# Critical behavior of the particle mass spectra in a family of gelling systems

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The critical and post-critical behavior of coagulating systems, where the coagulation efficiency grows with the masses of colliding particles $g$ and $l$ as $K(g,l)=0.5(g^{\alpha}l^{\beta}+g^{\beta}l^{\alpha})$, $\lambda=\alpha+\beta>1$, $\mu=|\alpha-\beta|<1$ is studied. The instantaneous sink that removes the particles with masses exceeding $G$ is introduced which allows one to describe the coagulation kinetics by a finite set of equations and define the gel as the deposit of particles with masses between $G+1$ and $2G$. This system displays the critical behavior (the sol-gel transition) in the limit $G\to\infty$ if $\lambda=\alpha+\beta>1$. The exact post-critical particle mass spectrum is shown to be an algebraic function of $g$ times a *growing* exponent. All critical parameters of the systems are determined as the functions of $\alpha$ and $\beta$.

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## I. INTRODUCTION

The phenomenon of coagulation is well familiar to everyone who encountered physics and chemistry of fractals [1], polymer formation [2,3], cloud physics [4–6], kinetics of nanoaerosol systems [1,4,6], boiling liquids [7], theories of planet formation [8], and even formation of traffic jams [9,10]. Theory of coagulation deals with the systems of particles that can coalesce thus producing larger and larger objects. The process continues until the moment when only one particle with the mass equal to the total mass of all particles remains in the system.

From the first sight it seems that sufficiently power computers are able to help to resolve any problem related to coagulation. Not all, however, is so cloudless. The point is that almost all existing theories describe the thermodynamically large systems, i.e., the systems in which the population numbers of the objects with a given property (let it be the particle mass) go to infinity together with the total volume of the system in such a way that their ratio remains finite. This thermodynamic consideration thus ignores the particles whose population numbers grow slower than the volume. Meanwhile, these low populated objects can seriously exert the behavior of the whole coagulating system [11].

The equation describing the time evolution of the particle mass spectrum was derived almost a century ago by Smoluchowski [12] and since then was studied by many authors in very diverse aspects, beginning with the direct applications of this equation to modeling the formation of aerosol hazes in the atmosphere and ending with the studies of rather delicate questions on the existence of the solution to this equation.

In spite of considerable efforts to attack the Smoluchowski equation theoretically and numerically (see recent review papers [13,14]) many aspects of the coagulation process remained in the shadow. Among them the fact that sometimes the coagulation process leads to gelation—the formation of giant objects with zero concentrations in the thermodynamic limit. I will try to explain in a few words what this means.

Let us consider a system of $N$ 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. This process is commonly referred to as coagulation. Symbolically it can be presented as a chain of irreversible binary chemical reactions

$$(g)+(l)\to(g+l). \tag{1}$$

Here $g$ and $l$ are the masses of colliding particles measured in units of a monomeric mass, i.e., the integers $g$ and $l$ are the numbers of monomers in the particles. The rate $K(g,l)$ of the process given by Eq. (1) (the coagulation kernel) is supposed to be a known homogeneous function of its arguments [4,5,15,16], i.e.,

$$K(ag,al)=a^{\lambda}K(g,l). \tag{2}$$

From the first sight the coagulation process looks absolutely offenseless. The particles coalesce producing new, larger ones. It is difficult to imagine that such simple phenomenon is able to lead to something unusual. And nevertheless it does. At $\lambda>1$ the coagulating systems experience the sol-gel transition, i.e., they separate into sol and gel fractions after a finite interval of time $t_c$ (see, e.g., review papers [13,14] and references therein). The sol part is a collection of $g$-mers whose concentrations $c_g(t)$ are the solutions to the kinetic equation of the process Eq. (1). Less clear is how to introduce the gel. It does not appear in the kinetic equation explicitly and only can be detected by the behavior of the sol mass which begins to drop down with time after $t=t_c$. The sol is considered to transfer a part of its mass to the gel whose mass begins to grow with time after $t=t_c$, although we see no gel in our equations.

Three scenarios of the sol-gel transition were proposed. The first scenario (see review paper [14] and references therein) considers the coagulation process going in a system of a finite number $M$ of monomers enclosed in a finite volume $V$. I will not discuss this scenario here.

The second (commonly accepted [3,13,15]) scenario assumes that after the critical time the coagulation process instantly transfers large particles to a gel state, the latter being an undefined object. In this case some interesting results were found by using the scaling hypothesis [3,13].

The third approach proposed more than two decades ago [17,18] (see also [14]) considers the coagulating systems with instantaneous sink of large particles, the particles with masses $g$ exceeding a cutoff mass $G$ being considered as a passive deposit. These particles do not interact with coagulating sol particles. The Smoluchowski equation thus reduces to a finite set of first-order differential equations which presumably cannot lead to the sol-gel catastrophe and allow therefore an analysis of the situation by permitting $G$ to go to infinity. This model was applied in [17,18] for the analysis of the sol-gel transition in the exactly solvable model with the coagulation kernel proportional to the product of masses of coalescing particles. It was found that the sol-gel transition reveals itself in the specifics of the evolution of the total particle mass concentration. The latter is conserved until the critical time and then almost abruptly (in the limit $G\to\infty$ abruptly) changes its regime. It begins to drop down as reciprocal time. In parallel the deposit begins to form.

Recently I discovered that the method used in these ancient works [16,17] can be applied to more general kernels [19] $K(g,l)=g^\alpha l^\alpha$. The present paper reports on the results that are applicable to a wider class of coagulation kernels leading to the sol-gel transition $K(g,l)\propto g^\alpha l^\beta+g^\beta l^\alpha$.

The remainder of the paper is organized as follows. The next section formulates the kinetic equation describing the coagulation process (the Smoluchowski equation), initial condition to it, and introduces the model coagulation kernels. A method for the solution of this equation proposed in Ref. [20] is described in Sec. III. A very important identity that proves $1/t$ dependence of the monomer number concentration is derived at the end of this section. This very identity allows for finding the critical times, where the sol-gel transition occurs. Section IV briefly reproduces the exact solution for the kernel $K(g,l)=gl$. The post-critical behavior of the sol spectrum is analyzed in Sec. V. The analysis is grounded on the idea of coherent behavior of the post-gel spectrum, i.e., the time dependence appears as a multiplier independent of the particle mass in the expression for the post-critical sol spectrum. The gel spectrum is also found together with the critical times. The mass spectrum in the vicinity of the transition point is investigated and the kinetics of formation of the gel spectrum is discussed. Section VI summarizes and discusses the results. This section also emphasizes that no indefinite proportionality coefficients appears in the asymptotic results presented in this paper. Concluding Sec. VII resumes the results. Two Appendixes introduce the reader to some technical details related to fractional differentiation of algebraic functions (Appendix A) and the details of the numerical procedure allowing for determining the critical times (Appendix B).

## II. BASIC EQUATIONS

Our starting point is the truncated Smoluchowski's equation describing the coagulating particles whose masses are limited with a maximal (cutoff) mass $G$. This truncated model is well adapted for considering the coagulation processes in the system with a sink that instantly removes the particles with the masses exceeding $G$ [14,17,18]. The truncated Smoluchowski equation can be written as follows:

$$\frac{dc_g(t)}{dt}=\frac{1}{2}\sum_{l=1}^{g-1}K(g-l,l)c_{g-l}(t)c_l(t)-c_g(t)\sum_{l=1}^{G}K(g,l)c_l(t). \tag{3}$$

Here $c_g(t)$ is the particle mass spectrum, the number concentration of the particles comprising exactly $g$ monomeric units at time $t$. The first term on the right-hand side of this equation describes the gain of $g$-mers due to reaction $(g-l)+(l)\to(g)$. The second term is responsible for $g$-mer losses by their sticking to all other particles. This second term contains the cutoff mass $G$, 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. Its mass spectrum is described by the following equation:

$$\frac{dc_g^+(t)}{dt}=\frac{1}{2}\sum_{l=g-G}^{G}K(g-l,l)c_{g-l}(t)c_l(t). \tag{4}$$

In Eqs. (3) and (4) the dimensionless units are used, i.e., the concentrations are measured in units of the initial particle concentration $c_1(0)$, and the unit of time is $1/K(1,1)c_1(0)$. The initial condition to Eq. (3) is chosen in the form

$$c_g(t=0)=\delta_{g,1}. \tag{5}$$

Here $\delta_{g,l}$ is the Kroneker delta which means that the coagulation process starts with a set of monomers whose total mass concentration $M=1$.

Now we specify the class of coagulation kernels which will be investigated further on. To this end we introduce two functions

$$u(x)=x^\alpha \quad \text{and} \quad v(x)=x^\beta \tag{6}$$

with $\lambda=\alpha+\beta$ and $\mu=|\alpha-\beta|$ (in what follows we consider $\alpha>\beta$). Then we can construct the homogeneous coagulation kernel as

$$K(g,l)=\frac{1}{2}[u(g)v(l)+v(g)u(l)]. \tag{7}$$

This simplified coagulation kernel is of great convenience for further analysis and reflects all specific features of realistic kernels [21]. So far only the case $\alpha=\beta$ is well studied [19].

## III. SOLUTION

In contrast to most approaches that apply a scaling hypothesis for analyzing the asymptotic stage of the coagulation processes I use the truncated model and a rather artificial trick proposed in [20] for solving Eq. (3). Although the problem cannot be resolved entirely exactly (like in the case of $\alpha=1$ [17,18]), the final results are asymptotically correct in the limit of large characteristic masses of the particle mass distribution, i.e., near the sol-gel transition. At the post-critical stage the results are asymptotically $(G\to\infty)$ exact.

Let us introduce new variable $\tau$ and new unknown functions $\nu_g(\tau)$,

$$\tau = \int_0^t c_1(t')dt', \quad \nu_g(\tau) = c_g(\tau)/c_1(\tau). \tag{8}$$

On substituting this into Eq. (3) yields two equations for $\nu_g(\tau)$ and $c_1(\tau)$ [20],

$$\frac{d\nu_g(\tau)}{d\tau} = \frac{1}{2}\sum_{l=1}^{g-1} K(g-l,l)\nu_{g-l}(\tau)\nu_l(\tau) - \nu_g(t)\sum_{l=1}^{G}[K(g,l)-K(1,l)]\nu_l(\tau) \tag{9}$$

with $\nu_1(\tau)=1$ and $\nu_g(0)=0$ $(g>1)$. This equation does not contain $c_1(\tau)$. The second equation allows one to find $c_1(\tau)$, once $\nu_g(\tau)$ are known,

$$\frac{dc_1(\tau)}{d\tau} = -c_1(\tau)\sum_{l=1}^{G} K(1,l)\nu_l(\tau). \tag{10}$$

The initial condition to this equation is $c_1(0)=1$.

For the kernel given by Eq. (7), Eqs. (9) and (10) reduce to

$$\frac{d\nu_g(\tau)}{d\tau} = \frac{1}{2}\sum_{l=1}^{g-1} u(g-l)v(l)\nu_{g-l}(\tau)\nu_g(\tau) - \frac{1}{2}[u(g)-1]\nu_g(\tau)\sum_{l=1}^{G} v(l)\nu_l(\tau) - \frac{1}{2}[v(g)-1]\nu_g(\tau)\sum_{l=1}^{G} u(l)\nu_l(\tau), \tag{11}$$

and

$$\frac{dc_1(\tau)}{d\tau} = -\frac{c_1(\tau)}{2}\left(\sum_{l=1}^{G} u(l)\nu_l(\tau) + \sum_{l=1}^{G} v(l)\nu_l(\tau)\right). \tag{12}$$

Let us try to find the solution to Eq. (11) in the form

$$\nu_g(\tau) = p^{u(g)-1}q^{v(g)-1}r_g(\tau), \tag{13}$$

where the functions $p(\tau)$ and $q(\tau)$ are defined by the equations

$$q\frac{dp}{d\tau} + \frac{1}{2}\sum_{l=1}^{G} v(l)p^{u(l)}q^{v(l)}r_l = \kappa_\alpha \tag{14}$$

and

$$p\frac{dq}{d\tau} + \frac{1}{2}\sum_{l=1}^{G} u(l)p^{u(l)}q^{v(l)}r_l = \kappa_\beta. \tag{15}$$

The initial conditions to these equations are

$$p(0) = q(0) = 0. \tag{16}$$

In Eqs. (14) and (15) $\kappa_\alpha$ and $\kappa_\beta$ are yet unknown constants.

On substituting $\nu_g(\tau)$ from Eq. (13) into Eq. (11) yields

$$\{\kappa_\alpha[u(g)-1] + \kappa_\beta[v(g)-1]\}r_g + pq\frac{dr_g}{d\tau} = \frac{1}{2}\sum_{l=1}^{g-1} u(g-l)v(l)r_{g-l}r_l p^{u(g-l)+u(l)-u(g)}q^{v(g-l)+v(l)-v(g)}. \tag{17}$$

The initial condition to this equation is readily derived from Eqs. (16) and (17). Setting $p=q=0$ in Eq. (17) gives $r_g(0)=\delta_{g,1}$. It is essential to notice that for deriving this initial condition the powers of $p$ and $q$ on the right-hand side of Eq. (17) should be positive. This condition is fulfilled only for $\alpha,\beta \le 1$.

A very important identity

$$c_1(t) = \frac{h(t)}{\kappa t} \tag{18}$$

follows from Eqs. (12)–(15). Here

$$h(t) = p(t)q(t) \quad \text{and} \quad \kappa = \kappa_\alpha + \kappa_\beta. \tag{19}$$

Indeed, combining Eqs. (12)–(15) yields $d_\tau \ln(c_1/h) = -\kappa/h$. Next, applying the definition of $\tau$ [Eq. (8)] leads to the closed equation for $c_1/h$, $d_t(c_1/h) = -\kappa(c_1/h)^2$ or $c_1/h = (\kappa t)^{-1}$. It is important to emphasize that the integration constant $t_0=0$, because the product $h(0)=p(0)q(0)=0$ [see Eq. (16)].

## IV. EXACTLY SOLVED MODEL

In this section I reproduce briefly the exact solution for the models $K(g,l)=gl$. The exact particle mass spectrum in this model is widely known in the limit $G=\infty$ and can be found, e.g., in [13]. The solution for finite $G$ appeared in [17,18] (see also [14]). Here I reproduce it following the scheme outlined in the preceding section.

We consider $\alpha=\beta=1$. In this case the right-hand side of Eq. (17) does not contain $p$ and $q$. The coefficients $r_g$ are then independent of $\tau$ and can be found from Eq. (17) without the last term on its left-hand side. On introducing $\kappa=2\kappa_1$ we have from Eq. (17),

$$\kappa(g-1)r_g = \frac{1}{2}\sum_{l=1}^{g-1}(g-l)lr_{g-l}r_l. \tag{20}$$

It is easy to derive the first-order differential equation for the generating function $D_0(z)=\sum_{g=1}^{\infty} r_g z^g$,

$$\kappa(zD_0' - D_0) = \frac{1}{2}(zD_0')^2. \tag{21}$$

Here, the prime stands for the derivative with respect to $z$. This equation appeared in the scientific literature already very long ago and its solution is also well known,

$$z = \phi e^{-\phi/\kappa}, \tag{22}$$

with $\phi(z)=zD_0'(z)$.

Let us differentiate Eq. (22) with respect to $z$ and find the value of $\phi(z_c)$ from the condition

$$d_\phi z = e^{-\phi/\kappa}(1 - \phi/\kappa) = 0 \tag{23}$$

defining the position of the singularity of the function $\phi(z)$. From this equation we find $\phi(1)=\kappa$. The requirement $z_c=1$ together with Eqs. (22) and (23) fix the separation constant $\kappa=e$ and give $\phi(1)=\kappa=e$. Thus $\phi(z)$ is expressed in terms of the tree function (see, e.g., [22]) as follows:

$$\phi(z) = eT(e^{z/e}), \tag{24}$$

where the tree function $T(x)$ is the solution to the transcendent equation,

$$x = Te^{-T}. \tag{25}$$

Now the exact particle mass spectrum can be restored from the Tailor expansion of the tree function [22],

$$T(x) = \sum_{g=1}^{\infty} \frac{g^{g-1}}{g!} x^g. \tag{26}$$

We thus have,

$$c_g(\tau) = r_g h^{g-1} = \frac{g^{g-2}}{g!} e^{-(g-1)} h^{g-1}, \tag{27}$$

where the function $h$ is the solution to the equation,

$$\frac{dh}{d\tau} + eT_G(h/e) = e. \tag{28}$$

Here

$$T_G(x) = \sum_{l=1}^{G} \frac{l^{l-1}}{l!} x^l \tag{29}$$

is the $G$ segment of the tree function [22].

In order to demonstrate the strategy of the present approach and the nature of the general results of this paper, I analyze the solution of Eq. (28) in the limit of large $G$.

Let us separate the variables in Eq. (28). The result is

$$\int_0^{h/e} \frac{ds}{1 - T_G(s)} = \tau. \tag{30}$$

If $G$ is finite, the function $T_G(x)$ is a polynomial with positive coefficients and the singularity of the integrand in Eq. (30) is a simple pole whose position is determined by the equation

$$T_G(h_m/e) = 1. \tag{31}$$

The integral on the left-hand side of Eq. (30) diverges at $s=h_m$ at any finite $G$.

The situation drastically changes if $G=\infty$ and $T_G$ is replaced by the tree function $T$ in the integrand in Eq. (30). The function $T(x/e)$ is equal to 1 at $x=1$ and has the square-root singularity at this point. Near $s=1$ the difference $1-T(s/e) \propto \sqrt{1-s}$ and the integral in Eq. (30) converges. The integration in Eq. (30) is readily performed if we replace $T_G$ by $T$. We introduce the new variable $x=T(s)$ and denote $\tilde{h}$ the solution to Eq. (28) at $G=\infty$. Then $ds=e^{-x}(1-x)dx$ and

$$\int_0^{\tilde{h}/e} \frac{ds}{1 - T(s)} = \int_0^{T(\tilde{h}/e)} e^{-x} dx = 1 - e^{-T(\tilde{h}/e)} = \tau. \tag{32}$$

From this equation we have

$$\tilde{h}(\tau) = e(1 - \tau)\ln \frac{1}{1 - \tau}. \tag{33}$$

This expression is valid for $\tau < \tau_{\max} = 1 - e^{-1}$ [$\tau_{\max}$ is the point, where the function $h(\tau)$ reaches the maximum]. At larger $\tau$ the function $\tilde{h}(\tau)=1$ is the solution to Eq. (28).

According to Eq. (18) $c_1=h(\tau)/(et)$. Then from Eqs. (8) and (18), we find

$$\frac{d\tau}{dt} = -\frac{(1 - \tau)\ln(1 - \tau)}{t}. \tag{34}$$

Integrating this equation yields

$$\tau(t) = 1 - e^{-t} \tag{35}$$

and

$$c_1(t) = \frac{d\tau}{dt} = e^{-t}. \tag{36}$$

As is known $t=t_c=1$ is the gelation point of the model $K(g,l)=gl$, $G=\infty$ (see, e.g., [13]). This $t_c$ corresponds to $\tau_{\max}$, i.e., $\tau(t_c)=\tau_c=\tau_{\max}$. At $t>t_c$ the mass concentration begins to drop down with time. The mass deficit is attributed to a gel formation. The gel itself does not appear explicitly in the kinetic equation.

Now we have the possibility to examine what is going on in the model with finite but large $G$. To this end we use the asymptotic expression for $r_g$ from Eq. (27),

$$r_g \approx \frac{1}{e\sqrt{2\pi} g^{5/2}}. \tag{37}$$

Equation (28) can be rewritten as

$$\frac{dh}{d\tau} + \sum_{g=1}^{G} g r_g (h^g - 1) = \sum_{g=G+1}^{\infty} g r_g. \tag{38}$$

The right-hand side of this equation is of the order of $G^{-1/2}$. The function $h(\tau)$ is seen to grow, reaches unity, and then slowly approaches the limiting steady-state value defined from the condition $d_\tau h=0$,

$$\sum_{g=1}^{G} g r_g (h_\infty^g - 1) = \sum_{g=G+1}^{\infty} g r_g. \tag{39}$$

At large $G$ we replace the sums in this equation with the integrals and try to look for the solution to this equation in the form $h_\infty = e^{\xi/G}$. We then come to the equation for $\xi$,

$$\int_0^1 \frac{e^{\xi x} - 1}{x^{3/2}} = 2. \tag{40}$$

Let us calculate the time dependence of the total mass concentration of the sol fraction,

$$M(\tau) = c_1(\tau)\sum_{g=1}^{G} \frac{g^{g-1}}{g!}\left(\frac{h}{e}\right)^{g-1}. \quad (41)$$

We can rewrite this expression as

$$M(\tau) = M_\infty(\tau) + M_1(\tau). \quad (42)$$

Here

$$M_\infty(\tau) = c_1(\tau)(\tilde{h}/e)T(\tilde{h}/e) = \theta(1-t) + t^{-1}\theta(t-1), \quad (43)$$

where $\theta(x)$ is the Heaviside step function. The correction term $M_1(\tau)$ is exponentially small (as a function of $G$) at the pregelation stage and is of order $G^{-1/2}$ at $\tau > \tau_c$.

The spectrum of the deposit is calculated in the next section [see Eqs. (69) and (71)].

## V. POST-CRITICAL SPECTRA

In this section I demonstrate the details of the solution of the Smoluchowski equation at the post-critical period.

### A. Sol spectrum

Now we do the decisive step: namely, we assume that at the critical time and after it the derivative $d_\tau r_g$ is small and can be ignored. Moreover, at $t > t_c$ the functions $p$ and $q$ are asymptotically independent of $\tau$ in the limit $G \to \infty$ [see Eq. (61)].

The above assumptions reduce Eq. (17) to the recurrence for $r_g(p,q)$,

$$\{\kappa_\alpha[u(g)-1] + \kappa_\beta[v(g)-1]\} r_g p^{u(g)} q^{v(g)} = \frac{1}{2}\sum_{l=1}^{g-1} u(g-l)v(l) r_{g-l} r_l p^{u(g-l)+u(l)} q^{v(g-l)+v(l)} \quad (44)$$

with $r_1 = 1$. We shall express the solution to Eq. (44) in terms of $\tilde{r}_g$ defined by a simpler recurrence,

$$\{\kappa_\alpha[u(g)-1] + \kappa_\beta[v(g)-1]\}\tilde{r}_g = \frac{1}{2}\sum_{l=1}^{g-1} u(g-l)v(l)\tilde{r}_{g-l}\tilde{r}_l, \quad (45)$$

with $\tilde{r}_1 = 1$.

Noticing that the combination $s_g = r_g p^{u(g)} q^{v(g)}$ entering Eq. (44) also meets Eq. (45) with a different first term of the sequence ($s_1 = pq$) allows us to express $r_g$ in terms of $\tilde{r}_g$, $p$, $q$, and $h = pq$,

$$r_g(p,q) = \tilde{r}_g h^g p^{-u(g)} q^{-v(g)}. \quad (46)$$

Equation (13) then gives

$$\nu_g = \tilde{r}_g h^{g-1}. \quad (47)$$

Let us return to the separation constants $\kappa_{\alpha,\beta}$ and then determine the asymptotic behavior of $\tilde{r}_g$ at large $g$. To this end we introduce the generating function for $g^\sigma \tilde{r}_g$,

$$D_\sigma(z) = \sum_{g=1}^{\infty} g^\sigma z^g \tilde{r}_g \quad (48)$$

(pay attention that here the summation goes up to $\infty$). From Eq. (45) one finds

$$\kappa_\alpha[D_\alpha(z) - D_0(z)] + \kappa_\beta[D_\beta(z) - D_0(z)] = \frac{1}{2}D_\alpha(z)D_\beta(z). \quad (49)$$

Now we choose the separation constants $\kappa_{\alpha,\beta}$ in such a way that the generating functions $D_\sigma(z)$ would have the nearest to $z=0$ singularity at $z=1$. This step removes the exponential factors from $\tilde{r}_g$.

We assume that

$$\tilde{r}_g \approx A g^{-\delta} \quad (50)$$

with $\delta > 2$ [see Eq. (55)]. Then at $z \approx 1$, the function $D_0(z)$ has the structure

$$D_0(z) \approx D_0(1) - D_1(1)(1-z) + b_0(1-z)^{\delta-1} + \cdots . \quad (51)$$

In Eq. (51) we used the identity $d_z D_0(z=1) = D_1(1)$.

We consider the case $1 < \delta - \sigma < 2$ ($\sigma = \alpha, \beta$). Then, the expansions of $D_\alpha(z)$ and $D_\beta(z)$ around $z=1$ contain the singular term,

$$D_\sigma(z) \approx D_\sigma(1) - b_\sigma(1-z)^{\delta-\sigma-1} + \cdots . \quad (52)$$

Again, $\sigma = \alpha, \beta$. Substituting these $D_\alpha$, $D_\beta$, and $D_0$ into Eq. (49) and equalizing the coefficient near similar powers of $1-z$ yield,

$$\kappa_\alpha = \frac{1}{2}D_\beta(1), \quad \kappa_\beta = \frac{1}{2}D_\alpha(1), \quad (53)$$

and

$$D_0(1) = \frac{D_\alpha(1)D_\beta(1)}{D_\alpha(1) + D_\beta(1)}. \quad (54)$$

The balance of power gives [we require $b_\alpha b_\beta (1-z)^{\delta-\alpha-1}(1-z)^{\delta-\beta-1} = \kappa D_1(1)(1-z)$],

$$\delta = \frac{3+\lambda}{2}. \quad (55)$$

In addition (see Appendix A), we can express the coefficients $b_{\alpha,\beta}$ in Eq. (52) in terms of $A$ and find

$$A = \sqrt{\frac{D_1\kappa(1-\mu^2)\cos(\pi\mu/2)}{2\pi}}. \quad (56)$$

The conditions $1 < \delta - \alpha < 2$ and $1 < \delta - \beta < 2$ in terms of $\lambda = \alpha + \beta$ and $\mu = |\alpha - \beta|$ turn into $1 < \lambda \leq 2$, $\mu < 1$. In deriving Eq. (56) we used Eqs. (A2)–(A5) and the identity $\Gamma(0.5+x)\Gamma(0.5-x) = \pi/\cos(\pi x)$.

Now we are ready for further analysis of Eq. (44). Equation (48) allows us to rewrite Eqs. (14) and (15) in the form

$$q\frac{dp}{d\tau} + \frac{1}{2}\sum_{l=1}^{G} v(l)p^{u(l)}q^{v(l)}r_l = \frac{1}{2}\sum_{l=1}^{\infty} v(l)r_l \quad (57)$$

and

$$p\frac{dq}{d\tau}+\frac{1}{2}\sum_{l=1}^{G}u(l)p^{u(l)}v^{v(l)}r_l=\frac{1}{2}\sum_{l=1}^{\infty}u(l)r_l. \qquad (58)$$

If we add these equations and use Eq. (46) we come to the closed equation for $h(\tau)=p(\tau)q(\tau)$,

$$\frac{dh}{d\tau}+\frac{1}{2}\sum_{l=1}^{G}l^{\alpha}\tilde{r}_l(h^l-1)+\frac{1}{2}\sum_{l=1}^{G}l^{\beta}\tilde{r}_l(h^l-1) =\frac{1}{2}\sum_{l=G+1}^{\infty}l^{\alpha}\tilde{r}_l+\frac{1}{2}\sum_{l=G+1}^{\infty}l^{\beta}\tilde{r}_l. \qquad (59)$$

Here we deciphered $u(l)=l^{\alpha}$ and $v(l)=l^{\beta}$ [see Eq. (7)]. This equation has exactly the same structure as just analyzed in Eq. (28). The function $h(\tau)$ grows with $\tau$, reaches unity, and then becomes stationary as $\tau\to\infty$. It is reasonable therefore to define the critical time as the root of the equation

$$h(\tau_c)=1. \qquad (60)$$

On reaching the critical value $h=1$ at $\tau=\tau_c$ the function $h(\tau)$ slowly grows. Its derivative over $\tau$ can be evaluated from Eq. (59),

$$\frac{dh}{d\tau}\propto\sum_{l=G+1}^{\infty}l^{\alpha}\tilde{r}_l\propto G^{-(1-\mu)/2}. \qquad (61)$$

Because $\Delta h\propto h_\infty-1\propto G^{-1}$, we can estimate the time necessary for reaching the limiting value of $h$ as $\Delta\tau\propto\Delta h/d_{\tau}h \propto G^{-(1+\mu)/2}$, i.e., this time is very short. The limiting value $h_\infty$ can be found from Eq. (59) by setting in it $d_{\tau}h=0$,

$$\sum_{l=1}^{G}l^{\alpha}\tilde{r}_l(h_\infty^l-1)+\sum_{l=1}^{G}l^{\beta}\tilde{r}_l(h_\infty^l-1)=\sum_{l=G+1}^{\infty}l^{\alpha}\tilde{r}_l+\sum_{l=G+1}^{\infty}l^{\beta}\tilde{r}_l. \qquad (62)$$

At large $G$ we can replace the sums in Eq. (59) with integrals and $\tilde{r}_g$ with its asymptotic form $\tilde{r}_g\approx Ag^{-(3+\lambda)/2}$. We then come to the equation for $\xi=G\ln h_\infty$,

$$\int_0^1 x^{-(3-\mu)/2}[\exp(\xi x)-1]dx=\frac{2}{1-\mu}. \qquad (63)$$

The terms coming from the integrals containing $g^{\beta}\tilde{r}_g$ disappear as $G\to\infty$ because their contribution of order $G^{-(1+\mu)/2}$ is small compared to the retained terms whose order is $G^{-(1-\mu)/2}$. The constant $\xi$ defined by Eq. (63) depends only on $\mu$.

### B. Gel spectrum

In the post-critical period $h=\exp(\xi/G)$. Hence, the spectrum has the form

$$c_g(t)=Bt^{-1}g^{-(3+\lambda)/2}\exp[\xi(g/G)], \qquad (64)$$

where

$$B=\frac{A}{(\kappa_\alpha+\kappa_\beta)}=\sqrt{D_1\frac{(1-\mu^2)\cos(\pi\mu/2)}{\pi[D_\alpha(1)+D_\beta(1)]}}. \qquad (65)$$

In order to understand what is going on in such systems in the post-critical period we calculate the rate of the sol mass transfer through the cutoff mass $G$,

$$\frac{dM_{\mathrm{sol}}}{dt}=-\frac{1}{2}\sum_{l,m}(l+m)K(l,m)c_lc_m, \qquad (66)$$

where $M_{\mathrm{sol}}(t)=\Sigma_{l=1}^{G}lc_l(t)$ and the summation on the right-hand side of Eq. (66) goes over all integers $l,m$ obeying the conditions $l,m\le G$ and $l+m>G$. On replacing the sum in this expression with the integral and keeping in mind the asymptotic structure of $c_g(t)$ in the post-critical period,

$$c_g=G^{-\gamma}Bt^{-1}c(x), \qquad (67)$$

where $x=g/G$ and $c(x)=x^{-\gamma}e^{\xi x}$, we find

$$\frac{dM_{\mathrm{sol}}}{dt}=\frac{G^{3+\lambda-2\gamma}}{2}(B/t)^2\int_0^1dx\int_{1-x}^1dy(x+y)K(x,y)c(x)c(y). \qquad (68)$$

One immediately sees that the rate of mass transfer through the cutoff mass is independent of $G$ if $\gamma=(3+\lambda)/2$.

Equation (4) permits for calculating the spectrum of the deposit. This spectrum stretches from $g=G$ to $g=2G$. At large masses the sum on the right-hand side of this equation can be converted to the integral. On doing this we get

$$c_g^{+}(t)=\frac{B^2}{2G^2}\left(\frac{1}{t_c}-\frac{1}{t}\right)F_\mu(s), \qquad (69)$$

where

$$F_\mu(s)=e^{\xi(1+s)}\int_s^1\frac{dy}{(1+s-y)^{(3+\mu)/2}y^{(3-\mu)/2}} \qquad (70)$$

and $s=(g-G)/G$. At $\mu=0$,

$$F_0(s)=\frac{4e^{\xi(1+s)}(1-s)}{(1+s)^2\sqrt{s}}. \qquad (71)$$

At $\alpha=1$,

$$c_g^{+}(\infty)=\frac{\exp[\xi(1+s)]}{\pi G^2}\frac{1-s}{(1+s^2)\sqrt{s}} \qquad (72)$$

(see [14,17,18]). We introduce the notation,

$$Q_\mu=\int_0^1(1+s)F_\mu(s)ds. \qquad (73)$$

At $\mu=0$ this integral is expected to be

$$Q_0=4\pi. \qquad (74)$$

This equality has been checked numerically.

### C. Critical times

As $t\to\infty$ all sol particles convert to gel whose total mass becomes equal to unity. Then $t_c$ can be determined from the condition $\int_G^{2G}c_g^{+}(\infty)gdg=1$ or

TABLE I. Parameter $\xi$ of the post-critical particle mass spectrum, Eq. (63) and critical times $t_c(\lambda)$, Eq. (75) as the functions of $\mu=\alpha-\beta$. Empty cells mean that the respective combinations of $\lambda$ and $\mu$ do not meet restrictions $0<\alpha,\ \beta<1$.

| $\mu$ | 0 | 0.2 | 0.4 | 0.6 | 0.8 |
|---|---|---|---|---|---|
| $\xi$ | 0.854 | 1.172 | 1.583 | 2.173 | 3.169 |
| $t_c(1.2)$ | 8.832 | 11.480 | 12.549 | 11.801 | 9.307 |
| $t_c(1.4)$ | 2.776 | 3.653 | 4.281 | 4.488 | |
| $t_c(1.6)$ | 1.661 | 2.206 | 2.655 | | |
| $t_c(1.8)$ | 1.231 | 1.642 | | | |
| $t_c(2.0)$ | 1 | | | | |

$$t_c = \frac{1}{2}Q_\mu B^2 = \left(\frac{(1-\mu^2)\cos(\pi\mu/2)Q_\mu}{4\pi}\right)\frac{2D_1(1)}{D_\alpha(1)+D_\beta(1)}. \tag{75}$$

At $\mu=0$ $(\alpha=\beta)$ Eq. (75) reproduces the result known from recent work [19],

$$t_c = \frac{D_1(1)}{D_\alpha(1)}. \tag{76}$$

## VI. RESULTS AND DISCUSSION

Here, we resume the main results of this paper.

It is shown that the exact particle mass spectrum has the form

$$c_g(t) = t^{-1}\tilde{r}_g(t)h^g(t). \tag{77}$$

Equations (59) and (45) determining the functions $h(t)$ and $r_g(t)$ are formulated. All subsequent results follow from the asymptotic analysis of these equations in the limit of large $g$ and $G$. These are the following:

(i) At the gel point the particle mass spectrum is algebraic,

$$c_g(t) = Bt_c^{-1}g^{-(3+\lambda)/2}.$$

The expression for the multiplier $B$ is given by Eq. (65). This expression has the same structure as that reported in Ref. [19]. The coefficient B, however, depends on $\mu=|\alpha-\beta|$.

The algebraic mass spectrum with the exponent $(3+\lambda)/2$ appeared several times in works on source enhanced coagulating systems [23–27]. As the critical exponent at the sol-gel transition point this dependence was derived in [27] for the kernels with $\alpha=\beta$.

(ii) At the post-critical period $t>t_c$ the functions $h(t)$ and $r_g(t)$ are independent of time. The function $h(t)$ is shown to be close to unity near $t=t_c$, $h(t_c)=1$ at $t=t_c$ and $h(t)=e^{\xi/G}$ at $t>t_c$. Hence, the post-critical mass spectrum has the form [Eq. (64)]

$$c_g(t) = Bt^{-1}g^{-(3+\lambda)/2}\exp[\xi(g/G)].$$

The constant $\xi$ depends on $\mu=|\alpha-\beta|$ and is found on solving Eq. (63) (see Table I).

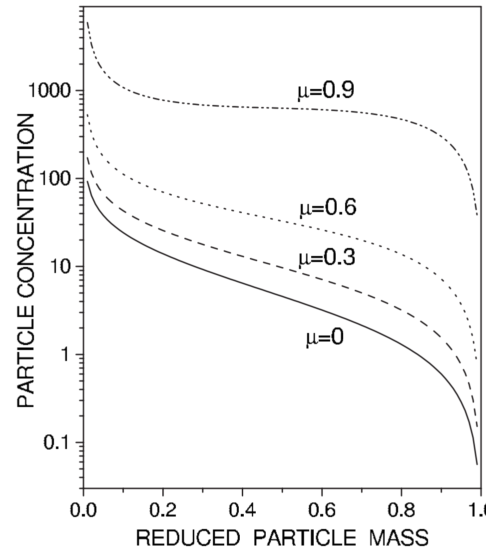


FIG. 1. Universal mass spectrum of the gel. As is seen from Eqs. (68) and (69) the gel forms after the critical time $t=t_c$. Its shape does not change with time [it is given by the function $F_\mu(x)$]. This function is shown in this figure.

(iii) The spectrum of the deposit is given by Eq. (69),

$$c_g^+(t) = \frac{B^2}{2G^2}\left(\frac{1}{t_c}-\frac{1}{t}\right)F_\mu(s),$$

where

$$F_\mu(s) = e^{\xi(1+s)}\int_s^1 \frac{dy}{(1+s-y)^{(3+\mu)/2}y^{(3-\mu)/2}}$$

and $s=(g-G)/G$. This spectrum is plotted in Fig. 1.

(iv) The exact expression for the critical time $t_c$ is derived [Eq. (75)],

$$t_c = \left(\frac{(1-\mu^2)\cos(\pi\mu/2)Q_\mu}{4\pi}\right)\frac{2D_1(1)}{D_\alpha(1)+D_\beta(1)}.$$

At $\alpha=\beta$

$$t_c = \frac{D_1(1)}{D_\alpha(1)}.$$

If $\alpha=1$ then $t_c=1$. Here $Q_\mu$ is an integral of the final spectrum of the deposit [see Eq. (73)] and $D_\sigma(1)=\Sigma_g g^\sigma r_g$. Numerical values of $t_c$ are given in Table I.

Remarkably, that the critical time depends not only on $\lambda$. The dependence of critical time on the parameter $\mu$ is also very essential, especially because it goes to 0 as $\mu\to 1$. In Ref. [3] an inequality giving the lower estimate for $t_c$ is derived. However, this derivation cannot be applied to the systems with finite $G$.

Although the truncated models of coagulation appeared more than two decades ago the model $G=\infty$ was (and still is) in the center of interest of studies on coagulation and gelation processes [28]. The point is that from the first sight the truncated models have only an auxiliary interest and should reproduce all features of the commonly accepted models as

$G\to\infty$. No essentially new results were expected to appear at finite but large $G$ especially if the characteristic scale of the developing mass distribution remains much less that the cut-off parameter $G$. This paper has demonstrated that there are many principal differences between the cases $G=\infty$ and $G<\infty$. First of all, the truncation leads to the occurrence of the terms depending on the ratio $g/G$. Moreover, these terms contribute to some integral characteristics (like $Q_\mu$ which determines the rate of mass transfer from sol to gel) in such a way, that their contribution does not disappear as $G\to\infty$. Next, these terms prevent a derivation of the equation for the moments of the particle mass distribution. In particular, the derivation of the upper limit for $t_c$ in the spirit of Ref. [3] becomes impossible at finite $G$. This is the reason why the numerical values of the critical times cited in Table I do not obey the inequality derived in [3].

There exists a number of numerical results on the kinetics of sol-gel transition (see especially [29]). The approach of this work is grounded on the scheme that conserves the mass concentration exactly. In the truncated models the couples of particles with masses exceeding $G$ are removed from the system, i.e., the principal moment of the present consideration is the violation of the mass conservation. This is the reason why I do not risk to compare the results of this paper with existing numerical calculations. On the other hand, because the truncated models operate with a finite number of differential equations they are very perspective for numerical studies.

## VII. CONCLUSION

The critical and post-critical behavior of coagulating systems, where the coagulation efficiency grows with the masses of colliding particles $g$ and $l$ as $K(g,l)=0.5(g^\alpha l^\beta+g^\beta l^\alpha)$ $(\lambda=\alpha+\beta>1,\mu=|\alpha-\beta|<1)$ has been studied. The model of the coagulation process includes instantaneous sink that removes the particles with masses exceeding $G$ which allows one to describe the coagulation kinetics by a finite set of equations and define the gel as a deposit of particles with masses between $G+1$ and $2G$. This system has been shown to display the critical behavior (the sol-gel transition) in the limit $G\to\infty$ at $\lambda=\alpha+\beta>1$. The exact post-critical particle mass spectrum has been shown to be an algebraic function of $g$ times a *growing* exponent. All post-critical parameters of the systems have been determined as functions of $\alpha$ and $\beta$.

The most essential feature of these results is that they do not contain any constants that should be determined from the numerical solution of the Smoluchowski equation for the initial stage of the coagulation process. The only not quite nontrivial computational problem is the calculation of $D_\sigma$. The recipe of these computations that I used here is given in Appendix B.

The particle mass spectra of coagulating systems with the coagulation kernels given by Eq. (7) have been found exactly and their asymptotic analysis has been done. For this class of coagulation kernels the picture of the gelation looks as follows. The coagulation process produces dimers, trimers, etc., from initially monodisperse particles. The particle mass spectrum is stretching but remains narrow (it contains an exponential dropping with the particle mass multiplier) during a *finite* interval of time $t<t_c$. At this initial stage the deposition process plays no role because the concentrations of particles with sizes exceeding $G$ is exponentially small. But at $t=t_c$ (it is important to emphasize that $t_c$ is independent of $G$ and remains finite as $G\to\infty$) the spectrum becomes algebraic and the deposition process goes with a finite rate. At the post-critical stage the spectrum acquires an exponentially growing multiplier and conserves its functional form until the end of the coagulation process. The coagulation process ends up with the formation of the deposit whose mass is equal to the total mass of the initial sol.

## APPENDIX A: ASYMPTOTIC BEHAVIOR OF MASS SPECTRA AND SINGULARITIES OF GENERATING FUNCTIONS

Let us consider an arbitrary sequence $a_g$ with an algebraic asymptotic tail at large $g$, $a_g\approx ag^{-\omega}$. I shall prove that the generating function $f(z)=\Sigma_{g=1}^{\infty}a_g z^g$ has the expansion around the point $z=1$ of the form

$$f(z)\approx a\Gamma(1-\omega)(1-z)^{\omega-1},$$

at $0<\omega<1$,

$$f(z)\approx f(1)-a\frac{\Gamma(2-\omega)}{\omega-1}(1-z)^{\omega-1},$$

at $1<\omega<2$,

$$f(z)\approx f(1)-f'(1)(1-z)+a\frac{\Gamma(3-\omega)}{(\omega-1)(\omega-2)}(1-z)^{\omega-1}, \tag{A1}$$

$2<\omega<3$, etc. I show how to prove the second equality. It is easy to do. Near $z=1$ we can write

$$f(z)=f(1)-\sum_{g=1}^{\infty}a_g(1-z^g)\approx a(1)-a\int_0^\infty g^{-\omega}(1-e^{-\zeta g})dg$$

$$=f(1)-a\frac{\Gamma(2-\omega)}{\omega-1}\zeta^{\omega-1}.$$

Here $\zeta=-\ln(z)\approx(1-z)$. I also converted the sum into the integral convergent at the low limit and replaced $a_g\approx ag^{-\omega}$. Other equality are proved similarly. If $\omega$ is an integer a logarithmic term comes up. For example, if $\omega=2$ we have

$$f(z)\approx f(1)+a(1-z)\ln(1-z).$$

Let $r_g\approx Ag^{-\gamma}$ with $\gamma=(3+\lambda)/2$. We want to find the coefficient $b_\alpha$ in the expansion around $z=1$,

$$D_\alpha(z)\approx D_\alpha(1)-b_\alpha(1-z)^{(1-\mu)/2}, \tag{A2}$$

where $\mu=\alpha-\beta$ $(\alpha>\beta)$,

$$D_\alpha(z)\approx D_\alpha(1)-[D_\alpha(1)-D_\alpha(z)]. \tag{A3}$$

The last difference on the right-hand side of this equation is

$$\sum_{g=1}^{\infty} g^{\alpha} r_g (1-z^g) \approx A \int_0^{\infty} \frac{1-e^{\zeta g}}{g^{\gamma-\alpha}} dg = A\zeta^{\gamma-\alpha-1} \int_0^{\infty} \frac{1-e^{-s}}{s^{\gamma-\alpha}} ds$$
$$= A\zeta^{\gamma-\alpha-1} \frac{\Gamma(2-\gamma+\alpha)}{\gamma-\alpha-1}. \quad \text{(A4)}$$

In this case $\gamma=(3+\lambda)/2$, $\gamma-\alpha-1=(1-\mu)/2$, $\gamma-\beta-1=(1+\mu)/2$, $2-\gamma+\alpha=(1+\mu)/2$, $2-\gamma+\beta=(1-\mu)/2$. Using these results we find

$$b_{\alpha} = \frac{2A}{1-\mu}\Gamma\left(\frac{1+\mu}{2}\right), \quad b_{\beta} = \frac{2A}{1+\mu}\Gamma\left(\frac{1-\mu}{2}\right). \quad \text{(A5)}$$

## APPENDIX B: NUMERICAL

This section explains how to find the numerical solution to Eqs. (49). Although nothing special comes up in this solution, an explanation is necessary, because the separation constants $\kappa_{\sigma}$ are chosen in such a way that the function $D_{\sigma}(z)$ has a singularity at $z=1$. Therefore although the series for $D_{\sigma}(1)$ converges, this convergence is very slow.

In order to find $\kappa_{\alpha,\beta}$ let us introduce $\kappa=\kappa_{\alpha}+\kappa_{\beta}$ and $\eta=\kappa_{\alpha}/\kappa_{\beta}$. Then Eq. (49) can be rewritten as

$$\kappa[\eta g^{\alpha} + (1-\eta)g^{\beta}]\tilde{r}_g = \frac{1}{2}\sum_{l=1}^{g-1} (g-l)^{\alpha} l^{\beta} \tilde{r}_{g-l}\tilde{r}_l. \quad \text{(B1)}$$

Let $\tilde{r}_g = \kappa^{g-1} p_g$. Then

$$[\eta g^{\alpha} + (1-\eta)g^{\beta}]p_g = \frac{1}{2}\sum_{l=1}^{g-1} (g-l)^{\alpha} l^{\beta} p_{g-l} p_l. \quad \text{(B2)}$$

The fact that $\tilde{r}_g$ is a power of $g$ allows one to find $\kappa$ from the test,

$$\kappa = \frac{p_{g-1}}{p_g}. \quad \text{(B3)}$$

This step defines the function $\kappa=\kappa(\eta)$. It is not a difficult numerical step. The value of $\eta$ is found from Eqs. (53). After several attempts it is possible to restore $\kappa_{\alpha,\beta}$ with the precision better than 0.01%.

The next step assumes the summation of thus found $g^{\sigma}\tilde{r}_g$. To this end it is necessary to find as many as possible terms in respective sums. I summed 5000 terms, but it is not enough for sufficiently precise calculations of $t_c$. The way out is simple. I replaced the sum $\Sigma_{5001}^{\infty} g^{\sigma}\tilde{r}_g$ with the respective integral and used the asymptotic expression for $\tilde{r}_g \approx A g^{(3+\lambda)/2}$. Thus found $D_{\sigma}(1)$ were used in the calculations of the critical times (see Table I). A more precise method of calculation of $D_{\sigma}(1)$ explains the difference between the previous calculations [19] and Table I of this paper.


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