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Cluster renormalization in the Becker–Döring equations

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Abstract. We apply ideas from renormalization theory to models of cluster formation in nucleation and growth processes. We study a simple case of the Becker–Döring system of equations and show how a novel coarse-graining procedure applied to the cluster aggregation space affects the coagulation and fragmentation rate coefficients. A dynamical renormalization structure is found to underlie the Becker–Döring equations, nine archetypal systems are identified, and their behaviour is analysed in detail. These archetypal systems divide into three distinct groups: coagulation-dominated systems, fragmentation-dominated systems and those systems where the two processes are balanced. The dynamical behaviour obtained for these is found to be in agreement with certain fine-grained solutions previously obtained by asymptotic methods. This work opens the way for the application of renormalization ideas to a wide range of non-equilibrium physicochemical processes, some of which we have previously modelled on the basis of the Becker–Döring equations.

1. Introduction

In this paper, we study the Becker–Döring cluster kinetic equations familiar from classical nucleation theory [1] in which the monomer concentration (c_1) is held constant

$$\dot{c}_r = J_{r-1} - J_r \qquad (r \geqslant 2) \qquad J_r = a_r c_r c_1 - b_{r+1} c_{r+1}. \tag{1}$$

Here c_r represents the concentration of clusters containing r-monomers, the dot implies a time derivative, and J_r is the flux from clusters of size r to those of size $r+1$. There are certain mathematical properties of the Becker–Döring system not immediately apparent from the equations but crucial to its wide-ranging physical applicability. Firstly, the partition function, Q_r, satisfies $a_r Q_r = b_{r+1} Q_{r+1}$ together with $Q_1 = 1$ and formally yields the equilibrium solution $c_r^{\mathrm{eq}} = Q_r c_1^r$. The relevance of this solution depends on the behaviour of Q_r in the limit $r \to \infty$; further analysis of this is given in section 5, where specific examples are analysed in detail. The function

$$V(\{c_r\}) = \sum_{r=1}^{\infty} c_r \left(\log\left(\frac{c_r}{Q_r c_1^r} \right) - 1 \right) \tag{2}$$

is monotonically decreasing and, provided it is bounded below, qualifies as a Lyapunov function guaranteeing the convergence of arbitrary initial data to the equilibrium solution. We note that

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the density $\varrho = \sum_{r=1}^{\infty} rc_r$ is not constant since monomers can be added to or removed from the system. Finally, there is a 'weak form' for the first equality in (1)

$$\sum_{r=2}^{\infty} g_r \dot{c}_r = g_1 J_1 + \sum_{r=1}^{\infty} [g_{r+1} - g_r] J_r. \tag{3}$$

In the forthcoming analysis we assume initial conditions $(c_r(0))$ which for large aggregation numbers decay faster than any exponential in r.

2. Coarse graining of cluster aggregation space

We now perform a coarse-graining contraction of the infinite set of Becker–Döring equations by systematically eliminating all the concentration variables except those which represent an aggregation number Λ_r, where

$$\Lambda_r = (r-1)\lambda + 1 \qquad r = 1, 2, 3, \ldots. \tag{4}$$

We then relabel the retained concentrations by $x_r = c_{\Lambda_r}$. The reduced fluxes are

$$L_r = \alpha_r x_r x_1^{\lambda_r} - \beta_{r+1} x_{r+1} \tag{5}$$

$$\alpha_r = T a_{\Lambda_r} a_{\Lambda_r+1} \ldots a_{\Lambda_{r+1}-1} \tag{6}$$

$$\beta_{r+1} = T b_{\Lambda_r+1} b_{\Lambda_r+2} \ldots b_{\Lambda_{r+1}} \tag{7}$$

where T is a constant which represents a change of timescale; the kinetic equations then reduce to

$$\dot{x}_r = L_{r-1} - L_r \qquad (r \geqslant 2). \tag{8}$$

This procedure is analogous to the Kadanoff block-spin renormalization procedure [5]; detailed information for cluster sizes between the aggregation numbers Λ_r is lost. For more details of this procedure, see [3, 8]. If the contracted system is to faithfully approximate the original system, we require that the special mathematical properties mentioned above are preserved under the coarse-grained rescaling. We can then draw on our renormalization procedure to extract the structurally stable phenomena present in the system.

The physical properties of the full Becker–Döring system (1) are shared by the contracted system (5)–(8): the partition function satisfies $\alpha_r Q_{\Lambda_r} = \beta_{r+1} Q_{\Lambda_{r+1}}$, hence $x_r^{\mathrm{eq}} = Q_{\Lambda_r} x_1^{\Lambda_r}$ is formally an equilibrium solution. The function $V(\{x_r\}) = \sum_{r=1}^{\infty} x_r(\log(x_r/Q_{\Lambda_r} x_1^{\Lambda_r}) - 1)$ has the same properties as (2). The weak form (3) is still valid if c_r is replaced by x_r and J_r by L_r. Finally, the density in the system is now defined by

$$\varrho = x_1 + \lambda \sum_{r=1}^{\infty} [(r-1)\lambda + 1] x_r. \tag{9}$$

To apply renormalization ideas to this theory, we consider the repeated application of the coarse-graining transformation (5)–(8), so we now reapply the contraction procedure with mesh size μ. Defining new variables $z_1 = x_1$, $z_r = x_{(r-1)\mu+1}$, and I_r as the flux from z_r to z_{r+1}, we find

$$\dot{z}_r = I_{r-1} - I_r \qquad (r \geqslant 2) \qquad I_r = A_r z_r z_1^{\lambda\mu} - B_{r+1} z_{r+1} \tag{10}$$

with A_r, B_r determined from α_r, β_r in an analogous way to (6), (7). A similar set of physical properties holds for this system of equations as for the original Becker–Döring equations. Thus, *a repetition of the coarse-grained contraction is identical to a single application with a larger mesh parameter* $\lambda\mu$. This shows that it is sufficient to consider a system of equations which has undergone a single contraction with large λ.

3. The case of constant coefficients

Although ultimately a theory capable of handling arbitrary forms of rate coefficients a_r and b_{r+1} is our goal, for the sake of simplicity let us start by considering constant coefficients—that is $a_r = a$, $b_r = b$. The parameter $\theta = ac_1/b$ enables the system's behaviour to be classified. The cluster partition function is defined by $Q_r = (a/b)^{r-1}$ and the forward coefficients in the reduced model by $\alpha_r = Ta^\lambda$, $\beta_{r+1} = Tb^\lambda$. Thus the size-independent rate coefficients $a_r = a$, $b_r = b$ are mapped to size-independent rate coefficients in the reduced model. This coarse-graining maps θ to θ^λ, leading to three fixed points, $\theta = 0, 1, \infty$. The large-time asymptotics of systems with constant coefficients have been analysed in detail in [8], where it is shown that the $\theta = 0$ case converges to the equilibrium solution, the $\theta = \infty$ case converges to the steady-state solution $x_r = x_1$ by a diffusive wave which moves through aggregation space in such a way that its position is given by $r = s(t) \sim t$, and the $\theta = 1$ case converges to the equilibrium solution $x_r = x_1$ by purely diffusive means ($x_r \sim x_1 \operatorname{erfc}(r/2\sqrt{t})$).

In [8] it is also shown that in order for the contracted system to preserve the correct large-time asymptotics, the parameter T in (6), (7) should take the value

$$T = \frac{ac_1 - b}{\lambda(a^\lambda c_1^\lambda - b^\lambda)}. \tag{11}$$

This temporal rescaling implies that our renormalization is *dynamic* [5]. Following this temporal rescaling, the large-time limit of the density of the original system with $\theta > 1$ then scales with $\frac{1}{2}c_1(ac_1 - b)t^2$, which is identical to the result given by the coarse-grained system (9); and both $V(\{c_r\})$ of equation (2) and $\lambda V(x)$ scale with $-\frac{1}{2}c_1(ac_1 - b)^2t^2 \log\theta$.

4. The case of power-law rate coefficients

In many systems the reaction rates are not independent of size as assumed above, but rather depend on the size of the cluster according to some power law. We assume $a_r = ar^p$, $b_{r+1} = br^p$, allowing us to model surface-limited aggregation in d dimensions with $p = 1 - 1/d$. The parameter $\theta = ac_1/b$ remains a useful tool for classifying behaviour; the partition function remains $Q_r = (a/b)^{r-1}$. The forward coefficients in the reduced model are

$$\alpha_r = a^\lambda \{[(r-1)\lambda + 1][(r-1)\lambda + 2] \ldots [r\lambda]\}^p . \tag{12}$$

For asymptotically large λ these can be approximated by

$$\log\alpha_r \sim \lambda \log a + p\lambda[\log(r\lambda) - 1 + (1-r)\log(1 - \frac{1}{r})] \tag{13}$$

so for simplicity we shall take $\alpha_r = (a\lambda^p r^p)^\lambda$, which is asymptotically correct at large r and differs only slightly at small values of r. In the same manner, the backward rate coefficients in the contracted model are given by $\beta_{r+1} = (b\lambda^p r^p)^\lambda$.

Our coarse-graining contraction maps the set of models with power law rate coefficients into itself. The coarse graining of power-law coefficients is only approximate when $p \neq 0$. However, the large-time asymptotics is qualitatively preserved, provided that a similar temporal rescaling is performed as in equation (11) [9]. For any given model the contraction maps the exponent p to λp. Following a contraction with large λ, there are three cases to consider: $p = 0$, and large positive or negative p. The reduced system also has a different θ-parameter, $\tilde{\theta} = \alpha_r x_1^\lambda/\beta_{r+1} = \theta^\lambda$; thus the contraction maps θ to θ^λ. The fixed points $\theta = 0, 1, \infty$ are, therefore, of most interest to us. Combining this information, there are nine fixed points of the coarse-grained contraction in (θ, p) parameter space, and these form the basis of the ensuing analysis.

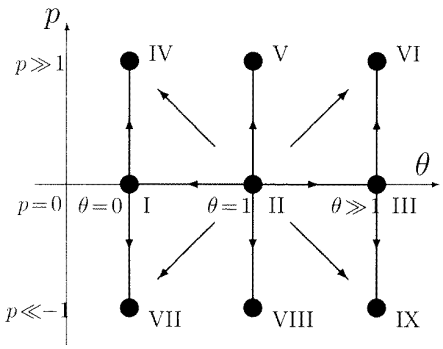

Figure 1. The effect of our coarse-graining dynamical renormalization on the two parameters θ, p in a Becker–Döring model with rate coefficients which vary as a power p of the cluster size r, and with ratio of aggregation to fragmentation rates θ. The dots show the fixed points of the mapping.

Figure 1 shows schematically the effect of the contraction. In phase plane terminology, II has the form of an unstable node, I, III, V, VIII are saddle points (although they are at the limits of the allowable domain, so only have trajectories on one side of the fixed point), and IV, VI, VII, IX are stable nodes. Cases I, IV, VII all have partition function $Q_r = 0$ for $r \geqslant 2$; in cases II, V, VIII the partition function satisfies $Q_r = 1$, whilst it is undefined in cases III, VI, IX since in all these cases the fragmentation rate is zero. Having no equilibrium configuration, these three cases approach a steady-state solution.

5. Effect of perturbations on the fixed points

There are two reasons for wanting to study noisy coefficients: firstly, any set of coefficients will be subject to uncertainties, whether derived from experimental data or a mathematical model. Secondly, systems are always susceptible to thermal (and in the models we study also spatial) fluctuations which locally alter the rate coefficients. In both cases it is necessary to know whether the models used are stable to minor variations in rate coefficients.

Firstly, we allow each reaction rate (a_r, b_{r+1} for $r = 1, 2, \ldots$) to be independently perturbed by a small-amplitude random fluctuation of the form

$$a_r = ar^p(1 + \nu\xi_r) \qquad b_{r+1} = br^p(1 + \nu\chi_{r+1}) \qquad r = 1, 2, \ldots \tag{14}$$

with $\nu \ll 1$ and ξ_r, χ_{r+1} being independent random variables with zero mean satisfying $\xi_r, \chi_{r+1} = \mathcal{O}(1)$. Such perturbations have no effect on the leading-order equilibrium or steady-state solutions, or the large-time asymptotics.

A more interesting case is that in which the presence of noise in the rate coefficients is allowed to alter their leading-order behaviour at large r. To examine these, we perturb the forward and backward rate coefficients according to

$$a_r = ar^p + \delta_r \qquad b_{r+1} = br^p + \varepsilon_{r+1} \qquad r = 1, 2, \ldots \tag{15}$$

where $\delta_r, \varepsilon_{r+1}$ have characteristic magnitude $\nu \ll 1$. We now investigate the effect of such perturbations on the equilibrium and steady-state solutions. Since we assume $c_1 = 1$, the partition function is the equilibrium solution. However, as described in [8], there are cases where the equilibrium configuration formally has infinite mass and is hence not relevant; the system then approaches one of the family of steady-state solutions in which all fluxes, J_r, are equal. The steady-state flux is determined by requiring the most rapid decay in c_r as $r \to \infty$. We now apply these ideas to the nine fixed points isolated earlier.

Case I: $p = 0, \theta = 0$. Since the non-perturbed case has $a_r = 0$ for all r, the partition function and the equilibrium solution are then zero; introducing perturbations removes this degeneracy, and the equilibrium solution then becomes rapidly decaying in r, namely $c_r = \mathcal{O}(\nu^{r-1})$, where ν is a small parameter representing the typical size of perturbations δ_r.

Case II: $p = 0$, $\theta = 1$. In this case, introducing perturbations to the rates modifies the partition function from $Q_r = 1$ to

$$Q_r \sim 1 + \sum_{k=1}^{r} (\delta_k - \varepsilon_{k+1}) \tag{16}$$

so small-amplitude noise in the coefficients does not affect the leading-order behaviour of the system.

Case III: $p = 0$, $\theta = \infty$. In the absence of perturbations, there is no partition function for this case; when present, $Q_r \sim \prod_{k=1}^{r-1}(1/\varepsilon_k)$. However, this case converges to a steady state rather than the equilibrium. When perturbations are included, the steady flux is $J = 1 + (\delta_1 - \varepsilon_2) + \mathcal{O}(\nu^2)$, which implies that the concentrations asymptote to $c_r = 1 + (\delta_1 - \varepsilon_2 + \varepsilon_{r+1} - \delta_r) + \mathcal{O}(\nu^2)$.

Case IV: $p \gg 1$, $\theta = 0$. As in case I, where noise is absent the partition function, Q_r, is zero for $r \geqslant 2$. Introducing noise removes this degeneracy, for small ν, $Q_r \sim \mathcal{O}(\nu^{r-1})$. Thus, as in case I, the equilibrium solution rapidly decays with r.

Case V: $p \gg 1$, $\theta = 1$. The balance of aggregation and fragmentation implies that $Q_r \equiv 1$ in the case with no noise. The addition of noise to the rates alters this, to

$$Q_r = 1 + \sum_{k=1}^{r-1} \left(\frac{\delta_k - \varepsilon_{k+1}}{k^p} \right) + \mathcal{O}(\nu^2) \tag{17}$$

wherein we see that the alteration to the partition function only affects the $\mathcal{O}(\nu)$ correction term, leaving the leading-order behaviour ($Q_r \sim 1$) unaltered.

Note that if $p > 1$ then the system does not evolve to the equilibrium solution, but instead is attracted to a steady-state solution with more rapid decay in the limit $r \to \infty$. Perturbing the rate coefficients modifies this state to

$$c_r = 1 - \frac{1}{\zeta(p)} \sum_{k=1}^{r-1} \frac{1}{k^p} + \sum_{k=1}^{r-1} \frac{\delta_k - \varepsilon_{k+1} - J_1}{k^p} \tag{18}$$

where $J_1 = (1/\zeta(p)) \sum_{k=1}^{\infty} (\delta_k - \varepsilon_{k+1})/k^p$, which has constant flux $J = 1/\zeta(p) + J_1$.

Case VI: $p \gg 1$, $\theta = \infty$. In this case the system approaches a steady-state solution, with flux $J = 1 + (\delta_1 - 2^{-p}\varepsilon_2) + \mathcal{O}(\nu^2)$, implying

$$c_r = \frac{1}{r^p} \left[1 + \left(\delta_1 - 2^{-p}\varepsilon_2 + \frac{\varepsilon_{r+1}}{(r+1)^p} - \frac{\delta_r}{r^p} \right) \right]. \tag{19}$$

Thus noise in the rate coefficients has a minor effect on the solution.

Case VII: $p \ll -1, \theta = 0$. Formally, we have,

$$Q_r = \prod_{k=1}^{r-1} \frac{\delta_k}{k^p + \varepsilon_{k+1}} \tag{20}$$

thus when $r = \mathcal{O}(1)$, $Q_r = \mathcal{O}(\nu^{r-1})$. However, when $r = r_c := \mathcal{O}(\nu^{1/p})$

$$c_r \sim [(\nu^{1/p})!]^{-p} \exp(\nu^{1/p} \log \nu). \tag{21}$$

For $r \geqslant r_c$, the perturbations have the same magnitude as the non-random part of the rate coefficient, thus all subsequent Q_r values depend strongly on the perturbations δ_k, ε_k and have the order of magnitude given by (20).

Case VIII: $p \ll -1, \theta = 1$. In the noiseless case this system converges to the equilibrium solution $c_r = 1$. When noisy coefficients are introduced, this solution may cease to be valid since at large r, the noise will be a leading-order effect. For small r we construct an asymptotic approximation to the modified equilibrium solution

$$c_r = 1 + \sum_{k=1}^{r-1} k^{-p}(\delta_k - \varepsilon_{k+1}) + \mathcal{O}(\nu^2). \tag{22}$$

This approximation to the solution ceases to be valid at large r, where $c_r = \mathcal{O}(1)$. We expect c_r to remain $\mathcal{O}(1)$ for all values of r, but to vary from $c_r = 1$ by significant amounts at large r.

Case IX: $p \ll -1, \theta = \infty$. In the absence of noise, this case approaches the divergent steady-state $c_r = r^{-p}$ (with flux $J = 1$). For small-amplitude noise, a modified form of this solution persists

$$c_r = \frac{1}{r^p}\left[1 + \left(\delta_1 - 2^{-p}\varepsilon_2 - \frac{\delta_r}{r^p} + \frac{\varepsilon_{r+1}}{(r+1)^p}\right)\right] + \mathcal{O}(\nu^2) \tag{23}$$

however, this ceases to be valid when $r = \mathcal{O}(\nu^{1/p})$. For values of r of this magnitude and larger, perturbations to the rates cannot be neglected as they constitute a leading-order effect in the system; and $c_r = \mathcal{O}(1/\nu)$ for all $r \geqslant \mathcal{O}(\nu^{1/p})$.

6. Effect of perturbations on the coarse-grained reaction rates

In this section we examine the effect which the coarse-graining contraction procedure has on the perturbed rate coefficients. In particular, we investigate whether small-amplitude noise in the full description of the model maps to small-amplitude noise in the reduced description. On inserting (15) into (6), (7) with $T = \lambda^{-p\lambda}$, we obtain

$$\alpha_r = a^\lambda r^{p\lambda} + \Delta_r \qquad \beta_{r+1} = b^\lambda r^{p\lambda} + E_{r+1} \tag{24}$$

where Δ_r, E_{r+1} represent the perturbations in the contracted descriptions and depend, respectively, on the δ_k, ε_k. For each of the nine fixed points (in which $a, b = 0, 1$) we calculate the leading-order form of this dependence.

Case I: $p = 0, \theta = 0$. Since $a = 0, b = 1$, we have $\alpha_r = \Delta_r = \mathcal{O}(\nu^\lambda)$, and $\beta_{r+1} = 1 + \mathcal{O}(\nu)$. Thus following contraction, the perturbations remain small.

Case II: $p = 0, \theta = 1$. Following the coarse-graining contraction, the reaction rates are given by $\alpha_r, \beta_r = 1 + \mathcal{O}(\nu)$. So the perturbations remain the same order of magnitude in the contracted model as in the full.

Case III: $p = 0, \theta = \infty$. The domination of aggregation is not altered by the presence of small noise, since $\alpha_r = 1 + \mathcal{O}(\nu)$ and $\beta_r = \mathcal{O}(\nu)$.

Case IV: $p \gg 1, \theta = 0$. The contracted rates are given by $\alpha_r = \mathcal{O}(\nu^\lambda)$ and $\beta_{r+1} = r^{p\lambda} + \mathcal{O}(\nu)$; in the latter, we have made the approximation (13) valid for large r. The system remains fragmentation dominated.

Case V: $p \gg 1$, $\theta = 1$. For large r, the rates in the contracted system have the form $\alpha_r, \beta_{r+1} = r^{p\lambda} + \mathcal{O}(\nu)$ Thus the noise will not cause any change to the leading-order form of the rate coefficients.

Case VI: $p \gg 1, \theta = \infty$. The domination of aggregation persists, since following contraction $\alpha_r = r^{p\lambda} + \mathcal{O}(\nu)$ whilst $\beta_{r+1} = \mathcal{O}(\nu^\lambda)$.

Cases VII–IX: $p \ll -1$. The formulae for Δ_r, E_{r+1} in these cases are identical to cases IV–VI, respectively. However, here $p < 0$ so that at large cluster sizes r, the perturbations will be of the same order of magnitude as the deterministic part of the rate coefficients. This occurs when $r = \mathcal{O}(\nu^{1/p})$.

In cases I–VI, the noise indeed remains small in the contracted description of the model hence these may be termed universality classes, whilst in cases VII–IX, this is not the case. In these last three cases, at large aggregation numbers, the noise in the full description is not small relative to the power-law component of the rate coefficient, and this is reflected in the contracted model. In cases VII–IX perturbations to the power-law rate coefficients play a major role in the kinetics at large cluster sizes r, as they do in the full model. Thus cases VII–IX may be termed universality classes if the added noise decays faster than the given power law as $r \to \infty$.

7. Conclusions

We have applied renormalization ideas to the Becker–Döring model of cluster formation. A novel feature of this work is that it is the cluster aggregation space which is rescaled, rather than a spatial dimension. Moreover, a dynamical renormalization is required to correctly maintain the timescales of the growth and fragmentation processes following the rescaling of aggregation space. In the case of the power-law model, nine fixed points of the renormalization procedure have been identified and analysed in greater detail, quantitatively providing nine types of large-time asymptotics which may be exhibited by the system. Five of these systems tend to equilibrium, and the remaining four to steady-state solutions. The pure fragmentation cases (I, IV, VII) all tend to the trivial equilibrium $x_r = \delta_{r,1}$.

In cases I, IV, VII, a diffusive wavefront invades the large-r region where cluster concentrations are zero, leaving the equilibrium solution behind the wavefront. In cases II, V, VIII the equilibrium solution is approached by purely diffusive mechanisms, no advection being present in the system. If $p > 1$ in case V, then the system approaches a steady-state solution rather than the equilibrium solution, since the steady state has faster decay at large aggregation numbers. This case is thus similar to cases III, VI, IX, all of which approach steady states rather than true thermodynamic equilibrium. However, their large-time asymptotics are more akin to cases I, IV, VII, being dominated by a diffusive wave which moves into the large r-domain.

Thus, for the first time we have identified universality classes present in the Becker–Döring equations, in that any system with power-law coefficients can be classified into one of the nine cases which correspond to fixed points of our contraction, and this qualitatively determines the system's large-time behaviour. In physical terms, our demonstration that a renormalization structure underpins the Becker–Döring equations carries with it the implication that universal behaviour can be identified in the approach of such systems to equilibrium or steady states. In a forthcoming paper [9], we shall discuss the temporal behaviour in detail. In the case of the Becker–Döring equations, this is a very welcome development, since it dispenses with the need to specify in full detail all the generally unknown fine-grained rate coefficients. For example the partition function is left unchanged by the coarse graining, as is the equilibrium solution and the steady-state solution. At the end of section 3 we showed that the large-time behaviour of both the density and the Lyapunov function (free energy) were left invariant by our coarse-grain rescaling. It is perhaps worth pointing out here, however, that consideration of the asymptotic limit implied by the renormalization procedure is not necessarily always appropriate, e.g. for systems in which it is crucial to retain some level of fine-grained detail in order to properly capture the dynamics.

The successful application of the renormalization techniques reported here opens the way for a study of generalized Becker–Döring equations using similar methods; it also furnishes a firm theoretical foundation for the analyses we have previously given of various generalizations of the basic Becker–Döring theory to a wide range of processes of physicochemical interest, including micelle and vesicle formation and self-reproduction [3, 4], generalized nucleation and growth phenomena [7], and macromolecular sequence selection in biopolymers [10].

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