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2008 J. Phys. A: Math. Theor. 41 072001

(http://iopscience.iop.org/1751-8121/41/7/072001)

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J. Phys. A: Math. Theor. **41** (2008) 072001 (6pp) doi:10.1088/1751-8113/41/7/072001

**FAST TRACK COMMUNICATION**

# Exact post-critical behavior of a source-enhanced gelling system

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Received 26 November 2007, in final form 16 January 2008
Published 5 February 2008
Online at stacks.iop.org/JPhysA/41/072001

**Abstract**

The critical behavior of a source-enhanced coagulating system, where the coagulation efficiency grows with the masses of colliding particles $g$ and $l$ as $K(g,l) = \kappa g l$, is studied. In addition to the continuously acting steady-state source of monomers of productivity $I$, an instantaneous sink that removes the particles with masses exceeding $G$ is introduced which allows one to define the gel as a deposit of particles with masses between $G+1$ and $2G$. This system displays a critical behavior (the sol–gel transition) as $G \longrightarrow \infty$. The exact post-critical particle mass spectrum is shown to be $c_g = A g^{-5/2}\, \mathrm{e}^{g\xi(t)/G}$. The function $\xi(t)$ drops down to a constant during a very short time of order $1/\sqrt{G}$ (in the system of units $I = \kappa = 1$). During this time, the sol mass concentration $M(t)$ jumps down from $M = \pi/2$ to $M = \sqrt{2}$.

PACS numbers: 79.60.Bm, 42.65.Lm, 03.65.−w, 52.90.+z

In this communication we consider a system of particles that move chaotically, collide and on colliding coalesce producing a daughter particle with the mass equal to the sum of masses of parent particles. Such a process is commonly referred to as coagulation. This process has received much attention because of its great scientific and practical importance (see Leyvraz (2003) and extensive citations therein). The kinetics of coagulation is described by the Smoluchowski equation which allows one to restore the particle mass spectrum at time $t$, once the initial conditions are known.

Less studied are the source-enhanced coagulating systems, where a spatially uniform external source produces the smallest particles which then grow by coagulation. Such systems are suspected to reach steady-state regimes under some special conditions imposed on the coagulation kernel. These conditions were formulated in a number of works (see, e.g., Lushnikov and Kulmala (2002), Connaughton *et al* (2004)). Moreover, the steady-state regimes can be realized in gelling systems, where the coagulation process leads to the formation of a giant cluster (gel) during a finite interval of time. Although the steady-state regimes in coagulating systems are already known more than three decades (Lushnikov and Smirnov 1975, 1977, 2002), nobody noticed that the total mass concentration in gelling systems experiences

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a finite jump at the critical point. This communication attempts to explain what is going on in the gelling systems right after the moment when the gel begins to form.

Let us consider a source-enhanced coagulating system. We assume that before the initial moment $t = 0$ the system was empty and then at $t > 0$ a source of monomers is turned on. The monomers begin to coalesce forming dimers, trimers, etc. When a particle reaches the mass $G + 1$ or more, it is considered to deposit and does not participate in the coagulation process furthermore. This is the truncated model of coagulation introduced very long ago by Lushnikov and Piskunov (1982, 1983) (see also Lushnikov (2006a)) and recently applied by me (Lushnikov 2007a, 2007b) for studying the post-critical behavior of free (no source) coagulating systems.

This work focuses on the critical behavior of the source-enhanced coagulating system with the product coagulation kernel $K(g, l) = \kappa gl$. This kernel won great popularity in the scientific community dealing with the coagulation processes not only because it describes some realistic processes such as polymerization (Ziff and Stell 1980, Hendrics *et al* 1983), evolution of random graphs (Ben-Naim and Krapivsky 2004, Lushnikov 2005), formation of aerogels (Lushnikov *et al* 1990), but also because, most important, this kernel allows for the exact analysis of the coagulation kinetics.

Fairly recently I found the exact solution of the respective coagulation equation for the scenario with the active gel, where after the critical time a giant superparticle formed that actively participated in the coagulation process by eating its smaller partners from the sol fraction (Lushnikov 2006b). In this communication I showed that the critical time is $t_c = \pi/2$ and the total mass concentration is also $M(t_c) = \pi/2$ (in what follows the system of units $I = \kappa = 1$ is used, $I$ and $\kappa$ being the source productivity and the dimension carrier of the coagulation kernel, respectively).

There is another scenario, where the gel is passive (see Leyvraz 2003). Of course, this scenario can be realized in source-enhanced systems. I knew about this scenario, but avoided it with silence in my just cited paper. The point is that the critical mass concentration $M(t_c)$ reaches the value $\pi/2$, whereas the most plausible candidate for the post-gel sol steady-state spectrum has a lower total mass ($M_{\text{gel}} = \sqrt{2}$). At that time, I did not know how to reconcile these two facts. Now I found the way out.

Our starting point is the truncated Smoluchowski's equation describing the coagulation kinetics of particles whose masses are limited with a maximal (cutoff) mass $G$. This truncated model used here describes the coagulation process in the system with a source of monomers and a sink that instantly removes the particles with the masses exceeding $G$. The Smoluchowski equation for the number concentrations $c_g(t)$ of actively coagulating particles (referred hereafter to as sol) comprising exactly $g$ ($g \leqslant G$) monomers at time $t$ looks as follows:

$$\frac{dc_g(t)}{\mathrm{dt}} = \delta_{g1} + \frac{1}{2}\sum_{l=1}^{g-1}(g-l)lc_{g-l}(t)c_l(t) - gc_g(t)M(t). \tag{1}$$

Here,

$$M(t) = \sum_{l=1}^{G} lc_l(t) \tag{2}$$

is the total particle mass concentration. The first term on the right-hand side of equation (1) is the source of monomers ($\delta_{gl}$ is the Kroneker delta), the second term describes the gain of $g$-mers due to the reaction $(g-l)+(l) \longrightarrow (g)$ and the third term is responsible for $g$-mer losses due to their sticking to all other particles. This third term contains the cutoff mass $G$ ($G \gg 1$), i.e. we assume that all particles with masses $G+1, G+2, \ldots, 2G$ do not participate

in the coagulation process and form a passive deposit (gel). We introduce its spectrum and denote the concentrations of deposited particles as $c_g^+(t)$. It is clear that only the gain term contributes to the rate of change to $c_g^+$:

$$\frac{dc_g^+(t)}{\mathrm{dt}} = \frac{1}{2}\sum_{l=g-G}^{G}(g-l)lc_{g-l}(t)c_l(t). \tag{3}$$

The initial condition to equation (1) is chosen in the form

$$c_g(t=0) = 0, \tag{4}$$

i.e. the coagulation process starts with an empty volume.

The pre-gelation stage does not depend on the gelation scenario; so we can use the results of my paper (Lushnikov 2006b).

In the post-gelation stage, we try to find the solution in the form

$$c_g(t) = \tilde{c}_g\,\mathrm{e}^{g\xi(t)/G}, \qquad t > t_c, \tag{5}$$

where $\tilde{c}_g$ are the steady-state concentrations $\tilde{c}_g = c_g(t=\infty)$. These concentrations meet the equation

$$\delta_{g1} + \frac{1}{2}\sum_{l=1}^{g-1}(g-l)l\tilde{c}_{g-l}\tilde{c}_l - g\tilde{c}_g\tilde{M} = 0 \tag{6}$$

with

$$\tilde{M} = \sum_{l=1}^{G} l\tilde{c}_l. \tag{7}$$

This equation is readily solved. To this end, we introduce the generating function

$$F(z) = \sum_{g=1}^{\infty} g\tilde{c}_g z^g. \tag{8}$$

From equation (6), we have

$$F^2 - 2\tilde{M}F + 2z = 0 \tag{9}$$

or

$$F(z) = \tilde{M} - \sqrt{\tilde{M}^2 - 2z}. \tag{10}$$

We thus find

$$\tilde{c}_g = \tilde{M}g^{-1}r_g\left(\frac{2}{\tilde{M}^2}\right)^g, \tag{11}$$

where

$$r_g = \frac{(2g-3)!!}{2^g g!} = \frac{(2g-3)!}{2^{2g-2}(g-2)!g!} \tag{12}$$

are the coefficients of the Taylor expansion of the function $1-\sqrt{1-z}$. At large $g$, we have

$$r_g \approx \frac{1}{2\sqrt{\pi g^3}}. \tag{13}$$

From equations (7) and (11), we find the equation for determining $M$:

$$1 = \sum_{g=1}^{G} r_g\left(\frac{2}{\tilde{M}^2}\right)^g. \tag{14}$$

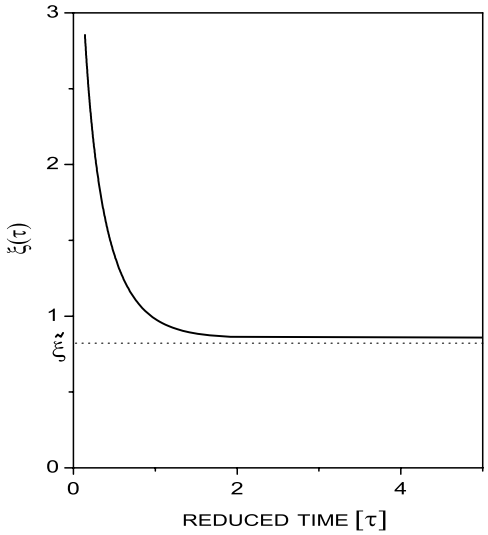


**Figure 1.** The dependence of $\xi(\tau)$ on the reduced time $\tau = 2\sqrt{\pi G}(t - t_c)$. The dotted line shows the limiting value $\xi(\infty) = \tilde{\xi}$.

We look for the solution to this equation in the form $M^2 = 2\mathrm{e}^{-\tilde{\xi}/G}$. The following chain of equalities solves the problem of finding $\tilde{\xi}$:

$$1 = \sum_{g=1}^{G} r_g \left(\frac{2}{\tilde{M}^2}\right)^g - \sum_{g=1}^{G} r_g + \sum_{g=1}^{G} r_g \approx \frac{1}{2\sqrt{\pi G}} \int_0^1 \frac{\mathrm{e}^{\tilde{\xi}x} - 1}{x^{3/2}}\,\mathrm{d}x + \sum_{g=1}^{G} r_g$$
$$= 1 + \frac{1}{2\sqrt{\pi G}} \left( \int_0^1 \frac{\mathrm{e}^{\tilde{\xi}x} - 1}{x^{3/2}}\,\mathrm{d}x - 2 \right).$$

We thus come to the equation for $\tilde{\xi}$:

$$\int_0^1 \frac{\mathrm{e}^{\tilde{\xi}x} - 1}{x^{3/2}}\,\mathrm{d}x = 2, \tag{15}$$

or on integrating twice by parts

$$(4\tilde{\xi} - 2)\,\mathrm{e}^{\tilde{\xi}} - 4\tilde{\xi}^2 \int_0^1 \sqrt{x}\,\mathrm{e}^{\tilde{\xi}x}\,\mathrm{d}x = 0. \tag{16}$$

In a different context, this equation already appeared in my works (see Lushnikov (2007a, 2007b) and references therein). Its solution is $\tilde{\xi} = 0.854\,033\,292$.

Now let us return to the transient period. Substituting equation (5) to equation (1) gives

$$\frac{g}{G}\dot{\xi}\tilde{c}_g = \delta_{g1}\,\mathrm{e}^{-\xi(t)/G} + \frac{1}{2}\sum_{l=1}^{g-1}(g-l)l\tilde{c}_{g-l}\tilde{c}_l - g\tilde{c}_g M(t). \tag{17}$$

As $G \gg 1$, we approximate $\mathrm{e}^{-\xi(t)/G} \approx 1$ and then use equation (6) to obtain

$$G^{-1}\dot{\xi} + M(t) - \tilde{M} = 0. \tag{18}$$

We finally come to the differential equation for $\xi(t)$:

$$\dot{\xi} + \frac{G^{1/2}}{2\sqrt{\pi}} \int_0^1 \frac{\mathrm{e}^{\xi x} - \mathrm{e}^{\tilde{\xi}x}}{x^{3/2}}\,\mathrm{d}x = 0 \tag{19}$$

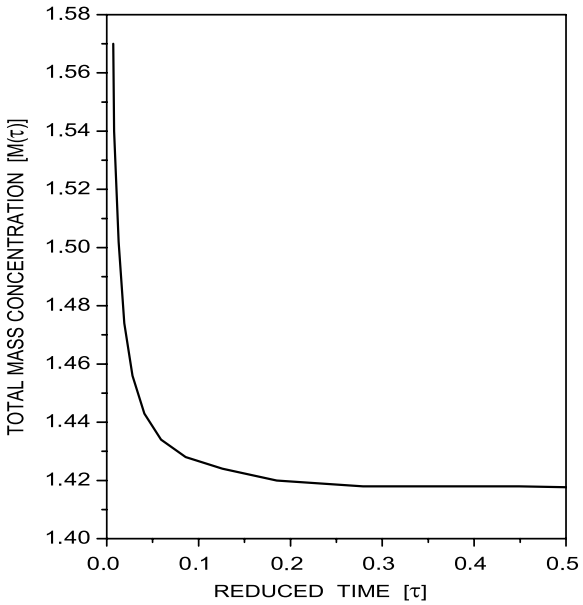


**Figure 2.** The dependence of the total mass concentration $M(\tau)$ of sol on the reduced time is $\tau = 2\sqrt{\pi G}(t - t_c)$.

with the initial condition $\xi(0) = \xi_0$, where $\xi_0$ is determined from the equation

$$\frac{1}{2\sqrt{\pi G}} \int_0^1 \frac{e^{\xi_0 x} - e^{\tilde{\xi} x}}{x^{3/2}} \, dx = M(t_c) - \tilde{M} = \frac{\pi}{2} - \sqrt{2}. \tag{20}$$

Equation (19) shows that $\xi(t)$ reaches its steady state during a very short time of order $t_c/\sqrt{G}$. On the other hand, as follows from equation (20) the value of $\xi_0$ is large (of order $\ln G$), but still much less than $G$. Equation (19) was solved numerically. The result is presented in figure 1. This solution was then used for calculating the total mass concentration of the sol fraction (see figure 2).

The main result of this study is the resolution of the paradox with the sharp jump between the sol and gel stages, where the total mass concentration of the sol state sharply drops down from the value $M(t_c) = \pi/2$ to $\tilde{M} = \sqrt{2}$. Now it has become clear that this jump has a very short finite duration.

As shown in my paper (Lushnikov 2006b), the sol spectrum becomes algebraic ($c_g \propto g^{-5/2}$) as the time approaches the critical value. After this two scenarios can be realized: either an active gel forms and the sol spectrum shrinks after the gel point or the spectrum remains algebraic and even modulated by the growing (with $g$) exponent. It is remarkable that the mass dependence of the steady-state spectrum coincides with that found for the case of free coagulation with passive gelation (see Lushnikov (2007a, 2007b) and references therein).

The mass of the gel fraction can be found from the mass balance, $M_{\rm gel} = t - M(t)$. After the short transient period, all mass produced by the source transfers to the gel whose mass grows with time linearly. The gel spectrum is readily found from equation (3). Its integration, as in the case of free coagulation, gives (see Lushnikov 2007a, 2007b)

$$c_g^+(\infty) = \frac{\exp[\xi(1+s)]}{\pi G^2} \frac{1-s}{(1+s)^2\sqrt{s}}(t - t_c). \tag{21}$$

Here, $s = (g - G)/G$.

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