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Evolution of a particulate assemblage due to coalescence combined with coagulation

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Abstract. — The final asymptotic stage of sol aging processes governed by the joint action of coalescence (Ostwald ripening) and coagulation (agglomeration) is considered. A self-similar solution of the kinetic and balance equations is obtained for a simple model example. The large-time particle size distribution density is shown to be essentially different from that due to coalescence alone in accordance with the conventional theory by Lifshitz and Slyozov.

Particulate assemblages (originated as a consequence of a bulk phase transition in a metastable medium as well as colloidal solutions under conditions of phase separation) usually evolve due to the growth of individual particles or aggregates, to a lasting formation of new critical nuclei and also to possible particle coagulation or agglomeration and disintegration processes. The study of the particle distribution density and the current degree of metastability of the ambient medium is a difficult problem of great significance in practice.

Three basic stages of the assemblage evolution have commonly to be distinguished while dealing with assemblages which are not subject to coagulation and disintegration. They are (i) an initial stage of critical nucleus formation when the surrounding medium may be approximately regarded as one being not affected by the nuclei and so preserving its original properties, (ii) an intermediate stage during which both particle growth and emergence of new nuclei under a condition of permanently reducing metastability are equally important, and (iii) a final stage at which the latter processes may be safely ignored because of the critical nucleus volume becoming rather large, and the whole of evolution is caused by the growth of larger particles at the expense of the dissolution of smaller ones.

The first stage was successively treated by many researchers, among whom Volmer and Zel’dovich should be named (for a review, see [1]). A modern theory of the third stage stems from the pioneering paper by Lifshitz and Slyosov [2]. On the contrary, investigation of the intermediate stage, that is responsible for the emanation of the main amount of a new phase from metastable surroundings, was met with serious obstacles until very recently. An effective method of approaching the problem and of getting its reliable solution in a tractable form has been suggested in [3] for molecular and in [4] for colloidal systems.
Among other inferences of [3, 4] there stands a conclusion that the density of the particle size distribution, that is reached in the very end of the second evolution stage and, thus, plays the role of an initial condition for the third stage, does not comply with the necessary requirements specific to the Lifshiz-Slyosov theory and so devalues it. Obviously, this questions the physical adequacy of the coalescence theory when applied to many real situations. This fact may well be disguised, however, by the occurrence of another mechanism of evolution due to coagulation of suspended particles as they approach each other, as a consequence of Brownian motion or for another reason, and, next, stick together. A similar role can be played by the particle disintegration. A time scale of coalescence or Ostwald ripening can often be proved to be of the same order of magnitude or even to noticeably exceed that of the coagulation. Therefore, one might expect the evolutionary process during the final stage to be less sensitive to initial conditions than it could be envisaged when accounting for coalescence alone. This means that a universal asymptotic size distribution is likely to be established at large times irrespectively of those conditions, but this distribution can well be different from that following from the conventional theory.

That such a situation frequently occurs in practice has been repeatedly acknowledged earlier and, at present, has become common knowledge. By way of putting forward rather an exotic example, we refer to rheocasting of metallic melts [5], when the effect of coagulation has been shown to lead to an asymptotic density of the size distribution that has happened to substantially deviate from that corresponding to the theory of coalescence with no allowance for coagulation.

It is worth noting right away that there is some confusion in relevant terminology (see [5]). Below we keep using the term « coalescence » for processes of the type of Ostwald ripening, as it was originally meant in [2], and understand « coagulation » (or « agglomeration ») as a process of particle merging.

Any attempt to modify the coalescence theory by allowing for particle coagulation requires, first of all, a new kinetic equation involving terms which are responsible for both mentioned mechanisms.

Formal representations of such an equation for the particle size distribution density have been suggested time and again in some articles and textbooks on the subject, examples of which are given by [6-8]. In spite of this, an effective method to solve the equation remains apparently absent, and either one of the above mechanisms is usually assumed to prevail or different approximate approaches to address the problem are brought into action.

The most popular and widespread approach of studying joint processes of coalescence and coagulation is seemingly presented by the method of particle distribution moments that has been applied to the problem in [8-14] and in some other papers. Its essence lies in reducing the kinetic equation to an infinite chain of simplified, mutually dependent, separate equations for the moments of different orders. The closure of the equations is commonly accomplished by means of the chain being arbitrarily cut off beginning with a certain integer order, whereas various moments of fractional orders are usually calculated with the help of a log-normal distribution that is postulated to hold good with no sufficient foundations.

Another approach has a bearing upon situations in which one of the mechanisms dominates, so that the conventional method of a small parameter can be employed to advantage. A representative example is to be found in [15] where a process of condensation that is only slightly influenced by coagulation has been successfully treated.

Neither of the approaches indicated can provide a reliable solution of the evolution problem for particulate assemblages whose particles grow at large times as a consequence of both coalescence and coagulation. To attack similar problems, some researchers have been proposing to look for self-similar solutions of the kinetic equation [16, 17]. That approach has
happened to meet with success when having been applied to coagulation processes unaffected by coalescence [18, 19], at it is proved by the experimental confirmation of the theoretical results in [19, 20]. As far as the present authors are aware of, however, it has never been used as regards processes of combined coagulation and coalescence.

In this paper, both mechanisms are simultaneously taken into account, and a long-time self-similar asymptotic is obtained, seemingly for the first time. For the sake of definiteness, we consider the aging of soles due to condensation from a supersaturated vapour, what does not limit in the least the applicability of the model being developed to systems of other physical origins.

The vapour supersaturation is presumed to be sufficiently small to prevent spontaneous formation of new critical nuclei of the liquid phase, since the critical nucleus volume, \( v_\ast \), is then large enough and comparable with the mean volume of droplets. If the volume \( v \) of a droplet exceeds \( v_\ast \), the droplet grows by condensation. Otherwise, it diminishes in size due to evaporation and eventually vanishes. When there is coagulation, a general picture becomes more complicated, since two small droplets which should normally evaporate are capable of merging to give rise to a larger droplet that would be bound, perhaps, to grow.

When introducing the droplet volume distribution density, \( f(t, v) \), normalized to the droplet number concentration \( n(t) \), and making use of familiar concepts [6], we arrive at a kinetic equation

\[
\frac{\partial f}{\partial t} + \frac{\partial (\varrho f)}{\partial v} = \frac{1}{2} \int_0^v A(w, v - w) f(t, w) f(t, v - w) \, dw - \int_0^\infty A(w, v) f(t, w) f(t, v) \, dw .
\]

(1)

Here \( A(v, w) \, dw \) denotes the frequency at which the droplets with volume between \( v \) and \( v + dv \) inside unit volume of the mixture coagulate with the droplets of volume within \((w, w + dw)\) and \( g = g(t, v) \) stands for an effective growth rate of a single droplet due to condensation-evaporation. Note that disintegration of the droplets is completely ignored to simplify equation (1).

To provide for a simple model example, we assume an equal coagulation rate for all the droplets irrespective of their volume. Then \( A(v, w) = A = \text{Cte} \). Further, we employ a well-known and widely used expression for the growth rate, that is,

\[
g(t, v) = \frac{dv}{dt} = \beta \left[ c(t) \frac{v^{1/3}}{\alpha} - 1 \right] , \quad c(t) = \frac{S(t) - S_\infty}{S_\infty} , \quad \beta = \frac{8 \pi \sigma D v' S_\infty}{kT} \quad \alpha = \frac{2(4 \pi/3)^{1/3} \sigma v'}{kT} .
\]

(2)

Here \( D \) and \( v' \) stand for the diffusivity and the molecular volume of a condensing substance in the vapour phase, respectively, \( \sigma \) is the surface tension coefficient and \( kT \) is the temperature in energy units. Quantity \( S(t) \) is understood as the gradually reducing volume concentration of the substance in the gaseous phase, \( S_\infty \) being its equilibrium value at a plane interface. This means that \( c(t) \) may be looked upon as a relative supersaturation. It is evident from equation (2) that the critical nucleus volume \( v_\ast = [\alpha/c(t)]^3 \) becomes progressively large as \( c(t) \) is approaching zero.

Complementary to the kinetic equation (1) is an equation that results from the balance law for the condensing substance, which is to be written out as follows:

\[
S(t) - S_\infty + \int_0^\infty v f(t, v) \, dv = Q = \text{Cte} .
\]

(3)
$Q$ playing the role of initial saturation if there were no droplets altogether.

Equations (1) and (3) must be supplemented with boundary and initial conditions, which may be taken in a traditional form.

$$f(0, v) = f_0(v), \quad S(0) = S_0 = Q - \int_0^{\infty} v f_0 \, dv + S_\infty, \quad f(t, \infty) = 0.$$  (4)

Thus we arrive at a highly nonlinear problem involving an integrodifferential equation, the solution of which is by no means a simple matter, and this ought not to be underestimated. Suffices it to say that a much easier problem that follows from the above one when dropping out the coagulation terms at all was a subject of an ingenious classical theory developed by Lifshitz and Slyosov.

In these circumstances, one can hardly hope to get a full solution of the problem even for the final evolution stage under consideration. It seems tempting, however, to look for a universal large-time asymptotic size distribution density resembling that calculated in [2]. As is often the case for quite different physical situations, asymptotics that are likely to be settled at sufficiently large times must be self-similar to be independent of initial conditions.

By applying a usual scaling method of the theory of dimensionality, we are able to set forth a solution that belongs to the indicated type as follows:

$$c(t) = \frac{K}{\tau^{1/3}}, \quad \tau = \frac{\beta t}{\alpha^3}, \quad f = \frac{K^3 \beta}{A \tau^2 \alpha^6} \phi(x), \quad \lambda = \frac{K^3 v}{\alpha^3 \tau}.$$  (5)

The parameter $K$ specifies the self similar solution. It cannot, however, be determined by considering the final self-similar stage alone, and thus must be supposed to be a preassigned quantity.

Substituting equation (5) into equations (1) and (2) gives an equation and normalizing condition

$$\frac{\partial \phi}{\partial x} = \frac{1}{x - K^3 (x^{1/3} - 1)} \left[ \left( \frac{K^3}{3 x^{2/3}} - 2 + \int_0^{\infty} \phi(y) \, dy \right) \phi - \frac{1}{2} \int_0^{x} \phi(y) \phi(x - y) \, dy \right], \quad (6)$$

$$\int_0^{\infty} x \phi(x) \, dx = \frac{K^3 A Q}{\beta} = R.$$  (7)

Solutions of equation (6) are distinguished by values of $R$ and $K$ which have to be regarded as some prescribed parameters. When $K \geq (27/4)^{1/3}$, equation (6) has no solution compatible with condition (7) because of divergence of the integral terms in the left-hand side of this equation. The divergence is caused by the denominator of the right-hand side of equation (6) going to zero at some point $x$ if $K \geq (27/4)^{1/3}$. This conclusion is to be drawn by closely following the same line of reasoning as in [2]. If $K < (27/4)^{1/3}$ and $x \rightarrow 1$ a function $2 \, b \, \exp(-bx)$ with constant $b$ can be proved to conform with both equation and condition (6) and may, thereby, be regarded as an appropriate explicit form of the wanted solution at large $x$. Note that a meaningful solution of a similar problem in the theory of coalescence [2] exists merely at $K$ strictly equalling $(27/4)^{1/3}$.

The last notion offers an opportunity to build up the whole self-similar solution by means of the following procedure. Let us choose certain values of $K$ and $b$ and set some sufficiently large $x = x_\infty$. Without loss of generality, we may assume $\phi(x) = 2 \, b \, \exp(-bx)$ at all $x > x_\infty$ and, next, find $\phi(x)$ everywhere within the range $0 < x < x_\infty$ numerically, with the help of the conventional iteration method. The result provides for calculation of the integral in the condition (6) and, thus, for defining $R$ as a function of $K$ and $b$. The last function can easily be reversed to yield $b$ as a function of the preassigned parameters, that is, of $K$ and $R$ (or $Q$).
Having the latter function at our disposal enables us to construct the desired solution at any \( K \) and \( R \) and to bring, in such a way, the matter of resolving the problem to completion.

The parameter \( b \) as a function of \( K \) at different \( R \) is shown in figure 1. The dimensionless distribution density at a fixed \( R \) and different \( K \) is plotted in figure 2. The smaller \( K \) (and the slower decrease in metastability), the steeper is the fall of \( \phi \) with \( x \). The presented curves substantially deviate from that resulting from the coalescence theory with no account for coagulation under similar conditions. The latter curve exists only at \( K = (27/4)^{1/3} \) what corresponds to the theory by Lifshitz and Slyosov [2], and the solution identically equals zero anywhere for \( x \geq 27/8 \). Thus the conventional theory of coalescence appears of not much use whenever discernable coagulation takes place.

By using scaling parameters introduced into equation (5) one can also get the dimensional distribution density. Representative curves \( f(t, v) \) at various moments are drawn in figure 3.

At last, we list useful formulae for the mean droplet radius and number concentration of the droplets. They read

\[
\langle r \rangle = \frac{\alpha}{K} \left( \frac{3 \tau}{4 \pi} \right)^{1/3} \int_0^\infty x^{1/3} \phi(x) \, dx \left( \int_0^\infty \phi(x) \, dx \right)^{-1},
\]

\[
n = \frac{\beta}{A \alpha^3 \tau} \int_0^\infty \phi(x) \, dx.
\]

![Fig. 1.](image1)

**Fig. 1.** — Dependence of \( b \) on \( K \) at different \( R \) shown by figures on the curves.

![Fig. 2.](image2)

**Fig. 2.** — Dimensionless size distribution density at \( R = 4 \) and \( K = 0.9, 1.2, 1.5 \) (curves 1-3, respectively); a dashed line corresponds to coalescence without coagulation.

![Fig. 3.](image3)

**Fig. 3.** — Distribution density at \( K = 1.2, R = 4 \). \( \alpha = 10^{-5} \) m, \( \beta = 10^{-13} \) m\(^3\)/s, \( A = 10^{-11} \) m\(^3\)/s, \( t = 1, 1.5, 2 \) s (figures on the curves).
Hence it follows that the mean radius grows as $t^{1/3}$ whereas the concentration is inversely proportional to $t$, as is the case for coalescence and Ostwald ripening processes without coagulation.

In a general case, replacing $A(v, w)$ with a constant and also using a simple representation of $g(t, v)$ given in equation (2) correspond to a rather crude approximation. The actual functions $A(v, w)$ and $g(t, v)$ characteristic of various processes are frequently determined empirically, by correlating experimental data. The former one is sometimes presented as a function of time, what is hardly anything more than a purely empirical action. Nonetheless, it can be used in practical calculations.

A comprehensive analysis of the final evolution stage under joint action of coalescence and coagulation at complicated $A(v, w)$ and $g(t, v)$ usually demands a very difficult problem to be solved. The task is, however, greatly simplified by the fact that almost any such problem possesses a self-similar solution, which appears to be only relevant. Then the formulation of a reduced problem, such as that stated by equation (6), becomes possible, and a number of conclusions can be drawn even without actually solving the problem.

To give an example, we return to the rheocasting process studied in [5], where it has been found that

$$g(t, v) = 4\pi r^2 \frac{dr}{dt} = 4\pi k_1 r^{2/3} \left( \frac{r}{r_*} - 1 \right),$$

(8)

$$A(v, w) = A(t) = \frac{\kappa}{r_*^{2/3} N(t)} \quad N(t) = \int_0^\infty f(v, t) dv$$

(9)

where \(\kappa, k_1\) are empirical kinetic coefficients and \(r_*(t)\) is to be understood as the critical nucleus radius.

By using again the theory of dimensionality and accounting for equations (8, 9) when dealing with equations (1) and (3), we get formulae

$$r_* = K_1 t^\gamma, \quad A = K_2 t^\delta \quad f(t, v) = \frac{K_3}{t^\rho} \quad u = \frac{K_4}{t^\nu}$$

(10)

\(K_j (j = 1, 2, 3, 4)\) being certain dimensional constants, and, further,

$$\gamma = 9/7, \quad \delta = 2/7, \quad \mu = 3/7, \quad \nu = 18/7,$$  

(11)

which provide for the proper scaling of the self-similar final stage of rheocasting process. Exponents (11) satisfy an evident identity, $\nu = \gamma + \delta + 1$, as they obviously have to do. There also follow new equations and condition for $\phi(u)$ which we are not going to write down here, in a preliminary publication on the subject, partly because of their complexity.

This notwithstanding, we can draw important inferences without solving such an equation. Really, the values of exponents that are listed in equation (11) enable us to conclude, in accordance with equations (8), (9), and (10), that the mean particle radius grows as $t^{3/7}$ and the number concentration decreases as $t^{-1}$, what are just the conclusions made on the basis of experiments of [5]. A more refined comparison with experimental data would require, of course, a lot of analytical and numerical calculations to be carried out and should comprise the subject of some future paper.

References

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