Sol-gel transition in a source-enhanced coagulating system

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This paper considers the time evolution of disperse systems in which binary coagulation and a source of fresh particles govern the temporal changes to the particle mass spectra. The source is assumed to produce fresh particles at a constant rate. The Smoluchowski equation describing the time evolution of the particle mass spectrum is solved exactly for the coagulation kernel proportional to the product of masses of two coalescing particles. It is shown that after a critical time t_c a gel forms in the system and the sol spectrum becomes an algebraic function of the particle mass at $t=t_c$. It begins to shrink after the critical time due to the mass loss supporting the growth of the gel mass. The pre- and post-critical behavior of the mass spectrum and its integral characteristics (total particle number and mass concentrations) are investigated for the source productivity $I(g)$ dropping down algebraically with the particle mass g as $I(g) \propto g^{-\gamma}$. The critical particle mass spectrum is proved to be a universal function of g (it drops down as $g^{-5/2}$) if the third moment of $I(g)$ is finite ($\gamma > 4$). Otherwise ($3 < \gamma \leq 4$) this and other critical exponents begin to depend on α. Still the mass spectrum remains self-similar, i.e., it depends on a combination of g and t. At smaller γ the gelation process is shown to begin at $t=0$. All critical characteristics of the particle mass spectrum are determined for this case.

I. INTRODUCTION

Let us consider a system of disperse particles comprising $g_1, g_2, \ldots, g_k, \ldots$ monomeric units. This system is assumed to evolve with time due to the processes of coalescence: two colliding particles coalesce forming a daughter one with the mass equal to the total mass of two mother particles,

$$(l) + (m) \rightarrow (l+m). \tag{1}$$

Here (x) denotes a particle containing x monomeric units. This process is referred to as coagulation. The coagulating systems are described by the mass spectrum $c_g(t)$, the concentration of the particles comprising g monomers (g-mers). There is not a problem to write down the kinetic equation governing the time evolution of the particle mass spectrum,

$$\frac{dc_g}{dt} = I_g + \frac{1}{2}\sum_{l=1}^{g-1} K(g-l,l)c_{g-l}c_l - c_g\sum_{l=1}^{\infty} K(g,l)c_l. \tag{2}$$

This is the famous Smoluchowski's equation. Here the coagulation kernel $K(g,l)$ is the transition rate for the process given by Eq. (1). The term I_g on the right-hand side (RHS) of Eq. (2) is the rate of production of fresh particles of mass g. The second term describes the gain in the g-mer concentration $c_g(t)$ due to coalescence of $(g-l)$- and l-mers, while the last one is responsible for the losses of g-mers due to their sticking to all other particles. More details can be found in review articles [1,2] and books [3–5].

Although the role of coagulation processes is widely recognized and has been thoroughly discussed in just cited reviews and books, very little attention was given to the systems where not mere coagulation that forms the mass distribution of particles. In particular, the processes in which a source adds fresh particles in the coagulating system were

passed over in attention. Still such systems are also of great importance. It is enough to mention secondary atmospheric aerosols that form due to some intra-atmospheric chemical and photochemical processes producing tiny embryos. These embryos then grow by condensation and coagulation and give the life to larger aerosol particles (see, e.g., Ref. [5]). The source term always presents in the atmospheric aerosol models [5,6]. There are many other examples.

The steady-state regimes in source-enhanced coagulating systems were first considered in Refs. [7,8]. The generating function method of Ref. [9] had been used in Ref. [8] for a general analysis of the shape of steady-state mass spectra. The results of this work had been applied for explaining the nature of algebraic particle size distributions observed in the atmosphere. The self-preserving regimes of coagulation in the presence of a source of fresh particles were investigated in Ref. [10] and especially in Ref. [11] (see also references therein).

Already very long ago it became clear [12,13] that the Smoluchowski approach to the description of the kinetics of coagulation sometimes leads to a paradox: the total particle mass concentration ceases to conserve after a finite interval of time. The reason for this is now clear. The coagulation process can develop so swiftly that some objects invisible in the thermodynamic limit appear. Meanwhile, the Smoluchowski approach entirely relies upon the thermodynamic notion like g-mer concentrations. The situations where very large objects with zero (in the thermodynamic limit) concentration result from the coagulation process cannot be described within this classical approach. Still the kinetic equation (2) describes well the precritical behavior of the coagulating system and the kinetics of the sol part (i.e., the behavior of the mass spectrum of the particles with thermodynamically large population numbers) even after the critical time.

The Smoluchowski approach had been used many times for the description of the sol-gel transition in free (no source) coagulating systems [1,2,14]. Another approach based on a

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stochastic consideration [15] had been used by me [16–18] for a more consecutive and full analysis of the sol-gel transition. Overwhelming majority of the constructive results in studying the sol-gel transition had been obtained for the kernel proportional to the product of the masses of a pair of coalescing particles.

Only two attempts [19,20] to study the gelation in the source-enhanced coagulating systems with the kernel proportional to the product of masses of coalescing particles are known to me. Reference [19] contains the results (with no derivation and analysis) of the solution to Eq. (2) for initially monodisperse system. The author of Ref. [20] reported on a steady-state asymptotic behavior of the sol spectrum at the post-critical period.

In this paper a full analysis of the gelation transition is given for the coagulating system with the kernel

$$K(g,l) = \kappa g l \qquad (3)$$

starting with the Smoluchowski approach. Here κ is a dimensional constant.

Of course, it would be better to start with the stochastic approach of Refs. [15–18] that allows for a more complete reproduction of the picture, especially at the transition point. But if we sacrifice the vicinity of the transition point, then the Smoluchowski approach can be applied for determining all macroscopic characteristics of the coagulating system below and even above the transition point.

The paper is organized as follows. The next section introduces the basic equations describing the coagulation process in the presence of a spatially uniform source of fresh particles. We demonstrate that the use of the kernel given by Eq. (3) leads to a divergency of the second moment of the particle mass spectrum after a finite interval of time t_c. This effect is associated with the appearance of a gel at $t=t_c$. In this section two possible scenarios of gelation are discussed. The exact solution to the Smoluchowski equation is found in Sec. III for nonzero external source of particles and the coagulation kernel given by Eq. (3). To this end the Laplace transform of the particle mass spectrum is introduced. This step reduces the integrodifferential kinetic equation to a partial differential equation which is then solved exactly. The details of the solution are given in Appendix A. The asymptotic analysis of the solution performed in Sec. IV shows that the particle mass spectrum at the critical point displays the universal behavior $c_g(t_c) \propto g^{-5/2}$, exactly as in the case of free coagulation. The analysis of the sol-gel transition for sources slowly damping with the particle size ($I_g \propto g^{-\gamma}$) demonstrates that if the source has the divergent third moment, i.e., I_g damps as a power of the particle mass with the exponent γ within the interval $3 < \gamma < 4$, then the universality of the critical behavior breaks down and the critical exponent in the power dependence of the critical mass spectrum begins to depend on γ. For the sources with the divergent second moment ($2 < \gamma < 3$) the gelation begins at $t=0$. Section V discusses the time behavior of the total particle number and mass concentrations. It is demonstrated how the gel forms in the coagulating system. A short resume of the results and a further discussion of the sol-gel transition are given in the concluding Sec. VI.

II. BASIC EQUATION

In what follows we consider the integral version of the Smoluchowski equation with a steady-state source [it follows from Eq. (2) after replacing the sums with the integrals] and specify the kernel as $K(gl) = \kappa gl$. Instead of Eq. (2) we thus write

$$\partial_t c(g,t) = I(g) + \frac{\kappa}{2} \int_0^g (g-l) l c(g-l,t) c(l,t) \mathrm{d}l - \kappa M g c(g,t),$$

$$(4)$$

where $I(g)$ is the rate of production of fresh g-mers, $M = M(t) = \int_0^\infty g c(g,t) dg$ is the total mass concentration of the coagulating system.

Equation (4) should be supplemented with the initial condition. In what follows we apply the zero initial condition (no particles exist at $t=0$):

$$c(g,0) = 0. \qquad (5)$$

A. Gelation catastrophe

One expects that $M(t) = I_1 t$, where I_1 is the first moment of the source distribution. However, as we will see below, this equality holds only during a finite interval of time $t \le t_c$. After this moment $\int_0^\infty g c(g,t) dg < I_1 t$. Moreover, the second moment of the particle mass distribution diverges at $t=t_c$. Indeed, let us multiply both sides of Eq. (4) by g^2 and integrate over all g. We then come to the equation for the second moment of the particle mass spectrum $Q(t) = \int_0^\infty g^2 c(g,t) dg$,

$$d_t Q = I_2 + \kappa Q^2. \qquad (6)$$

Here I_2 is the second moment of $I(g)$. Other moments are defined as

$$I_s(t) = \int_0^\infty g^s I(g) dg. \qquad (7)$$

The solution to Eq. (6) is [$Q(0)=0$]

$$Q(t) = \sqrt{\frac{I_2}{\kappa}} \tan(t\sqrt{\kappa I_2}). \qquad (8)$$

The condition $Q(t_c)=\infty$ defines the position of the critical point,

$$t_c = \frac{\pi}{2\sqrt{\kappa I_2}}. \qquad (9)$$

This catastrophe is attributed to the appearance of a gel, an object that cannot be described within the scopes of the Smoluchowski approach. The desire to know what the gel could be is quite understandable and natural. The clear answer to this question had been given about three decades ago in Ref. [16]. The gel can be a single giant particle whose mass is comparable to the total mass of the whole coagulating system (active gel). This particle is not noticeable in the thermodynamic limit (its concentration is zero) but the mass is so large that it is able to affect the dynamics of the coagu-

lation process. The details may be seen in Refs. [17,18].

An alternative introduction of the gel uses truncated models of coagulating systems, where an upper cutoff mass G is introduced. The particles with masses exceeding G are assumed to be instantly removed from the system and to form a deposit whose spectrum stretches from G to $2G$. This deposit models the passive gel [21] as $G \to \infty$. It is essential to emphasize that the coagulation of the sol (a collection of particles with nonzero concentrations) can always be described by the Smoluchowski equation.

B. Scenarios of gelation

We will see in Sec. V that the mass spectrum found from Eq. (4) does not conserve the total mass concentration defined as $\int_0^\infty gc(g,t)dg$ (it should be equal to $I_1 t$) and a gel is introduced *by hand* for correcting this defect of the Smoluchowski theory. At this step it should be emphasized that the introduction of the gel is a rather artificial step which does not follow from the Smoluchowski equation. There are two methods for introducing the gel:

(i) The *active* gel is able to grow by coalescing with the sol particles. The mass concentration $M(t)$ in Eq. (4) includes then the mass of the gel,

$$M(t) = I_1 t = M_{sol}(t) + M_{gel}(t). \quad (10)$$

Here M_{gel} is the mass of the gel.

(ii) An alternative way for introducing the gel is to accept that the mass $M(t)$ entering Eq. (4) is the mass of the sol fraction alone,

$$M(t) = M_{sol}(t) = \int_0^\infty c(g,t)g\,dg. \quad (11)$$

The fact that $M_{sol}(t)$ drops down with time may be attributed to the formation of a gel, whose mass, however, does not appear in Eq. (4). Thus the gel does not affect actively the post-critical behavior of the sol mass spectrum (the *passive* gel). Nevertheless, the total mass concentration includes the mass hidden in the gel and remains equal to $I_1 t$.

In the pregelation period the definitions Eqs. (10) and (11) of the total mass concentration $M(t)$ coincide,

$$M(t) = \int_0^\infty c(g,t)g\,dg = I_1 t. \quad (12)$$

A more thorough discussion of this problem is left up to Sec. V. Both these scenarios had been discussed in Ref. [14] (see also earlier citations therein) for free coagulating systems. The present paper considers only the first scenario [Eq. (10)].

III. EXACT SOLUTION

For the Laplace transform of the mass spectrum

$$\mathcal{F}(p,t) = \int_0^\infty c(g,t)e^{-pg}dg \quad (13)$$

we have from Eq. (4),

$$\partial_t \mathcal{F}(p,t) = \mathcal{I}(p) + \frac{\kappa}{2}[\partial_p \mathcal{F}(p,t)]^2 + \kappa M(t)\partial_p \mathcal{F}(p,t), \quad (14)$$

where $\mathcal{I}(p)$ is the Laplace transform of the source function,

$$\mathcal{I}(p) = \int_0^\infty I(g)e^{-pg}dg. \quad (15)$$

For a constant growth rate of the total mass concentration the solution to Eq. (14) can be found in the form (the proof is given in Appendix A)

$$\mathcal{F}(p,t) = tA(\xi) - \int_p^\xi \sqrt{\frac{2}{\kappa}[A(\xi) - A(s)]}\,ds + Q(p,t), \quad (16)$$

where

$$A(p) = \mathcal{I}(p) + \dot{M}p, \quad (17)$$

$$Q(p,t) = -pM(t) - \frac{\kappa}{2}\int_0^t M^2(t')dt', \quad (18)$$

and the function $\xi = \xi(p,t)$ appearing in Eq. (16) is introduced in such a way that $\partial_\xi \mathcal{F}(p,t) = 0$. Hence

$$t = \frac{1}{\sqrt{\kappa}}\int_p^\xi \frac{ds}{\sqrt{2[A(\xi) - A(s)]}}. \quad (19)$$

This equation defines the function $\xi(p,t)$. The term Q does not contribute to the particle mass spectrum and serves only for normalization purposes [the function $\mathcal{F}(p,t)$ should reproduce correctly the particle mass and number concentrations].

Instead of $c(g,t)$ we can introduce

$$b(g,t) = gc(g,t). \quad (20)$$

The Laplace transform for $b(g,t)$ is readily expressed in terms of $\mathcal{F}$,

$$\mathcal{G}(p,t) = \int_0^\infty b(g,t)e^{-pg}dg = -\partial_p \mathcal{F}(p,t). \quad (21)$$

On differentiating Eq. (14) with respect to p yields the equation for $\mathcal{G}$,

$$\partial_t \mathcal{G} = \kappa(M - \mathcal{G})\partial_p \mathcal{G} - \mathcal{I}'. \quad (22)$$

The solution to this equation has the form

$$\mathcal{G}(p,t) = M(t) - \sqrt{\frac{2}{\kappa}[A(\xi) - A(p)]}. \quad (23)$$

This result immediately follows from Eqs. (16), (19), and (21).

We also introduce $\tau(\xi)$ as

$$\tau(\xi) = \frac{1}{\sqrt{\kappa}}\int_0^\xi \frac{ds}{\sqrt{2[A(\xi) - A(s)]}}. \quad (24)$$

Then Eq. (19) takes the form

$$t = \tau(\xi) - \frac{1}{\sqrt{\kappa}} \int_0^p \frac{ds}{\sqrt{2[A(\xi) - A(s)]}}. \qquad (25)$$

The function $\tau(\xi)$ plays an important role, for it defines the time dependence of $\xi(t,0) = \xi_0(t)$ playing the role of the order parameter in the sol-gel transition.

Equation (23) allows for restoring the particle mass spectrum,

$$c(g,t) = -\frac{1}{2\pi i g} \int_C \sqrt{\frac{2}{\kappa}[A(\xi(p,t)) - A(p)]} e^{pg} dp. \qquad (26)$$

As usual, the integration contour C in the complex plane p goes from $-i\infty$ to $i\infty$ and passes to the right of all singularities of the integrand.

IV. ASYMPTOTIC ANALYSIS

The singularities of the functions $\mathcal{F}$ or $\mathcal{G}$ nearest to $p=0$ in the complex plane p define the asymptotic behavior of the particle mass spectrum at large masses. We analyze these singularities starting with Eqs. (19) and (23). It is convenient to introduce

$$\tilde{A}(x) = A(x) - A(0) = \mathcal{I}(x) - I_0 + I_1 x. \qquad (27)$$

It is worthwhile to notice that $A(\xi) - A(x) = \tilde{A}(\xi) - \tilde{A}(x)$. Thus the spectrum given by Eq. (26) is independent of the first two moments I_0 and I_1.

In Appendix B I will show that at small p the function $\xi(p,t)$ (see Fig. 1) is also small, but much larger than p [see Eq. (B13)]. We thus can ignore $A(p)$ in expression (23) and rewrite the part of $\mathcal{G}(p,t)$ responsible for the asymptotic behavior of the particle mass spectrum as

$$\mathcal{G}(p,t) \approx -\sqrt{2\tilde{A}(\xi)/\kappa}. \qquad (28)$$

The constant term in Eq. (23) does not contribute to the mass spectrum.

In what follows we consider separately two different types of sources:

(i) The source producing only small particles $I(g) \leq Ag^{-(3+\alpha)}$ ($0 < \alpha \leq 1$), so at least three first moments I_0, I_1, and I_2 of the function $I(g)$ are finite (in what follows such sources are referred to as narrow sources). The expansion in s of $\tilde{A}(s)$ can be thus written as

$$\tilde{A}(s) = A(s) - I_0 = I_2 s^2/2\,! - a_\alpha s^{2+\alpha} + \cdots. \qquad (29)$$

Here a_α is a constant. The generating function in this case is approximated as

$$\mathcal{G}(p,t) \approx -\sqrt{2\tilde{A}(\xi)/\kappa} \approx -\xi(p,t)\sqrt{I_2/\kappa}. \qquad (30)$$

Because the second moment I_2 is finite, gelation begins after a finite moment of time given by Eq. (9).

(ii) The source with a more flat algebraic tail $I(g) \leq Ag^{-(2+\alpha)}$ ($0 < \alpha < 1$) (wide source, in what follows). Such the source has the divergent second moment. Thus, according to Eq. (9), the gelation begins from the very outset of the coagulation process. In this case,
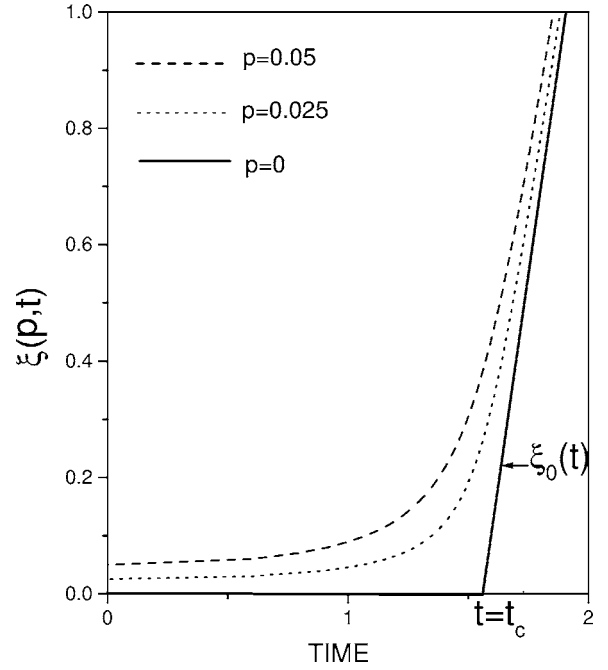

FIG. 1. The dependence of the function $\xi(p,t)$ on time. It is seen that as $p \to 0$ the curves approach to their limiting dependence $\xi_0(t)$. The latter function plays the role of an order parameter in the sol-gel transition. It remains zero at the precritical period $t < t_c$. Calculations are done for initially monodisperse particles. Here time is measured in units of $(\kappa I_2)^{-1/2}$. The function $\xi(p,t)$ is dimensionless.

$$\tilde{A}(s) = A(\xi) - I_0 = b_\alpha s^{1+\alpha} + \cdots. \qquad (31)$$

The approximate generating function in this case looks as follows:

$$\mathcal{G}(p,t) \approx -\sqrt{\frac{2\tilde{A}(\xi)}{\kappa}} \approx -[\xi(p,t)]^{(1+\alpha)/2}\sqrt{\frac{2b_\alpha}{\kappa}}. \qquad (32)$$

A. Narrow source

Here we consider the case, where the second moment of $I(g)$ is finite but the third one diverges. In this case the equation for $\xi(p,t)$ is derived in Appendix B [Eq. (B12)] and has the form

$$R\xi^{1+\alpha} - \tau\xi - p = 0, \qquad (33)$$

where $\tau = (t - t_c)/t_c$ and R is a constant defined by Eq. (B10). The solution to Eq. (33) can be expressed in terms of a universal function $z(x)$,

$$\xi(p,t) = (|\tau|/R)^{1/\alpha} z\left(\frac{pR^{1/\alpha}}{|\tau|^{(\alpha+1)/\alpha}}\right). \qquad (34)$$

The function $z(x)$ meets the equation

$$z^{1+\alpha} - \mathrm{sgn}(\tau)z - x = 0, \qquad (35)$$

where, as usual, $\mathrm{sgn}(\tau) = 1$ for positive τ and $\mathrm{sgn}(\tau) = -1$ otherwise.

Once the function $z(x)$ is known, the inversion theorem yields the mass spectrum,

$$c(g,\tau) = \frac{|\tau|^{1/\alpha}}{R^{1/\alpha} g_0 g} \sqrt{\frac{I_2}{\kappa}} Z\left(\frac{g}{g_0}\right), \qquad (36)$$

with $z(x)$ being the Laplace transform of $Z(s)$. Equation (34) defines the characteristic mass $g_0 = g_0(\tau)$,

$$g_0(\tau) = R^{1/\alpha} |\tau|^{-(1+\alpha)/\alpha}. \qquad (37)$$

Putting $p = 0$ in Eq. (33) yields the time dependence of the order parameter,

$$\xi_0(\tau) = \xi(p,0) = R^{-1/\alpha} |\tau|^{1/\alpha}. \qquad (38)$$

At $\tau < 0$ Eq. (33) has only the zero solution $\xi_0 = 0$.

Let us investigate the postcritical behavior ($\tau > 0$) of the mass spectrum. To this end we find the solution to Eq. (35) in the limit of small x. We apply the iterative procedure $z_{k+1}^{1+\alpha} = z_k + x$ with $z_0 = 1$ [this is the solution of Eq. (35) at $x = 0$]. The first approximation is enough for our purposes,

$$z(x) = (1+x)^{1/(1+\alpha)}. \qquad (39)$$

It is not difficult to restore the postcritical mass spectrum,

$$c(g,\tau) \propto g^{-(3+2\alpha)/(1+\alpha)} e^{-g/g_0(\tau)}. \qquad (40)$$

It is important to notice that the proportionality coefficient in this equation is independent of τ. In deriving Eq. (40) we use the Laplace inversion of p^γ,

$$p^\gamma \doteq \frac{\sin[\pi(\gamma+1)]}{\pi} \Gamma(\gamma+1) g^{-(\gamma+1)}. \qquad (41)$$

This formula will be of use in our further analysis.

At $\tau < 0$ (the precritical stage) we investigate the structure of the singularity starting with Eq. (33) and assuming that $|\tau|\xi \ll p$. We solve this equation by iterations taking $\xi = (p/R)^{1/(1+\alpha)}$ as the starting approximation.

The second iteration gives the final result,

$$\xi(p,\tau) \approx p^{1/(1+\alpha)} - \frac{\tau p^{(1-\alpha)/(1+\alpha)}}{(1+\alpha) R^{1/(1+\alpha)}}. \qquad (42)$$

Applying Eqs. (41) and (36) yields the asymptotic mass spectrum,

$$c(g,\tau) \propto g^{-(3+2\alpha)/(1+\alpha)} [1 - \mu(\alpha)(g/g_0)^{\alpha/(1+\alpha)}]$$
$$\approx g^{-(3+2\alpha)/(1+\alpha)} \exp\{-\mu(\alpha)[g/g_0(\tau)]^{\alpha/(1+\alpha)}\}, \quad (43)$$

where after a tedious algebra we find

$$\mu(\alpha) = \frac{\Gamma[2/(1+\alpha)]}{\Gamma[1/(1+\alpha)]} \frac{\sin[\pi(1-\alpha)/(1+\alpha)]}{\sin[\pi/(1+\alpha)]}. \qquad$$

The coefficient $\mu(\alpha) = 0$ at $\alpha = 1$. But in this case Eq. (33) is solved analytically. The result is

$$\xi(p,\tau) = \frac{1}{2}(\sqrt{\tau^2 + 4p} + \tau). \qquad (44)$$

The order parameter is

$$\zeta_0(\tau) = \frac{1}{2}(|\tau| + \tau). \qquad (45)$$

At $\tau < 0$ the order parameter is equal to zero, as should it be.

Equation (45) allows for restoring the particle mass spectrum in pre- and postgelation period,

$$c(g,t) \approx \frac{\sqrt{3}}{2} \frac{I_2}{\sqrt{\pi\kappa I_3}} g^{-5/2} e^{-g/g_0(t)} \propto g^{-5/2} e^{-g/g_0(t)}, \quad (46)$$

where

$$g_0(t) = \frac{4I_3}{3I_2} \frac{1}{\cos^2(t\sqrt{\kappa I_2})} \approx \frac{4I_3}{3\kappa I_2^2} \frac{1}{(t-t_c)^2} \propto \frac{1}{\tau^2}. \quad (47)$$

Here instead of the coefficient a_1 we introduced the third moment $I_3 = 3! a_1$.

B. Wide sources

If the second moment I_2 diverges, the gel formation begins at $t = 0$. There is no pregelation stage in this case. As follows from Eq. (B18) of Appendix B

$$\xi_0(t) = (t\sqrt{b_\alpha \kappa}/c_\alpha)^{2/(1-\alpha)}. \qquad (48)$$

The Laplace transform of the asymptotic particle mass spectrum is given by Eq. (B20),

$$\xi(p,t) \approx \xi_0(t)\left(1 + \frac{p}{c_\alpha \xi_0(t)}\right)^{2/(1-\alpha)}. \qquad (49)$$

The spectrum corresponding to this $\xi(p,t)$ has the form [see Eq. (32)]

$$c(g,t) \propto t^{(1+\alpha)/(1-\alpha)} g^{-(3-\alpha)/(1-\alpha)} e^{-g/g_0(t)}, \qquad (50)$$

where

$$g_0(t) = c_\alpha \xi_0(t). \qquad (51)$$

V. RESULTS AND DISCUSSION

A. Pregelation stage

Multiplying both sides of Eq. (4) by g and integrating over all g gives

$$\dot{M} = I_1 \quad \text{or} \quad M = I_1 t, \qquad (52)$$

i.e., in the pregelation period the total mass concentration grows linearly with time. This result is quite natural. Next, on integrating Eq. (4) over all g yields the equation for the particle number concentration

$$\dot{N} = I_0 - \frac{\kappa}{2} M^2, \qquad (53)$$

where $N(t) = \int_0^\infty c(g,t) dg$. Equation (13) gives in the pregelation period ($t < t_c$)

$$N(t) = I_0 t - \frac{\kappa}{6} I_1^2 t^3. \qquad (54)$$

One sees that $N(t)$ could become negative at $t > t_N = \sqrt{6I_0/\kappa I_1^2}$. This, however, never happens, for $t_N > t_c$ or, after some trivial algebra $\pi I_1/2\sqrt{6} < \sqrt{I_0 I_2}$. Indeed, $I_0 I_2 \geq I_1^2$ which immediately follows from the inequalities $\int_0^\infty (k$

$-l)^2 I(k)I(l)dkdl \geq 0$ and $I(x) \geq 0$. Below we will see that at $t \geq t_c$ the expression for $N(t)$ and $M(t)$ differ from those given by Eqs. (52) and (54).

If the three first moments of the source function $I(g)$ are finite, then as is seen from Eq. (46), the mass spectrum in the pregelation stage grows wider with time. In the vicinity of the critical point t_c it repeats the shape of the spectrum found for free coagulating system with the product kernel

$$c(g,t) \propto g^{-5/2} e^{-g/g_0}. \qquad (55)$$

At the critical point this spectrum drops down with the particle mass as $g^{-5/2}$, as in the case of free coagulation. As is seen from Eq. (46), the coefficient before $g^{-5/2}$ depends on the second and third moments I_2 and I_3 of the source rate distribution $I(g)$ and is independent of I_1 and I_0.

If the third moment of $I(g)$ diverges, then the precritical mass spectrum is given by Eq. (43),

$$c(g,\tau) \propto g^{-(3+2\alpha)/(1+\alpha)} \exp\{-\mu(\alpha)[g/g_0(\tau)]^{\alpha/(1+\alpha)}\}, \quad (56)$$

with $\mu(\alpha)=0$ at $\alpha=1$. The critical mass spectrum now is no longer universal and depends on the exponent α,

$$c(g,\tau) \propto g^{-(3+2\alpha)/(1+\alpha)}. \qquad (57)$$

It is interesting to notice that the critical exponents in Eqs. (55) and (56) defining the g dependence of the particle mass spectrum at the critical point coincide with those for free coagulation (see Ref. [2] and especially Appendix L of that paper). This fact is not so unexpected, because the partial differential equations for the Laplace transforms of the particle mass spectra are very similar in both these cases. The source term $\mathcal{I}(p)$ in Eq. (14) does not define the type of the singularity at $p=0$, if it is not very singular itself.

B. Postgelation stage

At the postgelation stage the situation drastically changes. The total particle mass concentration ceases to conserve. As follows from Eqs. (21) and (23)

$$M(t) = \mathcal{G}(0,t) = I_1 t - \sqrt{\frac{2}{\kappa}\{A[\xi_0(t)] - I_0\}}. \qquad (58)$$

The deficit of mass is attributed to the appearance of a gel. In Refs. [16–18] this gel is associated with a giant particle whose mass is comparable to the total mass of the whole system but the concentration is zero. This gel consumes the mass of the sol. Therefore in the thermodynamic limit we observe the mass loss. The dependence of the sol mass concentration on time is shown in Fig. 2.

The expression for the total number concentration also changes at the postgelation period,

$$N(t) = \mathcal{F}(0,t) = tA(\xi_0) - \int_0^{\xi_0} \sqrt{\frac{2}{\kappa}[A(\xi_0) - A(s)]}ds - \frac{\kappa}{6}I_1^2 t^3. \qquad (59)$$

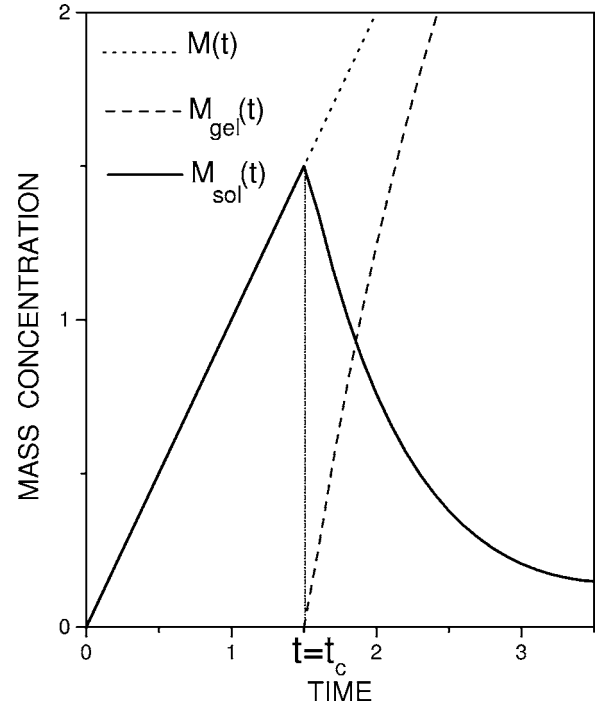On differentiating Eq. (59) over t we find

FIG. 2. Mass concentration vs time for initially monodisperse particles. Thick solid line displays the time dependence of the total sol mass concentration. This mass is seen to begin drop down with time after the critical time. Still no violation of the mass conservation is observed, for the gel mass (dashed line) is equal to the difference between $I_1 t$ and the sol mass. Mass concentration and time are given in units of $\sqrt{I_2/\kappa}$ and $(\kappa I_2)^{-1/2}$, respectively.

$$\dot{N} = A(\xi) - \frac{\kappa}{2}I_1^2 t^2 = I_0 - \frac{\kappa}{2}I_1^2 t^2 + \frac{\kappa}{2}M_{gel}^2, \qquad (60)$$

where

$$M_{gel} = \sqrt{\frac{2}{\kappa}\{A[\xi_0(t)] - I_0\}} \qquad (61)$$

is the mass of the gel. The dependence of the total particle number concentration is shown in Fig. 3.

For narrow sources (I_3 exists) the postcritical mass spectrum is given by Eq. (40). This equation holds also at $\alpha=1$. In the postcritical period this spectrum shrinks with time [the value of $g_0(\tau)$ decreases as τ increases].

If the third moment does not exist the mass scale g_0 depends on time as a power depending on α,

$$g_0(\tau) \propto |\tau|^{-(1+\alpha)/\alpha}, \qquad (62)$$

and $g_0 \propto \tau^{-2}$ otherwise. Similarly, the time dependence of the order parameter is also algebraic,

$$\xi_0(\tau) \propto |\tau|^{1/\alpha}. \qquad (63)$$

The dependence on α disappears if the third moment of the source is finite.

If the second moment I_2 diverges, the gel formation begins at $t=0$. There is no a pregelation stage. As follows from Eq. (B18) of Appendix B
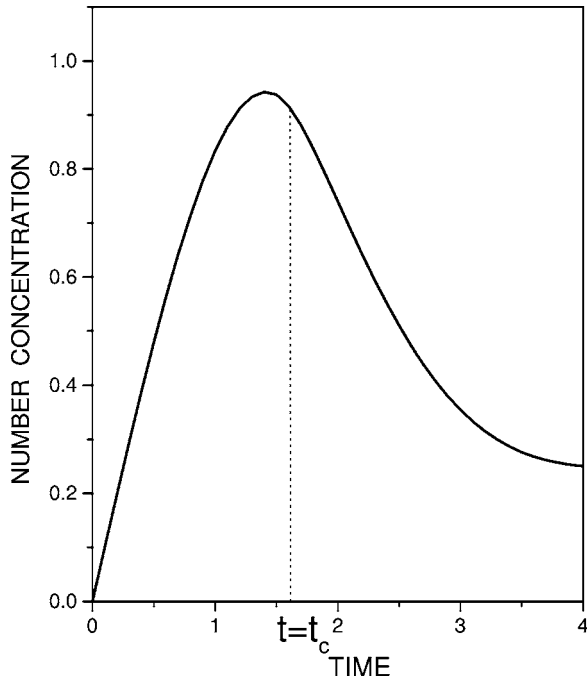
FIG. 3. Number concentration vs time for initially monodisperse particles. The gel does not contribute to $N(t)$, for its concentration in the thermodynamic limit is zero. The units are the same as in Fig. 2.

$$\xi_0(t) \propto t^{2/(1-\alpha)}. \tag{64}$$

The spectrum has the form

$$c(g,t) \propto t^{(1+\alpha)/(1-\alpha)} g^{-(3-\alpha)/(1-\alpha)} e^{-g/g_0(t)}, \tag{65}$$

where

$$g_0(t) = c_\alpha \xi_0(t). \tag{66}$$

VI. CONCLUSION

In this paper a "pathological" coagulating system has been considered, i.e., the system whose development in time leads to the formation of an object that is not provided for by the initial theoretical assumptions. In our case it is the gel whose appearance breaks the hypothesis that the kinetics of coagulation can be described in terms of the particle number concentrations defined as the thermodynamic limit of the ratio (occupation numbers)/volume.

The source-enhanced coagulating system with the kernel proportional to the product of the masses of two colliding particles has been the central object of the present study. The main decisive step that has been done in this paper is the analytical solution of the equation for the Laplace transform of the particle mass spectrum. The knowledge of the functions $\mathcal{F}(p,t)$ and its derivative $\mathcal{G}(p,t)$ has given the full information on the time behavior of the number and mass concentration in pre- and postgel periods and to find the expression for the critical time. The asymptotic analysis of the properties of $\mathcal{G}(p,t)$ has allowed us to investigate the shape of the particle mass spectrum near the critical point.

Only one scenario of gelation has been considered here. We assumed that as in the case of free coagulation the gel appears as one giant particle with the mass comparable to the mass of the sol. The gel concentration is zero in the thermodynamic limit, but it affects the dynamics of the sol evolution (see Refs. [16–18]).

The second (and the most widespread) scenario assumes that after the critical time the coagulation process instantly transfers large sol particles to a gel state, the latter being defined as an infinite cluster. This gel can be either passive (it does not interact with the coagulating particles) or active (coagulating particles can stick to the gel) [12–14]. In the latter case the gel should be taken into account in the mass balance and no paradox with the loss of the total mass comes up [14].

Still neither this definition nor the postgel solution to the Smoluchowski equation give a clear answer to the question, what is this, the gel?

The situation becomes more clear if one considers a class of so-called truncated models (see Refs. [2,21]). In these models a cutoff particle mass G is introduced. The truncation is treated as an instant sink removing very heavy particles with the masses $g > G$ from the system. So we have sacrificed with the mass conservation from the very beginning. The particles whose mass exceeds G form a deposit (gel) and do not contribute to the mass balance. Of course, the total mass of the active particles+deposit conserves. The time evolution of the spectrum of active particles (with masses $g < G$) is described by the Smoluchowski equation as before, with the limit ∞ in the loss term being replaced with the cutoff mass G. The set of kinetic equations then becomes finite and no a catastrophe is expected to come up. The solution of the Smoluchowski equation with the external source of particles for this scenario remains a hard nut.

APPENDIX A: EXACT GENERATING FUNCTION

For the Laplace transform of the mass spectrum

$$\mathcal{F}(p,t) = \int_0^\infty c(g,t) e^{-pg} dg \tag{A1}$$

we have from Eq. (3)

$$\partial_t \mathcal{F}(p,t) = \mathcal{I}(p) + \frac{\kappa}{2}[\partial_p \mathcal{F}(p,t)]^2 + \kappa M(t)\partial_p \mathcal{F}(p,t), \tag{A2}$$

where $\mathcal{I}(p)$ is the Laplace transform of the source function,

$$\mathcal{I}(p) = \int_0^\infty I(g) e^{-pg} dg. \tag{A3}$$

The solution to Eq. (A1) can be found in the form

$$\mathcal{F}(p,t) = tA(\xi) - \int_p^\xi \sqrt{\frac{2}{\kappa}[A(\xi) - A(s)]} ds + Q(p,t), \tag{A4}$$

where $\xi = \xi(p,t)$ is defined from the equality

$$t = \int_p^\xi \frac{ds}{\sqrt{2\kappa[A(\xi) - A(s)]}}, \qquad \text{(A5)}$$

and the functions $A(p)$ and $Q(p,t)$ are not yet specified. The function $\xi = \xi(p,t)$ which appeared first in Eq. (A4) is introduced in such a way that the partial derivative of the RHS of Eq. (4) with respect to ξ would be zero. Keeping this fact in mind we can find $Q(p,t)$ by differentiating both sides of Eq. (A4) with respect to p and t and substituting the results into Eq. (A2). We have

$$\partial_t \mathcal{F}(p,t) = A(\xi) + \partial_t Q \qquad \text{(A6)}$$

and

$$\partial_p \mathcal{F}(p,t) = \sqrt{\frac{2}{\kappa}[A(\xi) - A(p)]} + \partial_p Q. \qquad \text{(A7)}$$

On substituting Eq. (A4) into Eq. (A2) yields

$$\partial_t Q = \mathcal{I} + \frac{\kappa}{2}(\partial_p Q)^2 + \partial_p Q \sqrt{2\kappa[A(\xi) - A(p)]} + M(t)$$

$$\times \{\sqrt{2\kappa[A(\xi) - A(p)]} + \kappa \partial_p Q\}. \qquad \text{(A8)}$$

In order to get rid of $\sqrt{2\kappa[A(\xi) - A(p)]}$ we should put

$$\partial_p Q + M(t) = 0 \quad \text{or} \quad Q = -pM(t) + C(t). \qquad \text{(A9)}$$

The remainder of Eq. (A8) gives

$$-\dot{M}p + \dot{C} = \mathcal{I}(p) - A(p) - \frac{\kappa}{2}M^2. \qquad \text{(A10)}$$

From this equation we find

$$\dot{C} = -\frac{\kappa}{2}M^2 \quad \text{and} \quad A(p) = \mathcal{I}(p) + \dot{M}p. \qquad \text{(A11)}$$

Next, $\dot{M}$ should be independent of time, i.e., the above consideration works only for steady-state sources. Finally we have

$$C(t) = -\frac{\kappa}{2}\int_0^t M^2(t')dt'. \qquad \text{(A12)}$$

Collecting Eqs. (A9) and (A12) yields

$$Q(p,t) = -pM(t) - \frac{\kappa}{2}\int_0^t M^2(t')dt'. \qquad \text{(A13)}$$

The term Q does not contribute to the particle mass spectrum and serves only for normalization purposes [the function $\mathcal{F}(p,t)$ should reproduce correctly the particle mass and number concentrations].

APPENDIX B: EVALUATION OF INTEGRAL IN EQ. (19)

Here we evaluate the integral in Eq. (19) at small p and ξ. Let

$$J(\xi,p) = \int_p^\xi \frac{ds}{\sqrt{2[\tilde{A}(\xi) - \tilde{A}(s)]}}. \qquad \text{(B1)}$$

Here $\tilde{A}(s) = \mathcal{I}(s) - I_0 + I_1 s$. Below we consider separately narrow and wide sources.

1. Narrow sources

In evaluating the integral Eq. (B1) it is convenient to introduce the new integration variable y as

$$2\tilde{A}(s) = y^2, \quad \tilde{A}'(s)ds = ydy. \qquad \text{(B2)}$$

In these variables the function $J(\xi,p)$ takes the form

$$J(\xi,p) = \int_{\sqrt{2\tilde{A}(p)}}^{\sqrt{2\tilde{A}(\xi)}} \frac{ydy}{\tilde{A}_s'[s(y)]\sqrt{2\tilde{A}(\xi) - y^2}}. \qquad \text{(B3)}$$

Let us expand the ratio $y/A'[s(y)]$ over y. First of all, we notice that at small s

$$\tilde{A}'(s) \approx I_2 s - (2 + \alpha)a_\alpha s^{1+\alpha}. \qquad \text{(B4)}$$

The function $s(y)$ is defined from the approximate equation

$$I_2 s^2 - 2a_\alpha s^{2+\alpha} = y^2. \qquad \text{(B5)}$$

In the limit of small y we find

$$s(y) = \frac{y}{\sqrt{I_2}} + \frac{a_\alpha}{I_2^{(3+\alpha)/2}}y^{1+\alpha}. \qquad \text{(B6)}$$

Hence

$$\tilde{A}'[s(y)] = y\sqrt{I_2} - \frac{(1+\alpha)a_\alpha}{I_2^{(1+\alpha)/2}}y^{1+\alpha}, \qquad \text{(B7)}$$

and finally we have

$$\frac{y}{A'[s(y)]} \approx \frac{1}{\sqrt{I_2}} + \frac{(1+\alpha)a_\alpha}{I_2^{(3+\alpha)/2}}y^\alpha. \qquad \text{(B8)}$$

Everywhere below we use the approximations $p, \xi \ll 1$ and $\xi \gg p$. At small argument $\tilde{A}(s) \approx s\sqrt{I_2/2}$. Thus

$$J(\xi,p) \approx \frac{1}{\sqrt{I_2}}\arccos(p/\xi) + \frac{R}{\sqrt{I_2}}\xi^\alpha, \qquad \text{(B9)}$$

where

$$R = \frac{(1+\alpha)a_\alpha}{I_2}\int_0^1 \frac{x^\alpha dx}{\sqrt{1-x^2}}. \qquad \text{(B10)}$$

On taking cosine of both parts of Eq. (B9) and applying our convention on smallness of arguments we come to the following equation for ξ:

$$R\xi^{1+\alpha} + \xi\cos(t\sqrt{\kappa I_2}) - p = 0. \qquad \text{(B11)}$$

In the vicinity of the critical time we approximate $\cos(t\sqrt{\kappa I_2}) \approx \tau$, with $\tau = (t - t_c)/t_c$, then we come to the result

$$R\xi^{1+\alpha} - \tau\xi - p = 0. \qquad \text{(B12)}$$

At the critical point $\tau=0$ one finds

$$\xi(p,t_c) = (p/R)^{1/(1+\alpha)}. \tag{B13}$$

By the way, this result is the reason why we adopted the approximation $\xi \gg p$, at small p.

At $p=0$ Eq. (B11) yields at $\tau>0$ (after the sol-gel transition)

$$\xi_0(t) = (\tau/R)^{1/\alpha}. \tag{B14}$$

2. Wide sources

Here we consider the case when the second moment of $I(g)$ diverges, i.e., the critical time is zero and the gel appears from the outset of the coagulation process. In this case $\widetilde{A}$ is given by Eq. (31). Then

$$J(\xi,p) = \frac{1}{\sqrt{2b_\alpha}} \xi^{(1-\alpha)/2} \int_{p/\xi}^{1} \frac{dx}{\sqrt{1-x^{1+\alpha}}}. \tag{B15}$$

In the limit $\xi \gg p$ we find from Eq. (19)

$$\tau = \xi^{(1-\alpha)/2}\left(c_\alpha - \frac{p}{\xi}\right). \tag{B16}$$

Here we introduced the notation $\tau=t\sqrt{b_\alpha \kappa}$ and $c_\alpha=\int_0^1(1-x^{1+\alpha})^{-1/2}dx$. Equation (B16) defines the function $\xi(p,t)$. It can be solved by iterations. As the first approximation we adopt

$$\tau = c_\alpha \xi_0^{(1-\alpha)/2}. \tag{B17}$$

Hence

$$\xi_0 = (\tau/c_\alpha)^{2/(1-\alpha)}. \tag{B18}$$

The second approximation then gives

$$\tau = \xi_1^{(1-\alpha)/2}(c_\alpha - p/\xi_0). \tag{B19}$$

From this equation we finally get

$$\xi_1(p,\tau) \approx \xi_0(\tau)\left(1 + \frac{p}{c_\alpha \xi_0(t)}\right)^{2/(1-\alpha)}. \tag{B20}$$

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