The perturbation theory for the set of self-similar asymptotics

in diffusion-controlled Ostwald ripening.

Telyatnik Rodion
statphys@narod.ru

Department of Statistical Physics, Faculty of Physics,
Saint-Petersburg State University, Russia

Abstract

Since the set of self-similar asymptotics in addition to Lifshitz-Slyozov's [2] and Wagner's [4] ones were found computationally and analytically [6] in the theory of Ostwald ripening, the problem of time corrections to these asymptotics raised and to this day it wasn't resolved properly and completely, as most of the discussions are around the definition of asymptotics themselves only out of classic Ostwald ripening model [3],[8],[9].

Considering the perturbation theory for the complete system of equations for the classic diffusion-controlled Ostwald ripening, we got first-order power corrections to the concentration of metastable phase, to the critical radius of drops, to their concentration, and we found explicit form of self-similar correcting distribution functions that have power decay to their asymptotics. Their normalization and scaling, which depends on experimental parameters, were obtained computationally. Limiting Lifshitz-Slyozov's case was represented individually and it got formal similarities with the work of Marqusee and Ross [10].

Introduction

Ostwald ripening (OR), first described by Wilhelm Ostwald in 1896 [1], is the process of competitive growth of new-phase clusters, when for the molecules energetically favorable to leave the small droplets, causing their dissolving, and to be transferred to the bigger ones (total surface energy reduces in such a way). This phenomenon play important role in stability of dispersion systems, precipitation hardening of alloys, formation of surface structures, and synthesis of nanoparticles. First significant mathematical analysis of OR was given by Lifshits and Slyozov (LS) in 1958 [2] for the case when diffusion transfer in mean field of metastable phase concentration plays main role in OR (non-mean field theory accounts intersections between diffusive fields around drops with finite volume fraction in the system [3]). By default assumption of infinite spectrum of cluster sizes (i.e. no maximal drop exists) LS obtained self-similar asymptotic of distribution function (DF) clusters on sizes. In 1961 Wagner did the same derivation for the case of interface-kinetics dominance [4], i.e. the ability of a drop to catch or to emit a molecule. The latter case, as distinct from the first one, corresponds to the system, where the free path of a molecule is well over cluster size (for certain estimates see [5]).

In the later 1990s the set of self-similar asymptotics (LS and Wagner's ones are the limiting cases for them) were found [6] without mentioned LS assumption. Certain asymptotic depends on the character of initial DF in the vicinity of the maximal drop [7], as it obviously affects critically on the behavior of OR, which finally forgets original distribution of small drops. Since then, there were many attempts to determine pre-eminence of LS asymptotic DF with its exponential tail among others asymptotics with power-like tails by means out of classic LS model by taking into account coagulation effect [8], or fluctuations [9], i.e. second order Becker-Döring-Zeldovich equation on DF in the theory of nucleation instead of first order continuity equation. These works can meet criticism only in that, how sensitive can be fluctuations for big enough drops to consider continuous variables and DFs. It also can be perverse to seek determination of initial DF (note: its mean value over systems) by fluctuations in a certain system while fluctuations shake DF with Poisson distribution in ensemble of systems [10].

The aim of this work is to build the perturbation theory by the example of diffusion-controlled OR and to find explicit first-order time corrections to any possible asymptotic of classic theory.

1. Basic formulas in the theory of OR

Let us introduce following non-dimensional variables:

$$\tau \equiv t / t_1 \ , \quad n(\tau) \equiv N(\tau t_1) / N_\infty \ , \quad a(\tau) \equiv R(\tau t_1) / R_c(t_1) \tag{1.1}$$

$$\text{Where} \quad t_1 \equiv \frac{\mathrm{v}_l}{N_\infty D}\left(\frac{2\sigma}{kT}\right)^2 \left(n_1 - 1\right)^{-3} \ , \quad n_1 \equiv n(1) \tag{1.2}$$

Here τ is the time in the ratio to the chosen moment t_1 at which we know in line with (1.2) vapor concentration $N(t)$ that we write in relation to N_∞ – asymptotical equilibrium vapor concentration above flat boundary of liquid phase. D is the diffusive constant, v_l is the molecular volume in liquid phase, σ is the surface tension coefficient, kT – Boltzmann constant multiplied on temperature (by the way we neglect thermal effects of condensation). Finally, $a(\tau)$ is the radius of a globular drop in respect to critical radius at mentioned moment. Critical radius depends on supersaturation and it is expressed by the asymptotical formula:

$$R_c(t) = \frac{2\mathrm{v}_l\sigma}{kT}\frac{N_\infty}{N(t)-N_\infty}\ ,\ a_c(\tau) = \frac{n_1-1}{n(\tau)-1} \underset{\tau\to+\infty}{\to} +\infty \qquad (1.3)$$

If a drop has size less than current critical magnitude, it diminishes until dissolution, what can be seen from the growth equation for a drop during diffusive OR:

$$\frac{da(\tau)}{d\tau} = \frac{1}{a(\tau)}\left(\frac{1}{a_c(\tau)} - \frac{1}{a(\tau)}\right) \qquad (1.4)$$

This is the only equation in which diffusive and interface-kinetics ORs differ, and t_1 was obtained from non-dimensionalizing (1.4). Derivation of these equations one can see in [5]. Next two expressions are written for DF $F(a,\tau)$:

$$\frac{\partial}{\partial\tau}F(a,\tau) = -\frac{\partial}{\partial a}\left(\frac{da}{d\tau}\cdot F(a,\tau)\right) \qquad (1.5)$$

We regard the continuity equation as we suppose non-fluctuating smooth change in time of DF. This equation on DF is non-linear as it depends through (1.4) and (1.3) on vapor concentration, which we constrain with permanent total mass of liquid and vapor in isolated system by balance equation:

$$n(\tau) + \int_0^\infty a^3 F(a,\tau)da = z\ ,\ z = const \qquad (1.6)$$

DF is normalized proportionally to the concentration of drops:

$$\int_0^\infty F(a,\tau)da = \frac{4\pi}{3}\frac{R_c^3(t_1)}{\mathrm{v}_l}n_{drops}(\tau)\ ,\ n_{drops}(\tau) \equiv \frac{N_{drops}(\tau t_1)}{N_\infty} \qquad (1.7)$$

Factual integration limits extend from relatively minimal drop to the maximal one at the current time. Expressions (1.3) – (1.6) represent the complete system of equations of OR, that can be resolved for all included variables, their asymptotics and corrections, at least computationally.

2. The set of self-similar asymptotics

LS get their solution for (1.5) in the terms of variable $u(\tau) = a(\tau) / a_c(\tau)$. We will use more convenient variable $v(\tau) = a(\tau) / a_m(\tau) \in (0,1]$ in the ratio to the maximal radius $a_m(\tau)$ among all drops. By analogy with LS, with the new variable we also introduce new DF, but with its explicit dependence on time:

$$P(v,\tau) \equiv a_m^4(\tau) F(v a_m(\tau), \tau) \tag{2.1}$$

With such DF balance equation (1.6) preserves nearly the same form:

$$n(\tau) + \int_0^1 v^3 P(v,\tau) dv = z \tag{2.2}$$

Anzats (2.1) will lead us on substituting (1.4) to (1.5) to the following equation:

$$\left.\begin{aligned} &\gamma a_m^3 v^3 \frac{\partial P(v,\tau)}{\partial \tau} + G(v \mid \gamma) v \frac{\partial P(v,\tau)}{\partial v} = H(v \mid \gamma) P(v,\tau) \\ &G(v \mid \gamma) \equiv -(1-v)(v+v_1+1)(v_1-v) \ , \quad v_1(\gamma) \equiv \left(\sqrt{1+4\gamma}-1\right)/2 \\ &H(v \mid \gamma) \equiv 4v^3 + (\gamma+1)v - 2\gamma \end{aligned}\right\} \tag{2.3}$$

Where the next expressions define the key variable $\gamma(\tau)$ and give useful relation on it which results from (1.4) for the growth of the maximal drop with the radius $a_m(\tau)$:

$$\frac{1}{\gamma(\tau)} \equiv a_m^2(\tau) \frac{da_m(\tau)}{d\tau} \ , \quad \frac{1}{\gamma(\tau)} = \frac{a_m(\tau)}{a_c(\tau)} - 1 \tag{2.4}$$

Normalization (1.7) of the rescaled DF and its finite asymptotic (limited by the balance equation) take the form:

$$K(\tau) \equiv \int_0^1 P(v,\tau) dv = \frac{4\pi R_c^3(t_0)}{3v_l} n_{drops}(\tau) a_m^3(\tau) \underset{\tau\to\infty}{\to} K_0 \tag{2.5}$$

It is evidently from the second relation in (2.4) that self-similarity requires constant γ, and the self-similar asymptotic solution can be written in the form:

$$P(v,\tau) \underset{\tau\to\infty}{\to} K_0 P_0(v \mid \gamma_0) \ , \quad \int_0^1 P_0(v \mid \gamma_0) dv = 1 \ ; \ \gamma(\tau) \underset{\tau\to\infty}{\to} \gamma_0 \tag{2.6}$$

Without time dependence eq. (2.3) becomes separable and it can be simply integrated by fractions. Result is:

$$\left.\begin{aligned} &P_0(v\,|\,\gamma_0)=\frac{3}{\gamma_0}v^2\left(1-v\right)^{\mu_0}\left(1+\frac{v}{1+v_1}\right)^{\lambda_0-\mu_0-6}\left(1-\frac{v}{v_1}\right)^{-\lambda_0},\ v_1\equiv v_1(\gamma_0)\\ &\mu(\alpha,\gamma_0)\equiv\frac{5-\gamma_0+3\alpha}{\gamma_0-2},\ \mu_0\equiv\mu(0,\gamma_0)\geq 0\Rightarrow\gamma_0\in(2,5]\\ &\lambda(\alpha,\gamma_0)\equiv 2+\alpha+\frac{1}{2}\left(2+\alpha+\mu(\alpha,\gamma_0)\right)\left(1+3\Big/\sqrt{1+4\gamma_0}\right),\ \lambda_0\equiv\lambda(0,\gamma_0)\end{aligned}\right\}\quad(2.7)$$

Parameter α is needed for further corrections. DF must be physically limited in $v=1$, hence $\mu_0\geq 0$, and the set of self-similar asymptotics is defined in the certain interval of $\gamma_0\in(2,5]$. Accurate passage to the limit $\gamma_0\to 2+$ in (2.7) (at that $\lambda_0\sim\mu_0\sim\left(v_1-1\right)^{-1}\sim 3\big/\left(\gamma_0-2\right)$ and $\lambda_0-\mu_0\to -11/3$) will give us due to exponent in $\lim\limits_{\gamma_0\to 2+}\left[\left(1-v\right)\big/\left(1-v/v_1\right)\right]^{\lambda_0}$ LS DF in our variable v:

$$P_0^{(LS)}(v)=\frac{3}{2}\cdot\frac{v^2}{\left(1+v/2\right)^{7/3}\left(1-v\right)^{11/3}}\exp\left(-\frac{v}{1-v}\right)\qquad(2.8)$$

3. The perturbation theory

To build the equation on the first-order corrections we need to exclude from the eq. (2.3) the asymptotics for $P(v,\tau)$, $\gamma(\tau)$, and $a_m(\tau)$. For latter the long-time behavior can be simply derived by integrating from the definition of γ in (2.4):

$$\frac{1}{\gamma_0}\underset{\tau\to\infty}{\simeq}a_m^2(\tau)\frac{da_m(\tau)}{d\tau}=\frac{da_m^3(\tau)}{3d\tau}$$

So, all necessary asymptotics with corrections look like:

$$n(\tau)=1+\delta n(\tau)\qquad(3.1)$$

$$\gamma(\tau)=\gamma_0+\delta\gamma(\tau)\qquad(3.2)$$

$$a_m(\tau)=\left(3\tau\big/\gamma_0\right)^{1/3}\left(1+\delta a_m(\tau)\right)\qquad(3.3)$$

$$P(v,\tau\,|\,\gamma)=K(\tau)\left[P_0(v\,|\,\gamma_0)+\delta P(v,\tau\,|\,\gamma)\right],\ \int_0^1\delta P(v,\tau\,|\,\gamma)dv=0\qquad(3.4)$$

Correction to DF obviously should be normalized to zero. Also it can be shown from (2.5) and (3.3) that normalization can be replaced by its asymptotic value in first-order accuracy, which can be found with the help of balance equation (2.2) in main (asymptotic) order upon substituting (3.1) and (3.4) to it:

$$K_0(z,\gamma_0)=\left(z-1\right)\left(\int_0^1 v^3P_0(v\,|\,\gamma_0)dv\right)^{-1},\ K(\tau)=K_0+O\left(\left(\delta a_m(\tau)\right)^2\right)\qquad(3.5)$$

In next order balance equation connects corrections to $n(\tau)$ and DF:

$$\delta n(\tau \mid \gamma) = -K_0 \int_0^1 v^3 \delta P(v, \tau \mid \gamma) dv \qquad (3.6)$$

Connection of corrections to $a_m(\tau)$ and $\gamma(\tau)$ is derived from definition (2.4):

$$\delta\gamma(\tau) = -3\gamma_0 \left(\delta a_m(\tau) + \tau \frac{d\delta a_m(\tau)}{d\tau} \right) \qquad (3.7)$$

Substituting (3.3) and (3.2) with (3.7) in the second relation in (2.4) we will get expression for critical radius with its correction:

$$a_c(\tau) = \frac{\gamma_0}{1+\gamma_0} \left(\frac{3}{\gamma_0} \tau \right)^{1/3} \left(1 + \frac{\delta\gamma(\tau)}{\gamma_0 (1+\gamma_0)} + \delta a_m(\tau) \right) \qquad (3.8)$$

Its asymptotic is enough to get correction to vapor concentration from (1.3):

$$\delta n(\tau) = (n_1 - 1) \frac{1+\gamma_0}{\gamma_0} \left(\frac{3}{\gamma_0} \tau \right)^{-1/3} \qquad (3.9)$$

From (3.9) and (3.6) one can see that $\delta P(v, \tau \mid \gamma) \sim \delta n(\tau) \sim \tau^{-1/3}$ in main order for isolated system. But for open system with arbitrary rate of additional mass transfer when $z = z(\tau)$ in (2.2) such conclusion can't be made relying only on balance equation. General power law behavior for correction to asymptotical self-similar DF (if it exists in certain open system) is derived from equation on DF itself. Substituting (3.2), (3.3), (3.4) to (2.3), excluding asymptotical terms and eliminating high-order corrections we will get:

$$3v^3 \tau \frac{\partial \delta P(v,\tau)}{\partial \tau} = H(v \mid \gamma_0) \delta P(v,\tau) - G(v \mid \gamma_0) v \frac{\partial \delta P(v,\tau)}{\partial v} + \left[(v-2) P_0(v) + (1-v) v \frac{dP_0(v)}{dv} \right] \delta\gamma(\tau) \qquad (3.10)$$

It can be clearly seen that any power-time behavior (as well as power series) of both $\delta P(v, \tau)$ and $\delta\gamma(\tau)$ cancels time dependencies leading to self-similarity:

$$\delta P(\tau, v) = P_1(v) \tau^{-\alpha} \ , \ \delta\gamma(\tau) = \gamma_1 \tau^{-\alpha} \ , \ \alpha = const \ , \ \gamma_1 = const \qquad (3.11)$$

This general power law can be proven strongly relative to $\delta P(v, \tau)$ in the terms of eigenvalues and eigenfunctions for differential operator in the right side of the eq. (3.10) and the logarithmic time $\ln \tau$, that converts the equation in nonhomogeneous differential (by times) equation. The same power law for $\delta\gamma(\tau)$ obviously follows from time independence of $P_1(v)$, on which we now have nonhomogeneous differential (by sizes) equation instead of (3.10):

$$\left.\begin{aligned} \frac{dP_1(v)}{dv} &= \frac{H(v \mid \gamma_0) - 3\alpha v^3}{v G(v \mid \gamma_0)} P_1(v) + \gamma_1 Q(v \mid \gamma_0) P_0(v \mid \gamma_0) \\ Q(v \mid \gamma_0) &\equiv \left(5v^2 - v - 1 \right) (1-v)^{-1} \left(v + v_1 + 1 \right)^{-2} \left(v_1 - v \right)^{-2} \end{aligned}\right\} \qquad (3.12)$$

Where $Q(v\,|\,\gamma_0)$ was obtained from (3.10) by expressing $dP_0(v\,|\,\gamma_0)\big/dv$ via $P_0(v\,|\,\gamma_0)$ immediately from the differential equation (2.3) for asymptotic DF. Solution of the homogeneous part of the eq. (3.12) can be directly integrated by fractions alike (2.3) with the solution like (2.7) with the same designations but with arbitrary normalization:

$$P_1^H(v\,|\,\alpha,\gamma_0) = v^2\left(1-v\right)^{\mu}\left(1+\frac{v}{1+v_1}\right)^{\lambda-\mu-6-3\alpha}\left(1-\frac{v}{v_1}\right)^{-\lambda} \tag{3.13}$$

Full solution of (3.12) can be expressed with $P_1^H(v)$ by resolvent formula with the constant of integration fulfilling normalization of the DF to zero as in (3.4):

$$P_1(v\,|\,\gamma_0,\gamma_1,\alpha) = \gamma_1 P_1^H(v)\left(\int_0^v \frac{Q(v')P_0(v')}{P_1^H(v')}dv' - \int_0^1 P_1^H(v'')\int_0^{v''}\frac{Q(v')P_0(v')}{P_1^H(v')}dv'dv''\right) \tag{3.14}$$

Second term in brackets represents mentioned constant and it can be found computationally. Corrective DF corresponds to asymptotic DF by certain γ_0. We know power $\alpha = 1/3$ from balance equation on corrections (3.6). Scale γ_1 also results from there upon substituting (3.9) and $\delta P(\tau,v) = P_1(v)\tau^{-1/3}$:

$$\int_0^1 v^3 P_1(v\,|\,\gamma_0,\gamma_1)dv = -\frac{n_1-1}{K_0(z,\gamma_0)}\cdot\frac{1+\gamma_0}{\gamma_0}\left(\frac{\gamma_0}{3}\right)^{1/3} \tag{3.15}$$

With normalization K_0 from (3.5) one can find $\gamma_1(\gamma_0,n_1,z)$ numerically if experimental data γ_0, n_1 and z are specified. Finally, placing $\delta\gamma(\tau) = \gamma_1\tau^{-1/3}$ to (3.7) and solving differential equation we can get first-order correction to maximal radius and therewith to the critical one from (3.8):

$$a_m(\tau) = \left(\frac{3}{\gamma_0}\tau\right)^{1/3}\left(1-\frac{\gamma_1}{2\gamma_0}\tau^{-1/3}\right) \tag{3.16}$$

$$a_c(\tau) = \frac{\gamma_0}{1+\gamma_0}\left(\frac{3}{\gamma_0}\tau\right)^{1/3}\left(1-\gamma_1\frac{\gamma_0-1}{2\gamma_0\left(1+\gamma_0\right)}\tau^{-1/3}\right) \tag{3.17}$$

It is the concentration of drops is usually measured on experiment, and from (2.5), (3.5) and (3.16) we have in main and first orders:

$$n_{drops}(\tau) = \frac{\mathrm{v}_l}{4\pi R_c^3(t_1)}K_0\gamma_0\tau^{-1}\left(1+\frac{3\gamma_1}{2\gamma_0}\tau^{-1/3}\right) \tag{3.18}$$

The same time power without factor in first order was obtained in [11].

4. Lifshits-Slyozov case

LS case corresponds to $\gamma_0 = 2$ in all previous expressions except those for DFs with the limit passage $\gamma_0 \to 2+$. To make correction to $P_0^{(LS)}(v)$ from (2.8) we must execute limit in (3.13), that has the same exponential form as $P_0^{(LS)}(v)$:

$$P_1^{H(LS)}(v \mid \alpha) \equiv P_1^H(v \mid \alpha, \gamma_0 \to 2+) = \frac{2}{3} P_0^{(LS)}(v) \left(1 + v/2\right)^{-4\alpha/3} \left(1 - v\right)^{-5\alpha/3} \quad (3.19)$$

Therewith $P_1^{(LS)}(v)$ takes the form (3.14) with $P_0(v) \to P_0^{(LS)}(v)$ and $P_1^H(v) \to P_1^{H(LS)}(v)$ that resembles correction DF obtained by Marqusee and Ross in [11], but such correction was rightly criticized by Kukushkin and Osipov (KO) in [12] because of non-uniform convergence at $v = 1$. Indeed, in the vicinity of maximal drop $P_0(v) \sim P_1(v) \sim (1-v)^{\mu_0}$ and $P_0(v) / P_1(v) \to const$ but $P_1^{(LS)}(v) / P_0^{(LS)}(v) \sim \left(1 - v\right)^{-2} \to +\infty$. That's because in (3.14) and (3.12) $Q(v \mid \gamma_0 \neq 2) \sim \left(1 - v\right)^{-1}$ but $Q(v \mid \gamma_0 = 2) \sim \left(1 - v\right)^{-3}$.
So KO infer that LS solution can't be asymptotical at all and in [12] they proposed special treatment of OR equations with another than γ key parameter that leads to another asymptotical DF with exponential tail. But it is confusing that KO DF causes inequality between critical size and average radius of drops, while this nonrandom asymptotical equality can be established apart from equation on DF [5] and can be obtained computationally even much earlier asymptotical stage [13].

On the back of this we should notice that LS derived their asymptotic and logarithmic time correction to their $\tilde{\gamma} \equiv \left(a_c^2(\tau) da_c(\tau) / d\tau\right)^{-1}$ only from the growth equation (1.4), which in our variables and designations takes the form:

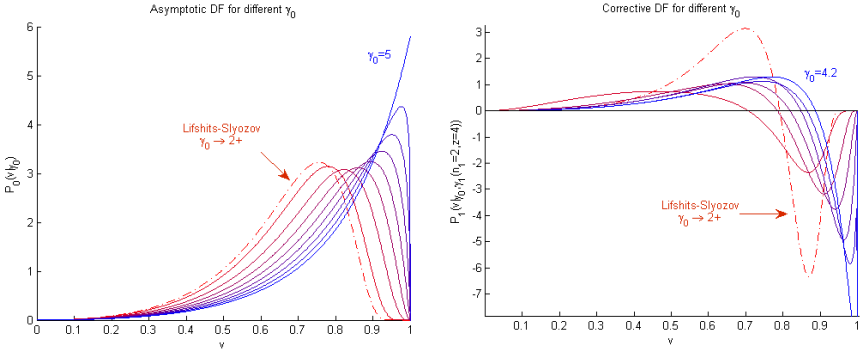
$$\frac{dv^3}{d\left(3 \ln a_m(\tau)\right)} = G(v \mid \gamma(\tau)) \quad (3.20)$$

LS considered infinite spectrum of drops sizes (i.e. no maximal drop exists and $v = 1$ LS called "locking point") and they argued that some drops occurred in the interval $v \in (1, v_1]$ will infinitely grow in view of positive sign of right side (4.2) thereby violating balance equation. So they chose specific asymptotic for gamma at which two roots (1 and v_1) of polynomial $G(v \mid \gamma_0)$ degenerate into one. The same logic LS iterated for correction to gamma. If we repeat their consideration of (4.2) in the vicinity of maximal drop for corrections to our gamma ignoring eq. (3.10) we also will obtain logarithmic law instead of powerlike $\gamma(\tau) = 2 + \gamma_1(\gamma_0 = 2, n_1, z)\tau^{-1/3}$:

$$\gamma(\tau) = 2 - 3/\ln\tau \qquad (3.21)$$

Which one behavior of gamma we should accept? At least it is doubtful that time correction (4.3) can be independent from non-self-similar DF (as nonlinear value can't evolve apart from DF) with its scale determined by the size of a system, while our consideration accounts DF with its normalization and balance equation in explicit form, but our treatment indeed isn't uniformly applicable for LS case, as it was stressed above.

Figures



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