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A finite version of Smoluchowski's coagulation equation

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Abstract. We formulate a finite version of Smoluchowski's coagulation equation in which molecules of size N react in the normal way whereas molecules of size N to $2N$ can be produced but cannot react. We prove that the solution converges to the solution of the infinite system of equations in the limit $N\to\infty$.

1. Introduction

It has been known for many years [1, 2] that the coagulation equation for the concentrations of k-mers $c_k(t)$, $k=1,2,3,\ldots$, $t\geqslant 0$,

$$\dot{c}_k=\tfrac{1}{2}\sum_{i+j=k} ijc_ic_j-kc_k\sum_{j=1}^{\infty} jc_j \tag{1}$$

with the initial condition $c_k(0)=\delta_{1k}$ has the solution

$$c_k=\frac{k^{k-2}}{k!}t^{k-1}\exp(-kt) \tag{2}$$

for $0\leqslant t<1$. During this time $\Sigma_{k=1}^{\infty} kc_k$ is conserved (and is conveniently normalized to 1) and all higher moments of the molecular weight distribution also exist. At $t=1$, however, a singularity occurs in the sense that the second moment (and all higher moments) diverge and for $t>1$, $\Sigma_{k=1}^{\infty} kc_k$ decreases, i.e. there is now no longer any mass conservation.

It is, however, possible to continue the solution [3–5] given above as

$$c_k=\frac{k^{k-2}}{k!}\mathrm{e}^{-k}t^{-1}\qquad (t\geqslant 1). \tag{3}$$

Note that we can write this solution as

$$c_k=\frac{k^{k-2}}{k!}t^{k-1}\exp[-k\phi^0(t)] \tag{4}$$

with

$$\phi^0(t)=\begin{cases} t & 0\leqslant t\leqslant 1\\ 1+\log t & t>1.\end{cases} \tag{5}$$

The $c_k(t)$ thus continued satisfies (1) and is everywhere differentiable with a continuous derivative. At $t=1$ the second derivative does not exist, however, and as mentioned above the second moment $\Sigma_{k=1}^{\infty} k^2c_k$ diverges.

2. A finite model

The above-mentioned divergence is commonly ascribed to the existence of a gel, an infinitely large molecule, which can be formed from the reaction described by (1), but which is not properly taken into account in this equation. That mass conservation breaks down, then means that there is a mass flux from sol to gel, with particles escaping to infinity. It is the purpose of this paper to elucidate this state of affairs by studying a finite system, whose size we will eventually allow to increase without bounds. We set

$$\sigma_k=\begin{cases} k & k\leqslant N \\ 0 & k>N \end{cases} \tag{6}$$

and write the coagulation equations as

$$\dot{c}_k=\tfrac{1}{2}\sum_{i+j=k}\sigma_i\sigma_j c_i c_j-\sigma_k c_k\sum_{j=1}^{\infty}\sigma_j c_j. \tag{7}$$

These equations were first considered by Lushnikov and Piskunov [6] as pointed out to us by an anonymous referee. Clearly these equations can form particles of size k with $2\leqslant k\leqslant 2N$, but only the particles $1\leqslant k\leqslant N$ can participate in the process of building up larger particles. In the language of polymer chemistry the k-mers with $1\leqslant k\leqslant N$ constitute the sol, whereas those with $N<j\leqslant 2N$ constitute the gel. It is easy to verify that $\Sigma_{k=1}^{2N} k\dot{c}_k=0$, i.e. we have mass conservation when we include the gel. The problem we shall study obviously has two sides to it. (1) Can the finite-dimensional equation (7) be solved—possibly approximately—for arbitrary N? (2) Can the limiting process $N\to\infty$ be carried out, and does any useful information accrue from this?

3. The limit $N\to\infty$

It is immediately obvious that by introducing

$$\begin{aligned}\phi_N(t)&=\sum_{k=1}^{N}\int_0^t \sigma_k c_k(t')\,\mathrm{d}t' \\ \dot{\phi}_N(t)&=\sum_{k=1}^{N} k c_k(t)\end{aligned} \tag{8}$$

we can write the solution to (7) corresponding to $c_k(0)=\delta_{k1}$ as

$$c_k(t)=\frac{k^{k-2}}{k!}t^{k-1}\exp[-k\phi_N(t)] \qquad 1\leqslant k\leqslant N \tag{9}$$

$$\begin{aligned}\dot{\phi}_N(t)&=\sum_{k=1}^{N}\frac{1}{k!}k^{k-1}t^{k-1}\exp[-k\phi_N(t)] \\ \phi_N(0)&=0 \qquad \dot{\phi}_N(0)=1.\end{aligned} \tag{10}$$

The expressions given in (9) and (10) are equivalent to (28)–(30) in [6]. The only differences are that the notation used here is more convenient for our purpose, and that we do not use the scaled time τ introduced by Lushnikov [6, 7]. Formally our equation (10) can be solved if, following Lushnikov, one introduces

$$\kappa_N(t)=t\exp[-\phi_N(t)].$$

This does not, however, lead to any useful explicit expression for the solution.

If in (10) we formally let $N\to\infty$, we get, with $\phi(t)$ equal to the formal limit of $\phi_N(t)$ as $N\to\infty$

$$\dot{\phi}(t)=\frac{1}{t}\,\psi(t\,e^{-\phi(t)}) \tag{11}$$

with

$$\psi(z)=\sum_{k=1}^{\infty} k^{k-1}z^k/k! \tag{12}$$

and

$$|t\exp[-\phi(t)]|\leqslant e^{-1}. \tag{13}$$

Comparing with lemma 2.1 in the paper by Kokholm [5], we see that (11) has $\phi^0(t)$ given by (5) as the solution. What we need to prove is that the limit of $\phi_N(t)$ as $N\to\infty$ exists and is identical to $\phi^0(t)$.

From mass conservation it follows that

$$0\leqslant\sum_{k=1}^{N} kc_k(t)\leqslant 1 \qquad t\geqslant 0 \tag{14}$$

and from this follows that

$$0<\phi_N(t)\leqslant t \qquad t>0 \tag{15}$$

and that $\phi_N(t)$ increases monotonically with t.

Comparing (10), (11) and (12) we see that

$$\left.\frac{d^n\phi_N(t)}{dt^n}\right|_{t=0}=\left.\frac{d^n\phi^0(t)}{dt^n}\right|_{t=0} \qquad 1\leqslant n\leqslant N$$

and for $n>1$ it follows from (5) that the right-hand side is zero. Furthermore, by a similar argument it can be seen that

$$\left.\frac{d^{N+1}\phi_N(t)}{dt^{N+1}}\right|_{t=0}=-(N+1)^{N-1}$$

and we now have:

Lemma. For every N there exists an $\varepsilon>0$ such that

$$\phi_N(t)<\phi_{N+1}(t) \qquad \text{for } 0<t<\varepsilon.$$

Now assume that for some N there exists a $t_0>0$ such that

$$\phi_N(t_0)=\phi_{N+1}(t_0)$$

then from (10) it follows that $\dot{\phi}_N(t_0)<\dot{\phi}_{N+1}(t_0)$. That is for $t<t_0$ we have $\phi_{N+1}(t)<\phi_N(t)$ which contradicts the lemma. Hence

$$\phi_N(t)<\phi_{N+1}(t) \qquad \text{for } 0<t \tag{16}$$

and comparing with (15) we see that there exists a function $\phi_\infty(t)$ such that

$$\phi_\infty(t)=\lim_{N\to\infty}\phi_N(t). \tag{17}$$

The above argument also holds for $\phi^0(t)$ instead of $\phi_{N+1}(t)$. Hence

$$\phi_N(t) < \phi^0(t) \qquad t > 0 \tag{18}$$

and thus

$$\phi_\infty(t) \leqslant \phi^0(t) \qquad t \geqslant 0. \tag{19}$$

From (8) we have

$$\ddot{\phi}_N(t) \leqslant 0 \qquad t > 0$$

that is $\phi_N(t)$ is concave and therefore so is $\phi_\infty(t)$. Since $\phi_\infty(t)$ is bounded, it is therefore continuous.

From (8) it also follows that

$$0 \leqslant \dot{\phi}_N(t) \leqslant 1 \qquad t \geqslant 0 \tag{20}$$

and from (16) and (10) it follows that

$$\dot{\phi}_N(t) \geqslant \frac{1}{t} \sum_{k=1}^{N} \frac{k^{k-2}}{k!} (t \exp[-\phi_\infty(t)])^k. \tag{21}$$

If there existed a $t_0 \geqslant 1$ such that

$$\phi_\infty(t_0) < \phi^0(t_0) = 1 + \log t_0$$

then $t_0 \exp[-\phi_\infty(t_0)] > \mathrm{e}^{-1}$ and this would imply according to Kokholm's lemma 2.1 that the sum

$$\sum \frac{k^{k-2}}{k!} (t_0 \exp[-\phi_\infty(t_0)])^k$$

would diverge. In particular it would imply that there existed an N_0 such that

$$\sum_{k=1}^{N_0} \frac{k^{k-2}}{k!} (t_0 \exp[-\phi_\infty(t_0)])^k > t_0.$$

When this is substituted in (21) we get $\dot{\phi}_N(t_0) > 1$ which contradicts (20). Thus we can conclude that

$$\phi_\infty(t) \geqslant \phi^0(t) \qquad \text{for } t \geqslant 1 \tag{22}$$

and comparing with (19) we get

$$\phi_\infty(t) = \phi^0(t) \qquad t \geqslant 1. \tag{23}$$

Since $\phi_\infty(t)$ is concave, it cannot lie under the cord connecting $(0, \phi_\infty(0))$ and $(1, \phi_\infty(1))$. Hence $\phi_\infty(t) \geqslant t$ for $0 < t < 1$ and this extends (23) to hold for all $t \geqslant 0$.

We have thus proved that the solution of the finite system of equations given by (7) in the limit $N \to \infty$ is the solution of the infinite system of equations (1) given by (4).

Since $\dot{\phi}_N(t)$ is bounded uniformly in t and N by (20), $\phi_N(t)$ $(N = 1, 2, \ldots)$ constitute an equicontinuous family, which in turn implies that the convergence of $\phi_N(t)$ to $\phi^0(t)$ is uniform in t for bounded intervals $(0 \leqslant t \leqslant t_0 < \infty)$. The uniform convergence of $c_k(t)$ (for given k) then follows from (9); since $c_k(t)$ is positive and decreases towards 0 as $t \to \infty$ there is no need to restrict t to bounded intervals in this case. Finally, the conservation equation $\Sigma_k kc_k(t) = 1$ implies $c_k(t) < 1/k$ and we have the following theorem.

Theorem. Define $c_{k,N}(t)$ for $k \leq N$ as the solution to (5) with the initial condition $c_{k,N}(0) = \delta_{k,1}$ and $c_{k,N}(t) = 0$ for $k > N$; then $c_{k,N}(t)$ converges uniformly in k and t for $t \geq 0$ to $c_k(t)$ given by (4) as $N \to \infty$.

4. Conclusion

It is proved that the solution of the system of equations given by (7) in the limit $N \to \infty$ will tend uniformly towards the solution of the infinite system of equations given by (1) whose existence was proved earlier [3, 5]. McLeod [1] using a slightly different method of truncation showed the convergence only for $0 < t \leq \theta$, where $\theta < 1$.

Kokholm [5] proved that the solution given by (4) is a unique solution to (1) if one requires that the concentrations $c_k(t)$ ($k = 1, 2, \ldots$) are continuously differentiable functions of t. By proving that this solution can also be obtained as a result of a natural limiting process, we hope to have shed more light on the physical meaning of the singularity in the infinite solution. In particular, it is seen that the solution for $t > 1$ is not an artefact of an infinite system.

Although we have only proved the convergence of the solution of the finite system to the solution of the infinite system for $\sigma_k = k$, one will of course expect this to be true for much more general forms of σ_k, and that the truncation introduced in this paper can form the basis for numerical investigations of equations like (1) only with the kernel ij replaced by the more general K_{ij}; in particular, since numerical calculations on the present model indicate that the convergence is rapid.

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