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FAST TRACK COMMUNICATION

Exact post-critical particle mass spectra in a family of gelling systems

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Abstract

The critical behaviour of the coagulating systems, where the coagulation efficiency grows with the masses of colliding particles g and l as $K(g,l) = g^\alpha l^\alpha$ $(1/2 < \alpha \leqslant 1)$ is studied. The 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 critical behaviour (the sol–gel transition) as $G \longrightarrow \infty$. 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 α including the critical times.

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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 an irreversible binary chemical reaction

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

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 simply the numbers of monomers in the particles. The rate of the process (1) $K(g,l)$ (the coagulation kernel) is supposed to be a known homogeneous function of its arguments, i.e., $K(ag, al) = a^\lambda K(g,l)$.

From the first sight the coagulation process looks absolutely offenceless. It is difficult to imagine that such simple systems are able to display something unusual. And nevertheless they do. 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., recent articles Leyvraz (2003, 2006), Ben-Naim and Krapivsky (2005a, 2005b), Lushnikov (2006), 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 (1). Less clear is how to introduce the gel. It does not appear in the kinetic equation explicitly and can only be detected by the behaviour 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. The sol part disappears either gradually or instantly. In the latter case the sol and the gel fractions cannot coexist. Below I consider only the first scenario.

My starting point is the truncated Smoluchowski's equation that describes the coagulating particles whose masses are limited with a maximal (cutoff) mass G. This truncated model describes the coagulation process in the system with a sink that instantly removes the particles with the masses exceeding G (Lushnikov and Piskunov 1982, 1983, Lushnikov 2006). The Smoluchowski equation for the number concentrations $c_g(t)$ of actively coagulating particles ($g \leqslant G$) comprising exactly g monomers at time t looks as follows:

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

The first term on the right-hand side (RHS) of this equation describes the gain of g-mers due to the reaction $(g-l)+(l) \longrightarrow (g)$. The second term is responsible for g-mer losses due to 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. 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^+,

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

In equations (2) and (3) 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 equation (2) is chosen in the form

$$c_g(t=0) = \delta_{g,1}, \tag{4}$$

i.e., the coagulation process starts with a set of monomers whose total mass concentration $M = 1$. In equation (4) $\delta_{g,l}$ is the Kroneker delta. The coagulation kernel

$$K(g,l) = g^\alpha l^\alpha \tag{5}$$

with $\lambda = 2\alpha > 1$ is used below. So far only the case $\alpha = 1$ is well studied, although many interesting results for more general coagulation kernels are reported in Hendriks *et al* (1983).

In what follows I demonstrate how the sol–gel transition can be investigated for the kernels given by equation (5). To this end I apply the truncated model of coagulation and a rather artificial trick proposed in Lushnikov (1973). Although the problem cannot be resolved entirely exactly (like in the case $\alpha = 1$), a full asymptotic analysis of the post-critical stage is possible.

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

$$\tau = \int_0^t c_1(t')\,\mathrm{d}t', \qquad \nu_g(\tau) = c_g(\tau)/c_1(\tau). \tag{6}$$

On substituting this into equation (2) yields two equations for $\nu_g(\tau)$ and $c_1(\tau)$:

$$\frac{\mathrm{d}\nu_g(\tau)}{\mathrm{d}\tau} = \frac{1}{2}\sum_{l=1}^{g-1} K(g-l,l)\nu_{g-l}(\tau)\nu_l(\tau) - \nu_g(t)\sum_{l=1}^{G}[K(g,l) - K(1,l)]\nu_l(\tau) \tag{7}$$

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 $v_g(\tau)$ are known,

$$\frac{dc_1(\tau)}{d\tau} = -c_1(\tau)\sum_{l=1}^{G} K(1,l)v_l(\tau). \tag{8}$$

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

For the kernel $K(g,l) = g^\alpha l^\alpha$ equations (7) and (8) reduce to

$$\frac{dv_g(\tau)}{d\tau} = \frac{1}{2}\sum_{l=1}^{g-1}(g-l)^\alpha l^\alpha v_{g-l}(\tau)v_g(\tau) - (g^\alpha - 1)v_g(\tau)\sum_{l=1}^{G} l^\alpha v_l(\tau), \tag{9}$$

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

Let us try to look for the solution to equation (9) in the form

$$v_g(\tau) = h^{(g^\alpha-1)}(\tau)r_g(\tau), \tag{11}$$

where the function $h(\tau)$ is introduced by the equation

$$\frac{dh}{d\tau} + \sum_{l=1}^{G} l^\alpha r_l h^{(l^\alpha)} = \kappa, \tag{12}$$

with κ being yet an unknown constant and $h(0) = 0$.

On substituting these $v_g(\tau)$ into equation (9) yields the set of differential equations for determining r_g,

$$\kappa(g^\alpha - 1)r_g + h\frac{dr_g}{d\tau} = \frac{1}{2}\sum_{l=1}^{g-1}(g-l)^\alpha l^\alpha r_{g-l}r_l h^{[(g-l)^\alpha + l^\alpha - g^\alpha]}. \tag{13}$$

A very important identity

$$c_1(t)/h(t) = 1/\kappa t \tag{14}$$

follows from equations (10) and (12). On combining these equations yields $d_\tau \ln(c_1/h) = -\kappa/h$. Next, applying the definition of τ (equation (6)) leads to the closed equation for c_1/h: $d_t(c_1/h) = -\kappa(c_1/h)^2$ or $c_1/h = (\kappa t)^{-1}$. Pay attention that the integration constant $t_0 = 0$ in this equation, because $c_1(0) = 1$ and $h(0) = 0$.

Now let us do the decisive step: namely, we assume that after the critical time the functions $r_g(\tau)$ are strictly independent of τ, i.e., the term containing $d_\tau r_g$ can be crossed out from equation (13). I shall justify this statement later on.

The above assumption allows us to find the coefficients r_g from the recurrence,

$$\kappa(g^\alpha - 1)r_g h^{(g^\alpha)} = \frac{1}{2}\sum_{l=1}^{g-1}(g-l)^\alpha l^\alpha r_{g-l}r_l h^{[(g-l)^\alpha + l^\alpha]} \tag{15}$$

with $r_1 = 1$. For determining the dependence of r_g on h let us introduce $\tilde{r}_g = r_g(1)$. From equation (15) one has

$$\kappa(g^\alpha - 1)\tilde{r}_g = \frac{1}{2}\sum_{l=1}^{g-1}(g-l)^\alpha l^\alpha \tilde{r}_{g-l}\tilde{r}_l. \tag{16}$$

Table 1. Parameter B of the post-critical particle mass spectrum, equation (29), critical time t_c, equation (35), and the separation constant κ, equation (21).

α	0.6	0.7	0.8	0.9	1.0
B	0.745	0.586	0.493	0.436	0.399
t_c	3.486	2.157	1.530	1.194	1.000
κ	3.503	3.215	3.005	2.842	2.718

Noticing that the combination $s_g = r_g h^{(g^\alpha)}$ entering equation (15) also satisfies equation (16) with a different first term of the sequence ($s_1 = h$) allows us to derive the explicit dependence of r_g on h,

$$r_g(h) = \tilde{r}_g h^{(g-g^\alpha)}. \tag{17}$$

Let us return to the separation constant κ and then determine the asymptotic behaviour of $\tilde{r}_g$ at large g. To this end we introduce two generating functions $D_0(z)$ and $D_\alpha(z)$, where

$$D_\sigma(z) = \sum_{g=1}^{\infty} g^\sigma z^g \tilde{r}_g \tag{18}$$

(pay attention that here the summation goes up to ∞). From equation (16) one finds

$$2\kappa[D_\alpha(z) - D_0(z)] = D_\alpha^2(z). \tag{19}$$

On solving this equation with respect to D_α yields

$$D_\alpha(z) = \kappa - \sqrt{\kappa^2 - 2\kappa D_0(z)}. \tag{20}$$

The separation constant is chosen as

$$\kappa = 2D_0(1) = D_\alpha(1). \tag{21}$$

This choice locates the singularity of both generating functions at $z = 1$ and removes thus the exponential factors from $\tilde{r}_g$.

Equation (20) was analysed in Hendriks *et al* (1983). The result is convenient to present in terms of $D_\sigma(1)$:

$$\tilde{r}_g \approx \kappa \sqrt{\frac{D_1(1)}{2\pi D_\alpha(1)}}\, g^{-(\alpha+3/2)}. \tag{22}$$

This expression is found by expanding $D_0(z)$ with respect to $z - 1$, using the Stirling formula for the expansion coefficients of the function $\sqrt{1-z}$, and the obvious formula $D_0'(1) = D_1(1)$. Here prime stands for the differentiation with respect to z. The values of $D_\alpha(1)$ and $D_1(1)$ can be determined from a numerical analysis of equation (16) (see table 1).

Now we are ready to analyse the solution of equation (12). Since $\kappa = D_\alpha(1) = \sum_{l=1}^{\infty} l^\alpha \tilde{r}_l$ (equation (21)), we can rewrite equation (12) in the form

$$\frac{\mathrm{d}h}{\mathrm{d}\tau} + \sum_{l=1}^{G} l^\alpha \tilde{r}_l (h^l - 1) = \sum_{l=G+1}^{\infty} l^\alpha \tilde{r}_l. \tag{23}$$

First we put $G = \infty$. Then the solution to equation (23) can be expressed in terms of $D_0(h)$,

$$\int_0^h \frac{\mathrm{d}h'}{D_\alpha(1) - D_\alpha(h')} = \tau. \tag{24}$$

The integral on the left-hand side of this equation converges at $h' = 1$ which means that $h(\tau)$ reaches unity during a finite interval of $\tau = \tau_c$. According to equations (6) and (14)

$\tau(t) \longrightarrow \infty$ as $t \longrightarrow \infty$, so the function $h(\tau) = 1$ and the particle mass spectrum remain algebraic after the sol–gel transition. Hence, the condition

$$h(\tau_c) = 1 \tag{25}$$

defines the critical value of τ. At finite G the situation is similar. The function $h(\tau)$, grows with τ, reaches the value $h = 1$ and then exceeds unity by a little becoming independent of τ. Let us try to find the limiting value of h in the form $h(\tau) = \exp(\xi/G)$. We substitute this h into equation (23) and replace the sums with the integrals. After some simple algebra we obtain the condition for determining ξ

$$\int_0^1 x^{-3/2}\,[\exp(\xi x) - 1]\,\mathrm{d}x = 2. \tag{26}$$

Remarkably, that $\xi = 0.854$ is independent of α.

In the post-critical period $h = \exp(\xi/G)$ which gives us the grounds to assume that r_g are independent of τ in the post-critical period. Indeed, $r_g(\tau) = r_g(h(\tau))$, because $\mathrm{d}r_g/\mathrm{d}\tau = (\mathrm{d}r_g/\mathrm{d}h)(\mathrm{d}h/\mathrm{d}\tau)$ and $\mathrm{d}h/\mathrm{d}\tau$ is a function of h (see equation (12)). Hence, the spectrum has the form

$$c_g(t) = \frac{1}{t}\sqrt{\frac{D_1(1)}{2\pi D_\alpha(1)}}\,g^{-(3+\lambda)/2}\exp[\xi(g/G)]. \tag{27}$$

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,

$$\frac{\mathrm{d}M_{\mathrm{sol}}}{\mathrm{d}t} = -\frac{1}{2}\sum_{l,m}(l+m)K(l,m)c_l c_m, \tag{28}$$

where $M_{\mathrm{sol}}(t) = \sum_{l=1}^{G} l c_l(t)$ and the summation on the right-hand side of equation (28) goes over all integers l, m obeying the conditions: $l, m \leqslant G$ 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,

$$c_g = G^{-\gamma} B t^{-1} c(x), \tag{29}$$

where $B = \sqrt{D_1(1)/(2\pi D_\alpha(1))}$, $x = g/G$ and $c(x) = x^{-\gamma}\,\mathrm{e}^{\xi x}$, we find

$$\frac{\mathrm{d}M_{\mathrm{sol}}}{\mathrm{d}t} = -\frac{1}{2}(B/t)^2 G^{3+\lambda-2\gamma}\int_0^1 \mathrm{d}x \int_{1-x}^1 \mathrm{d}y\,(x+y)K(x,y)c(x)c(y). \tag{30}$$

One immediately sees that the rate of mass transport through the cutoff mass is independent of G for any homogeneous kernels if $\gamma = (3+\lambda)/2$ and the integrals on the RHS of this equation converge.

The truncated model permits for calculating the spectrum of the deposit. This spectrum stretches from $g = G$ to $g = 2G$ (see equation (3)). At large masses the sum on the RHS of this equation can be converted to the integral. On doing this we get

$$c_g^+(t) = \frac{B^2}{2G^2}\left(\frac{1}{t_c} - \frac{1}{t}\right)F(s), \tag{31}$$

where

$$F(s) = \mathrm{e}^{\xi(1+s)}\int_s^1 \frac{\mathrm{d}y}{(1+s-y)^{3/2}y^{3/2}} = \frac{4\,\mathrm{e}^{\xi(1+s)}(1-s)}{(1+s)^2\sqrt{s}}. \tag{32}$$

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

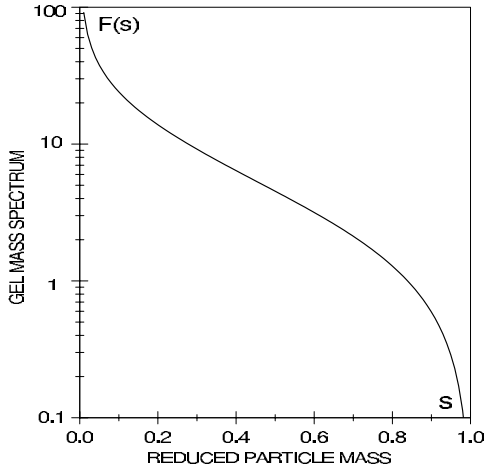

Figure 1. Universal mass spectrum of the gel. As is seen from equation (31) after the critical time the gel forms. Its shape does not change with time (it is given by the function $F(s)$, $s = g/G - 1$). This function is shown in this figure.

At $\alpha = 1$ (see Lushnikov (2006))

$$c_g^+(\infty) = \frac{\exp[\xi(1+s)]}{\pi G^2} \frac{1-s}{(1+s)^2\sqrt{s}} = \frac{1}{4\pi} F(s). \tag{33}$$

Since $\int_G^{2G} g c_g^+(\infty) = 1$ we can conclude from equation (33)) that

$$\int_0^1 (1+s) F(s)\, \mathrm{d}s = 4\pi. \tag{34}$$

As $t \longrightarrow \infty$ all sol particles convert to gel whose total mass becomes equal to unity. Then t_c can be determined from the condition $\int_G^{2G} c_g^+(\infty) g\, \mathrm{d}g = 1$ or (see equation (31) and (34))

$$t_c = \frac{B^2}{2} \int_0^1 (1+s) F(s)\, \mathrm{d}s = 2\pi B^2 = \frac{D_1(1)}{D_\alpha(1)}. \tag{35}$$

The last equality follows from the definition of B (see equation (29)).

The main result of this study is the expression for the exact post-critical particle mass spectrum equation (27). This spectrum contains the algebraic function $g^{-(3/2+\alpha)}$ accompanied with the growing exponent of the particle mass $\exp(\xi g/G)$. This exact post-critical solution of the Smoluchowski equation becomes possible, because the structure of the post-critical spectrum is much simpler than that at the pre-critical stage. We see that the time dependence is separated and is given by the t^{-1} multiplier. This is a consequence of the structure of the coagulation kernel.

Another important result is the spectrum of the deposit. It is universal (its functional form is independent of α (see figure 1)) as well as the rate of the mass transfer through the cutoff mass G. This rate is independent of G. This fact was known to the authors of van Dongen and Ernst (1986), Leyvraz 2006, but their expression for $\mathrm{d}M_{\mathrm{sol}}/\mathrm{d}t$ differs from equation (30) in two respects; it contains the integration over the interval $(1, \infty)$, whereas equation (30) assumes the integration from 1 to 2. Next, equation (29) contains the growing exponent which does not disappear even as $G \longrightarrow \infty$.

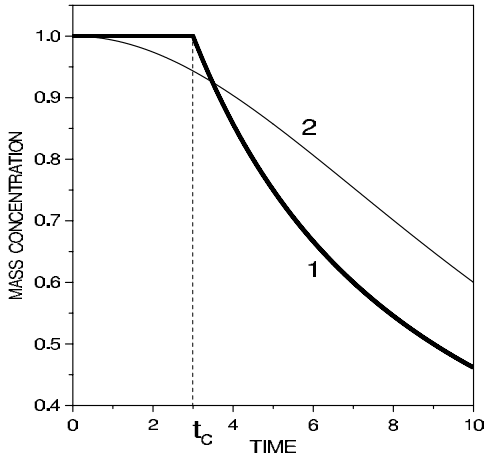

Figure 2. Gelling (1) and non-gelling (2) systems. Shown is the sol mass concentration $M_{\rm sol}(t)$ versus time. In the gelling system $M(t)$ is conserved until $t = t_c$, then a sharp transition to the gelation stage occurs during a very short transient time (of order $G^{-\alpha+1/2}$) and then the deposit (gel) forms. In non-gelling system the transient time is long (it contains a positive power of G).

The above consideration applies the model that sacrifices the mass conservation from the very beginning. In gelling and non-gelling system the coagulation process eventually results in the formation of the deposit. Moreover, neither a phase transition is expected in the system whose dynamics is described by a finite set of ordinary differential equations. So the question comes up how to reconcile this statement with the results of this communication? Figure 2 explains the difference between gelling and non-gelling systems. In the gelling systems the sol mass concentration is almost conserved ($1 - M_{\rm sol} \propto G^{-(\alpha-1/2)}$) until the transition time, then during a short transient time the deposit begins to form and the post-critical regime ensues. In the non-gelling systems the transient time is long and we observe a smooth deposition of the particles from the sol fraction.

References

Ben-Naim E and Krapivsky P L 2005a Percolation with multiple giant clusters *J. Phys. A: Math. Gen.* **38** L417–23
Ben-Naim E and Krapivsky P L 2005b Polymerization with freezing *J. Phys: Condens. Matter* **17** S4249–62
Hendriks E M, Ernst M H and Ziff R M 1983 Coagulation equation with gelation *J. Stat. Phys.* **31** 519–63
Leyvraz F 2003 Scaling theory and exactly solved models in the kinetics of irreversible aggregation *Phys. Rep.* **183** 95–212
Leyvraz F 2006 Scaling theory for gelling systems: work in progress *Physica* D **222** 21–8
Lushnikov A A 1973 Evolution of coagulating systems *J. Colloid Interface Sci.* **45** 549–59
Lushnikov A A and Piskunov V N 1982 Three new exactly solvable models in theory of coagulation *Dokl. Akad. Nauk SSSR (Sov. Phys. Dokl.)* **267** 127–30
Lushnikov A A and Piskunov V N 1983 Analytical solutions in theory of coagulation with sinks *Appl. Math. Mech.* **47** 931–9
Lushnikov A A 2006 Gelation in coagulating systems *Physica* D **222** 37–53
van Dongen P G J and Ernst M H 1986 On the occurrence of a gelation transition in Smoluchowski's coagulation equation *J. Stat. Phys.* **44** 785–92