From Sol to Gel Exactly

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The time evolution of a disperse system wherein the binary coagulation alone governs the temporal changes of particle mass spectra is studied under the assumption that the coagulation kernel is proportional to the product of masses of the coalescing particles. This model is known to reveal the sol-gel transition, i.e., the formation of a cluster with mass comparable to the total mass of the whole system. This Letter reports on the exact solution of this model. The single-particle mass spectrum is analyzed in the thermodynamic limit and it is demonstrated explicitly how the gel appears in the system.

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The term "coagulation" refers to a wide number of very diverse phenomena whose manifestations are related to coalescence of clusters—the parts of an evolving system. The simplest example of the coagulation process is the evolution of a system of M monomeric units that are able to form g-mers resulting from a chain of binary coalescence processes

$$(l_1) + (l_2) \longrightarrow (l_1 + l_2), \qquad (1)$$

where l are the numbers of monomers in an l-mer. Aging of aerosols and hydrosols [1–3], formation of traffic jams [4], cloud and precipitation formation [1,2], formation of fractals [3], evolution of random graphs [5], and formation of atmospheric aerosols [1,2] are only some of the phenomena in which coagulation plays a key role.

Of primary interest is the time evolution of the particle mass spectrum, i.e., the time dependence of the concentrations $c_g(t)$ of g-mers. Commonly accepted approach to the kinetics of coagulating systems relies upon the Smoluchowski kinetic equation governing the time dependence of these concentrations. In the simplest case of spatially uniform systems this equation claims

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

Here the coagulation kernel $K(g, l)$ is the transition rate for the process $(g) + (l) \longrightarrow (g + l)$. The first term on the right-hand side (rhs) of Eq. (2) describes the gain in the g-mer concentration due to coalescence of $(g - l)$- and l-mers while the second one is responsible for the losses of g-mers due to their sticking to all other particles.

There are some reasons not to trust to Eq. (2). Indeed, an attempt to calculate the second moment of the particle mass spectrum, $\phi_2 = \sum_g g^2 c(g)$ for $K(g, l) \propto gl$ leads to a strange result (see, e.g., [1])

$$\phi_2(t) \propto \frac{1}{t_c - t}, \qquad (3)$$

where the critical time t_c depends on the initial mass spectrum. And this is not yet all. The total mass concentration $m = \sum_g g c_g(t)$ conserves only until $t = t_c$. After the critical moment $t = t_c$, the mass concentration exponentially drops down with time, although according to Eq. (2) (and common sense), it should remain constant. Next, at $t = t_n > t_c$ the particle number concentration $N(t) = \sum_g c_g(t)$ crosses the t axis and becomes negative.

Of course, these unusual features of the solution to Eq. (2) did not remain unnoticed (see recent review article [6] and references therein). Many authors tried to answer the question, what is going on at the critical point and after. Most of the attempts had relied upon the use of the Smoluchowski equation. The mass nonconservation had been attributed to the appearance of a *gel*.

Two scenarios of the sol-gel transition had been proposed. The first one (see Refs. [6–9]) assumes that after the critical time, the coagulation process instantly transfers large particles to a gel state, the latter being an undefined object. I will not discuss this scenario here.

The second scenario [10–13] (see also review article [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. In this case any losses of mass are excluded "by definition." On the other hand, the consideration of finite systems calls for an alternative approach. Such an approach based on the scheme developed in [10] had been proposed in [11], where an attempt had been done to answer the question: what happens in *finite* coagulating system with $K(g, l) = 2gl$ in the thermodynamic limit? The answer is simple, but in no way apparent. In contrast to "normal" systems, where the time of formation of large objects grows with M, a giant object with the mass of the order of M forms during a *finite* (independent of V and M) time t_c. After $t = t_c$, this giant particle (referred to as "superparticle" in Ref. [11] and as "gel" in modern literature) actively begins to "eat" the smaller particles (in contrast to the first scenario). Although the probability for any two particles to meet is generally small [$\propto K(g, l)/V$], in the case of the gel this smallness compensates by a large value of the coagulation kernel proportional to the gel mass ($\propto M$), which is, in turn, proportional to V. Hence, this single gel particle whose concentration is zero in the thermodynamical limit can play a considerable role in the evolution of the whole system. The structure of the kernel is also the reason why only one gel particle can form. The point is that the time for the process $(l) + (m) \to (l + m)$ is short for $l, m \propto M$: $\tau \propto V/K(l, m) \propto V/M^2 \propto 1/V \to 0$ in the thermodynamic limit. Of course, the Smoluchowski equation is not able to detect the particles with zero concentration. Although the qualitative picture of the gelation process is more or less clear, the central problem remained unsolved: how to derive the correct particle mass spectrum starting with the master equation for the probability to find the coagulating system in a given state? This problem is resolved here.

An approach that is able to follow the fate of all particles relies upon the equation [11]

$$V\frac{\partial\Psi}{\partial t} = \frac{1}{2}\sum_{l,m} K(l, m)(x_{l+m} - x_l x_m)\frac{\partial^2\Psi}{\partial x_l \partial x_m}, \quad (4)$$

where Ψ is the generating functional for the probability $W(t; n_1, n_2 \ldots)$ to find in the system n_1 monomers, n_2 dimers, etc., at time t, $\Psi(t; x_1, x_2 \ldots) = \sum W(t; n_1, n_2 \ldots) x_1^{n_1} x_2^{n_2} \ldots$. Equation (4) is equivalent to the master equation for W. The solution to Eq. (4) for initially monodisperse particles and $K(g, l) = 2gl$ had been found in [11] in the form:

$$\Psi = \frac{M!}{2\pi i}\oint \frac{dz}{z^{M+1}} \exp\left[\sum_{g=1}^{\infty} z^g a_g(t) x_g\right]. \quad (5)$$

The integration contour passes counterclockwise around the origin of coordinates in the complex plane z. The average occupation numbers can be then found from the equality, $\bar{n}_g(t) = \partial_{x_g}\Psi(t; 1, 1 \ldots x_g \ldots)|_{x_g=1}$, or using Eq. (5),

$$\bar{n}_g(t) = \frac{M!}{2\pi i} a_g(t) \oint \frac{dz}{z^{M-g+1}} e^{G(z,t)}, \quad (6)$$

with $G(z, t)$ being the generating function for a_g. As had been shown in [11], $G(z, t) = \ln D(z e^{-Mt/V}, t)$, where

$$D(z, t) = \sum_{g=0}^{\infty} \frac{z^g}{g!} e^{g^2\tau}. \quad (7)$$

Equation (7) allows for expressing $a_g(t)$ in terms of polynomials of $e^{2t/V}$. Although a recurrence procedure for restoring these polynomials had been proposed in [11], no general result suitable for the analysis of the polynomials in the thermodynamic limit had been found at that time.

Only recently my colleagues prompted me a remarkable identity (see Ref. [15]) that allowed for moving ahead. It is,

$$\ln D(z, \tau) = \sum_{g=1}^{\infty} \frac{z^g e^{Mg\tau}}{g!}(e^{2\tau} - 1)^{g-1} F_{g-1}(e^{2\tau}), \quad (8)$$

where $\tau = 2t/V$ and $F_g(x)$ are the Mallows-Riordan polynomials discussed in [15]. Their exponential generating function $F(z, x) = \sum_{g=1}^{\infty} F_g(x) z^g/g!$ is known to obey the equation (see Ref. [15]),

$$\frac{\partial F}{\partial \xi} = F(\xi, x)\left(\frac{xF(x\xi, x) - F(\xi, x)}{x - 1}\right). \quad (9)$$

Now collecting Eqs. (6)–(8) yields the exact mass spectrum,

$$\bar{n}_g(\tau) = C_M^g e^{(g^2 - 2Mg + g)\tau}(e^{2\tau} - 1)^{g-1} F_{g-1}(e^{2\tau}). \quad (10)$$

The polynomials $F_g(x)$ can be restored step by step from the recurrence $[F_0(x) = 1]$,

$$F_g(x) = \sum_{l=1}^{g} C_{g-1}^{l-1}(1 + x + \ldots + x^{l-1}) F_{l-1}(x) F_{g-l}(x). \quad (11)$$

Hence, the exact mass spectrum is found. Now our task is to investigate the spectrum at finite t in the thermodynamic limit $M \longrightarrow \infty$, $V \longrightarrow \infty$, $M/V = m < \infty$. This asymptotic analysis is, however, far from being trivial.

The sol-gel transition happens at finite t. At large V the argument of F_{g-1} in Eq. (10) approaches unity. So we will solve Eq. (9) at $x = 1 + \delta$, where $\delta \ll 1$. We introduce the polynomials $P_g(\delta) = F_g(1 + \delta)$ and their exponential generating function,

$$y(\xi, \delta) = \sum_{g=0}^{\infty} \frac{\xi^g}{g!} P_g(\delta). \quad (12)$$

The equation for $y(\xi, \delta)$ follows from Eq. (9) after a single integration,

$$\ln y(\xi, \delta) = \xi \int_0^1 y[\xi(1 + u\delta), \delta] \mathrm{d}u. \quad (13)$$

At $\delta = 0$ the solution to Eq. (13) is readily found,

$$\ln y_0 = \xi y_0, \quad (14)$$

where we introduced $y_0(\xi) = y(\xi, 0)$.

Let us expand $y(\xi, \delta)$ over the powers of δ,

$$y(\xi, \delta) = \sum_{k=0}^{\infty} \frac{\delta^k}{k!} y_k(\xi), \quad (15)$$

where $y_k(\xi) = \partial_\delta^k y(\xi, \delta)|_{\delta=0}$. Equation (13) yields

$$\partial_\delta^n \ln y|_{\delta=0} = \sum_{m=0}^{n} \frac{\xi^{m+1}}{m + 1} C_n^m \frac{\partial^m}{\partial \xi^m} y_{n-m}(\xi). \quad (16)$$

It is easy to conclude that $y_k(\xi)$ is a linear combination of the functions $A(a, b, c; \xi) = \xi^a y_0^b (1 - \ln y_0)^{-c}$. For example, $y_1 = \frac{1}{2}A(2, 3, 2)$, $y_2 = \frac{5}{3}A(3, 4, 3) + \frac{1}{3}A(3, 4, 4) + \frac{3}{2}A(4, 5, 4) + \frac{5}{4}A(4, 5, 5)$. The functions A are seen to be singular at $\xi = e^{-1}$ [see Eq. (14)]. The stronger the singularity the higher power of g appears in A_g. Indeed,

$$A_g(a, b, c) = \frac{g!}{2\pi i} \oint \frac{y^b \mathrm{d}\xi}{\xi^{g-a+1}(1 - \ln y_0)^c}. \tag{17}$$

At large g ($g \gg a, bc$), one finds

$$A_g(a, b, c) \approx \frac{g^g}{(c-2)!} g^{(c-1)/2} 2^{(c-3)/2} \Gamma\left(\frac{c-1}{2}\right). \tag{18}$$

The central idea of the asymptotic analysis consists in the summation of the leading singularities in the expansion Eq. (15). The leading singularity in $y_k(\xi)$ corresponds to $c = 3k - 1$. We thus come to the conclusion that the leading singularities contribute to $y(\xi, \delta)$ as follows:

$$y(\xi, \delta) \approx \sum_{k=1}^{\infty} \frac{a_k \delta^k}{(1 - \ln y_0)^{3k-1}}. \tag{19}$$

Finally we find the following asymptotic estimation for the polynomial $P_g(\delta)$,

$$P_g(\delta) \approx g^{g-1}[1 + S_g(\delta)], \tag{20}$$

where

$$S_g(\delta) = \frac{e}{4} \sum_{k=1}^{\infty} \frac{(g^{3/2}\delta)^k \prod_{s=2}^{k}(3s-4)}{(3k-3)!} 2^{k/2} \Gamma\left(\frac{3k-2}{2}\right). \tag{21}$$

The sum $S_g(\delta)$ in Eq. (19) can be asymptotically converted to

$$S_g(\delta) \approx \sum_{k=1}^{\infty} k^{1/6} \left[\frac{\delta g^{3/2}}{\sqrt{12}}\right]^k e^{-0.5k \ln k + k/2}. \tag{22}$$

Let us evaluate this sum by the saddle point method. The saddle point locates at $k = k_s = g^3\delta^2/12$. In order to apply Eq. (18) [we have done it in deriving Eq. (21)], we must demand $k_s \ll g$ or $\delta g \ll 1$. This restriction, however, does not hinder us to investigate the vicinity of the transition point, because we expect that at small but finite differences $t - t_c \ll 1$, the gel will appear at small $g\delta \ll 1$. Hence, we have from Eq. (22)

$$S_g(\delta) \approx \exp\left(\frac{1}{24} g^3 \delta^2\right). \tag{23}$$

It is also possible to find the full asymptotic estimate for the polynomials $P_g(\delta)$. It is

$$P_g(\delta) \propto \frac{\sinh^g(g\delta/2)}{(\delta/2)^g}. \tag{24}$$

Now we are ready to restore the particle mass distribution. Let us exponentiate the rhs of Eq. (10) and replace F_{g-1} using the results of our asymptotic analysis [Eqs. (20) and (23)]. We find $\bar{n}_g(t) \propto e^{-M\Phi(\mu,\epsilon)}$ with

$$\Phi(\mu, \epsilon) = \frac{\mu(\mu - 4\epsilon)^2}{8}. \tag{25}$$

Here we introduced $\mu = g/V$, $\epsilon = t_c - t$. We also put $m = M/V = 1$. The extension of final results to the case of $m \neq 1$ is trivial ($t \longrightarrow mt$). Next, we will follow the route adopted from the theory of phase transitions, with the functions $\Phi(\mu, \epsilon)$ playing the role of free energy. It is easy to see that $\Phi(\mu, t)$ has a maximum at $\mu_+ = 4\epsilon/3$ and a minimum at $\mu_- = 4\epsilon$. It is important to notice that $\Phi_1(\mu_-, t) = 0$. On the other hand, the direct calculation of the mass of the gel particle gives [11]

$$t = \frac{1}{2\mu_c} \ln\frac{1}{1 - \mu_c}. \tag{26}$$

At small μ_c this equation gives $\mu_c = \mu_-$.

Let us write down the mass distribution in the variables g, ϵ

$$\bar{n}_g(t) = C(g, \epsilon) \exp\left(-\frac{g^3}{8M^2} + \epsilon\frac{g^2}{M} - 2g\epsilon^2\right). \tag{27}$$

The normalization factor $C(g, \epsilon)$ can be retrieved from the mass conservation,

$$C(g, \epsilon) = \frac{M}{\sqrt{2\pi g^5}} + \frac{\sqrt{\epsilon}\theta(\epsilon)}{\sqrt{2\pi M}}, \tag{28}$$

with $\theta(\epsilon)$ being the Heaviside step function. Indeed, below the transition point the total mass conserves and the asymptotic mass spectrum is known. Equations (27) and (28) reproduce the latter at $g \ll M$. Above the transition point the second term normalizes the peak appearing at $g = \mu_- M$ to unity, whereas the first term does not contribute to the mass at such large g.

Now it becomes possible to describe what is going on. Below the transition point (at $\epsilon < 0$), the mass spectrum exponentially drops down in increasing g. The terms containing the mass M in the denominators [see Eq. (27)] play a role only at $g \propto M$. At these masses, the particle concentrations are exponentially small. In short, in the thermodynamic limit and at $\epsilon < 0$ the first two terms in the exponent on the rhs of Eq. (27) can be ignored. The spectrum reduces to the well known form,

$$\bar{n}_g(t) = \frac{M}{\sqrt{2\pi g^5}} e^{-2g\epsilon^2}. \tag{29}$$

At the critical point ($t = t_c$ or $\epsilon = 0$), the spectrum acquires the form,

$$\bar{n}_g(t) = \frac{M}{\sqrt{2\pi g^5}} e^{-g^3/8M^2}. \tag{30}$$

Although the expression in the exponent contains M in the denominator, we have no right to ignore it, for this exponential factor provides the convergence of the integral for the second moment $\phi_2 = M^{-1} \sum g^2 \bar{n}_g$,

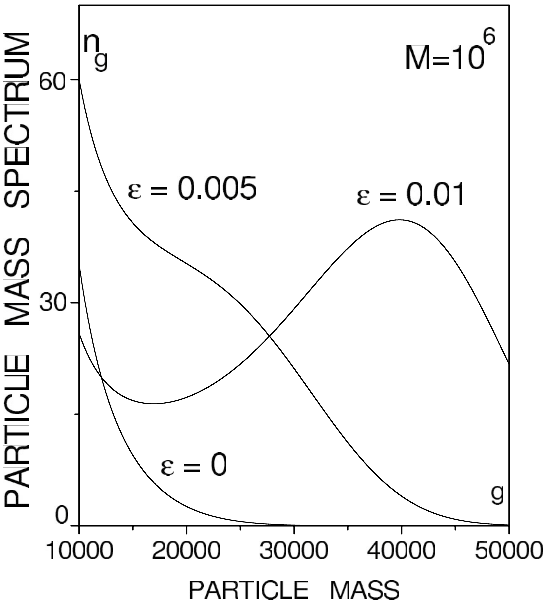

FIG. 1. The particle mass spectrum at $\epsilon = 0, 0.005, 0.01$. It is seen how the gel appears from nothing.

$$\phi_2(t_c) = \frac{1}{\sqrt{2\pi}} \int_0^M \frac{e^{-g^3/8M^2} \mathrm{d}g}{\sqrt{g}} \approx \frac{1}{3\sqrt{\pi}} \Gamma(1/6) M^{1/3}. \tag{31}$$

Here $\Gamma(x)$ is the Euler gamma function.

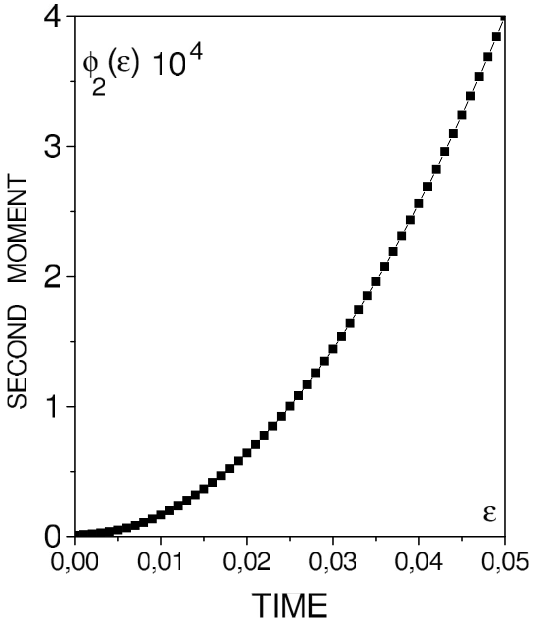

FIG. 2. The second moment ϕ_2 vs time ($\epsilon = t - t_c$) at the postcritical stage. On reaching the value $\phi_2 \propto M^{1/3}$ at $t = t_c$ (or $\epsilon = 0$) the second moment continues to grow solely because the gel actively eats smaller particles and grows. At the postcritical stage $\phi_2 = M\mu_c^2$.

It is seen that $\phi_2(t_c)$ does not diverge anymore. It remains finite, but now it contains the factor $M^{1/3}$ [compare with Eq. (3)].

Above the transition point the situation drastically changes. Figure 1 clearly demonstrates what is going on. Right after the critical time the particle mass distribution splits into two parts: the thermodynamically populated one whose behavior is described by the Smoluchowski equation at $g \ll M$ and a narrow peak with the mass exactly equal to the difference $M\mu_c(t) = M - M\mu_s(t)$, where $\mu_s(t)$ is the mass of the thermodynamically populated fraction. This peak can be now referred to as gel. The gel peak has the Gaussian form. Indeed, at $\mu \propto \mu_-$ Eq. (27) gives

$$\bar{n}_g = \frac{\sqrt{\epsilon}}{\sqrt{2\pi M}} e^{-M\epsilon(\mu-\mu_-)^2/2}. \tag{32}$$

The width of the gel peak is thus $\Gamma \propto 1/\sqrt{M\epsilon}$. This peak is well separated from the rest of the mass spectrum when its width much exceeds g_c, This happens after a very short time $\epsilon \propto 1/M$. Thus born gel actively "eats" smaller particles and grows.

In Fig. 2 the postcritical behavior of the second moment is displayed. On reaching the critical value [Eq. (31)] it instantly (for the times $\epsilon \propto M^{-1}$) reaches the value of the order of M^2 and continues to grow solely because the gel peak moves to the right along the particle mass axis.

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