Application of Statistical Field Theory to Reaction-Diffusion Problems

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1 Introduction

Statistical mechanics is one of the oldest branches in theoretical physics being still an up to date field of modern research. It deals with physical systems of which the macroscopic properties can be inferred from a microscopic description [1, 2]. Although mathematical tools have been developed successfully to study systems in thermodynamic equilibrium by ensemble theory, the examination of many-body systems in non-equilibrium is still a challenging task for theoretical physics, since more general and more elaborate concepts are needed. The requirement for the study of non-equilibrium statistical physics stems from its relevance to describe processes in nature. Most systems are exposed to an interaction to other systems yielding an exchange of energy and matter and thus cannot be described in terms of thermodynamic equilibrium physics.

The focus of this essay will lie on systems being comprised of many diffusing particles reacting with each other in a defined manner and the adequate modelling of them in order to explain the experimentally or computationally gained observations. We are always interested in two questions concerning these reaction-diffusion processes. The first point occupies the existence of a steady state, that is an unchanged particle density in time and in case of existence, its spatial dependence. The second question, being naturally much harder to answer, examines the way the system approaches the steady state. Since we look at the long-time behaviour of such systems, we can always assume to be in the so-called diffusion limited regime, where low particle densities are present and the dynamics will be dominated by the diffusion rates.
Macroscopically, the time evolution of these systems is often modelled by ordinary differential equations (ODEs) for the observable or quantity of interest. These variables could be, for instance, the mean particle or population density, chemical concentration or magnetisation.
By including also spatial degrees of freedoms, the variables become local functions and the mathematical frame would be shifted to partial differential equations (PDEs) revealing more complex behaviour such as spreading, front propagation and patterns [3].

However, due to the underlying interaction between the constituents of the system, correlations between the particles may arise, possibly leading to collective phenomena, which involve oscillations, pattern formation or phase transitions between different macroscopic states. Moreover, the system contains randomness in its variables, either because of its random kinetics (reaction of several reactants with a certain probability) or because of our ignorance by modelling the system, since it is mathematically not feasible to include all degrees of freedom for a many particle system.
It turns out that many systems show universal scaling behaviour as they evolve in time towards the steady state [4]. This critical behaviour may be described

by power laws with critical exponents for the order parameter characterising the large-scale and long-time properties of the system. For example, the effective reaction rate of the process can change in the presence of fluctuations and correlations.
However, the description of the temporal dependence of a stochastic many particle system performing reaction and diffusion processes in terms of ODEs and PDEs for the rates of the involved quantities entirely neglects correlations and spatial variations and is referred to as a mean-field description. It is often not possible to explain the right scaling behaviour and critical exponents by applying the theory of rate equations, but the appearance of these phenomena suggests the use of methods known from statistical field theory.

It has been one of the biggest successes of theoretical physics for the last decades to explain universality and scaling laws in condensed matter and particle physics and statistical field theory delivers the appropriate mathematical framework and tools to study these systems, namely renormalisation group techniques.

This essay deals with the application of these methods to reaction-diffusion systems in order to overcome the lack of the rate equation model. However, for the sake of lucidity, we will restrict our attention to the pair annihilation process $A + A \xrightarrow{\lambda} \emptyset$, a specific reaction-diffusion system, being explained more detailed later on.
First, the rate equation model is outlined and its features are compared to experiments and numerical simulations. In order to generalise the model and to apply methods from statistical field theory, the lattice approach to reaction-diffusion systems is introduced. Based on the description of reaction-diffusion processes on a lattice, the microscopic master equation is re-formulated in terms of creation and annihilation operators in analogy to quantum mechanics on a Fock space, which provides a natural framework for systems with changing particle numbers. This enables the path integral formulation and a field theory action is obtained. By renormalising the field theory, universal scaling behaviour and the right critical exponents for the way the system approaches its steady state can be extracted and qualitative results are stated for other reaction-diffusion systems.

2 Pair Annihilation Reaction-Diffusion Process

We shall examine and exemplify the features and problems arising at the analysis of reaction-diffusion systems on the single-species pair annihilation process,

$$A + A \xrightarrow{\lambda} \emptyset \; + \; \text{diffusion} \; . \tag{2.1}$$

The particles of species A are allowed to diffuse in space and annihilate each other with reaction rate λ. We investigate this simple reaction-diffusion system,

because all main features of critical behaviour can be extracted analytically for this pair annihilation process and the analysis stays manageable and traceable within the scope of this essay.

The steady state of such a process is very simple. Depending on the initial condition, whether we start the reaction-diffusion process with an even or odd number of particles, the steady state will contain either no particles (empty space) or only one particle left. Therefore, the focus of our analysis will lie on the question, how the system approaches the steady state.

3 Rate Equations

Reaction-diffusion systems are generally studied in terms of rate equations, being part of the analysis of partial differential equations (PDE) [5, 6, 7]. In d spatial and one time dimension they are equations for the mean particle density $\rho : \mathbb{R}^{d+1} \to \mathbb{R}$, which reads for the pair annihilation process (eq. 2.1) as follows,

$$\frac{\partial}{\partial t}\rho(x,t) = \underbrace{D \cdot \nabla^2 \rho(x,t)}_{\text{diffusion}} - \underbrace{\lambda \rho(x,t)^2}_{\text{reaction}} \tag{3.2}$$

$$\rho(x,0) = f(x) \;, \tag{3.3}$$

where suitable initial conditions may be imposed in eq. (3.3). The first term on the right-hand side is subject to diffusion, the second term takes care of the reaction process.

If we neglect the diffusive part in eq. (3.2) for a moment, we get the kinetic rate equation,

$$\frac{\partial}{\partial t}\rho(t) = -\lambda \rho(t)^2 \;, \tag{3.4}$$

which is a first order ordinary differential equation solved by,

$$\rho(t) = \frac{1}{1/\rho(0) + \lambda t} \;, \tag{3.5}$$

whereas $\rho(0)$ denotes the initial particle density at time $t_0 = 0$. This solution (3.5) behaves asymptotically like $\rho \sim t^{-1}$.

If we return to the inhomogeneous system, where the particle density $\rho(x,t)$ is considered to be local, diffusion effects have to be taken into account. Assuming uniformity of the particle density in spatial coordinates for all times [4], the solution of the full rate eq. (3.2) will perform the same scaling law for the asymptotic temporal behaviour as given in eq. (3.5).

However, experiments and computer simulations show that the long-time behaviour does indeed depend on the dimension d we are considering and hence

such a kinetic PDE approach inheres an inadequate description in some regimes. Some examples can be found in [8, 9, 10].
For the pair annihilation process, one finds,

$$\rho(x,t) \sim \begin{cases} t^{-1/2} & d=1, \quad \text{PDE prediction wrong} \\ \ln t \cdot t^{-1} & d=2, \quad \text{PDE prediction wrong} \\ t^{-1} & d>2, \quad \text{PDE prediction right} \end{cases} \tag{3.6}$$

This suggests the assumption that the PDE approach to reaction-diffusion problems may be too naive in some cases and does not predict the right long-time behaviour for all dimensions.
In fact it turns out, that such a PDE description neglects any spatial fluctuations and correlations in the system and corresponds to a mean-field description. This feature will be extracted in detail in due course.
Nevertheless, we want to predict the right long-time behaviour (3.6) for a given reaction-diffusion system. Hence, we will include statistical fluctuations in our analysis and rewrite the pair annihilation process in terms of field theoretic quantities by using the lattice model described in the next section. By applying dynamic renormalisation group methods, it will be shown, that the approach to the steady state is critical in the sense that it exhibits universal scaling behaviour and critical exponents.

4 Lattice Model for Reaction-Diffusion Systems

To model reaction-diffusion systems, starting from a microscopic description, we consider a lattice in d dimensions, whereas each lattice site is occupied by a certain number of particles of different particle species $\alpha = A, B, \ldots$ (cf. figure 4.1). The spatial difference between two neighbouring lattice sites is called a and the particle number for a specific particle species at a lattice point $i \in \mathbb{Z}^d$ is denoted by n_i^α. The total number of particles N occupying the lattice can be computed via $N = \sum_{i,\alpha} n_i^\alpha$. A configuration η is given by the specification of all particle numbers for all sites and particle species, that is $\eta = \{n_i^\alpha\}$.

The dynamics of such a system will be governed by two processes: reactions and diffusion. For each time step the particles are allowed to jump to a nearest neighbour lattice site. We assume that no spatial direction for the jump process is preferred and that it can be described by a diffusion process in the continuum limit with diffusion constant D_α, depending on the particle species α. Furthermore, reaction processes may take place on a single lattice site with a specific reaction rate λ. Possible reactions could include, for example [4]:

- Production: $\emptyset \xrightarrow{\lambda_1} A$

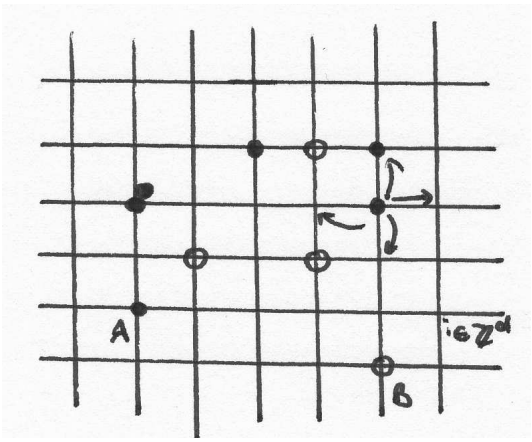

Figure 4.1: *Microscopic lattice model for reaction-diffusion systems.*

- Degradation: $A \xrightarrow{\lambda_2} \emptyset$
- Mutation: $A \xrightarrow{\lambda_3} B$
- Chemical reaction: $A + B \xrightarrow{\lambda_4} C$
- Dominance: $A + B \xrightarrow{\lambda_5} A + A$

Here, $\emptyset$ denotes an empty lattice site. If we perform the continuum limit by letting $a \to 0$ (or equivalently the volume of a spatial cell of volume $V_b = b^d \to \infty$ and $N \to \infty$) such that the ratio of the number of particles included in a cell of side length b and the volume of this cell b^d stays finite, we can define the particle density $\rho(x,t)$, where x labels then the continuous spatial coordinate in d dimensions.

For the pair annihilation process, we consider a lattice in d dimensions with only one particle species. The particles are allowed to hop on the lattice (corresponding to diffusion in the continuum limit with diffusion constant D) and if two particles meet each other at one site, they will annihilate irreversibly with reaction rate λ.

5 Field Theoretic Formulation

5.1 Operator Description

5.1.1 Master equation

The starting point of the description of the temporal evolution for the pair annihilation system (2.1) is the introduction of the time-dependent probability distribution $P(\eta, t)$, prescribing the probability of a configuration η to occur at time t.

The dynamics of the probability distribution is governed by a master equation,

$$\frac{\partial}{\partial t}P(\eta,t)=\sum_{\eta'}\left\{T_{\eta'\to\eta}P(\eta',t)-T_{\eta\to\eta'}P(\eta,t)\right\}\ , \tag{5.7}$$

which is a first order differential equation in time and represents the underlying assumption of a continuous Markov process, meaning that no memory is imposed. The next step in the time evolution of the probability distribution depends only on the probability distribution of the current time t simplifying the problem enormously. The master equation can be thought of as a balance between gain and loss terms. All transitions from a configuration η' to the configuration η, characterised by the transition rate $T_{\eta'\to\eta}$, contribute to a gain of probability at time t in configuration η, all transitions form η to other configurations, characterised by the transition rate $T_{\eta\to\eta'}$ result in a loss of $P(\eta,t)$. Note, that the transition rates are said to be independent of time t.

The initial condition is determined by a product of Poisson distributions over all lattice sites,

$$P(\eta,t=0)=\prod_i\left(\frac{\langle n_0\rangle^{n_i}}{n_i!}e^{-\langle n_0\rangle}\right)\ , \tag{5.8}$$

where $\langle n_0\rangle$ denotes the average number of particles per site. At each lattice site, we have a binomial distribution for the random variable X_m (= number of occupations) in a sequence of m independent yes/no experiments if we assume uniform, random initial conditions. Each occupation experiment yields an occupation number n with probability $p=\frac{\langle n_0\rangle}{m}$, thus $X_m\sim\mathrm{Bin}(m,p)$.
The law of rare events states [11] that for fixed $\langle n_0\rangle$ and for $X_m\sim\mathrm{Bin}(m,\frac{\langle n_0\rangle}{m})$ and $Y\sim\mathrm{Pois}(\langle n_0\rangle)$ one obtains for fixed n,

$$\lim_{m\to\infty}\mathbb{P}(X_m=n)=\mathbb{P}(Y=n)=\frac{\langle n_0\rangle^n}{n!}e^{-\langle n_0\rangle}.$$

5.1.2 Bosonic operator description

In the following, we will introduce a bosonic operator representation and map the master equation (5.7) onto a stochastic quasi-Hamiltonian description [12, 13]. However, it should be emphasized that this procedure reflects a classical approach and does not involve any quantum mechanical physics.

We define a Fock space on the lattice for this stochastic process. The empty lattice without any particles is called the vacuum state and will be denoted by $|0\rangle$. From this vacuum state, we can construct other states in analogy to the quantum mechanical Fock space by introducing creation and annihilation operators $a_i^\dagger, a_i$. For example, the creation operator $a_i^\dagger$ creates a particle of particle species A at

lattice site $i \in \mathbb{Z}^d$. The state $|n_i\rangle$ represents a configuration with n_i particles at site i. We impose the following constraints on our vacuum state, which naturally arise if we think of $|0\rangle$ being the vacuum state,

$$\begin{aligned} a_i|0\rangle &:= 0 \ , \\ \langle 0|0\rangle &:= 1 \ . \end{aligned}$$

Mathematically, the bosonic operators are defined on the Fock space, such that,

$$\begin{aligned} a_i^\dagger|n_i\rangle &:= |n_i+1\rangle \ , \\ a_i|n_i\rangle &:= n_i|n_i-1\rangle \ , \end{aligned} \tag{5.9}$$

which justifies the name for the creation and annihilation operator. A general configuration $\eta = \{n_i^\alpha\}$ corresponds to the state $|n_1, n_2, \dots\rangle$, being defined as,

$$|\eta\rangle = |\{n_i^\alpha\}\rangle = |n_1, n_2, \dots\rangle := \left(a_1^\dagger\right)^{n_1} \left(a_2^\dagger\right)^{n_2} \dots |0\rangle \ . \tag{5.10}$$

From these definitions, the well-known bosonic commutation relations can be obtained,

$$[a_i, a_j^\dagger] = a_i a_j^\dagger - a_j^\dagger a_i = \delta_{ij} \ , \tag{5.11}$$

$$[a_i^\dagger, a_j^\dagger] = [a_i, a_j] = 0 \ . \tag{5.12}$$

Furthermore, it turns out that $a^\dagger$ is the hermitian conjugate to the operator a. Note, however, the different normalisation in eq. (5.9) in comparison to the quantum mechanical analogue, where the operators are defined in such a way that the normalisation is conserved. If we apply definition (5.9, 5.10), we recognise that $\langle n|m\rangle = n! \cdot \delta_{nm}$. Nevertheless, the normalisation of states is not needed in this representation and the building-up process of states by acting with the creation operator on the vacuum state (5.10) becomes simpler.

We also define the particle number operator $\hat{n}_i := a_i^\dagger a_i$, whose eigenvectors are the occupation number states,

$$\hat{n}_i|n_i\rangle = n_i|n_i\rangle \ . \tag{5.13}$$

Next, the probability distribution $P(\eta, t)$ is mapped to a state vector $|\psi(t)\rangle$, being defined on the Fock space as follows,

$$|\psi(t)\rangle = \sum_\eta P(\eta, t)|\eta\rangle \ , \tag{5.14}$$

which is a sum over all possible configurations weighted by their probability to occur at time t. We can now study the time evolution of this state vector by applying the master equation (5.7) yielding a Schroedinger type equation,

$$\frac{\partial}{\partial t}|\psi(t)\rangle = -H(\{a_i^\dagger, a_i\})|\psi(t)\rangle \ , \tag{5.15}$$

where $H(\{a_i^\dagger, a_i\}$ represents the quasi-Hamiltonian acting on the Fock space. Formally, this equation is solved by,

$$|\psi(t)\rangle = e^{-Ht}|\psi(0)\rangle \ . \tag{5.16}$$

The initial condition of the master equation (5.8) is mapped in this occupation number representation to,

$$|\psi(t=0)\rangle = \sum_\eta P(\eta, t=0)|\eta\rangle = \sum_{\{n_i\}} \prod_i \left(\frac{\langle n_0 \rangle^{n_i}}{n_i!} e^{-\langle n_0 \rangle} \left(a_i^\dagger\right)^{n_i} \right) |0\rangle \tag{5.17}$$

$$= \prod_i e^{-\langle n_0 \rangle} e^{\langle n_0 \rangle a_i^\dagger} |0\rangle \ , \tag{5.18}$$

Let us examine the map to the Schroedinger type equation in more depth and illustrate the procedure of extracting H for a couple of examples.

Diffusion between two sites

Consider first the case, where particles are only allowed to jump from site 1 to site 2 with diffusion rate D (cf. figure (5.2)).

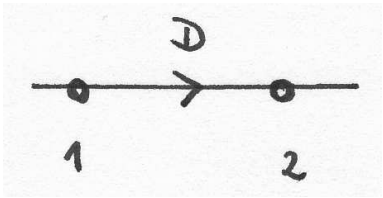

Figure 5.2: *Diffusion between two sites.*

$$\frac{\partial}{\partial t} P(n_1, n_2, t) = D(n_1 + 1) \cdot P(n_1 + 1, n_2 - 1, t) - D n_1 \cdot P(n_1, n_2, t) \ , \tag{5.19}$$

since we gain probability for $P(n_1, n_2, t)$ if we start in a configuration $\eta = (n_1 + 1, n_2 - 1)$ and a particle jumps to site 2 and we loose probability if a particle jumps from 1 to 2 out of a configuration $\eta = (n_1, n_2)$. The state vector for this simple example is defined as,

$$|\psi(t)\rangle = \sum_{n_1, n_2} P(n_1, n_2, t)|n_1, n_2\rangle = \sum_{n_1, n_2} P(n_1, n_2, t) \left(a_1^\dagger\right)^{n_1} \left(a_2^\dagger\right)^{n_2} |0\rangle \ . \tag{5.20}$$

Taking the time derivative of eq. (5.20) and inserting the master equation (5.19) yields,

$$\begin{aligned}
\frac{\partial}{\partial t}|\psi(t)\rangle &= \sum_{n_1,n_2} \frac{\partial}{\partial t} P(n_1,n_2,t) \left(a_1^\dagger\right)^{n_1} \left(a_2^\dagger\right)^{n_2} |0\rangle \\
&= \sum_{n_1,n_2} \Big(D(n_1+1)\cdot P(n_1+1,n_2-1,t) - Dn_1 \cdot P(n_1,n_2,t) \Big) \left(a_1^\dagger\right)^{n_1} \left(a_2^\dagger\right)^{n_2} |0\rangle \\
&= \sum_{n_1,n_2} D\cdot P(n_1+1,n_2-1,t)\; a_2^\dagger a_1 \left(a_1^\dagger\right)^{n_1+1} \left(a_2^\dagger\right)^{n_2-1} |0\rangle \\
&\quad - \sum_{n_1,n_2} D\cdot P(n_1,n_2,t)\; a_1^\dagger a_1 \left(a_1^\dagger\right)^{n_1} \left(a_2^\dagger\right)^{n_2} |0\rangle \\
&= D(a_2^\dagger a_1 - a_1^\dagger a_1)|\psi(t)\rangle = -H_{1\to 2}(a_1^\dagger, a_2^\dagger, a_1)|\psi(t)\rangle \;,
\end{aligned}$$

where $H_{1\to 2}(a_1^\dagger, a_2^\dagger, a_1) := -D(a_2^\dagger - a_1^\dagger)a_1$ was defined. From the second to the third line, we used the fact that the occupation number states are eigenvectors of the particle number operator (eq. (5.13)) together with the following conversion,

$$a\left(a^\dagger\right)^{n+1} = aa^\dagger \left(a^\dagger\right)^n = (\mathbb{I} + a^\dagger a)\left(a^\dagger\right)^n = (n+1)\left(a^\dagger\right)^n \;.$$

The big advantage of using the second-quantised occupation number formalism lies in its pictorial and intuitive understanding of the process. The first term of $H_{1\to 2}$ corresponds to a annihilation of a particle at site 1, whereas a particle at site 2 is created. This process takes place with a diffusion rate D. The second term is less obvious and reflects a consistency relation, because $H(\{a_i^\dagger = \mathbb{I}, a_i\}) = 0$ [4]. It is related to the conservation of probability in time due to the master equation (5.7). We will not go into further details at this point, but shall encounter this consistency term at several points.

The back hopping from site 2 to 1 leads in the same way to the same Hamiltonian with interchanged indices, $H_{2\to 1}(a_1^\dagger, a_2^\dagger, a_2) = -D(a_1^\dagger - a_2^\dagger)a_2$. The total hopping Hamiltonian between site 1 and 2 is the sum of $H_{1\to 2}$ and $H_{2\to 1}$, thus $H_{1\leftrightarrow 2}(a_1^\dagger, a_2^\dagger, a_1, a_2) = D(a_2^\dagger - a_1^\dagger)(a_2 - a_1)$.

Diffusion on the lattice

We can generalise this result to the diffusion on the whole lattice, since the particles are allowed to jump only to a nearest neighbour lattice site. Thus we end up with,

$$H_{\text{diff}}(\{a_i^\dagger, a_i\}) = D\cdot \sum_{\langle i,j\rangle} (a_i^\dagger - a_j^\dagger)(a_i - a_j) \;, \tag{5.21}$$

where the sum is carried out over all nearest neighbours $\langle i,j\rangle$.

Reaction $A + A \xrightarrow{\lambda} \emptyset$

The single site pair annihilation reaction can be treated in the same way as it was shown for the diffusion case. Again, one has to look at the gain and loss terms of the probability distribution $P(n,t)$. We can increase $P(n,t)$ if $n+2$ particles react at time t with each other and a reaction of two particles from a state with occupation number n at time t leads to a decrease of $P(n,t)$. Hence, the master equation (5.7) for the probability distribution $P(n,t)$ for this reaction at one lattice site reads as follows,

$$\frac{\partial}{\partial t}P(n,t) = \lambda(n+2)(n+1)\cdot P(n+2,t) - \lambda n(n-1)\cdot P(n,t)\ . \tag{5.22}$$

For the single site reaction, the state vector can be written as,

$$|\psi(t)\rangle = \sum_n P(n,t)|n\rangle = \sum_n P(n,t)\left(a^\dagger\right)^n|0\rangle\ , \tag{5.23}$$

and thus,

$$\begin{aligned}
\frac{\partial}{\partial t}|\psi(t)\rangle &= \sum_n \frac{\partial}{\partial t}P(n,t)\left(a^\dagger\right)^n|0\rangle \\
&= \sum_n \Big(\lambda(n+2)(n+1)\cdot P(n+2,t) - \lambda n(n-1)\cdot P(n,t)\Big)\left(a^\dagger\right)^n|0\rangle \\
&= \lambda\cdot\sum_n P(n+2,t)\ a^2\left(a^\dagger\right)^{n+2}|0\rangle - \lambda\cdot\sum_n P(n,t)\ \left(a^\dagger\right)^2 a^2\left(a^\dagger\right)^n|0\rangle \\
&= \lambda\cdot\left(a^2 - \left(a^\dagger\right)^2 a^2\right)|\psi(t)\rangle = -H(a^\dagger,a)|\psi(t)\rangle\ ,
\end{aligned}$$

where from the second to the third line,

$$(n+2)(n+1)|n\rangle = a^2|n+2\rangle,$$

and

$$\begin{aligned}
n(n-1)|n\rangle = (n^2-n)|n\rangle &= \left(\left(a^\dagger a\right)^2 - a^\dagger a\right)|n\rangle \\
&= \left(a^\dagger a a^\dagger a - a^\dagger a\right)|n\rangle = \left(a^\dagger(\mathbb{I}+a^\dagger a)a - a^\dagger a\right)|n\rangle \\
&= \left(a^\dagger\right)^2 a^2|n\rangle\ ,
\end{aligned}$$

were used. We defined in the last line $H(a^\dagger,a) := -\lambda\cdot(a^2 - \left(a^\dagger\right)^2 a^2)$. In the pair annihilation reaction, two particles are annihilated with rate λ and thus a term with $-\lambda\cdot a^2$ appears in the Hamiltonian. The second term represents the consistency relation as mentioned above.

For the whole lattice one obtains the Hamiltonian for the pair annihilation reaction by summing over all lattice sites,

$$H_{\text{react}}(\{a_i^\dagger, a_i\}) = -\lambda\cdot\sum_i\left(\mathbb{I} - \left(a_i^\dagger\right)^2\right)a_i^2\ , \tag{5.24}$$

Pair annihilation reaction-diffusion process on the lattice

To summarise the results from the above calculations, we can infer the Hamiltonian for the pair annihilation reaction-diffusion process on the lattice,

$$\begin{aligned} H(\{a_i^\dagger, a_i\}) &= H_{\text{diff}}(\{a_i^\dagger, a_i\}) + H_{\text{react}}(\{a_i^\dagger, a_i\}) \\ &= D \cdot \sum_{\langle i,j \rangle} (a_i^\dagger - a_j^\dagger)(a_i - a_j) - \lambda \cdot \sum_i \left(\mathbb{I} - \left(a_i^\dagger \right)^2 \right) a_i^2 \,, \end{aligned} \tag{5.25}$$

which will be the starting point for our further analysis. Note, that this Hamiltonian is normal-ordered, since all creation operators are to the left of all annihilation operators in products and thus the expectation value $\langle 0|H|0\rangle$ is zero.

Generalisation to other reactions, Lotka-Volterra model

If we were to write down the Hamiltonian for the Schroedinger type equation (5.15) for a general reaction-diffusion system, we can proceed in the same way as it was demonstrated above. The Hamiltonian for the diffusive part can be copied for every process from eq. (5.21).

The Hamiltonian for the reaction part can be constructed via the intuitive bosonic operator description and consists of two parts, both being normal ordered. The negative part takes care of the annihilated and created particles due to the reaction. For each annihilated particle of species α we insert an annihilation operator a_α, for each created particle a creation operator $a_\alpha^\dagger$. The positive part of the Hamiltonian reflects the consistency relation and includes a creation and an annihilation operator for each reactant.

Let us exemplify this procedure on the two-species Lotka-Volterra system [14]. In this model two species are in competition with each other: the predator A and the prey B. The interactions can be described by three reactions plus diffusion.

1. $A \xrightarrow{\mu} \emptyset \qquad \rightsquigarrow \quad H = -\mu(\mathbb{I} - a^\dagger)a$
   The predators die with a rate μ spontaneously.
2. $B \xrightarrow{\sigma} B + B \qquad \rightsquigarrow \quad H = -\sigma(\left(b^\dagger\right)^2 - b^\dagger)b$
   The preys reproduce with a rate σ spontaneously.
3. $A + B \xrightarrow{\lambda} A + A \quad \rightsquigarrow \quad H = -\lambda(\left(a^\dagger\right)^2 - a^\dagger b^\dagger)ab$
   The preys are consumed by the predators reproducing themselves at the same time with rate λ.

The Hamiltonian for the Lotka-Volterra reaction-diffusion system then reads as

follows,

$$\begin{aligned} H_{\mathrm{LV}}(\{a_i^\dagger, b_i^\dagger, a_i, b_i\}) &= H_{\mathrm{diff}}(\{a_i^\dagger, b_i^\dagger, a_i, b_i\}) + H_{\mathrm{react}}(\{a_i^\dagger, b_i^\dagger, a_i, b_i\}) \\ &= D_A \cdot \sum_{\langle i,j \rangle} (a_i^\dagger - a_j^\dagger)(a_i - a_j) + D_B \cdot \sum_{\langle i,j \rangle} (b_i^\dagger - b_j^\dagger)(b_i - b_j) \\ &\quad - \lambda \cdot \sum_i \left(\left(a_i^\dagger\right)^2 - a_i^\dagger b_i^\dagger \right) a_i b_i - \mu \cdot \sum_i \left(\mathbb{I} - a_i^\dagger \right) a_i - \sigma \cdot \sum_i \left(\left(b_i^\dagger\right)^2 - b_i^\dagger \right) b_i \, . \end{aligned} \tag{5.26}$$

This is the main reason, why we use the occupation number representation. Together with the Schroedinger type equation (5.15), it is a powerful tool to describe the time evolution, even for more sophisticated interacting stochastic many particle systems [15].

5.1.3 Expectation Values of Observables

In the end, we want to compute expectation values for specific observables, for example the mean particle number, and evaluate its dependence on time. On this account, we will rewrite expectation values $\bar{A}(t)$ of observables $A(\eta)$ in the bosonic operator representation. The expectation value of an observable is defined as,

$$\bar{A}(t) := \sum_\eta A(\eta) P(\eta, t) \, . \tag{5.27}$$

This expectation is equivalent to,

$$\bar{A}(t) = \langle 0 | e^{\sum_i a_i} A(\eta) | \psi(t) \rangle \, . \tag{5.28}$$

as one can see from the identity $1 = \langle 0 | e^{\sum_j a_j} \prod_j \left(a_j^\dagger\right)^{n_j} |0\rangle$, which follows directly from the bosonic commutation relations (5.11) and the following conversion,

$$\begin{aligned} \bar{A}(t) &= \sum_\eta A(\eta) P(\eta, t) \cdot 1 \\ &= \sum_\eta A(\eta) P(\eta, t) \cdot \langle 0 | e^{\sum_j a_j} \prod_j \left(a_j^\dagger\right)^{n_j} |0\rangle \\ &\overset{5.20}{=} \langle 0 | \prod_j e^{a_j} A(\eta) | \psi(t) \rangle \, . \end{aligned}$$

It is convenient to shift the $e^{\sum_j a_j}$ in front of the observable $A(\eta)$ in eq. (5.28) between the $A(\eta)$ and $|\psi(t)\rangle$ term by making use of the identity $e^{ca} f(a^\dagger) =$

$f(a^\dagger + c)\ e^{ca}$ for $c \in \mathbb{C}$. Hence, we obtain,

$$\begin{aligned}
\bar{A}(t) &= \langle 0|e^{\sum_j a_j} A(\{n_i\})|\psi(t)\rangle = \langle 0| \prod_j e^{1\cdot a_j} A(\{a_i^\dagger, a_i\}) e^{-H(\{a_i^\dagger, a_i\})t}|\psi(0)\rangle \\
&\overset{\text{shift}}{=} \langle 0|A(\{a_i^\dagger + \mathbb{I}, a_i\}) e^{-H(\{a_i^\dagger+\mathbb{I}, a_i\})t} \prod_j e^{1\cdot a_j}|\psi(0)\rangle \\
&\overset{5.18}{=} \langle 0|A(\{a_i^\dagger + \mathbb{I}, a_i\}) e^{-H(\{a_i^\dagger+\mathbb{I}, a_i\})t} \prod_j e^{a_j} e^{-\langle n_0\rangle} e^{\langle n_0\rangle a_j^\dagger}|0\rangle \\
&\overset{\text{shift}}{=} \langle 0|A(\{a_i^\dagger + \mathbb{I}, a_i\}) e^{-H(\{a_i^\dagger+\mathbb{I}, a_i\})t} \prod_j e^{-\langle n_0\rangle} e^{\langle n_0\rangle (a_j^\dagger+\mathbb{I})} e^{a_j}|0\rangle \\
&= \langle 0|A(\{a_i^\dagger + \mathbb{I}, a_i\}) e^{-H(\{a_i^\dagger+\mathbb{I}, a_i\})t} \prod_j e^{\langle n_0\rangle a_j^\dagger}|0\rangle\ .
\end{aligned}$$

According to literature [16], we denote,

$$\tilde{f}(\{a_i^\dagger, a_i\}) := f(\{a_i^\dagger + \mathbb{I}, a_i\})\ , \tag{5.29}$$

which is often referred to as Doi-shift.

In terms of Doi-shifted quantities, we finally arrive at,

$$\bar{A}(t) = \langle 0|\tilde{A}(\{a_i^\dagger, a_i\}) e^{-\tilde{H}(\{a_i^\dagger, a_i\})t} \prod_j e^{\langle n_0\rangle a_j^\dagger}|0\rangle\ . \tag{5.30}$$

Mean particle number

The starting point and motivation of all analysis was the question of how the particle density $\rho(x,t)$ evolves for large times. That is, we are particularly interested in the mean of the particle number operator $n = a^\dagger a$ as our observable that can be written as,

$$\begin{aligned}
\bar{n}(t) &= \langle 0|(a^\dagger + \mathbb{I})a\ e^{-\tilde{H}(\{a_i^\dagger, a_i\})t} \prod_j e^{\langle n_0\rangle a_j^\dagger}|0\rangle \\
&= \langle 0|a\ e^{-\tilde{H}(\{a_i^\dagger, a_i\})t} \prod_j e^{\langle n_0\rangle a_j^\dagger}|0\rangle\ .
\end{aligned} \tag{5.31}$$

5.2 Path Integral Formulation

After having transformed the expression for the mean value of an observable (5.27) into expression (5.30) via the bosonic operator description, we are now at the point to introduce the path integral formulation for a reaction-diffusion process.

Since we mapped the dynamics of such a reaction-diffusion system from the master equation (5.7) to a Schroedinger type equation (5.15, 5.16), we can perform the process of rewriting the theory into a path integral language in the same way as it is done in quantum field theory [17]. The result will be a field theoretic prescription of a reaction-diffusion process.

Let us explain the idea and outline the important steps of this transformation. The key point is to split the time interval $(0,t)$ into N pieces (cf. figure 5.3), such that each time piece has length $\delta t = t/N$, and express $e^{-\tilde{H}t}$ in eq. (5.30) as a limit as $\delta t \to 0$,

$$\begin{aligned} e^{-\tilde{H}t} &= \lim_{\delta t \to 0} (1 - \delta t \cdot \tilde{H})^{t/\delta t} \\ &= \lim_{\substack{\delta t \to 0 \\ N \to \infty}} \underbrace{(1 - \delta t \cdot \tilde{H}) \cdot (1 - \delta t \cdot \tilde{H}) \cdots (1 - \delta t \cdot \tilde{H})}_{N \text{ factors}} \ . \end{aligned} \tag{5.32}$$

We want to simplify the exponential of the Hamiltonian and write it therefore as the limit of a product of N factors, involving the Hamiltonian only linearly.

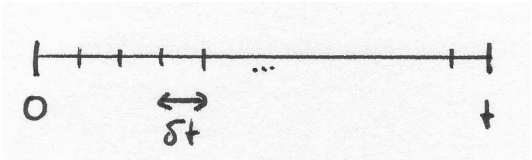

Figure 5.3: *Split of the time interval* $(0,t)$ *into* N *pieces of length* δt.

One can evaluate this product by sandwiching each linear term in the product by a suitable identity,

$$\underset{\uparrow\!\mathbb{I}}{(1 - \delta t \cdot \tilde{H})} \cdot \underset{\uparrow\!\mathbb{I}}{(1 - \delta t \cdot \tilde{H})} \cdot \cdots \cdot \underset{\uparrow\!\mathbb{I}}{(1 - \delta t \cdot \tilde{H})} \cdot \cdots \cdot \underset{\uparrow\!\mathbb{I}}{(1 - \delta t \cdot \tilde{H})} \ .$$

The question is always, which identity simplifies the product most.
In this case, where we are dealing with a normal ordered Hamiltonian $\tilde{H}(\{a_i^\dagger, a_i\})$, the eigenstates of the bosonic annihilation operator a_i provide an appropriate simplification.

It is an easy calculation (since the occupation number states $\{|n\rangle\}_{n\in\mathbb{N}}$ constitute an orthogonal set and in our convention $\langle m|n\rangle = n! \cdot \delta_{mn}$) that the eigenstates $|\phi\rangle$ of the bosonic annihilation operator a, fulfilling $a|\phi\rangle = \phi|\phi\rangle$ for $\phi \in \mathbb{C}$, can be written as [18],

$$|\phi\rangle = \phi_0 \sum_{n\geq 0} \frac{\phi^n}{n!} |n\rangle = \phi_0 \cdot e^{\phi a^\dagger} |0\rangle = e^{-\frac{1}{2}|\phi|^2 + \phi a^\dagger} |0\rangle \ , \quad \phi \in \mathbb{C} \ . \tag{5.33}$$

These states are normalised, $\langle\phi|\phi\rangle = 1$, overcomplete and referred to as coherent states.

By using $\delta_{mn} = \frac{1}{\pi m!}\int d^2\phi\ e^{-|\phi|^2}(\phi^*)^m\phi^n$, we obtain a presentation of the identity operator for a single lattice site,

$$\begin{aligned}\mathbb{I} &= \sum_{n\geq 0}\frac{1}{n!}|n\rangle\langle n| = \sum_{m,n\geq 0}\frac{1}{n!}|n\rangle\langle m|\ \delta_{mn}\\ &= \sum_{m,n\geq 0}\frac{1}{n!}|n\rangle\langle m|\cdot\frac{1}{\pi m!}\int\limits_{\phi\in\mathbb{C}} d^2\phi\ e^{-|\phi|^2}(\phi^*)^m\phi^n\\ &\overset{5.33}{=} \frac{1}{\pi}\int\limits_{\phi\in\mathbb{C}} d^2\phi\ |\phi\rangle\langle\phi| = \frac{1}{\pi}\int\limits_{\phi\in\mathbb{C}} d^2\phi\ e^{-|\phi|^2}e^{\phi a^\dagger}e^{\phi^* a}|0\rangle\langle 0|\ ,\end{aligned}$$

where the integration measure is $d^2\phi = d(\mathrm{Re}(\phi))\ d(\mathrm{Im}(\phi))$. Turning to the whole lattice, we introduce the multiple particle state $|\{\phi\}\rangle = |\phi_1\rangle\otimes|\phi_2\rangle\otimes\cdots$ and generalise the result from above to the identity operator on the whole lattice,

$$\mathbb{I} = \int\limits_{\phi_i\in\mathbb{C}}\prod_{i\in\mathbb{Z}^d}\left(\frac{d^2\phi_i}{\pi}\right)\ |\{\phi\}\rangle\langle\{\phi\}|\ . \tag{5.34}$$

By using identity (5.34) and inserting it into eq. (5.32) and eq. (5.30), we have to evaluate the following terms (for the sake of clarity given at one lattice site only) by applying again the Doi shift, the identity $e^{ca}f(a^\dagger) = f(a^\dagger + c)\ e^{ca}$ and its conjugate form as well as the normal ordering of the Hamiltonian and observables,

1. N bulk-terms,
   $\langle 0|e^{\phi^*(t)a}(1-\delta t\tilde{H}(a^\dagger,a))e^{\phi(t-\delta t)a^\dagger}|0\rangle = \cdots = e^{\phi(t-\delta t)\phi^*(t)}\Big(1-\delta t\tilde{H}(\phi^*(t),\phi(t-\delta t))\Big)$.
2. Two boundary terms,
   $\langle 0|\tilde{A}(a^\dagger,a)e^{\phi(t)a^\dagger}|0\rangle = \cdots = A(\phi(t))$,
   $\langle 0|e^{\phi^*(0)a}e^{\langle n_0\rangle a^\dagger}|0\rangle = \cdots = e^{\langle n_0\rangle\phi^*(0)}$.
3. $N+1$ factors of $e^{-|\phi(t)|^2}$.

Putting everything together, we get for one lattice site,

$$\begin{aligned}\bar{A}(t) = \frac{1}{\mathcal{N}}\lim_{\substack{\delta t\to 0\\ N\to\infty}}\int\prod_{k=0}^{N}\left(\frac{d\phi(t_k)d\phi^*(t_k)}{\pi}\right)\times\\ \times\exp\left\{-\sum_{j=0}^{N-1}\Big(\delta t\tilde{H}(\phi^*(t_j),\phi(t_j)) + |\phi(t_j+\delta t)|^2 - \phi(t_j)\phi^*(t_j+\delta t)\Big)\right\}\times\\ \times A(\phi(t))\cdot e^{\langle n_0\rangle\phi^*(o)-|\phi(0)|^2}\ ,\end{aligned}$$

where, $\mathcal{N}$ is the normalisation, obtained from averaging over the identity operator.
As it is usually done in literature, this cumbersome limit is abbreviated as follows,

$$\bar{A}(t) = \mathcal{N}^{-1} \int \mathcal{D}[\phi^*(t)]\mathcal{D}[\phi(t)]\ A(\phi(t)) \cdot e^{-S[\phi^*(t),\phi(t)]} \ ,$$

$$S[\phi^*(t),\phi(t)] = \int_0^t d\tau\ \left(\tilde{H}(\phi^*(\tau),\phi(\tau)) + \phi^*(\tau)\partial_\tau\phi(\tau)\right) - (\langle n_0\rangle - \phi(0))\phi^*(0) \ ,$$

which displays an average over all fields $\phi^*(t), \phi(t)$, weighted by the exponential of the stated action $S[\phi^*(t), \phi(t)]$. The boundary term in the action S ensures the initial condition $\phi(0) = \langle n_0\rangle$ since the path integral over $\phi^*(0)$ leads formally to a δ-function. The $\phi(0)\phi^*(0)$-term can be dropped due to the perturbation expansion, being developed in the next section, which has the feature that the propagator of this theory only connects earlier ϕ^* to later ϕ [4].

However, we have only performed the analysis for one single lattice site up to now and have to account for the whole lattice.
Furthermore, we carry out the spatial continuum limit by letting the lattice spacing $a \to 0$ in order to end up with a field theory. We will have to redefine the fields and parameters of our theory, since $\sum_{i\in\mathbb{Z}^d} a^d \ldots \mapsto \int d^dx \ldots$, as follows,

$$\frac{\phi_i(t)}{a^d} \mapsto \phi(x,t) \ , \quad \phi^*(t) \mapsto \tilde{\phi}(x,t) \ , \quad D \mapsto \frac{D}{a^2} \ , \quad \lambda \mapsto \frac{\lambda}{a^d} \ , \quad \langle n_0\rangle \mapsto \rho_0 = \frac{\langle n_0\rangle}{a^d} \ .$$

In case of our pair annihilation reaction-diffusion process (2.1), the Hamiltonian becomes in the continuum limit,

$$\begin{aligned} H(\{a_i^\dagger, a_i\}) &= D \cdot \sum_{\langle i,j\rangle} (a_i^\dagger - a_j^\dagger)(a_i - a_j) - \lambda \cdot \sum_i \left(\mathbb{I} - \left(a_i^\dagger\right)^2\right) a_i^2 \ , \\ &\overset{\text{Doishift}}{\longmapsto} \ \tilde{H}(\{\phi_i^*(t), \phi_i(t)\}) = D \cdot \sum_{\langle i,j\rangle} (\phi_i^* - \phi_j^*)(\phi_i - \phi_j) - \lambda \cdot \sum_i \left(\mathbb{I} - (\phi_i^* + \mathbb{I})^2\right) \phi_i^2 \ , \\ &\overset{\text{cont.limit}}{\longmapsto} \ \int d^dx\ \left(D\nabla\tilde{\phi}\cdot\nabla\phi + \lambda(\tilde{\phi}^2 + 2\tilde{\phi})\phi^2\right) \end{aligned}$$

Finally, we arrive at

$$\bar{A}(t) = \mathcal{N}^{-1} \int \mathcal{D}[\tilde{\phi}(x,t)]\mathcal{D}[\phi(x,t)]\ A(\phi(x,t)) \cdot e^{-S[\tilde{\phi}(x,t),\phi(x,t)]} \ , \tag{5.35}$$

whereas the action for the pair annihilation process (2.1) can be written as,

$$S[\tilde{\phi}(x,t),\phi(x,t)] = \int d^d\chi \left\{ \int_0^t d\tau \; \mathcal{L}[\tilde{\phi}(\chi,\tau),\phi(\chi,\tau)] - \rho_0\tilde{\phi}(\chi,0) \right\} , \tag{5.36}$$

$$\mathcal{L}[\tilde{\phi}(x,t),\phi(x,t)] = \underbrace{\tilde{\phi}(\partial_t - D\nabla_x^2)\phi}_{\text{pure diffusion}} + \underbrace{2\lambda\tilde{\phi}\phi^2 + \lambda\tilde{\phi}^2\phi^2}_{\text{reaction } A+A\xrightarrow{\lambda}\emptyset} , \tag{5.37}$$

where the bilinear part of the Lagrangian corresponds to the pure diffusion process and the higher order interactions represent the reaction term $A + A \xrightarrow{\lambda} \emptyset$. Eq. (5.35, 5.36, 5.37) will be the starting point of all further analysis. The path integral together with the action build up the basis of the field-theoretic examination of the pair annihilation process.

The mean particle number $\bar{n}$ in the continuum limit becomes the mean particle density ρ and is equal to the mean of the field $\rho(x,t) = \langle\phi(x,t)\rangle$ in this path integral formulation, so,

$$\rho(x,t) = \frac{\int \mathcal{D}[\tilde{\phi}(x,t)]\mathcal{D}[\phi(x,t)] \; \phi(x,t) e^{-S[\tilde{\phi}(x,t),\phi(x,t)]}}{\int \mathcal{D}[\tilde{\phi}(x,t)]\mathcal{D}[\phi(x,t)] \; e^{-S[\tilde{\phi}(x,t),\phi(x,t)]}} = \langle\phi(x,t)\rangle =: G_1(x,t) . \tag{5.38}$$

It will be shown in the next chapter how to evaluate eq. (5.38) perturbatively.

We could generalize this procedure to other reactions, too, the only change would concern the establishing of the Lagrangian of the theory, which goes back to finding the microscopic Hamiltonian on the lattice. For example, the Lotka-Volterra model (5.26) can be mapped to a field theory (5.35, 5.36) by carrying out the same steps as it was shown for the pair annihilation process, namely performing the Doi shift and carrying out the continuum limit, leading to the following Lagrangian [14],

$$\begin{aligned} \mathcal{L}[\tilde{\phi},\tilde{\psi},\phi,\psi] = {} & \tilde{\phi}(\partial_t - D_A\nabla_x^2 + \mu)\phi + \tilde{\psi}(\partial_t - D_B\nabla_x^2 - \sigma)\psi \\ & - \sigma\tilde{\psi}^2\psi - \lambda(\tilde{\phi}+1)(\tilde{\phi}-\tilde{\psi})\phi\psi . \end{aligned} \tag{5.39}$$

5.3 Remarks to Field Theory

5.3.1 Classical field equation

It is worth to investigate the classical field equations of action (5.36). In order to take the stationarity solutions of the field action, one has to compute,

$$\frac{\partial S}{\partial \phi} = \frac{\partial S}{\partial \tilde{\phi}} \stackrel{!}{=} 0 ,$$

which is, for example, solved by $\tilde{\phi} = 0$ and $(\partial_t - D\nabla_x^2)\phi + 2\lambda\phi^2 = 0$. Taking the expectation of the latter yields,

$$\begin{aligned} & (\partial_t - D\nabla_x^2)\langle\phi\rangle + 2\lambda\langle\phi^2\rangle = 0 \,, \\ \Rightarrow \quad & \frac{\partial}{\partial t}\rho(x,t) = D\nabla^2\rho(x,t) - 2\lambda\langle\phi^2\rangle \,, \end{aligned}$$

which has nearly the form of the rate equation (3.2). The difference between the two rate equations lies in the different interaction terms. If we assume a factorisation in the two-particle probability density and hence $\langle\phi^2\rangle = \langle\phi\rangle^2 = \rho^2$, we obtain the rate equation (3.2). But this assumption is only true in case of absence of spatial fluctuations and correlations in the system. Thus, the rate equation approach corresponds to a mean-field description as pointed out earlier.

5.3.2 Stochastic Langevin equations

A possible extension of the classical field equation approach is the application of the Langevin formalism, which formulates the problem in terms of a stochastic partial differential equation (SPDE). It will be shown, how the field theory characterised by action (5.36) and Lagrangian (5.37) can be cast into a Langevin equation.

Generally, a Langevin equation is written in the form [19],

$$\frac{\partial}{\partial t}\phi(t) = \underbrace{-\gamma\frac{\delta\mathcal{H}}{\delta\phi}}_{\text{deterministic}} + \underbrace{\xi(t)}_{\text{stochastic noise}} \,, \tag{5.40}$$

whereas $\mathcal{H}$ is the Hamiltonian from the last section in the continuum limit, γ a real parameter and $\xi(t)$ reflects a time-dependent random noise function with zero mean and two-point function,

$$\langle\xi(t)\xi(t')\rangle = 2\sigma\delta(t-t') \,. \tag{5.41}$$

The parameter σ determines the strength of the noise. Its characterisation will have interesting implications. Langevin equations are mostly used to describe equilibrium systems, such as Brownian motion of a mesoscopic particle suspended in a solution of smaller particles. The system is in thermal equilibrium with the heat bath being characterised by temperature T. For these stochastic processes, it turns out that the noise correlation is adequately described by Gaussian noise, that is $\sigma = D > 0$, the diffusion constant, which is related to parameter γ by the fluctuation-dissipation-theorem,

$$\gamma k_B T = D \,, \tag{5.42}$$

with k_B being Boltzmann's constant. We will see how the noise correlation changes if we describe the non-equilibrium pair-annihilation process (2.1) by a Langevin equation one would obtain from an equilibrium process.
In order to extract the correct form of the Langevin equation (5.40, 5.41), it is convenient to express the two-point function as an average over the noise ξ,

$$\langle\phi(t_1)\phi(t_2)\rangle = \left\langle \int \mathcal{D}[\phi]\ \phi(t_1)\phi(t_2)\delta[\phi(t) - \text{solution to (5.40)}] \right\rangle_{\xi(t)} .$$

By applying theorems from functional integration, the analysis results in (for details see [19], [4]),

$$\begin{aligned} \langle\phi(t_1)\phi(t_2)\rangle &= \int \mathcal{D}[\tilde{\phi}]\mathcal{D}[\phi]\ \phi(t_1)\phi(t_2)e^{-S[\tilde{\phi},\phi]} , \\ S[\tilde{\phi},\phi] &= \int dt\ \left\{ \tilde{\phi}\partial_t\phi + \tilde{\phi}\gamma\frac{\delta\mathcal{H}}{\delta\phi} - \sigma\tilde{\phi}^2 \right\} . \end{aligned} \tag{5.43}$$

A comparison of the field action yielded by the general Langevin approach (5.43) with the field action from the lattice approach (5.36) reveals the stochastic partial differential equation,

$$\begin{aligned} \partial_t\phi(t) &= D\nabla^2\phi - 2\lambda\phi^2 + \xi , \\ \langle\xi(t)\xi(t')\rangle &= -\lambda\phi^2\delta(t-t') , \end{aligned} \tag{5.44}$$

which can be regarded as an extension of the classical field equation including now stochastic noise. Note, that the noise correlator now includes the field itself and a minus sign. The former implicates a multiplicative noise, which can be understood qualitatively since the noise should vanish if the particle density is zero. The latter says that the noise ξ must be a complex field. In contrast to the description of equilibrium processes, the noise cannot be a real field and limits the phenomenological interpretation of the Langevin equation. It is not possible to simply extend the classical field equation by adding real Gaussian noise to the deterministic part of the classical equation.

However, eq. (5.44) could be the starting point for a perturbation analysis, which is realised in [20]. Nevertheless, the application of this approach is limited to reactions with two reactants only, since only these reactions can be transformed directly into a SPDE [4]. Therefore, further analysis will be carried out by starting from eq. (5.35, 5.36, 5.37).

6 Diagrammatic Expansion

Let us summarize the results derived in the last section. We managed to rewrite the microscopic stochastic description of the pair annihilation reaction (2.1) in

terms of a master equation (5.7) into a field theory (5.35, 5.36, 5.37) by virtue of the second quantised formalism and the continuum limit. We are now in the position to evaluate the one-point function $\langle\phi(x,t)\rangle$ via eq. (5.38), but, in contrast to the rate equation approach (3.2), including fluctuations and correlations in our analysis. However, being faced with this field theoretic problem, it is possible to apply the prosperous methods from field theory, in particular perturbation expansions and renormalisation methods to compute $\langle\phi(x,t)\rangle$. These methods are well established, for example in statistical and quantum field theory, but involve a lot of effort to derive them from scratch. Therefore, only the main steps and features of the field-theoretic description of this reaction-diffusion process will be presented in the following and specialties of the pair annihilation process will be pointed out.

In order to compute $\langle\phi(x,t)\rangle$, one defines the generating functional $Z[\tilde{h},h]$ by introducing external field sources $\tilde{h},h$ linearly coupled to the fields $\tilde{\phi},\phi$ in the action,

$$Z[\tilde{h},h] := \int \mathcal{D}[\tilde{\phi}]\mathcal{D}[\phi]\ \exp\left\{-S[\tilde{\phi},\phi] - \int\limits_{x,\tau}(\tilde{h}\tilde{\phi}+h\phi)\right\}, \tag{6.45}$$

where the shorthand notation $\int\limits_{x,\tau}\ldots := \int d^dx \int\limits_0^t d\tau\ldots$ was used.
Thus, the one-point function can be computed by taking the first functional derivative with respect to the field source h and setting $\tilde{h}=h=0$,

$$G_1 = \langle\phi\rangle = \frac{-1}{Z[0,0]}\cdot\frac{\delta}{\delta h}Z[\tilde{h},h]\bigg|_{\tilde{h}=h=0}. \tag{6.46}$$

The task is now shifted to the evaluation of the generating functional $Z[\tilde{h},h]$, which can be performed perturbatively.

6.1 Free Field Theory: Pure Diffusion

To evaluate the generating functional $Z[\tilde{h},h]$ and hence to compute eq. (5.38, 6.46) for the one-point function perturbatively, one has to establish a theory, normally referred to as free-field theory, that can be solved exactly. Usually, it will be the bilinear part in the field theory action, for which the path integral can be solved exactly (at least formally) by means of functional Gaussian integrals and around which a perturbation expansion can be formulated.

For the pair annihilation reaction-diffusion process, the bilinear part of the ac-

tion (5.36) is the following term, corresponding to pure diffusion,

$$S_0[\tilde{\phi},\phi] = \int d^dx \int_0^t d\tau\ \tilde{\phi}\underbrace{(\partial_\tau - D\cdot\nabla_x^2)}_{=:\mathcal{O}(\tau,x)}\phi\ , \tag{6.47}$$

where the diffusion operator was abbreviated, $\mathcal{O}(\tau,x) := \partial_\tau - D\cdot\nabla_x^2$. The related generating functional for this free-field theory $Z_0[\tilde{h},h]$ can be written as,

$$Z_0[\tilde{h},h] := \int \mathcal{D}[\tilde{\phi}]\mathcal{D}[\phi]\ \exp\left\{-\int_{x,\tau}\left(\tilde{\phi}\mathcal{O}\phi + \tilde{h}\tilde{\phi} + h\phi\right)\right\} \tag{6.48}$$

If we define the inverse operator $\mathcal{O}^{-1}$ of the diffusion operator as follows,

$$\mathcal{O}(x,t)\mathcal{O}^{-1}(x',t') = \delta(x-x')\delta(t-t')\ , \tag{6.49}$$

one can complete the square in eq. (6.48) by shifting the field $\phi \mapsto \phi + \int_{x,\tau}\mathcal{O}^{-1}\tilde{h}$ and carrying out the Gaussian integration, revealing,

$$\begin{aligned} Z_0[\tilde{h},h] &= \int \mathcal{D}[\tilde{\phi}]\mathcal{D}[\phi]\ \exp\left\{-\int_{x,\tau}\tilde{\phi}\mathcal{O}\phi + \int_{x,\tau}\int_{x',\tau'} h\mathcal{O}^{-1}\tilde{h}\right\}\ , \\ &= Z_0[0,0]\cdot\exp\left\{\int_{x,\tau}\int_{x',\tau'} h\mathcal{O}^{-1}\tilde{h}\right\}\ , \end{aligned} \tag{6.50}$$

which is an exact result for the free field theory as promised.

Propagator - Inverse of the Diffusion Operator

The explicit form of the inverse $\mathcal{O}^{-1}$ to the diffusion operator still has to be specified. This can be done by applying Fourier transform methods to eq. (6.49). This procedure is common in field theories, compare for example with fermionic field theory and the Dirac operator. Finally, one obtains in Fourier space,

$$\mathcal{O}^{-1}(q,\omega) = \frac{1}{-i\omega + Dq^2} =: G_0(q,\omega)\ . \tag{6.51}$$

Conveniently, the inverse operator of the free field theory is given an own label, here G_0, since it is the propagator of our field theory,

$$\langle\phi(q,\omega)\tilde{\phi}(q',\omega')\rangle_0 = (2\pi)^{d+1}\delta(q+q')\delta(\omega+\omega')G_0(q,\omega)\ ,$$

where averages with respect to the free field action (6.47) are denoted by the subscript $\langle\rangle_0$.
If we go back into the time domain by applying inverse Fourier transform only in the time coordinate, one obtains,

$$G_0(q,t) = \frac{1}{2\pi}\int d\omega\; e^{-i\omega t} G_0(q,\omega) = \Theta(t)\cdot e^{-Dq^2 t}\;, \tag{6.52}$$

with the Heaviside function,

$$\Theta(t) = \begin{cases} 1 & t \geq 0\;, \\ 0 & t < 0\;. \end{cases}$$

Thus, the propagator G_0 inherently represents a causal ordering of the fields ϕ and $\tilde{\phi}$, since only earlier fields $\tilde{\phi}$ are connected to later fields ϕ,

$$\langle \phi(q,t)\tilde{\phi}(q',t')\rangle_0 \propto \Theta(t-t')\cdot e^{-D(q-q')^2(t-t')}\;.$$

This is a crucial feature of the diffusion propagator, whereupon the structure of Feynman diagrams in the perturbation expansion will be restricted. This will be content of the next section.

6.2 Perturbation Around Diffusion

Let us go back to our initial aim of this chapter, the evaluation of the generating functional $Z[\tilde{h},h]$ for the full reaction-diffusion action (5.36, 5.37) and the computation of the one-point function $\langle\phi(x,t)\rangle$ via eq. (6.46). The generating functional can be rewritten as follows,

$$\begin{aligned}
Z[\tilde{h},h] &= \int \mathcal{D}[\tilde{\phi}]\mathcal{D}[\phi]\;\exp\left\{-S[\tilde{\phi},\phi] - \int\limits_{x,\tau}(\tilde{h}\tilde{\phi}+h\phi)\right\} \\
&= \int \mathcal{D}[\tilde{\phi}]\mathcal{D}[\phi]\; e^{-S_0}\exp\left\{-\int\limits_{x,\tau}\left(2\lambda\tilde{\phi}\phi^2+\lambda\tilde{\phi}^2\phi^2\right)\right\} e^{-\int\limits_{x,\tau}\tilde{h}\tilde{\phi}+h\phi} \\
&\qquad \text{with boundary condition: } \phi(x,0)=\rho_0(x) \\
&= \exp\left\{-\int\limits_{x,\tau}\left(2\lambda\frac{\delta}{\delta\tilde{h}}\frac{\delta^2}{\delta h^2}+\lambda\frac{\delta^2}{\delta\tilde{h}^2}\frac{\delta^2}{\delta h^2}\right)\right\} Z_0[\tilde{h},h]\;+\text{b.c.} \\
&\overset{6.50}{=} Z_0[0,0]\cdot\exp\left\{-\int\limits_{x,\tau}\left(2\lambda\frac{\delta}{\delta\tilde{h}}\frac{\delta^2}{\delta h^2}+\lambda\frac{\delta^2}{\delta\tilde{h}^2}\frac{\delta^2}{\delta h^2}\right)\right\}\exp\left\{\int\limits_{x,\tau}\int\limits_{x',\tau'} hG_0\tilde{h}\right\}\;+\text{b.c.}
\end{aligned} \tag{6.53}$$

The idea is now to expand the exponential with the reaction terms in orders of the coupling parameter λ according to $e^{\lambda x} = \sum_n (\lambda x)^n / n!$. By doing so, one ultimately ends up with an perturbation expansion around pure diffusion, where the reactions constitute the perturbations.
Physically, this way of expanding the generating functional makes sense, since we are interested in the long-time behaviour of the one-point function $\langle \phi \rangle$, that is in a regime being dominated by diffusion. The reactions are assumed to be only small corrections to the pure diffusive case.

For the reason of clarity and better understanding, one usually denotes this expansion series in terms of so called Feynman diagrams. Each diagram in this graphical notation corresponds to an integral expression in the perturbation expansion according to the following identification,

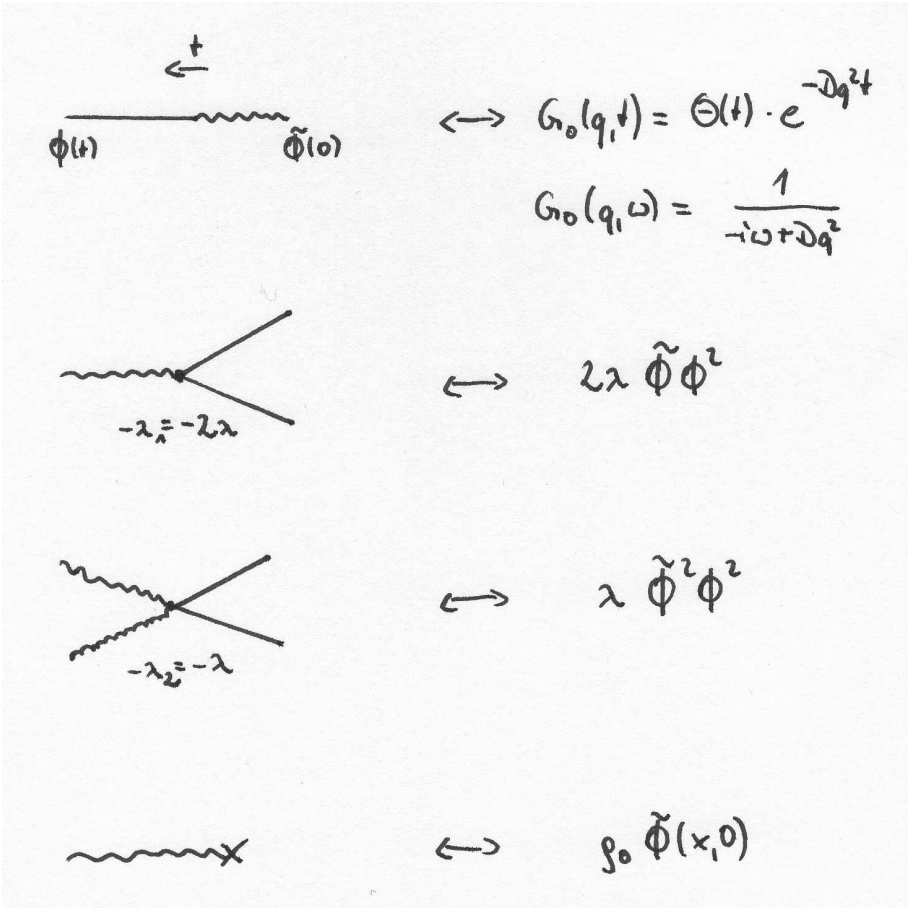

Figure 6.4: *Propagator and vertices for the pair annihilation reaction.*

For example, the $2\lambda\tilde{\phi}\phi^2$-term corresponds to a vertex that connects two incoming propagators with one outgoing propagator. The causal structure of the propagator for the reaction-diffusion process ensures time-ordering, hence, the time

increases from the right to the left in a Feynman diagram.

Since we are only interested in the one-point function, we do not have to compute all possible diagrams. After having differentiated $Z[\tilde{h}, h]$ with respect to the source h in eq. (6.46), we set all external fields to zero, $\tilde{h} = h = 0$. Therefore, all diagrams in the perturbation expansion for the one-point function will vanish unless they have one external leg.

The Feynman rules for drawing all diagrams contributing to $\langle \phi(x,t) \rangle$ resulting from eq. (6.46, 6.53) are most conveniently formulated in momentum space, since we are dealing with a translationally invariant system in space and time. They can be summarised as follows [17, 4],

- Draw all diagrams with one external leg on the left and with initial legs on the right.
- Each line corresponds to a propagator G_0 (figure 6.4).
- The two vertices (figure 6.4) connect internal lines together. A 3-vertex goes with a factor of $(-\lambda_1 = -2\lambda)$, a 4-vertex contributes with a factor of $(-\lambda_2 = -\lambda)$.
- Integrate over each undetermined loop momentum p with measure $\frac{1}{(2\pi)^d} \int d^d p \ldots$ and over each undetermined time t_0 with measure $\int_{t'}^{t''} dt_0 \ldots$
- Impose momentum conservation at each vertex. The final propagator must have $q = 0$ (spatial uniformity) and all propagators connected with an initial leg (figure 6.4) also have $q = 0$, because of the initial condition in Fourier space. Each initial leg comes with a factor of ρ_0.
- Include a symmetry factor for each diagram being equal to the number of possibilities to attach an inner propagator to a vertex.

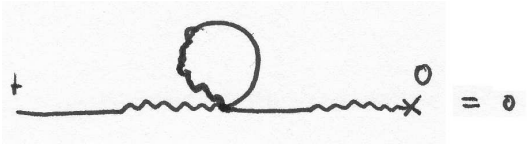

Figure 6.5: *Loops at one time yield zero because of the causal structure of the propagator.*

Note that loops at one specific time t' are not allowed (figure 6.5), due to the time-ordering principle and causal structure of our propagator $G_0(q,t) = \Theta(t) \cdot e^{-Dq^2 t}$.

An integration over such a loop is proportional to the integral,

$$\int_{t'}^{t'} dt\ G_0(p,0) = 0\ .$$

For the one-point function, the diagrammatic expansion, according to the Feynman rules, yields,

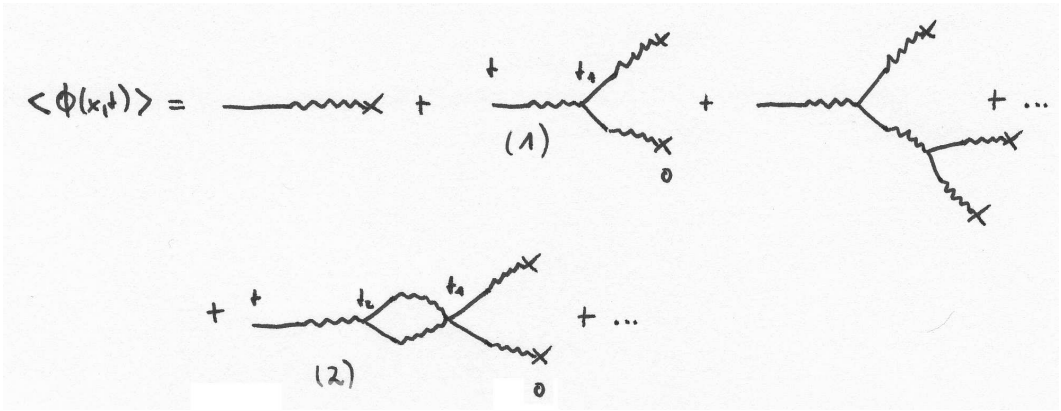

Figure 6.6: *Diagrammatic expansion for the one-point function.*

To exemplify the correspondence between the diagrams and the integral expressions, let us have a closer look at two integrals.

$$(1) = \int_0^t dt_1\ G_0(0,t-t_1)(-\lambda_1)G_0(0,t_1)^2\cdot\rho_0^2\ \propto -\lambda_1\rho_0^2 t\ ,$$

$$(2) = \int_0^t dt_2 \int_0^{t_2} dt_1\ G_0(0,t-t_2)(-\lambda_1)\times$$
$$\times \int \frac{d^dp}{(2\pi)^d}\ G_0(p,t_2-t_1)(-\lambda_2)G_0(-p,t_2-t_1)\cdot 2G_0(0,t_1)^2\rho_0^2\ .$$

The first integral (1) corresponds to a linear decrease of the initial density in time, but the second integral (2) demonstrates a problem of our naive proceeding in the perturbation expansion, since it diverges. To see this, consider the effective coupling λ_{eff}, being part of our integral expression above, given by the diagram depicted in figure 6.7,

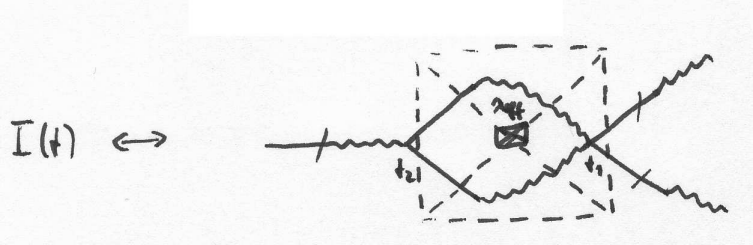

Figure 6.7: *Effective coupling.*

with (calculations for $d \neq 2, 4$),

$$I(t) =: -\lambda_{\text{eff}} = \int_0^{t_2} dt_1 \int \frac{d^d p}{(2\pi)^d} G_0(p, t_2 - t_1)(-\lambda_2) G_0(-p, t_2 - t_1) \cdot 2 \,,$$
$$\propto -\lambda_2 \cdot t^{1-d/2} \qquad (d \neq 2, 4) \,.$$

We have to distinguish between two cases for $I(t)$, depending on the dimension d. The qualitative behaviour changes at a critical dimension $d_c = 2$ [20, 4].

- $d < d_c = 2$
  For small times $t \to 0$, $I(t)$ is finite and the perturbation expansion results are reliable. This limit is also referred to as ultraviolet (UV) limit ($q, \omega \to \infty$).
  For large times $t \to \infty$, $I(t)$ diverges and the perturbation theory breaks down. This limit is also referred to as infrared (IR) limit ($q, \omega \to 0$).

- $d > d_c = 2$
  Perturbation theory breaks down for $t \to 0$, but works for $t \to \infty$.

The UV divergences for $d \geq 2$ are caused by the continuum limit, where the lattice spacing $a \to 0$. Physically, there will always be a short-distance cut-off Λ, which can be introduced by hand into the analysis and which resolves the UV divergence.
In contrast, the IR divergence for $d \leq 2$, thus the limit we are interested in, weighs more severe, since the naive perturbation series cannot be resolved by a physical argument as for the UV divergence.
Nevertheless, it is possible to extract the right scaling behaviour for the mean particle density even for $d \leq 2$ by means of renormalisation group, being described later on.

6.3 Tree Diagrams Correspond to Mean-Field Rate Equation

Let us have closer look at the so called tree diagrams, that is the Feynman diagrams not involving any loops.

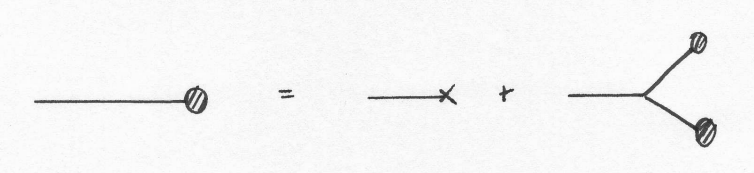

Figure 6.8: *Iterative expression for the tree diagrams.*

For the sum of all tree diagrams ρ_{tree}, one can infer on an iterative expression according to the Feynman rules from the last section (cf. figure 6.8).

$$\rho_{\text{tree}}(t) = \rho_0 - \lambda_1 \int_0^t dt_1 \; \rho_{\text{tree}}(t_1)^2 \; .$$

By taking the time derivative of this equation, one obtains the kinetic mean-field rate equation (3.4) for the pair-annihilation process with the correct initial condition.
Hence, all analysis on the tree diagram level corresponds to the mean-field PDE approach and fluctuation corrections are represented by the diverging loop integral expressions. The analysis of the fluctuation corrections will play the central part of the next section.

7 Renormalisation

In the last chapter, we have seen, how one can compute $\langle \phi(x,t) \rangle$ perturbatively. However, this perturbation expansion approach is too naive and leads to divergences in the IR limit for asymptotic times below a critical dimension $d_c = 2$.
Nevertheless, our aim is to extract the correct asymptotic behaviour of the particle density $\rho(x,t)$. To this end, first the UV divergences at $d = 2$ will be examined and scale invariance can be shown for the underlying reaction-diffusion system. Renormalisation methods will render finite results for the loop diagrams, but parameters of the theory will then depend on the introduced UV cut-off Λ. The scaling behaviour is extracted by means of dynamic renormalisation group (RG), leading to the identification of an IR-stable renormalisation group fixed point. The scale invariance for asymptotic times is used to derive scaling behaviour also

in the IR limit. Scaling laws in other dimensions $d < d_c = 2$ can finally be obtained by dimensional expansion around $d = d_c$ in a small parameter $\epsilon = d_c - d$, which will not be that small in the end, since we want to set $\epsilon = 1$, in order to get results for $d = 1$.

The detailed analysis, of how IR divergences are connected to UV singularities, can be found in [21].

7.1 Primitive UV Divergences

We want to investigate the primitive UV divergences, we have encountered in the diagrammatic expansion of $\langle\phi(x,t)\rangle$ in $d = 2$. These divergences are called primitive, since they are superficial and can be removed by a short-distance cut-off Λ^{-1}. The dependence on the physical lattice cut-off Λ will be rewritten in terms of dimensional regularisation.
Also, only amputated connected diagrams will be examined, since it was shown that loops and the corresponding effective couplings cause divergences. Amputated refers to the fact that propagators of external lines are neglected. The sum of all amputated connected n-point functions is denoted by $\hat{F}_n(q,\omega)$.

Primitive divergences have their origin in loop integrals, thus $\hat{F}$ can be written as,

$$\hat{F} \propto \int dp^{dL} \frac{1}{(-i\omega + Dp^2)^I} \propto \int_0^\infty d|p| \ |p|^{dL-1} \frac{1}{(-i\omega + Dp^2)^I} \ ,$$

where L denotes the number of loops in the Feynman diagram and I the number of internal lines. The diagram corresponds to a UV divergent integral if the superficial degree of divergence $DoD := dL - 2I \geq 0$.
From only topological reasons, it can be inferred that the superficial degree of divergence can be computed as [17],

$$DoD = (d-4)L + \sum_n (n-4)V_n - E + 4 \ . \tag{7.54}$$

V_n denotes the number of vertices of valence n and E the number of external legs. However, $DoD \leq 0$ does not guarantee that a diagram is finite, since subdivergences are not taken care of, meaning that also diagrams with $DoD \leq 0$ can have divergent subgraphs. Nevertheless, it turns out that the superficial degree of divergence is the right tool to analyse and resolve divergences via renormalisation techniques (cf. renormalisation theorem).
In our case, we have $d = 2$ and hence $DoD \geq 0 \Leftrightarrow -V_3 - E + 4 \geq 2L$. First of all, it can be derived that the more loops involved, the better the chance for the diagram to be well-defined. If the worst case with $L = 0$ is taken, only two situations have to be considered.

- $V_3 = 0$
  In case of no 3-vertex interaction, it follows the condition for superficial divergence: $E \leq 4$. Since the interaction involves vertices with always two incoming fields, only diagrams with one or two outgoing fields are allowed.

- $V_3 = 1$
  Now, the condition becomes $E \leq 3$ and only diagrams with one outgoing field are allowed.

$V_3 > 1$ is not possible since no outgoing fields could be included.
Hence, only two sets of Feynman diagrams carry UV divergences, because of the underlying vertex structure of the pair annihilation reaction, namely $\hat{F}_3(q, \omega)$ and $\hat{F}_4(q, \omega)$ (cf. figure 7.9).

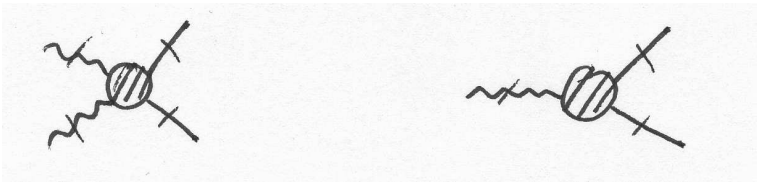

Figure 7.9: *$\hat{F}_4(q, \omega)$ (left) and $\hat{F}_3(q, \omega)$ (right) contain all Feynman diagrams that give rise to infinities in the diagrammatic expansion.*

Note that no superficial divergences can appear in $\hat{F}_2$ and hence $\hat{F}_2(q, \omega) = -i\omega + Dq^2$ (cf. figure 7.10).

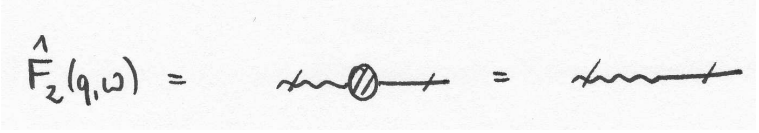

Figure 7.10: *No renormalisation is needed for the propagator.*

This is due to the structure of the pair annihilation interaction and the time-ordering property of the propagator with the consequence that no divergences occur for the propagator itself. Therefore, the propagator stays unchanged during the renormalisation process and the diffusion constant does not have to be renormalised. The same is true for the fields $\tilde{\phi}, \phi$ and in the language of renormalisation, we have $Z_{\tilde{\phi}} = Z_\phi = 1$ and $Z_D = 1$. This is a special feature of the pair annihilation process and in contrast to scalar quantum field theory with ϕ^4-interaction, for example, where the mass term has to be renormalised. It is then possible to set the diffusion constant to $D = 1$ to all orders in perturbation theory.

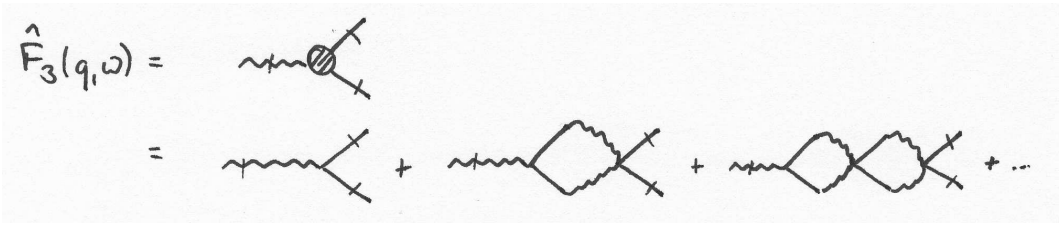

Figure 7.11: *Full diagrammatic expansion for $\hat{F}_3$.*

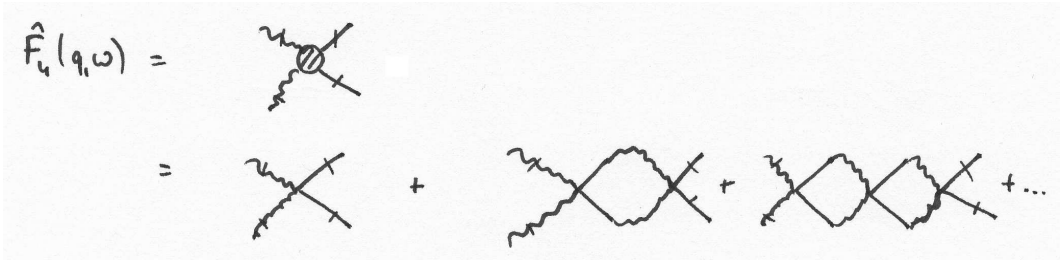

Figure 7.12: *Full diagrammatic expansion for $\hat{F}_4$.*

Moreover, we can immediately write down the full diagrammatic expansion for $\hat{F}_3$ and $\hat{F}_4$, again because of the structure of the vertices (figure 6.4) together with the causal structure of the propagator,

By assigning $J(q,\omega)$ to the integral expression of the loop, we can write $\hat{F}_3(q,\omega)$ as a geometric series,

$$\begin{aligned}\hat{F}_3 &= -2(-2\lambda) - (-2\lambda)J(-\lambda)2^2 - (-2\lambda)J(-\lambda)J(-\lambda)2^3 \\ &= 4\lambda(1 - 2J\lambda + 2^2J^2\lambda^2 \mp \dots) \\ &= 4 \cdot \frac{\lambda}{1+2\lambda J} =: 4 \cdot \lambda_R \,, \end{aligned} \tag{7.55}$$

which is an exact result to all orders in the loop expansion. This is again a feature, contrary to, for example, scalar quantum field ϕ^4-theory, where the evaluation can only be carried out order by order in the loop expansion. Thus, the whole analysis for the following renormalisation procedure simplifies enormously.
The loop integral $J(q,\omega)$ can be evaluated by dimensional regularisation, that is the occurring divergences are transformed to poles of functions depending on the small parameter $\epsilon = 2-d$, which describes the distance to the critical dimension.

Usually, one has $d \in \mathbb{Z}^+$, but one can regulate by analytic continuation to $d \in \mathbb{C}$.

$$\begin{aligned} J(q,\omega) &= \int \frac{d^d q'}{(2\pi)^d} \int \frac{d\omega'}{2\pi} \frac{1}{-i\omega' + q'^2} \frac{1}{-i(\omega'-\omega) + (q'-q)^2} \\ &\propto \int \frac{d^d q'}{-i\omega + (q'-q)^2 + q'^2} \overset{q' \mapsto q'/\sqrt{2}}{\propto} \int \frac{d^d q'}{q'^2 - 2q' \cdot \frac{q}{\sqrt{2}} + q^2 - i\omega} \\ &= \frac{\Gamma(1-d/2)}{(4\pi)^{d/2}\Gamma(1)} \cdot \frac{1}{(\frac{q^2}{2} - i\omega)^{1-d/2}} , \end{aligned}$$

where in the last step the Gamma-function was introduced ($\Gamma(\alpha) = 1/\alpha \cdot \Gamma(\alpha+1)$ and $\Gamma(1) = 1, \Gamma(1/2) = \sqrt{\pi}$) and the following integral identity was used [21],

$$\int \frac{d^d k}{(k^2 + 2k \cdot p + m^2)^s} = \frac{\Gamma(s - d/2)}{(4\pi)^{d/2}\Gamma(s)} \cdot \frac{1}{(m^2 - p^2)^{s-d/2}} .$$

With $\epsilon = 2 - d$, we finally arrive at,

$$J(q,\omega) = \frac{1}{(8\pi)^{d/2}} \cdot \Gamma\left(\frac{\epsilon}{2}\right) \cdot \left(-i\omega + \frac{q^2}{2}\right)^{-\epsilon/2} , \tag{7.56}$$

$$\hat{F}_3 = 4 \cdot \frac{\lambda}{1 + \frac{2\lambda}{(8\pi)^{d/2}} \cdot \Gamma\left(\frac{\epsilon}{2}\right) \cdot \left(-i\omega + \frac{q^2}{2}\right)^{-\epsilon/2}} . \tag{7.57}$$

One can now recognize the extracted divergence from above by looking at the parameter ϵ. If $q = 0$, the expression for $\hat{F}_3$ for $\epsilon > 0$ diverges as $\omega \to 0$, representing the IR singularity. The UV divergence is now expressed by the poles of the Γ-function for $\epsilon = 0, -2, -4, \ldots$, since $\Gamma\left(\frac{\epsilon}{2}\right) \sim \frac{2}{\epsilon}$ as $\epsilon \to 0$.
A similar result can be obtained for $\hat{F}_4$.

7.2 Renormalisation Procedure

7.2.1 Renormalisation Idea

Let us summarise the key points, we have encountered up to now. We started with a field theory whose Lagrangian can essentially be written as,

$$\begin{aligned} \mathcal{L} &= \mathcal{L}_0 + \mathcal{L}_{\text{int}} \\ &= \tilde{\phi}(\partial_t - D\nabla_x^2)\phi + 2\lambda\tilde{\phi}\phi^2 + \lambda\tilde{\phi}^2\phi^2 . \end{aligned}$$

It was derived that in two dimensions, the amputated connected n-point function $\hat{F}_n(q, \omega; \lambda, \Lambda)$ shows IR divergences (for $q \to 0$ and $t \to \infty$) and UV divergences due to the continuum limit for $n = 3, 4$. The good news is that $\hat{F}_2$ is well-defined and finite and hence no renormalisation of the fields and the diffusion coefficient

is needed. Furthermore, it was possible to compute $\hat{F}_3, \hat{F}_4$ to all orders in the loop expansion.
It was shown in eq. (7.55, 7.57) that if the continuum limit is carried out (corresponding to $\Lambda \to 0$ or equivalently $\epsilon \to 0$ in dimensional regularization), the effective coupling diverges.
However, in the theory, there must be a physical coupling λ_{phys}, being measured in an experiment and corresponding to an effective interaction,

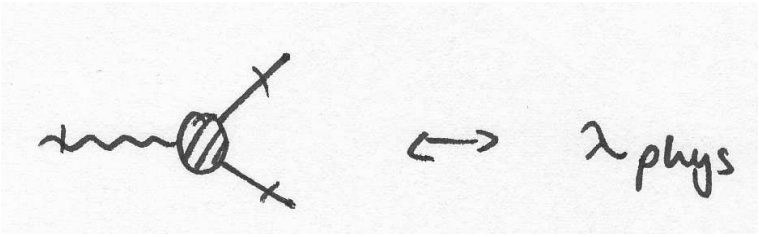

Figure 7.13: *Physical effective coupling.*

Thus, one makes the ansatz $\lambda_{\text{phys}} = \lambda + \tilde{\lambda} = \lambda(1 + \tilde{\lambda}/\lambda)$, whereby λ is the coupling appearing in the Lagrangian and $\tilde{\lambda}$ is an introduced shift in the parameter which depends on the cut-off Λ. So, the idea is to allow λ to depend on the cut-off Λ, $\lambda \mapsto \hat{\lambda}(\Lambda)$.
We want to carry out a more sophisticated limit, that is take $\Lambda \to 0$ with $\hat{\lambda}(\Lambda)$ varying, but λ_{phys} held fixed. We must get finite answers for all observable quantities in this limit. The existence of such a limit is non-trivial, but can be achieved for the pair annihilation process by introducing a finite number of additive terms to the Lagrangian, also known as counter terms (such a theory is called renormalisable). Note, that in general one would also allow $D, \tilde{\phi}, \phi$ to depend on the cut-off Λ, but this is not needed for the pair annihilation process as already mentioned.
We will see that this procedure removes divergences, but at the cost of running couplings, that is parameters and fields of the theory will depend on the cut-off in general.

In practice, the divergences can be cancelled by adding counter terms to the Lagrangian $\mathcal{L} \mapsto \mathcal{L} + \mathcal{L}_{\text{c.t.}}$. Normally this would have to be carried out order by order (in loops), but here we know the divergences to all orders and can immediately write down the needed counter terms to all loop orders,

$$\mathcal{L}_{\text{c.t.}} = A\tilde{\phi}\phi^2 + B\tilde{\phi}^2\phi^2 \ ,$$

by which new vertices are introduced to the field theoretic expansion of $\mathcal{L} + \mathcal{L}_{\text{c.t.}}$ in addition to figure 6.4, depicted in figure 7.14.

These new vertices are constructed and defined in order to subtract off exactly the divergences occurring in the original Lagrangian $\mathcal{L}$. Hence, by taking re-

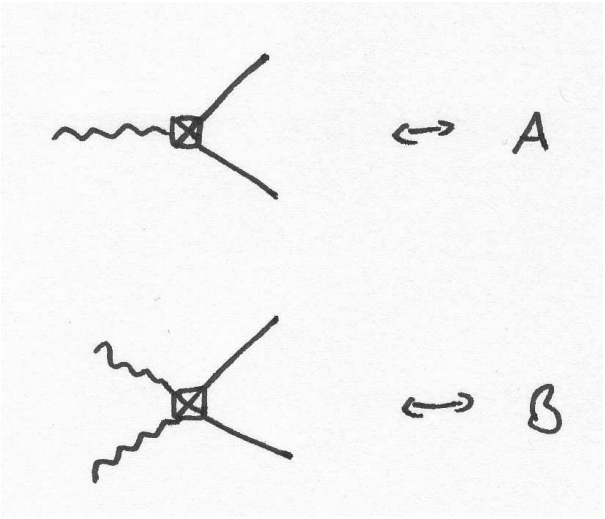

Figure 7.14: *New vertices due to counter terms.*

sult (7.55, 7.57) into account, one obtains,

$$A = \lambda_R = \frac{\lambda}{1 + \frac{2\lambda}{(8\pi)^{d/2}} \cdot \Gamma\left(\frac{\epsilon}{2}\right) \cdot \left(-i\omega + \frac{q^2}{2}\right)^{-\epsilon/2}} = \hat{\lambda} \; .$$

7.2.2 Dimensional Analysis

Before proceeding in the renormalisation analysis, a more precise dimensional analysis has to be carried out, since a perturbation expansion only makes sense in a dimensionless quantity. We will see that, apart from two dimensions, the coupling λ carries dimension ϵ and thus, a dimensionless quantity has to be introduced. Therefore, let us examine again the action from eq. (5.36, 5.37),

$$S[\tilde{\phi}(x,t), \phi(x,t)] = \int d^d\chi \left\{ \int_0^t d\tau \; \left(\tilde{\phi}(\partial_t - D\nabla_x^2)\phi + 2\lambda\tilde{\phi}\phi^2 + \lambda\tilde{\phi}^2\phi^2 \right) - \rho_0\tilde{\phi}(\chi, 0) \right\} \; .$$

The action S appears in the exponential in the path integral and thus has dimension 0, whereas quantities are measured in momentum units, for example Λ. Hence, $[S] = 0, [p] = 1, [x] = -1$ and we are free to choose $[D] = 0$, a dimensionless diffusion constant. It follows from the diffusion operator that $[1/x^2] = [1/t] \Rightarrow [t] = -2$. Furthermore, the way the continuum limit for the field theory was defined yields $[\tilde{\phi}] = 0$. But this implicates $[\phi] = d$ and $[\lambda] = 2 - d = \epsilon$. A dimensionless coupling g ($[g] = 0$) is defined in $d = 2 - \epsilon$ dimensions by introducing an arbitrary scale μ with $[\mu] = 1$, being also called the RG-scale,

$$\lambda = g \cdot \mu^\epsilon \quad \text{and} \quad \hat{\lambda} = \hat{g} \cdot \hat{\mu}^\epsilon \; .$$

7.2.3 Callan-Symanzik Equation and Beta-Function

In this subsection, the idea of renormalisation and the dimensional analysis are brought together and physical consequences are inferred.
We define the bare Lagrangian $\mathcal{L}_B$ as the shifted Lagrangian $\mathcal{L} + \mathcal{L}_{\text{c.t.}}$ now in terms of dimensionless couplings,

$$\begin{aligned}\mathcal{L}_B :&= \mathcal{L} + \mathcal{L}_{\text{c.t.}} \\ &= \tilde{\phi}(\partial_t - D\nabla_x^2)\phi + 2\hat{g}\cdot\mu^\epsilon\tilde{\phi}\phi^2 + \hat{g}\cdot\mu^\epsilon\tilde{\phi}^2\phi^2 + \hat{A}\cdot\mu^\epsilon\tilde{\phi}\phi^2 + \hat{B}\cdot\mu^\epsilon\tilde{\phi}^2\phi^2 \\ &= \tilde{\phi}_B(\partial_t - D_B\nabla_x^2)\phi_B + 2\hat{g}_B\cdot\mu^\epsilon\tilde{\phi}_B\phi_B^2 + \hat{g}_B\cdot\mu^\epsilon\tilde{\phi}_B^2\phi_B^2 \ .\end{aligned}$$

In the second line, the counter term couplings A, B have been expressed in terms of dimensionless couplings, for example,

$$\hat{A}(\epsilon) = \sum_{n\geq 1} g^n \hat{A}_n(\epsilon) = \frac{g}{1 + \frac{2g}{(8\pi)^{d/2}}\cdot\Gamma\left(\frac{\epsilon}{2}\right)\cdot\left(-i\omega + \frac{q^2}{2}\right)^{-\epsilon/2}} = \hat{g} \ , \tag{7.58}$$

and similar for $\hat{B}$. In the third line, we have rewritten the bare Lagrangian in the same form as the original Lagrangian by defining bare fields ($\tilde{\phi}_B := \tilde{\phi}, \phi_B := \phi$) and bare parameters ($D_B := D, \hat{g}_B := \hat{g} + \hat{A}$). Note, that the bare parameters and bare fields depend on the cut-off parameter ϵ, but are independent of the RG-scale μ. In contrast, the renormalised parameter $\hat{g} = \hat{g}(\mu)$ depends on the arbitrary RG-scale μ, but not on ϵ.

However, the arbitrariness of μ will lead to a constraint on the theory, which will be presented in the following.
We can rewrite the path integral in terms of bare quantities as follows,

$$S_B[\tilde{\phi}_B, \phi_B] = \int d^d\chi \left\{ \int_0^t d\tau \ \mathcal{L}_B[\tilde{\phi}_B, \phi_B] - \rho_0\tilde{\phi}_B(\chi, 0) \right\} \quad \text{and} \quad \mathcal{D}[\phi_B] = \mathcal{D}[\phi]$$

$$\Rightarrow \quad \langle\phi_B(x,t)\rangle = \frac{\int \mathcal{D}[\tilde{\phi}_B]\mathcal{D}[\phi_B] \ \phi_B \ e^{-S_B[\tilde{\phi}_B,\phi_B]}}{\int \mathcal{D}[\tilde{\phi}_B]\mathcal{D}[\phi_B] \ e^{-S_B[\tilde{\phi}_B,\phi_B]}} \stackrel{!}{=} \rho(x,t) \ . \tag{7.59}$$

The last step reflects the fact that physical predictions must not depend on the RG-scale μ, since this parameter was introduced as an arbitrary scale. Mathematically, the constraint reads for the one-point function as,

$$G_1^B(x,t;\hat{g}_B,\epsilon) \stackrel{!}{=} G_1(x,t;\hat{g},\mu) \ . \tag{7.60}$$

Since the left-hand side of eq. (7.60) does not depend on μ, the explicit dependence of G_1 on μ on the right-hand side has to be cancelled by the implicit dependence of $\hat{g}(\mu)$, being expressed by,

$$\mu\frac{d}{d\mu} \ G_1(x,t,D,\hat{g},\mu)\Big|_{\text{NP}} = 0 \ .$$

The normalisation point $|_{\text{NP}}$ is chosen for convenience at $q^2 = 0$ and $-i\omega^2 = \mu^2$ and corresponds to holding the bare parameter $\hat{g}_B$ fixed. Applying the last equation leads to,

$$\mu \frac{d}{d\mu}\bigg|_{\text{NP}} = \mu \frac{\partial}{\partial \mu} + \underbrace{\mu \frac{d\hat{g}}{d\mu}\bigg|_{\text{NP}}}_{=:\beta_g} \cdot \frac{\partial}{\partial \hat{g}} \, ,$$

where the beta-function $\beta_g(\hat{g})$ was defined. The beta-function can be calculated from eq. (7.58) again to all orders of loops, revealing,

$$\beta_g(\hat{g}) = -\epsilon \hat{g} + \epsilon \hat{g}^2 \frac{2}{(8\pi)^{d/2}} \cdot \Gamma\left(\frac{\epsilon}{2}\right) \, . \tag{7.61}$$

Finally, the constraint for the one-point function can be written as,

$$\left(\mu \frac{\partial}{\partial \mu} + \beta_g(\hat{g}) \frac{\partial}{\partial \hat{g}}\right) G_1 = 0 \, , \tag{7.62}$$

which is also known as the Callan-Symanzik equation.

Since the beta-function captures the scale dependence of the coupling parameter $\hat{g}$, its zeros correspond to scale invariance of the theory. If the parameter does not change with changing scale, the theory defined by the parameter $\hat{g}$ becomes scale invariant. The zeros of $\beta_g(\hat{g})$ lie at $\hat{g}_1 = 0$ and $\hat{g}_2 = \frac{(8\pi)^{d/2}}{2 \cdot \Gamma\left(\frac{\epsilon}{2}\right)}$.
The first zero at $\hat{g}_1 = 0$ corresponds to $\lambda = 0$, which means that only diffusion is in existence. The second zero, however, is non-trivial and corresponds to the special IR stable fixed point value for the coupling [4]. Since $\Gamma\left(\frac{\epsilon}{2}\right) \sim 1/\epsilon$, we get $\hat{g}_2 \sim \epsilon$ as $\epsilon \to 0$. Further details to this analysis can be found in [4, 22]. The fixed-point $\hat{g}_2$ is crucial for the scaling behaviour and determines the asymptotic behaviour of the one-point function as mentioned earlier.

Ultimately, we are interested in the time dependence of the one-point function $\langle \phi(x,t) \rangle$. From eq. (5.38) and the dimensional analysis $[\phi] = d$, it follows that $[G_1] = [\phi] = d$. Consequently, the one-point function may be rewritten as follows (omitting the spatial coordinate),

$$G_1(t, \hat{g}, \mu) = \mu^d \cdot \hat{G}_1(\mu^2 t, \hat{g})$$

Hence, one can transform the μ-derivative in the Callan-Symanzik equation (7.62) into a time-derivative,

$$\mu \frac{\partial}{\partial \mu} \, G_1(t, \hat{g}, \mu) = \mu \frac{\partial}{\partial \mu} \left(\mu^d \cdot \hat{G}_1(\mu^2 t, \hat{g})\right) = \left(d + 2t \frac{\partial}{\partial t}\right) G_1(t, \hat{g}, \mu) \, .$$

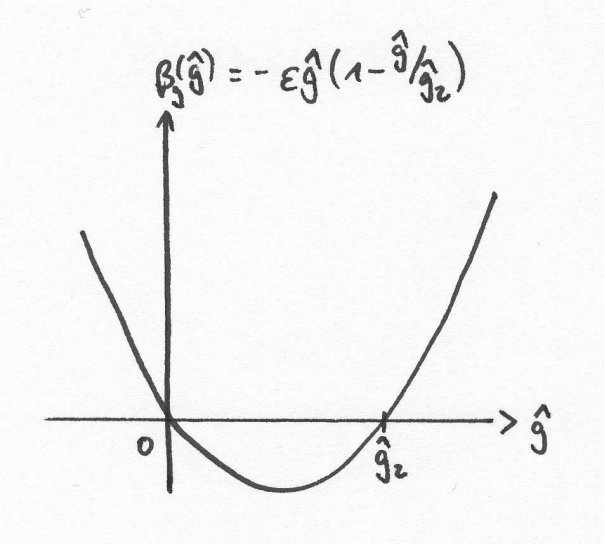

Figure 7.15: *Beta function* $\beta(\hat{g}) = -\epsilon\hat{g}(1 - \frac{\hat{g}}{\hat{g}_2})$.

However, a subtlety arises from the boundary term $\rho_0\tilde{\phi}(\chi, 0)$ in the field action (5.36). A mathematically rigorous analysis shows that an additional derivative term appears in the Callan-Symanzik equation due to the initial density. Finally, one obtains the converted Callan-Symanzik equation,

$$\left(d + 2t\frac{\partial}{\partial t} + \beta_g(\hat{g})\frac{\partial}{\partial \hat{g}} - d\rho_0\frac{\partial}{\partial \rho_0}\right)\rho(t, \hat{g}, \rho_0, \mu) = 0 \;, \tag{7.63}$$

which is a first order partial differential equation (PDE) for the renormalised particle density ρ that can be solved by the methods of characteristics being a standard method in the analysis of partial differential equations. One introduces a flow parameter l and chooses the right curves (characteristics) by which the PDE can be reduced to a set of ordinary differential equations (ODE). The solutions of the ODEs can be evaluated along the characteristics and deliver the solution for the PDE.

The important result of this standard procedure is $\rho(t, \hat{g}, \rho_0, \mu) \sim t^{-d/2}$ for $\epsilon = d_c - d = 2 - d > 0$ and a complete analysis (including $d = 2$) reveals,

$$\rho(t, \hat{g}, \rho_0, \mu) \sim t^{-d/2} = \begin{cases} \sim t^{-1/2} & d = 1, \\ \sim \ln t \cdot t^{-1} & d = 2, \\ \sim t^{-1} & d > 2, \end{cases} \tag{7.64}$$

which is exactly the result we encountered in eq. (3.6). Thus, this renormalisation group approach to the pair annihilation process exactly reproduces the long-time behaviour, suggested by experiments and computer simulations. The long-time behaviour of the rate equation (3.2) becomes exact above the upper critical

dimension $d_c = 2$. In lower dimensions ($d = 1$), the mean-field assumption (factorisation of the two-particle probability density) does not describe the scaling behaviour accurately, the $\rho \sim t^{-1}$ solution has to be renormalised to $\rho \sim t^{-1/2}$.

7.3 Heuristics

It was pointed out that the loop diagram expansion goes beyond the mean-field description of the pair annihilation reaction. Is it possible to understand physically, why the mean-field description becomes wrong for long times in one dimension?

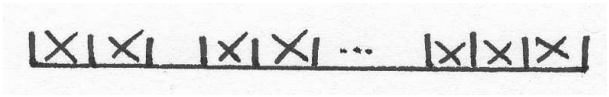

Figure 7.16: *Initial distribution on the lattice.*

Consider a one-dimensional lattice, where nearly all lattice sites are populated by particles of species A (cf. figure 7.16), such that the annihilation reaction $A + A \xrightarrow{\lambda} \emptyset$ can in principle take place everywhere. Thus, the initial dynamics is accurately described by the solution of the kinetic rate equation (3.2) with $\rho \sim t^{-1}$.

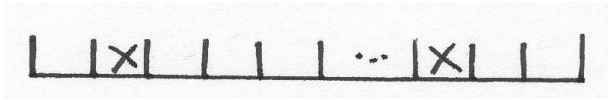

Figure 7.17: *Asymptotic distribution on the lattice.*

At later times, the lattice sites become more and more diluted (cf. figure 7.17) and the reaction rate is limited by the first passage time of a random walk in $d = 1$, scaling exactly with $t^{-1/2}$. Hence, the long-time behaviour of ρ is renormalised to $\rho \sim \ t^{-1}/t^{-1/2} = t^{-1/2}$.

It turns out that the dimensionality of the system is crucial, since it determines the dimensionality of the diffusion process and hence the underlying random walk process. It is known, that for $d = 1$, a random walk returns to a specific point in space in finite time almost certainly, whereas for $d > 2$ this does not hold [19]. Therefore, for $d > 2$, fluctuation and correlation corrections to the mean-field behaviour $\rho \sim t^{-1}$ become irrelevant.

8 Summary and Outlook

In this essay, the pair annihilation reaction $A + A \xrightarrow{\lambda} \emptyset$ was investigated by means of statistical field theory methods. It was shown that the rate equation approach does not capture the nature of spatial fluctuations and correlations due to interactions within the system and is hence inadequate to describe the critical long-time behaviour of observables, such as the mean particle density for dimensions $d \leq d_c = 2$. It corresponds to a mean-field description of the process.
However, the phenomenological rate equation can be extended to a stochastic Langevin equation by including random noise, whose two-point function is negative. A perturbation theory can be established (cf. [20]), but the phenomenological interpretation of the Langevin approach is limited and, moreover, is only applicable to reactions with only two reactants.

The presented field theoretic approach overcomes this constraint by starting from a microscopic lattice description. This concept generalises the approach to reaction-diffusion systems by systematically including fluctuations and correlations in the analysis. The microscopic probability description was transformed to a field theory by making use of the bosonic creation and annihilation operators and taking the continuum limit. In order to extract the asymptotic long-time behaviour of the mean particle density ρ, a perturbation expansion for the one-point function of this field theory was formulated, leading to divergences in the IR limit below the critical dimension $d_c = 2$. By applying renormalisation group techniques, scale invariance was shown for the critical dimension and the exact scaling laws were obtained for $d < d_c$ by a dimensional expansion in the parameter $\epsilon = d_c - d$ around d_c.
It turns out that the mean-field solution of the pair annihilation process $\rho \sim t^{-1}$ is exact for $d > d_c = 2$ and gets renormalised, due to higher-order terms in a divergent loop expansion, for $d < d_c = 2$ to $\rho \sim t^{-d/2}$ and logarithmic corrections lead to $\rho \sim \ln t \cdot t^{-1}$ for $d_c = 2$.
In contrast to the stochastic Langevin approach, the application of statistical field theory also allows the investigation of more complex many particle systems, reproducing the exact long-time behaviour in agreement with experiments and simulations. For example, the single-species reaction-diffusion process $kA \longrightarrow lA$ can be examined as a direct generalisation of the pair annihilation reaction and shows a similar qualitative behaviour [4, 3, 20, 19]. Fluctuations alter the critical power law for the long-time behaviour of the mean particle density predicted by mean-field rate equations below an upper critical dimension, depending on the number of reactants k, namely $d_c = 2/(k-1)$. Hence, if our attention is only caught by physical dimensions, the cases $k = 2$ (pair reaction) and $k = 3$ (triplet reaction) show a modification due to stochastic fluctuations for $d \leq d_c$ and $k > l$. One finds that the qualitative behaviour of the pair annihilation reaction is also obtained for the coagulation reaction $A + A \longrightarrow A$. It can be shown that

both reactions belong to the same universality class. For the triplet reaction $3A \longrightarrow lA$ $(l = 0, 1, 2)$, one gets, for instance, $\rho \sim (\ln t \cdot t^{-1})^{1/2}$ in $d = d_c = 1$ [4].

In order to investigate multi-species reactions, different propagators have to be introduced in the field theoretic analysis as indicated in the chapter on path integral formulation, but the concept of the renormalisation idea stays unchanged. However, the method is limited by the existence of an IR stable fixed point of the yielded β-function as outlined in the previous chapter. The analysis for multiple-species reactions, such as $A+B \longrightarrow \emptyset$, gets more involved and additional correlation effects (particle segregation, establishing of reaction zones) may occur that cannot be predicted by rate equations [4, 20]. For more complex systems, such as the Lotka-Volterra system, the analysis becomes even more sophisticated [14] and ends in open questions.
Nevertheless, numerical and chemical experiments support and justify the yielded results and underline the strength of the application of field theoretic methods to reaction-diffusion problems [8, 9, 10, 15, 14]. Spatial fluctuations and correlations can be non-negligible and even crucial for dynamical processes and can sometimes cause complex cooperative, non-equilibrium phenomena going beyond the scope of rate equations and Langevin theory.

But still, more chemical and biological experiments have to be carried out to verify the theoretical results and evaluate its relevance to physical phenomena and to deepen the understanding of many-body systems. The development of further non-perturbative renormalisation methods could resolve some open problems of the theoretical investigation of complex reaction-diffusion problems.
Finally, the study of non-equilibrium systems such as reaction-diffusion processes will remain an interesting and fruitful part of ongoing research in the future.

References

[1] R. R. Horgan. *Statistical Field Theory.* Lecture Notes, 2009.

[2] N. Goldenfeld. *Lectures On Phase Transitions And The Renormalization Group.* Westview Press, 1992.

[3] U. Tauber. Field-theoretic methods. *arXiv*, 2007.

[4] B. Vollmayr-Lee U. Tauber, M. Howard. Applications of field-theoretic renormalization group methods to reaction-diffusion problems. *Journal of Physics A: Mathematical and General*, 38(17):R79–R131, 2005.

[5] K. Fellner. *Reactions-Diffusion Equations.* Lecture Notes, 2009.

[6] P. C. Fife. *Mathematical Aspects of Reacting and Diffusing Systems.* Springer, 1979.

[7] J. Toth P. Erdi. *Mathematical Models of Chemical Reactions.* Manchester University Press, 1989.

[8] R. Kopelman E. Monson. Nonclassical kinetics of an elementary $a + b \rightarrow c$ reaction-diffusion system showing effects of a speckled initial reactant distribution and eventual self-segregation: Experiments. *Phys. Rev. E*, 69(2):021103, Feb 2004.

[9] A. Yethiraj B. J. Sung. Molecular-dynamics simulations for nonclassical kinetics of diffusion-controlled bimolecular reactions. *J. Chem. Phys.*, 123:114503, 2005.

[10] B. A. Reid, U. C. Tauber, and J. C. Brunson. Reaction-controlled diffusion: Monte carlo simulations. *arXiv*, 68(4):046121, oct 2003.

[11] V.I. Isham D.R. Cox. *Point Processes.* Chapman and Hall, 1980.

[12] M. Doi. Stochastic theory of diffusion-controlled reaction. *Journal of Physics A: Mathematical and General*, 9(9):1479–1495, 1976.

[13] M. Glasser D. Mattis. The uses of quantum field theory in diffusion-limited reactions. *Rev. Mod. Phys.*, 70(3):979, Jul 1998.

[14] U. Tauber M. Mobilia, I. Georgiev. Phase transitions and spatio-temporal fluctuations in stochastic lattice lotka-volterra models. *Journal of Statistical Physics*, 128(447), 2007.

[15] E. Frey T. Reichenbach, M. Mobilia. Mobility promotes and jeopardizes biodiversity in rock-paper-scissors games. *Nature*, 448, 2007.

[16] J. Cardy et. al. *Non-Equilibrium Statistical Mechanics and Turbulence*. Cambridge University Press, 2008.

[17] D.V. Schroeder M.E. Peskin. *An introduction to quantum field theory*. Addison-Wesley Pub. Co., October 1995.

[18] F. Schwabl. *Quantum Mechanics I*. Springer, 2004.

[19] J. Cardy. Reaction-diffusion processes. *Lecture notes at the LMS/EPSRC 'methods of non-equilibrium statistical mechanics in turbulence' school, University of Warwick*, 2006.

[20] J. Cardy. Renormalisation group approach to reaction-diffusion problems, 1996.

[21] U. Tauber. *Critical Dynamics*. http://www.phys.vt.edu/ tauber/, 2010.

[22] M. Le Bellac. *Quantum and Statistical Field Theory*. Oxford University Press, 1992.