Gelation in coagulation and fragmentation models

M. Escobedo

Abstract. We first present very elementary relations between climate and aerosols. Then we introduce the homogeneous coagulation equation as a simple model to describe systems of merging particules like polymers or aerosols. We next give a recent result about gelation of solutions. We end with some related open questions.

Gelificación en modelos de coagulación y fragmentación

Resumen. En primer lugar presentamos de una manera muy elemental las relaciones entre clima y aerosoles. Posteriormente se introduce la ecuación de coagulación en el caso homogéneo como un modelo sencillo para describir sistemas de partículas como polímeros o aerosoles. Finalmente se exponen algunos resultados recientes sobre gelificación de soluciones y algunos problemas abiertos.

1.   Aerosols, Contaminant & Climate.

1.1.   Chemical components of the atmosphere.

a.- Major chemical components: nitrogen, oxygen, water, carbon dioxide & noble gases.
b.- Trace gases: 1 part per million and even, 1 part per trillion parts of air. There are myriad of trace species. The role of trace species is disproportionate to their abundance. They are responsible for:

   -urban photochemical smog
   -acid deposition
   -stratospheric ozone depletion
   -potential climate change.

c.- Composition of the atmosphere is changing. Increase in long-lived so-called greenhouse gases:

   -carbon dioxide CO_2, methane CH_4, nitrous oxide N_2O.

   In the last century and in the North hemisphere, increase of:

   -concentration of tropospheric ozone O_3,
   -sulfate and carbonaceous aerosols.

These changes alter the basic chemistry of the atmosphere.

1.2.   Aerosols: Particles suspended in the atmosphere.

a.- They arise,
- either: directly from emissions of particles (e.g. carbonaceous soots)
- or: from conversion of certain gases to particles in the atmosphere (e.g. sulfates).

b.- The atmospheric aerosols interact with the cycles of trace gases. The aerosols particles affect the climate and interact chemically in heretofore unrecognized ways with atmospheric gases:
- volcanic aerosols in the stratosphere participate in the catalytic destruction of ozone.
- Aerosols reflect solar radiation back to space and contributes to the cooling of the Earth.
- Aerosols are the nuclei around which clouds droplets form:

No aerosols no clouds. Clouds are one of the most important elements of our climate system. So the effect of increasing global aerosol levels on the Earth's cloudiness is a key problem in climate studies.

1.3.   Athmospheric models.

In the athmospheric models we have:
A.- Primary meteorological variables:
-wind speed, wind direction,
-air temperature, air density, air pressure and water content.

These variables are simulated by solving a set of equations including:
-the momentum equation,
-the thermodynamic energy equation,
-the continuity equation for air,
-the equation of state
-the continuity equation for total water.

B.- Primary radiative variables:
-heating rates (used to calculate changes in the temperatures)
-actinic fluxes (used to calculate photolysis rate coefficients.[2]).

These two variables are calculated with the radiative transfer equation.

The radiative transfer equation gives the change in radiance and/or inradiance along a beam of electromagnetic energy at a point of the athmosphere. The radiance is used to calculate actinic fluxes, the inradiance is used to calculate heating rates.

The radiation is affected by different processes. All of them depend on the pollutant parameters which are the gas and aerosols concentrations.

1.4.   Specific projects underway.

a.- Measurement and theoretical description of the formation of secondary organic aerosols from the atmospheric oxidation of hydrocarbons.

b.- Thermodinamics of atmospheric organic aerosols.

c.- Aircraft measurement of aerosols (and clouds) to understand the effects of aerosols on the Earth's radiation balance and climate.

d.- Assessment of past and projected future effects of aerosols on climate using General Circulation Models coupled with models of detailed aerosol microphysics and tropospheric chemistry.

e.- Formation and growth of aerosols particles (in order for instance to develop strategies of particulate air pollution). Modelling of growth and aggregation of fine particles formed in combustion. This formation of fine particles in combustion and other industrial processes has been addressed in a number of studies. In coal combustion, fine particles are formed from volatilized metals and metal oxides. The particles tend to grow as low density aggregates that are not well-described by classical aerosol theories. The emission rates,

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[2]When a gas absorbs radiation, it often breaks into smaller molecules or atoms during photolysis

the thermochimistry of ash vaporisation must be known. Understand the influence of growing particles on the rate of homogeneous nucleation.

(C. M. Sorensen *et al.* at K.S.U and R. C. Flagan, J. H. Seinfeld *et al.* at Caltech.)

2. Coagulation fragmentation equations.

2.1. The simplest model: homogeneous coagulation.

Coagulation fragmentation equations are very simplified models to describe systems of particles merging to form clusters which can also merge to form larger and larger clusters. This may give rise to crowded states of dispersed particulate mater.

Such crowded states are ubiquitous in Nature and technology: gels, colloidal emulsions, self associating polymer networks and aerogelation in soot aerosols are all examples of a transition to a crowded or packed state.

We then consider a system of particles (or monomers) such that:

(i) Clusters composed of different numbers of monomers move through the space.

(ii) When two clusters- say composed of i and j monomers- are sufficiently close, they merge into single clusters of size $i + j$.

(iii) A cluster of size i and one of size j merge at a stochastic rate given by $K(i,j)/N$ where, N is the total number of particles and $K(i,j) \in \mathbb{R}$ defined as follows.

(iv) $K(i,j)$:   Given a cluster of size i. We assume that the instantaneous rate at which it merges with some cluster of size j is proportional to the density $n(j,t)$ of such clusters. The number $K(i,j)$ is the constant of proportionality. It is usually taken in the physical literature so that,

$$K(i,j) = K(j,i), \quad K(r\,i, r\,j) = r^\lambda\, K(i,j), \ \lambda \geq 0. \tag{1}$$

There is a great variety of such kernels in the physical chemistry literature, these are some examples:

$$K(i,j) = (i^{1/3} + j^{1/3})^2, K(i,j) = (i+c)(j+c)$$
$$K(i,j) = (i-j)^2 (i+j)^{-1}, K(i,j) = (i^{1/3} + j^{1/3})^{7/3}.$$

A more complete model would incorporate mass, position, velocity (or diffusive rates) of each cluster, together with the exact rule for coalescence of two clusters.

The equation obtained in that way, is known as Smoluchovski equation. It was introduced in 1916 by M. Smoluchovski [20] to model the coagulation of colloids moving according to Brownian motion. It describes the evolution of the concentration $n(k,t)$ of clusters of k monomers and reads:

$$\frac{d}{dt} n(k,t) = \frac{1}{2} \sum_{i+j=k} K(i,j)\, n(i,t)\, n(j,t) - n(k,t) \sum_{j=1}^{\infty} K(k,j)\, n(j,t). \tag{2}$$

This equation describes irreversible coagulation processes. This means that there is no equilibrium possible in this model. Alternatively, one may think of the system as being far from chemical equilibrium in the begining. The model then only holds as long as the system is still sufficiently far from equilibrium. In order to describe reversible systems of particles we need to introduce also a fragmentation process and coagulation fragmentation equations.

Remark 1 The Continuous model The corresponding continuous model is also considered in the scientific literature:

$$\frac{d}{dt}\, n(x,t) = \frac{1}{2} \int_0^x K(x-y, y)\, n(x-y, t)\, n(y, t)\, dy \tag{3}$$

$$-n(x,t) \int_0^\infty K(x,y)\, n(y,t)\, dy.$$

It appears as a limit when k ranges over a large range. In that case the kernel $K(x,y)$ satisfies similar properties:

$$K(x,y) = K(y,x), \quad K(r\,x, r\,y) = r^{\lambda}\,K(x,y). \quad \blacksquare$$

If one considers a system containing only at most N particles or monomers, no molecule of more than N particules may be formed and one obtains the equation,

$$\frac{d}{dt}n_N(k,t) = \frac{1}{2}\sum_{i+j=k} K(i,j)\,n_N(i,t)\,n_N(j,t) \tag{4}$$
$$-n_N(k,t)\sum_{j=1}^{N-j} K(k,j)\,n_N(j,t).$$

The equation (2) may then be formally seen as the limit of equation (4) as $N \to \infty$.
If we multiply the equation (4) by k and sum from $k=1$ to $k=N$, we obtain:

$$\frac{d}{dt}\sum_{k=1}^{N} k\,n_N(k,t) = 0, \quad \forall t > 0. \tag{5}$$

This reflects the conservation of the total number of particles or monomers. It is not possible to show in general the analogue of (5) for the infinite system (2). The reason for this is easy to understand. Let us assume that,

$$\begin{cases} \lim_{N\to\infty} n_N(k,t) = n(k,t), \ \ \forall k \geq 0, \forall t \geq 0; \\ \\ \sum_{k=1}^{N} k\,n_N(k,t) = 1, \ \forall N \geq 1, \ \forall t \geq 0. \end{cases} \tag{6}$$

Then,

$$\sum_{k=1}^{\infty} k\,n(k,t) = \lim_{M\to\infty}\sum_{k=1}^{M-1} k\,n(k,t) = \lim_{M\to\infty}\lim_{N\to\infty}\sum_{k=1}^{M-1} k\,n_N(k,t) =$$
$$\lim_{M\to\infty}\lim_{N\to\infty}\left(1 - \sum_{k=M}^{N} k\,n(k,t)\right) = 1 - \lim_{M\to\infty}\lim_{N\to\infty}\sum_{k=M}^{N} k\,n(k,t).$$

The last term need not vanish: If the dynamics (4) can produce, in finite time, a finite quantity of clusters, the size of which goes to infinity as N does, then clearly it will not vanish. This phenomenon is well known in chemistry as gelation.

As it can be seen in P. J. Flory ([10]) and W. H. Stockmayer [25] the Smoluchovski equation was used from the beginning in the study of the kinetics of polymer growth, and especially gelation, to describe the distribution law of N-particules system, to study the ocurrence of gelation as well as the post gelation behaviour of the system.

Sol Gel transition. The sol-gel transition is a phase transition in which there is a loss of mass from finite size clusters (sol particles) to the infinite cluster (gel particles). This loss of mass is due to the cascading growth of larger and larger clusters, where the process accelerates, as the clusters grow larger. Finally, a positive proportion of mass lies in infinite gel clusters.

The sol gel transition in colloidal and polymeric liquid solutions is a common and important phenomenon

in Nature and for the creation of materials of practical value. Much less examples seem to be known in aerosols. Nevertheless, aerogelation, induced by an applied electric field has been observed by A. A. Lushnikov *et al.* [18]. It has also been reported in aerosols of freely aggregating clusters like in flame soot aerosol (C. M. Sorensen *et al.* [21]). Carbonaceous soot is a common by-product of fossil fuel combustion and, as such, is a major atmospheric pollutant. Evidence of the formation of superagglomerates in a laminar acetylene/air diffusion flame has been recently reported by Sorensen *et al.*, ([21]) where this interconnecting web of superagglomerates is described as a gel state.

2.2. Mathematical results and questions.

Let us come now to the equation stated above:

$$\frac{d}{dt} n(k,t) = \frac{1}{2} \sum_{i+j=k} K(i,j)\, n(i,t)\, n(j,t) - n(k,t) \sum_{j=1}^{\infty} K(k,j)\, n(j,t).$$

Since the dynamics of the clusters is contained in the kernel $K(i,j)$ we may expect that the behaviour of the solutions of this equation will strongly depend on the properties of this kernel.
The first results about the existence of solutions to the Cauchy problem associated to the Smoluchovski equation,where obtained by M. Smoluchovski ([20]), W. H. Stockmayer ([25]), Z. A. Melzak ([19]).
Further and more general existence results where obtained by several authors J. B. McLeod ([17]) W. H. White ([26]), J. M. Ball & J. Carr ([2]) and may be summarized as follows. To this end, let us define, for every ℓ

$$m_\ell(t) = \sum_{k=1}^{\infty} k^\ell\, n(k,t).$$

Theorem 1 *For any kernel K such that,*

$$K(i,j) \leq K_0\, (1 + i + j)$$

for some positive constant K_0, and for any initial data $n(i,0)$ such that,

$$m_0(0) < \infty, \quad m_1(0) = 1, \quad m_2(0) < \infty$$

the Smoluchovski coagulation equation has a unique solution which satisfies the same conditions, $m_0(t) < \infty$, $m_1(t) = 1$ and $m_2(t) < \infty$ for all $t > 0$ □.

This result is based on the following formal argument. Multiplying the equation by k^2, using the condition on the kernel $K(i,j)$, and summing formally from $k = 0$ to ∞ we obtain

$$\frac{d}{dt}\, m_2(t) \leq K_0\, \left(2m_2(t)\, m_1(t) + m_1^2(t)\right).$$

This shows that $m_2(t)$ remains bounded as long as $m_1(t)$ is bounded. It is then easely deduced that $m_2(t)$ is finite for all $t > 0$. Moreover this shows that we may actually multiply the equation by k and sum from $k = 0$ to $+\infty$ and obtain,

$$m_1(t) = m_1(0), \quad \forall t \geq 0.$$

Gelling kernels.   In contrast, if we consider, for instance, the case $K(i,j) = i\, j$ the same formal argument gives,

$$\frac{d}{dt}\, m_2(t) = m_2(t)^2.$$

From where,

$$m_2(t) = m_2(0)(1-t)^{-1}.$$

This kernel is the prototype example where the process exhibits the gelation transition. It corresponds to the Flory-Stockmayer model of gelation.

A gelling solution is defined precisely as one for which, there exists a finite time, $T > 0$ such that

$$m_1(T) < m_1(0).$$

The gelation time T_{gel} is then the largest time $T > 0$ such that the solution satisfies $m_1(t) = m_1(0)$ for all $t < T$.

The gelling solutions are not unique in general. An explicit example of non uniqueness has been constructed in [24]. Nevertheless, in the case $K(i,j) = i\,j$ uniqueness of global solutions is proved in [13].

Sometimes in the physical literature the gelling phenomena is exhibited by showing that the second moment $m_2(t)$ blows up in finite time even if this is not enough to identify a gelation transition phenomena. Nevertheless, when $K(i,j) = i\,j$ it has been proved that the two phenomena coincide at the same time. It is an open question if this is always true or not.

The gelation phenomenon has been first exhibited in the physical literature, calculating explicit solutions as in W. H. Stockmayer ([25]), G. Stell and R.M. Ziff ([23]), F. Leyvraz and H.R. Tschudi ([16]), M.H. Ernst, R.M. Ziff and E.M. Hendriks, ([7]) and also, using scaling arguments E.M. Hendriks, M.H. Ernst, R.M. Ziff ([11]).
The first general and rigourous result on the ocurrence of gelation is furnished by F. Leyvraz and H.R. Tschudi ([16]) for the kernel $K(i,j) = i\,j$. They prove that for any kernel $K(i,j) \geq i\,j$ it can not be true that the solution satisfies

$$\sum_{k=1}^{\infty} k\,n(k,t) = \sum_{k=1}^{\infty} k\,n(k,0), \quad \forall t > 0.$$

Using probability arguments, I. Jeon ([12]) was able to construct gelling solutions for any initial datum and for the kernel $K(i,j) = (i\,j)^{\lambda}$ with $\lambda > 1$. More recently the following result has been proved.

Theorem 2 *([8]) Assume that $\lambda > 1$. Then, for every $n(\cdot,0)$ and every weak solution of the Smoluchovski equation, there exists a positive constant C_* depending on $m_0(0), m_1(0)$ and λ such that for every $t \geq 0$,*

$$m_1(t) \leq \frac{C_*}{(1+t)^{1/\lambda}}.$$

As a consequence, gelation occurs in finite time and

$$T_{gel} \leq \left(\frac{C_*}{m_1(0)}\right)^{\lambda}. \quad \square$$

The proof of this result is based on some a priori estimates which are true for any weak solution of the coagulation equation. We only give one of them in the continuous model contex (the same inequalities hold true in the discrete case and the proofs are essentially the same): for every $k \in [\lambda/2, \lambda/2 + 1/2)$, (and for $k = 1$ if $\lambda = 2$):

$$\int_T^{\infty} m_k^2(t)\,dt \leq C_k\,(m_0(T) + m_1(T)). \tag{7}$$

Notice that we immediatly deduce from (7) that $m_1 \in L^2(R^+)$ so that $m_1(t)$ can not be constant in time and gelation must occurs.

The proof of this estimate may be sketched as follows. Any weak solution of the continuous coagulation equation satisfies:

$$\frac{1}{2} \int_{t_0}^{t_1} \int_0^\infty \int_0^\infty a(y, y') \, f(t, y) \, f(t, y') \, (-\tilde\psi(y, y')) \, dy \, dy' \, dt = \tag{8}$$

$$= \int_0^\infty f(t_0, y) \, \psi \, dy - \int_0^\infty f(t_1, y) \, \psi \, dy.$$

for any $\psi \in L^\infty(0, +\infty)$ and where $\tilde\psi(y, y') = \psi(y + y') - \psi(y) - \psi(y')$.

Taking first $\psi \equiv 1$ we obtain that

$$\frac{1}{2} \int_{t_0}^{t_1} \int_0^\infty \int_0^\infty a(y, y') \, f(t, y) \, f(t, y') \, dy \, dy' \, dt = m_0(t_0) - m_0(t_1) \tag{9}$$

Choosing ψ such that $\psi(y) = \min(y, A)$ for $A > 0$ a fixed constant we obtain,

$$\int_{t_0}^{t_1} \left(\int_A^\infty y^{\lambda/2} \, f(t, y) \, dy \right)^2 dt \leq 2 \, \frac{m_1(t_0)}{A} \quad \forall \, A > 0. \tag{10}$$

Then, using Fubini's theorem

$$\int_{t_0}^{t_1} \left(\int_0^\infty \Phi'(A) \int_A^\infty f(t, y) \, y^{\lambda/2} \, dy \, dA \right)^2 dt \leq 2 \, C_\Phi^2 \, m_1(t_0),$$

for every increasing function Φ such that $\Phi(0) = 0$ and $\Phi'(\cdot) \, (\cdot)^{-1/2}$ is integrable over $(0, +\infty)$. If we choose now $\Phi(y) = \left(y^{1/2}/(\ln y)^\delta - r^{1/2}/(\ln r)^\delta \right)^+$ with $\delta > 1$ and $r = \exp(2\delta)$ we obtain

$$\int_T^\infty \left(\int_e^\infty f(t, y) \, \frac{y^{\lambda/2 + 1/2}}{(\ln y)^\delta} \, dy \right)^2 dt \leq C_\delta \, m_1(T) \tag{11}$$

Finally, for every $k \in [\lambda/2, \lambda/2 + 1/2)$ we have,

$$
\begin{aligned}
m_k^2(t) &\leq C_1 \left(\int_0^e y^{\frac{\lambda}{2}} f(t, y) \, dy + \int_e^\infty y^k f(t, y) \, dy \right)^2 \\
&\leq C_2 \left[m_{\lambda/2}^2(t) + \left(\int_e^\infty \frac{y^{\frac{\lambda}{2} + \frac{1}{2}}}{(\ln y)^2} f(t, y) \, dy \right)^2 \right]
\end{aligned}
$$

and (7) follows from (9) and (11).

Gelling profile. An interesting related question is to establish the profile of the solution at gelling time. It is conjectured in the physical chemistry literature that :

$$n(k, t) \sim (T_{\text{gel}} - t)^{\frac{3 + \lambda}{\lambda - 1}} \Phi\left(k \, (T_{\text{gel}} - t)^{\frac{2}{\lambda - 1}} \right)$$

as $k \to \infty$, $(T_{\text{gel}} - t) \to 0$ and $k(T_{\text{gel}} - t) \geq 1$, for some function Φ,

and that

$$n(k, t) \sim C(t) \, k^{-\frac{\lambda + 3}{2}}, \quad \text{as } k \to +\infty,$$

for every $t > T_{\text{gel}}$ (c.f. P.G.C. van Dongen & M. H. Ernst [4] for a discussion and some results).

Coagulation fragmentation system. The case of coagulation with fragmentation is also of great importance due to its greater generality and the possibility of describing reversible systems both near and far from equilibrium. The Smoluchovski equation generalized to include fragmentation reads,

$$\frac{d\, n(k,t)}{dt} = \frac{1}{2} \sum_{i+j=k} [K(i,j)\, n(i,t)\, n(j,t) - F(i,j)\, n_{i+j}] \tag{12}$$

$$- \sum_{j=1}^{\infty} [K(k,j)\, n(k,t)\, n(j,t) - F(k,j)\, n_{k+j}].$$

where $F(i,j)$ is the fragmentation kernel.

The first work on coagulation-fragmentation system appears to be that of P. J. Blatz & A. V. Tobolsky ([3]) who studied a polymerization-depolymerization reaction for the special case of constant-rate coefficients (homogeneity equal to zero for each kernel).

The dynamic of these system is of course much richer than that of the coagulation equation. Only partial results on the ocurrence of gelation for the weak solutions of such systems have been obtained up to know. They consider fragmentation kernels satisfying the following type of conditions:

$$F(i,j) = F(j,i) \leq B(i+j), \quad \text{with} \quad B(z) = \frac{B}{(1+z)^{\gamma}} \tag{13}$$

For instance it has been proved (cf. [9]) that when $\frac{\lambda}{2} + \gamma \geq \frac{3}{2}$ gelation occurs for all weak solution whose initial total mass $m_1(0)$ is large enough. On the other hand, if $\lambda + \gamma < 2$ it can be proved that for every initial data there exists at least one weak solution for which gelation does not occurs.

A more detailed introduction to the mathematical theory of coagulation equations may be found in the two survays [5] and [1] as well as in the monography [6]. The interested reader may find in [15] an example of model where spatial diffusion of the particles is taken in acount.

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M. Escobedo
Departamento de Matemáticas, Universidad del País Vasco
Apartado 644. Bilbao, Spain 48080
mtpesmam@lg.ehu.es