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LETTER TO THE EDITOR

Exact particle mass spectrum in a gelling system**A A Lushnikov**Department of Physical Sciences, University of Helsinki, PO Box 64.
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Online at stacks.iop.org/JPhysA/38/L35**Abstract**

This letter reports on the exact particle mass spectrum in a coagulating system with the coagulation kernel proportional to the product of masses of two coalescing particles. This model is known to reveal the sol–gel transition, i.e., formation of a cluster with the mass comparable to the total mass of the whole system. The single-particle mass spectrum is analyzed in the thermodynamic limit and it is demonstrated explicitly how the gel appears in the system.

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Various phenomena of quite different nature can be described as the aggregation processes of the type (see Drake (1972) and the recent review paper, Leyvraz (2003)),



where the notation (x) stands for an x -mer, a cluster comprising a given number x of elementary units (monomers). The kinetics of such aggregation processes is formulated in terms of $\bar{n}_g(t)$, the average numbers of g -mers in the system at time t . It is more common, however, to use the concentrations $c_g(t) = \bar{n}_g(t)/V$, 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. 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 $M \longrightarrow \infty$. Normally this step does not lead to dramatic consequences and the respective kinetic equations have found wide applications in many branches of science. However, there exist exceptions, where the description in the thermodynamic limit leads to an unexpected mass loss, the latter being attributed to the formation of a gel (a good reference list can be found in Leyvraz (2003)). Another approach (Lushnikov (1978)) does not introduce the gel ‘by hands’ and considers a *finite* system of coagulating particles in which case the mass conserves ‘by definition’. The gel still appears as a giant particle whose mass is proportional to the total mass of the system.

Below I consider the coagulation in a finite system and assume that the coagulation kernel is proportional to the product of masses of colliding particles. Although this problem was ‘almost’ solved in 1978, the particle mass spectrum had not been found. Here I report on

the exponential asymptotics of the particle mass spectrum. The form of this spectrum in the vicinity of the gel point has been recently reported in Lushnikov (2004).

Initially let there be M monomers in a volume V . The monomers move, coalesce, produce dimers, trimers etc along the scheme given by equation (1). Then let $Q = \{n_1, n_2, \dots, n_g \dots\}$ be the state of the system which is given by the set of integers n_g , the numbers of particles of mass g . A single coagulation act (collision of two particles + their coalescence) changes a preceding state $Q^- = \{n_1, \dots, n_l + 1, \dots, n_m + 1, \dots, n_g - 1 \dots\}$ to the state Q by coalescing the particles of masses l and m to one particle of mass g . In its turn, a next coagulation act transfers the state Q to the state Q^+ according to the scheme $Q^- \rightarrow Q \rightarrow Q^+$, $(Q^+)^- = Q$.

Let us introduce a set of variables $X = \{x_1, x_2, \dots, x_m \dots\}$ and call $X^Q = x_1^{n_1(Q)} x_2^{n_2(Q)} \dots x_m^{n_m(Q)}$. Then

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

and

$$x_l x_m \frac{\partial^2}{\partial x_l \partial x_m} X^Q = n_l(Q)(n_m(Q) - \delta_{l,m}) X^Q. \quad (3)$$

Here $\delta_{l,m}$ is the Kroneker delta. Let $W(Q, t)$ be the probability of finding the coagulating system in the state Q . The generating functional for $W(Q, t)$ is introduced as

$$\Psi(X, t) = \sum_Q W(Q, t) X^Q. \quad (4)$$

Equations (2) and (3) allow us to conclude that $\Psi(X, t)$ satisfies the following evolution equation:

$$V \frac{\partial \Psi}{\partial t} = \frac{1}{2} \sum_{l,m} K(l, m)(x_{l+m} - x_l x_m) \frac{\partial^2 \Psi}{\partial x_l \partial x_m}. \quad (5)$$

This equation is entirely equivalent to the Markov equation for $W(Q, t)$. Indeed, $K(l, m)/V$ is the probability per unit time for two particles to meet in the volume V and to coalesce, whereas the differential operations equations (2) and (3) produce the correct combinatorial factors.

For $K(g, l) = 2gl$ and initially monodisperse particles ($\Psi(X, 0) = x_1^M$) the solution to equation (5) had been found in the form (Lushnikov (1978)),

$$\Psi_M = \frac{M!}{2\pi i} \oint \frac{dz}{z^{M+1}} \exp \left[\sum_{g=1}^{\infty} z^g a_g(t) x_g \right]. \quad (6)$$

The integration contour in equation (6) surrounds the origin of coordinates in the complex plane z . The functions $a_g(t)$ are polynomials of $\exp(\tau)$ ($\tau = t/V$) (see Lushnikov (2004)),

$$\bar{n}_g(\tau) = \binom{M}{g} e^{(g^2 - 2Mg + g)\tau} (e^{2\tau} - 1)^{g-1} F_{g-1}(e^{2\tau}). \quad (7)$$

Here \bar{n}_g are the average numbers of g -mers in the system. The polynomials $F_g(x)$ are introduced by their exponential generating function (Knuth (1998), Flajolet *et al* (1998) and references therein),

$$F(\xi, x) = \sum_{n=0}^{\infty} F_n(x) \frac{\xi^n}{n!}. \quad (8)$$

As shown in Knuth (1998), the function F satisfies the equation,

$$F(z(x-1), x)W(z, x) = W'_z(z, x), \quad (9)$$

where

$$W(z, x) = \sum_{n=0}^{\infty} \frac{z^n}{n!} x^{n(n-1)/2}. \quad (10)$$

Combining equations (8)–(10) yields a set of linear recurrence relations for F_g ,

$$x^{g(g+1)/2} = \sum_{m=0}^g \binom{g}{m} F_{g-m}(x) (x-1)^{g-m} x^{m(m-1)/2}. \quad (11)$$

This recurrence is readily converted to a simpler one,

$$\sum_{m=0}^g \binom{g}{m} F_m(x) (x-1)^m x^{(m+1)(m-2g)/2} = 1. \quad (12)$$

A more elegant recurrence can be found for $A_g(x) = (x-1)^g F_g(x)$,

$$A_g(x) = x^{g(g+1)/2} - \sum_{m=0}^{g-1} \binom{g}{m} A_m(x) x^{(g-m)(g-m-1)/2}, \quad (13)$$

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 $g(g-1)/2$.

The recurrence equation (12) proves that the spectrum equation (7) conserves the total mass, i.e.,

$$\sum_g g \bar{n}_g(\tau) = M. \quad (14)$$

Indeed, let us apply equation (12) to $g = M - 1$ and use the notation $x = e^{2\tau}$. The following chain of equalities,

$$\begin{aligned} 1 &= \sum_{g=0}^{M-1} \binom{M-1}{g} (x-1)^g F_g(x) x^{(g+1)(g-2M+2)/2} \\ &= \sum_{g=1}^M \binom{M-1}{g-1} (x-1)^{g-1} F_{g-1}(x) x^{g(g-2M+1)/2} \\ &= M^{-1} \sum_{g=1}^M g \binom{M}{g} (x-1)^{g-1} F_{g-1}(x) x^{g(g-2M+1)/2}, \end{aligned}$$

proves equation (14).

At large (but finite) M and finite t ($t/M \ll 1$) it is more convenient to replace the polynomials $F_g(x)$ by $P_g(\delta) = F_g(1 + \delta)$. The exponential generating function for $P_g(\delta)$ satisfies the following nonlinear integral equation Lushnikov (2004):

$$\ln Y(\xi, \delta) = \xi \int_0^1 Y(\xi(1 + u\delta), \delta) du. \quad (15)$$

Here

$$Y(\xi, \delta) = \sum_{g=0}^{\infty} \frac{\xi^g}{g!} P_g(\delta) \quad (16)$$

The function $Y(\xi, \delta)$ can be expanded in powers of δ ,

$$Y(\xi, \delta) = \sum_{k=0}^{\infty} B_k(\xi) \delta^k. \quad (17)$$

Even more simple equation

$$\ln Y = \xi Y + \delta \frac{\xi^2}{2} Y'_\xi \quad (18)$$

can serve for the asymptotic analysis of the polynomials $P_g(\delta)$ as $\delta \rightarrow 0$, while the product $g\delta$ is finite. Still the asymptotic analysis remains extremely complex.

Below I wish to demonstrate a trick allowing one to pass by all these complexities. My idea is to apply the recurrence equation (12) which defines the polynomials F_g . More convenient is, however, to apply the mass conservation, which, as has been just shown, is entirely equivalent to equation (12).

My recent analysis Lushnikov (2003) prompts the functional form of $P_g(\delta)$ at large g and small δ . It is

$$P_g(\delta) \propto g^g f^g(g\delta). \quad (19)$$

This form is almost evident. The factor g^g reproduces $P_g(0)$. The product $g\delta$ inevitably should appear in the thermodynamic limit, as well as the exponent g . No other ways for g and δ to enter the asymptotic expression for $P_g(\delta)$ are seen, except for a pre-exponential factor.

Let us introduce $\mu = g/M$ and exponentiate the exact mass spectrum equation (7),

$$\bar{n}_g(t) = e^{M\Phi(\mu,t)}, \quad (20)$$

with $\Phi(\mu, t) \leq 0$. In the limit of finite μ and $M \rightarrow \infty$ we can write,

$$\Phi(\mu, t) = -(1 - \mu) \ln(1 - \mu) + (\mu^2 - 2\mu)t + \mu \ln 2t + \mu \psi(\mu t), \quad (21)$$

where $\psi(x) = \ln f(2x)$. We have not yet specified the function ψ and are doing this now using the condition of the total mass conservation, equation (14). To this end we note that the sum in equation (14) contains the terms exponentially dependent on M . This means that the terms with $\mu = \mu_c(t)$ defined from the condition $\Phi(\mu_c, t) = 0$ give the main contribution to the sum in equation (14), because $\Phi(\mu, t)$ cannot be positive (otherwise $\bar{n}_g(t)$ will be exponentially large). Hence, the function $\Phi(\mu, t)$ should have a maximum at $\mu = \mu_c(t)$, or $\Phi'_\mu(\mu_c, t) = 0$. These two conditions give two equations,

$$-(1 - \mu_c) \ln(1 - \mu_c) + (\mu_c^2 - 2\mu_c)t + \mu_c \ln 2t + \mu_c \psi(\mu_c t) = 0, \quad (22)$$

$$\ln(1 - \mu_c) + 1 + (2\mu_c - 2)t + \ln 2t + \psi(\mu_c t) + \mu_c t \psi'(\mu_c t) = 0. \quad (23)$$

Let us introduce the variable $x = \mu_c(t)t$ and two unknown functions, $\psi(x)$ and $t(x)$. Then these two equations can serve for determining these functions.

It is easy to check that

$$\psi(x) = \ln \frac{1 - e^{-2x}}{2x} + x \quad (24)$$

and

$$t(x) = \frac{x}{1 - e^{-2x}} \quad (25)$$

are the solution to the set of equations (22), (23). It is seen that $t(0) = 1/2$. At $t < 1/2$ only one extremal point $\mu = 0$ contributes to the total mass. At $t > 1/2$ both extremal points, $\mu = 0$ and $\mu = \mu_c(t)$ defined by the equation $t = t(\mu_c t)$ do. The total mass is then shared between the sol (the contribution of the point $\mu = 0$) and gel ($\mu = \mu_c(t)$). There are strong reasons to believe that only *one* giant particle forms at $\mu = \mu_c$ (see Lushnikov (1978), (2004)).

The mass of this particle is thus $g_c(t) = M\mu_c(t)$, where, as follows from equation (25), $\mu_c(t)$ is the root of the equation,

$$t = \frac{1}{2\mu_c} \ln \frac{1}{1 - \mu_c}. \quad (26)$$

Let us return to the function $f(x)$ from equation (19). Equation (24) gives,

$$f(x) = \frac{\sinh(x/2)}{x/2}, \quad (27)$$

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

$$P_g(\delta) \propto \frac{\sinh^g(g\delta/2)}{(\delta/2)^g}. \quad (28)$$

At small $g\delta$ this expression gives

$$p_g(\delta) \propto g^9 \exp(g^3 \delta^2 / 24) \quad (29)$$

This result had been reported in Lushnikov (2004).

The function Φ , an analogue of the free energy in statistical mechanics, has the form,

$$\Phi(\mu, t) = -(1 - \mu) \ln(1 - \mu) - \mu \ln \mu + 2(\mu^2 - \mu)t + \mu \ln(1 - e^{-2\mu t}). \quad (30)$$

Now it is possible to write down the asymptotic expression for the particle mass spectrum. It is

$$\bar{n}(g, t) = \frac{M}{\sqrt{2\pi}} \left(\frac{1}{\sqrt{g^5}} + \sqrt{\frac{|\Phi''_{\mu}(\mu_c, t)|}{M^3}} \theta(t - t_c) \right) \exp\{M[-(1 - \mu) \ln(1 - \mu) - \mu \ln \mu + 2(\mu^2 - \mu)t + \mu \ln(1 - e^{-2\mu t})]\} \quad (31)$$

where $\theta(x)$ is the Heaviside step-function and $t_c = 1/2$ is the critical time. The pre-exponential factor is restored on absolutely the same ground as in Lushnikov (2004). The first term correctly reproduces the mass of the sol ($g \ll M$). This term becomes very small at $g \propto M$, and the second term normalizing the gel peak to unity alone contributes to the sum in equation (14) at large g .

The main results of this short note can be summarized as follows.

- (i) Equation (31) gives the mass spectrum in the coagulating system with the coagulation kernel proportional to the product of masses of two coalescing particles. This final expression is surprisingly simple.
- (ii) A trick is proposed allowing for the asymptotic form of the polynomials $P_g(\delta)$ (equation (28)) to be established without a heavy analysis of equations (15) and (18). Of course, I tried to analyse these equations and not without success (see Lushnikov (2004)), but I was not (yet) able to derive equation (28) in this way.

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