Universal features of the order-parameter fluctuations: reversible and irreversible aggregation

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We discuss the universal scaling laws of order parameter fluctuations in any system in which the second-order critical behaviour can be identified. These scaling laws can be derived rigorously for equilibrium systems when combined with the finite-size scaling analysis. The relation between order parameter, criticality and scaling law of fluctuations has been established and the connexion between the scaling function and the critical exponents has been found. We give examples in out-of-equilibrium aggregation models such as the Smoluchowski kinetic equations, or of at-equilibrium Ising and percolation models.

I. INTRODUCTION

Fluctuations in many physical processes are difficult to analyze because they develop dynamically and often keep the memory of initial conditions. On the other hand, strong fluctuations are ubiquitous, as show examples of hadronization in strong interaction physics, polymerization, colloid aggregation, aerosol coalescence or the formation of large scale structures in the Universe. With the advent of recently developed advanced detection systems, the study of large fluctuations in physical observables became accessible in 'small systems', such as formed in ultrarelativistic collisions of hadrons, leptons and nuclei, in the heavy-ion collisions at the intermediate energies or in the collisions of atomic aggregates.

In theoretical studies, it is often assumed that fluctuations are irrelevant. In this spirit, many aggregation processes have been studied in the mean-field approximation. This problem has been revisited recently. It was shown that contrary to the usual believe, fluctuations in the size distribution of largest cluster are generally large in the aggregation processes. Large fluctuations in the cluster multiplicity distribution have also been reported in the binary fragmentation process with the inactivation mechanism.

This article deals with the features of fluctuations of physical quantities in a $N$-body, $d$-dimensional system, with $N$ essentially finite. Moreover, the system is not necessarily at the thermodynamic equilibrium. Both these aspects of our approach are important in many areas of physics where, for example, small and strongly fluctuating systems are produced in the violent collision processes. Consequently, these systems live shortly and the typical time-scales are such that standard methods of equilibrium statistical physics may not to applicable.

We shall be particularly interested in self-similar systems, such as the fractal objects or thermodynamic systems at the second-order phase transition. The self-similarity means in particular that one is unable to define the characteristic length $\sim (N^*)^{1/d}$, where $N^*$ is the characteristic size, which could be associated with the disappearance of fluctuations. Our aim in this work is the discussion of universal scaling laws of fluctuations of different observables in self-similar systems. In particular, we shall consider the order parameter fluctuations in any system, both equilibrium and non-equilibrium one, in which the second-order critical behaviour can be identified. These considerations will provide an understanding of the relation between the order parameter, the criticality and the scaling law of fluctuations. The notion of relevant variable (relevant observable) for the discussion of critical behaviour in finite systems will appear from this discussion.

The paper is organized as follows. In Sect. II the order parameter fluctuations in statistical systems are analyzed and the relation with the finite-size scaling analysis and Widom’s hypothesis is developed in details (Sect. II.B). The generic features of the tail of the scaling function is addressed in Sect. I.C. In Sects. II.E - II.H, the generalized scaling of the observable quantities, the $\Delta$-scaling, is discussed and the reasons for the deviations from the limiting cases $\Delta = 1$ and $\Delta = 1/2$ are presented.

Sects. III - VI are devoted to the detailed discussion of several well known generic models, using the results and methods of analysis proposed in Sect. II. In Sect. III, the non-critical fragmentation model is discussed which exhibits the power-law cluster size distribution. Results obtained in Potts model are discussed in Sect. IV. Sect. V is devoted to the discussion of the reversible aggregation, as modelled by the percolation model. Both realistic 3-dimensional bond percolation and the mean-field percolation on the Bethe lattice is being considered.
the Smoluchowski kinetic model are discussed in Sect. VI. Finally, the main conclusions are given in Sect. VII.

II. ORDER PARAMETER FLUCTUATIONS

A. Correlation function argument

Let us call $m$ the observable under investigation. For the reason of presentation, we shall restrict ourselves to the case where $m$ is a scalar quantity and takes real positive values. (In fact, this restriction is not a true limitation and, generally, one can consider $|m|^2$ as well.) Fluctuations of the order parameter in thermodynamic systems are expected to have different properties at the critical point and outside of it. Far from the critical behaviour, the correlations are short-ranged. Fluctuations of the extensive order parameter $m$ in this case resemble the ergodic Brownian motion of this variable in its proper configuration space. Consequently $< (m - < m >)^2 > / < m >$ is roughly a constant, meaning independent of the number of constituents in the sample. On the contrary, close to the second-order transition point, the fluctuations are correlated throughout the whole system and the correlation length $\xi$ for the infinite system becomes infinite as well. Let us now define in such a system the deviation $\epsilon$ of the driven parameter from its critical value, $m$ the local value of the order parameter and the field $h$ conjugated to $m$. The following isotropic correlation function is introduced:

$$
\sigma_n(\epsilon, h, \vec{r}_1, ..., \vec{r}_{n-1}) = < m(\vec{r}_0)m(\vec{r}_0 - \vec{r}_1) \ldots 
\ldots m(\vec{r}_0 - \vec{r}_{n-1}) > .
$$

(1)

Notation $< ... >$ in the above expression denotes the thermodynamic average at a given $\epsilon$ and over the position $\vec{r}_0$. For vanishing $\epsilon$, all the length scales disappear and the correlation length $\xi$ diverges algebraically as

$$
\xi \sim \epsilon^{-\nu}
$$

with a universal exponent $\nu$, which depends only on the universality class of the transition. Moreover, the scaling description of second-order critical phenomena leads to the fundamental postulate that the thermodynamic potential $G$ verifies

$$
G(\lambda \epsilon, \lambda^{2-\alpha-\beta} h) \sim \lambda^{2-\alpha} G(\epsilon, h),
$$

(2)

and this defines the two universal exponents $\alpha$ and $\beta$. Let us now go back to the correlation function $\sigma_n$ defined in (3). The integral of $\sigma_n$ over the $n-1$ space-variables : $\vec{r}_1, ..., \vec{r}_{n-1}$, is equal to the $n$-th derivative of $G$ with respect to the field $h$. Hence, to be consistent with (3), we must get the scaling relation:

$$
\sigma_n(\lambda \epsilon, \lambda^{2-\alpha-\beta} h, \lambda^{-\nu} \vec{r}_1, \ldots, \lambda^{-\nu} \vec{r}_{n-1}) \sim 
\sim \lambda^{n\beta} \sigma_n(\epsilon, h, \vec{r}_1, ..., \vec{r}_{n-1}).
$$

(3)

For $n = 1$, we recover the well-known scaling behaviour of the averaged order parameter with the critical exponent $\beta$. For any integer $n$, putting all the space-variables to 0 in formula (3) leads to the scaling of powers of the local order parameter:

$$
<m^n> (\lambda \epsilon, \lambda^{2-\alpha-\beta} h) \sim \lambda^{n\beta} < m^n > (\epsilon, h) .
$$

(4)

As a consequence, if we let $h = 0$ and $\lambda = 1/\epsilon$, one finds that the quantities $< m^n > / < m >^n$ are independent of $\epsilon$, when close to the transition. This means, by the finite-size analysis, that this ratio is independent of the size $N$ of the system at the transition point.

Let us now introduce the cumulants $\kappa_q$ from the general formula for the moment expansion of the order-parameter probability distribution $P[m]$ :

$$
\ln \left( \sum_{m=0}^{\infty} P[m] \exp(mu) \right) = \sum_{q=0}^{\infty} \frac{u^q}{q!} \kappa_q .
$$

(5)

Expanding the l.h.s. of the above expression in the power series in $u$, and comparing corresponding powers on l.h.s. and r.h.s., one derives the relations between ordinary moments of $P[m]$ and the cumulant moments :

$$
\kappa_1 = < m >
$$

$$
\kappa_2 = < m^2 > - < m >^2
$$

$$
\kappa_3 = < m^3 > - 3 < m^2 > < m > + 2 < m >^3
$$

$$
\kappa_4 = < m^4 > - 4 < m^3 > < m > - 3 < m^2 >^2 + 12 < m^2 > < m >^2 - 6 < m >^4
$$

...

In the case of the second-order phase transition, as a result of scaling relations (4), all cumulant moments scale like

$$
\kappa_q \sim < m >^q .
$$

Consequently, the generating function of the $m$-probability distribution (6) is only a function of the reduced variable $< m > u$. This can be written as :

$$
P[m] = \frac{1}{2\pi} \int_0^{2\pi} \hat{G}(iu) \exp(-imu)du
$$

(7)

where $\hat{G}$ is the generating function :

$$
\hat{G}(u) = \sum_{m=0}^{\infty} P[m] \exp(mu) .
$$

(8)

In the case when $< m >$ tends to $\infty$ but $m/ < m >$ remains finite, we can rewrite formula (8) in the more compact form :

$$
< m > P[m] = \Phi \left( \frac{m}{< m >} \right) ,
$$

(9)
which is valid at the critical point. \( \Phi \) is the scaling function of the single reduced variable \( m/ < m > \). As stated before, we can express this scaling as:

\[
\sum_{m=0}^{\infty} P_N[m] \exp(mu) = \Psi(<m > u) , \tag{9}
\]

which is the necessary and sufficient condition for the applicability of scaling law [3, 26]. This result implies also that if this scaling occurs for the fluctuations of the parameter \( m \) then it holds also for fluctuations of any power:

\[
X = N^a m^b
\]

of this parameter as well. This is a consequence of [1] and

\[
P_N[X]dX = P_N[m]dm . \tag{10}
\]

Till now, we did not specify reasons of changing \( < m > \). Indeed, under the condition that the scaling framework of second-order phase transition holds, the scaling relation [3] is valid independently of the explicit reasons of changing \( < m > \) and independently of any phenomenological details. In other words, the explicit relation between the size \( N \) of the system and \( < m > \) need not to be known at this stage. In the following section, we shall show how to derive supplementary informations about \( \Phi \) when the system is at the pseudo-critical point.

### B. Widom’s hypothesis and the finite-size scaling argument

The hypothesis of Widom states that in the thermodynamic limit of a system at thermal equilibrium, the free energy density close to the critical point scales as [3]:

\[
f(\lambda^\beta \eta, \lambda \epsilon) \sim \lambda^{2-\alpha} f(\eta, \epsilon) , \tag{10}
\]

where \( \alpha, \beta \) are the usual critical exponents, \( \eta \) is the intensive order parameter and \( \lambda \) is the scale parameter. Even though finite systems do not exhibit the critical behaviour, nevertheless their properties may resemble those of infinite systems if the correlation length \( \xi \) is larger or comparable to the typical length \( L \) of the system. In this case, one speaks about the pseudocritical point in a finite system at a distance

\[
\epsilon \sim cN^{-\gamma/2}\nu d
\]

from the true critical point [3]. The quantity \( N \) in (11) is the size of the \( d \)-dimensional system and \( c \) is some dimensionless constant which can be either positive or negative. This constant \( c \) is negative if the maximum of finite-size susceptibility or of any other divergent macroscopic quantity in the thermodynamic limit lies in the ordered phase, while \( c \) is positive if this maximum is in the disordered phase. One can then derive the finite-size scaling of the total free energy:

\[
F(\eta, \epsilon, N) = N f(\eta, \epsilon)
\]
at the pseudocritical point:

\[
F_c(\eta, N) \sim f(\eta N^{-\alpha/2} \gamma) . \tag{12}
\]

In deriving (12) we used the hyperscaling relation:

\[
2 - \alpha = \nu d . \tag{13}
\]

The canonical probability density of the order parameter \( P_N[\eta] \) is given by [3]:

\[
P_N[\eta] = \frac{1}{Z_N} \exp(-\beta_T F(\eta, \epsilon, N)) , \tag{13}
\]

where the coefficient \( \beta_T \) (\( \equiv 1/T \)) is independent of \( \eta \) (\( T \) is the temperature of the system). Using Eq. (14), one may calculate the most probable value of the order parameter, which is the solution to the equation

\[
\frac{\partial P_N[\eta]}{\partial \eta} = 0 ,
\]

as well as the average value of the order parameter and the partition function

\[
Z_N \sim N^{-\xi/c} \sim <\eta> \sim \eta^* . \tag{14}
\]

\( \eta^* \) in (14) denotes the most probable value of the order parameter. The average value of the order parameter vanishes for large values of \( N \), since both \( \beta \) and \( 2 - \alpha = 2\beta + \gamma \) are positive. The probability density \( P_N[\eta] \) obeys then the scaling law formally identical to Eq. (3):

\[
<\eta > P_N[\eta] = \Phi \left( \frac{\eta}{\eta^*} \right) \equiv \Phi(z) \tag{15}
\]

where, in addition,

\[
\Phi(z) \sim \exp(-\beta_T f(az, c)) . \tag{16}
\]

In the above formula, we have omitted the temperature-dependent multiplicative factor which can be determined by normalization of \( P_N[\eta] \). Coefficients \( a \) and \( c \) may both depend on \( \beta_T \). We can then rewrite the scaling (13) in a standard form for the extensive order parameter \( m = N\eta \):

\[
< m > P_N[m] = \Phi(z_{(1)}) \tag{17}
\]

with the scaling variable \( z_{(1)} \) defined by

\[
z_{(1)} = \frac{m - m^*}{< m >} . \tag{18}
\]
$m^*$ denotes the most probable value of the extensive order parameter. We call (17) with (18) the first-scaling law. The scaling domain is defined by this asymptotic behaviour of $P_N[m]$ when $m \to \infty$ and $\langle m \rangle \to \infty$, but $z_{(1)}$ has a finite value. The normalization of the probability distribution $P_N[\eta]$ and the definition of the average value of $m$, provide the two constraints:

$$\lim_{-m^*/<m>} \int \Phi(z_{(1)})dz_{(1)} = 1$$

$$\lim_{-m^*/<m>} \int z_{(1)}\Phi(z_{(1)})dz_{(1)} = 0$$

The first-scaling law (15) is a consequence of the self-similarity of the statistical system. The self-similarity means here that the fluctuations of the reduced order parameter $\eta/\langle \eta \rangle$ at different scales characterized by different values of the intensive order parameter $< \eta >$, have identical properties. This is a qualitative explanation for this scaling.

The logarithm of scaling function (16) corresponds to the non-critical free energy density at the renormalized distance $e = c$ from the critical point. If it happens that the order parameter is related to the number of fragments, like in the Fragmentation - Inactivation - Binary (FIB) process [11,12], then (16) can be written in an equivalent form to the Koba - Nielsen - Olesen (KNO) scaling [13], proposed some time ago as an ultimate symmetry of the $S$ - matrix in the relativistic field theory [14]. The multiplicity distribution of produced particles is intensely studied in the strong interaction physics where simple behaviour of much of the data on hadron-multiplicity distribution seems to point to some universality independent of the particular dynamical process.

If, instead of real positive scalar, the parameter under investigation is a vector of dimensionality $n : \vec{m} = [m_1, \cdots, m_n]$, then the first-scaling law (17,18) takes the more general form:

$$\langle |\vec{m}| \rangle >^n P_N[\vec{m}] = \Phi(\vec{z}_{(1)})$$

with

$$\vec{z}_{(1)} = \frac{\vec{m} - \vec{m}^*}{\langle |\vec{m}| \rangle}.$$  \hspace{1cm} (20)

The scaling limit in (19) is defined by the asymptotic behaviour of $P_N[\vec{m}]$ when $m_i \to \infty$ ($i = 1,\cdots,N$) and $\langle |\vec{m}| \rangle \to \infty$, but $z_{(1)}$ ($i = 1,\cdots,N$) have finite values.

C. The tail of the scaling function

The scaling function $\Phi$ introduced in the first-scaling law (17) has some typical features reminiscent of the non-Gaussian critical distribution of the order parameter. In this section, we are interested in the behaviour of scaling function for large values of the reduced parameter $m/\langle m \rangle$, so we have to study the system subject to the small field $h$ conjugated to the order parameter. This breaks the symmetry of the distribution by shifting $m$ and $\langle m \rangle$ towards larger values. More precisely, let us write the probability to get the value $\eta$ of intensive order parameter at the distance $e$ from the critical point as:

$$P_N[\eta,\epsilon,h] = P_N[\eta,\epsilon,0] \exp(\beta_T \eta Nh).$$  \hspace{1cm} (21)

Till now, we have studied the behaviour of $P_N[\eta,\epsilon,0]$ for which the first-scaling law holds when $\epsilon = 0$ (the critical point) or $\epsilon = cN^{-1+\nu d}$ (the pseudo-critical point). Substituting (12) and using (14), we obtain:

$$P_N[\eta,0,h] = N \times \exp \left( \ln \Phi \left( \frac{\eta N^{-1+\nu d}}{\langle m \rangle} \right) + \beta_T \eta Nh \right).$$

The most probable value

$$\eta^* \sim h^{1/\delta}$$

of the order parameter in the limit of small external field $h$, is given by the maximum of the term in the exponential. Since

$$\delta = \frac{2 - \alpha - \beta}{\beta},$$

we get:

$$\ln \Phi(h^{\ast} N^{-1+\nu d}) \sim -\beta_T h^{\ast} Nh.$$  \hspace{1cm} (22)

Relation (22) is valid for any value of $N$ if and only if

$$\Phi(z) \sim \exp(-az^{\delta+1}) \equiv \exp(-az^\nu),$$

with the coefficient $a$ which depends on the temperature regularly.

One can express this relation in a different way. The anomalous dimension for extensive quantity $m = N\eta$ can be defined as:

$$g = \lim _{N \to \infty} g_N = \lim _{N \to \infty} \frac{d}{d \ln N} (\ln < m >).$$  \hspace{1cm} (24)

One can see that due to both (14) and the Rushbrooke relation between critical exponents:

$$\alpha + 2\beta + \gamma = 2,$$

the anomalous dimension is:

$$g = 1 - \frac{\beta}{\gamma + 2\beta}.$$  \hspace{1cm} (25)

Since both $\alpha$ and $\beta$ are positive, therefore $g$ is contained between 1/2 and 1 for equilibrium systems at the critical point of the second-order phase transition. Because of these additional relations between critical exponents,
one may note that a behaviour of the tail of the scaling function (23) is governed by the exponent:

$$\nu = \frac{1}{1 - g} = \delta + 1 = \frac{2 - \alpha}{\beta},$$  \hspace{1cm} (26)$$

which is always larger than 2. The limiting case : $\nu = 2$, i.e. the Gaussian tail (see (23)), corresponds in this framework to the non-critical system. Moreover, the relation (27) derived for the second-order critical phenomenon is correctly recovered. One should emphasize, that the relation (29) is very general and its derivation does not depend on the assumption of thermodynamic equilibrium. In other words, the relation (29) is valid also for the off-equilibrium second-order phase transitions. We shall return to this point in Sect. VI.

The cluster multiplicity could be the order parameter whenever $\tau < 2$, though this cannot happen in the equilibrium phase transitions. Note that this argument to sort among different candidates for the order parameter requires only the knowledge of $\tau$, i.e. the complete information about the critical process is superfluous. We shall use this argument later in the case of percolation model and Smoluchowski model of gelation. Finally, we shall see below in the Mekjian model that we may have power-law size distribution with $\tau < 2$, in the absence of phase transition governed by the multiplicity as the order parameter.

D. Landau - Ginzburg theory of phase transitions

Let us consider the Landau - Ginzburg (LG) theory as an exactly solvable example of the second-order phase transition. The homogeneous LG free energy density is :

$$f(\eta) = \epsilon \eta^2 + b \eta^4 + \cdots$$

where $b$ is a positive constant. The most probable value of the order parameter $\eta$ in the disordered phase ($\epsilon < 0$) is implicitly set to 0. It is more convenient to work with the extensive order parameter $m = N \eta$ when dealing with the finite systems. The probability of a state $m$ for a given $\epsilon$ is:

$$P_N[m] = \frac{1}{Z_N} \exp \left[ -\beta \epsilon \frac{m^2}{N} + \frac{b m^4}{N^2} - \cdots \right] \hspace{1cm} (30)$$

$Z_N$ is defined by the normalization of $P_N[m]$. To remain consistent with other sections of this paper and without loss of generality, we consider now the case where $m$ is
positive. We will admit that \( N \) is so large that the first two terms in the free energy expansion are sufficient to study the phase transition. At the critical point: \( \epsilon = 0 \), the leading term of the free energy density is proportional to \( m^4 \). Standard integrations yield the values for the partition function \( Z_N \) and the average value of the order parameter \( < m > \), both proportional to \( N^{3/4} \). Introducing them in (30), one finds:

\[
<m> P_N[m] = \frac{4\sqrt{\pi}}{\Gamma^2[1/4]} \times \\
\times \exp\left(-\frac{\pi^2}{\Gamma^4[1/4]} \left(\frac{m}{<m>}\right)^4\right), \quad (31)
\]

which has the form of (8). Note that the scaling function \( \Phi(z) \sim \exp(-z^4) \), decreases very fast as one moves away from the most probable value. This result is consistent with the analysis done in the previous section.

The pseudo-critical point is the value of \( \epsilon \) for which the finite-size thermal susceptibility reaches its maximum. Writing that the inverse of this susceptibility is the second derivative of the free energy with respect to the order parameter, one finds:

\[
\epsilon = -6 \frac{\Gamma[3/4]}{\Gamma[1/4]} \left( \frac{b}{\beta T N} \right)^{1/2}. \quad (32)
\]

This result is correct at the first order in \( N^{-1/2} \). Replacing \( \epsilon \) in (30) by (32), leads to the scaling form of \( P_N[m] \):

\[
<m> P_N[m] = A \exp \left[ -\frac{\Gamma[3/4]^2}{\Gamma[1/4]^2} (m/ <m>)^4 - 6(m/ <m>)^2 \right], \quad (33)
\]

where \( A \) denotes a normalization constant. We recover indeed the first-scaling law with the exponential tail: \( \exp(-a m^4) \), for the large arguments.

Outside of the critical point in the disordered phase \( (\epsilon > 0) \), the leading term of the free energy is proportional to \( m^2 \), and the probability distribution \( P_N[m] \) is essentially Gaussian. Deriving, as previously, the values of \( Z_N \) and \( < m > \) (both behave like \( N^{1/2} \) in this case), we get the scaling form:

\[
<m> P_N[m] = \frac{4}{\pi} \exp \left(-\frac{4}{\pi} \left(\frac{m}{<m>}\right)^2\right) \quad (34)
\]

which is still under the form (13) but with a Gaussian scaling function reminiscent of the Gaussian fluctuations.

Finally, in the low temperature regime \( (\epsilon < 0) \), the most probable value of the order parameter is positive:

\[
m^* = \sqrt{-\frac{\epsilon}{2b} N}. \quad (35)
\]

Developing \( P_N[m] \) in (30) around this point leads to the expression:

\[
m^{*1/2} P_N[m] \simeq \left(-2\frac{\epsilon}{b a^2}\right)^{1/4} \times \\
\times \exp \left(\epsilon \sqrt{-2a b} \frac{(m - m^*)^2}{m^*}\right), \quad (36)
\]

which is no more in the standard form (13). In this case, the average value of the order parameter \( < m > \) is of the same order of magnitude as its most probable value \( m^* \) and one can rewrite (35) in the scaling form:

\[
<m> P_N[m] \sim \exp \left(-a \frac{(m - m^*)^2}{<m>}\right), \quad (37)
\]

where \( a \) is a positive constant. This particular scaling form will be discussed later in details.

### E. The \( \Delta \)-scaling law

One may ask, what happens if the observable quantity is not the order parameter but the \( N \)-dependent function of the order parameter like:

\[
m = N^{a_1} - N^{a_2} \eta, \quad (38)
\]

where

\[
a_1 > g + a_2 - 1. \quad (39)
\]

The latter condition ensures that the order parameter does not determine the leading behaviour of \( m \). For large \( N \):

\[
<m> \sim N^{a_1}. \quad (40)
\]

Writing (17) with \( m \) instead of \( \eta \) and taking into account that:

\[
P_N[\eta] d\eta = P_N[m] dm
\]

one finds the generalized law:

\[
<m>^\Delta P_N[m] = \Phi(z(\Delta)) \equiv \Phi\left(\frac{m - m^*}{<m>^\Delta}\right), \quad (41)
\]

where:

\[
\Delta = \frac{g + a_1 - 1}{a_1}, \quad (42)
\]

This generalized law will be called the following the \( \Delta \)-scaling law. The scaling function \( \Phi(z(\Delta)) \) depends only on one scaled variable:

\[
z(\Delta) = \frac{m - m^*}{<m>^\Delta}, \quad (43)
\]

The normalization of the probability distribution \( P_N[m] \) and the definition of the average value of \( m \) provide two constraints:
\[
\lim_{z \to -\infty} z\Phi(z)dz = 0
\]

which are consistent with \( \Delta \leq 1 \), because the scaling function \( \Phi \) is positive. The scaling function \( \Phi(z(\Delta)) \) has an identical form as \( \Phi(z(1)) \), except for the inversion of the abscissa axis. In particular, its tail for large \( z(\Delta) \) has the same form:

\[
\Phi(z(\Delta)) \sim \exp\left(-\frac{z}{\sqrt{\Delta}}\right) = \exp\left(-\frac{z}{\sqrt{1}}\right) \quad (41)
\]
as given in (23). One should mention in passing that if \( a_1 < g + a_2 - 1 \) in (37), then

\[
<m> \sim N^{a_2} \eta >
\]
and \( \Delta = 1 \), following the remark of Sect. II.A.

According to (14), the logarithm of scaling function \( \Phi(z(\Delta)) \) :

\[
\ln \Phi(z(\Delta)) = -\beta_T f(az(\Delta), c)
\]
is related to the non-critical free energy \( f \), in either ordered \((c > 0)\) or disordered \((c < 0)\) phase.

As an important example, we see from (37), (39), that the \( \Delta \)-scaling of the extensive variable :

\[
\hat{m} = N(1 - \eta) \equiv N\eta
\]
can be used to determine the anomalous dimension since in this case : \( \Delta = g \). For this reason, \( \hat{m} \) is a very useful variable in all phenomenological studies. At the phase transition :

\[
< N\eta > \sim N
\]
but the finite-size corrections are algebraic.

F. Off-critical scaling

\( \Delta = 1/2 \) with \( \Phi(z(\Delta)) \) nearly Gaussian, is a particular case of a \( \Delta \)-scaling associated with the non-critical systems [23]. This limit :

\[
<m>^{1/2} P_N[m] = \Phi\left(\frac{m - m^*}{<m>^{1/2}}\right) \equiv \Phi(z(1/2)) \quad (42)
\]
which is called the second-scaling law, has been found in the shattering phase of the non-equilibrium FIB process [24] and in the 'gaseous' phase of equilibrium percolation process [23]. We should recall also that this form of scaling function has been seen for LG model in the low temperature regime (see (23)).

More generally, let us suppose now that the extensive parameter \( m \) is not critical, \( i.e. \) either the system is in a critical state but the parameter \( m \) is not critical, or the system is outside of the critical region. The value of \( m \) at the equilibrium is obtained by minimizing the free energy. The free energy \( F \) is analytical in the variable \( m \) close to its most probable value \( m^* \) :

\[
F \sim N^{-1}(m - m^*)^2 \quad . (43)
\]

Using (43) one obtains

\[
<m> \sim \mu^* N
\]
where \( \mu^* \) is a positive (finite) number independent of \( N \) and :

\[
Z_N \sim N^{1/2} \sim <m>^{1/2} \quad . (44)
\]
The probability density \( P_N[m] \) verifies the second-scaling law (39) :

\[
<m>^{1/2} P_N[m] = \exp\left(-\beta_T \mu^* \left(\frac{m - <m>}{<m>^{1/2}}\right)^2\right) \equiv \Phi(z(1/2)) \quad . (45)
\]
This is a particular case of the \( \Delta \)-scaling law (\( \Delta = 1/2 \)) and the scaling function is now Gaussian [23]. This scaling (42) holds for \( m > N \) but now with the exponential finite-size corrections. This is a principle difference from the finite-size corrections and/or \( \Delta \)-scaling. The above arguments apply to any second order phase transition. In particular, they are not limited to LG theory of phase transitions (see Eq. (38)).

G. Finite-size cross-over effects

The discussion of previous section is valid for systems at the critical (and pseudo-critical) point or far from the critical point in the ordered phase. Let us suppose now that the system is prepared such that :

\[
<m> \sim N^{g'} \quad , \quad g' < 1
\]
and \( g' \) is not the anomalous exponent. Here, we would like to study how the finite system evolves when the control parameter \( \epsilon \) tends slowly to 0, namely :

\[
\epsilon \sim N^{2g' - 2} \quad .
\]

We shall address this question in the mean-field approximation using LG theory. Let us first write down the average value :
< m > = \int_{0}^{\infty} \frac{m \exp(-m^2/N-bm^4/N^3)dm}{\int_{0}^{\infty} \exp(-m^2/N-bm^4/N^3)dm}. \quad (46)

Hence, writing this definition with the new driving parameter \( \epsilon' = \epsilon N^{1/2} \) and using the rescaled variable \( m' = m/N^{3/4} \), the average value of \( m \) can be put in the form:

\[ < m > = N^{3/4} \phi(\epsilon N^{1/2}) \]

while its most probable value is:

\[ m* = \sqrt{-\frac{\epsilon}{2b}} N. \]

If the exponent \( \gamma' \) is not too small, i.e. if \( \epsilon \) does not vanish too fast, the two quantities: \( < m > \) and \( m* \), have to coincide. This is because the exponential weight term in \( (46) \) diverges as \( \sim \exp(\epsilon^2 N/4b) \) when

\[ \epsilon N^{1/2} \sim N^{4\gamma' - 2} \]

becomes large with increasing \( N \). As a consequence, the common behaviour of \( < m > \) and \( m* \) is: \( \sim N^\gamma \). The scaling form \( (52) \) in this case is:

\[ < m >_\Delta P_N[m] \sim \exp \left( -c \frac{(m-m*)^2}{< m >_{2\Delta}} \right) \]

with \( c \) a positive constant, and:

\[ \Delta = \frac{3}{2} \gamma' - 1. \]

We recover here the two cases previously discussed in Sect. II.B. When \( \gamma = 1, \) i.e. when \( \epsilon = \text{const} \), then this is the second-scaling law. When \( \gamma = 3/4, \) then this is the first-scaling law since the finite system is yet in the critical region \( (\gamma' = \gamma) \). In between these two limiting cases, \( \Delta \)-scaling holds with \( 1/2 < \Delta < 1 \). Note also that the scaling function in \( (48) \) has a Gaussian form, even for \( \Delta > 1/2 \), which is quite different from the case \( (23) \) of Sect. II.C.

**H. Summary : panorama of the \( \Delta \)-scaling for thermodynamic systems**

Several features of finite systems are important if one wants to study either the criticality of the corresponding infinite system or the distance to the critical point. One should name here: the \( \Delta \)-scaling (this includes the first-scaling law \( \Delta = 1 \) as well), the form of the tail of the scaling function \( \Phi \), and the anomalous exponent. All these features are closely related with the properties of the scaling function which characterizes finite system at the equilibrium. If the infinite system experiences a second-order phase transition, and if \( m \) is the scalar order parameter or the shifted scalar order parameter \( (37) \), then:

At the critical point, the corresponding finite system exhibits first-scaling law if \( m \) is the order parameter, or \( \Delta \)-scaling law if \( m \) is the shifted order parameter. In both cases, the tail of the scaling function \( \sim \exp(-z^\nu) \) is characterized by a large value of the exponent \( \nu = 1/(1-\gamma) > 2 \), with \( \gamma \) being the anomalous exponent, i.e. the exponent characterizing decrease of the extensive order parameter with the size \( N \) of the finite system. The values of \( \Delta \) are restricted to \( 0 < \Delta \leq 1 \), and the anomalous exponent \( \gamma \) takes values in between \( 1/2 \) and \( 1 \) for second-order at-equilibrium phase transition.

Far from the critical point, finite system exhibits second-scaling law with the Gaussian tail of the scaling function.

Close to the critical point when \( \epsilon \to 0 \) if \( N \to \infty \), the finite system exhibits the cross-over phenomenon from the first-scaling to the second-scaling law by a continuous \( \Delta \)-scaling law with Gaussian shape of the scaling function. One should remind here that the precise dependence of \( \epsilon(N) \) is irrelevant provided that: \( \gamma < \gamma' < 1, \) i.e. that the conditional point approaches 0 not faster than the pseudocritical point. This last remark is important in the phenomenological applications of the scaling theory to the situations where the \( N \) dependency of the conditional point is governed by an external control parameter with unknown relation to the system size.

Last but not least, if the parameter \( m \) is not singular at the transition, then all properties of its probability distribution are the same as in the case of non-critical systems.

In phenomenological applications, it is often difficult to get the probability distribution with sufficient accuracy for the values of scaling variable which are far from the most probable value since this corresponds to very small probabilities. It is then more judicious to work with moments of the distribution instead of the distribution itself. For example, when the system undergoes \( \Delta \)-scaling, the properly normalized cumulant moments \( (13) \):

\[ \frac{\kappa_q}{(\kappa_1)^{q\Delta}} \sim \text{const}, \quad (49) \]

are independent of the size of the system. An important consequence is that the generating function of the \( m \)-distribution:

\[ G(u) = \sum P[m] \exp(mu), \]

is a function of the reduced variable \( < m >^\Delta u \) only, generalizing a remark of Sect. II.A for the generating function in the first-scaling case.
III. A NON-CRITICAL MODEL: THE MEKJIAN MODEL

The Mekjian fragmentation model is an equilibrium model which describes the decomposition of system into an ensemble of fragments. The statistical weights for every configuration of fragments are given explicitly in this model. If \( n_s \) denotes the number of fragments of size \( s \) with the size-conservation: \( N = \sum n_s \), the weight function for the configuration \( \{ n_s \} \) is given by [13] :

\[
W_N(\{ n_s \}, x) = \prod_{s=1}^{N} \frac{x^n s^n}{n_s! s^n (x + s - 1)} ,
\]

with \( x \) being a real control parameter. Many exact results can be obtained in this simple model. Here, we are interested in the multiplicity distribution \( P_N[m] \), where the fragment multiplicity is \( m = \sum n_s \). We can show that [14] :

\[
P_N[m] = x^m |S_N^{(m)}| \frac{\Gamma(x)}{\Gamma(N + x)} ,
\]

where \( |S_N^{(m)}| \) are the signless Stirling numbers of the first kind. Knowing then the generating function for these Stirling numbers :

\[
\sum_{m=0}^{\infty} P_N[m] e^{mu} = \frac{\Gamma(x) \Gamma(xe^u + N)}{\Gamma(xe^u) \Gamma(x + N)}
\]

one obtains the average value of \( m \) :

\[
\langle m \rangle = \sum_{s=1}^{N} \frac{1}{x + s} = x \ln N + (x - 1)\gamma - \psi(x) + O(1/N) .
\]

Moreover, making an asymptotic development of \( \langle m \rangle \) for large \( N \) and small \( s \), one obtains :

\[
\sum_{m=0}^{\infty} P_N[m] e^{mu} \approx N^{x(e^u - 1)} .
\]

The latter approximation is known to be correct for finite values of \( u \) [13]. This means that \( P_N[m] \) is approximately a Poisson \( m \)-distribution with parameter \( x \ln N \). In the leading order we have then : \( \langle m \rangle \approx m^* \). Inverting [14] to get \( P_N[m] \) as a Fourier transform, and making \( N \) large yields the scaling formula :

\[
\langle m \rangle^{1/2} P_N[m] = \frac{1}{\sqrt{\pi}} \exp \left( -\frac{(m - \langle m \rangle)^2}{2 \langle m \rangle} \right) - (x - 1)(\gamma - \psi(x))m^{\langle m \rangle \rangle} + O \left( \frac{1}{\langle m \rangle} \right) .
\]

This is nothing else but the second-scaling law [14] for the multiplicity distribution when \( N \) becomes large enough, because \( \langle m \rangle \approx m^* \). When \( \langle m \rangle \) is large enough, the second term in (52) is always very small compared to the first one for a finite \( m \).

Different fixed values of the control parameter \( x \) mimic different situations of the fragmentation. For \( x \ll 1 \), one has the situation of a fused system. For \( x \sim 0.5 \), the fragmentation resembles the evaporation of light fragments. The limit \( x \gg 1 \) corresponds to the complete disassociation of the mass into light fragments (monomers). Each of this situation is characterized by a different fragment-size distribution. The case \( x = 1 \) is particular in this model since it leads to the power-law size-distribution with the exponent \( \tau = 1 \). Following discussion in Sect. II.C, cluster multiplicity could be the order parameter. On the other hand, the second-order equilibrium phase transition is associated with \( 2 < \tau < 3 \), what implies that the equilibrium model of Mekjian is a non-critical model. Indeed, that is what can be seen also in the cluster-multiplicity scaling law [13]. Hence, the power-law cluster-size distribution alone does not guarantee that the system exhibits the critical behaviour of any kind [13].

IV. EXAMPLE: THE POTTS MODEL

A generalization of the magnetic Ising spin model has been proposed by Domb [12] and studied in details by Potts [13]. In this model, one considers a system of \( N \) sites in the \( d \)-dimensional space. The magnetic state of each site \( i \) is characterized by a quantity called : a spin (say : \( s_i \)). Each spin is of the same constant modulus and points to one of the \( q \) equally spaced directions, labelled from 0 to \( q - 1 \). The ferromagnetic short-ranged Potts Hamiltonian is then :

\[
H_q = -J \sum_{i,j} \delta(s_i, s_j) ,
\]

where \( \delta \) is the Kronecker symbol, and \( J \) is the positive coupling constant. The sum is restricted to nearest-neighbour pairs. The site percolation corresponds to the \( q = 1 \) Potts model, and ferromagnetic Ising model to the \( q = 2 \) case. This model is one of the simplest non-trivial critical thermodynamic N-body system, and many exact or accurate results are known for standard values of \( (d, q) \). In particular, there exists a value \( q_c(d) \) (for example : \( q_c(2) = 4 \)), for which when \( q \leq q_c(d) \), then such an interacting system experiences a second-order phase transition at a finite critical temperature (for example : \( \beta_c J = \ln(1 + \sqrt{q}) \) at \( d = 2 \)), while for \( q > q_c(d) \) the transition is a first-order one.

Let us consider here the case of the second order phase transition. All the scalings described above should hold.
We have first to define the order parameter for the system. If for a given configuration of the system, we call $N_k$ the number of sites in the state $k$, where $k$ varies from 0 to $q - 1$, then the order parameter $m$ is given by:

$$m = \frac{q(N_{\text{max}}/N) - 1}{q - 1}. \quad (54)$$

$N_{\text{max}}$ in (54) is defined as the maximum of all $N_k$’s. Fig. 1 shows the $m$-distribution at the critical temperature in the $(d, q) = (2, 3)$ case, in the first-scaling form. The scaling is recovered very precisely, even for such small system sizes as $64 \times 64$. Note also the complicated shape of the scaling curve.

On the other hand, if the system is in the ordered phase, the average value of the individual spins is finite, say : $< s_i > = m$, and the same reasoning can be used for the variable : $(M - Nm)/\sqrt{N}$. This variable is of zero mean, finite variance and short-ranged correlated. So, its fluctuations are Gaussian and can be put in the second-scaling form:

$$< M >^{1/2} P[M] = \frac{1}{\sqrt{2\pi}} \exp \left( \frac{- (M - < M >)^2}{2 < M >} \right). \quad (56)$$

Of course, the most interesting case corresponds to the critical temperature. At this point, the spins are correlated throughout the system, and the magnetization cannot be evaluated by the central limit theorem. Instead, we can remark that the spin-correlations are power-law:

$$< s_{\vec{r}} s_{\vec{r} + \vec{r}_0} > \sim \frac{1}{r^{d - 2 + \eta}},$$

with $\eta$ a critical exponent whose value should be between $2 - d$ and 2. Looking at the total magnetization as the sum of $N$ correlated variables, one gets

$$< M^2 > = \sum_{i,j} < s_i s_j > = \sum_i < s_i^2 > +$$

$$+ N \int_1^L < s_\vec{r} s_{\vec{r}_1} > r^{d - 1} dr \quad (57)$$

with $L \sim N^{1/d}$ the typical macroscopic length of the system. This means that:

$$< M^2 > \sim N^{1 + \frac{2 - \eta}{d}}$$

as the leading behaviour. This non-trivial anomalous exponent

$$g = \frac{1}{2} + \frac{2 - \eta}{2d}$$

between 1/2 and 1, is here the sign of the criticality. The first-scaling law should hold in this case, as for the $(d, q) = (2, 3)$ Potts model discussed above, but the scaling function should be different since it depends on the precise form of the interactions. Only the tail can be linked to another critical exponent, as it has been written in Sect. II.C.

V. REVERSIBLE AGGREGATION - THE PERCOLATION MODEL

Percolation model can be defined as follows. In a box (a part of the regular lattice), each site corresponds to a monomer and a proportion $p$ of active bonds is set randomly between sites (the bond percolation model). Such a network results in a distribution of clusters defined as ensemble of occupied sites connected by active bonds.
For a definite value of \( p \), say \( p_{cr} \), a giant cluster almost surely spans the whole box. The sol-gel transition corresponds to the appearance of 'infinite' cluster (gel) at a finite time. 'Infinite' in this context means that gel contains the finite fraction of total mass of the system. The sol-gel transition in finite systems can be suitably studied using moments of the number-size-distribution \( n_s \), i.e. the number of finite clusters of size \( s \):

\[
M'_k = \sum_{s < s_{max}} s^k n_s ,
\]

where the summation is performed over all clusters with the exception of the largest cluster \( s = s_{max} \). The superscript ' recalls this constraint on summation in Eq. (58). The mass of the largest cluster is then : \( N - M'_1 \), with :

\[
N = \sum_{all \ s} s n_s .
\]

In infinite systems, one works with the normalized moments of the concentration-size-distribution \( c_s \), i.e. the concentration of clusters of size \( s \):

\[
m'_k = \sum_s s^k c_s ,
\]

where the summation in (59) runs over all finite clusters. Generally, concentrations are normalized such that :

\[
c_s = \lim_{N \to \infty} \frac{n_s}{N} .
\]

The probability that a monomer belongs to the infinite cluster (gel) is equal to \( 1 - m'_1 \), with :

\[
m'_1 = \lim_{N \to \infty} \frac{M'_1}{N} .
\]

For example, in the thermodynamic limit when the size of the box becomes infinite, a finite fraction of the total number of vertices belongs to this cluster. Therefore, we get the results : \( m'_1 = 1 \) for \( p < p_{cr} \) and \( m'_1 < 1 \) for \( p > p_{cr} \). Moreover, \( m'_1 \) is a decreasing function of the occupation probability. This typical behaviour is commonly (and incorrectly) called : 'the failure of mass conservation', but, as stated before, \( m'_1 \) is more simply the probability for a vertex to belong to some finite cluster.

**A. Percolation on the Bethe lattice**

The bond-percolation on the Bethe lattice with coordination number \( \hat{z} \), has been solved by Fisher and Essam [39]. Here the main result we are interested in, is the concentration-size-distribution [39] :

\[
c_s = \frac{((\hat{z} - 1)s)!}{((\hat{z} - 2)s + 2)! s!} p^{s-1}(1 - p)(\hat{z} - 2)s + \hat{z}
\]

and the first normalized moment :

\[
m'_1 = \left( \frac{1 - p}{1 - p^*} \right)^{2\hat{z} - 2} ,
\]

with \( p^* \) being the smallest solution of equation :

\[
p^*(1 - p^*)^{\hat{z} - 2} = p(1 - p)^{\hat{z} - 2} .
\]

Let us define :

\[
p_{cr} \equiv \frac{1}{\hat{z} - 1} .
\]

For \( p < p_{cr} \), the only solution of the above equation is : \( p^* = p \), but when \( p \) is larger than \( p_{cr} \), then there is a smaller non-trivial solution which behaves as \( p_{cr} - |p - p_{cr}| \) near \( p_{cr} \). Above this threshold, the moment \( m'_1 \) is smaller than 1 and behaves approximately as :

\[
m'_1 \approx 1 - \frac{2(p - p_{cr})}{1 - p_{cr}} .
\]

The marginal case \( \hat{z} = 2 \) corresponds to the linear-chain case.

Coming back to the concentrations, we can see that for large values of the size \( s \), the following Stirling approximation holds :

\[
c_s \sim s^{-5/2} \exp(-\alpha s)
\]

with \( \alpha \) given by :

\[
\alpha = \ln \left[ \frac{p}{p_{cr}} \left( \frac{1 - p}{1 - p_{cr}} \right)^{\hat{z} - 2} \right] .
\]

For this model, a power-law behaviour of the concentrations is seen at the threshold \( p_{cr} \), namely : \( c_s \sim s^{-\tau} \) with \( \tau = 5/2 \). Outside this threshold, an exponential cut-off is always present [40]. This sort of critical behaviour at equilibrium is analogous to the thermal critical phenomena, and in particular, there exist two independent critical exponents, for example \( \tau \) and \( \sigma \). The latter one is the exponent of the mean cluster-size divergence. Together, those two critical exponents : \( \tau = 5/2 \) and \( \sigma = 1 \), describe completely the critical features.

This singular behaviour is due to the appearance of a giant cluster, the so-called percolation cluster, at the transition point. More precisely, in the infinite system the probability for a given site to belong to this infinite cluster is zero below the critical threshold \( p_{cr} \) and positive above it. This probability is non-analytical at the critical point. Because of this behaviour, the extensive order parameter defined for finite systems is just the size of the largest cluster \( s_{max} \).

As discussed in Sect. II.C, the corresponding finite-size order parameter scales as

\[
s_{max} \sim N^{2/3} .
\]
Even though the system experiences the second-order critical phenomenon, fluctuations of the multiplicity distribution remain small and the KNO-scaling does not hold. Of course, $m'_0$ is not in this case an order parameter since $\tau > 2$ even though there is some irregularity in its behaviour passing the threshold. This non-analyticity can be illustrated by the exact result for bond-percolation on the Bethe lattice. In this mean-field case, the normalized $0^\text{th}$-moment is:

$$m'_0 = (1 - \frac{\hat{s}}{2/p^*}) \Bigg( \frac{1 - p}{1 - p^*} \Bigg)^{2\hat{s} - 2} \simeq \frac{\hat{s} - 2}{2(\hat{s} - 1)} - (\hat{s} - 1)\epsilon + (1 - \frac{\hat{s}}{2})|\epsilon|$$

with $\epsilon = p - p_c$, and $\epsilon \ll 1$. There is a jump of the first derivative of $m'_0$ with respect to $p$: $-\hat{s}/2$ for $p \rightarrow p_c^-$, and $(4 - 3\hat{s})/2$ for $p \rightarrow p_c^+$. 

**B. 3-dimensional percolation**

As shown by Botet et al.\[23\], the multiplicity distribution for the 3-dimensional bond percolation model on the cubic lattice at the infinite-network percolation threshold exhibits the $\Delta$-scaling with $\Delta = 1/2$, and hence the fragment multiplicity is not related to the order parameter in this process. This is shown in Fig. 2c as a typical example of non-critical parameter scaling. Note that the multiplicity distributions in Fig. 2c are plotted in semi-logarithmic form to show clearly the Gaussian behaviour (parabolic shape on the figure). The proper order parameter for this model is the normalized mass of the gel-phase, i.e. the mass of the largest cluster divided by the total mass of the system $s_{\text{max}}/N$. Different probability distributions $P_N[s_{\text{max}}/N]$ for different system sizes $N$ can be all compressed into a unique characteristic function (see Fig. 2a):

$$< \frac{s_{\text{max}}}{N} > P_N \left[ \frac{s_{\text{max}}}{N} \right] = \Phi \left( \frac{s_{\text{max}} - < s_{\text{max}} >}{< s_{\text{max}} >} \right)$$

which is analogous to the KNO-scaling function. As an application of results developed in Sect. II.E, Fig.2b shows the $\Delta$-scaling for the shifted order parameter : $M'_1 = N - s_{\text{max}}$. The value of $\Delta$ $(= 0.8)$, is consistent with the value of the anomalous dimension (25) : $g = 0.8435$, for the accepted values of the critical exponents $\beta, \gamma$ in the 3-dimensional percolation. One should also remember that $\Delta$ has been extracted from the small size $(N = 14^3, 20^3, 32^3)$ percolation network calculations at the infinite-network percolation threshold. This explains a small difference between the value for $\Delta$ from the scaling analysis and the expected value : $\Delta = g$, in the infinite network.

According to the results derived above for the second order phase transition, the second-scaling should hold outside of the critical point. This is correctly realized with the three variables $s_{\text{max}}$, $M'_1$ and $M_0$ for large or small values of the probability $p$. Fig. 3 shows such results for the value $p = 0.35$.

**Fig. 2.** (a) The first-scaling of $s_{\text{max}}$-distributions at the percolation threshold $(p = p_c = 0.2488)$ of the 3-dimensional bond percolation for lattices of different sizes : $N = 14^3$ (diamonds), $N = 20^3$ (squares), $N = 32^3$ (circles). The data corresponds to $10^5$ events. (b) The $\Delta$-scaling of the distributions of $M'_1 = N - s_{\text{max}}$ for the same conditions as in (a). (c) The second-scaling of the multiplicity distributions plotted in log-linear scale (i.e. $\log(< M_0 >^{1/2} P[M_0])$ vs $z_{(1/2)}$) for the same conditions as in (a).

Finally, it is instructive to see how the first-scaling is disappearing when the value of $p$ is slightly shifted away from its critical value. Fig. 4 illustrates the deviations from the first-scaling for the values of parameter $p$ close to $p_c$, on both sides of $p_c$. Even very close to the critical point, these deviations are quite significant and can be easily seen in this representation.
VI. IRREVERSIBLE AGGREGATION - EXAMPLE OF SMOLUCHOWSKI KINETIC MODEL

The irreversible sol-gel transition can be modelled using the coupled non-linear differential equations in distributions $c_s$ of clusters of mass $s$ per unit volume (the Smoluchowski equations [27]) :

$$\frac{dc_s}{dt} = \frac{1}{2} \sum_{i+j=s} K_{i,j} c_i c_j - \sum_j K_{s,j} c_s c_j . \quad (60)$$

Coefficients $K_{i,j}$ represent the probability of aggregation per unit of time between two clusters of mass $i$ and $j$. The Smoluchowski equations are derived from the master equation in the mean-field approximation [33] :

$$<c_k c_l> = <c_k> <c_l> .$$

The time $t$ includes both diffusion and reaction times. Eqs. (60) suppose irreversibility of the aggregation, i.e. the cluster fragmentation is excluded. One should notice however that the sum over $j$ in (60) does not include the

FIG. 3. (a) The second-scaling of $s_{max}$-distributions above the percolation threshold ($p = 0.35$) of the 3-dimensional bond percolation for lattices of different sizes : $N = 14^3$ (diamonds), $N = 20^3$ (squares), $N = 32^3$ (circles). The calculated data corresponds to $10^5$ events.

(b) The second-scaling of the distributions of $M'_1 = N - s_{max}$ for the same conditions as in (a).

(c) The second-scaling of the multiplicity distributions plotted in log-linear scale (i.e. $\log(<M_0>^{1/2} P[M_0])$ vs $z_{(1/2)}$) for the same conditions as in (a).

FIG. 4. (a) The $s_{max}$-distributions are plotted in the first-scaling form for parameters $p$ close to the percolation threshold of the 3-dimensional bond percolation : (a) $p = 0.252$ ; (b) $p = p_{cr} = 0.2488$ and (c) $p = 0.245$. The calculations are done for lattices of different sizes : $N = 14^3$ (diamonds), $N = 32^3$ (circles). The calculated data corresponds to $10^5$ events.
infinite cluster (gel) because:
\[ c_{j=\infty} = 1/\infty = 0 \, . \]

Experimentally known aggregation kernels \( K_{ij} \) are homogeneous functions \([28]\):
\[ K_{ai,aj} = \lambda^s K_{i,j} \]
with \( \lambda \) being the homogeneity index. Perhaps the simplest physically relevant example of a homogeneous kernel is: \( K_{ij} = (ij)^\mu \). It has been shown in this case that if \( \mu \) is larger than \( 1/2 \), then there exists a time \( t_{cr} \) \((t_{cr} < \infty)\) such that \( m'_1 = 1 \) for \( t \leq t_{cr} \) but \( m'_1 < 1 \) for \( t > t_{cr} \) \([29,30]\).

Let us consider now the case: \( K_{ij} = (ij)^\mu \) with \( \mu = 1 \) in more details. It was shown in this case that if \( \mu \) is larger than \( 1/2 \), then there exists a time \( t_{cr} \) such that \( m'_1 = 1 \) for \( t \leq t_{cr} \) but \( m'_1 < 1 \) for \( t > t_{cr} \) \([32]\).

The critical gelation time is:
\[ m_G = \lim_{N \to \infty} \frac{1}{N} < s_{\text{max}} > \]
as the order parameter. For one realization, \( s_{\text{max}} \) corresponds to the mass of the gel above \( t_c = 1 \).

For finite sizes, one makes the usual assumption that there exists a characteristic size diverging at the transition, say:
\[ N_c \sim |t - 1|^{-1/\sigma_N} \]
such that for the mass gel in the finite system one has:
\[ \frac{1}{N} < s_{\text{max}} > \sim (t - 1) f \left( \frac{N}{N_c} \right) \text{ for } t \geq 1 \]
In particular, at the gelation time one has:
\[ < s_{\text{max}} > \sim N^{1-\sigma_N} \sim N^g \, . \]

Using the formula \([29]\), which is valid both for the equilibrium and non-equilibrium systems, one can calculate the anomalous dimension. Given the value of \( \tau \) (see \([31]\)), one finds \( g = 2/3 \). Hence: \( \sigma_N = 1/3 \) can be deduced from \([32]\). The average value of the order parameter \( < s_{\text{max}} > \) increases logarithmically for \( t < 1 \), and is a finite proportion of the system size when \( t > 1 \).

\[ \Phi \left( Z_{(1)} \right) \]

FIG. 5. The first-scaling of the \( s_{\text{max}} \) variable in the Smoluchowski kinetic model with the kernel \( K_{ij} = ij \) at the critical time \( t = t_{cr} = 1 \). The calculation are performed for two system sizes: \( N = 2^{10} \) (diamonds) and \( N = 2^{14} \) (circles). Each data set corresponds to \( 10^3 \) independent events.

The illustration of the above discussion is shown in Figs. 5 and 6. Fig. 5 shows the distribution of \( s_{\text{max}} \) in the first-scaling variables for systems of different sizes. The results have been obtained in the Smoluchowski model with the kernel \( K_{ij} = ij \), at the critical time: \( t = t_{cr} = 1 \). Fluctuation properties of \( s_{\text{max}} \) outside of the critical time: \( t = 2t_{cr} \), are shown in Fig. 6.
The remaining parameters of the Smoluchowski calculations are the same as used in the calculations shown in Fig. 5. In this case, the data for different system sizes collapse into the universal curve in the scaling variables with $\Delta = 1/2$. One should keep in mind that in both cases, the fragment-size distribution is a power-law with $\tau = 5/2$ (see (61)).

\[ \Phi(z_{(1/2)}) \]

**FIG. 6.** The second-scaling of the $s_{\text{max}}$ variable in the Smoluchowski kinetic model with the kernel $K_{ij} = ij$ above the critical time $t = 2t_c$. The calculations are performed for two system sizes: $N = 2^{10}$ (diamonds) and $N = 2^{14}$ (circles). Each data set corresponds to $10^5$ independent events.

\[ \log[\Phi(z_1)] \]

**FIG. 7.** The plot of the large -$z_{(1)}$ tail of the decimal logarithm of the scaling function: $\log \Phi(z_{(1)})$, against $z_{(1)}$ for the system size $N = 2^{12}$. The calculated data correspond to $10^5$ independent events. The solid line shows the dependence: $\Phi(z_{(1)}) \sim \exp(-z_{(1)}^3)$, which is expected from the value of the anomalous dimension $g = 2/3$.

The relation between the form of tail of the scaling function and the anomalous dimension (26) was derived analytically in Sect. II.C for the equilibrium systems at the second-order phase transition. For non-equilibrium systems, we do not know equally rigorous derivation (see also Sect. VI.A). On the other hand, one may expect that the relation between the $N$-dependence of the average value of the order parameter and the asymptotic form of the scaling function in the limit $N \to \infty$, i.e. between $\hat{\nu}$ and $g$, is connected to the asymptotic stability of the limit distributions. Actually, there is a very close connection of the renormalization group ideas and the limit theorems in the probability theory. If true, then the relation (26) could be valid in a more general framework than the one provided by the equilibrium statistical mechanics. To check this assertion, in Fig. 7 we show the plot of the logarithm of the scaling function $\Phi(z_{(1)})$ (see Fig. 5) versus $z_{(1)}^3$ for large values of $z_{(1)}$. If the relation (26) is valid also for the non-equilibrium sol - gel second-order phase transition, then: $\Phi(z_{(1)}) \sim \exp(-z_{(1)}^3)$, and the tail of the scaling function should be a straight line in Fig. 7. That is indeed the case.

Figs. 8 and 9, show the $\Delta$-scaling for the shifted order parameter variable: $M_{i} = N - s_{\text{max}}$. Results of the Smoluchowski calculations with the kernel: $K_{ij} = ij$, are shown at $t = t_c$ (see Fig. 8), and at $t = 2t_c$ (see Fig. 9). One sees that the $M_{i}$ distribution exhibits a qualitative change while going from the critical time $t = t_c$, where $\Delta = 0.67$, to $t = 2t_c$ for which $\Delta = 1/2$. At $t = t_c$, the value of $\Delta$ obtained by superposing different $M_{i}$ distributions in the scaling plot (39), agrees perfectly with the value of the anomalous dimension $g (=2/3)$.

By comparing Figs. 5, 6 with Figs. 8, 9, one may see
also that the effect of changing the variable : \( s_{\text{max}} \to M'_I \), is seen only at the critical time (compare Figs. 5 and 8) where \( (\Delta = 1) \to (\Delta = 0.67) \), and is absent above the critical time (compare Figs. 6 and 9) where \( \Delta (=1/2) \) remains unchanged.

\[
\Phi(z_{(1/2)})
\]

\[
t = 2t_{cr}
\]

FIG. 9. The second-scaling of the distributions of \( M'_I \) shifted order parameter in the Smoluchowski kinetic model with kernel \( K_{ij} = ij \) above the critical time, at \( t = 2t_{cr} \). Two system sizes are considered : \( N = 2^{10} \) (diamonds) and \( N = 2^{14} \) (circles). The calculated data correspond to \( 10^5 \) independent events.

\[
\Phi(z_{(1/2)})
\]

\[
t = t_{cr}
\]

FIG. 10. The distributions of \( M'_I \) shifted order parameter in the Smoluchowski kinetic model with kernel \( K_{ij} = ij \) at the critical time \( t = t_{cr} = 1 \), are plotted in the scaling variables of second-scaling. Two system sizes are considered : \( N = 2^{10} \) (diamonds) and \( N = 2^{14} \) (circles). The calculated data correspond to \( 10^5 \) independent events. The failure of the second-scaling is clearly visible.

Finally, in Fig. 10 we show the size-dependence of the \( M'_I \)-distributions at \( t = t_{cr} \), when the distributions are plotted in the ‘wrong’ variables of the second-scaling \( \Delta = 1/2 \). The distributions for two system sizes are clearly displaced , showing the sensitivity of the scaling analysis and failure of the second-scaling.

A. The origin of fluctuations and the argument of Van Kampen

\( \Omega \)-expansion is a systematic expansion of the master equations in powers of \( 1/N \) \([2] \). Lushnikov was the first to express the generating functions as the contour integrals for quantities like the moments \( M'_k \) \([2] \). Then Van Dongen and Ernst \([38] \) used \( \Omega \)-expansion to calculate explicitly these integrals for the moments \( M'_k \) in some simple cases like : \( K_{ij} = ij \). For example, the result for \( M'_2 \) can be expressed in terms of the generating function for the \( s_{\text{max}} \)-distribution \( P_N[s_{\text{max}}] \), as :

\[
\sum_{s_{\text{max}}} P_N[s_{\text{max}}] e^{s_{\text{max}} u} = \frac{N!}{2\pi i} \int \frac{dz}{z^{N+1}} \times \exp \left[ \sum_{s=1}^{N} \frac{c_s}{N^{s-1}} e^{s(N-s)/(2N)} (ze^{-u})^s \right]
\]

Using then the identity :

\[
\frac{\partial^n}{\partial u^n} \left[ \exp \left( \sum_s \alpha_s e^{su} \right) \right] = \sum \frac{n!}{1! a_1! \ldots n! a_n!} \times \left[ \sum \alpha_s s^a e^{su} \right]^{a_1} \ldots \left[ \sum \alpha_s s^n e^{su} \right]^{a_n} \exp \left( \sum_s \alpha_s e^{su} \right)
\]

, where the sum runs over different sets \( \{ a_1, ..., a_n \} \) with the constraint : \( a_1 + \ldots + a_n = n \), and the particular result written down by Van Dongen and Ernst for the \( K_{ij} = ij \)-case \([38] \) :

\[
\exp \left[ \sum_{s=1}^{N} \frac{c_s}{N^{s-1}} e^{s(N-s)/(2N)} z^s \right] = \sum_{s=1}^{N} \frac{z^s}{s!} \exp \left[ -\frac{1}{2} \left( 1 - \frac{s}{N} \right) + O(1/N) \right]
\]

we can find :

\[
\sum_{s_{\text{max}}} P_N[s_{\text{max}}] \exp (s_{\text{max}} u) = \exp \left[ N \left( \sum_{k=1}^{\infty} \frac{m'_k (-u)^k}{k!} + u \right) \right]. \quad (64)
\]

Having the \( \Omega \)-expansion of the generating function of the \( s_{\text{max}} \)-distribution, we can conclude about the scaling at the gelation point. The moments \( m'_k \) of the size-distribution for infinite systems are known to diverge near the gelation time \([22] \) as :
\[m_k' \sim |t - 1|^{3-2k}.\]

For finite systems, using : \( \sigma_N = 1/3 \), one obtains :

\[m_k' \sim |t - 1|^{-2k+3} f_k(N|t - 1|^3) \sim N^{\frac{2k-3}{2k-1}} \quad (65)\]

at the gelation time. We have then found the asymptotic result :

\[Nm_k' \simeq a_k < s_{max} >^k,\]

where \( a_k \)'s are some positive constants. Inserting (66) in (24), one can show that the generating function for \( s_{max} \) is the function of a single variable : \(< s_{max} > u \), what is a sufficient condition for the validity of the first-scaling law (1).

We can have informations on similar scalings for various moment-distributions. \( \Omega \) - expansion leads to the results :

\[< M_k'^2 > - < M_k'^2)^2 = Nm_{2k}' - (1-t)m_{k+1}'^2\]

\[< M_k' > = Nm_k' \quad (66)\]

for the values of \( k \) when all the quantities are defined. At the transition \((t = 1)\), the relation (32) allows to calculate the reduced moments \( m_k' \). The results can be written in the compact form :

\[\frac{< M_k'^2 > - < M_k'^2)^2}{< M_k'^2 >^{2\Delta}} \sim \text{const},\]

with the following values of exponent \( \Delta \) :

- \( \Delta = 1/2 \) for \( k \leq 3/4 \)
- \( \Delta = 2k/3 \) for \( 3/4 \leq k \leq 3/2 \)
- \( \Delta = 1 \) for \( 3/2 \leq k \)

These are indications for \( \Delta \)-scaling according to the remark (99) in Sect. II.H. More precisely : The moments of order \( k < 3/4 \) are not critical (the second-scaling law), the moments of order \( k \) between 3/4 and 3/2 exhibit the \( \Delta \)-scaling with \( \Delta = 2k/3 \). In particular, for \( k = 1 \), one recovers the correct value : \( \Delta = g = 2/3 \), corresponding to the general argument of the shifted order-parameter (77) with \( a_1 = a_2 = 1 \). Finally, when the value of \( k \) is larger than 3/2, we obtain the first-scaling law for the distribution of moments \( M_k' \). This is also a consequence of the shifted order parameter argument, since in these cases :

\[< M_k' > \sim < s_{max}^k >.\]

Far from the critical point, all the reduced moments \( m_k' \) are independent of \( N \), since the correlation size :

\[\frac{1}{t - 1 + \ln t}\]

(see (11)) is finite. Then, for any value of \( k \), the second-scaling law holds, as expected from the general theory.

The above results about \( \Delta \)-scaling for various moments of the size-distribution in the Smoluchowski model with kernel \( K_{ij} = ij \), are not complete since the arguments involve only the second cumulant moment \( \kappa_2 \). In principle, as shown in Sect. II.H, all cumulants should be investigated. So, even though many exact results are known in this model, the complete analytical solution is not yet available.

The same study as presented above for gelling systems, can be performed also for non-gelling systems. An example of this kind is obtained for : \( K_{ij} = i + j \). In this case, the size-distribution is power-law with the exponent \( \tau = 3/2 \) and, following the discussion in Sect. II.C, the cluster multiplicity can be the order parameter. One can derive analytically, that the multiplicity distribution is binomial :

\[P_N[M_0,t] = \left( \frac{N - 1}{M_0 - 1} \right) (1 - \exp(-Nt))^{N-M_0} \times \exp[-(M_0 - 1)Nt]\]

and can be approximated for \( N \rightarrow \infty \) and for a finite value of \( < M_0 > / N \) by :

\[< M_0 >^{1/2} \quad P_N[M_0,t] \sim \frac{1}{\sqrt{2\pi(1 - e^{-Nt})}} \times \exp\left( -\frac{1}{2(1 - e^{-Nt})} \left( M_0 - < M_0 > \right)^2 \right) \quad (67)\]

what corresponds to the second-scaling. One may notice, that this binomial distribution is exactly equivalent to the bond percolation on a Bethe lattice with the occupation probability :

\[p = 1 - \exp(-Nt).\]

In spite of self-similar features in the fragment-size distribution at the infinite time, one does not see any critical behaviour in the cluster multiplicity distribution at any time in the non-gelling aggregation systems. This confirms the observation made in Sect. III.A in the Mekjian equilibrium model, that the power-law size-distribution alone does not guarantee that the system exhibits the critical behaviour.

The insight gained from the numerical simulations of Smoluchowski equations and the evidences from exact results for both gelling and non-gelling aggregation systems, provide strong hints that the discussion of Sect. II.H is valid not only for the equilibrium systems but also for the non-equilibrium ones. We see the same significance of the \( \Delta \)-scaling in non-equilibrium systems as found in thermodynamic systems, and not only at the critical point but also close to the critical point or even far from it. We believe that this universality, which is common to equilibrium and non-equilibrium systems, has
deeper foundation in the relation between renormalization group ideas for self-similar systems and the limit theorems of probability theory for the asymptotic scaling laws of order-parameter distributions. The concept of statistical equilibrium does not intervene at this level. One should also remember that the universality discussed in this work, is associated with only one critical exponent, and certainly does not exhaust all the singularity properties of the thermodynamical potential in second-order thermal phase-transition.

VII. CONCLUSIONS

We have presented in this paper the theory of universal scaling laws of the order parameter fluctuations in any system in which the second-order critical behaviour exist. These scaling laws, called $\Delta$-scaling laws, are rigorously derived for the equilibrium systems. Moreover, both analytical and numerical evidence is presented in favour of the general validity of the $\Delta$-scaling laws also for the off-equilibrium processes which exhibit the critical phenomenon of the second-order.

In this work we have discussed different aggregation models, both reversible and irreversible, finding the same connexion between scaling function properties and the anomalous dimension (critical exponents). These results can be important in the phenomenological analysis of 'critical behaviour' in finite systems, where the critical exponent analysis is dubious and, moreover, the precise mechanism of the process may be unknown. In these cases, the $\Delta$-scaling analysis allows to select both the relevant observable and the interesting initial conditions, which lead to the 'pseudocritical' behaviour in the studied process. Another interesting aspect of the $\Delta$-scaling analysis is the possibility of compressing data and, hence, the elimination of redundant dependences in the data on parameters like the system size, the total energy, or the total momentum etc.. This provides an obligatory intermediate step in any phenomenological analysis before the laws governing complicated dynamics can be found. Finally, one should stress that the scaling laws discussed in this paper are independent of whether one deals with an equilibrium or an off-equilibrium process. This is a crucial advantage in the studies of short-lived systems. Examples of the multifragmentation processes in the collisions of atomic nuclei or atomic clusters well illustrate this problematic [4]. In the absence of thermal equilibrium, which is a theoretical hypothesis difficult to verify in dynamically formed short-lived systems, we simply do not have at our disposal any other tool to address reliably the question of possible 'criticality' of the studied process.

As said before, the $\Delta$-scaling analysis developed in this work provides an alternative to the critical exponents analysis in the equilibrium systems and is the only tool for the analysis of the non-equilibrium systems. All essential information can be deduced from the scaling function, the value of $\Delta$ parameter, the form of the tail of the scaling function and the value of the anomalous exponent. With these informations it is possible to find out whether the studied process is at the critical point, in its neighbourhood or far away from it. Reference point in this analysis is the (approximate) self-similarity of the system. Generalization of the above scaling theory to discontinuous phase-order transitions for which the characteristic length can be defined, is in progress.

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This follows from expected validity of Feynman scaling for the many-body inclusive cross sections of particle production in ultrarelativistic collisions.

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Strictly speaking, the system with $K_{ij} = i + j$ is 'asymptotically critical', i.e. its critical time is infinite. The power-law cluster-size distribution with $\tau = 3/2$ is valid rigorously only in the limit $t \to \infty$. 

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