Reaction-diffusion processes

John Cardy
Rudolf Peierls Centre for Theoretical Physics
1 Keble Road, Oxford OX1 3NP, U.K.

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Abstract

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1 Introduction

The aim of this course is to introduce reaction-diffusion systems. These are non-equilibrium systems of diffusing classical particles, which undergo reactions such as pairwise annihilation. The system is governed by a master equation, but this may be expressed equivalently as a many-body quantum Hamiltonian. This allows perturbative solutions to correlation functions, including the mean number of particles in the system and density-density correlation functions. We will see that these systems, although non-equilibrium systems, have much in common with equilibrium systems governed by Langevin equations.

2 Brownian motion

As our first example of an equilibrium system, let us consider Brownian motion, which describes the motion of a mesoscopic particle, such as a grain of pollen, immersed in a bath of much smaller particles. We will work in one dimension for simplicity and set the mass of the particle to 1. Newton’s equation is

\[ \dot{v} = -\Gamma v + \xi(t) + F_{\text{ext}}, \]

in which \( v \) is the velocity of the particle, \( \Gamma \) is the strength of the Stokes friction, \( \xi \) is a random stochastic term drawn from a distribution with zero mean and \( F_{\text{ext}} \) is an external force. This stochastic equation is an example of a Langevin equation. We will examine more general Langevin type equations later. Note that the friction term may also be written as the derivative of the Hamiltonian, \( H \).

\[ -\Gamma v = -\Gamma \frac{\partial}{\partial v}(H = v^2/2). \]

The stochastic noise is characterised by its expectation values

\[ \langle \xi(t) \rangle = 0 \]

\[ \langle \xi(t)\xi(t') \rangle = f(t-t') \sim e^{-|t-t'|/\tau}, \]

with \( \tau \) the typical collision time, which is assumed short compared to all other time scales in the problem. A small particle may collide with the pollen, but will then have its velocity randomised by interactions with other small particles. Hence, later collisions are essentially uncorrelated. Since we
are interested in the behaviour on much longer time scales, we will take a delta function form for the second moment of the noise

\[ \langle \xi(t)\xi(t') \rangle = 2D\delta(t - t'). \]  

(5)

Note that \( \xi(t) \) is not a differentiable function, so the machinery of stochastic calculus should be used to interpret equation (1), but as we will always be integrating \( \xi \) over small times, we will sidestep this technicality.

### 2.1 The Einstein relation

Let us take \( F_{\text{ext}} = 0 \), then the system will come into thermal equilibrium with the heat bath at temperature \( T \). A result of the equipartition theorem is \( \langle v^2 \rangle = k_B T \), which may be used to derive a relation between \( \Gamma \) and \( D \). Starting from equation 1,

\[ v(t + \delta t) = (1 - \Gamma \delta t)v(t) + \int_t^{t+\delta t} \xi(t')dt' + O(\delta t^2) \]  

(6)

\[ \langle v(t + \delta t)^2 \rangle = (1 - 2\Gamma \delta t)\langle v(t)^2 \rangle + 2\int_t^{t+\delta t} \langle v(t)\xi(t') \rangle dt' \]

\[ + \int_t^{t+\delta t} \int_t^{t+\delta t} \langle \xi(t')\xi(t'') \rangle dt'dt'' + O(\delta t^2) . \]  

(7)

The expectation value \( \langle v(t)\xi(t') \rangle \) vanishes by causality, since the noise should be independent of the velocity at an earlier time. We may then substitute in equation (5) and use the equilibrium condition \( \langle v(t + \delta t)^2 \rangle = \langle v(t)^2 \rangle = k_B T \) to find

\[ k_B T = (1 - 2\Gamma \delta t)k_B T + 2D\delta t + O(\delta t^2) . \]  

(8)

Equating terms of order \( \delta t \) yields the Einstein relation for systems in equilibrium,

\[ \Gamma k_B T = D . \]  

(9)

### 2.2 Correlation function

We may also calculate the velocity two-point correlation function from equation 1. Let us continue to take \( F_{\text{ext}} = 0 \). The Fourier transform is

\[ -i\omega \tilde{v}(\omega) = -\Gamma \tilde{v}(\omega) + \tilde{\xi}(\omega) . \]  

(10)
Hence
\[ \langle \tilde{v}(\omega)\tilde{v}(\omega') \rangle = \frac{1}{-i\omega + \Gamma} \frac{1}{-i\omega' + \Gamma} \langle \tilde{\xi}(\omega)\tilde{\xi}(\omega') \rangle. \quad (11) \]

The Fourier transform of equation 5 is
\[ \langle \tilde{\xi}(\omega)\tilde{\xi}(\omega') \rangle = 2D\delta(\omega + \omega'). \quad (12) \]

Substituting this result into equation 11
\[ \langle \tilde{v}(\omega)\tilde{v}(\omega') \rangle = \frac{1}{\omega^2 + \Gamma^2} \delta(\omega + \omega'). \quad (13) \]

We may Fourier transform back to time
\[ \langle v(t)v(t') \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{2De^{-i\omega(t-t')}}{\omega^2 + \Gamma^2} = k_B T e^{-\Gamma|t-t'|}, \quad (14) \]

which shows that the velocity fluctuations are correlated over the relaxation time $1/\Gamma$.

### 2.3 Response function

Let us add a term $-f(t)v(t)$ to the energy, corresponding to a linear coupling to the variable $v(t)$ and examine how this affects the expectation value of $v(t)$. In $\omega$ space, equation 1 now takes the form
\[ -i\omega\langle \tilde{v}(\omega) \rangle = -\Gamma\langle \tilde{v}(\omega) \rangle + \Gamma \tilde{f}(\omega). \quad (15) \]

Solving for $\langle \tilde{v}(\omega) \rangle$,
\[ \langle \tilde{v}(\omega) \rangle = \frac{f(\omega)}{-i\omega/\Gamma + 1} = G(\omega)f(\omega). \quad (16) \]

This defines the response function $G(\omega)$. In $t$ space this is a convolution
\[ \langle v(t) \rangle = \int_{-\infty}^{\infty} G(t-t')f(t')dt'. \quad (17) \]

Hence this is equivalent to the definition in terms of the functional derivative of $\langle v(t) \rangle$,
\[ G(t-t') = \left. \frac{\delta \langle v(t) \rangle}{\delta f(t')} \right|_{f=0}. \quad (18) \]

For Brownian motion, therefore, the correlation and response functions are related by
\[ C(\omega) = \frac{2k_B T}{\omega} \text{Im}[G(\omega)]. \quad (19) \]

This is an example of the fluctuation-dissipation relation (FDT). We will derive the FDT for a more general Langevin equation in the next section.
3 More general Langevin equations

We have examined Brownian motion as an example of a stochastic process governed by a Langevin equation. We will now derive the correlation and response functions for a more general stochastic process with a single degree of freedom, labelled \( \phi(t) \). The Langevin equation takes the form

\[
\frac{d}{dt} \phi(t) = -\Gamma \frac{\partial H(\phi(t))}{\partial \phi(t)} + \xi(t),
\]

(20)

where \( \xi(t) \) is again a random term with zero time average and two-point correlation function

\[
\langle \xi(t) \xi(t') \rangle = 2D \delta(t - t').
\]

(21)

Equation 20 is equivalent to

\[
\phi(t + \delta t) = \phi(t) - \Gamma \frac{\partial H(\phi(t))}{\partial \phi(t)} \delta t + \int_t^{t+\delta t} \xi(t') dt'.
\]

(22)

Assuming that the system will relax to equilibrium in the presence of the noise, take the square of the above equation and average with respect to the Gibbs measure \( e^{-H(\phi)/k_B T} \) to find

\[
\langle \phi(t + \delta t)^2 \rangle - \langle \phi(t)^2 \rangle = -2\Gamma \langle \phi(t) \frac{dH(\phi(t))}{d\phi(t)} \rangle \delta t + 2D \delta t + O(\delta t^2).
\]

(23)

The term \( \langle \phi(t)H'(\phi(t)) \rangle \) may be integrated by parts and shown to be equal to \( k_B T \), so equating terms of order \( \delta t \), again leads to the Einstein relation

\[
D = \Gamma k_B T.
\]

(24)

3.1 The response function formalism

Expectation values of quantities such as \( \phi(t_1)\phi(t_2) \) may be formally evaluated using a functional integral

\[
\langle \phi(t_1)\phi(t_2) \rangle = \langle \int \phi(t_1)\phi(t_2) \delta[\phi(t) = \text{solution}] D\phi(t) \xi(t) \rangle,
\]

(25)

where the delta function ensures that \( \phi(t) \) is solution to the Langevin equation 20 and the average on the right hand side is now with respect to realisations of the noise \( \xi(t) \). The delta function may be rewritten as

\[
\delta[\phi(t) = \text{solution}] = \delta[\frac{d}{dt} \phi(t) + \Gamma \frac{\partial H(\phi(t))}{\partial \phi(t)} - \xi(t)] \times \text{Jacobian},
\]

(26)
with the Jacobian equal to unity, as equation 20 is being interpreted as an Itô stochastic equation, the Jacobian is the determinant of an upper triangular matrix with 1 on the diagonal. The delta function may be expressed as a functional integral.

\[
\delta[\frac{d}{dt}\phi + \Gamma \frac{dH}{d\phi} + \xi] = \int e^{-f(\phi(t)[\frac{d}{dt}\phi(t)] + \Gamma H'(\phi(t)) - \xi(t))} dt D\phi(t). \tag{27}
\]

The integral is over the field \( \tilde{\phi}(t) \), which is known as the response field. In this form, the average over realisations of the noise may be taken using

\[
\langle e^{\int \tilde{\phi}(t) \xi(t) dt} \rangle = e^{\frac{1}{2} \int \int dt' dt'' \tilde{\phi}(t') \tilde{\phi}(t'') \xi(t') \xi(t'')} = e^{D \int \tilde{\phi}(t)^2 dt}. \tag{28}
\]

Putting all this together, correlation functions, such as those in equation 25, may be expressed as

\[
\langle \phi(t_1) \phi(t_2) \rangle = \int \int \phi(t_1) \phi(t_2) e^{-S[\tilde{\phi}(t), \phi(t)]} D\phi D\tilde{\phi}, \tag{29}
\]

where the effective action, \( S \), is

\[
S = \int \left[ \frac{d}{dt} \phi(t) \right] \phi(t) + \Gamma H'(\phi(t)) - D \tilde{\phi}(t)^2 \right] dt. \tag{30}
\]

This is the response function formalism. Response functions may be obtained in this formalism by adding a linear coupling to \( \phi \) in the Hamiltonian, \( H \rightarrow H - f(t) \phi(t) \). Then \( S \rightarrow S - \Gamma \int f(t) \tilde{\phi}(t) dt \) and

\[
\langle \phi(t_1) \rangle = \int \int e^{-S[\phi(t), \tilde{\phi}(t)] + \Gamma f(t) \tilde{\phi}(t) dt} D\phi(t) D\tilde{\phi}(t). \tag{31}
\]

From the derivative of this equation follows the response function.

\[
G(t_2 - t_1) = \left. \frac{\partial \langle \phi(t_1) \rangle}{\partial f(t_2)} \right|_{f=0} = \Gamma \int \int \phi(t_1) \tilde{\phi}(t_2) e^{-S[\phi(t), \tilde{\phi}(t)]} D\phi(t) D\tilde{\phi}(t). \tag{32}
\]

Alternatively completing the square in \( \tilde{\phi}(t) \) in equation 31 and shifting integration variables \( \tilde{\phi}(t) \rightarrow \tilde{\phi}(t) + \Gamma f(t) / 2D \), the response function is

\[
G(t_1 - t_2) = \frac{-\Gamma}{2D} \langle \phi(t_1) \rangle \frac{d}{dt} \phi(t_2) + \Gamma H'(\phi(t_2)) \rangle = \frac{\Gamma}{2D} \hat{C}(t_1 - t_2) - \frac{\Gamma^2}{2D} \langle \phi(t_1) \rangle H'(\phi(t_2)) \rangle. \tag{33}
\]
Let us consider the symmetries of the above equation under time reversal. The response function is zero for \( t_1 < t_2 \) by causality. The derivative of the correlation function is odd with respect to time. The term involving the Hamiltonian is even under exchange of the times \( t_1 \) and \( t_2 \), since the equilibrium average is time reversal invariant. We therefore conclude that for \( t_1 > t_2 \)

\[
G(t_1 - t_2) = \frac{\Gamma}{D} \dot{C}(t_1 - t_2) = k_B T \dot{C}(t_1 - t_2).
\]

(34)

This is the fluctuation-dissipation relation again. In Fourier space, the FDT takes the form

\[
\tilde{C}(\omega) = \frac{2k_B T}{\omega} \text{Im}[\tilde{G}(\omega)].
\]

(35)

### 3.2 The master equation

The master equation is a first order linear equation expressing the rate at which a system moves between states labelled by \( \{\alpha\} \). At time \( t \), let the system be in state \( \alpha \) with probability \( P(\alpha,t) \) and consider the time derivative of \( P(\alpha,t) \). The change in \( P \) is due to transitions into and out of the state \( \alpha \). We will denote the rates of these processes by \( R_{\alpha \rightarrow \beta} \). Then the master equation is

\[
\frac{dP(\alpha,t)}{dt} = \sum_\beta R_{\beta \rightarrow \alpha} P(\beta,t) - R_{\alpha \rightarrow \beta} P(\alpha,t) \\
\equiv - \sum_\beta H_{\alpha \beta} P(\beta,t).
\]

(36)

The conservation of probability requires that

\[
0 = \frac{d}{dt} \sum_\alpha P(\alpha) = \sum_\beta R_{\beta \rightarrow \alpha} P(\beta,t) - R_{\alpha \rightarrow \beta} P(\alpha,t).
\]

(37)

In terms of \( H_{\alpha \beta} \), this is

\[
\sum_\alpha H_{\alpha \beta} = 0,
\]

(38)

so \( H \) has a zero eigenvalue.
3.3 Detailed balance

The equilibrium distribution \( P(\alpha) \propto e^{-H(\alpha)/k_B T} \) is stationary so \( \partial_t P = 0 \). Therefore,

\[
\sum_\beta R_{\beta \rightarrow \alpha} P(\beta, t) - R_{\alpha \rightarrow \beta} P(\alpha, t) = 0 .
\] (39)

The system satisfies detailed balance if this relation is valid term by term, ie

\[
\frac{R_{\beta \rightarrow \alpha}}{R_{\alpha \rightarrow \beta}} = \frac{e^{-H(\alpha)/k_B T}}{e^{-H(\beta)/k_B T}} .
\] (40)

This is the case for the Metropolis algorithm used in numerical simulations of equilibrium systems. For this example,

\[
\tilde{H}_{\alpha\beta} = e^{+H(\alpha)/k_B T} H_{\alpha\beta} e^{-H(\beta)/k_B T}
\] (41)

is symmetric \((\tilde{H}_{\alpha\beta} = \tilde{H}_{\beta\alpha})\), so has real eigenvalues. For the non-equilibrium particle systems we shall study, detailed balance is not valid.

4 Stochastic particle systems

We shall now turn our attention to non-equilibrium systems, in particular reaction-diffusion problems. These are classical systems with particles localised in space. These particles may be molecules, biological entities, fluctuating commodities in a market etc. There may be several species of particles in a given model, which will be labelled \( A, B, C \) and which reside on a lattice \( \mathbb{Z}^d \), labelled by site labels \( \{j\} \). They undergo diffusion with characteristic diffusion constants \( D_A, D_B \) and react with rates \( \lambda, \mu \) when inhabit the same lattice site. An example of such a reaction is represented by the equation

\[
A + B \rightarrow C .
\] (42)

The first example we shall consider contains a single particle species, \( A \), undergoing two particle annihilation, \( A + A \rightarrow 0 \). The steady state is not interesting; it is a single particle or zero particles, depending on whether the initial state of the system has an odd or an even number of particles. The interest in this model is the approach to the steady state. The starting point is the master equation. The states of the system are defined by the number of particles at each lattice site \( \{n_j\} \) and the rates in the master equation are related to the reaction rate \( \lambda \).
Although the system is a classical system, it may be re-expressed as a many-body quantum problem. The machinery associated with quantum mechanics then allows perturbative solutions to the correlation and response functions. The Fock space is composed of a vacuum state with zero particles, along with linear particle creation operators at each site \( a_j^\dagger \). A general state is

\[
|\{n_j\}\rangle = \prod_j a_j^{\dagger n_j} |0\rangle .
\]  

(43)

There are also particle annihilation operators, which are the Hermitian conjugates of the creation operators and remove particles at site \( j \). The algebra satisfied by the operators is

\[
[a_j, a_k^\dagger] = \delta_{j,k} 
\]

(44)

\[
[a_j^\dagger, a_k^\dagger] = [a_j, a_k] = 0 .
\]

(45)

Using this, it may be shown that the states are eigenstates of the particle number operators \( \{n_j\} = \{a_j^\dagger a_j\} \) with eigenvalue equal to the number of particles at site \( j \). We can associate a state in the Fock space with a set of probabilities at time \( t \)

\[
|\psi(t)\rangle = \sum_{\{n_j\} = (0,0,...)}^\infty p(\{n_j\}; t) \prod_j a_j^{\dagger n_j} |0\rangle .
\]

(46)

With this definition, the master equation may be rewritten as a Schrödinger-type equation

\[
\frac{d}{dt} |\psi(t)\rangle = -H(\{a\}, \{a^\dagger\}) |\psi(t)\rangle .
\]

(47)

Note that there are some differences from many-body quantum mechanics. The Schrödinger equation is real, so this is like Euclidean quantum mechanics. Our Hamiltonian is not (necessarily) hermitian. It may be shown that Hamiltonians coming from systems which satisfy detailed balance may be made symmetric and real by a similarity transformation. Also, the states are linear functions of the probabilities, rather than linear functions of the probability amplitudes as in quantum mechanics. We will return to this when we consider expectation values of observables, but first let us look at some examples of master equations and derive the associated Hamiltonians.
4.1 Particles hopping on a lattice

Consider a lattice consisting of two sites, 1 and 2. Particles hop from site 1 to site 2 only, with a rate $D$. The master equation is

$$\frac{dP(n_1, n_2, t)}{dt} = D(n_1 + 1)P(n_1 + 1, n_2 - 1, t) - Dn_1 P(n_1, n_2, t). \quad (48)$$

We may multiply the above equation by $a_1^\dagger n_1 a_2^\dagger n_2 |0\rangle$ and sum over all values of $n_1, n_2$. With the definition of the state $|\psi(t)\rangle$:

$$|\psi(t)\rangle = \sum_{n_1, n_2} P(n_1, n_2, t) a_1^\dagger n_1 a_2^\dagger n_2 |0\rangle, \quad (49)$$

we may rewrite the equation obtained as

$$\frac{d|\psi(t)\rangle}{dt} = D \sum_{n_1, n_2} \left[ p(n_1 + 1, n_2 - 1, t)(n_1 + 1) - p(n_1, n_2)n_1 \right] a_1^\dagger n_1 a_2^\dagger n_2 |0\rangle. \quad (50)$$

Substituting the ladder operators for the number operators and using their commutation relations, we obtain

$$\frac{d|\psi(t)\rangle}{dt} = D \sum_{n_1, n_2} p(n_1 + 1, n_2 - 1, t)a_2^\dagger n_2 a_1^\dagger n_1 + 1 a_1^\dagger n_1 - 1 |0\rangle$$

$$- D \sum_{n_1, n_2} p(n_1, n_2, t) a_1^\dagger n_1 a_2^\dagger n_2 a_2^\dagger n_2 |0\rangle. \quad (51)$$

With a relabelling of indices in the first sum we have arrived at the desired formula, of the form of equation 47, with

$$H = -D(a_2^\dagger - a_1^\dagger) a_1. \quad (52)$$

Had we also allowed hopping from site 2 to site 1 at the same rate, we would have obtained

$$H = D(a_2^\dagger - a_1^\dagger)(a_2 - a_1). \quad (53)$$

4.2 Two particle annihilation

As a second example, consider two particle annihilation $A + A \rightarrow 0$ on a single lattice site. The master equation is

$$\frac{dP(n)}{dt} = \lambda(n + 2)(n + 1)P(n + 2) - \lambda n(n - 1)P(n). \quad (54)$$
In terms of $|\psi(t)\rangle$, this is
\[
\frac{d|\psi(t)\rangle}{dt} = \lambda \sum_n (n + 2)(n + 1)P(n + 2,t)a^{\dagger n}\langle 0\rangle - \lambda \sum_n n(n - 1)P(n,t)a^{\dagger n}\langle 0\rangle \\
= \lambda \sum_n P(n + 2)a^2 a^{\dagger n+2}\langle 0\rangle - \lambda \sum_n P(n)a^{\dagger 2}a^2 a^{\dagger n}\langle 0\rangle.
\] (55)

Hence, we obtain a Schrödinger-type equation with
\[
H = -\lambda (1 - a^{\dagger 2})a^2.
\] (56)

Combining the two equations above, we find the Hamiltonian for the lattice annihilation model
\[
H = D \sum_{\langle ij \rangle} (a_i^{\dagger} - a_j^{\dagger})(a_i - a_j) - \lambda \sum_i (1 - a_i^{\dagger 2})a_i^2,
\] (57)

where the first sum is over pairs of nearest neighbour sites.

### 4.3 Averages of observables in the many-body formalism

For a given master equation, we have shown how to derive a Schrödinger-like equation for the evolution of the state of the system in the form of equation 47. This may be integrated as usual to find
\[
|\psi(t)\rangle = e^{-Ht}|\psi(0)\rangle.
\] (58)

A convenient choice for the initial probability distribution is an independent Poisson distribution at each site
\[
P(\{n_i\}, t = 0) = \prod_j e^{-\rho_0} \frac{\rho_0^{n_j}}{n_j!},
\] (59)

since this corresponds to the initial state of the system being a coherent state
\[
|\psi(0)\rangle = \prod_j e^{-\rho_0} e^{\rho_0 a_j^{\dagger}} |0\rangle.
\] (60)

The average value of an observable $A(\{n_j\})$ is defined as
\[
\overline{A} = \sum_{\{n_j\}} A(\{n_j\})p(\{n_j\}, t).
\] (61)
Using the identity $\langle 0|e^a a^+ n|0 \rangle = 1$, this may be rewritten as

$$\bar{A} = \langle 0| \prod_j e^{a_j} A(\{n_j\})|\psi(t)\rangle . \quad (62)$$

As an example, let us calculate the expectation value of the identity operator:

$$1 = \langle 0| \prod_j e^{a_j} e^{-H(\{a_j, a^+_j\}) t}|\psi(0)\rangle . \quad (63)$$

This can only be satisfied for all $t$ if $\langle 0| \prod_j e^{a_j} H(\{a_j, a^+_j\}) = 0$. Using $\langle 0|e^a a^+ = \langle 0|e^a$, we see that the Hamiltonian must satisfy

$$H(\{a_j\}, \{a^+_j = 1\}) = 0 . \quad (64)$$

This is an expression of the conservation of probability.

### 4.4 The Doi shift

The term $\prod_j e^{a_j}$ may be commuted through to the right in equation 62, by making use of the identity

$$e^a f(a^+) = f(a^+ + 1)e^a . \quad (65)$$

Note that this is simply a consequence of the commutation relations for the ladder operators. The resulting form of the expectation value of observables is

$$\langle 0|A(\{a^+_j + 1\}, \{a_j\})e^{-H(\{a^+_j + 1\}, \{a_j\}) t} e^{\sum_j a_j} |\psi(0)\rangle . \quad (66)$$

With the choice of a coherent state for the initial wavefunction, the ket takes the simple form

$$e^{\sum_j a_j} |\psi(0)\rangle = e^{\sum_j \rho a^+_j} |0\rangle . \quad (67)$$

The Hamiltonian with $\{a^+_j\} \rightarrow \{a^+_j + 1\}$ is known as the Doi shifted Hamiltonian. For our example of particles hopping on the lattice and pairwise annihilating, the shifted Hamiltonian takes the form

$$H_{\text{shifted}} = D \sum_{\langle ij \rangle} (a^+_i - a^+_j)(a_i - a_j) + \lambda \sum_j 2a^+_j a^2_j + a^2_j a^2_j . \quad (68)$$

Note that this Hamiltonian is normal ordered, with the consequence that its vacuum expectation value is zero.
4.5 Path integral representation

From the many-body description, we may use perturbation theory to calculate expectation values of observables. First it is convenient to re-express expectation values in terms of path integrals. Split a given time interval $t$ into small increments $\delta t$ and recall the identity

$$e^{-Ht} = \lim_{\delta t \to 0} (1 - \delta t H)^{t/\delta t}. \tag{69}$$

A complete set of coherent states

$$1 = \int \frac{d\phi d\phi^*}{\pi} e^{-\phi^* \phi} e^{\phi^* a} |0\rangle \langle 0| e^{\phi^* a}, \tag{70}$$

may be inserted into equation 62 at each time step. Thus, the expectation value is a product of terms like

$$\langle 0| e^{\phi^* (t+\delta t)a} [1 - \delta t H(a^+, a)] e^{\phi(t)a^+} |0 \rangle. \tag{71}$$

The exponentials may be commuted to the other side of the square bracket using equation 65 and the conjugate expression to obtain

$$\langle 0| 1 - \delta t H(a^+, \phi^* + \phi) |0 \rangle e^{\phi^* (t+\delta t)\phi(t)}. \tag{72}$$

As the Hamiltonian is normal ordered, this is equivalent to

$$\langle 0| 1 - \delta t H(\phi^* + \phi) |0 \rangle e^{\phi^* (t+\delta t)\phi(t)}. \tag{73}$$

Re-exponentiating the product of terms involving the Hamiltonian and taking the continuum time limit, we see that averages of observables are integrals over a pair of fields on the discrete lattice, with an effective action

$$\prod_j \left[ \int \int \frac{d\phi_j(t) d\phi^*_j(t)}{\pi} e^{-S[\phi^* , \phi]} \right] \tag{74}$$

$$S[\phi^*, \phi] = \int dt \sum_j \phi_j^* \partial_t \phi_j + H(\{\phi_j^*\}, \{\phi_j\}), \tag{75}$$

where the time dependence of $\phi$ and $\phi^*$ has been omitted. The action for $A + A \to 0$ is

$$S = \int dt \sum_j \phi_j^* \partial_t \phi_j + D \sum_{(ij)} (\phi_i^* - \phi_j^*)(\phi_i - \phi_j) + \lambda \sum_j (2\phi_j^* \phi_j^2 + \phi_j^* \phi_j^2). \tag{76}$$
Just as in the Hamiltonian, $a$† operators in the observables are replaced by $\phi^*$ fields and $a$ operators by $\phi$. We can now take a naive continuum limit, converting the product of integrals into functional integrals over the fields $\phi(t)$ and $\phi^*(t)$ and recasting $S$ for our example in the form

$$ S = \int dt \int d^d x \left[ \phi^* \partial_t \phi + D \nabla \phi^* \nabla \phi + \lambda (2 \phi^* \phi^2 + \phi^* \phi^2) \right]. \quad (77) $$

Originally, $\phi^*$ was taken to be the complex conjugate of $\phi$, but we may now treat them as independent variables, relabelling $\phi^*$ as $\tilde{\phi}$. After an integration by parts on the gradient terms, we obtain for our Lagrangian

$$ \tilde{\phi} [\partial_t \phi - D \nabla^2 \phi + 2 \lambda \tilde{\phi} \phi^2] + \lambda \tilde{\phi}^2 \phi^2. \quad (78) $$

This is the same form as the Langrangian we would obtain from an equilibrium problem with the Langevin equation

$$ \partial_t \phi = D \nabla^2 \phi - 2 \lambda \phi^2 + \xi. \quad (79) $$

In the next subsection we will show that $\langle \phi(t) \rangle = \bar{n}(t)$, the expected number of particles at time $t$. Taking expectation values of the above equation therefore yields

$$ \frac{dn}{dt} = D \nabla^2 n - 2 \lambda n^{(2)}, \quad (80) $$

where $n^{(2)} = \langle \phi(t)^2 \rangle$ is the probability of finding 2 particles at the same site at time $t$. If we approximate $n^{(2)} = n^2$, we obtain the rate equation. Since a diffusion process starting from a Poisson distribution in the absence of noise remains a Poisson distribution at later times, we deduce that the noise describes deviations from a Poissonian distribution. This noise is not white noise, however. Recall from section 3.1 that starting from white noise with the correlation function $\langle \xi(x,t) \xi(x',t') \rangle = 2D \delta(x' - x) \delta(t' - t)$, we obtain a term in the Lagrangian of the form $-D \tilde{\phi}^2$. Here, however, the Lagrangian contains a term $\lambda \tilde{\phi}^2$, so the correlations of the noise are

$$ \langle \xi(x,t) \xi(x',t') \rangle = -2 \lambda \phi^2 \delta(x' - x) \delta(t' - t). \quad (81) $$

Hence, the noise is complex. If we start with a real field $\phi$, it too becomes complex. There is a physical reason why we cannot simply have real white noise in this problem. A given particle, which hasn’t annihilated, will have swept out an area around it without any particles contained inside. So, particles must be anti-correlated. For the connected part of $\langle \phi(x_1,t_1) \phi(x_2,t_2) \rangle$ to
be negative, we require negatively correlated noise since the response function is positive

\[ \langle \phi(x_1, t_1) \phi(x_2, t_2) \rangle_c = \int \int G(t_1 - t', x_1 - x') G(t_2 - t'', x_2 - x'') \langle \xi(x', t') \xi(x'', t'') \rangle dt' dx' dt'' dx''. \]  

(82)

The explanation for this result is that \( \phi \), as a fluctuating quantity is not the same as the density. It is the expectation values of the two which are equal. One of the problems is to show that

\[ \bar{n}^2 = \langle \phi^2 \rangle + \langle \phi \rangle^2, \]  

(83)

from which it is clear that \( n \neq \phi \). The vanishing of \( \langle \phi^2 \rangle - \langle \phi \rangle^2 \) would simply result in \( \bar{n} \) having a Poissonian distribution.

### 4.6 The expected number of particles and the expectation value of \( \phi \)

In this short subsection, we will show that, on average, \( \phi \) is the same as \( n \), the number of particles.

\[ \pi = \langle 0 | e^a a^\dagger a e^{-Ht} | \psi(0) \rangle \]

\[ = \langle 0 | e^a a e^{-Ht} | \psi(0) \rangle, \]  

(84)

In the path integral picture

\[ \langle 0 | e^a a e^{-Ht} | \psi(0) \rangle = \frac{\int \int D\phi D\bar{\phi} e^{-S}}{\int \int D\phi D\bar{\phi} e^{-S}} = \langle \phi \rangle. \]  

(85)

So \( \pi = \langle \phi \rangle. \)

### 5 Feynman diagrams and the renormalization group

The form of the Lagrangian allows us to write down the propagator and vertex diagrams and so to formulate pertubative solutions to the correlation
functions of the theory. We will not proceed in this way, but instead start
from the stochastic equation
\[
\partial_t \phi(x, t) = D \nabla^2 \phi(x, t) - 2\lambda \phi(x, t)^2 + \xi(x, t) + \rho_0 \delta(t),
\]
with the following correlation function for the noise
\[
\langle \xi(x, t) \xi(x', t') \rangle = -2\lambda \phi(x, t)^2 \delta(t-t') \delta(x-x').
\]
Note that the term \( \rho_0 \delta(t) \) comes from the Doi shifted initial Poissonian (co-
herent) state. We find the formal solution to this differential equation
\[
\phi(x, t) = \int G_0(x-x', t-t')[-2\lambda \phi(x', t') + \xi(x', t') + \rho_0 \delta(t)] ,
\]
where the Green’s function, \( G_0(x, t) \), satisfies the equation
\[
(\partial_t - D \nabla^2)G_0(x, t) = \delta(x)\delta(t) .
\]
Equation 88 permits an iterative solution, which is most easily described
pictorially in terms of the Feynman diagrams in Fig 1. Time increases from
right to left, starting from \( t = 0 \) at the right hand side.

\[
\phi = \xi + \rho_0 \delta(t) + \xi + \rho_0 \delta(t) - 2\lambda + \ldots
\]

Figure 1: Feynman diagrams contributing to \( \phi \).

So, \( \phi \) is seen to be a sum of tree diagrams. If we switch off the noise, \( \xi \to 0 \),
we obtain the diagrams in Fig 2.

These diagrams may be expressed alternatively as a recursive relation, de-
scribed pictorially in Fig 3. Algebraically, these diagrams represent
\[
\phi(t) = \int d^d x G_0(t, x) \rho_0 - 2\lambda G_0 \circ \phi^2 ,
\]
where \( \circ \) denotes a convolution. This can be readily converted back to a
differential equation
\[
\partial_t \phi = D \nabla^2 \phi - 2\lambda \phi^2 + \rho_0 \delta(t) ,
\]
\[ \phi = \rho_0 \delta(t) - 2\lambda + \ldots \]

Figure 2: Feynman diagrams contributing to \( \phi \) in the absence of noise.

\[ \rho_0 \delta(t) \]

which is just the rate equation and shows that our results are consistent. If we assume spatial homogeneity, the rate equation has a simple solution

\[ \phi = \frac{\rho_0}{1 + 2\rho_0 \lambda t}, \tag{92} \]

which has the long time behaviour

\[ \phi(t \to \infty) = \frac{1}{2\lambda t}. \tag{93} \]

Note that this long time solution is independent of \( \rho_0 \). Now let us reinstate the noise and examine the average of \( \phi \), using

\[ \langle \xi(x,t) \rangle = 0 \]
\[ \langle \xi(x,t)\xi(x',t') \rangle = -2\lambda \phi(t)^2 \delta(x-x')\delta(t-t') \]
\[ \langle \xi^4 \rangle = \sum \text{pairs} \langle \xi^2 \rangle \langle \xi^2 \rangle. \tag{96} \]

The last identity follows from \( \xi \) having a Gaussian distribution. It is equivalent to Wick’s theorem in quantum field theory. Averaging leads to the pairwise contraction of \( \xi \) insertions, leading to diagrams with loops like those in Fig 4.

Each diagram is constructed from the set of components in Fig 5. Those familiar with quantum field theory would have been able to identify these
\[ \langle \phi \rangle = -2 \lambda \rho_0 \delta(t) + \rho_0 \delta(t) + \cdots \]

Figure 4: The average over noise of \( \phi \).

\[ G_0(x,t) = \int_0^\infty ds \int_{-\infty}^\infty \frac{d^d k}{(2\pi)^d} e^{ik \cdot x} e^{st + ik \cdot x} \] \hspace{2cm} (97)

In order to perform the vertex renormalizations, it is necessary to calculate the loop diagram in Fig 7:

\[ \int_0^\infty ds' \int_{-\infty}^\infty \frac{d^d k'}{(2\pi)^d} \frac{1}{s' + D k'^2} \frac{1}{s - s' + D (k - k')^2} \] \hspace{2cm} (98)
so the propagator doesn’t get renormalised.

Figure 6: The full propagator and vertex diagrams

Integrating over $s'$ and taking $k = 0$

$$= \int_{-\infty}^{\infty} \frac{d^d k'}{(2\pi)^d} \frac{1}{s + 2D k'^2}.$$  \hspace{1cm} (99)

The integral appears to diverge at large $k'$ for $d > 2$, but this is a consequence of discarding the lattice cut-off, which restricts the upper limit on $k'$. The divergence at $s = 0$ for $d < 2$ is more interesting. Above two dimensions, the integral is an analytic function of $s$. For $d \geq 2$, the loop corrections to the density give non-leading terms and simply renormalize $\rho_0$ and $\lambda$. We see then that the rate equation is (qualitatively) asymptotically correct for
\( d \geq 2 \). The loop diagram may be thought of as a correction due to annihilations between particles which have survived occupying the same site at an earlier time without annihilating. The dimensionality of the system is important because it determines the dimensionality of the random walk in relative particle coordinates. For \( d = 1 \), a random walk returns with almost certain probability to a point in space in finite time. For \( d > 2 \), the random walk almost certainly does not return in finite time, so corrections corresponding to the loop diagram above are irrelevant. \( d_c = 2 \) is known as the critical dimension of the theory. The renormalization group is a way of resumming series which are divergent in the limit \( s \to 0 \), such as those with loops in figure 6. Define \( \lambda_R(s) \) as the sum of diagrams contributing to the full three point propagator in figure 6 with total outgoing frequency \( s \). We see that the diagrams are convolutions in \((t,x)\) space, so are geometric series in \((s,q)\) space. Using equation 99 and doing the integral over \( k' \):

\[
\lambda_R(s) = \frac{\lambda_0}{1 + \frac{k_d}{\epsilon} \frac{2\lambda_0 s^{-\epsilon/2}}{D^{1-\epsilon/2}}}.
\]  

(100)

where \( \epsilon = 2 - d \) and \( k_d \) is finite for \( d = 2 \). It is defined as

\[
k_d = \frac{2\epsilon}{(8\pi)^{d/2}} \Gamma(1-d/2).
\]  

(101)

It is easiest to work with a dimensionless coupling constant. Looking at the denominator of equation 100, a suitable choice is

\[
g_R(s) = \lambda_R s^{-\epsilon/2} D^{\epsilon/2-1}.
\]  

(102)

The expected number of particles may be expressed as a function of the bare coupling constant, or alternatively as a function of the renormalized coupling constant and the scale \( s \). This scale was introduced arbitrarily, though, so
at fixed $\lambda_0$ the expected number of particles should not depend on $s$.

$$s \frac{d}{ds} \bigg|_{\lambda_0} \bar{n}(t, g_R, s) = 0,$$

(103)

where we have assumed that the asymptotic form of $\bar{n}$ does not depend on the initial density $n_0$. This assumption is not necessary for this derivation, but shortens the calculation. $g_R$ is a function of $s$, so this may be rewritten as

$$(s \frac{\partial}{\partial s} + \beta(g_R) \frac{\partial}{\partial g_R})\bar{n}(t, g_R, s) = 0,$$

(104)

where the derivative with respect to $s$ acts only on the explicit $s$ dependence of $\bar{n}$ and the beta function is defined by

$$\beta(g_R) \equiv s \frac{\partial}{\partial s} g_R(s) \bigg|_{\lambda}.$$

(105)

For our example, from equation 102

$$\beta(g_R) = \frac{-\epsilon}{2} g_R + \frac{k_d}{2} g_R^2.$$

(106)

Dimensional analysis determines the form of $\bar{n}$

$$\bar{n}(t, g_R, s) \sim (t)^{-d/2} f(st, g_R),$$

(107)

where $f$ is some function of its dimensionless parameters. This shows that

$$s \frac{\partial}{\partial s} \bar{n}(t, g_R, s) = (t \frac{\partial}{\partial t} + \frac{d}{2}) \bar{n}(t, g_R, s).$$

(108)

We have obtained the following partial differential equation for $\bar{n}$, known as the Callan-Symanzik equation:

$$\left(t \frac{\partial}{\partial t} + \beta(g_R) \frac{\partial}{\partial g_R} + \frac{d}{2}\right)\bar{n}(t, g_R, s) = 0.$$

(109)

The solution to this partial differential equation is obtained via the method of characteristics

$$\bar{n}(t, g_R, s) = (ts)^{-d/2} \bar{n}(t = s^{-1}, \tilde{g}(t), s),$$

(110)

where $\tilde{g}(t)$ is known as the running coupling and satisfies the equation

$$t \frac{d}{dt} \tilde{g}(t) = -\beta(\tilde{g}(t)).$$

(111)
For $d > 2$, $\epsilon$ is negative

$$
t \frac{d}{dt} \tilde{g}(t) = -\left(-\frac{\epsilon}{2}\right) \tilde{g}(t),
$$

so the running coupling flows to zero as $t \to \infty$. In this case, we are not justified in neglecting the long time dependence of $\overline{\pi}$ on $n_0$. For $d < 2$, $\tilde{g}(t)$ flows to the zero of the beta function $g^* = \epsilon/k_d$. We may evaluate $\overline{\pi}$ in the right hand side of equation 110 for small $s$, since this corresponds to late times. Therefore, we may use the long time solution of the rate equation 93 to find

$$
\overline{\pi}(t) \sim (st)^{-d/2} \frac{1}{2\lambda s^{-1}} \sim (t)^{-d/2} \frac{1}{2D^{1-\epsilon/2}g^*} \sim (Dt)^{-d/2} A(\epsilon).
$$

$A(\epsilon)$ is known as a universal amplitude, since it depends only on the dimensionality of the system. We have shown here that $A = (1/4\pi\epsilon)(1 + O(\epsilon))$. To find the higher order terms, we need to evaluate the higher loop diagrams in perturbation theory.

### 5.1 The critical dimension

At $d_c = 2$, the equation for the running coupling constant 111

$$
t \frac{d\tilde{g}(t)}{dt} = \frac{-k_2}{2} \tilde{g}(t)^2
$$

has solution

$$
\tilde{g}(t) = \frac{4\pi}{\ln t}.
$$

Hence, substituting this into the solution for $\overline{\pi}$, we obtain

$$
\overline{\pi}(t) \sim \frac{1}{8\pi} \frac{\ln t}{Dt}.
$$

The coefficient $1/8\pi$ is exact and universal and we see the well-known logarithmic corrections in the critical dimension.
6 Other reaction-diffusion processes

The methods we have learnt are applicable to a range of other reaction-diffusion processes. The general strategy is to write down a Hamiltonian, formulate a field theory and renormalize this field theory. We will examine two examples for which this method fails however, due to conservation laws. These laws lead to different types of fluctuations and slow dynamics.

6.1 $A + B \rightarrow 0$

The first example has two species, labelled $A$ and $B$. For convenience, they will have identical properties, except their labels. They react via $A + B \rightarrow 0$ with rate $\lambda$. This reaction is realised in electrodynamics by the annihilation of oppositely charged particles. Note that the reaction conserves $n_a - n_b$ locally, since the reactions are local. From the master equation, the following Hamiltonian may be derived

$$H = H_{\text{hopping}} - \lambda \sum_j (a_j b_j - a_j^\dagger b_j^\dagger a_j b_j).$$

(117)

The path integral representation therefore has an effective action

$$S = \int dt \int d^d x \left[ a^* \partial_t a + b^* \partial_t b + D \nabla a^* \nabla a + D \nabla b^* \nabla b - \lambda (ab - a^* b^* a b) \right].$$

(118)

$S$ must be dimensionless, since it appears as the argument of an exponential function in the functional integral. In terms of units of wavenumber, $k$, the fields have the following dimensions

$$[a a^*] = [b b^*] = k^d$$

(119)

$$[\lambda] = 2 - d.$$

(120)

Hence, the upper critical dimension for the theory is $d_c = 2$. However, it turns out that in certain circumstances fluctuations are still important for $d > 2$. We would like to investigate the evolution of the system from a spatially homogeneous initial state, such as when the distribution of $A$ and $B$ particles is an independent Poisson distribution at each site. For $d > 2$ we can use the inhomogeneous rate equations

$$\partial_t a = D \nabla^2 a - \lambda ab$$

(121)

$$\partial_t b = D \nabla^2 b - \lambda ab,$$

(122)
where \( a = n_a \), etc. Subtract the above equations to see that \( \langle \chi \rangle = \langle a - b \rangle \) satisfies a simple diffusion equation, with formal solution

\[
\chi(x, t) = \int \mathrm{d}^d x' G_0(t, x - x') \chi(x', 0).
\]

\( \chi(x', 0) \) is a random variable with mean zero. However, \( \chi(x, 0) \) is a fluctuating quantity. Assuming

\[
\langle \chi(x', 0) \chi(x'', 0) \rangle = \Delta \delta(x' - x''),
\]

where \( \Delta \propto \rho_0 \), it follows that

\[
\langle \chi(x, t)^2 \rangle = \Delta \int \mathrm{d}^d x' G(t, x - x')^2 \sim \frac{\Delta}{t^{d/2}}.
\]

Define also \( \phi \equiv a + b \), which satisfies the equation

\[
\partial_t \phi = D \nabla^2 \phi - \lambda \phi^2 + \lambda \chi^2 + \text{noise}.
\]

Considering average values,

\[
\partial_t \langle \phi \rangle = D \nabla^2 \langle \phi \rangle - \lambda \langle \phi^2 \rangle + \lambda \langle \chi^2 \rangle.
\]

For solutions with translational invariance, the \( \nabla^2 \) term vanishes. We may replace \( \langle \phi^2 \rangle \) with \( \langle \phi \rangle^2 \) to find an upper bound for our solution. Thus,

\[
\partial_t \langle \phi \rangle = -\lambda \langle \phi \rangle^2 + \frac{\lambda \Delta}{t^{d/2}}.
\]

On setting \( \Delta = 0 \), we see that \( \phi \sim 1/\lambda t \). This is asymptotically correct for \( d > 4 \) if \( \Delta \neq 0 \) by dimensional analysis. If \( d < 4 \), the two terms on the right hand side balance asymptotically, so that

\[
\langle \phi \rangle \sim \sqrt{\frac{\Delta}{t^{d/2}}} \sim \frac{1}{t^{d/4}}.
\]

Hence, the critical dimension is 4 and so three dimensions displays interesting non-mean field behaviour. Locally \( \phi^2 \approx \chi^2 \), so \( a + b = |a - b| \). This means that either \( a \gg b \) or \( a \ll b \). Therefore, most parts of the system are dominated by one particle type separated by relatively narrow reaction zones. This is known as segregation.
6.2 \( A + A \rightarrow C \)

Consider now the process \( A + A \leftrightarrow C \), where the reaction proceeds from left to right at rate \( \lambda \) and from right to left at rate \( \mu \). The quantity \( n_a + 2n_c \) is conserved by the reaction and this conservation law again leads to interesting dynamics. The rate equations are

\[
\begin{align*}
\partial_t a &= -2\lambda a^2 + 2\mu c \\
\partial_t b &= \lambda a^2 - \mu c, 
\end{align*}
\]

with the constraint that

\[
\partial_t (a + 2c) = 0.
\]

The steady state solution is

\[
\lambda a^2_\infty = \mu c_\infty,
\]

with

\[
a_\infty + 2c_\infty = a_0 + 2c_0.
\]

Expanding the rate equations in terms of \( c = c_\infty + \delta c \) and \( a = a_\infty + \delta a \), we find an exponentially fast approach to the steady state \( \delta a, \delta c \sim e^{-t/t_0} \), but this is not what actually happens; fluctuations play an important role. The Hamiltonian is

\[
H = H_{\text{diff}} - \lambda (c^\dagger a^2 - a^\dagger a^2) - \mu (a^\dagger c - c^\dagger c).
\]

The Doi shifts \( c^\dagger \rightarrow c^\dagger + 1 \) and \( a^\dagger \rightarrow a^\dagger + 1 \) lead to the following form for the shifted Hamiltonian:

\[
H_{\text{shifted}} = H_{\text{diff}} + \lambda (a^\dagger a^2 + 2a^\dagger - c^\dagger) a^2 - \mu (a^\dagger a^2 + 2a^\dagger - c^\dagger c).
\]

The effective Lagrangian is equivalent to the rate equations

\[
\begin{align*}
\partial_t a &= D \nabla^2 a - 2\lambda a^2 + 2\mu c + \xi \\
\partial_t b &= D \nabla^2 b + \lambda a^2 - \mu c,
\end{align*}
\]

There is no noise term in equation 137, since the Lagrangian does not contain a \( c^\dagger a^2 \) term. The noise in equation 136 satisfies

\[
\langle \xi(x,t)\xi(x',t') \rangle = (\mu c - \lambda a^2)\delta(x - x')\delta(t - t').
\]

Note that the noise vanishes in the equilibrium steady state. This is not to say there are no fluctuations, but instead that the density distribution is a
product of local Poisson distributions. The stochastic equation for $\chi = a + 2c$ is

$$\partial_t \chi = D \nabla^2 \chi + \xi. \tag{139}$$

This may be solved for a given realisation of the noise

$$\chi = \chi_0 + \int d^dx' \int dt G_0(x - x', t - t') \xi(x', t'). \tag{140}$$

$\chi_0$ is the conserved piece so that $\langle \chi \rangle = \chi_0$. Let us look at the two point correlation function for $\chi$

$$\langle \chi(t)^2 \rangle - \langle \chi(t) \rangle^2 = \int d^dx' \int dt' G_0(x - x', t - t')^2 \langle \mu c(x', t') - \lambda a^2(x', t') \rangle. \tag{141}$$

The expectation value is equivalent to $-\partial_{t'} \langle c(t') \rangle$ which is supposed to be independent of $x'$. Thus the spatial integral may be performed to find

$$\langle \chi(t)^2 \rangle - \langle \chi(t) \rangle^2 = -\int dt' \frac{1}{(t - t')^{d/2}} \frac{\partial}{\partial t'} \langle c(t') \rangle. \tag{142}$$

For large times, this integral is dominated by $t' \ll t$ and we obtain

$$\langle \chi(t)^2 \rangle - \langle \chi(t) \rangle^2 = \frac{c_0 - c_\infty}{t^{d/2}}. \tag{143}$$

We conclude that particles become correlated or anti-correlated depending on whether the initial density of $C$ particles is larger than the equilibrium density or smaller than the equilibrium density. The asymptotic solution to the stochastic differential equations can be found systematically, but a faster route to the solution is to assume local equilibrium $\lambda a^2 = \mu c$. We also have that

$$a + 2c = a_0 + 2c_0 + \delta \chi. \tag{144}$$

Solving these equations locally gives

$$a = -\mu + \sqrt{\mu^2 + 8\mu \lambda (a_0 + 2c_0 + \delta \chi)} \over 4\lambda. \tag{145}$$

The fluctuations in $\delta \chi$ affect the approach to equilibrium of $a$ since $a = f(\delta \chi)$ so that

$$\langle a \rangle = \langle f(\delta \chi) \rangle = f(0) + \frac{1}{2} f''(0) \langle \delta \chi^2 \rangle. \tag{146}$$

As the fluctuations in $\delta \chi$ scale as $t^{-d/2}$, so does the approach to equilibrium of $a$

$$\langle a \rangle = a_\infty + C t^{-d/2}, \tag{147}$$

where $C$ is a calculable constant.