A new functional for the entropy that is asymptotically correct both in the high and low density limits is proposed. The new form is
\[ S = S^{(ad)} + S^{(ln)} + S^{(r)} + S^{(c)} \]
where the new term \( S^{(c)} \) depends on the p-bodies density fluctuations \( \alpha_p \) and has the form
\[ S^{(c)} = \langle N \rangle \left\{ \ln 2 - 1 + \sum_{p=2}^{\infty} \frac{(\ln 2)^{p}}{p!} \alpha_p - \left[ \exp(\alpha_2 - 1) - \alpha_2 \right] \right\} + \hat{S} \]
\( \hat{S} \) renormalizes the ring approximation \( S^{(r)} \). This result is obtained by analyzing the functional dependence of the most general expression of the entropy: Two main results for \( S^{(c)} \) are proven: i) In the thermodynamic limit, only the functional dependence on the one body distribution function survives and ii) by summing to infinite order the leading contributions in the density a new numerical expression for the entropy is proposed with a new renormalized ring approximation included. The relationship of these results to the incompressible approximation to entropy is discussed.

I. INTRODUCTION

Entropy is one of the very important and challenging thermodynamic quantities in statistical mechanics; this is so because it depends on all the n-particle distribution functions. The problem is not the lack of exact expressions but to derive equations that are both accurate and manageable from a theoretical and numerical point of view. Amongst the exact expressions we cite the classical work of Nettleton and Green [1], and, more recently, [2,3], while approximate expressions can be found in [3–7]. In [4] we have shown how an infinite subset of terms (dependent exclusively on the one- and two- body distribution functions) can be analytically summed giving rise to the so-called ring approximation and, through a minimization of the free energy functional, the well known HNC approximation [8] is obtained as an optimized superposition approximation. Later on, Bush et al [5] derived sets of integral equations by analyzing several levels of approximation to the grand potential function and, in a recent and very interesting article, Puoskari [3] extends the ring approximation to three particle functions showing how the HNC2 equations either of the Wertheim [9] or the Baxter [10] variety can be obtained. Baranyai and Evans [6] showed that, even though the derivations are done in the grand canonical ensemble, the entropy equations are, in fact, ensemble invariants if local expressions are used for the entropy. In this way, the comparison with canonical ensemble numerical simulations is justified. They also analyze the convergence range of some needed integrals showing how this range increases at high densities. Wallace [7] also worked with the same type of expression and, by analyzing the behaviour of density fluctuations, proposed an incompressible approximation for the entropy of dense fluids (which, as Wallace himself states, is decidedly wrong in the low density regime). He then concluded that the dilute gas and dense liquid regimes occupy different regions of the phase space. These conclusions have been criticized [8]. Laird and Haymet [11] have extended the ring approximation to mixtures and applied it to electrolytes. They found that the correct Debye-Huckel expression for the entropy in the low concentration limit is obtained when the ring approximation is included. They have also discussed [12] the incompressible approximation in dense fluids, proposed an expression that differs from the one of Wallace, and applied it with good numerical results.

Summarizing, these works show that, at low densities the inclusion of the ring approximation gives a very accurate entropy equation and the incompressible approximation is hopelessly wrong, while, at high densities, the ring term overestimates the entropy and the incompressible approximation is reasonably accurate. It has been suggested that
more than two bodies correlations must be incorporated in order to have an accurate expansion and, in this respect, Puoskari’s work [3] is quite promising. It is the purpose of this article to elaborate on the compressibility related contribution to entropy and improve the entropy expansion when truncated to the pair distribution level. In Section II we discuss the conceptual structure of the entropy when written as a functional of the n-bodies distribution function. In Section III it is shown by functional differentiation that the compressibility related contribution only depends on the one body distribution function as well as on thermodynamic parameters and, in Section IV, by summing three subsets of terms, we shed some light on the nature of the incompressible approximation and show how the correct low density limit can also be obtained. In Section V we present our conclusions and propose a new entropy equation.

II. ENTROPY STRUCTURE

We can think on two different criteria for the analysis of the entropy. The first one can be called the functional criterium; is the one we take when interested in the entropy dependence on distribution functions, e.g., when a variational principle is formulated. The second point of view is the numerical one, i.e. the main goal is numerical accuracy. It is clear that it is not necessarily true that the same expression will fulfill satisfactorily both goals. In particular, the incompressible approximation (see eq. (10)) is numerically correct at high densities, but has the wrong behaviour at low densities and also lacks a sound theoretical foundation.

When the entropy dependence on all the n-bodies distribution functions is explicitly written, we obtain an approximate expression with the following distinct structure contributions [3,4]:

i) The ideal gas contribution

$$S^{(id)}_k = \langle N \rangle \left[ \frac{5}{2} - \ln(\rho \lambda^3) \right]$$

where $\rho$ is the number density and $\lambda$ the thermal wavelength.

ii) The ever present logarithmic contribution

$$S^{(ln)}_k = -\sum_{p\geq1} \int d\{p\} n_p(\{p\}) \omega_p(\{p\})$$

where $n_p(\{p\})$ is the p-particles distribution function and $\omega_p(\{p\})$ the irreducible p-bodies contribution to the potential of average force. More specifically, the link with the more usual notation is

$$g_p(\{p\}) = \frac{n_p(\{p\})}{\prod_i n_i(1)}$$

$$e^{\omega_p(\{p\})} = \frac{n_p \prod_{p-2} \subset(\{p\}) {n_{p-2}} \prod_{p-4} \subset(\{p\}) {n_{p-4}} \cdots}{\prod_{p-1} \subset(\{p\}) {n_{p-1}} \prod_{p-3} \subset(\{p\}) {n_{p-3}} \cdots}$$

As usual, we have that $g_2 = 1 + h_2$ and, through the use of the generalized superposition approximation (GSA) [13] we can write that, e.g.

$$g_3(\{3\}) = [1 + \Delta_3(\{3\})] \prod_{\{2\} \subset(\{3\})} g_2(\{2\})$$

$$g_4(\{4\}) = [1 + \Delta_4(\{4\})] \prod_{\{3\} \subset(\{4\})} g_3(\{3\}) \prod_{\{2\} \subset(\{4\})} g_2(\{2\})$$

$$= [1 + \Delta_4(\{4\})] \prod_{\{3\} \subset(\{4\})} [1 + \Delta_3(\{3\})] \prod_{\{2\} \subset(\{4\})} g_2(\{2\})$$

which introduces the family of $\Delta_p$ functions that, when different from zero, correct for the difference with the GSA. They can also be written as

$$\Delta_p(\{p\}) = e^{\omega_p(\{p\})} - 1$$

This $S^{(ln)}$ contribution is the one that, when functionally differentiated, gives rise to the $\ln g$ contribution in the integral equations.
ii) The ring term, which in its simplest, two-body version, is

\[
\frac{S^{(r)}}{k} = \frac{1}{2} \sum_{p \geq 3} \frac{(-1)^{p-1}}{p} \int d\{p\} \prod_{i=1}^{p} n_1(i) h_2(12) h_2(23) \ldots h_2(p1) 
\]  

(7)

and it can be summed in homogeneous systems [4]. This term is the responsible of the contribution \(h_2 - c_2\) in the integral equations. The three bodies version is derived in [3].

iv) The compressibility related contribution

\[
\frac{S^{(c)}}{k} = \sum_{p \geq 2} \frac{1}{p!} \int d\{p\} \prod_{i=1}^{p} n_1(i) \Delta_p(\{p\}) \Gamma_p(\{n_p\}) 
\]  

(8)

\[
\Gamma_p(\{n_p\}) = \frac{\prod_{\{p-1\} \subset \{p\}} g_{p-1} \prod_{\{p-3\} \subset \{p\}} g_{p-3} \ldots}{\prod_{\{p-2\} \subset \{p\}} g_{p-2} \prod_{\{p-4\} \subset \{p\}} g_{p-4} \ldots} 
\]  

(9)

Its first term is essentially the compressibility \((\Delta_2 \equiv \Delta)\) and the sequence of products in eq. [3] stops when reaching either \(g_3\) or \(g_2\). As far as we know there are no previous studies of the whole series given in eq. [3]; the compressibility approximation focuses on the first term of this series, which for a one component homogeneous system is

\[
\frac{S^{(c)}}{k} = \langle N \rangle \frac{\rho}{2} \int d\rho h_2(\rho) = \langle N \rangle \frac{e^{-\langle N \rangle}}{2} (-1 + \alpha_2) 
\]  

(10)

As in the dense liquid limit is \(\alpha_2 \ll 1\), the incompressible approximation considers \(\alpha_2 = 0\) in the whole \(\rho - T\) space.

### III. FUNCTIONAL DEPENDENCE

Here we prove that, in the thermodynamic limit, all the functional derivatives of the compressibility contribution with respect to the distribution functions can be summarized in the equation

\[
\frac{\delta S^{(c)}}{\delta n_p(\{p\})} = -\delta_{1p} + O(e^{-\langle N \rangle}) 
\]  

(11)

Therefore,

\[
\frac{S^{(c)}}{k} = - \int d\{1\} n_1(\{1\}) + C(\rho, T) + O(e^{-\langle N \rangle}) 
\]  

(12)

\(C\) is an integration constant as far as the functional integration refers but, in fact, it depends on \(\rho, T\).

The derivation is straightforward. The origin of the compressibility term \(S^{(c)}\) is quite clear and eqs. (38-41) of Ref. [2] are the equations to look at. Equation (38) is our eq. (11) and in eqs. (39-41) we see that each one of them has, amongst other terms, the integral \(\int \prod n_1 g_p d\{p\}\). When the GSA for \(g_p\) is used (eq. [6]), the integral decomposes into a sum of two integrals \(\int \prod n_1 \Gamma_p [1 + \Delta_p] d\{p\}\). The term without \(\Delta_p\) contributes to the ring approximation plus neglected terms (such as those shown in Ref. [1]) and the term with \(\Delta_p\) contributes to \(S^{(c)}\).

As \(\Gamma_p\) can also be written as

\[
\Gamma_p(\{n_p\}) = \frac{\prod_{\{p-1\} \subset \{p\}} n_{p-1} \prod_{\{p-3\} \subset \{p\}} n_{p-3} \ldots}{\prod_{\{p-2\} \subset \{p\}} n_{p-2} \prod_{\{p-4\} \subset \{p\}} n_{p-4} \ldots} 
\]

using eqs. [7] and [8] we conclude that

\[
\frac{S^{(c)}}{k} = \sum_{p \geq 2} \frac{1}{p!} \int d\{p\} \left[ n_p - \frac{\prod_{\{p-1\} \subset \{p\}} n_{p-1} \prod_{\{p-3\} \subset \{p\}} n_{p-3} \ldots}{\prod_{\{p-2\} \subset \{p\}} n_{p-2} \prod_{\{p-4\} \subset \{p\}} n_{p-4} \ldots} \right] 
\]  

(13)

It is somewhat clear that each one of these integrals is related to \(p\)-bodies density fluctuations but a clearer explanation is to be found in the next section. This explains the origin of naming this contribution as compressibility related. Written in this way it is straightforward to show that the functional derivatives are
\[
\frac{\delta S^{(c)}/k}{\delta n_1(x)} = \sum_{p \geq 1} (-1)^p \frac{\langle N \rangle^p}{p!} \left[ 1 + \bigcirc \left( \frac{1}{\langle N \rangle} \right) \right] = -1 + \bigcirc \left( e^{-\langle N \rangle} \right)
\] (14)

\[
\frac{\delta S^{(c)}/k}{\delta n_s(\{x_s\})} = \frac{1}{s!} \sum_{p \geq 0} (-1)^p \frac{\langle N \rangle^p}{p!} \left[ 1 + \bigcirc \left( \frac{1}{\langle N \rangle} \right) \right] = \bigcirc \left( e^{-\langle N \rangle} \right)
\] (15)

and we arrive to eq. (14).

This result shows that, in the thermodynamic limit, the compressibility term does not contribute to any set of equations we may derive by functional differentiation of a functional that includes the entropy; it only contributes to the constraint of fixed density. Therefore, if we are after a set of equations which are the consequence of a variational principle, we can rightly put the compressibility term aside from all the others, while if we are after a numerical approximation to the entropy we can assume, on physical grounds, absolute convergence of the whole entropy series and feel free to mix the compressibility term with all the others if numerical convergence is improved.

**IV. SERIES SUMMATION**

For the sake of this numerical goal we will cut the GSA to third order; in this way \( g_p \) can be written in two equivalent forms

\[
g_p(\{p\}) = \left\{ 1 + \frac{\sum_{\{2\} \subseteq \{p\}} h_2(\{2\}) + \sum_{\{3\} \subseteq \{p\}} h_3(\{3\}) + \ldots h_p(\{p\})}{\prod_{\{3\} \subseteq \{p\}} [1 + \Delta_3(\{3\})] \prod_{\{2\} \subseteq \{p\}} [1 + h_2(\{2\})] } \right\}
\] (16)

In eq. (13) for the compressibility contribution we will sum to infinite order three subsets of terms. These subsets are clearly identified in the \( p = 3 \) summand of eq. (13), i.e.

\[
\frac{S^{(c)}}{k} = \frac{1}{3!} \int d\{3\} \prod_{i=1}^{3} n_1(\{i\}) \left[ g_3(\{3\}) - \prod_{\{2\} \subseteq \{3\}} [1 + h_2(\{2\})] \right] = \sum_{i=1}^{3} \prod_{i=1}^{3} n_1(\{i\}) \left[ h_3(\{3\}) - \prod_{i=1}^{3} h_2(\{i\}) - h_2(\{12\}) h_2(\{13\}) h_2(\{23\}) \right]
\] (17)

A) The first subset includes the contribution of the integrals \( \int h_p d\{p\}, p \geq 2 \). The series is

\[
\frac{S^{(c)}}{k} = \frac{1}{3!} \int d\{3\} \prod_{i=1}^{3} n_1(\{i\}) h_3(\{3\}) - \prod_{\{2\} \subseteq \{3\}} [1 + h_2(\{2\})] \]
\] (17)

\[
\frac{S^{(c)}}{k} = \frac{1}{3!} \int d\{3\} \prod_{i=1}^{3} n_1(\{i\}) \left[ h_3(\{3\}) - \prod_{i=1}^{3} h_2(\{i\}) - h_2(\{12\}) h_2(\{13\}) h_2(\{23\}) \right]
\] (17)

The moment-cumulant relation [8] is

\[
C_M(\{M\}) = h_M(\{M\}) \prod_{i=1}^{M} n_1(\{i\}) = \sum_{k=1}^{M} \left( k\{m_i\}_M \right) (-1)^{k-1} (k-1)! \prod_{i=1}^{k} n_{m_i}(\{m_i\})
\] (19)

Here, the partition of the coordinate set \( \{M\} \) in \( k \) disjoint subsets \( \{m_i\}_M, 1 \leq i \leq k \) is symbolized by \( \{k\{m_i\}_M\} \) and therefore \( \sum_{k=1}^{M} \left( k\{m_i\}_M \right) \) indicates the sum over all the partitions in \( k \) subsets and for each \( k \) is \( 1 \leq i \leq k \). In this way \( \langle C_p \rangle \) is related to the integrals \( \langle n_p \rangle = \int dp_1 n_p \). On the other hand, \( \langle n_p \rangle \) can be expanded in terms of \( \langle N^k \rangle \) [14]

\[
\langle n_p \rangle = \langle N(N-1) \ldots (N-p+1) \rangle = \sum_{k=1}^{p} s(p,k) \langle N^k \rangle
\] (20)

for \( p \geq 1 \), where \( s(p,k) \) are the Stirling numbers of first kind. One of its definitions is that \(-1)^{p-k} s(p,k)\) is the number of permutations of \( p \) elements which contain exactly \( k \) cycles. They satisfy the recurrence relation

\[
s(p+1,k) = s(p,k-1) - ps(p,k), 1 \leq k \leq p
\]
with starting values

\[ s(p, 0) = s(0, k) = \delta_{kn} \]

We also define the r-bodies density fluctuations \( \alpha_r \) by

\[ \alpha_r = \begin{cases} \frac{1}{(\langle N-<N>\rangle)^r} & r = 1 \\ \frac{1}{<N>} & r > 1 \end{cases} \tag{21} \]

The first few \( \langle C_p \rangle \) are then expressed in terms of the \( \alpha_r \) and Stirling numbers as

\[ \langle C_2 \rangle = \langle N \rangle (1 + \alpha_2) = \langle N \rangle \sum_{i=1}^{2} s(2, i) \alpha_i \tag{22} \]

\[ \langle C_3 \rangle = \langle N \rangle (2 - 3\alpha_2 + \alpha_3) = \langle N \rangle \sum_{i=1}^{3} s(3, i) \alpha_i \tag{23} \]

\[ \langle C_4 \rangle = \langle N \rangle (-6 + 11\alpha_2 - 6\alpha_3 + \alpha_4) + 3 \langle N \rangle^2 \alpha_2^2 = \langle N \rangle \sum_{i=1}^{4} s(4, i) \alpha_i + 3 \langle N \rangle^2 \alpha_2^2 \tag{24} \]

The \( 3 \langle N \rangle^2 \alpha_2^2 \) term and similar ones from higher order \( \langle C_p \rangle \) will be included in the next partial sum. In order to sum to infinite order the contribution of each r-bodies density fluctuations we need the result [14]

\[ \sum_{t=k}^{\infty} \frac{s(t, k)}{k!} x^k = \frac{[\ln(1+x)]^t}{t!} \]

Therefore, the \( \alpha_r \) contribution is

\[ \Gamma_{\alpha_r} = \begin{cases} \frac{\ln 2 - 1}{(\ln 2)^r / r!} & r = 1 \\ \frac{\ln 2 - 1 + \sum_{p=2}^{\infty} \frac{\ln 2}{p!} \alpha_p}{r \geq 2} \end{cases} \tag{25} \]

and our first partial sum, which includes contributions to infinite order of all the \( \alpha_r \), is

\[ \frac{S_b^{(c)}}{k} = \sum_{p=2}^{\infty} \frac{\langle C_p \rangle}{p!} = \langle N \rangle \left\{ \ln 2 - 1 + \sum_{p=2}^{\infty} \frac{\ln 2}{p!} \alpha_p \right\} \tag{26} \]

Let us remark on some characteristics of this result: i) \( \ln 2 - 1 \) is the contribution in the absence of density fluctuations and it is also its high density limit \( \alpha_p \ll 1 \), ii) as \( \alpha_p \to 1 \) when \( \rho \to 0 \), eq. (24) vanishes in the low density limit, iii) the series is rapidly convergent. Therefore, this sum goes in the right direction to improve on the incompressible approximation, both in its numerical results and in its theoretical foundation. This analysis makes also clear why this contribution is referred to as compressibility related. Lastly, the \( \alpha_p \) are easily expressed as integrals of the correlation functions; the first ones are

\[ \alpha_2 = 1 + \frac{1}{\langle N \rangle} \int d\{2\} \prod n_1(i) h_2(\{2\}) \]

\[ \alpha_3 = -2 + 3\alpha_2 + \frac{1}{\langle N \rangle} \int d\{3\} \prod n_1(i) h_3(\{3\}) \]

B) When in the p-th term of eq. (23) the expansions given in eqs. (16) are inserted, each \( h_k, k < p \) expanded in terms of \( h_2, \Delta_3 \) and terms like the \( 3 \langle N \rangle^2 \alpha_2^2 \) which were left aside in the first partial series included, then all the unconnected (in the graph theory sense) terms cancel out and the first two sets of connected diagrams are those depicted in eq. (17). We first evaluate the sum of ”star ” products of \( h_2 \) bonds

\[ \frac{S_b^{(c)}}{k} = \sum_{p=3}^{\infty} \Psi_p = -\sum_{p=3}^{\infty} \frac{1}{p!} \sum_{t=1}^{p} \int d\{i\} n_1(i) \prod_{k \neq i} \int d\{k\} n_1(k) h_2(\{ik\}) \tag{27} \]

Each summand is easily evaluated as
\[
\Psi_p = \frac{\langle N \rangle}{(p-1)!} (-1 + \alpha_2)^{p-1}
\]

and the second partial sum is

\[
\frac{S_k^{(c)}}{k} = -\langle N \rangle [\exp(\alpha_2 - 1) - \alpha_2]
\]  \hspace{1cm} (28)

Its low and high density limits are 0 and \(-e^{-1}\) respectively.

C) This series is a sum of rings very similar to eq. \([6]\), its first term is given in eq. \([17]\) and, as the symmetry number of p-rings is 2p, it can be written as

\[
\frac{S_k^{(c)}}{k} = -\frac{1}{2} \sum_{p \geq 3} \frac{1}{p} \int d\{p\} \prod_{i=1}^{p} n_1(i) h_2(12) h_2(23) \ldots h_2(p1)
\]  \hspace{1cm} (29)

which can be summed for homogeneous systems in the same way as the original ring approximation was \([1]\)

\[
\frac{S_k^{(c)}}{k} = -\frac{\langle N \rangle}{2p} \int d\mathbf{k} \left\{ \ln \left(1 - \rho h_2(k)\right) - \rho \tilde{h}_2(k) - \frac{\left(\rho \tilde{h}_2(k)\right)^2}{2} \right\}
\]  \hspace{1cm} (30)

where \(\tilde{h}_2(k) = \int d\mathbf{r} h_2(\mathbf{r}) \exp(2\pi i \mathbf{k} \cdot \mathbf{r})\) is the Fourier transform of \(h_2(\mathbf{r})\) and the integration is over the \(\mathbf{k}\)-space. This contribution can be added to the original ring approximation giving a renormalized ring approximation \(\tilde{S}^{(c)}\), which is

\[
\frac{\tilde{S}^{(c)}}{k} = -\frac{\langle N \rangle}{2} \int d\mathbf{k} \left\{ \ln \left(1 - (\rho h_2(k))^2\right) + \left(\rho \tilde{h}_2(k)\right)^2 \right\}
\]  \hspace{1cm} (31)

a sum over all even order rings and, for homogeneous systems, the result is

\[
\tilde{S}^{(c)} = \frac{\langle N \rangle}{2} \int d\mathbf{k} \left\{ \ln \left(1 - (\rho h_2(k))^2\right) + \left(\rho \tilde{h}_2(k)\right)^2 \right\}
\]  \hspace{1cm} (32)

V. CONCLUSIONS

Collecting together the different results obtained, i.e. eqs. \([26]\), \([28]\) and \([29]\) with eqs. \([1] and [2]\) we arrive to a new entropy equation which includes a partial summation of the compressibility related contribution, i.e.

\[
\frac{S}{k} = \langle N \rangle \left[ \frac{5}{2} - \ln(\rho \lambda^3) \right] - \sum_{p \geq 1} \int d\{p\} n_p\{p\} \omega_p\{p\} +
\]

\[
+ \frac{\langle N \rangle}{2p} \int d\mathbf{k} \left\{ \ln \left(1 - (\rho h_2(k))^2\right) + \left(\rho \tilde{h}_2(k)\right)^2 \right\} +
\]

\[
+ \langle N \rangle \left\{ \ln 2 - 1 + \sum_{p=2}^{\infty} \frac{(\ln 2)^p}{p!} \alpha_p \right\} - \langle N \rangle [\exp(\alpha_2 - 1) - \alpha_2]
\]  \hspace{1cm} (33)

If, for just a moment, we neglect the renormalization in the ring approximation, the contribution due to the r-bodies density fluctuations gives not only a theoretical understanding on the nature of the incompressible approximation, but also a description that is essentially correct in the low and high density limits (0 and \(\ln 2 - 1 - e^{-1}\) respectively). As the ring approximation grows quite steeply when the density increases \([11,12]\), its renormalization should have the right asymptotic behaviour. Let us also mention that these results extend trivially to mixtures (see, e.g. \([12]\) and, in this case, it is more convenient to work with the entropy per unite volume.

We have also shown that, in the thermodynamic limit, the compressibility term only depends (as a functional) on the one body distribution function. Therefore, this functional dependence is such that it only enters in the constant density constraint and, in this way, the conceptual structure of the equation for the entropy is significantly simplified.
As our results apply to the full entropy functional, they are valuable to any functional minimization as, e.g., those in [4,5]. It can also be mentioned that this theorem does not conflict with Laird-Haymet [11]. They obtained the correct Debye-Hückel low density expression for the entropy by including the $S^{(id)}$, $S^{(ln)}$, $S^{(r)}$ plus the compressibility related contribution of eq. [10]. As this term and, in fact, all the sums we did, vanish when $\rho \to 0$ (including the one that renormalizes the ring approximation), there is no contradiction between ours and theirs results. Lastly, as this result does not depend on the potential, it is also valid for the associative Wertheim-Ornstein-Zernike equation [15,16] as well as systems with directional forces [17].

This new functional provides a robust and systematic way to develop fully analytical theories of liquids [18–20], which will be examined in future work.

VI. ACKNOWLEDGMENTS

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