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## LETTER TO THE EDITOR

**Sol–gel transition in a coagulating mixture****A A Lushnikov**

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Online at [stacks.iop.org/JPhysA/38/L383](http://stacks.iop.org/JPhysA/38/L383)**Abstract**

The time evolution of a coagulating mixture in which binary coagulation governs the temporal changes to the particle mass and composition spectra is studied under the assumption that the coagulation kernel is proportional to the product of masses of the first and the second components in the coalescing particles. This model is shown 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 evolution equation for the generating functional defining all properties of coagulating systems is solved exactly for this particular kernel. The single-particle mass spectrum is analysed in the thermodynamic limit and it is demonstrated how the gel appears in this mixed system.

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In contrast to the coagulation of unary systems which has been studied comparatively well (see the review article by Leyvraz (2003)), little is known about the behaviour of coagulating mixtures. My earlier paper (Lushnikov 1976) was probably the first where the coagulation mixtures were considered. The evolution of the particle composition spectrum is of importance and it can be often determined from simple combinatorial considerations, especially if the collision efficiency leading to the particle coalescence depends on the total mass of the colliding particles rather than on their composition.

The model proposed below considers a coagulating mixture wherein the efficiency of coagulation principally depends on the particle composition. For two particles comprising respectively  $m_1, n_1$  and  $m_2, n_2$  monomers (green and red ones, for definiteness) this efficiency (coagulation kernel) is introduced as

$$K(m_1, n_1 | m_2, n_2) \propto m_1 n_2 + m_2 n_1. \quad (1)$$

This kernel gives a dimensionless rate of the process  $(m_1, n_1) + (m_2, n_2) \longrightarrow (m_1 + m_2, n_1 + n_2)$ . The kernel (1) describes realistic processes such as copolymerization (see e.g., a review of Soteris and Whittington (2004)) or time evolution of bipartite graphs (better to say, a bipartite forest, where an appearing edge is forbidden to create cycles). In the latter case,

the number of ways for the edge to join two trees having respectively  $m_1, n_1$  and  $m_2, n_2$  green and red vertices is exactly  $K$  given by equation (1). Next, coagulation in such systems leads to the sol–gel transition, i.e., a giant object containing a macroscopic number of monomers (gel) (or a giant component in an evolving random graph (Albert and Barabasi 2002)) appears in a finite interval of time (see the details in my recent articles (Lushnikov 2004, 2005)). The kinetics of pregelation stage of the coagulating mixture had been studied by Domilovskii, Lushnikov and Piskunov (1978).

In what follows I apply the approach (Marcus 1968, Lushnikov 1978, 2004, 2005) that operates with the occupation numbers (numbers of  $m, n$ -mers) and the probability to find a given set of occupation number at time  $t$ . The generating functional  $\Psi$  for this probability obeys the evolution equation,

$$V \partial_t \Psi = \hat{\mathcal{L}} \Psi, \quad (2)$$

where the generating functional depends on the set of variables  $X = \{x(m, n)\}$ ,  $V$  is the volume of the coagulating system and the evolution operator  $\hat{\mathcal{L}}$  has the form:

$$\hat{\mathcal{L}} = \frac{1}{2} \left[ \sum_{m,n} (m_1 n_2 + m_2 n_1) x(m_1 + m_2, n_1 + n_2) \frac{\partial^2}{\partial x(m_1, n_1) \partial x(m_2, n_2)} - \hat{M}_r M_g - M_r \hat{M}_g \right], \quad (3)$$

where  $\hat{M}_{g,r}$  is the operator of the total mass of green or red monomers respectively,  $\hat{M}_g = \sum_{m,n} m x(m, n) \partial_{x(m,n)}$  and  $\hat{M}_r = \sum_{m,n} n x(m, n) \partial_{x(m,n)}$ . The integers  $M_g$ , and  $M_r$  are the eigenvalues of these operators, the total numbers of green and red monomers respectively. The coagulation process does not change these numbers.

Below we shall follow the route that I have applied to the model  $K \propto gl$  (Lushnikov 2004, 2005). We construct the mass conserving solution in the form

$$\Psi = M_g! M_r! \text{Coef}_{\xi, \eta} \xi^{-M_g-1} \eta^{-M_r-1} \exp \left[ \sum_{m,n} x(m, n) a_{m,n}(t) \xi^m \eta^n \right]. \quad (4)$$

Here the notation Coef introduced by Egorychev (1977) is used instead of contour integrals. The point is that this operation allows for dealing with divergent series, where a normal integration is inapplicable. The operation Coef is defined as

$$\text{Coef}_{\xi, \eta} \sum_{m,n} b_{m,n} \xi^m \eta^n = b_{-1, -1}. \quad (5)$$

If the sum on the left-hand side of this equation converges the operation Coef can be replaced by respective integrals. The operation Coef displays many features of ordinary residues. It is easy to check that the functional  $\Psi$  given by equation (4) is the eigenfunctional of  $\hat{M}_g$  and  $\hat{M}_r$ .

The particle mass spectrum  $\bar{n}_{m,n}(t)$  is expressed in terms of  $a_{m,n}(t)$  as follows:

$$\bar{n}_{m,n}(t) = \partial_{x(m,n)} \Psi|_{X=1} = M_g! M_r! a_{m,n}(t) \text{Coef}_{\xi, \eta} \xi^{-M_g+m-1} \eta^{-M_r+n-1} \exp[G(\xi, \eta; t)]. \quad (6)$$

Here  $G(\xi, \eta; t) = \sum_{m,n} a_{m,n}(t) \xi^m \eta^n$  is the bivariate generating function for  $a_{m,n}(t)$ .

Substituting  $\Psi$  in the form (4) into equation (2) yields the following set of equations for  $a$ ,

$$V d_t a_{m,n}(t) = \sum_{k,l=0}^{m,n} (m-l) k a_{m-l,n-k}(t) a_{l,k}(t) + m n a_{m,n}(t) - \frac{1}{2} (M_r m + M_g n) a_{m,n}(t). \quad (7)$$

This set is subject to the condition corresponding to initially monodisperse particles,  $a_{m,n}(0) = \delta_{m,1} \delta_{n,0} + \delta_{m,0} \delta_{n,1}$ .

The equation for the generating function  $G$  can be readily derived from equation (7),

$$V \frac{\partial G}{\partial t} = \xi \frac{\partial G}{\partial \xi} \eta \frac{\partial G}{\partial \eta} + \xi \eta \frac{\partial^2 G}{\partial \xi \partial \eta} - \frac{1}{2} \left( M_r \xi \frac{\partial G}{\partial \xi} + M_g \eta \frac{\partial G}{\partial \eta} \right). \tag{8}$$

The initial condition to this equation is  $G(\xi, \eta; 0) = \xi + \eta$ .

Now let  $G(\xi, \eta; t) = D(\xi e^{-\mathcal{M}_r t/2}, \eta e^{-\mathcal{M}_g t/2}; t)$ , where  $\mathcal{M}_g = M_g/V, \mathcal{M}_r = M_r/V$ . Then, instead of equation (7) we find a linear equation for  $e^D$ ,

$$V \frac{\partial e^D}{\partial t} = \xi \eta \frac{\partial^2 e^D}{\partial \xi \partial \eta}. \tag{9}$$

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

$$e^D = \sum_{m,n} \frac{\xi^m \eta^n}{m!n!} \exp(mnt/V). \tag{10}$$

From this equation we can find

$$\text{Coef}_{\xi, \eta} \xi^{-M_g + m - 1} \eta^{-M_r + n - 1} \exp[G(\xi, \eta; t)] = \frac{\exp(-m\mathcal{M}_r t/2 - n\mathcal{M}_g t/2 + mnt/V)}{(M_g - m)!(M_r - n)!}. \tag{11}$$

The central difficulty is how to find  $a_{m,n}(t)$ . The identity

$$\ln \left( \sum_{m,n=0}^{\infty} \frac{\xi^m \eta^n}{m!n!} x^{mn} \right) = \sum_{m,n=0}^{\infty} \frac{\xi^m \eta^n}{m!n!} (1-x)^{m+n-1} F_{m-1,n-1}(x), \tag{12}$$

solves this problem. Here  $F_{0,-1}(x) = F_{0,-1}(x) = 1$  and  $F_{-1,-1}(x) = 0$ . The polynomials  $F_{m,n}(x)$  are introduced by the recurrence

$$F_{m+1,n+1}(x) = \sum_{p,q} \binom{m+1}{m+1-q} \binom{n+1}{n+1-p} F_{m-q,p}(x) F_{q,n-p}(x) \frac{x^{p+1} - 1}{x - 1}. \tag{13}$$

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

$$F_{1,1}(x) = x + 3, \quad F_{1,2}(x) = F_{2,1}(x) = x^2 + 4x + 7, \\ F_{2,2}(x) = x^4 + 5x^3 + 15x^2 + 29x + 31, \dots$$

Another set of polynomials  $P_{m,n}(\delta) = F_{m,n}(1 + \delta)$  is more convenient. These polynomials are introduced by two bivariate exponential generating functions

$$X_\delta(\xi, \eta) = \sum P_{m,n-1}(\delta) \frac{\xi^m \eta^n}{m!n!} \quad Y_\delta(\xi, \eta) = \sum P_{m-1,n}(\delta) \frac{\xi^m \eta^n}{m!n!}. \tag{14}$$

These functions satisfy a set of integral equations,

$$\ln X_\delta(\xi, \eta) = \eta \int_0^1 Y_\delta[\xi, (1 + u\delta)\eta] du, \quad \ln Y_\delta(\xi, \eta) = \xi \int_0^1 X_\delta[(1 + u\delta)\xi, \eta] du. \tag{15}$$

These equations are given here without a derivation. The limited scopes of the letter do not permit me to reproduce it here, but the analogy between  $F_{m,n}(x)$  and the Mallows–Riordan polynomials used in my recent works (Lushnikov 2004, 2005; see also references therein) is apparent. The derivation of equations (13)–(15) follows the same route as in these works and will be given elsewhere.

Equations (6), (11) and (12) allow us to restore the exact particle composition spectrum,

$$\bar{n}_{m,n}(t) = \binom{M_g}{m} \binom{M_r}{n} e^{mnt/V - m\mathcal{M}_r t - n\mathcal{M}_g t} (e^{t/V} - 1)^{m+n-1} F_{m-1,n-1}(e^{t/V}). \tag{16}$$

In order to investigate the behaviour of the composition spectrum in the thermodynamic limit, we need an asymptotic formula for  $P_{m,n}(\delta)$  in the limit  $m, n \rightarrow \infty, \delta \rightarrow 0, \mu,$

$\nu = m/V, n/V < \infty$ . This formula can be derived exactly along the same line as equation (28) of Lushnikov (2005). The final result is

$$P_{m,n}(\delta) \propto m^n n^m h^m(n\delta) h^n(m\delta), \quad (17)$$

where  $h(x) = 2x^{-1} \sinh x/2$ .

Applying the Stirling formula to equation (16) and using equation (17) yield

$$n_{m,n}(t) \propto e^{\mathcal{F}(\mu, \nu; t)}. \quad (18)$$

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

$$\begin{aligned} \mathcal{F}(\mu, \nu; t) = & -M_g[(1-\mu)\ln(1-\mu) + \mu\ln\mu] - M_r[(1-\nu)\ln(1-\nu) + \nu\ln\nu] \\ & - M_g M_r (\mu + \nu - 2\mu\nu)t/V + M_r \nu \ln(1 - e^{\mathcal{M}_g \mu t}) + M_g \mu \ln(1 - e^{\mathcal{M}_r \nu t}). \end{aligned} \quad (19)$$

Now I am showing that the function  $\mathcal{F}(\mu, \nu; t) < 0$  at  $t < t_c$  where

$$t_c = 1/\sqrt{\mathcal{M}_g \mathcal{M}_r}. \quad (20)$$

Indeed, the function  $\mathcal{F}$  cannot be positive, otherwise  $\bar{n}_{m,n}(t)$  would be exponentially large (as a function of  $V$ ). Next, on differentiating  $\mathcal{F}$  over  $\mu$  and  $\nu$  we arrive at two equations  $\partial_\mu \mathcal{F} = 0$  and  $\partial_\nu \mathcal{F} = 0$  determining the position of the maximum. It is easy to check that

- (i) the maximum of the function  $\mathcal{F}$  is located at the point  $\mu = \mu_c(t), \nu = \nu_c(t)$  in the plane  $\mu, \nu$ , where

$$t = \frac{1}{\nu_c \mathcal{M}_r} \ln \frac{1}{1 - \mu_c} = \frac{1}{\mu_c \mathcal{M}_g} \ln \frac{1}{1 - \nu_c}. \quad (21)$$

These equations have a nonzero solution only at  $t > t_c$ .

- (ii) The function  $\mathcal{F}(\mu_c(t), \nu_c(t); t) = 0$ .

In order to elucidate the meaning of this result let us consider the Smoluchowski limit ( $m/M_g, n/M_r \rightarrow \infty$ ) of the composition distribution (equation (16)). The concentration  $c_{m,n}(t) = \bar{n}_{m,n}(t)/V$  is then,

$$c_{m,n}(t) = \mathcal{M}_g^m \mathcal{M}_r^n \frac{P_{m-1, n-1}(0)}{m!n!} t^{m+n-1} \exp[-(m\mathcal{M}_r + n\mathcal{M}_g)t] \quad (22)$$

(note that  $P_{m-1, n-1}(0) = m^{n-1} n^{m-1}$ ).

The total mass concentrations of green and red monomers are seen to be expressed in terms of  $X_0(\xi_0, \eta_0)$  and  $Y_0(\xi_0, \eta_0)$  as follows:

$$\sum_{m,n} m c_{m,n}(t) = t^{-1} \xi_0 X_0(\xi_0, \eta_0) = \mathcal{M}_g [1 - \mu_d(t)] \quad (23)$$

and

$$\sum_{m,n} n c_{m,n}(t) = t^{-1} \eta_0 Y_0(\xi_0, \eta_0) = \mathcal{M}_r [1 - \nu_d(t)], \quad (24)$$

where the functions  $1 - \mu_d(t)$  and  $1 - \nu_d(t)$  define the deficit of the mass concentrations due to formation of a gel particle. Other notation are  $\xi_0(t) = \mathcal{M}_g t e^{-\mathcal{M}_r t}$  and  $\eta_0(t) = \mathcal{M}_r t e^{-\mathcal{M}_g t}$ .

At  $\delta = 0$ , the set of integral equations (15) reduces to a simple set of transcendent equations,  $X_0 = e^{\eta_0 Y_0}, Y_0 = e^{\xi_0 X_0}$ . Then equations (23) and (24) allow one to derive the set of equations for  $\mu_d$  and  $\nu_d$ . This set is identical to equation (21), i.e. the deficits of the total mass concentrations of green and red monomers coincide with  $\mu_c$  and  $\nu_c$  defining the position of the maximum of  $\mathcal{F}$ . This fact unequivocally provides evidence in favour of the formation of one gel particle whose composition is defined by the set of equations (21).

In the limit of large  $m, n$  the spectrum  $c_{m,n}(t)$  takes the form

$$c_{m,n}(t) \approx \frac{1}{2\pi} \mathcal{M}_g^m \mathcal{M}_r^n m^{n-m-1/2} n^{m-n-1/2} t^{m+n-1} \exp[-(m\nu + n\mu)t]. \quad (25)$$

At  $t = t_c = (\mu\nu)^{-1/2}$  and  $m\sqrt{\nu} = n\sqrt{\mu}$  the spectrum becomes powerlike,

$$c_{m,n}(t) \approx \frac{\sqrt{\mu\nu}}{2\pi m^{3/2} n^{3/2}}. \quad (26)$$

Equation (25) allows us to derive the equation for the particle number concentration  $N(t) = \sum c_{m,n}(t)$ ,

$$\frac{dN}{dt} = -\mathcal{M}_g \mathcal{M}_r [1 - \mu_c(t)\nu_c(t)]. \quad (27)$$

The main results of this letter can be summarized as follows:

1. The time evolution of a coagulating mixture with the model coagulation kernel (equation (1)) has been investigated. Equation (16) expresses the exact composition spectrum in terms of the polynomials  $F_{m,n}(x)$  introduced by recurrence (13).
2. It is shown that after the critical time  $t_c = 1/\sqrt{\mu\nu}$  the gel appears in the system. Its composition is determined by the set of equations (21).

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