

From Becker-Döring to Lifshitz-Slyozov: deriving the non-local boundary condition of a non-linear transport equation

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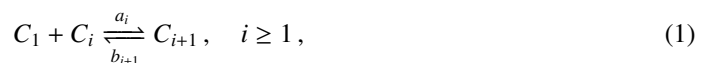
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Abstract.

We investigate the connection between two classical models of phase transition phenomena, the (discrete size, Markov chain or infinite set of ODE) Becker-Döring equations and the (continuous size, PDE) Lifshitz-Slyozov equation. Contrary to previous studies, we use a weak topology that includes the boundary of the state space, allowing us to rigorously derive a boundary value for the Lifshitz-Slyozov model. This boundary condition depends on a particular scaling and is the result of a separation of time scales.

1 Introduction

We address the link between two models of coagulation-fragmentation describing different stages of cluster growth. The Becker-Döring (BD) model [1] represents the microscopic stages, and describes the size repartition of clusters (or aggregates) using a discrete structure variable $i \in \mathbb{N}^*$, according to the set of chemical reactions



where C_i stands for the clusters consisting of i particles and C_1 the free particles. Here, the coefficients $a_i > 0$ and $b_{i+1} > 0$ denote respectively the rates of aggregation and fragmentation.

In the limit of a large number of particles, the time evolution of the concentration of clusters subject to the set of chemical reactions (1) is given by the solution of an infinite system of ordinary differential equations. Namely, the deterministic BD model is given, for all $t \geq 0$, by

$$\begin{cases} \frac{d}{dt} C_1(t) &= -2j_1(t) - \sum_{i \geq 2} j_i(t), \\ \frac{d}{dt} C_i(t) &= j_{i-1}(t) - j_i(t), \quad i \geq 2, \end{cases} \quad (2)$$

with

$$j_i(t) = a_i C_1(t) C_i(t) - b_{i+1} C_{i+1}(t), \quad i \geq 1, \quad (3)$$

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where the restriction $a_i = O(i)$ is imposed to ensure global existence, see [2, 7]. The initial condition is subjected to $(C_i(0))_{i \geq 1} \subset \mathbb{R}^+$, and $\sum_{i \geq 1} iC_i(0) =: M < \infty$.

Alternatively, considering a finite number of particles, such model (1) may be interpreted mathematically as a Markov Chain on a finite subset of a lattice. Denoting by Y_i^+ (resp. Y_i^-) the standard Poisson process associated to the aggregation (resp. fragmentation) reaction of clusters of size $i \geq 1$ (resp. $i \geq 2$), the stochastic version of the BD model is given for $t \geq 0$ by

$$\begin{cases} C_1(t) &= C_1(0) - 2J_1(t) - \sum_{i \geq 2} J_i(t), \\ C_i(t) &= C_i(0) + J_{i-1}(t) - J_i(t), \quad i \geq 2, \end{cases} \quad (4)$$

with

$$J_i(t) = Y_i^+ \left(\int_0^t a_i C_1(s) (C_i(s) - \delta_i^1) ds \right) - Y_{i+1}^- \left(\int_0^t b_{i+1} C_{i+1}(s) ds \right), \quad i \geq 1, \quad (5)$$

where $\delta_i^1 = 1$ if $i = 1$ and $\delta_i^1 = 0$ if $i \geq 2$. The initial condition is subjected to $(C_i(0))_{i \geq 1} \subset \mathbb{N}$, and $\sum_{i \geq 1} iC_i(0) =: M < \infty$.

The second model is the Lifshitz-Slyozov (LS) model [3, 6, 8], and describes the cluster growth at a macroscopic scale. The size of the clusters are represented by a continuously varying variable $x > 0$. If $f(t, x)$ denotes the size distribution function, the LS model is given by

$$\begin{aligned} \partial_t f(t, x) + \partial_x [(a(x)u(t) - b(x))f(t, x)] &= 0, \quad t \geq 0, \quad x > 0, \\ u(t) + \int_0^\infty x f(t, x) &= \text{const.} =: m, \quad t \geq 0, \end{aligned} \quad (6)$$

where $a(x)$ and $b(x)$ are respectively the aggregation and fragmentation rates. Note that in such a model, $u(t)$ plays the *analog* role of the concentration of free particles $C_1(t)$ in the BD model. If $a(x)u(t) - b(x) > 0$ near $x = 0$, such formulation lacks a proper *boundary condition* at $x = 0$. It is the goal of this work to derive such boundary condition, using a rescaling of either Eq. (2) or Eq. (4).

2 Rescaling and results

2.1 Rescaled equations

The classical approach to operate a scaling is to write the equations in a dimensionless form. We follow [9] and introduce the following characteristic values:

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|---|--|--|
| <ul style="list-style-type: none"> • \bar{T} : characteristic time, • \bar{C}_1 : characteristic value for C_1, • \bar{C} : characteristic value for C_i, for $i \geq 2$, • \bar{M}_c : characteristic value for M, | | <ul style="list-style-type: none"> • \bar{A}_1 : characteristic value for a_1, • \bar{B}_2 : characteristic value for b_2, • \bar{A} : characteristic value for a_i, $i \geq 2$, • \bar{B} : characteristic value for b_i, $i \geq 3$. |
|---|--|--|

We introduce the scaling parameter $\varepsilon > 0$ and assume the following choices of relation:

$$\bar{C}/\bar{C}_1 = \varepsilon^2, \quad \bar{A}\bar{C}_1\bar{T} = \bar{B}\bar{T} = \frac{1}{\varepsilon}, \quad \bar{M}_c/\bar{C}_1 = 1, \quad \bar{A}_1 = \varepsilon^2\bar{A}, \quad \bar{B}_2 = \varepsilon^\eta\bar{B}, \quad (7)$$

with $\eta \in [0, 1]$ to be chosen later. Thus, we define the dimensionless quantities

$$\tau = t/\bar{T}, \quad u^\varepsilon(\tau) = C_1(\tau\bar{T})/\bar{C}_1, \quad c_i^\varepsilon(\tau) = C_i(\tau\bar{T})/\bar{C}, \quad m^\varepsilon = M/\bar{M}_c, \quad (8)$$

and (we use different letters at the boundary to emphasize this point)

$$\alpha^\varepsilon := a_1/\bar{A}_1, \quad \beta^\varepsilon := b_2/\bar{B}_2, \quad \text{and } a_i^\varepsilon = a_i/\bar{A}, \quad b_{i+1}^\varepsilon = b_{i+1}/\bar{B}, \quad i \geq 2. \quad (9)$$

We define the macroscopic reaction rates and fluxes

$$a^\varepsilon(x) := \sum_{i \geq 2} a_i^\varepsilon \mathbf{1}_{\Lambda_i^\varepsilon}(x), \quad b^\varepsilon(x) := \sum_{i \geq 3} b_i^\varepsilon \mathbf{1}_{\Lambda_i^\varepsilon}(x), \quad \text{and } j^\varepsilon(\tau, x) = \sum_{i \geq 2} (a_i^\varepsilon u^\varepsilon(\tau) - b_{i+1}^\varepsilon) \mathbf{1}_{\Lambda_i^\varepsilon}(x),$$

where $\Lambda_i^\varepsilon = [(i - 1/2)\varepsilon, (i + 1/2)\varepsilon]$. The clusters quantities given by (2) (resp. by (4)) are now represented by a continuously varying variable $x > 0$, and we let, for all $t \geq 0$ and all $\varepsilon > 0$,

$$f^\varepsilon(\tau, x) = \sum_{i \geq 2} c_i^\varepsilon(\tau) \mathbf{1}_{\Lambda_i^\varepsilon}(x), \quad x \geq 0. \quad (10)$$

Hence, using relations (7)-(8)-(9) the deterministic BD system (2)-(3) reads, for all $\tau \geq 0$,

$$\begin{cases} \frac{d}{d\tau} u^\varepsilon &= -\varepsilon j_1^\varepsilon - \varepsilon \sum_{i \geq 1} j_i^\varepsilon, \\ \frac{d}{d\tau} c_i^\varepsilon &= \frac{1}{\varepsilon} [j_{i-1}^\varepsilon - j_i^\varepsilon], \quad i \geq 2, \end{cases} \quad (11)$$

where the rescaled fluxes are defined by

$$j_1^\varepsilon = \alpha^\varepsilon (u^\varepsilon)^2 - \beta^\varepsilon \varepsilon^\eta c_2^\varepsilon, \quad \text{and } j_i^\varepsilon = a_i^\varepsilon u^\varepsilon c_i^\varepsilon - b_{i+1}^\varepsilon c_{i+1}^\varepsilon, \quad i \geq 2. \quad (12)$$

Then, for each $\varepsilon > 0$ and all $\varphi \in W_{loc}^{1,\infty}$ such that $\partial_x \varphi \in L^\infty$, we have from Eq. (11)-(12) for all $\tau \geq 0$

$$\begin{aligned} \int_0^{+\infty} f^\varepsilon(\tau, x) \varphi(x) dx &= \int_0^{+\infty} f^{in,\varepsilon}(x) \varphi(x) dx + \int_0^\tau j_1^\varepsilon(s) \frac{1}{\varepsilon} \int_{\Lambda_2^\varepsilon} \varphi(x) dx ds \\ &\quad + \int_0^\tau \int_0^{+\infty} [a^\varepsilon(x) u^\varepsilon(s) f^\varepsilon(s, x) \Delta_\varepsilon \varphi(x) - b^\varepsilon(x) f^\varepsilon(s, x) \Delta_{-\varepsilon} \varphi(x)] dx ds, \end{aligned} \quad (13)$$

with $\Delta_h \varphi(x) = (\varphi(x+h) - \varphi(x))/h$ for $h \in \mathbb{R}$ and $u^\varepsilon(\tau) + \int_0^\infty x f^\varepsilon(\tau, x) dx = m^\varepsilon$.

Similarly, using additionally $\bar{C} = 1$, with relations (7)-(8)-(9) the stochastic BD system (4)-(5) reads

$$\begin{cases} u^\varepsilon(\tau) &= u^\varepsilon(0) - 2\varepsilon^2 J_1^\varepsilon(\tau) + \sum_{i \geq 2} \varepsilon^2 J_i^\varepsilon(\tau), \\ c_i^\varepsilon(\tau) &= c_i^\varepsilon(0) + J_{i-1}^\varepsilon(\tau) - J_i^\varepsilon(\tau), \quad i \geq 2, \end{cases} \quad (14)$$

with the rescaled flux

$$\begin{aligned} J_1^\varepsilon(\tau) &= Y_1^+ \left(\int_0^\tau \varepsilon^{-1} \alpha^\varepsilon u^\varepsilon(s) (u^\varepsilon(s) - \varepsilon^2) ds \right) - Y_2^- \left(\int_0^\tau \varepsilon^{-1} \beta^\varepsilon \varepsilon^\eta c_2^\varepsilon(s) ds \right) \\ J_i^\varepsilon(\tau) &= Y_i^+ \left(\int_0^\tau \varepsilon^{-1} a_i^\varepsilon u^\varepsilon(s) c_i^\varepsilon(s) ds \right) - Y_{i+1}^- \left(\int_0^\tau \varepsilon^{-1} b_{i+1}^\varepsilon c_{i+1}^\varepsilon(s) ds \right), \quad i \geq 2. \end{aligned} \quad (15)$$

Then, from Eq. (14)-(15), we obtain the stochastic infinitesimal generator of f^ε constructed by Eq. (10),

$$\begin{aligned} \mathcal{L}^\varepsilon \psi(f) &= \frac{\psi(f + \mathbf{1}_{\Lambda_2^\varepsilon}) - \psi(f)}{\varepsilon} \alpha^\varepsilon u^\varepsilon (u^\varepsilon - \varepsilon^2) + \frac{\psi(f - \mathbf{1}_{\Lambda_2^\varepsilon}) - \psi(f)}{\varepsilon} \beta^\varepsilon \varepsilon^\eta c_2^\varepsilon \\ &\quad + \sum_{i \geq 2} \frac{\psi(f + \mathbf{1}_{\Lambda_{i+1}^\varepsilon} - \mathbf{1}_{\Lambda_i^\varepsilon}) - \psi(f)}{\varepsilon} a_i^\varepsilon u^\varepsilon c_i^\varepsilon + \sum_{i \geq 3} \frac{\psi(f - \mathbf{1}_{\Lambda_i^\varepsilon} + \mathbf{1}_{\Lambda_{i-1}^\varepsilon}) - \psi(f)}{\varepsilon} b_i^\varepsilon c_i^\varepsilon, \end{aligned} \quad (16)$$

where $c_i^\varepsilon = \varepsilon^{-1} \int_{\Lambda_\varepsilon^i} f(t, x) dx$, $i \geq 2$, and $u^\varepsilon = m^\varepsilon - \int x f(t, x)$. In particular, with $\psi(f) = \langle f, \varphi \rangle$ and $\varphi \in C_b$, we obtain an L^2 -martingale given by

$$\begin{aligned} \mathcal{M}^{\varepsilon, \tau, \varphi} := & \int_0^{+\infty} f^\varepsilon(\tau, x) \varphi(x) dx - \int_0^{+\infty} f^{in, \varepsilon}(x) \varphi(x) dx \\ & - \int_0^\tau [a^\varepsilon u^\varepsilon(s)(u^\varepsilon(s) - \varepsilon^2) - \beta^\varepsilon \varepsilon^\eta c_2^\varepsilon(s)] \frac{1}{\varepsilon} \int_{\Lambda_2^\varepsilon} \varphi(x) dx ds \\ & - \int_0^\tau \int_0^{+\infty} [a^\varepsilon(x) u^\varepsilon(s) f^\varepsilon(s, x) \Delta_\varepsilon \varphi(x) - b^\varepsilon(x) f^\varepsilon(s, x) \Delta_{-\varepsilon} \varphi(x)] dx ds. \end{aligned}$$

2.2 Results

To obtain the convergence of $\{f^\varepsilon\}$, we use the measure space $\mathcal{X} := \{\nu \in \mathcal{M}_f(\mathbb{R}^+) : \int_0^\infty x \nu(dx) < +\infty\}$, equipped with the weak topology, that is $\{f^\varepsilon(x) dx\}$ converges to μ in \mathcal{X} if

$$\int_0^\infty (1+x) \varphi(x) f^\varepsilon(x) dx \rightarrow \int_0^\infty (1+x) \varphi(x) \mu(dx), \quad \forall \varphi \in C_b([0, +\infty)).$$

We assume standard convergence properties of the reactions rates $\alpha^\varepsilon, \beta^\varepsilon, a^\varepsilon(\cdot)$ and $b^\varepsilon(\cdot)$ towards (resp.) $\alpha, \beta, a(\cdot)$ and $b(\cdot)$, together with convergence of the initial condition u^ε and $f^{in, \varepsilon}(\cdot)$ towards (resp.) u^{in} and $\mu^{in}(\cdot)$. In order to derive the boundary condition, we need to know precisely the behavior of the rate functions near 0. For that, we suppose there exist $r_a, r_b \in [0, 1]$, and $\bar{a}, \bar{b} > 0$ such that

$$\begin{array}{l|l} 0 \leq r_a < 1, & r_a \leq r_b, \\ a(x) \sim_{0^+} \bar{a} x^{r_a}, & b(x) \sim_{0^+} \bar{b} x^{r_b}, \\ a^\varepsilon(\varepsilon i) = a(\varepsilon i) + o((\varepsilon i)^{r_a}), \quad i \geq 2, & b^\varepsilon(\varepsilon i) = b(\varepsilon i) + o((\varepsilon i)^{r_b}), \quad i \geq 3. \end{array}$$

where o is the Landau notation in $\varepsilon \rightarrow 0^+$ (independent on i). We also define the critical quantity

$$\rho := \lim_{x \rightarrow 0^+} \frac{b(x)}{a(x)} = \lim_{x \rightarrow 0^+} \frac{\bar{b}}{\bar{a}} x^{r_b - r_a} \in [0, +\infty).$$

Under reasonable assumptions on the macroscopic reaction rates, we are able to prove (see [4]) compactness property on f^ε in \mathcal{X} (for both the deterministic Eq. (13) and the stochastic Eq. (16)) Then, for any convergent subsequence, we prove that the candidate limit $\mu \in C([0, T]; \mathcal{X})$ and $u \in C([0, T])$ satisfy, for all $\varphi \in C_c^1(0, +\infty)$ and $t \geq 0$

$$\begin{aligned} \int_0^\infty \varphi(x) \mu(t, dx) &= \int_0^\infty \varphi(x) \mu^{in}(dx) + \int_0^t \int_0^\infty \varphi'(x) (a(x) u(s) - b(x)) \mu(t, dx) ds, \\ u(t) + \int_0^\infty x \mu(t, dx) &= m. \end{aligned} \tag{17}$$

Note that Eq. (17) is formally the weak form of Eq. (6). Moreover, for any $T > 0$ such that the limit satisfies $\inf_{t \in [0, T]} u(t) > \rho$, then for all $\varphi \in C_b^1([0, +\infty))$ and $t \geq 0$

$$\langle \mu(t), \varphi \rangle = \langle \mu^{in}, \varphi \rangle + \int_0^t \int_0^\infty \varphi'(x) (a(x) u(s) - b(x)) \mu(t, dx) ds + \varphi(0) \int_0^t N(s) ds. \tag{18}$$

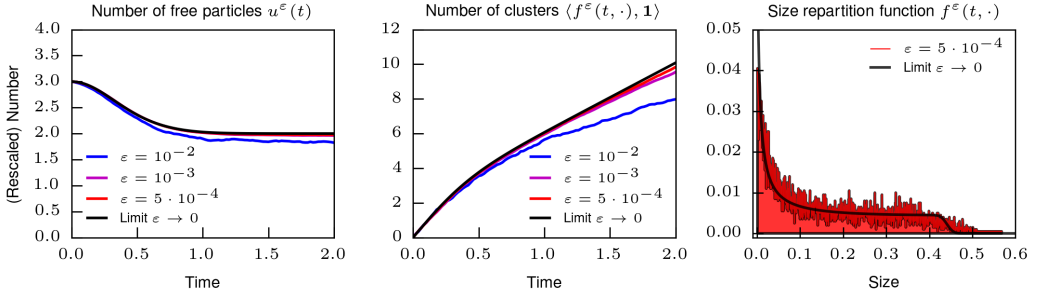


Figure 1. Agreement between numerical simulations and our limit theorem. We plot the time evolution of the (rescaled) number of free particles $u^\varepsilon(t)$ (left) and the total (rescaled) number of clusters $\langle f^\varepsilon(t, \cdot), \mathbf{1} \rangle$ (middle) for different ε (see legend), together with the deterministic solution (in black) of the moment equations obtained from the weak form of the LS equation (18) with respectively $\varphi = x$ and $\varphi = 1$. Right, we plot one snapshot at time $t = 1$ of the size distribution function $f^\varepsilon(t, \cdot)$ for $\varepsilon = 5 \cdot 10^{-4}$, together with the numerical solution of the LS equation (standard upwind scheme). We used the scaling given in Section 2.1 with constant rate coefficients $a^\varepsilon(x) \equiv 1$ and $b^\varepsilon(x) \equiv 2$, $\alpha^\varepsilon = 1$, and $\beta^\varepsilon = 1$, under incoming characteristics, i.e. $u(0) = m = 3 > \rho = \frac{b}{a} = 2$.

with for all $t \in [0, T]$

$$N(t) = \begin{cases} \alpha u(s)^2 & \text{if } \eta > r_a \\ \alpha u(s)^2 \frac{2^\eta u(s)}{2^\eta u(s) + \beta} & \text{if } \eta = r_a < r_b \\ \alpha u(s)^2 \frac{\bar{a}u(s) - \bar{b}}{\bar{a}u(s) - \bar{b} + \beta/2^\eta} & \text{if } \eta = r_a = r_b \\ 0 & \text{if } \eta < r_a < r_b \end{cases} \quad (19)$$

Thus the precise expression of the boundary condition Eq. (19) is dependent on the behavior of the rate functions near 0 and on the scaling factor η , that measures the relative speed of the fragmentation rate for $i = 2$ with the fragmentation rates for $i > 2$ (equal to r_b for the latter). The case $\eta = 1 > r_a$ was treated for the stochastic Eq. (16) in [4] and all cases for the deterministic Eq. (13) in [5].

3 Illustration and Discussion

We illustrate our theoretical results with the help of a numerical simulation, see Figure 1. We show the good agreement between the rescaled solution of the stochastic BD system (14) and the limit given by Eq. (18). The importance of deriving such results is both numerical, in order to design fast numerical scheme to approximate large discrete system, and theoretical, to derive steady-state and time-dependent properties of the original discrete system from a (simpler) continuous one [10, 11]. In our scaling, each cluster of size initially $i \geq 2$ is seen as a cluster of size roughly $i\varepsilon \in \mathbb{R}_+$, and our scaling consists in an acceleration of the fluxes (by $1/\varepsilon$) in Eq. (11) (resp. Eq. (14)) so that it can reach an “infinite” size $i = x/\varepsilon$ in finite time. This requires a large amount of free particles, of order $1/\varepsilon^2$ compared to the amount of clusters. The first aggregation rate a_1 has been rescaled differently for the others for $i \geq 2$. This is due to the particular role played by the free particles in the BD model. Indeed, since we have assumed a large excess of free particles compared to the number of clusters (to

form large ones), to keep such properties through time, one has to “slow down” the first nucleation rate a_1 , that transform free particles into clusters (of size 2). If this is not satisfied, we hypothesize that the pool of free particles would deplete, leading to a different version of the LS, namely the Lifshitz-Slyozov-Wagner model (work in progress, see also [7]).

From those previous work [7, 9], the originality of our work [4] resides in being able to derive the boundary condition of the limit equation. Such boundary condition is needed when the characteristics of the transport equation are incoming (*i.e.* the small clusters tend to grow). This result was obtained as an averaging result. In order to form large clusters, we have to accelerate the fluxes (by $1/\varepsilon$). Then, each individual size, and *a fortiori* the minimal size $i = 2$, evolves in a fast time scale. By proving a quasi steady-state result, we were able to prove that each discrete size tend to equilibrate to a value given by the stationary state of an auxiliary system, very similar to the original deterministic BD model (but in a linear version).

Finally, second order approximation and large deviation phenomena of the stochastic discrete BD system (14) were observed numerically [10]. In particular, when the formation of large cluster is (asymptotically) very unlikely, the latter appears as a large deviation from the mean-field limit and gives a suitable framework to describe phase transition phenomena, as *inherent infrequent stochastic processes*, in contrast to classical nucleation theory. The precise quantification is left for future work.

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