Multiscaling of correlation functions in single species reaction-diffusion systems

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We derive the multi-scaling of probability distributions of multi-particle configurations for the binary reaction-diffusion system $A+A \rightarrow \emptyset$ in $d \leq 2$ and for the ternary system $3A \rightarrow \emptyset$ in $d=1$. For the binary reaction we find that the probability $P_j(N,\Delta V)$ of finding $N$ particles in a fixed volume element $\Delta V$ at time $t$ decays in the limit of large time as $(\ln t)^d/(\ln \Gamma)^{N(N-1)/2}$ for $d=2$ and $e^{-N(N-1)/24\chi^2 c^2}$ for $d<2$. Here $\varepsilon=2-d$. For the ternary reaction in one dimension we find that $P_j(N,\Delta V) \sim (\ln t)^{-N(N-1)(N-2)/6}$. The principal feature of our study is the dynamical renormalization group. We compare predictions of $P_j(N,\Delta V)$ for a binary reaction in one dimension against the exact known results. We conclude that the $\varepsilon$ corrections of order two and higher are absent in the previous answer for $P_j(N,\Delta V)$ for $N=1,2,3,4$. Furthermore, we conjecture the absence of $\varepsilon^2$ corrections for all values of $N$.

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I. INTRODUCTION

Modeling chemical reactions is an important practical and theoretical problem. Systems of reacting particles are typical of complex irreversible nonequilibrium systems. The popular description of these systems in terms of simple rate equations currently adopted in chemical kinetics [1] does not appear to have a firm theoretical foundation and often produces wrong results.

Interacting particle systems provide a good model for simple chemical reactions. Well-known examples include systems of diffusing-coalescing and diffusing-annihilating particles describing reactions $A+A \rightarrow A$ and $A+A \rightarrow \emptyset$, respectively. Extensive studies of these particle systems in low dimensions have shown that the rate equations yield incorrect results for the computation of average concentrations of reactants; see [2] for review. Rate equations fail in low dimensions due to the presence of large fluctuation effects, which violate mean-field theory (MFT) assumptions underlying their derivation. The study of diffusive annihilation (or coalescence) [20] is a good starting point for analyzing large fluctuation effects in more complicated nonequilibrium statistical systems. For example, the system $A+A \rightarrow A$ was used to analyze the aggregation of massive diffusing particles [5].

Our aim in the current paper is to fully characterize the effects of large fluctuations on the statistics of local density for the reactions $A+A \rightarrow \emptyset$ and $A+A+A \rightarrow \emptyset$ in the regime where standard mean field arguments fail. Namely, we will study the temporal scaling of the probability of finding $N$ particles in the fixed volume in the limit of large times. For small spatial dimensions we discover the multiscaling of probabilities, in the sense that the corresponding scaling exponents depend nonlinearly on $N$. As a result, the probability of finding $N$ particles in the volume does not scale as the $N$th power of particle density. This type of scaling reflects the breakdown of self-similarity of the PDF of local particle density, and is impossible to obtain using either mean field or Smoluchowski approximations. As a consequence of our study, reactions of ternary and binary annihilation can be added to the small list of statistical systems for which multiscaling is verified analytically.

Large fluctuation effects are accounted for in binary reaction-diffusion models using Empty Interval methods (EIM) and its generalizations [6–9]. This approach is restricted to $d=1$ and does not extend to higher dimensions. There are rigorous results on the average density of particles in $d=1,2$ [10]. The Smoluchowski approximation gives correct answers for average concentrations [11] but cannot be used for higher order correlation functions. In the early 90s, the work of Cardy and Lee [4,12] used field theoretic methods, in particular the renormalization group (RG), to obtain an answer for the average density as well as its amplitude for $d \leq 2$. The study of $A+A \rightarrow \emptyset(A)$ has also introduced the concept of stochastic rate equations with imaginary multiplicative noise [3,4].

In this paper we derive the multiscaling of correlation functions in the systems $A+A \rightarrow \emptyset$ and $3A \rightarrow \emptyset$ using the RG method. The main aim is the study of violation of self similarity of the probability distribution function of local particle density. This is done by analyzing the large time temporal scaling of $P_j(N,\Delta V)$, the probability of finding $N$ particles in a small volume $\Delta V$. Note that $P_j(N,\Delta V)$ is the integral of the $N$th moment of the PDF of local particle density.

For the $A+A \rightarrow \emptyset$ reaction-diffusion system, we are interested in $d \leq 2$. We do not consider higher dimensions, as the answers there are given by MFT. Most studies have concentrated on computing the average density of particles ($N=1$) [4,12]. To the best of our knowledge, the computation of multiparticle probabilities are only considered in [6–8], with the analysis restricted to one dimension. The dynamical RG

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method allows us to obtain answers for the large time limit in the form of an $e$ expansion ($e=2-d$ for $d<2$ and logarithmic corrections to the MF scaling for $d=2$:

$$P_x(N,\Delta V)/P_x(1,\Delta V)^N \sim \begin{cases} r^{(N-1)e^2/4+O(e^2)}, & d < 2, \\ (\ln t)^{-N(N-1)/2} \cdot \left[1 + O\left(\frac{1}{\ln t}\right)\right], & d = 2, \end{cases}$$

(1)

where [12]

$$P_x(1,\Delta V) \sim \begin{cases} r^{d/2}, & d < 2, \\ \ln t, & d = 2. \end{cases}$$

Equation (1) represents the multiscaling or the deviation of $P_x(N,\Delta V)$ from $P_x(1,\Delta V)^N$. More precisely, one needs infinitely many exponents to describe the scaling of distribution functions $P_x(N,\Delta V)$: As can be derived from (1), the probability of finding $N$ particles in the volume $\Delta V$ conditioned on it containing at least $N-1$ particles is

$$P_x(N,\Delta V|N-1) \sim \left(\frac{1}{\ln t}\right)^d \left(\frac{1}{N^2}\right)^{e(N-1)}.$$ 

(2)

The first scaling factor on the rhs of (2) agrees with Slomuchowski or, equivalently, the renormalized mean field theory approximation. The second scaling factor, $\beta_N=(1/\sqrt{t})^{eN}$, where $e_N=e(N-1)$ describes the reduction of the probability of finding an additional particle in the volume already containing at least $N-1$ particles. The value of $e_N$ depends on $N$, which implies the multiscaling of probabilities $P_x(N,\Delta V)$. It is worth noting an analogy between the multiscaling picture presented previously and phenomenological multifractal models of turbulence, see [14], Chap. 8, for a review. We also note that as

$$\lim_{t \to \infty} P_x(N,\Delta V)/P_x(1,\Delta V)^N = 0.$$ 

(3)

Equation (1) reflects the anticorrelation between particles in the large time limit. The multiscaling in (2) gives the law of an increase of the strength of anticorrelation with the number of particles.

For the ternary reaction-diffusion system $3A \to \emptyset$, we restrict our attention to $d=1$. MFT provides the answers in higher dimensions [12]. The average density has been studied in [12,13], and the two-point function in [12]. Higher order correlations have not been considered. The method of empty intervals does not extend to the ternary reaction. The RG method produces asymptotically exact results for $d=1$:

$$P_x(N,\Delta V)/P_x(1,\Delta V)^N \sim \ln^{-N(N-1)(N-2)/6} r^{(N-1)e^2},$$

(4)

where [12]

$$P_x(1,\Delta V) \sim \left(\ln t\right)^{1/2}.$$ 

The paper is organized as follows: an introduction to the lattice model of $A+A \to \emptyset$ is given in Sec. II A; its field-theoretic reformulation is given in Sec. II B, followed by a summary of the mean field results in Sec. II C. Section III contains the RG analysis of the binary annihilation system for $d=2$, starting with the description of the renormalization procedure in Sec. III A. Section III B contains the RG analysis of the binary annihilation system for $d=2$, starting with the description of the renormalization procedure in Sec. III A. Section III B contains the derivation of the corresponding Callan-Symanzik equation for the theory, its solution, and the derivation of large time asymptotics of multiparticle probabilities. We prove the exactness of our result for $P_x(N=2, \Delta V)$ using the first Hopf equation of the theory. In Sec. III C, we compare our results in $d=1$ against results from [6] and establish their equivalence for $N=1,2,3,4$. Further, we conjecture the exactness of our one-loop answer in $d=1$ for general values of $N$. In Sec. IV we extend our analysis to the ternary reaction in $d=1$ using the same methodology.

**II. FIELD-THEORETIC FORMULATION AND MEAN-FIELD LIMIT OF $A+A \to \emptyset$ MODEL**

**A. The model**

Consider a set of point particles performing random walks, characterized by diffusion coefficient $D$, on the lattice $\mathbb{Z}^d$. Any two particles positioned at the same site can annihilate each other according to an exponential process with rate $\lambda$. For the simplicity of our analysis we assume finite reaction rates. However, the large time asymptotics of our model belongs to the universality class of an instantaneous annihilation-diffusion model (see the end of Sec. III B). It is assumed that the initial distribution of particle number at each site is an independent Poisson with mean $N_0$.

Let the random variable $N_t(x)$ represent the occupation number for site $x$ at time $t$. The configuration vector $N_t = \{N_t(x)\}_{x \in \mathbb{Z}^d}$ specifies the state of the system at time $t$ by encoding the occupation number at all sites. $N_t$ is also termed a microstate. Let $P_t(N)$ be the probability of finding the system in microstate $N$ at time $t$. Correlation functions of $N_t(x)$ can be obtained by averaging functions of $N(x)$ with respect to $P_t(N)$. For example, the average density is given by

$$\overline{N(x)} = \sum_{[N]} N(x)P_t(N).$$ 

(5)

Due to translational invariance, this will be independent of $x$. Our main object of interest is the large time limit asymptotics of $P_t(N(x) = N)$, the probability of finding $N$ particles at site $x$. It turns out that in the low density limit this probability is proportional to the $N$th factorial moment of $N(x)$, which we denote by $M_N(x,t)$. This can be verified as follows:

$$M_N(x,t) = \frac{\left[N_t(x) - (N-1)\right] \ldots \left[N_t(x) - 1\right]}{N!}$$

$$= \sum_{[N]} \prod_{k=0}^{N-1} \left[N(x) - k\right] P_t[N]$$

$$= \sum_{[N]} \prod_{n=0}^{N-1} \sum_{k=0}^{n} \left[n-k\right] \delta_{N(x),n} P_t[N].$$
\[
\approx \frac{N}{N-1} \sum_{n=N_1}^{N-1} \prod_{k=0}^{N-1} \left( n-k \right) P_\tau[N(x) = n] \\
= \sum_{n=N_1}^{N-1} \prod_{k=0}^{N-1} \left( n-k \right) P_\tau[N(x) = n] \\
= N \left\{ \prod_{n=0}^{N-1} \left( N - n \right) \right\} \\
= \sum_{n=0}^{N-1} \prod_{k=0}^{N-1} \left( n-k \right) P_\tau[N(x) = n] \\
= N ! \left\{ \prod_{n=0}^{N-1} \left( N - n \right) \right\}, \tag{6}
\]

where \( \delta_{ab} \) is the Kronecker delta symbol. In the above derivation, the first five lines are exact relations. The last line is due to the fact that in the large time limit we expect the particle density to be low and particles are anticorrelated [4,6,8,12]. Hence the configurations with the smallest possible value of \( N_1 = N \) will give the dominant contribution.

The coarse-grained counterpart of \( P_\tau[N(x) = N] \) is \( P_\tau(N, \Delta V) \), the probability of finding \( N \) particles in the volume element \( \Delta V \). Let \( \Delta N(x) \) be the number of particles in a volume \( \Delta V \) (centered at \( x \)) at time \( t \):

\[
\Delta N_t(x) = \int_{\Delta V} d^3y \, n_t(y), \tag{7}
\]

where \( n_t(y) \) stands for the density of particles at time \( t \) at a point \( y \). It should be mentioned that, upon averaging, \( \Delta N_t(x) \) is independent of \( x \) due to translational invariance. In the limit of large time and fixed \( \Delta V \), factorial moments of \( \Delta N \) are related to \( P_\tau(N, \Delta V) \) via a relation analogous to (6):

\[
P_\tau(N, \Delta V) = \frac{1}{N!} M_N(t) \\
= \frac{1}{N!} \prod_{k=0}^{N-1} \left( \Delta N_t(x) - k \right). \tag{8}
\]

As we will demonstrate in the next section, the factorial moments of \( \Delta N_t(x) \) admit a simple representation in terms of polynomial moments of Doi’s fields.

### B. Path-integral representation

In the previous section it was shown that to obtain correlation functions of interest, we need to know moments of \( N(x) \) with respect to \( P_\tau(N) \). It is possible to evaluate these moments in a path-integral setting. The formalism is due to Doi-Zeldovich-Ovchinnikov, and we refer the reader to [3,4] for details. We simply present a schematic derivation. The time evolution of the probability measure \( P_\tau \) on the space of microstates is given by the master equation. The master equation is a linear first order autonomous differential equation with respect to time, which implies that its evolution operator can be expressed as a path integral. Thus we can find a path-integral representation for any correlation function. As we are interested in universal properties of the system at scales much larger than the lattice spacing, it is convenient to work with the continuum (coarse-grained) limit of the lattice model, which corresponds to some effective field theory in imaginary time. The continuum limit in the path integral is taken according to the rules

\[
\lambda(\Delta x)^d \to \lambda, \quad D(\Delta x)^2 \to D,
\]

where \( \Delta x \) denotes the lattice spacing. The reader is asked to refer to [12] for more details. The resulting field theory is given by the effective action \( S \):

\[
S = \int_0^\tau dt \int d^3x \, \bar{\phi}(\partial_t - \Delta) \phi + 2\lambda \bar{\phi} \phi^2 + \lambda \bar{\phi}^2 - n_0 \bar{\phi} \phi(t), \tag{9}
\]

where \( n_0 \) is the initial average particle density. We will be working in the large \( n_0 \) limit. The diffusion coefficient \( D \) can be set to 1, as it is not renormalized by fluctuations [12]. The \( \bar{\phi} \) field is a response field. The \( \phi \) field is related to the local density field, \( n_t(x) \), in the sense that there is a one-to-one correspondence between correlation functions of \( n_t \) and \( \phi \). Let \( \langle \cdot \rangle \) be the averaging with respect to the path-integral measure \( e^{-S} \). Then the average density is [12]

\[
\bar{n}_t(x) = \langle \phi(x,t) \rangle = \int D\bar{\phi}(x,t) D\phi(x,t) \phi(x,t) e^{-S[\phi,\bar{\phi}]}. \tag{10}
\]

Let us introduce the quantity \( \Delta\phi \):

\[
\Delta \phi(x) = \int_\Delta V d^3y \phi(y), \tag{11}
\]

where the volume \( \Delta V \) is centered at \( x \). Averaging (11) results in an \( x \)-independent quantity due to the translational invariance of the system. Let us consider the statistics of \( \Delta N_t(x) \) defined in Eq. (7). Moments of \( \Delta N \) and moments of \( \Delta \phi \) are related as follows:

\[
\langle \Delta \phi \rangle = \Delta N_t, \tag{12}
\]

\[
\langle \Delta \phi^2 \rangle = \Delta N_t(\Delta N_t - 1). \tag{13}
\]

The relations (12), (13) follow from [12]. Let us note that (12) gives us a path-integral representation of the average number of particles in a volume \( \Delta V \). More generally [15],

\[
\langle \Delta \phi^N \rangle = M_N(t), \tag{14}
\]

where \( M_N \) is defined by Eq. (8). In the previous section it was shown that in the large-time limit the factorial moment is approximately equal to the probability of finding \( N \) particles in a volume element \( \Delta V \). Hence,

\[
P_\tau(N, \Delta V) = \frac{1}{N!} \langle \Delta \phi^N \rangle. \tag{15}
\]

As we mentioned previously, we are interested in the limit \( \Delta V \to 0 \). Physically this limit corresponds to \( \Delta V \ll \ell^d \), where the correlation length \( \ell \sim \sqrt{t} [4] \). By working in the large time limit we are effectively dealing with the case \( \Delta V \to 0 \). Then we may write:

\[
\langle \Delta \phi^N \rangle = \int_{\Delta V} dx_1 \ldots dx_N \langle \phi(x,x_1) \ldots \phi(x,x_N) \rangle, \tag{16}
\]

where
to the mean density, diagrams with $m$ renormalizable dc scaling of $Pt=n_{cl}$ also termed the classical density, denoted coupling regime the main contribution to the mean density $d_{n}/H_{20849}$ must be dimensionless; thus in length dimensions of the relevant parameters must be.

The critical dimension is $d_{c}=2$, where the reaction rate is dimensionless. For $d=2$ the field theory is super-renormalizable, where all Feynman integrals converge. For $d=2$ we use dimensional regularization to ensure the convergence of Feynman integrals.

The bare dimensionless reaction rate is given by $g_{d}(t)=\lambda t^{1-d/2}$, which grows with time in $d<2$. A combinatorial argument shows that an $n$-loop diagram contributing to the mean density is proportional to $g_{d}^{-1}(t)$ [12]; thus in the weak coupling regime the main contribution to the mean density comes from the sum of tree diagrams. This is equivalent to the mean-field approximation. This sum (tree diagrams) is also termed the classical density, denoted $n_{cl}(t)$. In $d<2$, MFT is valid for small times given the initial density is large. This agrees with our intuition: for small times, local fluctuations around the mean value of the density are small. At large times, $g_{d}(t)$ grows and MFT breaks down. To compute corrections to the mean-field answers, one must compute higher loop contributions. In particular, this involves summing infinite sets of diagrams for a fixed number of loops. These can be resummed in a more compact form using the classical density ($n_{cl}$) and the classical response function ($G_{t_{0}}$). The classical response function consists of the sum of all tree diagrams with one outgoing and one incoming line. The diagrammatic form of the integral equations satisfied by these two quantities are given in Fig. 2. The solution to these equations are

$$\langle \phi(x_{1}) \cdots \phi(x_{N}) \rangle = F(x_{1} \cdots x_{N})|_{dc} [1 + \mathcal{O}(\Delta V^{1/d})].$$

$F(x_{1} \cdots x_{N})$ is the leading coefficient of Wilson’s operator product expansion (OPE) [16]. The limit $\Delta V \to 0$ corresponds to the ultraviolet ($x_{i} \to 0, \forall i$) asymptotics of $\langle \phi(x_{1} + x_{1}) \cdots \phi(x_{i} + x_{N}) \rangle$, which is given by the renormalized average of the composite operator $\phi^{N}$. We conclude that multi-scaling of $P_{t}(N, \Delta V)$ is described by anomalous dimensions $\xi$ of $\phi^{N}$. The spectrum of anomalous dimensions of $\phi^{N}$ will be computed in Sec. III.

C. Mean field limit and loop expansion

The Feynman rules for the perturbative computation of correlation functions are derived from the action $S$, Eq. (9). They are given by Fig 1. The propagator $G_{0}$ is the Green’s function of the standard diffusion equation. The perturbative expansion of $\langle \phi^{m} \rangle$ in powers of $\lambda$ is given by the sum of all diagrams with $m$ outgoing lines; hence diagrams contributing to the mean density, $\langle \phi \rangle$, have one outgoing line. The action $S$ must be dimensionless; thus in length ($L$) units, the dimensions of the relevant parameters must be

$$[\lambda] = L^{2}, \quad [\bar{\phi}] = L^{0}, \quad [\phi] = L^{-d}, \quad [\chi] = L^{d-2}.$$ (18)

\[ \text{FIG. 1. Feynman rules for } A+A \to \phi \text{-field theory.} \]

The dynamical renormalization group method allows one to extract large time asymptotics of correlation functions of the theory (9). The first step is to eliminate all $\varepsilon \to 0$ singularities of Feynman integrals at some reference time $t_{0}$. The process of removing these divergences is called renormalization. This is done by introducing a renormalized reaction rate, renormalized fields, etc. The number of renormalization constants needed to eliminate all divergences is finite for $d \approx d_{c}$ due to the renormalizability of (9). Individual terms in the renormalized perturbative series for any correlation function $C(t)$ depend on the reference time $t_{0}$. The lack of dependence of the unrenormalized version of $C(t)$ on the unphysical parameter $t_{0}$ leads to a renormalization group (Callan-Symanzik) equation for the correlation function. This is solved subject to the initial condition at $t_{0}$ given by the perturbative expansion for $C(t)$ at $t=t_{0}$. This procedure is equivalent to resumming all leading $\varepsilon$ singularities in $d < d_{c}$ at all orders of the loop expansion [17]. Consequently, using $n_{cl}$ and $G_{t_{0}}$ in combination with the vertices of Fig. 1, we arrive at Feynman rules generating finitely many diagrams for a given number of loops.

Using $n_{cl}$ and $G_{t_{0}}$ in combination with the vertices of Fig. 1, we arrive at Feynman rules generating finitely many diagrams for a given number of loops. The solution to these equations are

\[ \text{FIG. 2. (a) The classical density; (b) the classical response function.} \]

$$n_{cl}(t) = \frac{1}{2\lambda t}$$

$$G_{e}(x_{2}, t_{1}^{2}; x_{1}, t_{1}) = \left( n_{cl}(t_{2}) / n_{cl}(t_{1}) \right) G_{0}(x_{2}, t_{2}^{2}; x_{1}, t_{1}).$$ (20)

In this form we see that for small $g_{d}(t)$ the loop corrections are small. Then we may formulate the following mean-field answer for the probability of finding $N$ particles in volume $\Delta V$:

$$P_{t}(N, \Delta V) = \frac{1}{N!} \langle \Delta \phi^{N} \rangle = \frac{1}{N!} \langle \Delta \phi \rangle^{N} \sim \langle \Delta V \rangle^{N} \gamma^{N}.$$ (22)

Comparing (22) with results from [6–8] in $d=1$, we find the linear temporal scaling of MFT to be incorrect in the large time limit. We will compute the correct scaling in the subsequent section.

III. RENORMALIZATION GROUP ANALYSIS OF $P_{t}(N, \Delta V)$

The dynamical renormalization group method allows one to extract large time asymptotics of correlation functions of the theory (9). The first step is to eliminate all $\varepsilon \to 0$ singularities of Feynman integrals at some reference time $t_{0}$. The process of removing these divergences is called renormalization. This is done by introducing a renormalized reaction rate, renormalized fields, etc. The number of renormalization constants needed to eliminate all divergences is finite for $d \approx d_{c}$ due to the renormalizability of (9). Individual terms in the renormalized perturbative series for any correlation function $C(t)$ depend on the reference time $t_{0}$. The lack of dependence of the unrenormalized version of $C(t)$ on the unphysical parameter $t_{0}$ leads to a renormalization group (Callan-Symanzik) equation for the correlation function. This is solved subject to the initial condition at $t_{0}$ given by the perturbative expansion for $C(t)$ at $t=t_{0}$. This procedure is equivalent to resumming all leading $\varepsilon$ singularities in $d < d_{c}$ at all orders of the loop expansion [17]. Consequently,
one obtains scaling laws for correlation functions in terms of an $\varepsilon$ expansion. The knowledge of $O(\varepsilon)$ terms in the loop expansion in $d<d_c$ yields leading order logarithmic corrections to the mean-field answers in $d=d_c$.

We will now apply the method described above to compute both temporal and spatial scaling exponents of $P_i(N,\Delta V)$ for an $A+A\rightarrow \emptyset$ ($d_c=2$) reaction.

### A. One-loop renormalization of composite operator $\phi^N$

Dimensional analysis shows that renormalization of the correlation function $\langle \prod_{i=1}^{N} \phi(x_i,t) \rangle$, where $x_i \neq x_j$, requires reaction rate renormalization only [4,12]. However, we are interested in single-point correlation functions of the form $\langle \phi^N(x,t) \rangle$; see (17). The operator $\phi^N$ is called a composite operator for $N \gg 2$. It is well known that the insertion of composite operators under the sign of averaging leads to new types of divergences in the corresponding loop expansion [16]. These divergences cannot be eliminated by reaction rate renormalization and require multiplicative renormalization of the corresponding composite operators. As we will see below, these extra divergences are responsible for the multi-scaling of probabilities $P_i(N,\Delta V)$.

For the theory (9) the first instance of such a divergence occurs in the correlator $\langle \phi^2(y,t) \rangle=\lim_{\varepsilon \rightarrow 0} \langle \phi(x,t) \phi(y,t) \rangle$, as $\varepsilon \rightarrow 0$. We will see that it is specifically this singularity that leads to the multiscale of $P_i(N,\Delta V)$ for $N \gg 2$. The tree-level answer is quoted below for $d<2$ [12,18,19]

$$
\langle \phi(x,t) \phi(y,t) \rangle = \frac{1}{8\pi g_0^d} \left\{ \frac{1}{\varepsilon} \left[ \frac{|x-y|}{\sqrt{t}} \right]^{-\varepsilon} - 1 \right\} + O(\varepsilon^0).
$$

The averaging $\langle \cdots \rangle_c$ denotes connected correlation functions. It is clear from Eq. (23) that for $x \neq y$ there is no divergence in the limit $\varepsilon \rightarrow 0$. However, if $x=y$, there will be a $1/\varepsilon$ divergence (as $\varepsilon \rightarrow 0$) despite (23) being a tree-level answer. This divergence cannot be regularized by reaction rate renormalization. It requires multiplicative renormalization, where the divergent function is multiplied by a renormalizing factor that will eliminate the singularity. This procedure violates naive dimensional arguments according to which $\langle \phi^N \rangle$ should scale as $\langle \phi \rangle \sim r^{-N/2d}$ for $d<2$. Multiplicative renormalization leads to a nontrivial anomalous dimension that depends nonlinearly on the order of the composite operator. Multiplicative renormalization is not required for the average density $\langle \phi \rangle$, which explains its lack of anomalous scaling [4].

Let $M_N(t)=\langle \phi^N(t) \rangle$. Our aim is to renormalize $M_N$ at (arbitrary reference) time $t_0$. Let $g_0=\lambda_0^{\frac{1}{2d}}$ be the bare (dimensionless) reaction rate. The renormalized rate $g$ is also defined at reference time $t_0$ and is given by [12]:

$$
g = \frac{g_0}{1 + g_0 g^*},
$$

where $g^*=\varepsilon/C_d = 2\pi\varepsilon + O(\varepsilon^2)$ is the nontrivial stable fixed point of the RG flow in the space of effective reaction rates. The constant $C_d$ is given by

$$
C_d = \frac{2\pi}{(8\pi)^{d/2}} \Gamma\left(\frac{d-2}{2}\right).
$$

$C_d$ is regular at $d=2$ and takes the value $1/2\pi$. Expressing $g_0$ as a power series in $g$ and substituting into $M_N(t_0)$ enables us to obtain $M_N$ as a power series in $g$:

$$
M_N(t_0) = \left[ n_c(g_0,t_0) g_0 g^* \right]^N \left( 1 + \sum_{n=1}^{\infty} c_{N,n} g^n \right).
$$

The expression for $M_N(t_0)$ to $O(g^{1-N})$ is summarized by the diagrams in Fig. 3. The first term in this series is just $n_c^N$ and is given by Fig. 3(a). Expanding $n_c$ in $g$ using relation (24) will generate a term proportional to $1/g \sim 1/\varepsilon$. This term acts as a counter term to the diagram shown in Fig. 3(b). It eliminates the singularity in the one-loop correction to mean density $n^{(1)}$ [12]. The first divergence that cannot be eliminated by the renormalized reaction rate appears in the coefficient $c_{N,1}$. The origin of this singularity is, from averaging, the composite operator $\phi^2$. Let $Z_N$ be the renormalizing factor of $M_N$:

$$
Z_N = 1 + \sum_{n=1}^{\infty} a_{N,n} g^n.
$$

It is chosen in such a way that the renormalized correlation function $M_{N,R}$ is nonsingular at $\varepsilon=0$ at all orders. By definition [21],

$$
M_{N,R}(g,t_0) = Z_N(g,\varepsilon) \cdot M(g,t_0,\varepsilon).
$$

The coefficients $a_{N,n}$ are chosen to cancel the singularities in the coefficients $c_{N,n}$. This is known as the minimal subtraction scheme. In particular
\[ a_{N,1} = -[c_{N,1}], \quad (29) \]

where \([\cdot]\) extracts the singular part of an expression. Let us look at the calculation in more detail. Using Fig. 3 we may write

\[ M_N(t_0) = \left( \frac{1}{2g t_0^d} \right)^N \left( 1 - \frac{N(N-1)}{4\pi\epsilon} \cdot g + O(g^2) + \text{finite} \right). \quad (30) \]

The \(O(g)\) term is computed as follows: we need \( n_c^{(N-2)} \), there are \( \gamma C_2 \) diagrams of type c, and finally by setting \( x = y \) in (23), which gives \([M_2(t_0)]_c = (-1/8\pi\epsilon)t_0^{-2}\). Hence

\[ Z_N = 1 + \frac{N(N-1)}{4\pi\epsilon} \cdot g + O(g^2). \quad (31) \]

**B. RG computation of multiscaling**

The knowledge of renormalization laws (24) and (31) can be used to compute \(M_N(t)\) for \( t > t_0 \) as follows. The Markov property of the evolution operator \( U \) for the bare theory, namely \( U(t, t_0)U(t_0, 0) = U(t, 0) \), tells us that the bare function \( M_N(t) \) is independent of \( t_0 \) for \( t > t_0 \). Hence

\[ t_0 \frac{\partial}{\partial t_0} M(t_0) = t_0 \frac{\partial}{\partial t_0} [Z_N^{-1} \cdot M_N(t_0, t_0)] = 0. \quad (32) \]

The function \( M_{N,R}(t) \) is a function of \((t, t_0, g)\), leading to the ansatz: \( M_{N,R}(t) = t_0^{-N_n^{[d/2]}} \Phi(t/t_0, g(t_0)) \), where \( \Phi \) is a function with dimensionless arguments. The choice of \( t_0 \) is arbitrary, but we choose it small enough so that MFT is still valid. This motivates the choice of the prefactor \( t_0^{-N_n^{[d/2]}} \). Upon substitution of this ansatz into (32), we obtain the Callan-Symanzik equation:

\[ \left( \frac{\partial}{\partial t} + \beta(g) \frac{\partial}{\partial g} + \frac{N}{2} + \gamma_N(g) \right) M_N(t, t_0, g) = 0, \quad (33) \]

where the \( \beta \) and \( \gamma_N \) functions of the theory are given by

\[ \beta(g) = -t_0 \frac{\partial}{\partial t_0} g = \frac{1}{2} (C_g g^2 - e g), \quad (34) \]

\[ \gamma_N(g) = -\beta(g) \frac{\partial}{\partial g} \ln Z_N = \frac{N(N-1)}{8\pi} g + O(g^2). \quad (35) \]

The initial condition (at time \( t_0 \)) is given by the loop expansion of \( \langle \phi^N \rangle \) with the most dominant contribution coming from the MFT answer:

\[ M_{N,R}(t_0, g) = n_0^{N}(t_0, g). \quad (36) \]

Equation (33) subject to initial condition (36) is solved using the method of characteristics and has the following solution for \( d < 2 \):

\[ M_{N,R}(t, g(t, t_0)) = \left( \frac{t}{t_0} \right)^{-N_n^{[d/2]}} n_0^{N}(t_0, g(t, t_0)) \cdot \frac{\langle g(t, t_0) - g^* \rangle^{[N(N-1)/4\pi\epsilon]g^*}}{g^*}, \quad (37) \]

\[ g(t, t_0) = \frac{g^*}{1 - \left( 1 - \frac{g^*}{g} \right) \left( \frac{t}{t_0} \right)^{d/2}}. \quad (38) \]

The running coupling \( g(t, t_0) \) is the effective RG flow of the reaction rate. It can be verified that \( \lim_{t \to 0} g(t, t_0) = g^* \), which is of order \( e \). Hence, for large times we can convert the loop expansion to an \( e \) expansion. To obtain answers in \( d = 2 \), we take the limit \( e \to 0 \) in Eqs. (37) and (38):

\[ M_{N,R}(t, g(t, t_0)) = \left( \frac{t}{t_0} \right)^N n_0^{N}(t_0, g(t, t_0)) \cdot \frac{\langle g(t, t_0) \rangle^{N(N-1)/2}}{g^*}, \quad (39) \]

\[ g(t, t_0) = \frac{g^*}{1 + \frac{g^*}{4\pi} \ln \left( \frac{t}{t_0} \right)^{d/2}}. \quad (40) \]

For large times \( g(t, t_0) \sim 4\pi/\ln(t/t_0) \). Then in the large time limit we obtain the following scaling in \( t \) [recall \( M_{N,R}(t) = \langle \phi^N(t) \rangle_R \)]:

\[ M_{N,R}(t) \sim \left( r^{-N_n^{[d/2]} - [N(N-1)/2]} + O(c^2) \right), \quad (41) \]

where \( \Delta V \) dependence is restored using dimensional arguments. The physical interpretation of (42) is that in the large-time limit particles are anticorrelated [recall Eq. (3)]: given the same average density the probability of finding \( N \) reacting particles in \( \Delta V \) goes to zero faster than the probability of finding \( N \) nonreacting particles in \( \Delta V \). The origin of anticorrelation can be traced back to the recurrence property of random walks in \( d \leq 2 \).

Let us compare (42) with exact results for \( N = 1, 2 \). For \( N = 1 \) there is no anomaly and our formula is in agreement with the well-known result found in [12] for \( d \leq 2 \). Let us examine the case \( N = 2 \) by studying the Langevin SDE [4]:

\[ \frac{\partial}{\partial t} \phi - \Delta \phi = -2\lambda \phi^2 + \text{complex multiplicative Itô noise term}, \quad (43) \]

which is equivalent to the field theory (9). Here \( \Delta \) denotes a \( d \)-dimensional Laplacian. Taking averages of both sides and using spatial homogeneity yields the first Hopf equation:

\[ \langle \phi \rangle = -2\lambda \langle \phi^2 \rangle. \quad (44) \]

For \( d < 2 \) we know \( \langle \phi \rangle \sim t^{-d/2} \). Substituting this into the Hopf equation gives \( \langle \phi^2 \rangle \sim t^{-(1-d/2)} = t^{-(4d/2)} \). In \( d = 2 \), \( \langle \phi \rangle \sim \ln t/t \) and using this in the Hopf equation yields...
\( \langle \phi^2 \rangle \sim \ln t/t^2 \). These are exact relations and are in agreement with our formula (41) with \( O(e^2) = 0 \). We conjecture that for \( N=2 \), the \( O(e^2) \) corrections are absent in (41). Note that due to the diffusion term in (43), it is impossible to generalize the previous computation to calculate the scaling of \( \langle \phi^2 \rangle \) for \( N > 2 \).

Finally, note from Eq. (24) that \( \lim_{t \to \infty} g = g^* \). Thus, for \( d \leq 2 \), the limit \( \lambda \to \infty \) for finite \( t \) yields the same asymptotics as the limit \( t \to \infty \) for finite \( \lambda \). Therefore the large time asymptotics of the model at hand belongs to the universality class of instantaneous annihilation.

C. Comparison of results of \( e \) expansion with exact results in \( d=1 \)

Equation (42) gives us an asymptotically exact result in \( d=2 \) (\( e=0 \)). In the previous section we have also confirmed that order-\( e \) expansion of the scaling exponent of \( P(2, \Delta V) \) given by the first equation in (42) is exact in all dimensions \( d \leq 2 \). As it turns out, (42) yields an exact answer for multiscaling of probabilities in \( d=1 \) for all values of \( N \). We are fortunate to have some exact results for multipoint correlation functions in the problem of diffusion-limited annihilation \( A+A \to \emptyset \) for \( d=1, \lambda \infty \) [6]. For more details please refer to [6–8]. Using MATHEMATICA and recurrence relations derived in [6] we were able to compute exact analytical expressions for \( P_1(N, \Delta V) \) for \( N=1, 2, 3, 4 \). Based on the results, we find that the \( O(e^2) \) terms are absent in the \( e \) expansion (42). This leads us to conjecture that in \( d=1 \) the one-loop answer for the scaling exponents are exact.

To substantiate our claims, let us review the key results from [6]. The reaction rate is infinite, hence we do not expect to find more than one particle at a given site. We will use the notation used in [6–8]. The correlation function \( \rho_N(x_1, \ldots, x_N; t) \) represents the joint probability density of finding \( N \) particles positioned at \( x_1, \ldots, x_N \) at time \( t \). In particular, \( \rho(t) = \rho_1(t) \) is the average density. There is also the convention that \( x_i < x_j \) for \( i < j \). In the limit of large times:

\[
P_1(N, \Delta V) = \int_{\Delta V} dx_1 \ldots dx_N \, \rho_N(x_1, \ldots, x_N; t).
\]  
(44)

In the large time limit the following answers hold true:

\[
\rho(t) = \frac{1}{\sqrt{8\pi Dt}},
\]  
(45)

\[
\frac{\rho_2(x_1, x_2; t)}{\rho^2(t)} = 1 - e^{2z_{21}^2} + \sqrt{\pi z_{21}} e^{-z_{21}^2} \text{erfc}(z_{21}),
\]  
(46)

\[
z_{ji} = \frac{x_i - x_j}{\sqrt{8Dt}},
\]  
(47)

where \( D \) is the diffusion coefficient [6]. Note that as \( x_2 \to x_1 \) (or vice versa), the correlation function vanishes. This is a reflection of anticorrelations between particles. For small separations, it can be easily shown that

\[
\frac{\rho_2(x_1, x_2; t)}{\rho^2(t)} = \sqrt{\pi z_{21}} + O(z_{21}^2).
\]  
(48)

The previous expression for \( \rho_2 \) is valid in the limit of large time and fixed separation \( \Delta = x_2 - x_1 \), as in this limit \( z_{21} \to 0 \).

Due to (44) the scaling for (48) agrees with our answer for \( N=2 \) in (42):

\[
\frac{P_1(2, \Delta V)}{P_1(1, \Delta V)^2} \sim \frac{\Delta}{t^{1/2}}.
\]  
(49)

With the aid of MATHEMATICA and using similar arguments as previous, it can be shown that \( \rho_3(x_1, x_2, x_3; t)/\rho^3(t) \sim t^{-3/2} \) and \( \rho_4(x_1, x_2, x_3, x_4; t)/\rho^4(t) \sim t^{-3} \), which are in agreement with our conjecture for the cases \( N=3 \) and \( N=4 \), respectively.

The formal reason for anomalous scaling for \( N=2 \) is vanishing of the two-particle probability distribution function at \( x_1 = x_2 \). This is the most clear indication of anticorrelation between annihilating particles. This same phenomenon is responsible for zeros of multiparticle distribution functions as well. To explore the nature of these zeros, starting from the exact recurrence relations of [5] we were forced to use MATHEMATICA: exact expressions for correlation functions are written as a linear combination of a variety of terms involving products of \( \exp(-z_{ji}^2), \text{erfc}(z_{ji}), z_{ji} \).

At small separations these expressions simplify due to a number of cancellations that are not obvious. Using MATHEMATICA to break through the tedious computations, we find

\[
\frac{\rho_2(x_1, x_2; t)}{\rho^2(t)} = \sqrt{\pi z_{21}},
\]  
(50)

\[
\frac{\rho_3(x_1, x_2, x_3; t)}{\rho^3(t)} = 6\sqrt{\pi z_{21} z_{31} z_{32}},
\]  
(51)

\[
\frac{\rho_4(x_1, x_2, x_3, x_4; t)}{\rho^4(t)} = 2\pi z_{21} z_{31} z_{32} z_{41} z_{42} z_{43}.
\]  
(52)

Note that all distribution functions above vanish as the first power of separation between any pair of particles. Hence we can make a conjecture about the spatiotemporal behavior of distribution functions for arbitrary \( N \):

\[
\frac{\rho_N(x_1, \ldots, x_N; t)}{\rho^N(t)} \sim \prod_{1 \leq i < j \leq N} z_{ji}.
\]  
(53)

The previous expression is a direct generalization of (52) based on permutation symmetry and self-similarity. It states that the spatial dependence of the probability density is given by the Van-der-Monde determinant of particles’ coordinates.

Conjecture (53) reproduces the temporal scaling derived in (41) as the right-hand side contains \( N(N-1)/2 \) factors \( z_{ji} \), each contributing \( t^{-1/2} \) to the scaling. We will present a rigorous proof of this conjecture in a separate publication.

Our main aim in the current section was to verify RG predictions in one dimension. However, conjecture (53) constitutes a new result for one-dimensional diffusion-limited annihilation, even though the exact formulas for all correlation functions have been derived in [6]. The exact expression
for $\rho_N$ in [6] is in the form of alternating sum of $(2N-1)$!! terms. As a result the direct derivation of (53) from the formulas in [6] for an arbitrary $N$ is an impossible task due to nonobvious cancellations that occur at small separations. Even for small values of $N$, such a derivation is very nontrivial. For example, the exact expression for $\rho_3$ contains 105 terms, which forced us to use MATHEMATICA to compute the small distance asymptotics of this probability.

IV. REACTION 3A → $\emptyset$ IN CRITICAL DIMENSION $d=1$

In the final section of this paper, we extend the preceding analysis to the problem 3A → $\emptyset$, where reactions occur in triples. Unlike in the binary case, we cannot apply EIM to analyze this reaction in $d=1$. Thus we will adopt the field-theoretic approach. We give a brief introduction to the important quantities in the model [12]. The action $S$, given by

$$S = \int d^d x \int_0^T dt \bar{\phi} (\partial_t - \Delta) \phi + 3\lambda \bar{\phi} \phi^3$$

$$+ 3\lambda \bar{\phi}^2 \phi^2 + \lambda \bar{\phi}^3 \phi^3 - n_0 \bar{\phi} \phi(t). \tag{54}$$

The Feynman rules are shown in Fig. 4. The action must be dimensionless, which requires the following:

$$[T] = L^2 \quad [\phi] = L^{-d} \quad [\bar{\phi}] = L^0 \quad [\lambda] = L^{2d-2}. \tag{55}$$

The reaction rate is dimensionless at $d=1$, which is the critical dimension for this problem. Hence, in $d=1$ we expect the system to be characterized by MFT, with logarithmic corrections. As for the binary system, we use the classical (MF) versions of the density and response functions to study the loop expansion. The integral equations satisfied by the classical density and classical response function are shown in Fig. 5. Their solutions are given by

$$n_{cl}(t) = \left( \frac{1}{6\lambda t} \right)^{1/2}, \tag{56}$$

FIG. 5. (a) The classical density; (b) the classical response function.

$$G_{cl}(x_2,x_1,t_1) = \frac{n_{cl}(t)}{n_{cl}(t_1)} G_0(x_2,x_1,t_1). \tag{57}$$

Power counting shows that reaction rate renormalization takes care of singularities of correlation functions that do not contain any composite operators. Moreover, it turns out that all divergences of $\langle \phi \rangle$ are also eliminated by reaction rate renormalization. For higher order composite operators one needs multiplicative renormalization.

Let $g_0 = \lambda t_0^0$ be the bare (dimensionless) reaction rate, where $t_0$ is our arbitrary reference time. Note that here $\epsilon = 1-d$. To eliminate divergences associated with reaction rate renormalization we need an expression for $g_0$ in terms of $g$. The relation (24) holds, but $g^* = 2\pi \epsilon / \sqrt{3} + O(\epsilon^2)$. The lowest order diagrams contributing to $M_N = \langle \phi^N \rangle$ are shown in Fig. 6. The only divergence at the one-loop level associated with composite operators comes from the connected three-point function. This determines $Z_N$ and hence the anomalous scaling.

The Callan-Symanzik equation in $d=1$ takes the form

$$\left( \frac{\partial}{\partial t} + \beta(g) \frac{\partial}{\partial g} + \frac{N}{2} + \gamma_\delta(g) \right) M_{N,R}(t,t_0,g) = 0, \tag{58}$$

where
\[ \beta(g) = \frac{\sqrt{3}}{2\pi} g^2, \quad (59) \]

\[ \gamma(g) = \frac{N(N-1)(N-2)}{4\pi \sqrt{3}} \ln g + O(g^2). \quad (60) \]

Once again we choose the reference time \( t_0 \) small so that the dominant contribution at \( t_0 \) is given by MFT,

\[ M_{N,R}(t_0,g) = n^N_{\phi}(t_0,g). \quad (61) \]

The solution of (58) is given by

\[ M_{N,R}(t,g(t,t_0)) = \left( \frac{t}{t_0} \right)^{N/2} n^N_{\phi}(t_0,g(t,t_0)) \cdot \frac{g(t,t_0)}{g(t_0)} \right)^{N(N-1)(N-2)/6}, \quad (62) \]

\[ g(t,t_0) = \frac{g}{1 + \frac{\sqrt{3}g}{2\pi} \ln \left( \frac{t}{t_0} \right)}. \quad (63) \]

Recall \( M_{N,R}(t) = \langle \phi^N(t) \rangle_R \). For large times, we obtain the following scaling behavior of composite operators:

\[ \langle \phi^N(t) \rangle_R \sim A_N \left( \ln \frac{t}{t_0} \right)^{N/2} \cdot \left( \ln t \right)^{-N(N-1)(N-2)/6} \cdot \left[ 1 + O\left( \frac{1}{\ln \ln t} \right) \right], \quad (64) \]

where

\[ A_N = \left( \frac{1}{\sqrt{6}} \right)^N \cdot \left( \frac{\sqrt{3}}{2\pi} \right)^{N(N-1)(N-2)/6}. \quad (65) \]

Using the relation (15) between composite operators and probabilities,

\[ P_N(N,\Delta V) \sim P_N(1,\Delta V)^N \cdot \left[ \ln \left( \frac{t}{\Delta V} \right) \right]^{-N(N-1)(N-2)/6} \cdot \left[ 1 + O\left( \frac{1}{\ln \ln t} \right) \right]. \quad (66) \]

The result (66) reflects the anticorrelation of particles as stated in Eq. (3). We know from [12] that \( \langle \phi \rangle - \ln t / t^{12} \), which agrees with (64) upon setting \( N=1 \). There is no anticorrelation between pairs of particles, as reactions only occur in triples. Therefore the anomaly should vanish for \( N=2 \), which agrees with (64) and (66). Due to the absence of singularities associated with \( \langle \phi^2 \rangle \), we know that the dominant contribution comes from the disconnected \( n_{i,i} \) diagrams for \( N=2 \). Then \( \langle \phi^2 \rangle \sim \ln t / t^{12} \) [12] which is also in agreement with (64). Finally, to check (64) for \( N=3 \), we can use the first Hopf equation for the theory: \( \delta \langle \phi \rangle = -3\lambda \langle \phi^3 \rangle \). As \( \langle \phi \rangle \sim \ln t / t^{12} \), the Hopf equation implies that \( \langle \phi^3 \rangle \sim t^{-3/2} \ln t / t^{12} \) exactly. This agrees with (64) as well.

V. SUMMARY

The main finding of this paper was the multiscaling of the probability distributions of multiparticle configurations for single species reaction-diffusion systems. The scaling was indicative of particles being anticorrelated in the large time limit. In particular, the quadratic scaling exponent in the binary system reflects pairwise anticorrelation. For the ternary case, the scaling exponent is cubic, which shows anticorrelation within particle triples. We obtained our results in a field-theoretic setting by identifying probability distributions of multiparticle configurations, at scales much smaller than the correlation length, with composite operators in Doi-Zeldovich field theory. The origin of the multiscaling can therefore be traced back to the anomalous dimensions of the corresponding composite operators.

We obtained exact logarithmic corrections to scaling for the binary system in \( d=2 \) and for the ternary reaction in \( d=1 \). We computed scaling exponents for the binary system in \( d=2 \) using \( \varepsilon \) expansion. By analyzing the first Hopf equation for the binary system, we proved that the one-loop \( \varepsilon \)-expansion gives the exact answer for the probability of finding two particles in a fixed volume. A similar computation for the ternary system confirms the result of the RG computation for the probability of finding three particles in the fixed volume.

RG analysis led us to several conjectures for scaling exponents for the \( A+A \rightarrow \emptyset \) system in \( d=1 \). First, by comparing one-loop answers with the exact results in one dimension [6] for \( N=1,2,3,4 \), we conjecture that two and higher loop corrections are absent in \( d=1 \) for an arbitrary number of particles \( N \); see (42). Second, based on the previous conjecture and dimensional analysis, we propose that the spatial dependence of the multi-particle probability density is given by the absolute value of the Van-der-Monde determinant of particles’ positions; see (53). We have recently found a rigorous proof of the stated conjectures, which will be published separately.

In conclusion, we would like to stress the importance of the RG method for the analysis of nonequilibrium systems. Most previous applications of RG to reaction-diffusion systems dealt with the computation of the average density of particles. In this case RG analysis just confirms the result of Smoluchowski approximation. In contrast, as shown in this paper, RG analysis seems to be the only systematic method of extracting multiscaling of high order correlation functions for these systems. The computation of multiscaling in terms of the spectrum of anomalous dimensions of composite operators carried out in the paper can be extended to more complex systems such as directed percolations.

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[20] Both systems belong to the same universality class [4] in a sense that the correlation functions for both systems are identical apart from the amplitude. For more details see [6].

[21] Lack of operator mixing produces this simple form for Eq. (28). This is due to the fact that in our theory all processes (diagrams) reduce the particle number. For more see [15].