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Exact kinetics of sol-gel transition in a coagulating mixture

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The formation of a gel in a two component disperse system wherein binary coagulation governs the temporal changes to particle composition spectra is studied under the assumption that the coagulation kernel is proportional to $m_1n_2+m_2n_1$, with m,n being the numbers of monomers of the first and the second component in the coalescing pair of particles. This model is shown 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 within the Marcus-Lushnikov stochastic scheme. The evolution equation for the generating functional of the probability to find in the system a given set of occupation numbers (the numbers of particles containing m and n monomers of each component) at time t is formulated and solved exactly. The expression for the particle composition spectrum is derived and analyzed in the thermodynamic limit. It is shown that after a critical time a giant single particle (the gel) appears. The time evolution of its composition is found. Special attention is given to the transition point, where the gel is appearing. The time dependencies of the gel composition, the number concentration, and the second moments of the particle composition spectrum are found.

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I. INTRODUCTION

A wide variety of phenomena of quite a different nature can be described as an aggregation process of the type

$$(k,l)+(p,q)\to(m,n)=(k+p,l+q), \qquad (1)$$

where the notation m,n stands for an $(m+n)$-mer comprising m and n monomers of the first and the second component, respectively. The most evident example is coagulation of a binary mixture, where a gas of $M+N$ monomers of two sorts begins to form mixed clusters containing m and n monomers of each sort. This type of coagulation had been considered almost three decades ago in Ref. [1].

Although the role of coagulation processes is commonly recognized and has been discussed in detail in papers [2–4], very little attention was given to coagulating mixtures. So far this problem remained clear of the main stream of works on theory of coagulation, although its importance is beyond any doubt. It is enough to mention such phenomena like formation of atmospheric aerosols [5] and especially coagulation of charged particles [6].

The motivation of the present paper is, however, different. It extends the results of Refs. [7–9] to a nontrivial and a very instructive example of a coagulating mixture, wherein the sol-gel transition occurs.

The first paper, where the pregelation behavior of a coagulating mixture had been studied was the work of my group [10]. In this paper we investigated the coagulation of a binary mixture starting with the traditional approach based on the Smoluchowski equation

$$d_tc_{m,n}(t)=\sum_{k,l,p,q}\mathcal{K}(m,n|k,l;p,q)c_{k,l}(t)c_{p,q}(t), \qquad (2)$$

where

$$\mathcal{K}(m,n|k,l;p,q)=\tfrac{1}{2}K(k,l;p,q)[\delta_{m,k+p}\delta_{n,l+q}-\delta_{m,k}\delta_{n,l}-\delta_{m,p}\delta_{n,q}]. \qquad (3)$$

Here the coagulation kernel $K(k,l;p,q)$ is the transition rate for the process given by Eq. (1). The first term on the right-hand side (RHS) of Eq. (3) describes the gain in the $(m+n)$-mer concentration due to coalescence of $(k+l)$- and $(p+q)$-mers ($k+p=m$, $l+q=n$), while the second one is responsible for the losses of $(m+n)$-mers due to their sticking to all other particles. The notation $\delta_{i,k}$ stands for Kroneker's δ. In Eq. (2) and throughout the paper we do not indicate explicitly the interval of summation if it stretches from 0 to ∞, i.e., Σ_m means $\Sigma_{m=0}^{\infty}$, $\Sigma_{m,n}=\Sigma_{m=0}^{\infty}\Sigma_{n=0}^{\infty}$, $m=n\neq 0$, etc.

The initial condition for Eq. (2) is

$$c_{m,n}(0)=\mathcal{M}\delta_{m,1}\delta_{n,0}+\mathcal{N}\delta_{m,0}\delta_{n,1}, \qquad (4)$$

where $\mathcal{M},\mathcal{N}$ are the mass concentrations of the species. This condition corresponds to the system initially containing monomeric particles of the first and the second sort, respectively. The coagulation process merges them forming mixed $m+n$-mers, the values $\mathcal{M},\mathcal{N}$ remaining unchanged with time. It is clear that the particles with $m=n=0$ never appear in the coagulating system, i.e., $c_{0,0}(t)=0$ for all t.

In this paper we investigate the coagulation process for the coagulation kernel of the form

$$K(k,l;p,q)=\kappa(kq+lp). \qquad (5)$$

Here κ is a dimension carrier of the kernel K. This kernel describes realistic processes like copolymerization [11] or time evolution of bipartite graphs [12], the problem bearing on the structures of weblike random nets [13], percolation

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*Electronic address: alex.lushnikov@helsinki.fi transitions [14], and second-order phase transitions [15,16]. Coagulation in such systems leads to the sol-gel transition, i.e., to formation of a giant object containing a macroscopic number of monomers (a gel) (or a giant component in an evolving random graph [17]) that appears in a finite interval of time.

In what follows it is convenient to assume that

$$\mathcal{M}+\mathcal{N}=1, \tag{6}$$

which means that all concentrations are measured in units of the total number concentration C_0 of the monomers and the unit for time is $1/\kappa C_0$.

For the coagulation kernel (5) the Smoluchowski equation looks as follows:

$$d_t c_{m,n}(t)=\sum_{k,l=0}^{m,n}(m-k)l c_{m-k,n-l}(t)c_{k,l}(t)-(m\mathcal{N}+n\mathcal{M})c_{m,n}(t). \tag{7}$$

The exact solution to this equation found almost a quarter of century ago in Ref. [10] had shown that the mass concentrations of each component are conserved only at $t<t_c$, where t_c is a critical time [defined below by Eq. (18)]. After the critical time a single giant particle (gel) forms and the traditional Smoluchowski scheme [Eq. (7)] fails to reproduce the kinetics of the coagulation process.

This is the reason why here I apply an alternative approach based on the evolution equation for the generating functional for the probabilities to have a given set of occupation numbers (the numbers of $m+n$-mers) at time t (see [9] and extensive citations therein). As has been shown in [7–9] this approach is appropriate when considering the sol-gel transition and can be successfully applied to gelling mixtures [18].

In order to illustrate the main idea of this approach let us consider a simple chemical reaction $A+B\rightarrow P$, where two substances A and B react producing a passive product P. Let κ_o be the rate constant of this reaction. Then we can write down two equations governing the kinetics of the reaction

$$\frac{dc_A}{dt}=-\kappa_o c_A c_B, \quad \frac{dc_B}{dt}=-\kappa_o c_A c_B, \tag{8}$$

where c_A and c_B are the concentrations of the A and B components, respectively. These equations are well known and nobody doubts in their validity.

We, however, can apply a different approach for describing the kinetics of this simple reacting mixture. Let us consider a volume V, wherein molecules A and B move chaotically, collide, and on colliding react producing P. Only pair collisions of A and B are taken into account. The states of our system can be characterized by two occupation numbers N_A and N_B. Each collision act leads to the jump from the state N_A+1, N_B+1 to the state N_A, N_B with the rate κ_o/V.

At this step we introduce the probability $W(N_A,N_B;t)$ to find exactly N_A and N_B molecules in our system at time t and write down the set of equations governing the time evolution of the probability W

$$\frac{dW(N_A,N_B;t)}{dt}=\frac{\kappa_o}{V}[(N_A+1)(N_B+1)W(N_A+1,N_B+1;t)-N_A N_B W(N_A,N_B;t)]. \tag{9}$$

The products of the occupation numbers appearing on the RHS of this equation is just the number of ways to create an efficiently reacting pair of A and B molecules.

Now we are ready for the last step. Let us introduce the generating function

$$\Psi(x,y:t)=\sum W(N_A,N_B;t)x^{N_A}y^{N_B}, \tag{10}$$

where the summations goes over all nonnegative integers N_A and N_B. It is easy to see that

$$V\frac{\partial\Psi}{\partial t}=\kappa_o(1-xy)\frac{\partial^2\Psi}{\partial x\,\partial y}. \tag{11}$$

This equation contains a full information on the evolution of the reacting mixture. For example, the concentration $c_A=\bar{N}_A/V=V^{-1}\partial_x\Psi(x,1)|_{x=1}$, where $\bar{N}_A=\Sigma N_A W(N_A,N_B;t)$ is the average occupation number of the component A.

Equations (8) can be derived from Eq. (11) in the thermodynamic limit ($N_X\rightarrow\infty$, $V\rightarrow\infty$ with $0<N_X/V<\infty$ being finite. Here $X=A,B$.)

Of course, Eq. (11) is much more complex than Eq. (8). On the other hand, Eq. (11) allows for considering the situations, where the number of reacting molecules is not large, such as chemical reactions at the surface of an aerosol particles [19]. This approach is absolutely irreplaceable in considering the sol-gel transitions in coagulating system, for it permits the consideration of finite number of coagulating particles avoiding thus the paradox of the mass losses due to gelation and the so-called gelation catastrophe (the divergency of the second moments of the composition spectrum).

The remainder of the paper is divided as follows. Section II demonstrates that a gelation catastrophe occurs if the coagulation kernel is given by Eq. (5). To this end the second moments of the particle composition spectrum are demonstrated to have a singular behavior at $t\rightarrow t_c$, where $t_c=(\mathcal{M}\mathcal{N})^{-1/2}$ is the critical time. In Sec. III the evolution equation governing the time dependence of the generating functional for the probabilities to find a given set of occupation numbers (the numbers of monomers having exactly m and n monomers) is formulated. This equation is solved exactly in Sec. IV and the particle composition spectrum is found in terms of polynomials analogous to those introduced in Refs. [7–9] in considering the gelation in monocomponent coagulating system and earlier in [20–22] for other purposes. Section V analyzes the spectrum in the thermodynamic limit. It is shown that a single giant particle whose mass and composition define the deficits of masses of each component in the sol fraction of the spectrum eventually forms after the critical time. The asymptotic expression for the composition spectrum is derived and analyzed at $t=t_c$. After the critical time the composition distribution has a narrow maximum located exactly at the point in the m,n plane corresponding to the gel particle. Two Appendixes introduce the set of polynomials necessary for the exact solution of the problem and for the analysis of the thermodynamical limit of the composition spectrum.

II. GELATION CATASTROPHE

In the case of monocomponent system the divergency of the second moment of the particle mass distribution evidences on the sol-gel transition. Below we will see that similar behavior of the second moments is also observed in gelating mixtures.

Let us calculate the time dependence of three second moments of the composition distribution

$$\phi_{20}(t) = \sum_{m,n} m^2 c_{m,n}(t), \quad \phi_{02}(t) = \sum_{m,n} n^2 c_{m,n}(t),$$

$$\phi_{11}(t) = \sum_{m,n} mnc_{m,n}(t). \tag{12}$$

Equation (7) allows one to derive the closed set of ordinary differential equations for the moments

$$d_t\phi_{20} = 2\phi_{11}\phi_{20}, \quad d_t\phi_{02} = 2\phi_{11}\phi_{02},$$

$$d_t\phi_{11} = \phi_{20}\phi_{02} + \phi_{11}^2, \tag{13}$$

with the initial conditions $\phi_{20}(0)=\mathcal{M}$, $\phi_{02}(0)=\mathcal{N}$, and $\phi_{11}(0)=0$. On introducing the variable $x=2\int_0^t\phi_{11}(t')dt'$ reduces the two first equations of set (13) to two linear equations of the form $d_x\phi=\phi$, the solutions to which are

$$\phi_{20}(x) = \mathcal{M}e^x, \quad \phi_{02}(x) = \mathcal{N}e^x. \tag{14}$$

Now, from the third equation of the set Eq. (13) we have

$$\frac{d\phi_{11}^2}{dx} - \phi_{11}^2 = \mathcal{M}\mathcal{N}e^{2x}, \tag{15}$$

or

$$\phi_{11}(x) = \sqrt{2\mathcal{M}\mathcal{N}e^x(e^x-1)}. \tag{16}$$

The time dependence of x is readily restored from its definition $d_t x=2\phi_{11}$

$$e^x = \frac{1}{1-(t/t_c)^2}, \tag{17}$$

where the critical time t_c is

$$t_c = \frac{1}{\sqrt{\mathcal{M}\mathcal{N}}}. \tag{18}$$

The final output of this calculation is the time dependence of all three second moments

$$\phi_{20} = \frac{\mathcal{M}}{1-(t/t_c)^2}, \quad \phi_{02} = \frac{\mathcal{N}}{1-(t/t_c)^2},$$

$$\phi_{11} = \sqrt{\mathcal{M}\mathcal{N}}\frac{t/t_c}{1-(t/t_c)^2}. \tag{19}$$

As in the case of gelling monocomponent systems (see Refs. [9,23,24]) this singular behavior of the second moments evidences on the gel formation at $t>t_c$.

III. EVOLUTION EQUATION

The approach of Refs. [23,24] is known to be able to answer the question what is going on at and after the critical time. Instead of the concentrations $c_{m,n}(t)$ this approach operates with the occupation numbers $n_{m,n}$ (numbers of m,n-mers) and the probability $W(\{n_{m,n}\},t)$ to find a given set $\{n_{m,n}\}$ of occupation numbers at time t. Let us introduce the generating functional $\Psi(\{x_{m,n}\},t)$ for this probability

$$\Psi(\{x_{m,n}\},t) = \sum_{\{n_{m,n}\}} W(\{n_{m,n}\},t)x_{0,1}^{n_{0,1}}x_{1,0}^{n_{1,0}}, \ldots, x_{m,n}^{n_{m,n}}. \tag{20}$$

The summation on the RHS of this equation goes over all possible sets $\{n_{m,n}\}$. The derivation of the evolution equation for Ψ repeats the scheme described in detail in Ref. [9] and outlined above [Eqs. (8)–(11)]. The final result is

$$V\partial_t\Psi = \hat{\mathcal{L}}\Psi, \tag{21}$$

where the generating functional depends on the set of *formal* variables $\{x_{m,n}\}$, V is a volume of the coagulating system, and the evolution operator $\hat{\mathcal{L}}$ has the form

$$\hat{\mathcal{L}} = \frac{1}{2}\sum_{m,n,k,l} K(m,n;k,l)[x_{m+k,n+l} - x_{m,n}x_{k,l}]\frac{\partial^2}{\partial x_{m,n}\,\partial x_{k,l}}. \tag{22}$$

Equation (21) is entirely equivalent to the Master equation for the probability W. Its derivation reminds in many respects that of Eq. (11) and repeats all the steps necessary for deriving Eq. (17) of Ref. [9].

For the kernel (5) the evolution operator Eq. (22) can be rewritten as

$$\hat{\mathcal{L}} = \frac{\kappa}{2}\left\{\left[\sum_{m,n,k,l}(ml+nk)x_{m+k,n+l}\frac{\partial^2}{\partial x_{m,n}\,\partial x_{k,l}}\right] - \hat{N}M - N\hat{M}\right\}, \tag{23}$$

where $\hat{M}$ and $\hat{N}$ are the operators of the total masses of the first and the second component, respectively

$$\hat{M} = \sum_{m,n} mx_{m,n}\frac{\partial}{\partial x_{m,n}}, \quad \hat{N} = \sum_{m,n} nx_{m,n}\frac{\partial}{\partial x_{m,n}}.$$

The evolution operator $\hat{\mathcal{L}}$ commutes with $\hat{M}$ and $\hat{N}$, which means that the functional Ψ can be chosen as an eigenfunctional of these mass operators

$$\hat{M}\Psi_{M,N}(\{x_{m,n}\},t) = M\Psi_{M,N}(\{x_{m,n}\},t),$$

$$\hat{N}\Psi_{M,N}(\{x_{m,n}\},t) = N\Psi_{M,N}(\{x_{m,n}\},t).$$

The nonnegative integers M and N (the total numbers of the monomers of the first and the second component, respectively) are the eigenvalues of these operators.

In what follows it is convenient to define the time scale by the equality $M+N=V$ and to introduce the mass concentrations of monomers $\mathcal{M}=M/V$, $\mathcal{N}=N/V$. The total mass concentration of monomers is then $\mathcal{M}+\mathcal{N}=1$ in agreement with the convention Eq. (6).

IV. EXACT SOLUTION

The solution to Eq. (21) with the evolution operator given by Eq. (23) can be found exactly in the same way as has been done in Refs. [7–9] in solving the evolution equation with the kernel proportional to the product of masses of coalescing particles.

We construct the mass conserving solution in the form

$$\Psi = M\,!\,N\,!\,\mathrm{Coef}_{\xi,\eta}\left[\xi^{-M-1}\eta^{-N-1}\exp\left(\sum_{m,n} x_{m,n}a_{m,n}(t)\xi^m\eta^n\right)\right], \tag{24}$$

where the coefficients $a_{m,n}(t)$ will be defined later on [see Eq. (28)]. The notation Coef introduced in Ref. [25] is used instead of contour integrals. The point is that in what follows we will deal with divergent series, where normal integration is not applicable. The operation Coef is introduced as follows:

$$\mathrm{Coef}_{\xi,\eta}\left[\sum_{m,n=-\infty}^{\infty} b_{m,n}\xi^m\eta^n\right] = b_{-1,-1}. \tag{25}$$

If the sum on the left-hand side (LHS) of this equation converges the operation Coef can be replaced by respective integrals. The operation Coef displays many features of ordinary residues.

The functional Ψ given by Eq. (24) is the eigenfunctional of $\hat{M}$ and $\hat{N}$. Indeed

$$\begin{aligned}\hat{M}\Psi &= M\,!\,N\,!\,\mathrm{Coef}_{\xi,\eta}\left[\xi^{-M-1}\eta^{-N-1}\sum_{m,n} m a_{m,n}x_{m,n}(t)\xi^m\eta^n\right.\\ &\quad\left.\times\exp\left(\sum_{m,n} x_{m,n}a_{m,n}(t)\xi^m\eta^n\right)\right]\\ &= M\,!\,N\,!\,\mathrm{Coef}_{\xi,\eta}\left[\xi^{-M-1}\eta^{-N-1}\xi\partial_\xi\right.\\ &\quad\left.\times\exp\left(\sum_{m,n} x_{m,n}a_{m,n}(t)\xi^m\eta^n\right)\right]\\ &= M\Psi.\end{aligned}$$

The last equality of this chain follows from the identity $\mathrm{Coef}_\xi[\xi^{-M}F'(\xi)]=M\mathrm{Coef}_\xi[\xi^{-M-1}F(\xi)]$ (an analog of the integration by parts).

The particle mass spectrum (the average number of $m+n$-mers) $\bar{n}_{m,n}(t)$ can be expressed in terms of $a_{m,n}(t)$ as follows:

$$\begin{aligned}\bar{n}_{m,n}(t) &= \left.\frac{\partial\Psi(\{x_{m,n}\},t)}{\partial x_{m,n}}\right|_{\{x_{m,n}\}=\{1\}}\\ &= M\,!\,N\,!\,a_{m,n}(t)\mathrm{Coef}_{\xi,\eta}\{\xi^{-M+m-1}\eta^{-N+n-1}\\ &\quad\times\exp[G(\xi,\eta;t)]\}.\end{aligned} \tag{26}$$

Here

$$G(\xi,\eta;t) = \sum_{m,n} a_{m,n}(t)\xi^m\eta^n \tag{27}$$

is the bivariate generating function for $a_{m,n}(t)$.

On substituting Ψ in the form (24) into Eq. (23) yields the set of equations for $a_{m,n}(t)$

$$\begin{aligned}Vd_t a_{m,n}(t) &= \sum_{k,l=0}^{m.n}(m-l)k a_{m-l,n-k}(t)a_{l,k}(t) + mna_{m,n}(t)\\ &\quad-\tfrac{1}{2}(Mn+Nm)a_{m,n}(t).\end{aligned} \tag{28}$$

This set is subject to the condition corresponding to initially monodisperse particles

$$a_{m,n}(0) = \delta_{m,1}\delta_{n,0} + \delta_{m,0}\delta_{n,1}. \tag{29}$$

Indeed, the condition (29) corresponds to $\Psi|_{t=0}=x_{1,0}^M x_{0,1}^N$.

The equation for the generating function G can be readily derived from Eqs. (27) and (28)

$$V\frac{\partial G}{\partial t} = \xi\frac{\partial G}{\partial\xi}\eta\frac{\partial G}{\partial\eta} + \xi\eta\frac{\partial^2 G}{\partial\xi\,\partial\eta} - \frac{1}{2}\left(N\xi\frac{\partial G}{\partial\xi} + M\eta\frac{\partial G}{\partial\eta}\right). \tag{30}$$

The initial condition for this equation is

$$G(\xi,\eta;0) = \xi + \eta. \tag{31}$$

Now let

$$G(\xi,\eta;t) = D(\xi e^{-\mathcal{N}t/2}, \eta e^{-\mathcal{M}t/2}; t). \tag{32}$$

Then, instead of Eq. (30) we find a linear equation for e^D

$$V\frac{\partial e^D}{\partial t} = \xi\eta\frac{\partial^2 e^D}{\partial\xi\,\partial\eta}. \tag{33}$$

The *formal* solution to this equation with the initial condition $e^{D(\xi,\eta;0)}=e^{\xi+\eta}$ is

$$e^D = \sum_{m,n}\frac{\xi^m\eta^n}{m\,!\,n!}\exp(mnt/V). \tag{34}$$

From Eqs. (32) and (34) we find

$$\begin{aligned}&\mathrm{Coef}_{\xi,\eta}\xi^{-M+m-1}\eta^{-N+n-1}\exp[G(\xi,\eta;t)]\\ &\quad= \frac{\exp(-m\mathcal{N}t/2 - n\mathcal{M}t/2 + mnt/V)}{(M-m)\,!\,(N-n)!}.\end{aligned} \tag{35}$$

Next, the coefficients $a_{m,n}(t)$ are readily restored from Eqs. (32), (34), and (A15),

$$a_{m,n}(t) = \frac{\exp(-m\mathcal{N}t/2 - n\mathcal{M}t/2)}{m\,!\,n!} \times (e^{t/V}-1)^{m+n-1}F_{m-1,n-1}(e^{t/V}). \tag{36}$$

Using Eqs. (26), (35), and (36) we come to the final result

$$\bar{n}_{m,n}(t) = \binom{M}{m}\binom{N}{n} e^{mnt/V - m\mathcal{N}t - n\mathcal{M}t} \times (e^{t/V}-1)^{m+n-1}F_{m-1,n-1}(e^{t/V}). \tag{37}$$

The polynomials $F_{m,n}(x)$ are introduced in Appendix A.

V. THERMODYNAMIC LIMIT

The sol-gel transition happens at finite t. Therefore, as had been done in [7–9] we investigate the exact mass spectrum given by Eq. (37) assuming $M, N, V \to \infty$, the total mass concentrations of each component $\mathcal{M}$, $\mathcal{N}$, and t being finite. At large V and finite t the argument of $F_{m,n}$ in Eq. (37) approaches unity.

A. The Smoluchowskii composition spectrum

At $t < t_c$ (no gel has formed) we can replace $F_{m,n}$ by $F_{m,n}(1)$ [see Eq. (B3)]

$$F_{m,n}(1) = P_{m,n}(0) = (m+1)^n (n+1)^m. \tag{38}$$

We can thus write down the composition spectrum at $m,n \ll M,N$. On introducing the concentrations $c_{m,n}(t) = \bar{n}_{m,n}(t)/V$ yields

$$c_{m,n}(t) = \mathcal{M}^m \mathcal{N}^n \frac{m^{n-1}n^{m-1}}{m\,!\,n!} t^{m+n-1} e^{-(m\mathcal{N}+n\mathcal{M})t}. \tag{39}$$

As had been shown in Ref. [8] this spectrum is the solution to the Smoluchowski equation (7), with the initial condition given by Eq. (4).

In the limit of large m,n we get

$$c_{m,n}(t) \approx \frac{1}{2\pi t m^{3/2} n^{3/2}} e^{\mathcal{F}_s(m,n;t)}, \tag{40}$$

where

$$\mathcal{F}_s(m,n;t) = m[1 + \ln(\mathcal{M}t) - \mathcal{N}t] + n[1 + \ln(\mathcal{N}t) - \mathcal{M}t] + (n-m)\ln\frac{m}{n}. \tag{41}$$

It is easy to check that at $t = t_c = (\mathcal{M}\mathcal{N})^{-1/2}$

$$\mathcal{F}_s(m,n;t_c) = \frac{\sqrt{\mathcal{M}} - \sqrt{\mathcal{N}}}{\sqrt{\mathcal{M}\mathcal{N}}}(m\sqrt{\mathcal{N}} - n\sqrt{\mathcal{M}}) - (m-n)\ln\frac{m\sqrt{\mathcal{N}}}{n\sqrt{\mathcal{M}}}. \tag{42}$$

At $t = t_c$ and $m\sqrt{\mathcal{N}} = n\sqrt{\mathcal{M}}$ the function $\mathcal{F}_s$ is zero together with its first derivatives with respect to m and n, the spectrum becomes algebraic, as should it be at the critical point

$$c_{m,n}(t_c) \approx \frac{\sqrt{\mathcal{M}\mathcal{N}}}{2\pi m^{3/2} n^{3/2}}. \tag{43}$$

In what follows we need the generating function $\Theta(\xi,\eta;t)$ for $c_{m,n}(t)$, which can be expressed in terms of the bivariate exponential generating function $\Phi(\xi,\eta;x)$ for the polynomials $F_{m-1,n-1}(x)$ introduced in Appendix A by Eq. (A16). The result is

$$\Theta(\xi,\eta;t) = \sum c_{m,n}(t)\xi^m\eta^n = \frac{1}{t}\Phi(t\mathcal{M}e^{-\mathcal{N}t}\xi, t\mathcal{N}e^{-\mathcal{M}t}\eta; 1). \tag{44}$$

B. Mass concentrations

Here we use Eq. (44) in order to show that at $t > t_c$ the spectrum Eq. (39) does not conserve the total mass concentrations of the monomers, i.e.

$$\sum_{m,n} m c_{m,n}(t) = \frac{1}{t}\xi_0\Phi'_\xi(\xi_0,\eta_0;1) = \mathcal{M}[1 - \mu_g(t)], \tag{45}$$

and

$$\sum_{m,n} n c_{m,n}(t) = \frac{1}{t}\eta_0\Phi'_\eta(\xi_0,\eta_0;1) = \mathcal{N}[1 - \nu_g(t)], \tag{46}$$

where the functions $1-\mu_g(t)$ and $1-\nu_g(t)$ define the deficit of the mass concentrations due to formation of a gel particle. Other notation

$$\xi_0(t) = \mathcal{M}te^{-\mathcal{N}t} \quad \text{and} \quad \eta_0(t) = \mathcal{N}te^{-\mathcal{M}t}. \tag{47}$$

Our aim now is to determine the functions $\mu_g(t)$ and $\nu_g(t)$.

From Eq. (A9) we conclude that at $x=1$

$$\Phi'_\xi = e^{\eta\Phi'_\eta}, \quad \text{and} \quad \Phi'_\eta = e^{\xi\Phi'_\xi}. \tag{48}$$

On combining Eqs. (45), (46), and (48) finally gives

$$\mathcal{N}\nu_g t = \ln\frac{1}{1-\mu_g}, \quad \mathcal{M}\mu_g t = \ln\frac{1}{1-\nu_g} \tag{49}$$

or

$$\nu_g = 1 - e^{-\mathcal{M}\mu_g t}, \quad \mu_g = 1 - e^{-\mathcal{N}\nu_g t}. \tag{50}$$

This set of equations has the solution $\mu_g(t) = \nu_g(t) = 0$ at $t < t_c = 1/\sqrt{\mathcal{M}\mathcal{N}}$. A nontrivial nonzero solution appears only after the gel point $t = t_c$. Indeed, at small μ_g, ν_g Eq. (50) can be expanded up to the second order in μ_g, ν_g. The result is

$$\mu_g = \mathcal{N}\nu_g t - \frac{(\mathcal{N}\nu_g t)^2}{2}, \quad \nu_g = \mathcal{M}\mu_g t - \frac{(\mathcal{M}\mu_g t)^2}{2}. \tag{51}$$

There are two solutions to this set of equations, $\mu_g = \nu_g = 0$ and a nontrivial one which at small $t - t_c$ has the form

$$\mu_g \approx \frac{4\mathcal{N}\sqrt{\mathcal{M}}(t-t_c)}{\sqrt{\mathcal{M}} + \sqrt{\mathcal{N}}}, \quad \nu_g \approx \frac{4\mathcal{M}\sqrt{\mathcal{N}}(t-t_c)}{\sqrt{\mathcal{M}} + \sqrt{\mathcal{N}}}. \tag{52}$$

The positive nontrivial solution is seen to exist only at $t > t_c = 1/\sqrt{\mathcal{M}\mathcal{N}}$.

C. Number concentration

Again, Eq. (44) allows the total number concentration to be expressed in terms of the function Φ

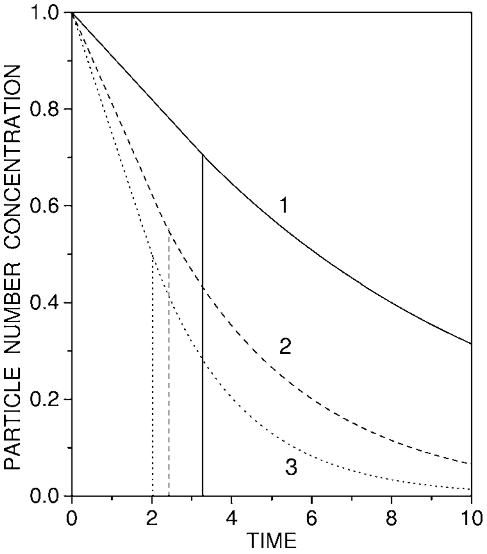

FIG. 1. Particle number concentration vs time (all values are dimensionless). Curves 1, 2, 3, correspond to the mass concentrations $\mathcal{M}=0.1, 0.25, 0.5$, respectively. Vertical lines show respective critical times, $t_{c1}=3.33$, $t_{c2}=2.31$, and $t_{c3}=2$. It is clearly seen that below the transition point these dependencies are linear and only after the gelation time they become more complex.

$$C(t)=\sum_{m,n} c_{m,n}(t)=\frac{1}{t}\Phi(\xi_0,\eta_0;1). \tag{53}$$

In order to calculate $C(t)$ we use Eq. (B5). Noticing that $\ln X_0(\xi_0,\eta_0)=\mathcal{N}t(1-\nu_g)$ and $\ln Y_0(\xi_0,\eta_0)=\mathcal{M}t(1-\mu_g)$ we come to the following expression for the total number concentration:

$$C(t)=\mathcal{M}(1-\mu_g)+\mathcal{N}(1-\nu_g)-\mathcal{M}\mathcal{N}t(1-\mu_g)(1-\nu_g). \tag{54}$$

Let us derive the differential equation for $C(t)$. To this end we differentiate both sides of Eq. (54) with respect to time

$$\begin{aligned}\dot{C}=&-\mathcal{M}\dot{\mu}_g-\mathcal{N}\dot{\mu}_g-\mathcal{M}\mathcal{N}(1-\mu_g)(1-\nu_g)\\&+\mathcal{M}\mathcal{N}t[\dot{\mu}_g(1-\nu_g)+\dot{\nu}_g(1-\mu_g)],\end{aligned}$$

and use Eq. (49) for expressing $\dot{\mu}_g$ and $\dot{\nu}_g$ in terms of μ_g and ν_g

$$\dot{\mu}_g=\mathcal{N}(1-\mu_g)(\nu_g+t\dot{\nu}_g), \quad \dot{\nu}_g=\mathcal{M}(1-\nu_g)(\mu_g+t\dot{\mu}_g).$$

After some simple algebra one finds

$$\frac{dC}{dt}=-\mathcal{M}\mathcal{N}[1-\mu_g(t)\nu_g(t)]. \tag{55}$$

This equation shows that the concentration $C(t)$ drops down linearly with time at $t<t_c$. Figure 1 clearly demonstrates this fact. The slowest dependence $C(t)$ on time realizes at small concentration of one of the monomer. The shortest pregelation period corresponds to the equal mass concentrations of both components $\mathcal{M}=\mathcal{N}=0.5$.

D. Particle composition spectrum

Assuming m,n to be large we approximate the exact spectrum Eq. (37) as follows:

$$\bar{n}_{m,n}(t)\approx\frac{1}{2\pi m^{3/2}n^{3/2}\sqrt{(1-\mu)(1-\nu)}}e^{\mathcal{F}(\mu,\nu;t)}. \tag{56}$$

Here $\mu=m/V$, $\nu=n/V$, $V=M+N$, and

$$\begin{aligned}\mathcal{F}(\mu,\nu;t)=&-M[(1-\mu)\ln(1-\mu)+\mu\ln\mu]\\&-N[(1-\nu)\ln(1-\nu)+\nu\ln\nu]\\&-MN(\mu+\nu-2\mu\nu)t/V\\&+N\nu\ln(1-e^{-\mathcal{M}\mu t})+M\mu\ln(1-e^{-\mathcal{N}\nu t}).\end{aligned} \tag{57}$$

In deriving this expression we used Eqs. (B9) and (B15). Equation (B9) shows that

$$\mathcal{F}(\mu,\nu;t)=\Omega(M,N,\mu,\nu;t/V). \tag{58}$$

Hence, according to Eqs. (B13), (B16), and (58) the function $\mathcal{F}(\mu,\nu;t)$ has a maximum at $\mu=\mu_g(t)$ and $\nu=\nu_g(t)$ given by Eq. (49). Next, $\mathcal{F}[\mu_g(t),\nu_g(t);t]=0$ [see Eq. (B13)].

E. Critical point

Let us analyze the behavior of the composition spectrum Eq. (57) at the critical point $t=t_c=(\mathcal{M}\mathcal{N})^{1/2}$ at small μ and ν $(\mu,\nu\ll 1)$. To this end we expand $\mathcal{F}(\mu,\nu;t_c)$ in powers of μ,ν and retain the terms up to the third order. As we will see below this approximation is enough to get rid of the divergencies in the sums defining the second moments of the particle composition spectrum. It is more convenient to present the result in the variables m,n

$$\begin{aligned}\mathcal{F}(m,n;t_c)\approx&\frac{\sqrt{M}-\sqrt{N}}{\sqrt{MN}}(m\sqrt{N}-n\sqrt{M})+(m-n)\ln\frac{n\sqrt{M}}{m\sqrt{N}}\\&-\frac{1}{2MN}(m\sqrt{N}-n\sqrt{M})^2\\&-\frac{1}{6}\left(\frac{m^3}{M^2}+\frac{n^3}{N^2}-\frac{m^2n}{4MN}-\frac{mn^2}{4MN}\right).\end{aligned} \tag{59}$$

One easily recognizes $\mathcal{F}_s(m,n;t_c)$ in the first two terms of this equation [see Eq. (42)]. Other terms give the correction related to the finiteness of the systems. They are finite only if m,n are comparable to the total volume V. The situation here is exactly the same as in the case of gelation of a monocomponent system (details see in Ref. [7]).

In what follows we will evaluate the moments $\phi_{\alpha,\beta}$ of the distributions given by Eq. (56) with $\mathcal{F}(m,n;t_c)$, where

$$\phi_{\alpha,\beta}=\frac{1}{2\pi}\sum_{m,n} m^{\alpha-3/2}n^{\beta-3/2}e^{\mathcal{F}(\mu,\nu;t_c)}. \tag{60}$$

In the above equation we ignore μ, ν in the preexponential multiplier of Eq. (56). This step will be justified below [right after Eq. (67)]

Let us introduce the polar coordinates

$$m = r\cos\varphi, \quad n = r\sin\varphi, \tag{61}$$

and the angle

$$\varphi_0 = \tan^{-1}(\sqrt{N/M}). \tag{62}$$

In these variables the function $\mathcal{F}$ has the form

$$\begin{aligned}\mathcal{F}(r,\varphi;t_c) = {} & -r\left[\frac{\cos\varphi_0 - \sin\varphi_0}{\sin\varphi_0\cos\varphi_0}\sin(\varphi-\varphi_0)\right.\\ & \left. + (\sin\varphi - \cos\varphi)\ln(\tan\varphi\cot\varphi_0)\right]\\ & - \frac{r^2}{2V\sin^2\varphi_0\cos\varphi_0}\sin^2(\varphi-\varphi_0) - \frac{r^3}{6V^2}\left(\frac{\cos^3\varphi}{\cos^2\varphi_0}\right.\\ & \left. + \frac{\sin^3\varphi}{\sin^2\varphi_0} - \frac{\cos^2\varphi\sin\varphi}{4\sin\varphi_0\cos\varphi_0} - \frac{\cos\varphi\sin^2\varphi}{4\sin\varphi_0\cos\varphi_0}\right).\end{aligned} \tag{63}$$

In the limit $V\to\infty$ the following approximations can be done:

(1) The sums in Eq. (60) are replaced by integrals.

(2) The function $e^{\mathcal{F}}$ differs from zero in a very narrow interval of φ in the vicinity φ_0. All functions depending on φ are then expanded up to the second power of the difference $\varphi-\varphi_0$.

(3) The interval of integration over ϕ is extended from $-\infty$ to ∞.

(4) The second term on the RHS of Eq. (63) does not contribute to the integral.

(5) In the third term on the RHS of Eq. (63) we put $\varphi=\varphi_0$.

The validity of these approximation will be justified later on.

The above-listed approximations allow for considerable simplifications in Eq. (63),

$$\mathcal{F} = -rA(\varphi-\varphi_0)^2 - \frac{r^3}{V^2}B, \tag{64}$$

where

$$A = \frac{\cos\varphi_0 + \sin\varphi_0}{2\sin^2\varphi_0\cos^2\varphi_0}, \quad B = \frac{1}{8}(\cos\varphi_0 + \sin\varphi_0). \tag{65}$$

The expression for $\mathcal{F}$ can be rewritten as

$$\mathcal{F} = -\frac{r\sigma^2}{r_0\sigma_0^2} - \frac{r^3}{r_0^3}, \tag{66}$$

where $\sigma=\phi-\phi_0$ and

$$r_0 = V^{2/3}B^{-1/3} \quad \text{and} \quad \sigma_0 = V^{-1/3}A^{-1/2}B^{1/6}. \tag{67}$$

Now let us justify the approximations leading to Eq. (64). Equation (67) shows that the characteristic intervals of integration in the expression for $I(\alpha,\beta)$ [Eq. (60)] are of the order of $r_0 \propto V^{2/3}$ and $\sigma_0 \propto V^{-1/3}$. The second term on the RHS of Eq. (63) is estimated as $r^2\sigma^2/V \propto V^{-1/3}$ and can be ignored as $V\to\infty$. We thus have

$$\phi_{\alpha,\beta} = \frac{1}{2\pi}r_0^{\alpha+\beta-1}\sigma_0\cos^{\alpha-3/2}\varphi_0\sin^{\beta-3/2}\varphi_0 I_{\alpha,\beta}, \tag{68}$$

where

$$I_{\alpha,\beta} = \int_0^\infty dx\int_{-\infty}^{\infty} d\sigma x^{\alpha+\beta-2}e^{-\sigma^2x-x^3}. \tag{69}$$

On integrating yields

$$\phi_{\alpha,\beta} = r_0^{\alpha+\beta-1}\sigma_0\cos^{\alpha-3/2}\varphi_0\sin^{\beta-3/2}\varphi_0\frac{1}{6\sqrt{\pi}}\Gamma\left(\frac{\alpha+\beta}{3} - \frac{1}{2}\right). \tag{70}$$

This equation allows us to obtain the critical values of the second moments. The results are

$$\begin{aligned}\phi_{11} & = \frac{1}{3\sqrt{2\pi}}\Gamma\left(\frac{1}{6}\right)V^{1/3}\frac{\sqrt{\sin\varphi_0\cos\varphi_0}}{(\sin\varphi_0+\cos\varphi_0)^{2/3}}\phi_{20}\\ & = \frac{1}{3\sqrt{2\pi}}\Gamma\left(\frac{1}{6}\right)V^{1/3}\frac{\sqrt{\cot\varphi_0}\cos\varphi_0}{(\sin\varphi_0+\cos\varphi_0)^{2/3}},\phi_{02}\\ & = \frac{1}{3\sqrt{2\pi}}\Gamma\left(\frac{1}{6}\right)V^{1/3}\frac{\sqrt{\tan\varphi_0}\sin\varphi_0}{(\sin\varphi_0+\cos\varphi_0)^{2/3}}.\end{aligned} \tag{71}$$

These formulas for the second moments can be summarized as

$$\phi_{\alpha,\beta} = \rho_{\alpha,\beta}V^{1/3}. \tag{72}$$

The values of the reduced moments $\rho_{\alpha,\beta}$ can be expressed in terms of $\mathcal{M}$ and $\mathcal{N}$ ($\mathcal{M}+\mathcal{N}=1$)

$$\rho_{1,1} = \frac{\mathcal{M}^{1/4}\mathcal{N}^{1/4}}{(\sqrt{\mathcal{M}}+\sqrt{\mathcal{N}})^{2/3}}, \quad \rho_{2,0} = \frac{\mathcal{M}^{5/4}\mathcal{N}^{-1/4}}{(\sqrt{\mathcal{M}}+\sqrt{\mathcal{N}})^{2/3}}. \tag{73}$$

Interchanging $\mathcal{M}$ and $\mathcal{N}$ in the last formula gives $\rho_{0,2}$. At the critical point the second moments begin to depend on the total volume of the coagulating system. As in the case of one component system this dependence is algebraic ($V^{1/3}$). However, the coefficients $\rho_{\alpha,\beta}$ (reduced second moments) depend on the composition of the gelating mixture. This dependence is displayed in Fig. 2.

VI. CONCLUDING REMARKS

Starting with the approach based on the evolution equation for the generating functional for the probabilities to have a given set of occupation numbers (the numbers of m,n-mers) at time t (Sec. III) the sol-gel transition in the coagulating mixture has been considered. Section II has demonstrated that the gelation catastrophe similar to that in one component systems occurs if the coagulation kernel is given by Eq. (5). To this end the second moments of the particle mass composition has been shown to have a singular behavior at $t\to t_c$, where $t_c=(\mathcal{M}\mathcal{N})^{-1/2}$ is the critical time. The evolution equation governing the time dependence of the generating functional for the probabilities to find a given set of occupation numbers formulated in Sec. III has been solved exactly (Sec. IV). The particle composition spectrum

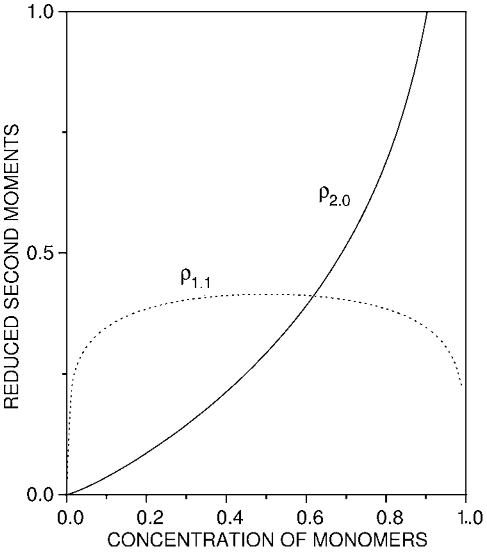

FIG. 2. Reduced second moments $\rho_{\alpha,\beta}$ as the functions of $\mathcal{N}$ ($\mathcal{M}+\mathcal{N}=1$). The moment $\rho_{2,0}$ displays less symmetric dependence on $\mathcal{N}$ than $\rho_{1,1}$.

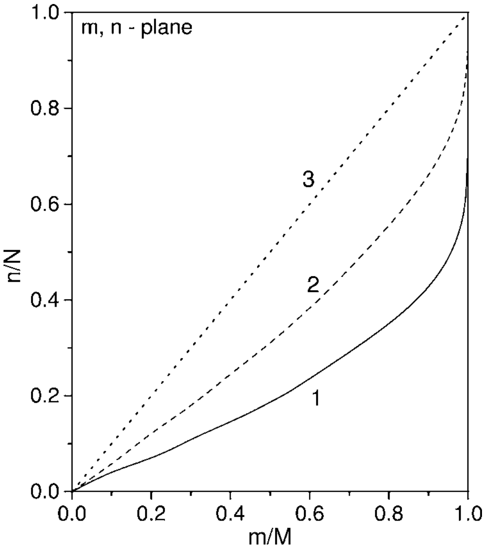

FIG. 3. After the critical time a very narrow maximum (the gel) in the particle composition distribution appears which then moves along the trajectories in the m,n plane. These trajectories are shown for $\mathcal{M}=0.1$, 0.25, 0.5 (curves 1–3, respectively).

has been expressed in terms of special polynomials $F_{m,n}(x)$ introduced and considered in detail in Appendixes A and B. The analysis of the composition distribution in the thermodynamic limit has been performed in Sec. V. It has been shown that a single giant particle whose mass and composition define the deficits of masses of each component in the sol fraction of the spectrum eventually forms after the critical time. The asymptotic expression for the composition spectrum has been derived and analyzed at $t=t_c$. After the critical time the composition distribution has been shown to have a narrow maximum located exactly at the point in the m,n plane corresponding to the gel particle. The trajectory of this maximum in the m,n plane is described by Eqs. (49) which can be rewritten as

$$n\ln(1-n/N)=m\ln(1-m/M). \tag{74}$$

This trajectory is shown in Fig. 3.

The similarity with the gelation in one component systems is apparent, although the description of the process in mixtures is much more complex. As in one component systems only one gel particle forms after the critical time. The critical values of the second moments grow with the volume of the system as $V^{1/3}$ (exactly as in the one component system), but the coefficients $\rho_{\alpha,\beta}$ in two component system depend on the composition of the coagulating system. It is also interesting to emphasize that the ratio of concentrations of two components in the gel particle right after the critical time is $M\mu_g/N\nu_g=\sqrt{\mathcal{M}\mathcal{N}}$ [Eq. (52)].

The approach described above can be applied to other systems. The most general form of the coagulation kernel that admits the exact solution of Eq. (21) in the form Eq. (24) is

$$\begin{aligned}K(k,l:p,q)&=kf_0(q)+lf_0(p)+pf_0(l)+qf_0(k)+kf_1(p)\\&\quad+pf_1(k)+qf_2(l)+pf_2(k),\end{aligned} \tag{75}$$

where the functions $f_i(x)$ are arbitrary. It is seen that the kernel $K(k,l:p,q)$ is symmetric, i.e., $K(k,l:p,q)=K(p,q:k,l)$. Equation (75) is an extension of linear models introduced in Ref. [10].

APPENDIX A: POLYNOMIALS $F_{m,n}$

Here we pass the route from Eq. (26) to Eq. (37). To this end we introduce the function

$$Q(\xi,\eta;x)=\sum_{m,n}\frac{\xi^m\eta^n}{m!\,n!}x^{mn}, \tag{A1}$$

and

$$W(\xi,\eta;x)=\ln Q(\xi,\eta;x)=\sum_{m,n}C_{m,n}(x)\frac{\xi^m\eta^n}{m!\,n!}, \tag{A2}$$

with $C_{1,0}=C_{0,1}=1$ and $C_{0,0}=0$.

Let us now rewrite equation (A1) in the form

$$Q(\xi,\eta)=\sum_n\frac{\eta^n}{n!}e^{\xi x^n}=e^{\xi}\sum_n\frac{\eta^n}{n!}e^{\xi(x^n-1)}. \tag{A3}$$

Hence, the function

$$W(\xi,\eta)=\xi+\ln\left[\sum_n\frac{\eta^n}{n!}e^{\xi(x^n-1)}\right], \tag{A4}$$

generates all $C_{m,n}$. For example

$$\partial_\eta W(\xi,\eta)|_{\eta=0}=e^{(x-1)\xi},$$

and thus $C_{m,1}=(x-1)^m$. Next

$$\partial^2_{\eta,\eta}W(\xi,\eta)|_{\eta=0}=e^{(x^2-1)\xi}-2e^{2(x-1)\xi}.$$

This function generates all $C_{m,2}$

$$C_{m,2}=(x-1)^m[(x+1)^m-2^m].$$

It is not so difficult to continue in this spirit

$$C_{m,3}=(x-1)^m[(x^2+x+1)^m-3(x+2)^m+2\times 3^m].$$

In particular, we find

$$C_{2,2}=(x-1)^3(x+3),\quad C_{23}=(x-1)^4(x^2+4x+7),$$

$$C_{33}=(x-1)^5(x^4+5x^3+15x^2+29x+31). \tag{A5}$$

Equation (A2) allows for deriving two sum rules for $C_{m,n}(x)$. It is evident that

$$Q\partial_\xi W=\partial_\xi Q \quad \text{and} \quad Q\partial_\eta W=\partial_\eta Q. \tag{A6}$$

On substituting here expansions (A1) and (A2) gives

$$\sum_{p,q=0}^{m,n}\binom{m}{p}\binom{n}{q}x^{-pn-qm+pq}C_{p+1,q}(x)$$

$$=\sum_{p,q=0}^{m,n}\binom{m}{p}\binom{n}{q}x^{-pn-qm+pq}C_{p,q+1}(x)=1. \tag{A7}$$

These identities are of use in deriving the expression for the composition spectrum in the thermodynamic limit.

Now let us derive the set of recurrence relations for $C_{m,n}(x)$ [Eq. (A12)], it is easy to see that

$$\partial_\xi Q(\xi,\eta;x)=Q(\xi,x\eta;x),$$

and

$$\partial_\eta Q(\xi,\eta;x)=Q(x\xi,\eta;x). \tag{A8}$$

Hence,

$$\partial_\xi W(\xi,\eta,x)=e^{W(\xi,x\eta;x)-W(\xi,\eta;x)},$$

and

$$\partial_\eta W(\xi,\eta,x)=e^{W(x\xi,\eta;x)-W(\xi,\eta;x)}. \tag{A9}$$

On combining Eqs. (A9) and (A2) yields

$$\sum_{m,n}C_{m+1,n}(x)\frac{\xi^m\eta^n}{m!\,n!}=\exp\left[\sum_{m,n}C_{m,n}(x)\frac{\xi^m\eta^n}{m!\,n!}(x^n-1)\right]. \tag{A10}$$

Next, we apply Eq. (A9) for finding $\partial^2W/\partial\xi\partial\eta$

$$\frac{\partial^2W}{\partial\xi\,\partial\eta}=\sum_{m,n}C_{m+1,n+1}\frac{\xi^m\eta^n}{m!\,n!}$$

$$=\sum_{\alpha,\beta}C_{\alpha,\beta+1}\frac{\xi^\alpha\eta^\beta}{\alpha!\,\beta!}(x^{\beta+1}-1)\sum_{\gamma,\delta}C_{\gamma+1,\delta}\frac{\xi^\gamma\eta^\delta}{\gamma!\,\delta!}. \tag{A11}$$

The summations in the two above equations go over all nonnegative integers.

Equation (A11) is equivalent to the set of recurrence relations

$$C_{m+1,n+1}=\sum_{p,q=0}^{m,n}\binom{m}{m-q}\binom{n}{n-p}C_{m-q,p+1}C_{q+1,n-p}(x^{p+1}-1). \tag{A12}$$

At this stage we introduce the polynomials $F_{m,n}(x)$. They are defined as

$$C_{m+1,n+1}(x)=(x-1)^{m+n+1}F_{m,n}(x). \tag{A13}$$

On substituting Eq. (A13) into Eq. (A12) gives the recurrence for the polynomials $F_{m,n}(x)$

$$F_{m+1,n+1}(x)=\sum_{p,q=1}^{m,n}\binom{m+1}{m+1-q}\times\binom{n+1}{n+1-p}F_{m-q,p}(x)F_{q,n-p}(x)\frac{x^{p+1}-1}{x-1}. \tag{A14}$$

The lowest order polynomials are, $F_{0,0}=0$, $F_{0,1}=F_{1,0}=1$, and

$$F_{1,1}(x)=x+3,\quad F_{1,2}(x)=F_{2,1}(x)=x^2+4x+7,$$

$$F_{2,2}(x)=x^4+5x^3+15x^2+29x+31,\ \ldots\ .$$

We finally come to the central identity allowing for deriving the exact mass spectrum (37)

$$\ln\left(\sum_{m,n}\frac{\xi^m\eta^n}{m!\,n!}x^{mn}\right)=\sum_{m,n=1}^{\infty}\frac{\xi^m\eta^n}{m!\,n!}(x-1)^{m+n-1}F_{m-1,n-1}(x)+\xi+\eta. \tag{A15}$$

The exponential generating function for the polynomials $F_{m,n}(x)$ is introduced as

$$\Phi(\xi,\eta;x)=\sum_{m,n=1}^{\infty}F_{m-1,n-1}(x)\frac{\xi^m\eta^n}{m!\,n!}+\xi+\eta. \tag{A16}$$

On the other hand, using Eq. (A13) we find

$$\Phi[(x-1)\xi,(x-1)\eta;x]=(x-1)W(\xi,\eta;x). \tag{A17}$$

Equation (A9) allows us to derive the set of equations for $\Phi(\xi,\eta;x)$. We introduce $(x-1)\xi=a$ and $(x-1)\eta=b$. Then Eq. (A17) can be rewritten as

$$\Phi(a,b;x)=(x-1)W\left(\frac{a}{x-1},\frac{b}{x-1};x\right). \tag{A18}$$

On differentiating both sides of this equation with respect to a and b and using Eq. (A9) yield the set of functional equations for Φ

$$\frac{\partial\Phi(a,b;x)}{\partial a}=\exp\left[\frac{\Phi(a,xb;x)-\Phi(a,b;x)}{x-1}\right],$$

$$\frac{\partial\Phi(a,b;x)}{\partial b}=\exp\left[\frac{\Phi(xa,b;x)-\Phi(a,b;x)}{x-1}\right]. \tag{A19}$$

APPENDIX B: POLYNOMIALS $P_{m,n}(\delta)$

Equations (A19) can be rewritten in a more symmetric form

$$\ln X_\delta(a,b) = b\int_0^1 Y_\delta[a,(1+u\delta)b]du,$$

$$\ln Y_\delta(a,b) = a\int_0^1 X_\delta[(1+u\delta)a,b]du. \tag{B1}$$

Here $\delta = x-1$ and

$$X_\delta(a,b) = \partial_a\Phi(a,b;1+\delta), \quad Y_\delta(a,b) = \partial_b\Phi(a,b;1+\delta).$$

It is clear that X_δ and Y_δ are the bivariate exponential generating functions for the polynomials $P_{m,n-1}(\delta)=F_{m,n-1}(1+\delta)$ and $P_{m-1,n}(\delta)=F_{m-1,n}(1+\delta)$

$$X_\delta(\xi,\eta) = \sum P_{m,n-1}(\delta)\frac{\xi^m\eta^n}{m!\,n!},$$

$$Y_\delta(\xi,\eta) = \sum P_{m-1,n}(\delta)\frac{\xi^m\eta^n}{m!\,n!}. \tag{B2}$$

1. The case $\delta=0$

It is easy to show that

$$P_{m,n}(0) = (m+1)^n(n+1)^m. \tag{B3}$$

Indeed, let us introduce

$$u(\xi,\eta) = \ln X(\xi,\eta;0) \quad \text{and} \quad v(\xi,\eta) = \ln Y(\xi,\eta;0).$$

From Eq. (B1) we find

$$u = \eta e^v, \quad v = \xi e^u. \tag{B4}$$

Then we can find $P_{m,n}(0)$ from the following chain of equalities

$$P_{m,n}(0) = m!\,(n+1)!\,\mathrm{Coef}_{\xi,\eta}\frac{X(\xi,\eta;0)}{\xi^{m+1}\eta^{n+2}}$$
$$= m!\,(n+1)!\,\mathrm{Coef}_{u,v}\frac{e^{u(m+2)+v(n+2)}}{v^{m+1}u^{n+2}}e^{-(u+v)}(1-uv).$$

Elementary algebraic transformations prove Eq. (B3). The multiplier $e^{-(u+v)}(1-uv)$ in the last term is just the Jacobian appearing in replacing the variables $\xi,\eta \to u,v$.

It is easy to find the first several polynomials. From Eq. (A15) we have

$$P_{1,1}(\delta) = \delta+4, \quad P_{1,2}(\delta) = P_{2,1}(\delta) = \delta^2+6\delta+12,$$

$$P_{2,2}(\delta) = \delta^4+9\delta^3+36\delta^2+78\delta+81, \ldots .$$

The generating function $\Phi(\xi,\eta;1)$ can be expressed in terms of $X_0(\xi,\eta)$ and $Y_0(\xi,\eta)$ as follows:

$$\Phi(\xi,\eta;1) = \ln X_0 + \ln Y_0 - \ln X_0 \ln Y_0. \tag{B5}$$

In order to prove this identity it is enough to differentiate Eq. (B5) with respect to η. The left-hand side gives simply $\Phi'_\eta(\xi,\eta;1)=Y_0(\xi,\eta)$. We will show that the right-hand side of this equation reproduces the same result. Indeed, as it follows from Eq. (B1) X_0 and Y_0 obey the set of transcendent equations

$$\ln X_0 = \eta Y_0, \quad \ln Y_0 = \xi X_0.$$

These equations allow us to find the derivatives

$$\frac{\partial X_0}{\partial\eta} = \frac{Y_0}{1-\ln X_0\ln Y_0}, \quad \frac{\partial Y_0}{\partial\eta} = \frac{Y_0\ln Y_0}{1-\ln X_0\ln Y_0}.$$

Now we differentiate the right-hand side of Eq. (B5)

$$\ln'_\eta X_0 + \ln'_\eta Y_0 - \ln'_\eta X_0 \ln Y_0 - \ln X_0 \ln'_\eta Y_0$$
$$= \ln'_\eta X_0(1-\ln \eta Y_0) + \ln'_\eta Y_0(1-\ln \eta X_0)$$
$$= \frac{Y_0(1-\ln Y_0) + Y_0\ln Y_0(1-\ln X_0)}{1-\ln X_0\ln Y_0} = Y_0.$$

This result proves Eq. (B5).

2. Asymptotic analysis

Now we use Eq. (A7) for deriving the asymptotic formula for the polynomials $P_{m,n}(\delta)$ in the limit $m,n\to\infty$, $\delta\to 0$, $m\delta, n\delta < \infty$. The answer can be easily guessed

$$P_{m,n}(\delta) \propto m^n n^m h^m(n\delta)h^n(m\delta), \tag{B6}$$

where

$$h(x) = \frac{\sinh x/2}{x/2}. \tag{B7}$$

The analogy with my recent result [5–7] is clearly seen.

In order to prove Eq. (B6) we rewrite the first Eq. (A7) in the exponential form

$$\sum_{p,q} e^{\Omega(m,n,p',q';\delta)} = 1, \tag{B8}$$

where $p'=p/m$, $q'=q/n$, and

$$\Omega(m,n,p',q';\delta) = -m[(1-p')\ln(1-p') + p'\ln p']$$
$$-n[(1-q')\ln(1-q') + q'\ln q']$$
$$-mn(p'+q'-p'q')\delta + mp'H(nq'\delta)$$
$$+nq'H(mp'\delta). \tag{B9}$$

The idea is that the terms of the order of unity contribute to the right-hand side of Eq. (B8). Next, these terms correspond to the maximum of e^Ω. We assumed also that $C_{p,q} \approx e^{pH(q\delta)+qH(p\delta)}$, in accordance with Eq. (B6)

Let us analyze the condition for the maximum of Ω with respect to p'. It gives

$$-m[-\ln(1-p') + \ln p'] - mn\delta(1-q') + mH(nq'\delta)$$
$$+ mnq'\delta H'(mp'\delta) = 0. \tag{B10}$$

Now we introduce the variables $x=mp'\delta$ and $y=nq'\delta$ and rewrite Eq. (B10) in terms of these variables

$$\ln(1-p') - \ln p' - \frac{y}{q'} + y + H(y) + yH'(x) = 0. \tag{B11}$$

Similar equation holds for q'

$$\ln(1-q') - \ln q' - \frac{x}{p'} + x + H(x) + xH'(y) = 0. \tag{B12}$$

Together with the condition

$$\Omega(m,n,p',q';\delta) = 0. \tag{B13}$$

we have three equations for determining p', q', and H as the functions of x and y.

Equations (B11) and (B12) can be resolved under the condition that $p'(x,y)=f(y)$ and $q'(x,y)=f(x)$. In this case a separation of variables is possible and both Eqs. (B11) and (B12) give one and the same couple of equations for $f(\zeta)$ and $H(\zeta)$

$$\frac{\ln(1-f) - \ln f + \zeta + H(\zeta)}{\zeta} = \frac{1}{f} - H'(\zeta) = a. \tag{B14}$$

Here a is a separation constant. Its value determined from the condition (B13) is $a=1/2$. Then we find from Eq. (B14),

$$f(\zeta) = 1 - e^{-\zeta} \quad \text{and} \quad H(\zeta) = \ln[2\sinh(\zeta/2)]. \tag{B15}$$

It is easy to check that

$$p'(x,y) = 1 - e^{-nq'(x,y)\delta}, \quad q'(x,y) = 1 - e^{-mp'(x,y)\delta}. \tag{B16}$$

meet equation (B13).

At small ζ we find

$$H(\zeta) \approx \ln\zeta + \frac{\zeta^2}{24}. \tag{B17}$$

3. Polynomials $P_{m,n}$ and graphs

In conclusion of this appendix, I will show that the polynomial $P_{m-1,n-1}(\delta)$ allows one to find the number $C_{m,n;\nu}$ of linked bipartite labeled graphs of the order of m,n with given number of edges ν. Namely, I will prove that the combination $\delta^{n+n-1}F_{m-1,n-1}(\delta)$ generate $C_{m,n;\nu}$, i.e.

$$\delta^{n+n-1}P_{m-1,n-1}(\delta) = \sum_{\nu=m+n-1}^{mn} C_{m,n;\nu}\delta^{\nu}. \tag{B18}$$

The idea of the proof is adopted from Ref. [13], where similar theorem is proved for ordinary graphs (having one type of vertices).

The number of ways to connect m,n vertices of a bipartite graphs by ν edges is $\binom{nm}{\nu}$. Then the polynomial $(1+\delta)^{mn}$ is the generation function for the number of labeled graphs with given number of edges. The bivariate exponential generating function for all bipartite graphs is

$$\sum_{m,n} \frac{\xi^m \eta^n}{m!\,n!}(1+\delta)^{mn}.$$

The reader readily recognizes the function $Q(\xi,\eta;1+\delta)$ given by [Eq. (A1)]. Hence, Q is the generating function for all labeled bipartite graphs. According to the Riddel theorem [26] the function $W=\ln Q$ is the generating function for all linked bipartite graphs. Then Eq. (A15) immediately follows from Eq. (B18).

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