phi) \alpha \cdot (\mathbf{r}_3 + \mathbf{r}_2)] \end{aligned} \quad (\text{B6a})$$

where we have used the relation d_ϕ , d'_ϕ , and d . On the other hand, if the function s is invariant under conformal transformation, we must have^(19,20)

$$\delta s(1, 2, 3) = -s(1, 2, 3) \sum_{1 \leq i < j \leq 3} [r_{ij}(\partial s(r_{ij})/\partial r_{ij}) \alpha \cdot (\mathbf{r}_i + \mathbf{r}_j)] \quad (\text{B6b})$$

From (B6a) and (B6b) we get

$$\begin{aligned} r_{12}(\partial s(r_{12})/\partial r_{12}) &= r_{13}(\partial s(r_{13})/\partial r_{13}) = -d'_\phi \\ r_{23}(\partial s(r_{23})/\partial r_{23}) &= d - 3d_\phi \end{aligned} \quad (\text{B7})$$

and finally

$$s(1, 2, 3) = S(r_{23})^{d-3d_\phi} (r_{12}r_{13})^{-(d-d_\phi)} \quad (\text{B8})$$

where S is a constant.

B3. Properties of $s^{(3)}$

In the dimensional analysis, $s^{(3)}$ behaves as $s^{(3)} = (1/\xi)^{d+d_\phi} s_\xi^{(3)}$, where $s_\xi^{(3)}$ represents the function $s^{(3)}$ in which the lengths are in ξ units. It is easy to verify that this result also can be obtained from the definition of $s^{(3)}$ and the dimension of its ingredients.

In the expression of $s^{(3)}$, the quantity $d - 3d_\phi = (-d + 6 - 3\eta)/2$ is positive because in Section 2.2 we established that $\eta < (4 - d)/2$. Thus, in the expression of $s^{(3)}$ the numerator increases with r_{23} ; however, $s^{(3)}$ remains finite, as shown in the following limiting cases. For a configuration in which $r_{12} \approx r_{13} \approx r_{23}$ then $s^{(3)} \approx (1/r_{23})^{d+d_\phi}$, it is noteworthy that the exponent is the same as the one in the dimensional analysis. Let us now consider configurations where two length scales are introduced. For example, the case where $r_{12} \approx r_{13} \approx \xi$ and $r_{23} \approx \alpha$ with $\alpha \ll \xi$, the dimensional

analysis, which does not take into account the constraint that 2 and 3 are close to each other, would give the above result $s^{(3)} \approx (1/\xi)^{d+d_\phi}$. The correct result is $s^{(3)} \approx \alpha^{d-3d_\phi} \xi^{-2(d-d_\phi)}$, which is used in Section 3.3. Note that this result is as though the constraint that 2 and 3 are close had the effect of forcing the field points of $c^{(3)}$ to remain in a α^d volume centered around root point 1. This is related to another configuration of interest, where this time $r_{13} \approx r_{23} \approx \xi$ and $r_{12} \approx \alpha$; the result is $s^{(3)} \approx \alpha^{-d+d_\phi} \xi^{-2d_\phi}$. We find that this result is coherent with the rule given in Section 3.3 according to which the field points give the main contribution when integrated in the vicinity of the corresponding group, in this case root points 1 and 2. These examples clearly show that the dimensional analysis, as expected, does not give the correct bound in a configuration where there are two different length scales.

B4. Integrals of $s^{(3)}$

In the estimation of the diagrams involved in the S_3 representation, we need to consider convolutions of $s^{(3)}$ functions. The integration volumes for each field point of $s^{(3)}$ can be judiciously partitioned when two length scales are involved; α and λ , with $\alpha \ll \lambda$, in a similar way to what has been presented in Section 4.3 for the analysis of Fig. 5. We will take $\lambda \approx \xi$, but the results can be generalized to any large λ . We give here the integral of $s^{(3)}$ in the relevant cases. We define $i(r_{23})$ by

$$i(r_{23}) = \int s(1, 2, 3) d\mathbf{r}_1 = \int S[(r_{23})^{d-3d_\phi} (r_{12}r_{13})^{-(d-d_\phi)}] d\mathbf{r}_1 \quad (B9)$$

We split the integration range into a volume α^d and the remaining volume $\xi^d - \alpha^d$; the integral $i(r_{23})$ will be performed over a volume V , which can be restricted to α^d . In what follows $I(x_{12}, x_{13}, x_{23})$ is the integral $i(r_{23})$ written in reduced variables $x_{ij} = r_{ij}/\alpha$ or r_{ij}/ξ , such that x_{ij} is bounded by 1; the choice for α or ξ is relative to whether the integration volume V is restricted to α^d around root points 2 or 3. We make the assumption that the lower bound for x_{ij} , namely the σ scale, introduces no singularity. We now examine different situations.

(a) $r_{23} \approx \xi$; $V = \xi^d - \alpha^d$:

$$i_a(r_{23}) \approx SI(x_{23}) \xi^{-d_\phi} \approx \xi^{-d_\phi} \quad (B10)$$

(b) $r_{23} \approx \xi$; $V = \alpha^d$ centered on the point 2 (or the point 3):

$$\begin{aligned} i_b(r_{23}) &\approx SI(r_{13}/\alpha, r_{12}/\xi, r_{23}/\xi) \alpha^{d_\phi} \xi^{-2d_\phi} \\ &\approx \alpha^{-d_\phi} (\xi/\alpha)^{-2d_\phi} \end{aligned} \quad (B11)$$

(c) $r_{23} \approx \xi$; $V = \alpha^d$ located at a distance ξ from both points 2 and 3:

$$\begin{aligned} i_c(r_{23}) &\approx SI(r_{13}/\xi, r_{12}/\xi, r_{23}/\xi) \alpha^d \xi^{-d_\phi} \\ &\approx \xi^{-d_\phi} (\xi/\alpha)^{-d} \end{aligned} \tag{B12}$$

(d) $r_{23} \approx \alpha$; $V = \alpha^d$ centered in the neighborhood of both points 2 and 3:

$$\begin{aligned} i_d(r_{23}) &\approx SI(r_{13}/\alpha, r_{12}/\alpha, r_{23}/\alpha) \alpha^{-d_\phi} \\ &\approx \alpha^{-d_\phi} \end{aligned} \tag{B13}$$

(e) $r_{23} \approx \alpha$; $V = \xi^d - \alpha^d$:

$$\begin{aligned} i_c(r_{23}) &\approx SI(r_{23}/\alpha) \alpha^{d-3d_\phi\xi^{-d}+2d_\phi} \\ &\approx \alpha^{-d_\phi} (\xi/\alpha)^{-d+2d_\phi} \end{aligned} \tag{B14}$$

(f) $r_{23} \approx \alpha$; $V = \alpha^d$ centered at a distance ξ from 2 and 3:

$$\begin{aligned} i_f(r_{23}) &\approx SI(r_{13}/\xi, r_{12}/\xi, r_{23}/\alpha) \alpha^{2d-3d_\phi\xi^{-2d}+2d_\phi} \\ &\approx \alpha^{-d_\phi} (\xi/\alpha)^{-2(d+d_\phi)} \end{aligned} \tag{B15}$$

Now, because of the convolution involving the various $s^{(3)}$ functions, the integration volumes are related to one another; the points attached to the $h^{(2)}$ bonds of an $s^{(3)}$ function are possibly also attached to a $c_1^{(3)}$ of another function. An element Q which is an element of the partition of the integration volume then corresponds to a set of i_i , $i \in \{a, b, \dots, f\}$, estimates. The estimation of S_3 is then typically written

$$S_3 = \sum_Q \left\{ \prod_{i \in \{a, b, \dots, f\}} i_i \right\} \tag{B16}$$

It is beyond the scope of this article to investigate the S_3 representation for any $h^{(n)}$ and any possible partition of the root points into group configurations. Let us point out that the interest of the S_3 representation is that it is possible in this particular case to verify the rules given in Section 3.3. First, the leading contribution comes from integration of $s^{(3)}$ performed in the vicinity of the corresponding group, as can be seen from i_i integrals (the largest one being i_d). Second, the leading graphs are the ones where the minimal number of $s^{(3)}$ functions are shared between different groups.

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