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Multi-particle critical correlations

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We study the role of multi-particle spatial correlations in the appearance of a liquid–vapour critical point. Our analysis is based on the exact infinite hierarchy of equations relating spatial integrals of $(k+1)$-particle correlations to the k-particle ones and their derivatives with respect to the density. Critical exponents corresponding to generalised compressibility equations resulting from the hierarchy are shown to grow linearly with the order of correlations. We prove that the critical behaviour requires taking into account correlation functions of arbitrary order. It is however only a necessary condition. Indeed, approximate closures of the hierarchy obtained by expressing higher order correlations in terms of lower order ones (Kirkwood's superposition approximation and its generalisations) turn out to be inconsistent with the critical behaviour.

Keywords: spatial correlations; critical point; generalised compressibility equations

1. Introduction

Phase transitions are accompanied by qualitative changes in the behaviour of correlation functions. In the case of an approach toward the liquid–vapour critical point along the critical isotherm, the monotonic exponentially damped decay of pair correlations between the density fluctuations turns into a power-like non-integrable decay leading to a divergence of the isothermal compressibility. This important relation between the behaviour of correlations and the appearance of singularities in the thermodynamic functions suggests that also higher order correlations carry a similar information. It is the aim of this study to elucidate the fundamental role of multi-particle correlations for the appearance of a critical point and the related singularities.

In order to study this question, we use the infinite hierarchy of equations derived by Baxter [1]. The hierarchy relates the spatial integrals of $(k+1)$-particle correlation functions to k-particle correlations and their derivatives with respect to the density, for $k = 2, 3, \ldots$ (Section 2). Our choice is dictated by the fact that the hierarchy is valid in any dimension and for any potential of interaction. It reflects thus the essential structure of the equilibrium Gibbs ensemble.

There are two kinds of questions which we study and answer in the present paper. The first concerns the evaluation of critical exponents characterising the divergence of spatial integrals of multi-particle correlation functions. The discussion of this topic is presented in Section 4.

The second type of problems focuses on the criteria for the occurrence of a critical point when an approximate closure of the hierarchy is adopted. For instance, we show that

it is necessary to take into account correlations of arbitrary order (Section 3). All multi-particle correlations play thus a crucial role in the appearance of a critical point.

A related question concerns the possibility of predicting a critical point within an approximation which expresses higher order correlation functions in terms of lower order ones. A well-known example is the Kirkwood superposition approximation (KSA) discussed in Section 5. It turns out that this approximation applied to the exact hierarchy yields a closed equation for the pair correlation function inconsistent with a critical behaviour [2]. In Section 6, we present arguments suggesting the impossibility of describing criticality even within generalised superposition approximations (GSA) where higher order correlation functions are approximated in terms of the lower order ones. The paper ends with concluding comments in Section 7.

2. Multi-particle correlation functions

Let us consider a fluid in equilibrium made of N particles in a volume V. The (reduced) k-particle density $n_k(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_k)$ is defined (in the canonical ensemble) as [3]

$$n_k(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_k) = \lim_{\infty} \frac{N!}{Q_N(N-k)!}$$
$$\times \int_V d\mathbf{r}_{k+1} \cdots \int_V d\mathbf{r}_N \, e^{-\beta \Phi_N(\mathbf{r}^N)}, \qquad (1)$$

where $\beta = 1/k_B T$ is the inverse temperature parameter, $\Phi_N(\mathbf{r}^N)$ is the potential energy (with the shorthand notation

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$r^N \equiv \{r_1, r_2, \ldots, r_N\}$) and

$$Q_N = \lim_\infty \int_V dr_1 \cdots \int_V dr_N \, e^{-\beta \Phi_N(r^N)} \qquad (2)$$

is the configuration integral. In Equations (1) and (2),

$$\lim_\infty \equiv \lim_{V \to \infty, N/V = n = \text{const}} \qquad (3)$$

denotes the thermodynamic limit. Invariance of the potential energy $\Phi_N(r^N)$ under spatial translation implies that the same property holds for the particle densities, i.e., $n_k(r_1, r_2, \ldots, r_k) = n_k(r_1 + a, r_2 + a, \ldots, r_k + a)$ with an arbitrary vector a.

The particle densities n_k depend on the temperature T and on the number density n of the system. In 1964, Baxter [1] proved an elegant hierarchy relating the derivative of n_k with respect to density with an integral of n_{k+1}, namely

$$\left(\chi_T n \frac{\partial}{\partial n} - k \right) n_k(1, \ldots, k) = \int d(k+1)$$
$$\times \, [n_{k+1}(1, \ldots, k, k+1) - n n_k(1, \ldots, k)], \quad (4)$$

where

$$\chi_T(n, T) = k_B T \left(\frac{\partial n}{\partial p} \right)_T \qquad (5)$$

is the isothermal compressibility multiplied by $n k_B T$, p being the pressure. In Equation (4), the shorthand notations $n_k(1, \ldots, k) \equiv n_k(r_1, \ldots, r_k)$ and $d(k+1) \equiv dr_{k+1}$ have been introduced.

In an ideal gas, $\Phi_N(r^N) = 0$ and thus $n_k^{\text{id}} = n^k$. In that trivial case, Equation (4) yields $\chi_T^{\text{id}} = 1$, as expected. In general, however, the interactions among particles induce spatial correlations and therefore $n_k \neq n^k$. Consequently, one can introduce the k-particle distribution function $g_k(1, 2, \ldots, k)$ as [3]

$$n_k(1, 2, \ldots, k) = n^k g_k(1, 2, \ldots, k). \qquad (6)$$

It is also convenient to define the correlation functions h_k by the cluster expansion [4]

$$g_1(1) = h_1(1) = 1, \qquad (7a)$$

$$g_2(1, 2) = h_1(1) h_1(2) + h_2(1, 2), \qquad (7b)$$

$$g_3(1, 2, 3) = h_1(1) h_1(2) h_1(3) + \mathbf{3} h_1(1) h_2(2, 3)$$
$$+ h_3(1, 2, 3), \qquad (7c)$$

$$g_4(1, 2, 3, 4) = h_1(1) h_1(2) h_1(3) h_1(4)$$
$$+ \mathbf{6} h_1(1) h_1(2) h_2(3, 4) + \mathbf{3} h_2(1, 2) h_2(3, 4)$$
$$+ \mathbf{4} h_1(1) h_3(2, 3, 4) + h_4(1, 2, 3, 4), \quad (7d)$$

and so on. Here, a numerical coefficient in boldface means that there exist a number of analogous terms (except for particle labelling) to the indicated canonical term. Note that, even though the one-particle correlation function h_1 is equal to unity, it is included in Equations (7b)–(7d) to make the general cluster structure clear. Expressed in terms of the correlation functions, the hierarchy (4) becomes [1]

$$\left(\chi_T n \frac{\partial}{\partial n} - k \right) n^k h_k(1, \ldots, k)$$
$$= n^{k+1} \int d(k+1) \, h_{k+1}(1, \ldots, k, k+1). \quad (8)$$

In particular, setting $k = 1$ in Equation (8), we obtain

$$\chi_T - 1 = n \int d2 \, h_2(1, 2). \qquad (9)$$

This is nothing else but the well-known compressibility equation, conventionally derived within the grand canonical ensemble [3].

Our main goal is to exploit Equation (8) for $k \geq 2$. To that end, let us define the correlation integrals

$$I_k(n, T) \equiv n^k \int d2 \cdots \int dk \, h_k(1, 2, \ldots, k). \qquad (10)$$

Note that, because of translational invariance, I_k is independent of r_1. Integrating over the coordinates of particles $2, \ldots, k$ in both sides of Equation (8), one has

$$I_{k+1} = \mathcal{L}_k I_k, \qquad (11)$$

where the operator $\mathcal{L}_k$ is

$$\mathcal{L}_k \equiv \chi_T n \partial_n - k. \qquad (12)$$

By iteration,

$$I_{k+1} = \mathcal{L}_k \mathcal{L}_{k-1} \cdots \mathcal{L}_2 n(\chi_T - 1), \quad (k \geq 2). \qquad (13)$$

Equations (11) and, equivalently, (13) define *generalised compressibility equations*.

Equation (13) can be written in an alternative equivalent form. This follows immediately from the identity

$$\chi_T n \frac{\partial}{\partial n} = k_B T n \frac{\partial n}{\partial p} \frac{\partial}{\partial n}$$
$$= k_B T \frac{\partial}{\partial \mu} = z \frac{\partial}{\partial z}, \qquad (14)$$

where all partial derivatives are calculated at constant temperature, μ denotes the chemical potential, $z = e^{\beta \mu}$ is the fugacity and the thermodynamic relation $n = \partial p / \partial \mu$ has been used. Thus, Equation (13) becomes

$$I_{k+1} = (z \partial_z - k) \cdots (z \partial_z - 2)(z \partial_z - 1) n. \qquad (15)$$

The formal expansion of density as a series in powers of fugacity is [5]

$$n(T, z) = \sum_{\ell=1}^{\infty} c_\ell(T) z^\ell, \qquad (16)$$

where each coefficient c_ℓ is proportional to the sum of all the cluster diagrams (reducible and irreducible) with ℓ points. Inserting Equation (16) into Equation (15) one can easily obtain

$$I_{k+1}(T, z) = \sum_{\ell=k+1}^{\infty} \frac{(\ell-1)!}{(\ell-k-1)!} c_\ell(T) z^\ell. \qquad (17)$$

Therefore, seen as a function of temperature and fugacity (grand canonical ensemble), the correlation integral I_{k+1} is of order z^{k+1}.

To illustrate the importance of the existence of multiparticle correlations as measured by the functions h_k, in the next section we analyse the solution of the generalised compressibility Equation (15) resulting from the approximate closure $I_{k+1} = 0$.

3. Solution of the generalised compressibility equation by neglecting correlations

As said above, if one neglects pair correlations ($h_2 = 0$), Equation (9) yields the ideal-gas result $\chi_T^{id} = 1$. An interesting problem is to find out what happens if $h_2, \ldots, h_{k_0}$ are retained but $(k_0 + 1)$-particle correlations are neglected, i.e., $h_{k_0+1} = 0$. In that case, Equation (15) with $I_{k_0+1} = 0$ becomes a linear equation whose general solution is *polynomial*,

$$n(T, z) = \sum_{\ell=1}^{k_0} c_\ell(T) z^\ell. \qquad (18)$$

Thus, the exact series (16) is truncated after $\ell = k_0$. The (reduced) isothermal compressibility corresponding to the approximation (18) is

$$\chi_T(T, z) = k_B T \frac{\partial n}{\partial p} = n^{-1} z \partial_z n = n^{-1} \sum_{\ell=1}^{k_0} \ell c_\ell(T) z^\ell$$

$$= 1 + n^{-1} \sum_{\ell=2}^{k_0} (\ell-1) c_\ell(T) z^\ell. \qquad (19)$$

Noting again that $\partial_\mu p = \beta z \partial_z p = n$, the pressure reads

$$\beta p(T, z) = \sum_{\ell=1}^{k_0} \frac{c_\ell(T)}{\ell} z^\ell. \qquad (20)$$

Taking into account that $\beta \mu^{id} = \ln[n\Lambda^d(\beta)]$, where $\Lambda(\beta)$ is the thermal de Broglie wavelength and d is the dimensionality of the system, it follows that $c_1 = \Lambda^{-d}$.

The remaining coefficients $\{c_2, c_3, \ldots, c_{k_0}\}$ are directly related to the virial coefficients $\{B_2, B_3, \ldots, B_{k_0}\}$. For instance, $c_2/c_1^2 = -2B_2$, $c_3/c_1^3 = \frac{3}{2}\left(4B_2^2 - B_3\right)$, $c_4/c_1^4 = -\frac{4}{3}\left(16B_2^3 - 9B_2 B_3 + B_4\right), \ldots$.

It remains to find the positive real root of the polynomial (18) as a function of the density n and insert the result into Equation (20) to obtain the equation of state. This can be done analytically only if $k_0 \leq 4$. In particular, in the case $k_0 = 2$ (neglect of triplet correlations) one simply has

$$\chi_T(n, T) = 2 - \frac{1 - \sqrt{1 - 8B_2(T)n}}{4B_2(T)n}, \qquad (21a)$$

$$Z(n, T) \equiv \frac{p}{nk_B T} = \frac{1}{2} + \frac{1 - \sqrt{1 - 8B_2(T)n}}{8B_2(T)n}. \qquad (21b)$$

The equation of state (21b) is real-valued only if $n \leq 1/8B_2(T)$. At $n = 1/8B_2(T)$, one has $Z = \frac{3}{2}$ and $\chi_T = 0$. From Equation (21b), one can obtain higher virial coefficients in terms of B_2 as

$$B_j = \frac{(2j-3)!!}{j!} 2^{2j-3} B_2^{j-1}, \quad j \geq 2. \qquad (22)$$

In the more general case, $k_0 \geq 3$, Equations (18) and (20) allow us to estimate B_{k_0+1} and higher virial coefficients from the knowledge of $\{B_2, B_3, \ldots, B_{k_0}\}$.

As a test of the reliability of the equation of state, let us study the prediction of B_{k_0+1} for (three-dimensional) hard spheres as obtained from the approximation $h_{k_0+1} = 0$ when the *exact* values [6–13] of $\{B_2, B_3, \ldots, B_{k_0}\}$ are used. The results for $k_0 + 1 = 3$–8 are displayed and compared with the exact coefficients B_{k_0+1} in Table 1. As can be seen, neglecting h_{k_0+1} in Equation (13) and imposing the virial coefficients $\{B_2, B_3, \ldots, B_{k_0}\}$ yield an extremely poor prediction of the next virial coefficient B_{k_0+1}. The predicted coefficients alternate in sign and are progressively much larger (in absolute value) than the known exact ones. The poor performance of the approximation defined by Equations (18) and (20) for hard spheres is confirmed by Figure 1, where the equation of state is plotted for a sequence of values of $k_0 + 1$. The results suggest that the sequence of approximations $\{h_3 = 0, h_4 = 0, \ldots\}$ has an asymptotic character

Table 1. Comparison between the first few values of the ratio $B_{k_0+1}/B_2^{k_0}$ for hard spheres as obtained from the approximation $h_{k_0+1} = 0$ and the exact values [6–13].

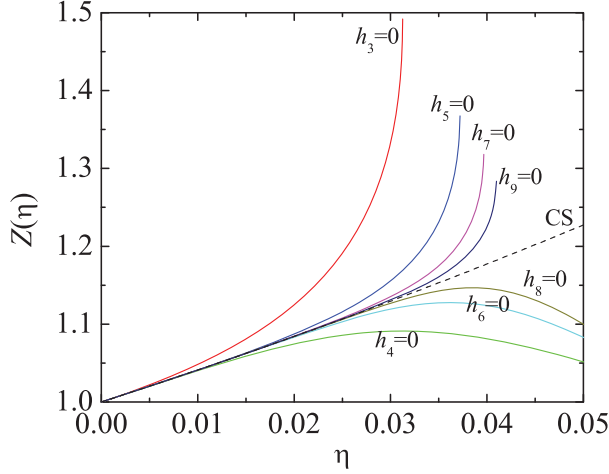| $k_0 + 1$	$h_{k_0+1} = 0$	Exact
3	4	0.62500
4	−10.375	0.28695
5	33.985	0.11025
6	−109.15	0.03888
7	356.96	0.01302
8	−1181.3	0.00418

Figure 1. Compressibility factor Z as a function of the packing fraction η for (three-dimensional) hard spheres as obtained from Equation (13) with the closures $h_3 = 0, \ldots, h_8 = 0$. The dashed line represents the Carnahan–Starling equation of state [3,14].

only. It is interesting to note that the curves corresponding to the approximations $h_{k_0+1} = 0$ with $k_0 + 1 =$ odd terminate with a branch point (where $\chi_T = 0$) at certain values of the packing fraction ($\eta = \frac{1}{32} \simeq 0.0313, 0.0372, 0.0397$ and 0.0410 for $h_3 = 0, h_5 = 0, h_7 = 0$ and $h_9 = 0$, respectively).

We now depart from the hard-sphere case and assume that the potential energy function Φ_N is such that a liquid–vapour critical point exists at a certain temperature $T = T_c$ and density $n = n_c$. A simple argument shows that an approximate theory which neglects completely correlations beyond some fixed order k_0 loses the possibility of describing such a critical point. The proof proceeds by *reductio ad absurdum* as follows. If a critical point exists, then the approximation (18) yields $n_c = \sum_{\ell=1}^{k_0} c_\ell(T_c) z_c^\ell$, where z_c is the fugacity at the critical point. Since $n_c =$ finite, one must have $z_c =$ finite and $c_\ell(T_c) =$ finite for $1 \le \ell \le k_0$. Consequently, according to Equation (19), $\lim_{n \to n_c, T \to T_c} \chi_T = n_c^{-1} \sum_{\ell=1}^{k_0} \ell c_\ell(T_c) z_c^\ell =$ finite. But this is in contradiction with the existence of a critical point where the isothermal compressibility diverges.

4. Multi-particle correlations near the critical point. Generalised critical exponents δ_k

Once we have shown the relevance of keeping multi-particle correlations in the generalised compressibility Equation (13), let us turn to the main topic of this work, namely the behaviour of the integrals I_k near the critical point.

We suppose again that a liquid–vapour critical point exists at $T = T_c$ and $n = n_c$. The singular behaviour of the relevant thermodynamic functions at criticality is characterised by the so-called *critical exponents* [15]. In particular, the critical exponent δ measures how the pressure p tends to its critical value p_c as the density n approaches its critical

value n_c along the critical isotherm $T = T_c$:

$$\frac{p - p_c}{n_c k_B T_c} \approx (\pm 1) B \left| \frac{n}{n_c} - 1 \right|^\delta, \quad T = T_c, \quad (23)$$

where B is a dimensionless critical amplitude and $(\pm 1) \equiv \text{sgn}(n - n_c)$, i.e., $+$ and $-$ correspond to the branches $n > n_c$ and $n < n_c$ of the critical isotherm, respectively. Since the critical isotherm must present an inflection point at the critical point, that is, $\partial^2 p / \partial n^2 |_c = 0$, one must have $\delta > 2$. The behaviour (23) implies that the (reduced) isothermal compressibility χ_T diverges at the critical point according to the law

$$\chi_T \approx A \left| \frac{n}{n_c} - 1 \right|^{-(\delta-1)}, \quad T = T_c, \quad (24)$$

where we have called $A \equiv 1/B\delta$. From Equation (9) it follows that

$$I_2 \equiv n^2 \int d2\, h_2(1, 2) \approx A n_c \left| \frac{n}{n_c} - 1 \right|^{-(\delta-1)}, \quad T = T_c. \quad (25)$$

The divergence of the integral I_2 at the critical point is directly linked to the development of long-range *pair* correlations.

It is physically expected that the clusters of three, four, five, ... particles are also highly correlated near the critical point in such a way that the generalised integrals I_k defined by Equation (10) diverge at criticality. In order to characterise this behaviour on the critical isotherm, let us define the *generalised* critical exponents δ_k by

$$I_k \approx (\pm 1)^k A_k n_c \left| \frac{n}{n_c} - 1 \right|^{-(\delta_k-1)}, \quad T = T_c. \quad (26)$$

In particular, $\delta_2 = \delta$ and $A_2 = A$. Equation (26) implies that

$$\partial_n I_k \approx -(\pm 1)^{k+1} (\delta_k - 1) A_k \left| \frac{n}{n_c} - 1 \right|^{-\delta_k}, \quad T = T_c. \quad (27)$$

Combining this with Equation (24),

$$\chi_T n \partial_n I_k \approx -(\pm 1)^{k+1} (\delta_k - 1) A_k A n_c \left| \frac{n}{n_c} - 1 \right|^{-(\delta_k+\delta-1)}, \quad T = T_c. \quad (28)$$

Clearly, $\chi_T n \partial_n I_k \gg k I_k$ near the critical point. Therefore, insertion of Equations (26) (with $k \to k+1$) and (28) into Equation (11) yields

$$\delta_{k+1} = \delta_k + \delta, \quad (29a)$$

$$A_{k+1} = -A A_k (\delta_k - 1). \quad (29b)$$

The solutions to the above recursion relations are

$$\delta_k = (k-1)\delta, \tag{30a}$$

$$A_k = (-1)^k A^{k-1}(\delta - 1)(2\delta - 1)\cdots[(k-2)\delta - 1]. \tag{30b}$$

It is instructive to rederive Equations (30) from Equation (15). Note first that the thermodynamic relation $n = \beta z \partial_z p$, together with Equation (23), yields

$$\frac{n}{n_c} - 1 \approx (\pm 1) B^{-1/\delta} \left| \frac{z}{z_c} - 1 \right|^{1/\delta}, \quad T = T_c. \tag{31}$$

This is equivalent to $(p - p_c)/n_c k_B T_c \approx (z/z_c - 1)$. At $T = T_c$ and for $n \approx n_c$, the most divergent term on the right-hand side of Equation (15) is $z_c^k \partial_z^k n$ and thus

$$I_{k+1} \approx z_c^k \partial_z^k n \approx n_c \frac{B^{-1/\delta}}{\delta} \frac{\Gamma\left(k - \delta^{-1}\right)}{\Gamma\left(1 - \delta^{-1}\right)} \left| \frac{z}{z_c} - 1 \right|^{1/\delta - k}$$
$$\approx (\pm 1)^{k+1} A^k n_c (-\delta)^{k-1} \frac{\Gamma\left(k - \delta^{-1}\right)}{\Gamma\left(1 - \delta^{-1}\right)} \left| \frac{n}{n_c} - 1 \right|^{-(k\delta - 1)}. \tag{32}$$

Comparison between Equations (26) (with $k \to k + 1$) and (32) yields $\delta_{k+1} = k\delta$ and $A_{k+1} = A^k(-\delta)^{k-1}\Gamma(k - \delta^{-1})/\Gamma(1 - \delta^{-1})$, in agreement with Equations (30).

Equations (30) are the basic results of this paper. Equation (30a) implies that, near the critical point, the correlation integral over all the coordinates of a cluster of k particles diverges with a critical exponent that increases *linearly* with k. As shown by Equation (32), this linear growth is a direct consequence of the exact formula (15). In addition, according to Equation (30b), the critical amplitude alternates in sign and its absolute value grows almost exponentially with k. Moreover, the presence of the factor $(\pm 1)^k$ in Equation (26) means that I_k with $k =$ odd diverges to either $-\infty$ or $+\infty$ depending on whether the critical point is reached along the critical isotherm with $n > n_c$ or $n < n_c$, respectively. To understand this peculiar property, let us focus on I_3 and note that, according to Equation (11), this quantity is related to the curvature of the isotherm by

$$I_3 = n(\chi_T - 1)(\chi_T - 2) - \frac{n^2}{k_B T} \chi_T^3 \frac{\partial^2 p}{\partial n^2}. \tag{33}$$

Near the critical point, the first term on the right-hand side of Equation (33) is dominated by the second one, i.e.,

$$I_3 \approx -\frac{n_c^2}{k_B T_c} \chi_T^3 \frac{\partial^2 p}{\partial n^2}. \tag{34}$$

The second derivative $\partial^2 p/\partial n^2$ along the critical isotherm is positive for $n > n_c$ and negative for $n < n_c$ and therefore I_3

has the opposite behaviour. In addition, $\partial^2 p/\partial n^2 \to 0$ and $\chi_T \to \infty$ as given by Equations (23) and (24), respectively. As a consequence,

$$I_3 \approx -(\pm 1) A^2 (\delta - 1) n_c \left| \frac{n}{n_c} - 1 \right|^{-(2\delta - 1)}, \quad T = T_c, \tag{35}$$

in consistency with Equations (26) and (30).

5. Kirkwood's superposition approximation

The standard approximation to eliminate the triplet distribution function in favour of the pair distributions is KSA [5,16]. It reads

$$g_3(1, 2, 3) = g_2(1, 2) g_2(1, 3) g_2(2, 3). \tag{36}$$

Making use of the cluster relations (7b) and (7c), it turns out that the KSA is equivalent to

$$h_3(1, 2, 3) = h_2(1, 2)h_2(1, 3) + h_2(1, 2)h_2(2, 3) + h_2(1, 3)h_2(2, 3) + h_2(1, 2)h_2(1, 3)h_2(2, 3). \tag{37}$$

Thus, in this approximation

$$I_3 = 3\frac{I_2^2}{n} + n^3 \int d2 \int d3\, h_2(1, 2)h_2(1, 3)h_2(2, 3). \tag{38}$$

Let us now see that Equation (38) is incompatible with the existence of a critical point, i.e., the approximation (38) is incompatible with the exact relation (11) (with $k = 2$) near the critical point [2]. To that end, we start by assuming that a critical point does exist. If that was the case, Appendix 1 shows that the second term on the right-hand side of Equation (38) would be negligible versus the first term near the critical point, yielding

$$I_3 \approx 3\frac{I_2^2}{n_c} \approx 3A^2 n_c \left| \frac{n}{n_c} - 1 \right|^{-2(\delta - 1)}, \quad T = T_c. \tag{39}$$

This is in contradiction with the exact relation (35) at least in two important points: (1) the divergence of I_3 is weaker (by a difference of unity in the exponent) in Equation (39) than in Equation (35) and (2) the sign of I_3 in Equation (39) is always positive regardless of whether $n < n_c$ or $n > n_c$, in contrast to Equations (34) and (35). In other words, the true long-range nature of the triplet correlation function h_3 is stronger than the one induced by that of h_2 in the KSA (37).

We can reformulate the inconsistency between Equations (35) and (39) as follows. Let us define a residual,

non-KSA term as

$$\Delta h_3(1, 2, 3) = h_3(1, 2, 3) - [h_2(1, 2)h_2(1, 3)$$
$$+ h_2(1, 2)h_2(2, 3) + h_2(1, 3)h_2(2, 3)$$
$$+ h_2(1, 2)h_2(1, 3)h_2(2, 3)]. \quad (40)$$

Then, near the critical point,

$$J_3 \equiv n^3 \int \mathrm{d}2 \int \mathrm{d}3 \, \Delta h_3(1, 2, 3) \approx I_3 - 3\frac{I_2^2}{n_c}. \quad (41)$$

Since $I_2^2/I_3 \sim |n/n_c - 1| \to 0$, it follows that $|J_3| \gg I_2^2/n_c$. This means that the integral J_3 of the residual function Δh_3 diverges near the critical point more rapidly than I_2^2 and therefore cannot be neglected (as the KSA does) near the critical point.

Thus, we conclude that the KSA is inconsistent with the existence of a critical point. The *no-go* arguments of this section are essentially equivalent to the proof presented in Ref. [2].

6. Generalised superposition approximations

The KSA (36) has been extended to express the *k*-particle distribution function in terms of pair distributions [17–19]:

$$g_k(1, 2, \ldots, k) = \prod_{1 \le i < j \le k} g_2(i, j). \quad (42)$$

However, this cannot be considered as a true GSA closure since in the latter g_k must be expressed in terms of $g_2, \ldots, g_{k-1}$ and not only of g_2 [16,20]. For instance, a GSA at the level of g_4 is [16,21]

$$g_4(1, 2, 3, 4)$$
$$= \frac{g_3(1, 2, 3)g_3(1, 2, 4)g_3(1, 3, 4)g_3(2, 3, 4)}{g_2(1, 2)g_2(1, 3)g_2(1, 4)g_2(2, 3)g_2(2, 4)g_2(3, 4)}. \quad (43)$$

Inserting Equations (7b)–(7d) into Equation (43) it is possible to express h_4 in terms of h_3 and h_2. The full expression is rather long and will be omitted here. It has the structure

$$h_4(1, 2, 3, 4)$$
$$= \frac{1}{D_4(1, 2, 3, 4)}\{\mathbf{12}h_2(1, 2)h_3(1, 3, 4)$$
$$+ \mathbf{6}h_3(1, 2, 3)h_3(1, 3, 4) - \mathbf{12}h_2(1, 2)h_2(1, 3)h_2(2, 4)$$
$$- 2[\mathbf{4}h_2(1, 2)h_2(1, 3)h_2(1, 4)] + \cdots\}, \quad (44)$$

where

$$D_4(1, 2, 3, 4) \equiv g_2(1, 2)g_2(1, 3)g_2(1, 4)$$
$$\times g_2(2, 3)g_2(2, 4)g_2(3, 4). \quad (45)$$

In Equation (44), the ellipsis represents terms expressed as products by (at least) a factor h_2 or h_3 of terms similar to the indicated ones. Moreover, as in Equations (7c) and (7d), a numerical coefficient in boldface represents the number of equivalent terms obtaining by relabelling of 1–4. The origin of these combinatorial coefficients just lies in the fact that the correlation function $h_4(1, 2, 3, 4)$ is a symmetric function of its arguments.

To proceed, we need to resort to heuristic arguments, similar to the ones followed in Appendix 1. Assuming that a critical point does exist, the integral I_4 near the critical point is dominated by configurations where particles 1–4 are widely separated from each other. In those configurations, $h_2 \to 0$ (even if it decays algebraically) and therefore we can replace $g_2 \to 1$ in Equation (45) and set $D_4 \to 1$ when integrating both sides of Equation (44). By the same argument, the terms represented by the ellipsis in Equation (44) can be neglected versus the displayed ones. Therefore,

$$I_4 \approx n^4 \int \mathrm{d}2 \int \mathrm{d}3 \int \mathrm{d}4[12h_2(1, 2)h_3(1, 3, 4)$$
$$+ 6h_3(1, 2, 3)h_3(1, 3, 4) - 12h_2(1, 2)h_2(1, 3)h_2(2, 4)$$
$$- 8h_2(1, 2)h_2(1, 3)h_2(1, 4)], \quad (46)$$

where we have taken into account that all the equivalent terms give the same integral. It follows from Baxter's Equation (7) that the term $\int \mathrm{d}2 \int \mathrm{d}4 \, h_2(1, 2)h_3(1, 3, 4)$ is linear in $h_2(1, 3)$ whereas the integral $\int \mathrm{d}2 \int \mathrm{d}4 \, h_3(1, 2, 3)h_3(1, 3, 4)$ yields an expression quadratic in $h_2(1, 3)$, thus decaying faster than the former one when $r_{13} \to \infty$. Therefore, the second term in the integrand of Equation (46) can be neglected versus the first term and thus

$$I_4 \approx 4I_2 \frac{3I_3 - 5I_2^2/n_c}{n_c}. \quad (47)$$

As a final step, we note that, as discussed in Section 5, $|I_3| \gg I_2^2/n_c$ near the critical point, so that

$$I_4 \approx 12\frac{I_2 I_3}{n_c} \approx -(\pm 1) \, 12A^3(\delta - 1)n_c \left|\frac{n}{n_c} - 1\right|^{-(3\delta-2)},$$
$$T = T_c, \quad (48)$$

where use has been made of Equations (25) and (35). Equation (48) is the GSA counterpart of the KSA relation (39). Analogously to the latter case, Equation (48) is inconsistent with Equations (30), according to which $\delta_4 - 1 = 3\delta - 1 > 3\delta - 2$ and $A_4 = A^3(\delta - 1)(2\delta - 1) \ne -12(\pm 1)A^3(\delta - 1)$. Thus, we conclude that the GSA closure (43) is also incompatible with the existence of a critical point.

Suppose now a generalisation of both (39) and (48) where the correlation integral I_{k_0+1} (with $k_0 \ge 4$) is

approximated near the (potential) critical point by

$$I_{k_0+1} \sim \prod_{j=2}^{k_0} I_j^{x_j}, \qquad (49)$$

where x_j are non-negative integer exponents satisfying the constraint

$$\sum_{j=2}^{k_0} j x_j = k_0 + 2. \qquad (50)$$

For instance, $k_0 = 2$ and $x_2 = 2$ in Equation (39), while $k_0 = 3$ and $x_2 = x_3 = 1$ in Equation (48). The constraint (50) implies that

$$\sum_{j=2}^{k_0} x_j \geq 2, \qquad (51)$$

since $\sum_{j=2}^{k_0} x_j = 1$ is possible only if $x_j = \delta_{j j_0}^{\mathrm{Kr}}$ with some $2 \leq j_0 \leq k_0$ (where $\delta_{ij}^{\mathrm{Kr}}$ is the Kronecker symbol), thus violating Equation (50).

According to Equations (26) and (49),

$$\delta_{k_0+1} - 1 = \sum_{j=2}^{k_0} x_j (\delta_j - 1). \qquad (52)$$

Using Equation (30a) for δ_j with $2 \leq j \leq k_0$, one has

$$\delta_{k_0+1} = 1 + (k_0 + 2)\delta - (\delta + 1) \sum_{j=2}^{k_0} x_j$$
$$\leq k_0 \delta - 1. \qquad (53)$$

In the first equality use has been made of Equation (50), while in the second step the inequality (51) has been used. As in the cases of Equations (39) and (48), the GSA (49) violates the exact condition $\delta_{k_0+1} = k_0 \delta$ by at least a unity.

Therefore, one can conclude that neglecting residual correlations beyond a certain finite order in a GSA eliminates the critical point from the resulting approximate theory. Stated in an alternative way, a necessary condition to describe a critical isotherm is to take into account correlations of arbitrary order not accounted for by lower order correlations.

7. Concluding comments

Although the hierarchy (4) contains most fundamental information about equilibrium correlations, it has been rarely used up to now. Our study shows clearly its predicting power as far as the description of critical phenomena is concerned. In an integrated form, the hierarchy permits to express the spatial integral of the $(k + 1)$-particle correlation function in terms of thermodynamic derivatives involving the

isothermal compressibility, as shown by Equation (13). The study of these generalised compressibility equations lead to the following conclusions.

(1) Correlations of any order contribute in an essential way to the occurrence of a critical point. In other words, approximations which neglect correlations beyond some fixed order cannot predict critical behaviour.
(2) If a fluid undergoes a liquid–vapour phase transition, the critical exponents characterising the divergence of spatial integrals of $(k + 1)$-particle correlation functions grow linearly with k, Equation (30a).
(3) Not only the KSA but also its generalisations are inconsistent with the existence of a critical point.

An open problem suggested by these results is the validity of the conjecture stating that any theory which expresses three-particle correlations in terms of two-particle ones loses the possibility of describing a critical point (a specific example is here the KSA). A stronger conjecture would claim that once the higher order correlations are assumed to be functionals of the lower order ones the resulting theory becomes inconsistent with a critical behaviour.

As an additional comment, let us remark that, from a strict point of view, the inconsistency of the KSA with the existence of a critical point follows when it is used as a closure for the Baxter hierarchy (8). This leaves a question on whether the KSA would lead to the same conclusion when applied as a closure to the Yvon–Born–Green hierarchy [3,5]. However, numerical results combined with analytical techniques [22–27] suggest that also in this case a true critical behaviour does not appear for three-dimensional systems. A challenging theoretical problem is to work out an exact analytic answer also to this question.

Finally, it must be noted that we focused entirely on the effect of multi-particle correlations on the existence of a critical point via the critical exponent δ. This is because the generalised compressibility Equations (13) are directly related to the isothermal compressibility and its derivatives with respect to density at constant temperature. Therefore, the problems associated with other critical exponents different from δ have not been studied. Of course, if the conditions for criticality are not satisfied, we should not expect any singularity not only in the isothermal compressibility but also in other thermodynamic quantities, such as, for instance, in the specific heat along the critical isochore (as measured by the critical exponent α).

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Appendix A. Right-hand side of Equation (38) near the critical point

In this Appendix we show by heuristic arguments that the second term on the right-hand side of Equation (38) can be neglected versus the first term near the critical point. To that end, let us compare the integrals

$$K \equiv \int \mathrm{d}2 \int \mathrm{d}3\, h_2(1,2)h_2(1,3)h_2(2,3), \quad \text{(A1a)}$$

$$\frac{I_2^2}{n^4} = \int \mathrm{d}2 \int \mathrm{d}3\, h_2(1,2)h_2(1,3). \quad \text{(A1b)}$$

The factor $h_2(2,3)$ in the integrand of Equation (A1a) is replaced by unity in Equation (A1b). Near the critical point, where the pair correlations become long-ranged, both integrals are dominated by configurations where particles 1, 2 and 3 are widely separated from each other. In those configurations, even if $h_2(2,3)$ decays algebraically with r_{23}, the replacement $h_2(2,3) \to 1$ when going from K to I_2^2/n^4 makes K diverge much more slowly than I_2^2/n^4.

To refine the above qualitative argument, note that Equations (A1) can be rewritten as

$$K = \frac{1}{2\pi} \int \mathrm{d}q\, \left[\widetilde{h}_2(q)\right]^3, \quad \text{(A2a)}$$

$$\frac{I_2^2}{n^4} = \left[\widetilde{h}_2(0)\right]^2 \quad \text{(A2b)}$$

where

$$\widetilde{h}_2(q) = \int \mathrm{d}r\, h_2(r)\mathrm{e}^{\mathrm{i}q\cdot r} \quad \text{(A3)}$$

is the Fourier transform of the pair correlation function. As a toy function, let us consider a three-dimensional geometry and the (classical) asymptotic form

$$h_2(r) \sim \frac{\mathrm{e}^{-\kappa r}}{r}, \quad \kappa r \gg 1, \quad \text{(A4)}$$

where κ is the inverse correlation length, which goes to zero as the critical point is approached. The Fourier transform of (A4) is

$$\widetilde{h}_2(q) \sim \left(\kappa^2 + q^2\right)^{-1}, \quad q/\kappa \ll 1. \quad \text{(A5)}$$

Thus, I_2^2 near the critical point diverges as

$$I_2^2 \sim \kappa^{-4}. \quad \text{(A6)}$$

In contrast, the integral K behaves as

$$K \sim \int \mathrm{d}q\, \left(\kappa^2 + q^2\right)^{-3} = \kappa^{-3} \int \mathrm{d}q^* \left(1 + q^{*2}\right)^{-3}$$
$$\sim \kappa^{-3}. \quad \text{(A7)}$$

Therefore, $K/(I_2^2/n^4) \to 0$, as expected.