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Exact kinetics of the sol-gel transition

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The formation of a gel in a disperse system wherein 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 coalescing particles. This model is known to reveal the sol-gel transition, i.e., the formation of *one* giant cluster with the mass comparable to the total mass of the whole system. This paper reports on the exact solution of this model for a finite total mass of the coagulating system. The evolution equation for the generating functional defining all properties of coagulating systems is solved exactly for this particular kernel. The final output is the exact expression for the single-particle mass spectrum as a function of time. The analysis of the spectrum in the thermodynamic limit shows that after a critical time a giant single particle (the gel) appears. Although the concentration of this giant gel particle is zero in the thermodynamic limit, it actively interacts with smaller particles "eating" them and thus growing in mass. Special attention is given to the transition point, where the gel is appearing. It is demonstrated that the sol-gel transition reminds the second-order phase transition. The time dependencies of the gel mass, the number concentration, and the second moment of the particle mass spectrum are found.

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I. INTRODUCTION

Various phenomena having a quite different nature can be often described as aggregation–fragmentation processes of the type,

$$\sum (m_k) \rightleftarrows \sum (n_k), \tag{1}$$

where the notation (x) stands for an x-mer, a cluster comprising a given number x of elementary units (monomers). The numbers of terms in the sums are normally nonequal. Very many examples of such processes are listed in review articles [1–3]. The kinetics of aggregation-fragmentation processes is formulated in terms of $\overline{n_g}(t)$, the average numbers of g-mers in the system at time t. It is more common, however, to use the concentrations $c_g(t)=\overline{n_g}(t)/V$, where V is the volume of the system proportional to M, the total number of monomeric units. Of course, M conserves during the whole process, once there are neither sources nor sinks of g-mers in the system. This thermodynamic description silently assumes that the average occupation numbers are proportional to M, and if not, the respective concentrations are simply equal to zero as $M\to\infty$. Normally this step does not lead to some dramatic consequences and the respective kinetic equations have found wide applications in many branches of science.

One of them is the famous Smoluchowski equation describing the kinetics of the coagulation process, the simplest example of which is the evolution of a system of monomeric units that are able to form g-mers resulting from a chain of binary irreversible coalescence processes,

$$(m_1) + (m_2) \to (m_1 + m_2). \tag{2}$$

In the simplest case of spatially uniform systems this equation claims

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

Here the coagulation kernel $K(g,l)$ is the transition rate for the process $(g)+(l)\to(g+l)$. The first term on the right-hand side (rhs) of Eq. (3) 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.

In what follows we use the dimensionless form of Eq. (3), i.e., all concentrations are measured in units of the initial monomer concentration M/V and time in units of $V/MK(1,1)$.

Already more than three decades ago I began to suspect that the Smoluchowski equation can lead to some unpleasant consequences [4]. In particular, if the coagulation kernel $K(g,l)$ is a homogeneous function of the masses g and l, i.e., $K(ag,al)=a^\lambda K(g,l)$, and $\lambda>1$, the moments of particle mass spectrum behave reasonably only during a finite interval of time. Moreover, there are not physical principles that would forbid the exponent λ to exceed unity and quite realistic coagulation kernels with $\lambda>1$ are not rarities (see Refs. [1,2] and references therein). One of them is the kernel proportional to the product of masses of coagulating particles, $K(g,l)\propto gl$ describing the formation of needlelike aerosol particles in external electric fields [5,6]. In this case $\lambda=2$, and the Smoluchowski equation should work only during a finite interval of time. Indeed, an attempt to calculate the second moment of the particle mass spectrum, $\phi_2 = \Sigma_g g^2 c(g)$ for $K(g,l)\propto gl$ leads to a strange result (see, e.g., [1])

$$\phi_2(t) \propto \frac{1}{t_c - t}, \tag{4}$$

where the critical time t_c depends on the initial mass spectrum, and this is not yet all. The total mass concentration

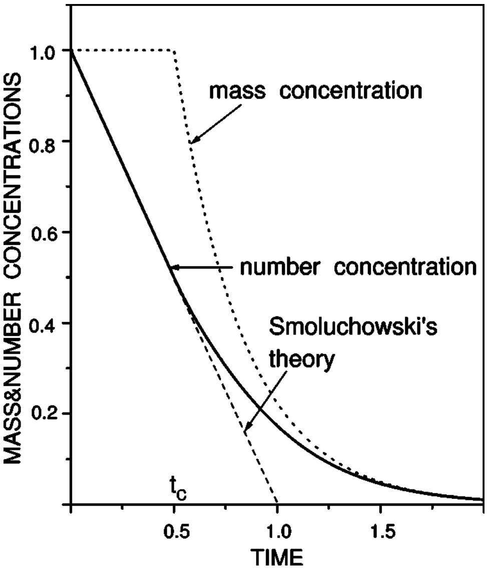

FIG. 1. The total number and total mass concentrations of sol particles are shown as the functions of time (dimensionless units). After the critical time $t=t_c=0.5$ the mass concentration decreases with time because a massive gel particle forms and begins to consume the mass of the sol. On the other hand, the number concentration does not feel the loss of one (although very big) gel particle. Still the postcritical behavior of the curve differs from that predicted by the Smoluchowski equation [$n(t)=1-t$, dashed line].

$m(t)=\Sigma_g g c_g(t)$ 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. (3) (and common sense) it should remain constant. Next, at $t>t_c$ the particle number concentration $n(t)=\Sigma_g c_g(t)$ crosses the t axis and becomes negative (see Fig. 1).

Of course, these unusual features of the solution to Eq. (3) did not remain unnoticed and a considerable literature exists, where this problem had been considered in detail [1,3,7–16]. Many authors have attempted to answer the question, what is going on at the critical point and after. Most of these attempts relied upon the use of the Smoluchowski equation (see especially review articles [1–3]). The loss of the mass was attributed to the appearance of a *gel*.

Two scenarios of the sol-gel transition had been proposed (see, e.g., [1–3,9,13]). The first one (and the most widespread) assumes that after the critical time the coagulation process instantly transfers large particles to a gel state, the latter being defined as an infinite cluster [17–23]. This gel can be either passive (it does not interact with the coagulating particles) or active (coagulating particles can stick to the gel). 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 (see Ref. [22]).

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

The situation had become more clear after the papers [24,25], where a class of so-called truncated models had been considered. In these models a cutoff particle mass G was introduced. The truncation was treated as an instant sink removing very heavy particles with the masses $g>G$ from the system. In such systems the mass cannot conserve. Very big particles form a deposit 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 catastrophe is expected to come up. The exact analysis of Refs. [24,25] had shown that indeed, nothing wrong happens even for the coagulation kernel $K\propto gl$. The total mass concentration of active particles drops down with time, as it should be, for the largest particles settle out to deposit. But as $G\to\infty$ the total mass concentration of active particles almost conserves at $t<t_c$ and only very shortly before the critical time ($t_c-t\propto G^{-1/2}$) the deposit begins to form and the mass drops down with time. After the critical time the total mass of active particles diminishes as reciprocal time. The mass spectrum of the deposit had been found in Refs. [24,25]. It is clear that the deposit is entirely identical to the gel of works [17–23].

The second scenario considers the coagulation process 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." The gel appears as a *single* giant particle of mass g comparable to the total mass M of the whole system. Although this scenario is also of rather vulnerable age, very few works [9–14] appeared attempting to analyze the kinetics of sol formation in finite systems.

The consideration of finite systems calls for an alternative approach. Such an approach based on the scheme developed in Ref. [26] had been proposed in Ref. [9] and applied in this work to the model $K(g\cdot l)\propto gl$. Although the solution to the evolution equation for $K\propto gl$ had been found, it contained a recurrence procedure that did not open a gate for a straightforward asymptotic analysis of the result. The main goal of this paper is to find the exact analytical expression for the particle mass spectrum in the finite coagulating system with the kernel $K(g,l)=2gl$.

From the first sight, the coagulation process cannot lead to something wrong. Indeed, let us consider a *finite* system of M monomers in the volume V. If the monomers move, collide, and coalesce on colliding, the coagulation process, after all, forms one giant particle of the mass M. The concentration of this M-mer is small, $c_M\propto 1/M$. Better to say, it is zero in the thermodynamic limit V, $M\to\infty$, $M/V=m<\infty$. In other words, no particles exist in coagulating systems after a sufficiently long time.

What happens then in the system with $K(g,l)\propto gl$ if we consider the thermodynamic limit? The answer is simple, although in no way apparent [9]. In contrast to "normal" systems, where the time of formation of a large object 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. [9] and as gel in modern literature) actively begins to "eat" the smaller particles. Although the probability for any two particles to meet is generally small [$\propto K(g,l)/V$], in the case of the superparticle this smallness is compensated by the large value of the coagulation kernel proportional to the particle mass M, which is, in turn, proportional to V. Hence the superparticle whose concentration is zero in the thermodynamic 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 superparticle 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. An alternative approach should be used.

Such an approach had been proposed by Marcus [26] and then by several authors [27,28]. However, this approach did not find wide recognition because of its complexity and the absence of the areas of application. In short, its application was considered as a tool for constructing practical numerical recipes for Monte Carlo modeling [11,28].

However, later this approach was reformulated in Ref. [9] in a more compact form. The idea to replace the Master equation by the equation for the generating functional had opened the gate for analyzing a class of so-called linear models with the kernels

$$K(g,l) = gf(l) + lf(g). \tag{5}$$

Here $f(x)$ is an arbitrary (but still a reasonable) function. The model $K(g,l)=2gl$ belongs to this class. The analysis of Ref. [9] allowed the answers to many questions, but the real exact solution had not yet been found. This step is completed after more than a quarter of a century in this paper (see also Ref. [29,30]). It became possible after a fairly recent paper [31], where a key identity so necessary for solving the present task had been derived.

Below the exact solution of the model of the coagulating system with the kernel $K=2gl$ is presented and analyzed in the thermodynamic limit. This solution is of great importance not only because it describes a phase transition but admits an exact analysis. The coagulating system with $K=2gl$ is a very rare example of exactly soluble model that refers to a realistic process. In this case this is the aerosol-aerogel transition observed in several laboratories [5,6,32].

The reminder of the paper is organized as follows. The next section outlines the basics of the approach and formulates the equation describing the time evolution of coagulating systems. The solution of the evolution equation for the kernel $K(g,l)=2gl$ is given in Sec. III. Section IV contains the asymptotic analysis of the postgel behavior of the particle number and mass concentration. An exact expression is derived for the second moment of the particle mass spectrum. The thermodynamic limit of the particle mass spectrum is also restored in this section. A summary of the results and some additional comments are presented in concluding Sec. V. Some important properties of the polynomials entering the expression for the exact mass spectrum [Eq. (35)] are given in Appendixes A and B.

II. APPROACH AND BASIC EQUATION

The description of the coagulation process in terms of occupation numbers (numbers of g-mers considered as random variables) had been first introduced by Marcus [26]. This approach had been then reformulated by me [9] in a form strongly resembling the second quantization. Here I outline this approach and introduce some useful extensions.

A. Free coagulation

Let there be M monomers in a volume V. The monomers move, coalesce, produce dimers, trimers, etc., along the scheme (2). Let then

$$Q = \{n_1, n_2, \dots, n_g, \dots\} \tag{6}$$

be the state of the system given by the set of integers n_g, the numbers of particles of mass g, with g being the number of monomeric units in a g-mer. A single coagulation act (the collision of two particles + their coalescence) changes a preceding state

$$Q^- = \{n_1, \dots, n_l + 1, \dots, n_m + 1, \dots, n_g - 1, \dots\} \tag{7}$$

if $l \neq m$ and

$$Q^- = \{n_1, \dots, n_l + 2, \dots \ \dots, n_g - 1, \dots\} \tag{8}$$

if $l=m$, $2l=g$ to the state Q by coalescing the particles with masses l and m to one particle with mass g. In its turn, a next coagulation act transfers the state Q to the state Q^+ according to the scheme

$$Q^- \to Q \to Q^+, \quad (Q^+)^- = Q. \tag{9}$$

The probability per unit time for two particles to collide and coalesce is $K(l,m)/V$, where $K(l,m)$ is the coagulation kernel (the efficiency of the coagulation process). The rate of the process (2) is then

$$A(Q,Q^-) = \frac{K(l,m)}{2V} n_l(Q^-)[n_m(Q^-) - \delta_{l,m}]. \tag{10}$$

Here $\delta_{a,b}$ stands for the Kroneker delta. The combinatorial multiplier here is just the number of ways to get a successfully coalescing pair of l- and m-mers.

Next, we introduce the probability $W(Q,t)$ to find the system in the state Q at time t. We can write down the Master equation for the probability $W(Q,t)$. It is

$$\frac{dW(Q,t)}{dt} = \sum_{Q^-} A(Q,Q^-)W(Q^-,t) - \sum_{Q^+} A(Q^+,Q)W(Q,t). \tag{11}$$

Technically it is much more convenient to deal with the generating functional

$$\Psi(X,t) = \sum_Q W(Q,t)X^Q \tag{12}$$

rather than with the probability $W(Q,t)$. Here X stands for the set $x_1, x_2, \dots$ and $X^Q = x_1^{n_1(Q)} x_2^{n_2(Q)} \cdots$.

Of course,

$$\Psi(X=1,t) = 1, \tag{13}$$

which corresponds to the normalization of $W(Q,t)$ to unity, i.e., $\Sigma_Q W(Q,t)=1$.

The equation for Ψ is readily derived from Eq. (11). Indeed, noticing that

$$x_{l+m}\frac{\partial^2}{\partial x_l \partial x_m}X^Q = [n_l(Q)n_m(Q) - \delta_{l,m}n_m(Q)]X^{Q^+}$$

and

$$x_l x_m\frac{\partial^2}{\partial x_l \partial x_m}X^Q = [n_l(Q)n_m(Q) - \delta_{l,m}n_m(Q)]X^{Q}$$

we find instead of Eq. (11),

$$V\frac{\partial \Psi}{\partial t} = \hat{\mathcal{L}}\Psi, \tag{14}$$

where the evolution operator $\mathcal{L}$ is defined as

$$\hat{\mathcal{L}} = \hat{\mathcal{L}}_0 = \frac{1}{2}\sum_{l,m} K(l,m)(x_{l+m} - x_l x_m)\frac{\partial^2}{\partial x_l \partial x_m}. \tag{15}$$

At this step we introduce the operators of occupation numbers, total particle number, and total particle mass. They are

$$\hat{n}_j = x_l\frac{\partial}{\partial x_l}, \quad \hat{N} = \sum_l \hat{n}_l, \quad \hat{M} = \sum_l l\hat{n}_l. \tag{16}$$

Any average value of interest can be expressed in terms of Ψ. For example, the average mass spectrum $\overline{n_g}(t) = \Sigma_Q n_g(Q)W(Q,t)$ is

$$\overline{n_g}(t) = \hat{n}_g\Psi(X,t)|_{X=1}. \tag{17}$$

It can be readily checked that $\hat{M}$ commutes with the evolution operator,

$$[\hat{\mathcal{L}},\hat{M}] = 0, \tag{18}$$

which means the total mass conservation.

The analogy with the second quantization is now clearly seen: the operator ∂_x acts as an annihilation operator and x as a creation operator. Their commutator $\partial_x x - x\partial_x = 1$. Hence the first term on the rhs of Eq. (15) replaces two particles with masses l and m by one with the mass equal $l+m$. The second term written as $\hat{n}_l\hat{n}_m - \hat{n}_l\delta_{m,l}$ removes the pair of particles with masses l and m from a given state of the coagulating system. The rate of both these processes is $K(l,m)$.

B. Source and sink

The spatially uniform external sources of particles can substantially change the kinetics of the coagulation process. Let the source produce g-mers with the rate $I(l)/V$. Then the processes changing the numbers of g-mers by one should be taken into account in the evolution equation. The respective evolution operator is

$$\hat{\mathcal{L}}_I = \sum_l I(l)(x_l - 1). \tag{19}$$

The structure of this operator is absolutely transparent: the first term adds an l-mer from any preceding state containing $n_l - 1$ l-mers and the second one gives the number of ways to leave the state with a given occupation number.

Similarly we can introduce the sink proportional to the number of l-mers. The respective evolution operator is

$$\hat{\mathcal{L}}_\lambda = \sum_l \lambda_l(1 - x_l)\frac{\partial}{\partial x_l}. \tag{20}$$

Here λ_l is the rate of sinks.

C. Fragmentation

Let $B(g|l,m)$ be the rate of the fragmentation process $(g) \to (l) + (m)$. The transition goes from the state $Q^+ = (\ldots, n_l - 1, \ldots, n_{m-1}, \ldots, n_{g+1}, \ldots)$ to the state $Q = (\ldots, n_l, \ldots, n_m, \ldots, n_g, \ldots)$. The operator

$$\hat{\mathcal{L}}_f = \sum_{g,l,m} B(g|l,m)(x_l x_m - x_{l+m})\frac{\partial}{\partial x_{l+m}} \tag{21}$$

then introduces the fragmentation process.

If we want to take into account all the processes altogether we must use $\hat{\mathcal{L}} = \Sigma\hat{\mathcal{L}}_s$ in Eq. (14).

III. EXACT SOLUTION

Considerable simplifications of Eq. (14) arise for the kernels given by Eq. (5). In particular, for $f(x) = x$ one finds (see also Ref. [9]),

$$\hat{\mathcal{L}} = \sum_{l,m} lm x_{l+m}\frac{\partial^2}{\partial x_l \partial x_m} + \sum_l l^2\hat{n}_l - \hat{M}^2. \tag{22}$$

If we work with the functionals belonging to a given mass M, i.e.,

$$\hat{M}\Psi_M = M\Psi_M, \tag{23}$$

then the operator $\hat{M}$ in Eq. (22) can be replaced by c-number M.

The functional $\Psi_M(X,t)$ can be now constructed in the form

$$\Psi_M = \frac{M!}{2\pi i}\oint \frac{dz}{z^{M+1}}\exp\left[\sum_{g=1}^{\infty} z^g a_g(t)x_g\right]. \tag{24}$$

The integration contour in Eq. (24) surrounds the origin of coordinates in the complex plane z.

It is easy to check that

(1) the functional Ψ_M corresponds to initially monodisperse sol $\Psi_M(X) = x_1^M$ if $a_g(0) = \delta_{g,1}$;

(2) the functional Ψ_M meets Eq. (23);

(3) the functional Ψ_M is the solution to Eq. (14) with $\hat{\mathcal{L}}$ given by Eq. (22) if the coefficients $a_g(t)$ are determined from the set of equations,

$$V\frac{da_g}{dt} = \sum_{l=1}^{g-1} l(g-l)a_l a_{g-l} - Mga_g + g^2 a_g; \tag{25}$$

(4) the functional Ψ_M satisfies the normalization condition $\Psi_M(1,t) = 1$.

Let us introduce the generating function $G(z,t)$ for $a_g(t)$,

$$G(z,t) = \sum_{g=1}^{\infty} a_g(t) z^g. \tag{26}$$

On multiplying both sides of Eq. (25) by z^g and summing over all g give the closed equation for $G(z,t)$,

$$V\frac{\partial G}{\partial t} = \left(z\frac{\partial G}{\partial z}\right)^2 - Mz\frac{\partial G}{\partial z} + z\frac{\partial}{\partial z}z\frac{\partial G}{\partial z}. \tag{27}$$

The substitution

$$G(z,t) = \ln D(ze^{-Mt/V},t) \tag{28}$$

allows Eq. (27) to be cast into the linear equation for $D(z,t)$,

$$V\frac{\partial D}{\partial t} = z\frac{\partial}{\partial z}z\frac{\partial D}{\partial z}. \tag{29}$$

According to Eqs. (17) and (24) the average occupation numbers are expressed as

$$\overline{n_g}(t) = \frac{M!}{2\pi i} a_g(t) \oint \frac{dz}{z^{M-g+1}} e^{G(z,t)}. \tag{30}$$

It is convenient to introduce the variable

$$\tau = \frac{t}{V}. \tag{31}$$

The solution to Eq. (29) is then readily found as a *formal* series (see Refs. [33,34] and references therein),

$$D(z,t) = \sum_{g=0}^{\infty} \frac{z^g}{g!} e^{g^2\tau}. \tag{32}$$

Here z is a formal variable whose power g just defines the coefficient before z^g. It is admissible to perform exact operations with such functions as with the normal one. For example, $\oint f(z)dz$ where $f(z)=\Sigma a_g z^g$ is defined as $\oint f(z)dz = 2\pi i a_{-1}$ irrespective of what this a_g is. Such objects are successfully used in combinatorial analysis for deriving combinatorial identities [33,34].

We thus can find the integral entering Eq. (30). It is

$$\frac{1}{2\pi i}\oint \frac{dz}{z^{M-g+1}} e^{G(z,\tau)} = \frac{1}{2\pi i}\oint \frac{dz}{z^{M-g+1}} D(ze^{-M\tau},\tau)$$
$$= \frac{1}{(M-g)!} e^{(g^2-Mg)\tau}. \tag{33}$$

In order to restore $a_g(t)$ we use the identity [31],

$$\ln D(z,\tau) = \sum_{g=1}^{\infty} \frac{z^g e^{Mg\tau}}{g!} (e^{2\tau}-1)^{g-1} F_{g-1}(e^{2\tau}), \tag{34}$$

where $F_g(x)$ are the Mallows-Riordan polynomials discussed in Refs. [35,36]. (The derivation of this identity is given in Appendix A).

Combining this result with Eqs. (30) and (33) we finally find the exact particle mass spectrum,

$$\overline{n_g}(\tau) = C_M^g e^{(g^2-2Mg+g)\tau} (e^{2\tau}-1)^{g-1} F_{g-1}(e^{2\tau}). \tag{35}$$

The recurrence Eq. (A12) proves that the spectrum Eq. (35) conserves the total mass, i.e., $\Sigma_g g\overline{n_g}(\tau)=M$. Indeed, let us apply Eq. (A12) to $g=M-1$ and use the notation $x=e^{2\tau}$. We have,

$$1 = \sum_{g=0}^{M-1} C_{M-1}^g (x-1)^g F_g(x) x^{(g+1)(g-2M+2)/2}$$
$$= \sum_{g=1}^{M} C_{M-1}^{g-1} (x-1)^{g-1} F_{g-1}(x) x^{g(g-2M+1)/2}$$
$$= M^{-1} \sum_{g=1}^{M} g C_M^g (x-1)^{g-1} F_{g-1}(x) x^{g(g-2M+1)/2}.$$

This is exactly what we wanted.

IV. THERMODYNAMIC LIMIT

The sol-gel transition happens at finite t. Therefore it is important to explore the asymptotic behavior of the mass spectrum given by Eq. (35) at finite t and V, $M \to \infty$, $M/V = m < \infty$ (the thermodynamic limit). At large V the argument of F_{g-1} in Eq. (35) approaches unity. So we are trying to analyze Eq. (35) at $\tau \propto M^{-1} \ll 1$.

A. The Smoluchowski spectrum

We begin the analysis by considering the limit of finite g and M, $V \to \infty$. Here and below we put $m=M/V=1$. The replacement $t \to mt$ restores the dependence of the results on m.

As is known [31,35,36]

$$F_g(1) = (g+1)^{g-1}. \tag{36}$$

We thus can write down the mass spectrum at $g \ll M$,

$$\overline{n_g}(t) \approx \overline{n_g^{(s)}}(t) = M\frac{g^{g-2}}{g!} e^{-2gt} (2t)^{g-1}. \tag{37}$$

The notation $\overline{n_g^{(s)}}(t)$ stands for the exact solution to the Smoluchowski equation (3). It is seen that we can introduce concentrations $c_g(t)=\overline{n_g^{(s)}}(t)/V$ which are independent of M. No traces of the catastrophe at $t=t_c$ are yet seen. All functions $\overline{n_g^{(s)}}(t)$ are well defined at all t. However, as we will see below, the total mass of the spectrum $\overline{n_g^{(s)}}(t)$ does not conserve at $t > t_c$.

B. Mass concentration

Here we find the time dependence of the mass concentration $m(t)=M(t)/V$ and the particle number concentration $n(t)=N(t)/V$. To this end we introduce the generating function for the spectrum $c_g(t)$,

$$\Theta(z,t) = \frac{1}{M}\sum_{g=1}^{\infty} z^g n_g(t) = e^{-2t}\int_0^z y_o(\xi \cdot 2te^{-2t}) d\xi. \tag{38}$$

Here $y_o(s)$ is the exponential generating function for $F_g(1)$ [31,35,36],

$$\ln y_o(s) = s y_o(s). \tag{39}$$

The total mass concentration is readily expressed in terms of y_o as follows:

$$m(t) = e^{-2t} y_o(2te^{-2t}) = 1 - \mu_c(t), \tag{40}$$

where the function $\mu_c(t)$ describes the deficit of the mass concentration after the critical time t_c. From Eqs. (39) and (40) we find,

$$2t = \frac{1}{\mu_c(t)} \ln \frac{1}{1-\mu_c(t)}. \tag{41}$$

This equation has only one root $\mu_c(t)=0$ at $t<t_c$ and two roots at $t>t_c$. It is clear why we should choose the positive nonzero root after the critical time. The point is that the spectrum Eq. (37) *shrinks* after the critical time, so its mass cannot remain constant.

C. Number concentration

The total particle number concentration can also be expressed in terms of the function $y_o(s)$,

$$n(t) = \frac{N(t)}{M} = e^{-2t} \int_0^t y_o(\xi 2te^{-2t}) d\xi = \frac{1}{2t} \int_0^{2te^{-2t}} y_o(s) ds.$$

The integration on the rhs of this equation can be readily performed. Replacing the variable $s \to y_o = y$ gives

$$\begin{aligned} n(t) &= \frac{1}{2t} \int_0^{2te^{-2t}} y(s) ds \\ &= \frac{1}{2t} \int_0^{y_0} y \frac{1-\ln y}{y^2} dy \\ &= \frac{1}{2t} \left(\ln y_0 - \frac{1}{2} \ln^2 y_0 \right) = m(t) - tm^2(t), \end{aligned} \tag{42}$$

where we used $y_0(t) = y_o(2te^{-2t}) = e^{2t} m(t)$.

D. Gel comes up

Now let us calculate the derivative $\dot{n}$.

$$\dot{n} = \dot{m}(t) - m^2(t) - 2tm(t)\dot{m}(t) = \dot{m}(t)[1 - 2tm(t)] - m^2(t).$$

But, as follows from Eq. (41),

$$\dot{m}(t) = \frac{2\mu_c(t) m(t)}{1 - 2m(t)t}$$

and

$$\dot{n} = 2\mu_c(t) m(t) - m^2(t) = -1 + \mu_c^2(t). \tag{43}$$

On the other hand, we can derive the equation for $N(t)$ from Eqs. (14), (16), (17), and (22). On applying the operator $\hat{N}$ to both sides of Eq. (14) one finds

$$V \frac{dN}{dt} = -M^2 + \varphi_2, \tag{44}$$

where φ_2 is the second moment of the particle mass spectrum,

$$\varphi_2(t) = \sum_{g=1}^{\infty} g^2 \overline{n_g}(t).$$

Comparing this with Eq. (43) yields

$$\lim \frac{\varphi_2}{V^2} = \mu_c^2(t). \tag{45}$$

Equation (45) can hold only if at $t>t_c$ the mass spectrum $\overline{n_g}(t)$ has a narrow peak at $g = M\mu_c(t)$. This result gives evidence in favor of the following facts.

(1) A giant particle with mass $g(t) = \mu_c(t) M$ forms after the critical time t_c.

(2) In the limit $M \to \infty$ the peak in the particle mass distribution has the zeroth width (the squared gel mass is equal to the second moment of the particle mass distribution).

E. Particle mass spectrum

At large (but finite) M and finite t ($t/M \ll 1$) it is more convenient to replace the polynomials $F_g(x)$ by $P_g(\delta) = F_g(1+\delta)$. As follows from Eq. (35) $\delta = 2t/M$. In order to investigate the particle mass spectrum we need to know the asymptotical behavior of $P_g(\delta)$ as $g \to \infty$, $\delta \to 0$, and $g\delta < \infty$. The respective asymptotical analysis is extremely complex (see Refs. [29,35]) and is able only to give a hint on possible functional form of $P_g(\delta)$ at large g and small δ [29]. It is,

$$P_g(\delta) \propto g^g f^g(g\delta). \tag{46}$$

The function $f(x)$ has been found in Ref. [29] for $x \ll 1$. Below the function $f(x)$ is restored in full by using very restricted information on the location of the gel peak in the particle mass distribution Eq. (41).

Let us introduce $\mu = g/M$ and exponentiate the exact mass spectrum Eq. (35),

$$\overline{n_g}(t) = e^{M\Phi(\mu,t)}. \tag{47}$$

In the limit of finite μ and $M \to \infty$ we can write,

$$\Phi(\mu,t) = -(1-\mu)\ln(1-\mu) + (\mu^2 - 2\mu)t + \mu \ln 2t + \mu\psi(\mu t), \tag{48}$$

where $\psi(x) = \ln f(2x)$. In deriving this expression the asymptotic formula for the binomial coefficients has been used,

$$C_M^g \propto e^{-M[\mu \ln \mu + (1-\mu)\ln(1-\mu)]}.$$

We have not yet specified the function ψ and will do this even not resorting to the definition of the polynomials. It is enough to know that the gel particle produces a maximum in the particle mass distribution and the position of this maximum is given by Eq. (41). The derivative $\Phi'_\mu(\mu_c) = 0$ or

$$\ln(1-\mu_c) + 1 + (2\mu_c - 2)t + \ln 2t + \psi(\mu_c t) + \mu_c t \psi'(\mu_c t) = 0,$$

where the prime stands for the differentiation over full argument. On introducing $x = \mu_c(t) t$ gives instead of Eq. (41),

$$t(x) = \frac{x}{1-e^{-2x}},$$

and we come to the ordinary linear differential equation for $\psi(x)$,

$$1 - \frac{2x}{1-e^{-2x}} + \ln\frac{2x}{1-e^{-2x}} + x\psi' + \psi = 0.$$

The solution to this equation is

$$\psi(x) = \ln\frac{1-e^{-2x}}{2x} + x. \tag{49}$$

The function $f(x)$ from Eq. (46) thus has the form

$$f(x) = \frac{\sinh(x/2)}{x/2}$$

and the exponential asymptotic formula for the polynomial $P_g(\delta)$ is

$$P_g(\delta) \propto \frac{\sinh^g(g\delta/2)}{(\delta/2)^g}. \tag{50}$$

Another derivation of this asymptotic formula is given in the end of Appendix B.

At small x this expression gives

$$\psi(x) \approx \frac{x^2}{6}. \tag{51}$$

These results had been reported in Refs. [29,30].

The function Φ, an analog of the free energy is statistical mechanics, has the form

$$\Phi(\mu,t) = -(1-\mu)\ln(1-\mu) - \mu\ln\mu + 2(\mu^2-\mu)t + \mu\ln(1-e^{-2\mu t}). \tag{52}$$

Now let us find the second derivative of Φ determining the width of the gel peak. At $\mu=\mu_c$ we have,

$$\Phi''(\mu_c,t) = -\frac{1}{1-\mu_c} - \frac{1}{\mu_c} + \frac{4t}{\mu_c}(1-te^{-2\mu_c t}). \tag{53}$$

At small ϵ, $\mu=4\epsilon$, $t=1/2+\epsilon$. Hence

$$\Phi''(\mu_c t) = -\frac{\mu_c}{1-\mu_c} - \frac{4\epsilon^2}{\mu_c} + 4\epsilon^2 \approx -\epsilon. \tag{54}$$

At large t we can approximate $1/(1-\mu_c) \approx e^{2\mu_c t} \approx e^{2t}$ and find $\Phi''(\mu_c t) = -e^{2t}$.

The function $\Phi(\mu_c,t)=0$ (arbitrary $t>t_c$).

F. Transition point

In the vicinity of the transition point we expand $\Phi(\mu,t)$ [Eq. (52)] in powers of μ and $\epsilon=t_c-t$. The result is

$$\Phi(\mu,\epsilon) \approx -\frac{\mu(\mu-4\epsilon)^2}{8}. \tag{55}$$

Next, we will follow the route adopted from 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 $\mu_m=4\epsilon/3$ and a minimum at $\mu_c=4\epsilon$. It is important to notice that $\Phi_1(\mu_c,t)=0$.

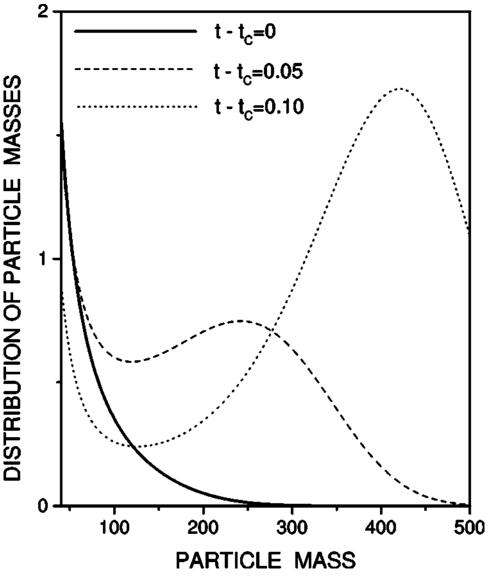

FIG. 2. The distributions of the particle masses $g\overline{n_g}(t-t_c)$ over g are shown at $t<t_c$, $t=t_c$, and $t>t_c$. Right after the critical time $t=t_c$ the gel peak begins to form and to move to the right along the g axis. All variables are dimensionless.

The mass distribution in the variables g,ϵ has the form (see also Ref. [29]),

$$\overline{n_g}(t) = C(g,\epsilon)\exp\left(-\frac{g^3}{8M^2} + \epsilon\frac{g^2}{M} - 2g\epsilon^2\right). \tag{56}$$

Unfortunately, our asymptotic analysis does not allow for restoring the normalization factor $C(g,\epsilon)$. Still some conclusions on its form can be retrieved from the mass conservation,

$$C(g,\epsilon) = \frac{M}{\sqrt{2\pi g^5}} + \frac{\sqrt{\epsilon}\theta(\epsilon)}{\sqrt{2\pi M}}, \tag{57}$$

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 (56) and (57) reproduce the latter at $g \ll M$. Above the transition point the second term normalizes the peak appearing at $g=\mu_c M$ to unity.

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. (56)] 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. (56) can be ignored. The spectrum reduces to the well-known form

$$\overline{n_g}(t) = \frac{M}{\sqrt{2\pi g^5}}e^{-2g\epsilon^2}. \tag{58}$$

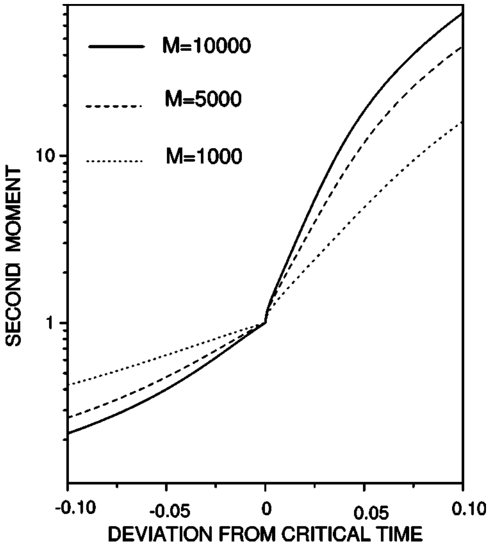

FIG. 3. The near-critical behavior of the second moment $\phi_2(\epsilon)/\phi_2(0)$, ($\epsilon = t - t_c$) at the pre- and postcritical stages. On reaching the value $\phi_2 \propto M^{1/3}$ at $t = t_c$ (or $\epsilon = 0$) the second moment continues to grow solely because the gel actively eats smaller particles and grows. The cusps on the curves at $\epsilon = 0$ signal the begining of the gel formation. All variables are dimensionless.

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

$$\overline{n_g}(t) = \frac{M}{\sqrt{2\pi g^5}} e^{-g^3/8M^2}. \tag{59}$$

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 $\phi_2 = M^{-1}\Sigma g^2 \overline{n_g}$ in the limit $M \to \infty$. We thus have

$$\phi_2(t_c) = \frac{1}{\sqrt{2\pi}} \int_0^M \frac{e^{-g^3/8M^2} dg}{\sqrt{g}} \approx \frac{1}{3\sqrt{\pi}} \Gamma(1/6) M^{1/3}. \tag{60}$$

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

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. (4)].

Above the transition point the situation drastically changes. Figure 2 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 $\mu \propto \mu_c$ Eq. (56) gives

$$\overline{n_g} = \frac{\sqrt{\epsilon}}{\sqrt{2\pi M}} e^{-M\epsilon(\mu - \mu_c)^2/2}. \tag{61}$$

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 greatly 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. 3 the near–critical behavior of the second moment is displayed. On reaching the critical value [eq. (60)] it instantly (for the times $\epsilon \propto M^{-1}$) reaches the value of the order of M^2 and continues to grow as the gel peak moves to the right along the particle mass axis.

V. CONCLUDING REMARKS

The main results of this paper are the exact mass spectrum in a gelling system, Eq. (35), and the analysis of the sol-gel transition given in Secs. IV E and IV F. We can see explicitly how the gel peak appears from nothing in a coagulating system (see also my preliminary communication [29]).

It is clear that gelation is not a property of this particular coagulating system alone. As has been mentioned in the Introduction there are many other coagulating systems under suspicion. Among them are the coagulating systems with the homogeneous kernels $K(ag, al) = a^\lambda K(g, l)$ with $\lambda > 1$ (see Refs. [2,4]). At present time there are neither clear ideas on the nature of the sol-gel transition in such systems nor regular methods for the study of this remarkable phenomenon. I hope that the exact model considered above will help to crack this hard nut.

APPENDIX A: POLYNOMIALS F_g

Here we pass the route from Eq. (32) to Eq. (34). To this end we, following Ref. [31], introduce the function

$$W(z,x) = \sum_{n=0}^{\infty} \frac{z^n}{n!} x^{n(n-1)/2}. \tag{A1}$$

Then Eq. (32) yields

$$D(z,\tau) = W(ze^\tau, e^{2\tau}). \tag{A2}$$

It is evident that

$$\partial_z W(z,x) = W(xz,x). \tag{A3}$$

Let us introduce $w(z,x)$ as

$$W(z,x) = e^{w(z,x)}. \tag{A4}$$

Using Eqs. (A3) and (A4) yields

$$\partial_z w(z,x) = e^{w(xz,x) - w(z,x)}. \tag{A5}$$

Let us now define the function $F(z,x)$ by the equality

$$\partial_z w(z,x) = F(z(x-1),x). \tag{A6}$$

Then we have from Eq. (A5)

$$F(z(x-1),x) = e^{w(xz,x) - w(z,x)}. \tag{A7}$$

On substituting here $z(x-1) = \xi$ gives

$$F(\xi,x) = \exp\left[w\left(\frac{x\xi}{x-1}, x\right) - w\left(\frac{\xi}{x-1}, x\right)\right]. \tag{A8}$$

Differentiating this equation over ξ and using Eq. (A6) give the functional equation for $F(\xi,x)$ [36],

$$F'_{\xi}(\xi,x) = F(\xi,x)\left(\frac{xF(x\xi,x) - F(\xi,x)}{x-1}\right). \qquad \text{(A9)}$$

Equation (A9) defines the exponential generating function for the polynomials $F_n(x)$

$$F(\xi,x) = \sum_{n=0}^{\infty} F_n(x)\frac{\xi^n}{n!}. \qquad \text{(A10)}$$

Equations (A10) and (A4) allow one to derive a simple set of linear recurrence relations for the polynomials $F_n(x)$. On differentiating both sides of Eq. (A4) over z gives $w'_z(z,x)W(z,x)=W'_z(z,x)$. Let us substitute here Eqs. (A1) and (A10) and equalize the coefficients at equal powers of z. We then obtain the recurrence,

$$x^{g(g+1)/2} = \sum_{m=0}^{g} C_g^m F_{g-m}(x)(x-1)^{g-m}x^{m(m-1)/2}. \qquad \text{(A11)}$$

After a simple algebra this recurrence can be rewritten as

$$\sum_{m=0}^{g} C_g^m F_m(x)(x-1)^m x^{(m+1)(m-2g)/2} = 1. \qquad \text{(A12)}$$

If we introduce $A_g(x)=(x-1)^g F_g(x)$, we find a more elegant recurrence for $A_g(x)$,

$$A_g(x) = x^{g(g+1)/2} - \sum_{m=0}^{g-1} C_g^m A_m(x) x^{(g-m)(g-m-1)/2}, \qquad \text{(A13)}$$

with $A_0(x)=1$. From this equation we see that $A_g(x)$ is a polynomial of degree $g(g+1)/2$, while $F_g(x)$ has degree $g(g-1)/2$.

Another recurrence is cited in Refs. [31,35,36]

$$F_n(x) = \sum_{l=1}^{n} C_{n-1}^{l-1}(1 + x + \cdots + x^{l-1})F_{l-1}(x)F_{n-l}(x). \qquad \text{(A14)}$$

The first four polynomials are $F_0(x)=F_1(x)=1$, and

$$F_2(x) = x + 2, \quad F_3(x) = x^3 + 3x^2 + 6x + 6,$$

$$F_4(x) = x^6 + 4x^5 + 10x^4 + 20x^3 + 30x^2 + 36x + 24.$$

Let us return to a_g. The generating function G [Eq. (26)] is expressed in terms of w as follows:

$$\begin{aligned} G(z,\tau) &= \ln D(ze^{-M\tau},\tau) = \ln W(ze^{-(M-1)\tau},e^{2\tau}) \\ &= w(ze^{-(M-1)\tau},e^{2\tau}). \end{aligned} \qquad \text{(A15)}$$

The following chain of equalities restores $a_g(t)$:

$$\begin{aligned} a_g(\tau) &= \frac{1}{2\pi i}\oint \frac{dz}{z^{g+1}} w(ze^{-(M-1)\tau},e^{2\tau}) \\ &= \frac{1}{2\pi i}e^{-g(M-1)\tau}\oint \frac{dz}{z^{g+1}} w(z,e^{2\tau}) \\ &= \frac{1}{2\pi i g}e^{-g(M-1)\tau}\oint \frac{dz}{z^{g}} w'_z(z,e^{2\tau}) \\ &= \frac{1}{2\pi i g}e^{-g(M-1)\tau}\oint \frac{dz}{z^{g}} F[z(e^{2\tau}-1),e^{2\tau}]. \end{aligned}$$

Hence

$$a_g(\tau) = e^{-g(M-1)\tau}\frac{1}{g!}(e^{2\tau}-1)^{g-1}F_{g-1}(e^{2\tau}). \qquad \text{(A16)}$$

APPENDIX B: POLYNOMIALS P_g

Sometimes it is more convenient to use the polynomials $P_g(\delta)$ defined as

$$P_g(\delta) = F_g(1 + \delta). \qquad \text{(B1)}$$

The first four of them are

$$P_2(\delta) = 3 + \delta, \quad P_3(\delta) = 16 + 15\delta + 6\delta^2 + \delta^3,$$

$$P_4(\delta) = 125 + 222\delta + 205\delta^2 + 120\delta^3 + 45\delta^4 + 10\delta^5 + \delta^6.$$

We also introduce their exponential generating function,

$$y(\xi,\delta) = \sum_{n=0}^{\infty} \frac{\xi^n}{n!}P_n(\delta). \qquad \text{(B2)}$$

The integral equation for y follows from Eq. (A9) after a single integration,

$$\ln y(\xi,\delta) = \xi\int_0^1 y(\xi(1 + u\delta),\delta)du. \qquad \text{(B3)}$$

At $\delta=0$

$$\ln y_o = \xi y_o, \qquad \text{(B4)}$$

where we introduced $y_o(\xi)=y(\xi,0)$. This result allows us to find $P_g(0)$ (see Refs. [31,35,36]),

$$P_g(0) = F_g(1) = (g + 1)^{g-1}. \qquad \text{(B5)}$$

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

$$y(\xi,\delta) = \sum_{k=0}^{\infty} \frac{\delta^k}{k!}y_{\delta}^{(k)}(\xi,0). \qquad \text{(B6)}$$

Equation (B3) allows us to derive the recurrence for determining the derivatives $y_{\delta}^{(k)}(\xi,0)$

$$\left.\frac{\partial^n \ln y(\xi,\delta)}{\partial\delta^n}\right|_{\delta=0} = \sum_{m=0}^{n} \frac{\xi^{m+1}}{m+1}C_n^m \frac{\partial^m}{\partial\xi^m}\frac{\partial^{n-m}}{\partial\delta^{n-m}}\, y(\xi,\delta)\Big|_{\delta=0}. \qquad \text{(B7)}$$

It is important to notice that if we know the nth derivative over δ then it is possible to find the $n+m$th mixed derivative over δ (n times) and ξ (m times). It is easy to find first several derivatives $y_{\delta}^{(k)}$ and to discover that they have singularity of the type $[1-\ln y(\xi,0)]^s$ and that the maximal power $s=3k-1$.

Now we show how the asymptotic formula Eq. (50) can be derived directly from Eq. (A12). The idea is very simple.

The maximal value of each term in the sum on the rhs of Eq. (A12) should be of the order of unity. If we represent each term in the exponential form $e^{-g\Phi}$ and introduce $\mu = m/g$, $\alpha = g\delta$, and $\Psi = \ln[\delta^m P_m(\delta)]$ we find that

$$\Phi = \mu \ln \mu + (1-\mu)\ln(1-\mu) - \mu\Psi(\mu\alpha) - \frac{\alpha}{2}\mu(\mu-2) = 0 \tag{B8}$$

and $\Phi'_\mu = 0$,

$$\ln \mu - \ln(1-\mu) - \mu\alpha\Psi'(\mu\alpha) - \Psi(\mu\alpha) - \alpha(\mu-1) = 0. \tag{B9}$$

We introduce the variable $x = \mu\alpha$ and two unknown functions, $\mu(x)$ and $\Psi(x)$. Then we have two equations for determining these functions

$$\mu \ln \mu + (1-\mu)\ln(1-\mu) - \mu\Psi(x) - \frac{x}{2}(\mu-2) = 0 \tag{B10}$$

and

$$\ln \mu - \ln(1-\mu) - [x\Psi(x)]' - x(1-1/\mu) = 0. \tag{B11}$$

It is easy to find that

$$\mu(x) = 1 - e^{-x}, \quad \Psi(x) = \ln[2\sinh(x/2)]. \tag{B12}$$

The direct substitution trivially shows that the solution Eq. (B12) is correct. Equation (B12) is equivalent to Eq. (50).

It is important to notice that if we return to the variables μ, t, then there are two solutions for the mass, $\mu = 0$ (for all t) and $\mu = 1 - e^{2\mu t}$ (upper root) for $\mu > 1/2$. This fact is quite remarkable.

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