Challenges in Stochastic Simulation Methods, Research Problems in Computational Physics no. 3, Problem no. 1: "Existence and Form of Scaling Function Solutions for Generalized Smoluchowski Equations"

Problem description and background for the workshop on Computational Problems in Physics, Helsinki, Finland, May 23 - 27, 2005
by

T. Ala-Nissilä (ala@fyslab.hut.fi), M. Rusanen (mtr@fyslab.hut.fi) and I.T. Koponen (ismo.koponen@helsinki.fi)

4th May 2005

1 Introduction

Rate equations are ubiquitous in nature, and can be used to describe a wide variety of different problems ranging from chemical reactions to population dynamics [1]. They offer a way to carry out coarse-grained descriptions of many dynamical problems, which are too difficult to solve on a "microscopic" level. There are also very efficient numerical algorithms for solving rate equations using stochastic computer simulation techniques. However, rate equations are notoriously difficult to solve analytically. The problem presented here – which actually comprises several parts – deals with constructing analytic solutions to a class of rate equations, also called Smoluchowski equations by physicists, which describe systems where there are competing processes. Typical processes of this type are growth (aggregation) of clusters of single particles, and fragmentation of such clusters. Aided by physical intuition and computer simulations, particular type of solutions are expected to exist, as will be described below. The aim here is to find such solutions and study their existence.

2 Rate equations

2.1 Smoluchowski equation

The starting point here is the Smoluchowski rate equation, originally derived to describe aggregation of particles in a colloidal solution. The number density n_s of clusters of size s, comprising s "atoms", evolves as

$$\frac{dn_s}{dt} = \frac{1}{2} \sum_{i+j=s} K(i,j) n_i n_j - \sum_{j=1}^{\infty} K(j,s) n_j n_s, \tag{1}$$

with the initial condition $n_s(t=0) = \delta_{s,1}$, where $\delta_{i,j} = 1$ is the Kronecker delta function. The quantity $K(j,s)$ is called the reaction kernel, which denotes the rate of aggregation of clusters of sizes i and j. The rate equation allows so-called scaling solutions (see below) if the kernels have homogeneous form, *i.e.* $K(ai, aj) = a^{\lambda} K(i,j)$ (physically it can be argued that $\lambda \leq 2$).

To define what the scaling solutions mean, we first define a quantity called the mean cluster size as $\bar{s} = \sum_s s^2 n_s / \sum_s s n_s$. The scaling solutions to Eq. (1) are separable solutions of the form

$$n_s(t) = g(t) f(s/\bar{s}). \tag{2}$$

Physical mass conservation requires (for $\lambda < 1$) that $g(t) = M_1/\bar{s}^2$, where $M_1 = \sum s n_s$ is the total mass of the system (note that for $1 < \lambda \leq 2$ an infinite cluster appears at some finite time $t = t_c$). Inserting the corresponding scaling form

$$n_s = M_1 \bar{s}^{-2} f(s/\bar{s}) \tag{3}$$

into Eq. (1), and taking the continuum limit $s, \bar{s} \to \infty$, $x = s/\bar{s}$, $y = j/\bar{s}$, we get an integro-differential equation of the form

$$-w[xf'(x) + 2f(x)] = \lim_{\epsilon\to 0}\left[\frac{1}{2}\int_{\epsilon x}^{(1-\epsilon)x} dy K(y, x-y) f(y) f(x-y) - f(x)\int_{\epsilon x}^{\infty} K(x,y) f(y)\right], \quad (4)$$

where w is the separation constant (for t and x dependence) such that $M_1 w = \bar{s}^{-\lambda} d\bar{s}/dt$. This gives for the mean cluster size

$$\bar{s} = [C + (1-\lambda) M_1 w t]^z, \quad (5)$$

where C is an integration constant, and the so-called dynamic scaling exponent is defined by

$$z \equiv 1/(1-\lambda), \quad (6)$$

for $\lambda < 1$. Existence and uniqueness of the solution is guaranteed if $K(i,j) \le K_0(i+j)$, which means that usually n_s decays exponentially fast for large x. The corresponding solution is of the form

$$f(x) = Ax^{-\lambda} \exp(-ax), \quad (7)$$

where A and a are constants. The small x behavior depends on convergence of the integrals: classifying the kernel according to the asymptotic behavior $K(i,j) \sim i^\mu j^\nu$ ($j \gg i$) we have the following cases:

- For $\mu > 0$, $f(x) = Bx^{-\tau}$ ($x \to 0$) with $\tau = 1 + \lambda$, $B = const.$;
- For $\mu = 0$, $f(x)$ as in (i), but $\tau = 2 - M_\lambda/w$, where $M_\lambda = \int dx x^\lambda f(x)$;
- For $\mu < 0$ (where all integrals converge at the lower limit), $f(x) \sim \exp(-x^{-|\mu|})$, whose exact algebraic form depends on the kernel (e.g. $K(i,j) = x^{-\mu} + y^{-\mu}$, $\mu > 0$, gives $f(x) \sim x^{-1}\exp(-x^{-\mu})$).

2.2 First Generalized Smoluchowski Equation: Cluster Fragmentation

Since it is physically possible that some of the growing clusters of size s can break up to smaller fragments, we add the so-called cluster fragmentation term into Eq. (1) (with the initial condition $n_s(t=0)=\delta_{s,1}$), which gives the rate equation

$$\frac{dn_s}{dt} = \frac{1}{2}\sum_{i+j=s}\left[K(i,j)n_i n_j - \kappa F(i,j)n_{i+j}\right] - \sum_{j=1}^{\infty}\left[K(j,s)n_j n_s - \kappa F(j,s)n_{j+s}\right]. \tag{8}$$

Here it is also assumed that the fragmentation kernel is a homogeneous function $F(ai,aj)=a^{\alpha}F(i,j)$, and κ is a parameter indicating the relative importance of fragmentation with respect to aggregation. Since now there are two competing but opposite processes, we can assume on physical grounds that a steady state can be reached, at least in a limited region of the parameter space of the rate equation. We insert the scaling ansatz into this (and set $M_1=1$), and taking the continuum limit gives

$$-\frac{\dot{\bar{s}}}{\bar{s}^2}\left[f(x)+xf'(x)\right] = \bar{s}^{\lambda-3}G_1(x) - \bar{s}^{\alpha-1}\kappa G_2(x), \tag{9}$$

where $\dot{\bar{s}}$ is the time derivative, and the functions $G_1(x)$ and $G_2(x)$ are given by

$$G_1(x) = \frac{1}{2}\int_{\epsilon x}^{(1-\epsilon)x} dyK(y,x-y)f(y)f(x-y) - f(x)\int_{\epsilon x}^{\infty} dyK(x,y)f(y);$$
$$G_2(x) = \frac{1}{2}\int_{\epsilon x}^{(1-\epsilon)x} dyF(y,x-y)f(x) - \int_{\epsilon x}^{\infty} dyF(x,y)f(x+y). \tag{10}$$

There is at least one physically sensible scaling function in the steady state which satisfies the equation, given by

$$f(x) \sim x^{\delta}\exp(-x), \tag{11}$$

where $\delta=-\lambda+\alpha+1$, if we assume that the integrals above converge.

The equation for the mean cluster size $\bar{s}$ is obtained by multiplying Eq. (8) with s^2, summing over s, and taking the continuum limit with the scaling ansatz inserted. This gives

$$\frac{d\bar{s}}{dt} = A\bar{s}^{\lambda} - B\kappa\bar{s}^{\alpha+2}, \tag{12}$$

where

$$
\begin{aligned}
A &= \int_0^\infty dx \int_0^\infty dy\, xyK(x,y)f(x)f(y); \\
B &= \int_0^\infty dx \int_0^\infty dy\, xyF(x,y)f(x+y).
\end{aligned} \tag{13}
$$

From this it can be shown that the steady state value $\bar{s}_0$ scales as $\bar{s}_0 \sim \kappa^q$ with $q = 1/(2-\lambda+\alpha)$. Linear stability analysis predicts that this value is stable as long as $q > 0$.

2.3 The Generalized Smoluchowski Equation II: Cluster Fragmentation and Monomer Addition

Next we generalize Eq. (8) to include monomer addition (or atom deposition) into the system. This introduces a source term in the rate equation, which now reads as

$$
\begin{aligned}
\frac{dn_s}{dt} &= \Phi\delta_{1,s} + \frac{1}{2}\sum_{i+j=s}[K(i,j)n_i n_j - \kappa F(i,j)n_s] \\
&\quad - \sum_{j=1}^{\infty}[K(s,j)n_s n_j - \kappa F(s,j)n_{s+j}],
\end{aligned} \tag{14}
$$

where Φ is the new addition rate.

To derive the continuum integro-differential equation for Eq. (14) we insert the scaling form of Eq. (2) into it, take the continuum limit $s, i, \bar{s} \to \infty$, $s/\bar{s} = const.$, and redefine time as $\tilde{t} = \Phi t$. This gives

$$
\frac{1}{\bar{s}^2}f(x) - \frac{\tilde{t}\dot{\bar{s}}}{\bar{s}^3}\left[2f(x) - xf'(x)\right] = \mathcal{R}\left[\tilde{t}^2\bar{s}^{\lambda-3}G_1(x) - \kappa\, \tilde{t}\bar{s}^{\alpha-1}G_2(x)\right], \tag{15}
$$

where $\dot{\bar{s}}$ denotes the time derivative, $f'(x) = df/dx$, $x = s/\bar{s}$ (and $\mathcal{R} = 1/\Phi$ and κ are constants, as before). Note that the deposition term vanishes in the continuum limit and the only effect of deposition is to increase time. The functions $G_{1,2}(x)$ are given by

$$\begin{aligned} G_1(x) &= \frac{1}{2}\int_{\epsilon x}^{(1-\epsilon)x} dy K(y,x-y)f(y)f(x-y) - f(x)\int_{\epsilon x}^{\infty} dy K(x,y)f(y); \\ G_2(x) &= \frac{1}{2}\int_{\epsilon x}^{(1-\epsilon)x} dy F(y,x-y)f(x) - \int_{\epsilon x}^{\infty} dy F(x,y)f(x+y). \end{aligned} \tag{16}$$

In the following, we assume that all the integrals converge, and set $\epsilon = 0$.

There are two limits where the solutions to Eq. (15) are of interest here:

1. On physical grounds, at the onset of growth the fragmentation term is negligible (since the clusters have not grown yet), and we are left with the equation

$$\bar{s}f(x) - 2\tilde{t}\dot{\bar{s}}f(x) - \tilde{t}\dot{\bar{s}}xf'(x) = \tilde{t}^2\bar{s}^\lambda \mathcal{R}G_1(x). \tag{17}$$

Apparently, the only way that the t and x dependence can be separated is that $\bar{s}$ follows an algebraic form in time, i.e. $\bar{s} \sim \mathcal{R}^\gamma t^\beta$. Matching the powers of the various terms in Eq. (17) gives the following results for the scaling exponents:

$$\begin{aligned} \gamma &= \frac{1}{2}\beta; \\ \beta &= \frac{2}{1-\lambda}. \end{aligned} \tag{18}$$

These are in contrast to the original Smoluchowski equation Eq. (6), where $\beta = z = 1/(1-\lambda)$ and the exponent γ does not even exist since it is due to the new deposition term.

If we assume that the scaling function has the form

$$f(x) \sim x^\delta \exp(-x), \tag{19}$$

(as is the case when fragmentation is included), the scaling exponent δ for the size distribution function follows through the x dependence of Eq. (17):

$$\delta = 1 - \lambda. \tag{20}$$

These results have been found to be valid numerically to a good degree of accuracy.

2. The second regime is at later times where fragmentation becomes important and one presumably has a quasi-stationary state where only time increases. Requiring the right hand side of Eq. (15) equals to zero gives $\bar{s} \sim \kappa^{-\beta} t^{\beta}$, similar to the fragmentation case, with the scaling exponent
$$\beta = 1/(-\lambda + \alpha + 2). \tag{21}$$
The scaling exponent of the scaling function is obtained by requiring that $G_1(x) \propto G_2(x)$. Inserting Eq. (19) into the relation between $G_{1,2}(x)$ gives
$$\begin{aligned} G_1(x) &= C_1 \mathrm{e}^{-x}\ x^{\lambda+2\delta-1}; \\ G_2(x) &= C_2 \mathrm{e}^{-x}\ x^{\delta+\alpha}, \end{aligned} \tag{22}$$
where C_1 and C_2 are constants depending on the explicit form of the reaction kernels. Equating the powers of x of these expressions gives
$$\delta = -\lambda + \alpha + 1. \tag{23}$$

3 Formulation of the Research Problem

The research problem formulated here concentrates on studying the existence and nature of solutions to the generalized Smoluchowski rate equation of Eq. (15). For simplicity, it can be assumed that the kernels $K(i,j)$ and $F(i,j)$ are homogenous, as discussed in the previous sections. In addition, it may or may not be important to consider limitations to the corresponding parameters λ and α, as discussed in the text. More specifically:

1. Study the existence and nature of possible scaling solutions to Eq.(9) in order to obtain more insight into the most general case of Eq. (17).
2. Study Eq. (15) in the quasi-stationary limit (i.e. where the right hand size equals zero).
3. Study Eq. (15) without any assumptions about vanishing terms.

Even if it were impossible to find exact analytic solutions to all of these equations, it would be important to know under what conditions scaling type of solutions might possibly exist.

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