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Asymptotic form of the approach to equilibrium in reversible recombination reactions

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Abstract. The reversible reactions $A + A \rightleftharpoons C$ and $A + B \rightleftharpoons C$ are investigated. From the exact Langevin equations describing our model, we set up a systematic approximation scheme to compute the approach of the density of C particles to its equilibrium value. We show that for a sufficiently long time t, this approach takes the form of a power law $At^{-d/2}$, for any dimension d. The amplitude A is also computed exactly, but is expected to be model dependent. For uncorrelated initial conditions, the C density turns out to be a monotonic time function. The cases of correlated initial conditions and unequal diffusion constants are investigated as well. In the former, correlations may break the monotonicity of the density or in some special cases they may change the long time behaviour. For the latter, the power law remains valid, only the amplitude changes, even in the extreme case of immobile C particles. We also consider the case of segregated initial condition for which a reaction front is observed, and confirm that its width is governed by mean-field exponent in any dimension.

1. Introduction

During the last two decades, diffusion-limited chemical reactions have attracted considerable interest. In particular, the one- and two-species annihilation reactions $A + A \rightarrow C$ and $A + B \rightarrow C$ are known to exhibit anomalous kinetics in lower dimension. For the one-species case, the upper critical dimension—the dimension above which the rate equation $\dot{n}_a(t) = -kn_a^2(t)$ (where $n_a(t)$ is the concentration of A particles) gives qualitatively correct results—is two [1–5]. For the two-species case, the situation is more complex, because of the presence of a conserved quantity, namely the difference concentration of A and B particles. Depending on the initial conditions, the upper-critical dimension is four (for homogeneous conditions with the same initial concentration of both particle types) or two (for segregated initial conditions or non-equal initial A and B concentration, etc) [1, 6–9]. Among other methods, those results have been derived using renormalization group techniques, drawing a rather complete picture of the different universality classes involved in these reactions [4,5,8,9].

In this paper, the question we want to address is the following: what happens if the backward decombination reaction is allowed with a given probability? In most physically interesting systems it is unlikely that this possibility is totally forbidden. Although for extremely small backward probability, one expects the effects to be very small (and even unnoticeable for not too large observation time), a fundamental change occurs in the system. Instead of decreasing toward a non-equilibrium steady state, the system should eventually reach an equilibrium state. Moreover a new conserved quantity can be constructed reflecting the conservation of mass or energy: $n_a(t) + 2n_c(t)$ for the one-species reversible reaction

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$A + A \rightleftharpoons C$ and $n_a(t) + n_b(t) + 2n_c(t)$ for the two-species reaction $A + B \rightleftharpoons C$ (where $n_b(t)$ and $n_c(t)$ are respectively the B and C particles concentration).

At the mean-field level, the rate equations give an exponential approach toward the equilibrium state. However it was soon recognized [10–13] that the conserved quantity obeys a diffusion equation, and thus its initial fluctuations should decay with a power law: $t^{-d/2}$ (d is the dimension of the system). In the long time limit, this power will always overcome the exponentially fast decay of the rate equations, for *any* dimension $d > 0$. The upper critical dimension is thus infinity. Although, at first sight this may seem surprising, this result has been confirmed in various ways. For the single-species reaction, Zeldovich and Ovchinnikov [11] obtained the approach to equilibrium in the low density limit of a field theory in three dimensions. This result was extended later [13] for arbitrary dimensions, but in the framework of an uncontrolled approximation. In the $A + B \rightleftharpoons C$ case, the power law decay was first obtained in three dimensions [10] from heuristic considerations. Later Kang and Redner [12], using an argument based on the fluctuations, and Burlastky *et al* [13], assuming a closure of the hierarchy, extended this result to arbitrary dimensions, but with different amplitudes. Our purpose in this paper is to derive, using field theory techniques and Langevin equations, the asymptotic approach to equilibrium in a controlled and exact way. Whereas we are able to show the universality of the power law exponent, the amplitude proves to be model-dependent.

The paper is organized as follows. In section 2 we consider the single-species $A + A \rightleftharpoons C$ reaction. From the master equation describing our model, we map the problem to a set of two Langevin equations for the random variables a and c, with complex noise. The concentrations $n_a(t)$ and $n_c(t)$ are then given by the average of the random variables a and c over the noise: $n_a = \langle a \rangle$ and $n_c = \langle c \rangle$. Exploiting the fact that $n_a(t) + 2n_c(t)$ is conserved by the dynamics, i.e. that $a + 2c$ obeys a noisy diffusion equation, we can write down the long time behaviour of its two-point correlation:

$$\langle (a + 2c)^2 \rangle - \langle a + 2c \rangle^2 \sim (c_\infty - c_0)(8\pi Dt)^{-d/2} \tag{1}$$

(c_∞ is the steady-state density of C particles, c_0 the initial one, and D the diffusion constant of both A and C particles). We can then set up a controlled approximation scheme to obtain the approach to the equilibrium, based on the fact that the previous correlation goes to zero as t grows to infinity. We find that

$$\langle c \rangle - c_\infty \sim \frac{2\lambda\mu^2}{(4\lambda a_\infty + \mu)^3}(c_0 - c_\infty)(8\pi Dt)^{-d/2} \tag{2}$$

(λ and μ are respectively the rate of the forward and backward reactions and a_∞ is the equilibrium density of A particles). The exponent of the power law is universal, as it comes from the conservation law, but the amplitude is model-dependent. However, it is interesting to note that Burlatsky *et al* [13] found the same result (up to a factor of 2) for a slightly different model, their results relying, nevertheless, on an uncontrolled approximation (the closure of the hierarchy). Note that the final approach to equilibrium is governed by the sign of $c_0 - c_\infty$. In fact, the density is expected to reach its equilibrium value monotonically.

In section 3 we consider the reaction $A + B \rightleftharpoons C$. Using the same method (in this case there is a second quantity for which the Langevin equation can also be solved exactly), we find

$$\langle c \rangle - c_\infty \sim \frac{\lambda}{2\sigma_{AB}^3}[\sigma_{AB}^2 + \mu^2 - \lambda^2(a_0 - b_0)^2](c_0 - c_\infty)(8\pi Dt)^{-d/2} \tag{3}$$

where $\sigma_{AB} = \lambda(a_0 + b_0 + 2c_0 - 2c_\infty) + \mu$, and a_0 and b_0 are the initial A and B particle densities. An equivalent expression were obtained by Burlatsky *et al* [13] when $a_0 = b_0$. Similar conclusions concerning universality and monotonicity can be drawn.

In section 4 various generalizations are considered. First we investigate the case of pair correlations between the reactants (i.e. A–A pairs for $A + A \rightleftharpoons C$ and A–B pairs for $A + B \rightleftharpoons C$). We show that, depending on the initial fraction of correlated particles, the approach to equilibrium can become non-monotonic, or even, in some special cases, the power law may change to a faster decay. The second part of this section is devoted to the interesting problem of unequal diffusion constants for the different species. Even in extreme cases (such as immobile C particles), the power law is unchanged and only the amplitude is modified. The last generalization we consider is the case of segregated initial conditions. When initially the A and B particles are spatially separated, a reaction front will develop. One natural question to ask is to which rapidity the width of this front will grow. We are able to confirm the scaling results obtained by Chopard *et al* [14] showing that this increase is governed by the mean-field behaviour $w(t) \sim t^{1/2}$. This result is also valid for immobile C particles. Final remarks are made in section 5.

2. The $A + A \rightleftharpoons C$ reaction

2.1. The model and the formalism used

Our starting point is the following continuous-time master equation

$$\begin{aligned}\frac{\partial}{\partial t}P(\{m\},\{n\};t) = {} & \frac{D_a}{\ell^2}\sum_i\sum_{e_i}[(m_{e_i}+1)P(\ldots,m_i-1,m_{e_i}+1,\ldots,\{n\};t) \\ & -m_iP(\{m\},\{n\};t)] \\ & +\frac{D_c}{\ell^2}\sum_i\sum_{e_i}[(n_{e_i}+1)P(\{m\},\ldots,n_i-1,n_{e_i}+1,\ldots;t)-n_iP(\{m\},\{n\};t)] \\ & +\lambda_0\sum_i[(m_i+2)(m_i+1)P(\ldots,m_i+2,\ldots,\{n\};t) \\ & -m_i(m_i-1)P(\{m\},\{n\};t)] \\ & +\mu\sum_i[(n_i+1)P(\{m\},\ldots,n_i+2,\ldots;t)-n_iP(\{m\},\{n\};t)]. \end{aligned} \tag{4}$$

The set $\{m\}$ ($\{n\}$) denotes the occupation numbers of A (C) particles in each lattice site and $P(\{m\},\{n\};t)$ is the probability to find the configuration $\{m\}$, $\{n\}$ at time t. This equation describes the evolution of the probability P in time. A given configuration can change due to four processes: by diffusion of A particles (first and second lines of (4), where D_a is the diffusion constant of the A particles and ℓ is the lattice constant); by diffusion of C particles (with diffusion constant D_c, third line). It will also change when two A particles merge into one C, with a microscopic reaction rate λ_0 (fourth and fifth lines) or, as shown in the last line of (4), when a C particle reacts producing two A (the corresponding rate is denoted by μ). In the diffusion terms, the sum over e_i stands for a summation over all the nearest neighbours of site i. In this respect, equation (4) then models the time-continuous evolution of the reversible reaction $A + A \rightleftharpoons C$ on a d-dimensional hypercubic lattice, allowing for multiple occupancy on each site.

For the time being, we choose the initial conditions to be given by an uncorrelated Poissonian distribution on each site and for each species:

$$P(\{m\},\{n\};0) = \mathrm{e}^{-\tilde{a}_0-\tilde{c}_0}\prod_i\frac{\tilde{a}_0^{m_i}}{m_i!}\frac{\tilde{c}_0^{n_i}}{n_i!} \tag{5}$$

where $\tilde{a}_0$ ($\tilde{c}_0$) is the average occupation number per lattice site for the A (C) particles. A correlated initial condition will be considered later, in section 4.

More than twenty years ago, Doi [15] (see also [16]) developed a procedure mapping the master equation to a second quantized representation by introducing sets of creation and annihilation operators. In turn this second quantized form can be mapped to a field theory (see [17]). Today these various steps are well known and we shall only quote the results we need.

Let us introduce the (complex) fields a, $\bar{a}$, c and $\bar{c}$. In terms of these fields, the A particle density is given by $n_a(\boldsymbol{x}, t) = \langle\langle a(\boldsymbol{x}, t)\rangle\rangle$ where $\langle\langle\cdot\rangle\rangle$ denotes an average over e^{-S}, where S is an action. In general,

$$\langle\langle \mathcal{A}[a, c]\rangle\rangle = \int \mathcal{D}a\mathcal{D}\bar{a}\mathcal{D}c\mathcal{D}\bar{c}\mathcal{A}[a, c]\mathrm{e}^{-S} \Big/ \int \mathcal{D}a\mathcal{D}\bar{a}\mathcal{D}c\mathcal{D}\bar{c}\mathrm{e}^{-S}. \tag{6}$$

The script $\mathcal{D}$ denotes functional integration and S is the action corresponding to our reaction, obtained by the mapping of the master equation (4)

$$S = \int \mathrm{d}^d x \int_0^{t_t} \mathrm{d}t\, [\bar{a}(\partial_t - D_a\nabla^2)a + \bar{c}(\partial_t - D_c\nabla^2)c + (\bar{a}^2 + 2\bar{a} - \bar{c})(\lambda a^2 - \mu c) - \delta(t)(a_0\bar{a} + c_0\bar{c})] \tag{7}$$

where $\lambda = \lambda_0\ell^d$, $a_0 = \tilde{a}_0/\ell^d$ and $c_0 = \tilde{c}_0/\ell^d$. For convenience, the continuous space limit ($\ell \to 0$) has been taken. However, an equivalent result can be written keeping the lattice structure. Note that any observable $\mathcal{A}$ can always be written as an expression which depends solely on the fields a and c and not on the response fields $\bar{a}$ and $\bar{c}$ (this comes from probability conservation). The double bracket notation in (6) stresses the fact that average is taken over both the dynamics and the initial conditions (the δ term).

The density correlation function for the A particles is given by

$$C_a(\boldsymbol{x}, t) = \langle\langle [a(\boldsymbol{x}, t) + \delta^d(\boldsymbol{x})]a(0, t)\rangle\rangle. \tag{8}$$

Similar relations hold for the C particles.

The analysis of the action using the renormalization group formalism has proved to be extremely powerful for various types of reaction (see [4, 5, 8, 9] for some recent examples). In particular, it is especially well suited to distinguish universality classes. However, in our case, this analysis is not well adapted because the upper critical dimension is infinite and an expansion around it will clearly fail. In fact, to treat this problem, we prefer to use the formalism of Langevin equations. These equations can be very easily obtained by replacing the quartic piece of the action with an integral over a noise variable:

$$\exp[-\bar{a}^2(\lambda a^2 - \mu c)] \sim \int_{-\infty}^{+\infty} \mathrm{d}\zeta\ \exp[\bar{a}\zeta - \tfrac{1}{4}\zeta^2/(\mu c - \lambda a^2)] \tag{9}$$

and integrating out the response fields $\bar{a}$ and $\bar{c}$. One then obtains the two following equations:

$$(\partial_t - D_a\nabla^2)a(\boldsymbol{x}, t) = -2\lambda a(\boldsymbol{x}, t)^2 + 2\mu c(\boldsymbol{x}, t) + \zeta(\boldsymbol{x}, t) \tag{10}$$

$$(\partial_t - D_c\nabla^2)c(\boldsymbol{x}, t) = \lambda a(\boldsymbol{x}, t)^2 - \mu c(\boldsymbol{x}, t) \tag{11}$$

where ζ is a complex Gaussian noise with zero mean value, whose correlation is given by

$$\langle\zeta(\boldsymbol{x}, t)\zeta(\boldsymbol{x}', t')\rangle = 2\langle\mu c(\boldsymbol{x}, t) - \lambda a(\boldsymbol{x}, t)^2\rangle\delta^{(d)}(\boldsymbol{x} - \boldsymbol{x}')\delta(t - t'). \tag{12}$$

Here, the single bracket notation stands for the average over the noise. There is no longer any need to average over the initial conditions as it has been explicitly performed when integrating over the response field.

Note that by using (11), one has, for homogeneous initial conditions,

$$\langle\zeta(\boldsymbol{x}, t)\zeta(\boldsymbol{x}', t')\rangle = -2\partial_t\langle c(t)\rangle\delta^{(d)}(\boldsymbol{x} - \boldsymbol{x}')\delta(t - t'). \tag{13}$$

As the density is expected to reach a (reversible) stationary state, the noise correlation should vanish in the long time limit ($\lim_{t\to\infty} \partial_t \langle c(t)\rangle = 0$). We emphasize that this property does not imply that the reaction stops at equilibrium. It just shows that the complex quantities a and c (which are *not* the densities) do not fluctuate any more. As we shall see later, the true densities always fluctuate, even at equilibrium. This, together with the fact that the equation for the variable $c(\boldsymbol{x}, t)$ comes without explicit noise (except through the a dependence), are the central points of our analysis.

These Langevin equations look very similar to the rate equations, with the addition of the noise. One then might question the necessity of deriving them in a such complicated way, as it would have been easier just to add noise to the rate equation. In fact this method allows us to derive exactly the noise and its noise–noise correlation function. In particular one sees that the noise is complex, a result which is at odds with the usual guess made when writing heuristic Langevin equations. It should also be emphasized that the variables $a(\boldsymbol{x}, t)$ and $c(\boldsymbol{x}, t)$ do *not* represent the density, because they are complex. The mean density $n_a(t)$ ($n_c(t)$) is given by the average of $a(\boldsymbol{x}, t)$ ($c(\boldsymbol{x}, t)$) over the noise. One easily convinces oneself that this average gives a real value for the density.

An immediate consequence of the vanishing of the fluctuations at equilibrium is the possibility of computing the actual values of the equilibrium densities, which are simply given by their mean field values. Denoting by a_∞ and c_∞ such densities, one has

$$\lambda a_\infty^2 = \mu c_\infty \tag{14}$$

which together with the conservation law

$$a_\infty + 2c_\infty = a_0 + 2c_0 \tag{15}$$

give us

$$a_\infty = \frac{\mu}{4\lambda}\left(\sqrt{1 + 8\lambda(a_0 + 2c_0)/\mu} - 1\right). \tag{16}$$

It is easy to check that this result is a solution of the detailed balance condition of the master equation (4), which should hold as the stationary state is an equilibrium state. Note that we do not expect this result to be universal, i.e. apply for all models describing a reversible $A + A \rightleftharpoons C$ reaction. In fact this result strongly relies on the multiple occupancy property and single-site reactions of our model. It can indeed be shown [18] that, in one dimension, a spin chain model of this reaction with exclusion process leads to a different steady-state density (equation (14) is replaced by another condition). However, in the small density limit (dilute gas) the latter result converges toward the mean field value which is expected to be universal in this regime.

2.2. Conservation law

The next step in our analysis of the model is, of course, to obtain the approach toward equilibrium. It is easily seen that the rate equations give an exponential decay. The fluctuations are expected, however, to change this law. Our starting point to analyse this problem will be the two equations (10) and (11) which, with the noise–noise correlation, completely describe our model. In order to simplify, we shall now consider the case of equal diffusion constant $D_a = D_c \equiv D$. The case for which $D_a \neq D_c$ will be considered in section 4.

First one remarks that the quantity $\chi = a + 2c$ obeys a noisy diffusion equation:

$$(\partial_t - D_a\nabla^2)\chi(\boldsymbol{x}, t) = \zeta(\boldsymbol{x}, t). \tag{17}$$

This reflects the fact that the quantity $n_a(\boldsymbol{x}, t) + 2n_c(\boldsymbol{x}, t) = \langle\chi(\boldsymbol{x}, t)\rangle$ is conserved by the dynamics, which in turn is a statement about mass (or energy) conservation. Equation (17) is

easily solved, and one finds

$$\chi(\boldsymbol{x},t)=\int_0^t \mathrm{d}t' \int \mathrm{d}^d x'\, G_0(\boldsymbol{x}-\boldsymbol{x}',t-t')\zeta(\boldsymbol{x}',t') + \int \mathrm{d}^d x'\, G_0(\boldsymbol{x}-\boldsymbol{x}',t)\chi(\boldsymbol{x}',0) \tag{18}$$

where $\chi(\boldsymbol{x},0)$ is the initial condition and $G_0(\boldsymbol{x},t)$ is the free propagator:

$$G_0(\boldsymbol{x},t)=\theta(t)(4\pi Dt)^{-d/2}\exp\left(-\frac{x^2}{4Dt}\right) \tag{19}$$

($\theta(t)$ is the usual Heaviside step function). Using $\langle\zeta\rangle=0$,

$$\langle\chi(\boldsymbol{x},t)^2\rangle-\langle\chi(\boldsymbol{x},t)\rangle^2=-2\int_0^t \mathrm{d}t_1\,[8\pi D(t-t_1)]^{-d/2}\partial_t\langle c(t_1)\rangle \tag{20}$$

with $\langle\chi(\boldsymbol{x},t)\rangle = a_0+2c_0$. Although the exact structure of $\langle c(t)\rangle$ is not known (as this is precisely the quantity we want to compute), we do not need it to obtain $\langle\chi(\boldsymbol{x},t)^2\rangle$ for long time, as, when $t\to\infty$

$$\langle\chi(\boldsymbol{x},t)^2\rangle-\langle\chi(\boldsymbol{x},t)\rangle^2=-2[8\pi Dt]^{-d/2}\int_0^\infty \mathrm{d}t_1\,\partial_t\langle c(t_1)\rangle=-2(c_\infty-c_0)[8\pi Dt]^{-d/2}. \tag{21}$$

At this stage several remarks have to be made. First, the integrand of expression (20) diverges when $t_1\to t$. For $d\geqslant 2$ the integral is thus singular. This divergence is, however, artificial as it comes from the continuous space limit we took when writing the action, and it can be avoided by putting a short distance cut-off of the order of ℓ in the space integration. In turn, once the integration over space is performed, this small distance cut-off will produce a cut-off function $\mathcal{C}_{\mathrm{cf}}(\ell^2/D(t-t_1))$ which multiplies the integrand of equation (20). The exact form of this cut-off function is unimportant. It should be a rapidly decreasing function for large x and it should go to 1 when x goes to 0 (for example a possible candidate could be $\mathcal{C}_{\mathrm{cf}}(x)\sim\exp(-x^2)$). In the following, such regularization will always been understood when facing ultra-violet divergent integrals. A second remark concerns the sign of the variance of χ which can be positive or negative, depending on the initial densities a_0 and c_0, i.e. on the sign of c_0-c_∞. (Note that c_∞ depends both on a_0 and c_0 and it is always possible to adjust a_0 such that $c_\infty<c_0$, or $c_\infty>c_0$.) The possibility of having negative variance plays a central role. In particular, as shown in section 2.3, it guarantees a monotonic approach towards equilibrium, at least for times at which our analysis applies. Whereas this result is not really surprising as it was already obtained by the rate equation, one should note that it refutes the results of a common method of solving such problems. From the two Langevin equations (10) and (11), a natural approximation for the density would be to consider the standard rate equations

$$(\partial_t-D\nabla^2)\hat{a}(\boldsymbol{x},t)=-2\lambda\hat{a}(\boldsymbol{x},t)^2+2\mu\hat{c}(\boldsymbol{x},t) \tag{22}$$

$$(\partial_t-D\nabla^2)\hat{c}(\boldsymbol{x},t)=\lambda\hat{a}(\boldsymbol{x},t)^2-\mu\hat{c}(\boldsymbol{x},t) \tag{23}$$

with Poissonian random initial conditions. Whereas this approximation gives perfectly good results, both for short and long times (but not for intermediate times), for the two species annihilation reaction $A+B\to\emptyset$ (see for example [8, 19]), in our case it fails to predict the anti-correlation of the conserved field. Indeed, it is easy to solve the equation for $\hat{\chi}=\hat{a}+2\hat{c}$. One has

$$\hat{\chi}(\boldsymbol{x},t)=\int \mathrm{d}^d x'\, G_0(\boldsymbol{x}-\boldsymbol{x}',t)\hat{\chi}(\boldsymbol{x}',0). \tag{24}$$

Denoting the average over the initial conditions by $\langle\cdot\rangle_{\mathrm{p}}$, one readily finds that the density $\langle\hat{\chi}\rangle_{\mathrm{p}}$ is conserved:

$$\langle\hat{\chi}(\boldsymbol{x},t)\rangle_{\mathrm{p}}=a_0+2c_0. \tag{25}$$

However, due to the Poissonian initial conditions which imply

$$\langle \hat{a}(\boldsymbol{x},0)\hat{a}(\boldsymbol{x}',0)\rangle_{\mathrm{p}} = a_0^2 + a_0\delta^{(d)}(\boldsymbol{x}-\boldsymbol{x}') \tag{26}$$

$$\langle \hat{c}(\boldsymbol{x},0)\hat{c}(\boldsymbol{x}',0)\rangle_{\mathrm{p}} = c_0^2 + c_0\delta^{(d)}(\boldsymbol{x}-\boldsymbol{x}') \tag{27}$$

one finds

$$\langle \hat{\chi}(\boldsymbol{x},t)^2\rangle_{\mathrm{p}} = (a_0+2c_0)^2 + (a_0+4c_0)(8\pi Dt)^{-d/2}. \tag{28}$$

This approximation gives satisfactory results concerning the power law approach to equilibrium, however, it is unable to predict the correct sign of the correlations. As a consequence of this erroneous sign, the density of the C particles would always approach its stationary value from above, leading to a non-monotonic behaviour, when $c_0 < c_\infty$.

2.3. Approximation scheme for the concentration of C particles

In this section, we would like to compute the approach of the density to its stationary value. Let us define $\delta c(\boldsymbol{x},t) = c(\boldsymbol{x},t) - c_\infty$ and $\delta\chi(\boldsymbol{x},t) = \chi(\boldsymbol{x},t) - (a_0+2c_0)$. The Langevin equation for δc is then given by

$$\begin{aligned}(\partial_t - D\nabla^2 + \sigma_{\mathrm{AA}})\delta c(\boldsymbol{x},t) &= 4\lambda\delta c(\boldsymbol{x},t)^2 - 4\lambda\delta\chi(\boldsymbol{x},t)\delta c(\boldsymbol{x},t) + \lambda\delta\chi(\boldsymbol{x},t)^2 \\ &\quad + \tfrac{1}{2}(\sigma_{\mathrm{AA}}-\mu)\delta\chi(\boldsymbol{x},t)\end{aligned} \tag{29}$$

where we put $\sigma_{\mathrm{AA}} = 4\lambda a_\infty + \mu$. The explicit solution of (29) is unknown. However, we can obtain the large time behaviour of $\langle\delta c\rangle$, by exploiting that $\delta\chi$ is a Gaussian random variable with vanishing variance when t goes to infinity. The formal solution of (29) can be written in the form

$$\delta c = \mathcal{G}_0[\delta c] + \mathcal{G}[4\lambda\delta c^2 - 4\lambda\delta\chi\delta c + \lambda\delta\chi^2 + \tfrac{1}{2}(\sigma_{\mathrm{AA}}-\mu)\delta\chi] \tag{30}$$

where to simplify our notation we have introduced

$$\mathcal{G}[f](\boldsymbol{x},t) = \int_0^t \mathrm{d}t \int \mathrm{d}^d x'\, \mathrm{e}^{-\sigma_{\mathrm{AA}}(t-t')} G_0(\boldsymbol{x}-\boldsymbol{x}', t-t') f(\boldsymbol{x}',t') \tag{31}$$

and

$$\mathcal{G}_0[f](\boldsymbol{x},t) = \int \mathrm{d}^d x'\, \mathrm{e}^{-\sigma_{\mathrm{AA}}t} G_0(\boldsymbol{x}-\boldsymbol{x}', t) f(\boldsymbol{x}',0). \tag{32}$$

The first term in (30) comes from the initial condition. It simply reduces to $(c_0 - c_\infty)\mathrm{e}^{-\sigma_{\mathrm{AA}}t}$.

Iterating this solution will give eventually a series in $\mathcal{G}_0[\delta c]$, $\mathcal{G}[\delta\chi]$ and $\mathcal{G}[\delta\chi^2]$, with appropriate insertions of the operator $\mathcal{G}$. Three kinds of terms then occur: terms containing only power of $\mathcal{G}_0[\delta c]$, terms containing only power of $\mathcal{G}[\delta\chi]$ and $\mathcal{G}[\delta\chi^2]$, and mixed terms. One can easily see that the first kind of terms gives exponential decay in the long time limit, they can thus be discarded as we are interested in the asymptotic time regime of $\langle\delta c\rangle$ and $\langle\delta c^2\rangle$. After averaging, and due to the particular structure of the operator $\mathcal{G}_0$, the mixed terms will also give exponential decay when $t\to\infty$. They can thus be discarded. Therefore, in the long time limit, $\langle\delta c\rangle$ reads:

$$\langle\delta c\rangle = \lambda\mathcal{G}[\langle\delta\chi^2\rangle] - 2\lambda(\sigma_{\mathrm{AA}}-\mu)\mathcal{G}[\langle\delta\chi\mathcal{G}[\delta\chi]\rangle] + \lambda(\sigma_{\mathrm{AA}}-\mu)^2\mathcal{G}[\langle\mathcal{G}[\delta\chi]^2\rangle] + \cdots \tag{33}$$

where the ellipsis stands for terms containing at least a fourth power of $\delta\chi$. In the following, we shall show that they give sub-leading contributions to the asymptotic time behaviour of $\langle\delta c\rangle$. Let us now analyse the first term of that equation. It reads

$$\mathcal{G}[\langle\delta\chi^2\rangle] = \int_0^t \mathrm{d}t' \int \mathrm{d}^d x\, \mathrm{e}^{-\sigma_{\mathrm{AA}}(t-t')} G_0(\boldsymbol{x}-\boldsymbol{x}', t-t')\langle\delta\chi(\boldsymbol{x}',t')^2\rangle. \tag{34}$$

The large time behaviour of this expression can be obtained in several ways. One would be to integrate over the space dependence, and then to use the property

$$\int_0^t \mathrm{d}t' \, \mathrm{e}^{-\alpha(t-t')} f(t') = \frac{1}{\alpha} f(t) + \mathrm{O}(f'(t)) \qquad (t \to \infty) \tag{35}$$

which is of course only valid if $f'(t)$ is negligible with respect to $f(t)$ (in particular this property is false when $f(t)$ is an exponential). In our case, one could safely use it, as $\langle \delta\chi^2 \rangle$ (which plays the role of $f(t)$) decays with a power law. Thus one finds

$$\mathcal{G}[\langle \delta\chi^2 \rangle] = \frac{1}{\sigma_{\mathrm{AA}}} \langle \delta\chi^2 \rangle. \tag{36}$$

Another equivalent way to obtain this result is to note that the leading behaviour of the time integral is obtained when $t' \to t$, i.e. one can simply replace $\mathrm{e}^{-\sigma_{\mathrm{AA}}(t-t')}$ with the delta function $\delta[\sigma_{\mathrm{AA}}(t-t')]$ and then use that

$$G_0(\boldsymbol{x} - \boldsymbol{x}', 0) = \delta^{(d)}(\boldsymbol{x} - \boldsymbol{x}'). \tag{37}$$

In other words, in the long time limit, the operator $\mathcal{G}$ can simply be replaced by $\sigma_{\mathrm{AA}}^{-1}$. Applying this method for all the other terms of (33), one readily obtains the large time behaviour for $\langle \delta c \rangle$:

$$\langle \delta c \rangle = \left(\frac{\lambda}{\sigma_{\mathrm{AA}}} - \frac{2\lambda(\sigma_{\mathrm{AA}} - \mu)}{\sigma_{\mathrm{AA}}^2} + \frac{\lambda(\sigma_{\mathrm{AA}} - \mu)^2}{\sigma_{\mathrm{AA}}^3} \right) \langle \delta\chi^2 \rangle + \cdots. \tag{38}$$

Note that the same result would have been obtained using the property (35). The terms containing higher powers of $\mathcal{G}[\delta\chi]$ can be treated in the same way. They will give (sub-leading) contributions of order $\langle \delta\chi^2 \rangle^n$, with $n \geqslant 2$. Finally, one finds

$$\langle \delta c \rangle = \frac{\lambda\mu^2}{\sigma_{\mathrm{AA}}^3} \langle \delta\chi^2 \rangle + \cdots = \frac{2\lambda\mu^2}{\sigma_{\mathrm{AA}}^3} (c_0 - c_\infty)(8\pi D t)^{-d/2} + \cdots. \tag{39}$$

Sub-leading corrections to that result are of order t^{-d} or $t^{-d/2-1}$, and will generally depend on microscopic details such as the lattice constant, etc.

In summary, using the fact that $\delta\chi$ is a Gaussian variable with a vanishing variance, we have written δc as a power series in $\delta\chi$, in a systematic way (formally, using this method, one can compute the sub-leading corrections, however the calculation may become rather tricky). The same method may be used to obtain $\langle \delta c^2 \rangle$, yielding

$$\begin{aligned} \langle \delta c^2 \rangle &= \left(\frac{\sigma_{\mathrm{AA}} - \mu}{2\sigma_{\mathrm{AA}}} \right)^2 \langle \delta\chi^2 \rangle + \cdots \\ &= \frac{1}{2} \left(\frac{\sigma_{\mathrm{AA}} - \mu}{\sigma_{\mathrm{AA}}} \right)^2 (c_0 - c_\infty)(8\pi D t)^{-d/2} + \cdots \end{aligned} \tag{40}$$

which is not necessarily positive, as c_0 can be less than c_∞.

Equation (40) implies that $\langle \delta c \rangle$ is not a self-averaging quantity. Indeed, the relative density fluctuations are given by

$$\left| \frac{\langle \delta c^2 \rangle - \langle \delta c \rangle^2}{\langle \delta c \rangle^2} \right|^{1/2} = \frac{1}{\sqrt{2}} \frac{\sigma_{\mathrm{AA}} - \mu}{\lambda\mu^2} \sigma_{\mathrm{AA}}^2 |c_0 - c_\infty|^{-1/2} (8\pi D t)^{d/4}. \tag{41}$$

They diverge in the long time limit.

As pointed out previously, the field $c(\boldsymbol{x}, t)$ does not fluctuate at equilibrium. What happens for the true density $\langle c \rangle$? From equation (8) the density correlation is easily calculated. Introducing

$$\delta C_c(t) = \frac{1}{L^d} \int \mathrm{d}^d x \, \langle \delta c(0, t) \delta c(\boldsymbol{x}, t) \rangle \tag{42}$$

(where L is the system size), one finds

$$C_c(t) = \frac{1}{L^d}\int \mathrm{d}^d x\, C_c(\boldsymbol{x},t) = \frac{1}{L^d}\int \mathrm{d}^d x\, \langle c(\boldsymbol{x},t)c(0,t)\rangle + \frac{1}{L^d}\langle c(0,t)\rangle$$
$$= c_\infty^2 + 2c_\infty\langle \delta c\rangle + \delta C_c(t) + \frac{1}{L^d}(c_\infty + \langle \delta c\rangle). \tag{43}$$

Its variance is given by

$$C_c(t) - \langle c\rangle^2 = \frac{1}{L^d}(c_\infty + \langle \delta c\rangle) + \delta C_c(t) - \langle \delta c\rangle^2. \tag{44}$$

In the asymptotic time limit, where our analysis applies, one easily verifies, by computing $\delta C_c(t)$, that this variance is, as expected, positive, the density being a physical quantity. At equilibrium, $C_c(\boldsymbol{x},t) - \langle c\rangle^2$ reduces to $\delta^{(d)}(\boldsymbol{x})c_\infty$, the statement that the steady state is just independent Poisson distributions of A and C particles, so the fluctuations in the local density of C are proportional to the density itself.

Intriguingly, the same results for the density and its correlations could be obtained by imposing $(\partial_t - D\nabla^2)\,\delta c = 0$ in equation (29) and then solving the quadratic equation for δc. However, this approximation is uncontrolled, and only the lowest-order terms can be obtained. It is possible to explain why such a crude approximation works, by noting that even though δc is a random variable, it should not vary too rapidly, as it only depends on $\delta\chi$ and not directly on the noise ζ.

Note that the sign of $\langle \delta c\rangle$ is given by $\langle \delta\chi^2\rangle$ (or equivalently by $c_0 - c_\infty$). This means that if initially $\langle \delta c\rangle$ is positive, so will it be for large time (note that if $\langle \delta\chi^2\rangle$ were a positive function, $\langle \delta c\rangle$ would not have been a monotonic function of time when $c_0 < c_\infty$). No information is given for intermediate times, but a non-monotonic behaviour would be surprising.

The computation of the density correlation functions goes along the same lines. Using that $a = a_\infty + \delta\chi - 2\delta c$ and equation (8), one obtains (when $t \to \infty$)

$$C_a(\boldsymbol{x},t) = a_\infty^2 + \delta^{(d)}(\boldsymbol{x})a_\infty + \frac{\mu^2}{\sigma_{\mathrm{AA}}^3}(a_\infty - a_0)(8\pi Dt)^{-d/2}(\mu \mathrm{e}^{-x^2/8Dt} - 2\lambda\delta^{(d)}(\boldsymbol{x})) \tag{45}$$

where the Gaussian factor $\mathrm{e}^{-x^2/8Dt}$ comes from the expression for $\langle \delta\chi(\boldsymbol{x},t)\delta\chi(0,t)\rangle$ (which is easily obtained from (18)). The correlation length ξ_a is given by

$$\xi_a^2 = \left|\frac{\int \mathrm{d}^d x\, x^2[C_a(\boldsymbol{x},t) - a_\infty^2]}{\int \mathrm{d}^d x\,[C_a(\boldsymbol{x},t) - a_\infty^2]}\right| = \frac{4d\pi Dt|a_\infty - a_0|}{a_\infty - a_0 + a_\infty\sigma_{\mathrm{AA}}^3/\mu^3}. \tag{46}$$

The absolute values ensure the positiveness of ξ_a^2 (note that $a_\infty - a_0 + a_\infty\sigma_{\mathrm{AA}}^3/\mu^3 \geqslant 0$). When $a_0 > a_\infty$, the second moment of $C_a(\boldsymbol{x},t) - a_\infty^2$ is negative, indicating that the A particles are negatively correlated. The same conclusion holds for the C particles.

3. The two-species reversible reaction $A + B \rightleftharpoons C$

3.1. The model

In this section we study the reversible $A + B \rightleftharpoons C$ reaction using the previous approach. As before, our starting point is the continuous time master equation describing the process on a d-dimensional hypercubic lattice, allowing multiple occupancy. Let $P(\{l\},\{m\},\{n\};t)$ be the probability to find the configuration $\{l\},\{m\},\{n\}$ at time t. The set $\{l\}$ describes the occupation numbers on each lattice site for the A particles, $\{m\}$ is used for the B particles and $\{n\}$ for the

C's. The master equation is then

$$\begin{aligned}\frac{\partial}{\partial t}P(\{l\},\{m\},\{n\};t) = \frac{D_a}{\ell^2}\sum_i\sum_{e_i}[&(l_{e_i}+1)P(\ldots,l_i-1,l_{e_i}+1,\ldots,\{m\},\{n\};t)\\ &-l_iP(\{l\},\{m\},\{n\};t)]\\ +\frac{D_b}{\ell^2}\sum_i\sum_{e_i}[&(m_{e_i}+1)P(\{l\},\ldots,m_i-1,m_{e_i}+1,\ldots,\{n\};t)\\ &-m_iP(\{l\},\{m\},\{n\};t)]\\ +\frac{D_c}{\ell^2}\sum_i\sum_{e_i}[&(n_{e_i}+1)P(\{l\},\{m\},\ldots,n_i-1,n_{e_i}+1,\ldots;t)\\ &-n_iP(\{l\},\{m\},\{n\};t)]\\ +\lambda_0\sum_i[&(l_i+1)(m_i+1)P(\ldots,l_i+1,\ldots,m_i+1,\ldots,\{n\};t)\\ &-m_i(m_i-1)P(\{l\},\{m\},\{n\};t)]\\ +\mu\sum_i[&(n_i+1)P(\{l\},\{m\},\ldots,n_i+2,\ldots;t)-n_iP(\{l\},\{m\},\{n\};t)].\end{aligned}\tag{47}$$

This master equation has the same structure as equation (4), and the same notation is used (D_b is the diffusion constant of B particles). For the time being, we choose homogeneous initial conditions given by an uncorrelated Poissonian distribution on each site and for each species:

$$P(\{l\},\{m\},\{n\};0) = \mathrm{e}^{-\tilde{a}_0-\tilde{b}_0-\tilde{c}_0}\prod_i\frac{\tilde{a}_0^{l_i}}{l_i!}\frac{\tilde{b}_0^{m_i}}{m_i!}\frac{\tilde{c}_0^{n_i}}{n_i!}\tag{48}$$

where $\tilde{b}_0$ is the initial average occupation number of B particles.

In the field theory formalism, the action is given by

$$\begin{aligned}S = \int \mathrm{d}^dx\int_0^{t_\mathrm{f}}\mathrm{d}t\,[&\bar{a}(\partial_t - D_a\nabla^2)a + \bar{b}(\partial_t - D_b\nabla^2)b + \bar{c}(\partial_t - D_c\nabla^2)c\\ &+(\bar{a}\bar{b}+\bar{a}+\bar{b}-\bar{c})(\lambda ab-\mu c) - \delta(t)(a_0\bar{a}+b_0\bar{b}+c_0\bar{c})]\end{aligned}\tag{49}$$

where $b_0 = \tilde{b}_0/\ell^d$. In terms of Langevin equations we find

$$(\partial_t - D_a\nabla^2)a(\boldsymbol{x},t) = -\lambda a(\boldsymbol{x},t)b(\boldsymbol{x},t) + \mu c(\boldsymbol{x},t) + \zeta_a(\boldsymbol{x},t)\tag{50}$$

$$(\partial_t - D_b\nabla^2)b(\boldsymbol{x},t) = -\lambda a(\boldsymbol{x},t)b(\boldsymbol{x},t) + \mu c(\boldsymbol{x},t) + \zeta_b(\boldsymbol{x},t)\tag{51}$$

$$(\partial_t - D_c\nabla^2)c(\boldsymbol{x},t) = \lambda a(\boldsymbol{x},t)b(\boldsymbol{x},t) - \mu c(\boldsymbol{x},t)\tag{52}$$

where ζ_a and ζ_b are two complex Gaussian noises with zero mean value and whose correlations are given by

$$\langle\zeta_a(\boldsymbol{x},t)\zeta_a(\boldsymbol{x}',t')\rangle = \langle\zeta_b(\boldsymbol{x},t)\zeta_b(\boldsymbol{x}',t')\rangle = 0\tag{53}$$

$$\begin{aligned}\langle\zeta_a(\boldsymbol{x},t)\zeta_b(\boldsymbol{x}',t')\rangle &= 2\langle\mu c(\boldsymbol{x},t) - \lambda a(\boldsymbol{x},t)b(\boldsymbol{x},t)\rangle\delta^{(d)}(\boldsymbol{x}-\boldsymbol{x}')\delta(t-t')\\ &= -2\partial_t\langle c(t)\rangle\delta^{(d)}(\boldsymbol{x}-\boldsymbol{x}')\delta(t-t')\end{aligned}\tag{54}$$

(for homogeneous initial conditions). As for the $A + A \rightleftharpoons C$ reaction, the noise vanishes at equilibrium. The equilibrium densities are thus given by their mean-field solution:

$$\lambda a_\infty b_\infty = \mu c_\infty\tag{55}$$

which together with the two conservation laws

$$a_\infty + b_\infty + 2c_\infty = a_0 + b_0 + 2c_0\tag{56}$$

$$a_\infty - b_\infty = a_0 - b_0\tag{57}$$

permits us to obtain the equilibrium densities as a function of the initial conditions.

3.2. Conserved quantities

The approach toward equilibrium will be obtained through the same steps as before. First we write the Langevin equation for the conserved quantities and then, once these equations are solved, we can set up a systematic approximation scheme for δc.

Let us introduce $\psi = a - b$ and $\chi = a + b + 2c$. From equations (50)–(52), one readily obtains the two following Langevin equations:

$$(\partial_t - D\nabla^2)\psi(\boldsymbol{x}, t) = \zeta_\psi(\boldsymbol{x}, t) \tag{58}$$

$$(\partial_t - D\nabla^2)\chi(\boldsymbol{x}, t) = \zeta_\chi(\boldsymbol{x}, t) \tag{59}$$

where in order to simplify, we supposed $D_a = D_b = D_c \equiv D$ (the case of different diffusion constants will be considered in section 4). The noises ζ_ψ and ζ_χ have a vanishing mean and their two-point correlations are

$$\begin{aligned}\langle \zeta_\psi(\boldsymbol{x}, t)\zeta_\psi(\boldsymbol{x}', t')\rangle &= -\langle \zeta_\chi(\boldsymbol{x}, t)\zeta_\chi(\boldsymbol{x}', t')\rangle \\ &= 2\partial_t\langle c(t)\rangle\delta^{(d)}(\boldsymbol{x} - \boldsymbol{x}')\delta(t - t')\end{aligned} \tag{60}$$

$$\langle \zeta_\psi(\boldsymbol{x}, t)\zeta_\chi(\boldsymbol{x}', t')\rangle = 0. \tag{61}$$

The solution of these two Langevin equations has the same form as equation (18), with appropriate initial conditions ($\psi(\boldsymbol{x}, 0) = a_0 - b_0$ and $\chi(\boldsymbol{x}, 0) = a_0 + b_0 + 2c_0$). ψ and χ then have a Gaussian distribution with a non-vanishing mean

$$\langle\psi\rangle = a_0 - b_0 \qquad \langle\chi\rangle = a_0 + b_0 + 2c_0 \tag{62}$$

and their variance is

$$\langle\psi^2\rangle - \langle\psi\rangle^2 = -(\langle\chi^2\rangle - \langle\chi\rangle^2) = 2\int_0^t \mathrm{d}t_1[8\pi D(t - t_1)]^{-d/2}\partial_t\langle c(t_1)\rangle. \tag{63}$$

In the long time limit, we again find the power law decay:

$$\langle\psi^2\rangle - \langle\psi\rangle^2 = 2(c_\infty - c_0)(8\pi Dt)^{-d/2} \qquad (t \to \infty). \tag{64}$$

3.3. Approximation scheme

The next step is to set up our approximation scheme for $\langle\delta c\rangle \equiv c - c_\infty$. Let us define $\delta\psi = \psi - (a_0 - b_0)$ and $\delta\chi = \chi - (a_0 + b_0 + 2c_0)$. The Langevin equation for δc reads

$$\begin{aligned}(\partial_t - D\nabla^2 + \sigma_{\mathrm{AB}})\delta c(\boldsymbol{x}, t) &= \lambda\delta c(\boldsymbol{x}, t)^2 - \lambda\delta\chi(\boldsymbol{x}, t)\delta c(\boldsymbol{x}, t) + \tfrac{1}{4}\lambda[\delta\chi(\boldsymbol{x}, t)^2 - \delta\psi(\boldsymbol{x}, t)^2] \\ &\quad + \tfrac{1}{2}(\sigma_{\mathrm{AB}} - \mu)\delta\chi(\boldsymbol{x}, t) - \tfrac{1}{2}\lambda(a_0 - b_0)\delta\psi(\boldsymbol{x}, t)\end{aligned} \tag{65}$$

where we put $\sigma_{\mathrm{AB}} = \lambda(a_0 + b_0 + 2c_0 - 2c_\infty) + \mu$. This equation possesses the same structure as equation (29). By repeating the same scheme, we may then obtain the large time behaviour of $\langle\delta c\rangle$. Finally, we find

$$\langle\delta c\rangle = \frac{\lambda\mu^2}{4\sigma_{\mathrm{AB}}^3}\langle\delta\chi^2\rangle - \frac{\lambda}{4\sigma_{\mathrm{AB}}}\left[1 - \left(\lambda\,\frac{a_0 - b_0}{4\sigma_{\mathrm{AB}}}\right)^2\right]\langle\delta\psi^2\rangle + \cdots \tag{66}$$

or, by putting the large time expression for $\langle\delta\chi^2\rangle$ and $\langle\delta\psi^2\rangle$

$$\langle\delta c\rangle = \frac{\lambda}{2\sigma_{\mathrm{AB}}^3}[\sigma_{\mathrm{AB}}^2 + \mu^2 - \lambda^2(a_0 - b_0)^2](c_0 - c_\infty)(8\pi Dt)^{-d/2} + \cdots. \tag{67}$$

Note that $\sigma_{\mathrm{AB}}^2 + \mu^2 - \lambda^2(a_0 - b_0)^2 = 2\mu(\sigma_{\mathrm{AB}} + 2\lambda c_\infty) > 0$.

Similarly, one obtains the C-particle correlation:

$$\langle\delta c^2\rangle = \frac{2\lambda\mu c_\infty}{\sigma_{\mathrm{AB}}^2}(c_0 - c_\infty)(8\pi Dt)^{-d/2} + \cdots. \tag{68}$$

Sub-leading corrections to these laws are of order t^{-d} or $t^{-d/2-1}$.

4. Extensions

4.1. Correlations in the initial condition

Recently, Yang *et al* [20] showed that in the $A + B \rightleftharpoons C$ case, and for correlated initial conditions, the power law approach (68) could be modified. More precisely, for a particular initial condition, they found that in one and three dimensions the approach to equilibrium was of the order $t^{-d/2-1}$, i.e. faster than in the uncorrelated case. Whereas it seems to be at odds with the fact that the power law should be universal (see the final section), we shall show in this section how such a behaviour can be obtained within our approach.

Let us consider the reaction $A + A \rightleftharpoons C$, when initially a fraction of the total density of the A particles are not distributed independently, but are disposed in pairs having a separation radius σ (each A–A pairs are supposed to be independently distributed). We still denote the total density by a_0, and the density of pairs will be denoted by n_0. In order to take this condition into account in our formalism, one should add the following term in the action (7)

$$-\frac{n_0}{s_d\sigma^{d-1}}\int \mathrm{d}^d x \int \mathrm{d}^d y\, \bar{a}(\boldsymbol{x},0)\bar{a}(\boldsymbol{y},0)\delta(|\boldsymbol{x}-\boldsymbol{y}|-\sigma). \tag{69}$$

(s_d is the surface of d dimensional sphere of radius unity). In the language of Langevin equations, this new term translates into a new contribution to the noise correlation, namely

$$\langle\zeta(\boldsymbol{x},t)\zeta(\boldsymbol{x}',t')\rangle = -2\partial\langle c(t)\rangle\delta^{(d)}(\boldsymbol{x}-\boldsymbol{x}')\delta(t-t') + \frac{n_0}{s_d\sigma^{d-1}}2\delta(|\boldsymbol{x}-\boldsymbol{x}'|-\sigma)\delta(t)\delta(t'). \tag{70}$$

The only relevant effect of this new contribution is to affect the variance of χ, to which one should add

$$\begin{aligned}\langle\delta\chi^2\rangle_{\mathrm{corr}} &= \frac{2n_0}{s_d\sigma^{d-1}}\int \mathrm{d}^d x' \int \mathrm{d}^d x''\, G_0(\boldsymbol{x}-\boldsymbol{x}',t)G_0(\boldsymbol{x}-\boldsymbol{x}'',t)\delta(|\boldsymbol{x}-\boldsymbol{x}'|-\sigma)\\ &= 2n_0\exp(-3\sigma^2/4Dt)(8\pi Dt)^{-d/2}.\end{aligned} \tag{71}$$

For long time, $\langle\delta\chi^2\rangle$ then becomes (we used that $2(c_0 - c_\infty) = a_\infty - a_0$)

$$\langle\delta\chi^2\rangle = [a_\infty - (a_0 - 2n_0)](8\pi Dt)^{-d/2} + \cdots \tag{72}$$

$a_0 - 2n_0$ represents the initial density of uncorrelated A particles. Inserting this result into formula (39) one obtains the C-particle density:

$$\langle\delta c\rangle = \frac{\lambda\mu^2}{\sigma_{\mathrm{AA}}^3}(a_\infty - a_0 + 2n_0)(8\pi Dt)^{-d/2} + \cdots. \tag{73}$$

Initial correlations could then lead to non-monotonic behaviour of $\langle\delta c\rangle$, as $a_\infty - a_0$ and $a_\infty - a_0 + 2n_0$ do not have necessarily the same sign (see [13, 21]).

A case of special interest occurs when we choose $2n_0$ to be exactly $a_\infty - a_0$. The amplitude of the leading term of the approach to equilibrium vanishes and one should consider the sub-leading corrections to $\langle\delta\chi^2\rangle$. As a consequence the approach to equilibrium will be faster. It is easy to verify that these corrections will be of order $t^{-d/2-1}$, with an amplitude that depends on microscopic parameters such as σ, the initial correlation length, or ℓ, the lattice constant. Note that the condition $2n_0 = a_\infty - a_0$ can be easily obtained experimentally: consider a system where A and C particles are at equilibrium. At time $t = 0$, we excite some fraction of C particles such that they break up into pairs of correlated A particles (this excitation can be for example obtained by a photo-flash [20]). Let us denote by $\tilde{a}_\infty$ and $\tilde{c}_\infty$ the concentrations of A and C particles before the excitation (note that we were at equilibrium: $\lambda\tilde{a}_\infty^2 = \mu\tilde{c}_\infty$). At time $t = 0$, the initial densities will be $a_0 = \tilde{a}_\infty + 2n_0$ and $c_0 = \tilde{c}_\infty - n_0$. Now, as

$a_0 + 2c_0 = \tilde{a}_\infty + 2\tilde{c}_\infty$, one must then have $a_\infty = \tilde{a}_\infty$, which implies $2n_0 = a_0 - a_\infty$. This initial condition correspond exactly to the case studied by Yang *et al* [20], for the two-species reaction.

Similar conclusions can be drawn for the $A + B \rightleftharpoons C$ reaction when initially a given amount of A and B particles are distributed in pairs of radius σ (initial correlations among particles of the same species will not be considered, as they should decay exponentially fast). The action gets modified in the same way as previously, by adding a new initial term:

$$-\frac{n_0}{s_d \sigma^{d-1}} \int \mathrm{d}^d x \int \mathrm{d}^d y \, \bar{a}(\boldsymbol{x}, 0)\bar{b}(\boldsymbol{y}, 0)\delta(|\boldsymbol{x} - \boldsymbol{y}| - \sigma). \tag{74}$$

In terms of the Langevin equation it also modifies the noise ζ, leading to a new contribution for both $\langle \delta\psi^2 \rangle$ and $\langle \delta\chi^2 \rangle$ (see (71)). Finally, one gets

$$\langle \delta\chi^2 \rangle = -\langle \delta\psi^2 \rangle = [a_\infty - (a_0 - n_0)](8\pi Dt)^{-d/2} + \cdots. \tag{75}$$

Here n_0 is the initial concentration of correlated pairs, it is also the initial density of correlated A (or B) particles. In contrast to the irreversible $A + B \to \emptyset$ case, the presence of correlations in the initial state does not modify the long time behaviour (except in some special limits as discussed above).

4.2. Unequal diffusion coefficient

The case of unequal diffusion constant is of special interest, because if, for some reasons, one kind of particle moves very slowly compared to the other, one could legitimately question the validity of our previous results. In fact we shall see that even in the worse case (one species at rest) the power law does not change, only the amplitude is affected.

Let us consider first the $A + A \rightleftharpoons C$ reaction, the generalization to the $A + B \rightleftharpoons C$ reaction being straightforward. The two Langevin equations associated with that model are

$$(\partial_t - D_a\nabla^2)\delta\chi + 2(D_a - D_c)\nabla^2 \delta c = \zeta \tag{76}$$

$$(\partial_t - D_c\nabla^2 + \sigma_{\mathrm{AA}})\,\delta c = 4\lambda\delta c^2 - 4\lambda\delta\chi\delta c + \lambda\delta\chi^2 + \tfrac{1}{2}(\sigma_{\mathrm{AA}} - \mu)\delta\chi. \tag{77}$$

The first consequence of having two different diffusion constants lies in the fact that the Langevin equation for $\delta\chi$ is no longer closed, but contains a term proportionnal to δc. The main question we want to address, is how does this extra term affect the large time behaviour of the $\langle \delta\chi^2 \rangle$? One quick and false answer would be to say that, as δc is a slowly varying random variable for large time, it should not modify the large time behaviour of $\delta\chi$. However, this picture is not true, as δc itself depends on $\delta\chi$ in a non-trivial way. In fact, a better way to treat this term is to insert it into the propagator, which is then no longer diagonal. Also putting in it the term proportional to $\delta\chi$ in equation (77) (which was previously treated like an interaction term), the propagator is given, in Fourier and Laplace transform representation, by the inverse of the following matrix:

$$\mathcal{M} = \begin{pmatrix} s + D_a p^2 & -2(D_a - D_c)p^2 \\ -\frac{1}{2}(\sigma_{\mathrm{AA}} - \mu) & s + D_c p^2 + \sigma_{\mathrm{AA}} \end{pmatrix} \tag{78}$$

where $\boldsymbol{p}$ and s are the Fourier and Laplace conjugated variables of space and time (this last expression is very easily obtained in the field theory formalism by considering the quadratic terms). For the $\delta\chi\delta\chi$ propagator, one then finds in the $(\boldsymbol{p}, s)$ representation

$$G_{\delta\chi\delta\chi,0}(\boldsymbol{p}, s) = \frac{s + D_c p^2 + \sigma_{\mathrm{AA}}}{(s + D_a p^2 + \sigma_{\mathrm{AA}})(s + D_c p^2) + (D_a - D_c)\mu p^2}. \tag{79}$$

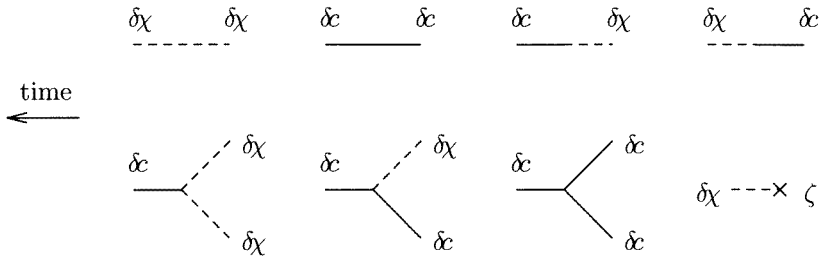

Figure 1. Set of propagators (upper part) and vertices (lower part) needed for the diagrammatic representation of the Langevin equations. The noise term is represented beginning with a cross. The arrow on the left represents the direction of the time.

Figure 2. Diagrammatic representation of $\langle \delta\chi^2 \rangle$. The dot stands for noise–noise correlation.

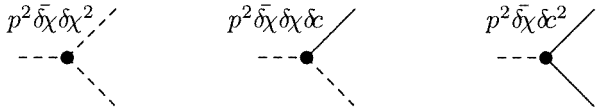

Figure 3. Effectives vertices appearing in all diagrams besides the first one of figure 2. They all give a sub-leading contribution to $\langle \delta\chi^2 \rangle$.

The $\delta\chi\delta c$ propagator is given by

$$G_{\delta\chi\delta c,0}(\boldsymbol{p}, s) = \frac{2(D_a - D_c)p^2}{(s + D_a p^2 + \sigma_{\mathrm{AA}})(s + D_c p^2) + (D_a - D_c)\mu p^2}. \tag{80}$$

The two other propagators could be obtained in the same way, but we are not interested in them. Our purpose now is to compute the large time limit of $\langle \delta\chi^2 \rangle$. Once this obtained, we shall then use our approximation scheme (applied to equation (77)), in order to derive its large time behaviour.

For computing the second moment of $\delta\chi$, it is easier to consider a diagrammatic representation (in this paragraph, we follow the line of reasoning developed in [8] for the irreversible reaction $A + B \to \emptyset$, when $D_a \neq D_C$). A $\delta\chi\delta\chi$ propagator will be represented by a dashed line and a $\delta c\delta c$ propagator by a full line. Off-diagonal propagators will be represented by mixing of the two lines (see figure 1). From the Langevin equation (77), three different vertices (four with the noise) can be identified, their representation is also given in figure 1. As we shall eventually average over the noise, only diagrams containing two merging noise lines at their beginning can subsist. To obtain the second moment of $\delta\chi$, we simply have to draw all diagrams ending with two merging $\delta\chi$ lines (see figure 2). If $D_a = D_c$, only the first diagram would give a non-vanishing contribution (in agreement with equation (20)). In fact, the subsequent terms of the sum all contain at least one of the three sub-diagrams shown in figure 3. However, in the language of field theory, these sub-diagrams give rise to effective vertices of the form $\bar{\delta\chi}\nabla^2\delta\chi^2$, $\bar{\delta\chi}\nabla^2\delta\chi\delta c$ and $\bar{\delta\chi}\nabla^2\delta c^2$, which, by simple power counting, turn out to be irrelevant. They will only give a sub-leading contribution to $\langle \delta\chi^2 \rangle$. Hence, its leading term is only given by the first diagram of figure 2.

To compute this contribution one first needs to obtain $G_{\delta\chi\delta\chi,0}$ in $(\boldsymbol{p}, t)$ space. Inverting

the Laplace transform, one finds

$$G_{\delta\chi\delta\chi,0}(\boldsymbol{p},t) = \frac{1}{r(\boldsymbol{p})}\exp[-\tfrac{1}{2}(D_a+D_c)p^2t - \tfrac{1}{2}\sigma_{\mathrm{AA}}t] \times\{[\sigma_{\mathrm{AA}} - (D_a-D_c)p^2]\sinh[\tfrac{1}{2}r(\boldsymbol{p})t] + r(\boldsymbol{p})\cosh[\tfrac{1}{2}r(\boldsymbol{p})t]\}\theta(t) \tag{81}$$

where

$$r(\boldsymbol{p}) = ((\sigma_{\mathrm{AA}} + (D_a-D_c)p^2)^2 - 4\mu(D_a-D_c)p^2)^{1/2}. \tag{82}$$

One is now in position to obtain $\langle\delta\chi^2\rangle$. To leading order, it is given by

$$\langle\delta\chi^2\rangle = -2\int_0^t \mathrm{d}t' \int \frac{\mathrm{d}^d p}{(2\pi)^d}[G_{\delta\chi\delta\chi,0}(\boldsymbol{p},t-t')]^2\partial_t\langle\delta c(t')\rangle \tag{83}$$

whose large time behaviour (which can be obtained by taking the large σ_{AA} and μ limit) reads

$$\langle\delta\chi^2\rangle = -2(8\pi D_{\mathrm{eff}})^{-d/2}\int_0^t \mathrm{d}t'\,(t-t')^{-d/2}\partial_t\langle\delta c(t')\rangle + \cdots \tag{84}$$

with

$$D_{\mathrm{eff}} = D_c + (D_a - D_c)\frac{\mu}{\sigma_{\mathrm{AA}}}. \tag{85}$$

This is the same as but the result of equation (20), with D replaced by D_{eff}.

We can now come back to the Langevin equation for δc which is exactly the same as the one written for equal diffusion constant (equation (29)), with D replaced by D_c, and then use our approximation scheme as before. The final expression for $\langle\delta c\rangle$ will then be given by equation (39) with D replaced by D_{eff}.

It is particularly interesting to consider the cases when either D_a or D_c vanish. If $D_c = 0$, one finds $D_{\mathrm{eff}} = D_a\mu/\sigma_{\mathrm{AA}}$. Although the C particles do not move, one still observes a power law decay of the concentration, but with a smaller diffusion constant than when $D_c = D_a$ ($\mu \leqslant \sigma_{\mathrm{AA}}$). The fact that the C particles are at rest is compensated by the movement of the A particles, which leads to an effective diffusion of the C particles. More surprising is the case $D_a = 0$. At first sight, one could expect that because the A particles do not move, the forward reaction is essentially inoperative (only A particles at the same site could react), however, one should not forget that the C particles still move and that they effectively carry two A particles (thus allowing some mixing of the A particles), and secondly this motion still allows the fluctuations of $\delta\chi$ to be smoothened diffusively.

For the $A + B \rightleftharpoons C$ reaction, the case where D_c differs from $D_a = D_b$ can be studied in exactly the same way. All we said for the $A + A \rightleftharpoons C$ reaction is still valid, with the modification that, as $\delta\psi$ only depends on the random variables a and b, it is not modified. Only $\delta\chi$ changes. As a consequence, the formula (64) is still valid, and for $\delta\chi$ one finds

$$\langle\delta\chi^2\rangle = 2(c_\infty - c_0)(8\pi D_{\mathrm{eff}}t)^{-d/2} \qquad (t\to\infty) \tag{86}$$

where D_{eff} is given by equation (85) with σ_{AA} replaced by σ_{AB}. The expression for $\langle\delta c\rangle$ then becomes

$$\langle\delta c\rangle = \frac{\lambda}{2\sigma_{\mathrm{AB}}^3}\left[\mu^2\left(1 - \frac{\sigma_{\mathrm{AB}}-\mu}{\sigma_{\mathrm{AB}}}\frac{D_a-D_c}{D_a}\right)^{-d/2} + \sigma_{\mathrm{AB}}^2 - \lambda^2(a_0-b_0)^2\right] \times(c_0-c_\infty)(8\pi D_a t)^{-d/2}. \tag{87}$$

When $D_c = 0$, the amplitude is slightly modified (compared to the case $D_c = D_a$) but one could still consider the diffusion constant to be D_a. Note that the case $D_a = 0$ cannot be treated by this formalism.

The case where all the diffusion constants are different can be considered as well. We shall not treat it here, but the result should not differ too much from the previous one. Indeed the main new ingredient is that $\langle \delta\psi^2 \rangle$ is modified. However, it has been shown that, for the $A + B \to \emptyset$ reaction, this leads only to a change in the amplitude [8]. We expect this result to be only slightly modified in the reversible case. For $\delta\chi$ the same analysis as before applies, but with more complicated expressions. The cases $D_a = 0$ or $D_b = 0$ cannot be treated with this formalism.

4.3. Segregated initial conditions

Our approach can also be extended to other initial conditions. The $A + B \rightleftharpoons C$ reaction with initially segregated reactants (say, the A particles on the right, the B ones on the left and no C particles) is of particular interest, mainly due to the dynamics of the reaction front. In the irreversible case, it is now well established that the width of the front increases with a power law $w(t) \sim t^{\alpha}$ [22–24]. Two different cases may be distinguished: above two dimensions, the exponent takes its mean-field value $\alpha = \frac{1}{6}$, whereas below two dimensions fluctuation effects play a dominant role, leading to $\alpha = 1/[2(d+1)]$. Extrapolating our previous results, one could expect that the fluctuations in the conserved quantities will play an important role. In fact it appears that the width of the front indeed increases with a power law $w(t) \sim t^{\alpha}$, but this exponent takes its mean-field value ($\alpha = \frac{1}{2}$) for *any* dimensions. These surprising results have already been obtained by Chopard *et al* [14] using scaling arguments and numerical simulations. In this section, we shall show how this behaviour can be confirmed within our formalism.

The problem is described by the Langevin equations (50)–(52) with the initial conditions

$$\psi(\boldsymbol{x}, 0) = n_0[\theta(x_1) - \theta(-x_1)] \tag{88}$$

$$\chi(\boldsymbol{x}, 0) = n_0 \tag{89}$$

$$c(\boldsymbol{x}, 0) = 0. \tag{90}$$

For simplicity we have chosen the particle to have the same diffusion constants; moreover both reacting species A and B are supposed to be homogeneously distributed (with density n_0) in their respective semi-infinite sub-space. Let us denote by $\hat{c}$ the mean-field C particles density. One easily shows that in the long time limit, it takes a scaling behaviour:

$$\hat{c}(\boldsymbol{x}, t) \simeq c_{\infty}(\xi) \tag{91}$$

where $\xi = x_1/\sqrt{4Dt}$. The exact form of $c_{\infty}(\xi)$ is unimportant. It can be obtained by equating to zero the right-hand side of the rate equation for the C particles. Defining the width of the front by the square root of the second moment of the C particles density, one immediately obtains, in the mean-field case, the exponent $\alpha = \frac{1}{2}$ for the reaction front.

In order to take into account the fluctuations, one first needs to integrate the equation for the conserved quantities ψ and χ. In the long time limit, one can show that

$$\langle \delta\psi^2 \rangle = -\langle \delta\chi^2 \rangle \simeq -(8\pi Dt)^{-d/2} \int_{-\infty}^{+\infty} \frac{\mathrm{d}y}{\sqrt{\pi}} \mathrm{e}^{-y^2} c_{\infty}(\xi - y). \tag{92}$$

The Langevin equation for the C particles can be rewritten using $\delta c \equiv c - \hat{c}$, so that

$$[\partial_t - D\nabla^2]\delta c = \tfrac{1}{4}\lambda(\delta\chi^2 - \delta\psi^2) + \lambda\delta c^2 - \lambda\delta\chi\delta c + \tfrac{1}{2}[\sigma(x_1, t) - \mu]\delta\chi$$
$$-\tfrac{1}{2}\lambda n_0 \operatorname{erf}(\xi)\delta\psi + \sigma(x_1, t)\delta c \tag{93}$$

where $\sigma(x_1, t) = \lambda n_0 - 2\lambda\hat{c}(x_1, t) + \mu$, and erf is the error function. This equation is very similar to equation (65), with the difference that σ has become time and position dependent.

As a consequence, we are unable to write in a closed form the propagator related to this equation, and thus to apply our approximation scheme. However, we can still deduce the large time behaviour of the density $\langle \delta c \rangle$ by equating the right-hand side to zero and solving the quadratic equation in δc. This crude approximation has proven to give accurate results in the homogeneous one- and two-species reactions. In addition, the same results are obtained by assuming (on physical grounds and by examining its differential equation) that the propagator behaves like

$$G(\boldsymbol{x}, \boldsymbol{x}', t, t') \simeq \exp[-\sigma(x_1, t)(t - t')] G_0(\boldsymbol{x} - \boldsymbol{x}', t - t') \tag{94}$$

when $t' \to t$ (note that in the homogeneous case, this limit gave the asymptotic time behaviour).

Finally, one finds

$$\langle c \rangle = \hat{c}(x_1, t) + \frac{\lambda}{4\sigma(x_1, t)^3} \{\mu^2 + \sigma(x_1, t)^2 - \lambda^2 n_0^2 [\mathrm{erf}(\xi)]^2\} \langle \delta \chi^2 \rangle. \tag{95}$$

As in the homogeneous case, the mean-field asymptotic solution is approached with a power law. From the last equation one immediately obtains that the width of the front is governed by its mean-field exponent $\alpha = \frac{1}{2}$. This result is easily explained: the spreading of the front is given by the diffusion of the C particles. Moreover, once the backward reaction is allowed, it has been shown that the C particles will always diffuse with a non-vanishing effective diffusion constant (even when $D_c = 0$). Hence the width of the front should grow like the square root of time, independently on the fluctuations which are governing only the approach to the equilibrium, and not the spreading of the C particles.

5. Discussion and concluding remarks

As we mentioned in the beginning, our model allows for multiple occupancy of each site and contains only single-site reactions, a property which has considerably simplified our analysis (leading in particular to the simple form of the Langevin equations). It is thus natural to question about the universality of our results.

To answer this question, let us consider the following two Langevin equations

$$(\partial_t - D\nabla)\Psi = \zeta \tag{96}$$

$$(\partial_t - D\nabla)\Phi = \sum_{\substack{i,j \\ i+j \geqslant 1}} a_{i,j} \Psi^i \Phi^j \tag{97}$$

with $\langle \zeta \rangle = 0$ and

$$\langle \zeta(\boldsymbol{x}, t) \zeta(\boldsymbol{x}', t') \rangle = \Gamma(t) \delta^{(d)}(\boldsymbol{x} - \boldsymbol{x}') \delta(t - t') \tag{98}$$

(homogeneous case). By writing these two equations, we have implicitely assumed that initially $\Psi(x, 0) = 0$ and that $\lim_{t \to \infty} \langle \Phi \rangle = 0$ (otherwise a constant term $a_{00} \neq 0$ should be added). From equation (96), one immediately obtains in the long time limit

$$\langle \Psi^2 \rangle = (8\pi D)^{-d/2} \int_0^t \mathrm{d}t' \, (t - t')^{-d/2} \Gamma(t') \tag{99}$$

(to cure the divergence when $t' \to t$, the integrand should be multiplied by a cut-off function), leading to the following long time behaviour for $\langle \Phi \rangle$

$$\langle \Phi \rangle = -\frac{1}{a_{01}^3} (a_{01}^2 a_{20} - a_{01} a_{11} a_{10} + a_{02} a_{10}^2)(8\pi D)^{-d/2} \int_0^t \mathrm{d}t' \, (t - t')^{-d/2} \Gamma(t'). \tag{100}$$

If $a_{01} \neq 0$, the leading behaviour is given by $\int_0^t \mathrm{d}t' \, (t - t')^{-d/2} \Gamma(t')$ (as long as $a_{01}^2 a_{20} - a_{01} a_{11} a_{10} + a_{02} a_{10}^2 \neq 0$). If $\int_0^\infty \mathrm{d}t' \, \Gamma(t')$ is finite (this implies in particular that the noise dies

out at equilibrium), one recovers the $t^{-d/2}$ power law. This shows us that in general the power law does not depend on the structure of the equation for Φ, but only on the presence of Ψ, i.e. of a diffusive conserved mode in the model. The condition $a_{01} \neq 0$ (here a_{01} plays the role of σ_{AA} or σ_{AB}) implies the presence of a non-vanishing mass in the field theory for the field Φ. This is responsible for the presence of an exponential decay in time of the $\Phi\Phi$ propagator, which, in turn, plays a central role in the large time behaviour.

Equation (100) shows that the amplitude depends only on the most relevant operators (the value of the coefficient $a_{i,j}$, with $1 \leqslant i + j \leqslant 2$). In particular, a model with an exclusion principle on each lattice site can be handled in the same way. Whereas the exclusion condition will give rise to new contributions for the noise correlation and for various operators, one can reasonably expect on physical grounds that the conserved quantity will behave diffusively, leading to the $t^{-d/2}$ power law. However, the equation for the evolution of Φ will be modified, leading to new expressions for the steady-state densities (which are again simply obtained by solving the corresponding mean-field equation) and the amplitude. Note that the exact expression of the equilibrium densities depends explicitly on the complete equation for (the unshifted version of) Φ, but as the noise dies out at equilibrium, it is still given by a mean-field equation.

The addition of a new diffusive conserved mode (like in the case of the $A + B \rightleftharpoons C$ reaction) clearly does not alter the power law, but the amplitude. A generalization of our analysis is also straightforward for the reversible aggregation $A_m + A_n \rightleftharpoons A_{m+n}$, for which the total number of monomers A is conserved (see [25]). However, it is not possible to extend our results for the reversible coagulation process $A + A \rightleftharpoons A$, for which no such conservation law occurs. In fact this last reaction can be described by an action equivalent to the one obtained for directed percolation, in the active phase. One expects thus the upper critical dimension to be four.

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