SOME RECENT RESULTS ON THE KINETIC THEORY OF PHASE TRANSITIONS

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Abstract. This paper gives a summary of our recent work on the Becker-Döring (BD) and Lifshitz-Slyozov (LS) models. The main issues addressed are existence, uniqueness and large time behaviour for the LS system, and its connection with the BD system. More precisely, we show how the BD system may be rescaled so as to yield the LS system as a first order approximation. Finally by carrying the expansion to second order, we propose a diffusive correction to the classical LS system, which has the form of a Focker-Planck equation.

Key words. Phase transitions, Lifshitz-Slyozov equations, Becker-Döring equations, Integro-differential equations

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1. Introduction and physical background. This paper presents an account of our recent work on some aspects of the kinetic theory of phase transitions. The simplest way to introduce the physical situation considered here is perhaps to recall the Becker-Döring picture [2]. In this setting one considers a population of grains (or *clusters*) which are made up of a certain number of particles (or *monomers*), closely packed together. The grains are supposed to be immersed in a bath of monomers, with which they interact by gaining or shedding particles. These two elementary reactions are called "coagulation" (or agglomeration) and "fragmentation" respectively. Depending on the relative importance of these two mechanisms, the average cluster size may increase or decrease. If one thinks of sufficiently large clusters as a new phase emerging from the original one, then this simple physical picture has the potential to generate a phase transition.

Depending on the mass transfer mechanism between clusters and monomers, and whether the size of the clusters is considered as a discrete or continuous variable, this physical picture gives rise to a variety of mathematical models. Here we will restrict ourselves to two well-known cases, the Becker-Döring model, and the Lifshitz-Slyozov model. The mathematical questions addressed here revolve around three issues: well-posedness, large-time behaviour, and rescaling. These form the contents of the following three sections.

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First of all let us detail further the physical background of the following Lifshitz-Slyozov equation

$$
\left\{
\begin{array}{l}
\partial_t f(t,x) + \partial_x (V(t,x) f(t,x)) = 0 \ \text{ in } \mathbb{R}_t^+ \times \mathbb{R}_x^+ ,\\
V(t,x) = a(x)c(t) - b(x),\\
c(t) + \displaystyle\int_0^\infty x f(t,x)\, dx = \rho > 0,\\
f_{|t=0} = f_0 \ \text{ in } \mathbb{R}_x^+, \qquad c_{|t=0} = c_0.
\end{array}
\right. \tag{1.1}
$$

This equation has been introduced by LIFSHITZ-SLYOZOV [17] in 1961 and it is intended to describe the evolution of some dilute solutions and the formation of clusters. The dynamics is governed by addition to or removal from the clusters of single molecules, or monomers. Hence, the unknowns $f(t,x) \geq 0$ and $c(t) \geq 0$ are the density of aggregates having at time t the size $x \geq 0$, and the monomers concentration, respectively. Accordingly, the third relation in (1.1) can be interpreted as the conservation of the total mass ρ within the solution: the sum of the mass of the aggegates and the mass of the monomers remains constant. The coefficients $a, b \geq 0$ are interpreted as rates at which these reactions occur and $V = \frac{dX}{dt}$ represents the rate of growth of the cluster of size x. More precisely, if ones considers a cluster of size x in a bath of monomers with concentration $c(t)$, the growth process depends on the ratio between $c(t)$ and the equilibrium concentration $c_e(x)$ at the boundary of the cluster: if $c(t) < c_e(x)$, the cluster losses molecules and shrinks, if $c(t) > c_e(x)$, it gains monomers and expands. The equilibrium concentration, for instance given by the Gibbs-Thomson law, is a decreasing function of the size, which leads to the fact that large grains grow at the price of shriking of the small ones, a phenomenom known as the Ostwald ripening. The precise expression of the kinetic coefficients a, b depends on the details of this mass transfer mechanism (e.g. assuming it to be diffusion-limited, or surface-attached, or other...). Here we restrict to a phenomenological level, in which the non negative coefficients $a(x), b(x)$ are given. In the seminal paper [17], it is assumed that the growth process is driven by diffusion mechanism which yields

$$
a(x) = 3x^{1/3}, \qquad b(x) = 3. \tag{1.2}
$$

For further details we refer to the recent review of SAGALOVICH-SLYOZOV [21] and to the classical reference of LIFSHITZ-PITAEVSKI [16]. Note also that we naturally have, in view of the physical mechanism described below,

$$
a(0)\rho - b(0) \leq 0, \tag{1.3}
$$

so that (1.1) does not need boundary condition at $x = 0$ (since the characteristics, which will be defined precisely below, are always outgoing).

The paper is organized as follows. First, we show that the problem (1.1) is well-posed for a wide class of initial data and coefficients. Section

3 is devoted to some remarks on the asymptotic behaviour of the solution. In Section 4, we describe some connections to discrete models. We shall only highlight the main results and sketch the proofs, referring for detailed versions to [4], [6]-[10],[14].

2. Some existence results. Let us give the following existence-uniqueness statement concerning the system (1.1), when dealing with regular coefficients, as discussed in [6].

THEOREM 2.1. *[6] Assume that a, b are C^1 functions on $[0, +\infty[$ satisfying*

$$\left\{ \begin{array}{l} a(x) \geq 0, \qquad b(x) > 0, \\ a(0)\rho - b(0) \leq 0, \\ |a'(x)| + |b'(x)| \leq K, \end{array} \right. \tag{2.1}$$

Let the initial data f_0 be nonnegative and satisfy

$$\int_0^\infty f_0(x)\, dx < \infty, \qquad \int_0^\infty x f_0(x)\, dx \leq \rho.$$

Then the system (1.1) has a unique solution

$$(c, f) \in C^0([0,T]) \times C^0([0,T], w - L^1(\mathbb{R}^+)).$$

Let us sketch the main steps of the proof. Forget temporarily the coupling in (1.1) and suppose that c is a given function of time. The regularity of the coefficients allows us to define the characteristic curves $X(t; s, x)$ associated to V as follows

$$\frac{\partial}{\partial t} X(t; s, x) = V(t; X(t; s, x)), \qquad X(s; s, x) = x. \tag{2.2}$$

We note that

$$\frac{\partial}{\partial x} X(t; s, x) = J(t; s, x) = \exp\left(\int_s^t \partial_x V(\sigma, X(\sigma; s, x))\, d\sigma \right),$$

and $J(t; s, x)$ corresponds to the jacobian of the change of variable $y = X(t; s, x)$. If f solves the transport equation in (1.1), we remark that

$$\frac{d}{dt}\big(f(t, X(t; s, x))\big) = (\partial_t f + V \partial_x f)(t, X(t; s, x)) = -(\partial_x V f)(t, X(t; s, x)).$$

This suggests to introduce the following mild formulation

$$f(t, x) = f_0(X(0; t, x)) J(0; t, x). \tag{2.3}$$

Integrating against smooth test functions, this formula means

$$\int_0^\infty f(t, x) \psi(x)\, dx = \int_{X(0;t,0)}^\infty f_0(y) \psi(X(t; 0, y))\, dy$$

(which can be used to extend Theorem 2.1 to measure-valued solution). We can check that f defined by (2.3) preserves positivity and moment properties of the initial data f_0. Furthermore, we can justify that

$$M_1(t) = \int_0^\infty x f(t,x)\,dx$$

is a C^1 function of t with the following formally obvious relation

$$\frac{d}{dt} M_1(t) = \int_0^\infty V(t,x) f(t,x)\,dx. \tag{2.4}$$

Now, it remains to organize a fixed point argument. Set

$$\mathcal{C} = \{c \in C^0([0,T]),\ 0 \le c(t) \le \rho\}.$$

We introduce the map $\mathcal{T}$ defined on $\mathcal{C}$ by

$$\mathcal{T}(c(t)) = \big[\rho - M_1(t)\big]_+$$

where M_1 is the first moment of f associated to c by (2.3). Thanks to the cut-off, $\mathcal{T}$ applies $\mathcal{C}$ into itself, and it can be shown, by using the properties of the characteristics, that $\mathcal{T}$ is continuous ($C^0([0,T])$ being endowed with the uniform norm). On the other hand (2.4) proves that $\mathcal{T}(c)$ is actually uniformly Lipshitz on $[0,T]$. Hence, the Schauder theorem gives the existence of a fixed point $\mathcal{T}(c) = c$. For such a fixed-point, reasoning by contradiction, we obtain that $c(t) > 0$ and the cut-off to the positive part can be removed, so that the pair (c,f) is a solution of (1.1). It remains to prove the uniqueness statement. More precisely, we have the following continuity result.

LEMMA 2.1. *For $i \in \{1,2\}$, let f_i, c_i be a solution of (1.1) with initial data $f_{0,i} \in L^1(R^+,(1+x)\,dx)$, and total mass ρ_i. Then, there exists a constant C, depending only on $K, \rho_i, f_{0,i}$ and T, such that*

$$\|c_2 - c_1\|_{C^0(0,T)} \le C\left(|\rho_2 - \rho_1| + \|f_{0,2} - f_{0,1}\|_{L^1(R^+,x dx)}\right).$$

The uniqueness result immediately follows. Indeed if $\rho_2 = \rho_1$ and $f_{0,2} = f_{0,1}$ we obtain $c_2 = c_1$, which yields the equality of the characteristic curves, thus $f_2 = f_1$.

Proof of Lemma 2.1 follows from the direct evaluation of

$$|c_2(t) - c_1(t)| \le |\rho_2 - \rho_1| + I_1 + I_2 + I_3,$$

in terms of integrals involving f_1, f_2

$$\begin{cases} I_1 = \displaystyle\int_{X_1(0;t,0)}^\infty |z(t;0,y)| f_{0,2}(y)\,dy, \\ I_2 = \displaystyle\int_{X_1(0;t,0)}^\infty X_1(t;0,y) |f_{0,2}(y) - f_{0,1}(y)|\,dy, \\ I_3 = \left|\displaystyle\int_{X_2(0;t,0)}^{X_1(0;t,0)} X_2(t;0,y) f_{0,2}(y)\,dy\right|, \end{cases}$$

where z stands for the difference between the characteristics $X_2 - X_1$. Using carefully the properties of the characteristics, one is led to the following estimate

$$\begin{aligned}&|c_2(t) - c_1(t)| \le |\rho_2 - \rho_1| \\ &+C_T \int_0^t |c_2(s) - c_1(s)|\, ds + C_T M_1(|f_{0,2} - f_{0,1}|),\end{aligned}$$

on $[0, T]$. Applying Gronwall's lemma gives the asserted result.

We end this section by indicating some possible extensions of the results given here:

• Measure-valued data, like Dirac masses, can also be considered, up to some technicalities (see [6]): Theorem 2.1 applies with initial data $\mu_0 \in \mathcal{M}^1_+([0, +\infty[)$ verifying

$$\int_0^\infty d\mu_0 < \infty, \qquad \int_0^\infty x\, d\mu_0 \le \rho.$$

• We can take into account coalescence effects through the following Smoluchowski collision integral in the right hand side of the first equation in (1.1)

$$\begin{aligned} Q(f) \quad = \quad & 1/2 \int_0^x \omega(x-y, y) f(t, x-y) f(t, y)\, dy \\ & - \int_0^\infty \omega(x, y) f(t, x) f(t, y)\, dy \end{aligned}$$

It is related to coagulation effects where a collision between a cluster with size w with a cluster with size z produces a cluster with size $w + z$. This situation has been analyzed in [7], still for regular coefficients a, b and bounded kernel ω.

• We should finally mention that comparable existence-uniqueness results have been obtained independently, by using a different technical approach, by B. Niethammer-R. Pego [18]. We also refer to P. Laurençot [15] for the treatment of more singular coefficients, as for instance in (1.2).

3. Remarks on the asymptotic behaviour for large time. This Section is devoted to the asymptotic large time behaviour of solution (c, f) of the system (1.1), a crucial question in physical chemistry.

3.1. Simple examples. First, let us investigate the very simple case where the kinetic coefficients depend on the size variable as powers

$$a(x) = ax^r, \quad b(x) = bx^r, \tag{3.1}$$

where $r \ge 0$. Note that there is no critical radius: since we assume that the same power arises in the definition of a and b, at any given time, all grains shrink or expand, according to the sign of the quantity $c(t) - b/a$. Nevertheless, we can perform some explicit computations and, despite the simplicity of the dynamics considered here, non-trivial and interesting asymptotic behaviour can be observed.

For $r = 0$ or $r = 1$ the solution can be explicitly computed. Let us summarize the various formulae we obtained.

PROPOSITION 3.1. *If $r = 0$, assume that $f_0(0) = 0$ and extend f_0 by the value zero for negative numbers. Assume that $ac(0) - b \geq 0$ (or $ac(0) - b < 0$ with* $\mathrm{supp}(f_0) \subset (R, \infty)$*, where R is large enough). Then, the solution to (1.1) is given by*

$$\begin{cases} f(t,x) = f_0(x - \gamma(t)), \qquad c(t) = b/a + (c_0 - b/a)\exp(-M_0 a t), \\ \gamma(t) = (c(0) - b/a)/M_0\ (1 - \exp(-M_0 a t)). \end{cases}$$

Here M_0 denotes the zeroth moment of the density function which remains constant.

If $r = 1$, then the solution to (1.1) is given by $f(t,x) = \beta(t) f_0(x\beta(t))$, and

$$\begin{cases} \text{if} \quad a\rho - b \neq 0: \quad c(t) = \dfrac{\rho(ac_0 - b)\exp((b - a\rho)t) + b(\rho - c_0)}{(ac_0 - b)\exp((b - a\rho)t) + a(\rho - c_0)}, \\ \text{if} \quad a\rho - b = 0: \quad c(t) = \dfrac{c_0 + \rho(\rho - c_0)at}{1 + (\rho - c_0)at}. \end{cases}$$

with

$$\begin{cases} \text{if} \quad a\rho - b \neq 0: \quad \beta(t) = \dfrac{(ac_0 - b)\exp((b - a\rho)t) + k(\rho - c_0)}{(a\rho - b)}, \\ \text{if} \quad a\rho - b = 0: \quad \beta(t) = 1 + (\rho - c_0)at. \end{cases}$$

Hence, for $r = 0, 1$ the asymptotic behaviour may be directly read from the explicit expression of the solution given above. For general r, our existence result does not apply (the derivatives of a, b blow up and the regularity requirement on the coefficients in (2.1) is not fulfilled) and we are not able to obtain explicit solutions. However, some formal manipulations can be made which give information on the asymptotic behaviour of the possible solutions. Let $r \neq 1$ and integrate the differential equation (2.2). We get

$$X(s;t,x) = [x^{1-r} + (r-1)\int_s^t (ac(\sigma) - b)\, d\sigma]^{1/(1-r)}. \tag{3.2}$$

and the definition of a mild solution gives

$$\begin{cases} f(t,x) = \beta^r(t,x) f_0(x\beta(t,x)) \\ \beta(t,x) = [1 + (r-1)\gamma(t)x^{r-1}]^{1/(1-r)}, \qquad \gamma(t) = \displaystyle\int_0^t (ac(s) - b)\, ds. \end{cases}$$

We compute also the first moment by using (2.3)

$$(3.3)\int_0^\infty x f(t,x)\,dx = \int_{X(0;t,0)}^{X(0;t,\infty)} [1-(r-1)\gamma(t)y^{r-1}]^{1/(1-r)} y f_0(y)\,dy.$$

The endpoints involved in this last integral are given by (3.2). For instance if $r<1$ and $\gamma(t)\le 0$ we obtain

$$X(0;t,0) = [(r-1)\gamma(t)]^{1/(1-r)}, \quad X(0;t,\infty)=\infty.$$

If $ac(t)-b\ge 0$, the problem has to be supplemented with a boundary condition since the characteristics are ingoing: we choose $f(t,0)=0$ in order to conserves the zeroth moment. Therefore, the integration in (3.3) is taken as starting from 0. In other words, the data $f_0(x)$ has been extended by 0 for negative x and, accordingly, if $\beta(x)<0$ for some value of $x>0, t>0$, then $f(t,x)=0$. It is also worth mentioning that these formulae provide some counter-examples to the existence of solutions: for $r=2$, $ac_0-b>0$, and an initial data f_0 which never vanishes, it is easy to check that the first moment instantaneously blows up (Note that (2.1) imply that $a(x), b(x)$ cannot grow faster than $1+x$; this kind of non existence result is comparable to the situation known for discrete models, see [1]). Using these formulae, we are led to the following asymptotic behaviour.

PROPOSITION 3.2. *Assume the kinetic coefficients are given by (3.1) with $0\le r\le 1$, that the initial data f_0 has finite zeroth and first moments, and that the system has a unique global solution. Then as $t\to\infty$ the behaviour of the solution is as follows:*

- *If $\rho\le b/a$, then $M_1(f)\to 0$ and $c\to\rho$.*
- *If $\rho\ge b/a$, then $f\to f_\infty$ pointwise, and $c\to b/a$ where f_∞ is given by*

$$f_\infty(x) = \beta_\infty(x)^r f_0(x\beta_\infty(x)), \quad \beta_\infty(x) = [1+(r-1)\gamma_\infty x^{r-1}]^{1/(1-r)},$$

and the number γ_∞ is uniquely determined by the following condition

$$\begin{cases} b/a + \displaystyle\int_{[(r-1)\gamma_\infty]^{1/(1-r)}}^\infty [1+(1-r)\gamma_\infty y^{r-1}]^{1/(1-r)} y f_0(y)\,dy = \rho \\ \qquad\qquad\qquad\qquad \text{if} \quad c_0 < b/a, \\ b/a + \displaystyle\int_0^\infty [1+(1-r)\gamma_\infty y^{r-1}]^{1/(1-r)} y f_0(y)\,dy = \rho \\ \qquad\qquad\qquad\qquad \text{if} \quad c_0 > b/a. \end{cases}$$

The proof uses the explicit relations for the solutions together with the equation

$$\frac{d}{dt}M_s = \big(a(\rho-M_1)-b\big)sM_{s-1+r},$$

for the $r-$th moment, and the relation

$$\frac{dc}{dt} = -(ac-b)M_r.$$

This last relation shows that c is a monotonous function of time. Indeed since $b/a \neq \rho$ and $M_r \neq 0$ for $c(t) \neq \rho$, the time derivative of c is non zero in a neighborhood of b/a (except precisely at the equilibrium value b/a). Thus the quantity $ac - b$ maintains a constant sign, and γ also is monotonous. The result follows from a discussion of the limit of these quantities. Details can be found in [6].

3.2. The real problem. The previous examples deal with kinetic coefficients which are too simple. Indeed, they exclude the physical effects of Ostwald ripening where grains whose radius is smaller than a critical size $x_{c(t)}$ shrink whereas grains whose radius is larger expand. Indeed, the crucial assumption on the coefficients is related to the existence and uniqueness, at each time t, of a critical point $x_c(t)$ where the growth rate

$$V(t, x) = a(x)c(t) - b(x)$$

changes sign. Therefore, the rates a and b are required to satisfy

$$\begin{cases} a(x) > 0, \qquad b(x) > 0 \qquad \text{for } x > 0, \\ q(x) = b(x)/a(x) \text{ is strictly decreasing from } (0, +\infty) \text{ to } (q(\infty) = 0, q(0)), \end{cases} \tag{3.4}$$

where $[0, \rho]$ is strictly contained in $[0, q(0))$ (we can have $q(0) = +\infty$ as in (1.2)). Then, the following definition of the critical size associated to a density c makes sense

$$x_c = q^{-1}(c).$$

For the coefficients (1.2), we have $x_{c(t)} = c(t)^{-3}$. In this case, LIFSHITZ-SLYOZOV claimed that $c(t)$ tends to 0 monotically and behaves for large time as $t^{-1/3}$. Furthermore, as $t \to \infty$, the solution f can be described by an asymptotic profile, independent on what was the initial data. This remains a challenging open question for mathematicians. We have studied in [8] whether the first claim ($c(t)$ converges to 0) is fullfilled. In fact two cases can appear depending on the initial repartition of mass: $c(t)$ converges either to 0 or to ρ although the total number of clusters converges to 0 in both cases.

THEOREM 3.1. *[8] Assume that $b(x) = b > 0$ and a is non decreasing. We suppose that $\Phi(f_0) \in L^1(\mathbb{R}^+)$ for some convex function $\Phi : \mathbb{R}^+ \longmapsto \mathbb{R}^+$ satisfying*

$$\Phi(0) = 0, \qquad \lim_{s \to +\infty} \frac{\Phi(s)}{s} = +\infty.$$

Then, as t goes to ∞, one has

$$f(t, x) \rightharpoonup 0 \text{ in } L^1(\mathbb{R}^+).$$

Accordingly, the total number of clusters $M_0(t)$ goes to 0 while the monomers concentration $c(t)$ either tends to 0 or ρ. In particular, if there exists $\delta > 0$

such that $\mathrm{supp}(f_0) \cap [x_{c(0)} + \delta, \infty[\neq \emptyset$, *then* $c(t) \to 0$. *If* $\mathrm{supp}(f_0)$ *belongs to* $[0, x_{c(0)}]$, *the two behaviours are certainly possible, depending on the initial repartition of the mass.*

The proof relies on the construction of an entropy-like functional and on the study of its dissipation. This method can be compared to the study of large-time behaviour of the Boltzmann equation (see [5] and the references therein). It is based of the following lemma which can be seen as a "H-Theorem".

LEMMA 3.1. *[8] Let* $k : \mathbb{R}^+ \longrightarrow \mathbb{R}^+$ *be a* C^1, *strictly increasing and concave function satisfying* $k(0) = 0$. *We denote* $q(x) = b/a(x)$ *which is a strictly decreasing function. Then the critical size associated to some* $c > 0$ *is defined by* $x_c = q^{-1}(c)$. *Set*

$$\begin{cases} K(c) = \displaystyle\int_0^c k'(q^{-1}(s))\, ds, \\ H(t) = \displaystyle\int_0^\infty k(x) f(t,x)\, dx + K(c(t)), \\ D(t) = \displaystyle\int_0^\infty [k'(x) - k'(x_{c(t)})] V(t,x) f(t,x)\, dx. \end{cases}$$

Then, we have $\frac{dH}{dt} = D \leq 0$.

By the definition of k, the integral $K(c)$ makes sense since for $0 \leq s \leq \rho$ we have $k'(q^{-1}(s)) \leq k'(q^{-1}(\rho))$.

First, notice that suprisingly this lemma does not insure that $c(t)$ is monotonous. Indeed, it shows that compensated effects can occur between the function $K(c)$ and $\int k(x) f\, dx$ although the sum of this terms are non-increasing. Moreover, from the definition of D, it follows that the only solution with no loss of entropy lying in $L^\infty(\mathbb{R}^+; L^1(\mathbb{R}^+))$ is the null function.

The proof of Theorem 3.1 uses the following sequences obtained by shifting the solution

$$f_n(t,x) = f(t + t_n, x), \qquad c_n(t) = c(t + t_n),$$

with a sequence t_n increasing to ∞. As a consequence of the estimates obtained in the existence results, we can assume (at least for a subsequence) that

$$\begin{cases} f_n(t,x) \rightharpoonup f_\infty(t,x) \text{ weak * in } L^\infty_w(\mathbb{R}^+; \mathcal{M}^1(\mathbb{R}^+)), \\ c_n(t) \to c_\infty(t) \text{ uniformly in } C^0([0,T]). \end{cases}$$

Here $\mathcal{M}^1(\mathbb{R}^+)$ stands for the set of bounded measures on Ω; it identifies with the dual of the space $C^0_0(\mathbb{R}^+)$ of continuous functions vanishing at infinity. We denote by $L^\infty_w(\mathbb{R}^+; \mathcal{M}^1(\mathbb{R}^+))$ the space of weakly-* measurable functions $\mathbb{R}^+ \to \mathcal{M}^1(\mathbb{R}^+)$ that are essentially bounded, which identifies to the dual of $L^1(\mathbb{R}^+; C^0_0(\mathbb{R}^+))$, see [12]. We check also here that the limit has a finite first moment on $\mathbb{R}^+$. The limit solution has no loss of entropy while the integrability property on f_0 is propagated which ensures that f_∞ belongs to $L^\infty(\mathbb{R}^+; L^1(\mathbb{R}^+))$. Therefore, we have $f_\infty = 0$. Then the entropy is equal to $K(c_\infty)$ and since it is constant, c_∞ does not depend on time. It is then possible to show that c_∞ is either 0 or ρ and does not depend on the chosen subsequence t_n.

Finally, notice that the predictions on the asymptotic profile of the solution presented by LIFSHITZ-SLYOZOV have given rise to a very controversial debate, both on physical and mathematical viewpoins. We refer to CARR-PENROSE [3] and NIETHAMMER-PEGO [19] for more references and very nice results which contradict in part the analysis of [17]. We mention also the recent numerical study [4].

4. Connection to discrete models. Eventually, we investigate the connection between (1.1) and the BECKER-DÖRING equations, see [2]

$$\frac{d}{dt} c_i = J_{i-1} - J_i \qquad \text{for } i \geq 2, \tag{4.1}$$

$$J_i = a_i c_1 c_i - b_{i+1} c_{i+1} \qquad \text{for } i \geq 1, \tag{4.2}$$

$$\frac{d}{dt} c_1 = -2J_1 - \sum_{i=2}^{\infty} J_i, \tag{4.3}$$

Here, the size of the aggregates is described by the discrete variable i and the unknown is the infinite sequence of functions $\{c_i,\ i \in \mathbb{N}^*\}$, while a_i, b_i are given positive coefficients. The quantity $c_i(t)$ for any $i \geq 2$ stands for the concentration of clusters containing i particles (or $i-$mers, denoted by X_i in the sequel) at time t, and $c_1(t)$ denotes the concentration of free particles (or monomers, denoted by X_1 in the sequel). Equation (4.1) is the kinetic equation for the c_i's deriving from a straightforward application of mass-action kinetics to the reactions

$$X_i + X_1 \rightleftharpoons X_{i+1},$$

by which $i-$mers can gain or loss monomer. Therefore quantity J_i denotes the rate of this reaction, and a_i, b_{i+1} stand for the coagulation and fragmentation rates, respectively. Equation (4.3) for c_1 takes into account that monomers are involved in infinitely many reactions. At least formally, (4.1)-(4.3) yields

$$m_1 \sum_{i=1}^{\infty} i c_i(t) = \rho,$$

which means conservation of the total amount of monomers present in the solution. Here, we interpret this relation as a mass conservation and m_1 denotes the mass of one monomer. An extensive study of the Becker-Döring system for nonnegative initial data with finite total mass ρ is due to BALL-CARR-PENROSE [1]. Here we will place ourselves in situations where the existence and uniqueness results of [1] apply. More precisely we will make use of the following results (see Th.2.5 and Th.3.7 in [1]).

THEOREM 4.1. *[1] i) Consider the problem (4.1)-(4.3) with initial data* $c_{i,|t=0} = c_i^0 \geq 0$ *verifying* $\sum_{i=1}^{\infty} i c_i^0 = \rho < \infty$. *Assume that the coefficients satisfy* $a_i, b_i = \mathcal{O}(\sqrt{i})$. *Then the problem (4.1)-(4.3) admits one and only one solution.*

ii) Let c be a solution to (4.1)-(4.3), and φ_i *be a non negative sequence satisfying the following assumptions:*

$$\begin{cases} \displaystyle\int_{t_1}^{t_2} \sum_{i=1}^{\infty} |\varphi_{i+1} - \varphi_i| a_i c_i(t)\, dt < \infty, \quad \sup_t \sum_{i=1}^{\infty} \varphi_i c_i(t) < \infty, \\ \varphi_{i+1} - \varphi_i \geq 0 \quad \text{for} \quad i \quad \text{large enough.} \end{cases}$$

Then for any $m \geq 2$ *the following relation holds true*

$$\begin{aligned} \sum_{i=m}^{\infty} c_i(t_2)\varphi_i \quad &+ \quad \int_{t_1}^{t_2} \left\{ \sum_{i=m}^{\infty} b_{i+1} c_{i+1}(s)(\varphi_{i+1} - \varphi_i) \right\} ds \\ &= \sum_{i=m}^{\infty} c_i(t_1)\varphi_i + \int_{t_1}^{t_2} \left\{ \sum_{i=m}^{\infty} a_i c_1(s) c_i(s)(\varphi_{i+1} - \varphi_i) \right\} ds \\ &\quad + \int_{t_1}^{t_2} \varphi_m (a_{m-1} c_1(s) c_{m-1}(s) - b_m c_m(s))\, ds. \end{aligned} \tag{4.4}$$

We will use these formula with $\varphi_i = i^\alpha$ for any $\alpha \geq 1$, or $\varphi_i = 1$, or any sequence which has only finitely many nonzero terms.

4.1. Convergence to the Lifschitz-Slyozov system. Since the Lifshitz-Slyozov model treats size as a continuous variable, our aim is to recover that model from the Becker-Döring system as a "macroscopic limit", in the spirit of hydrodynamic limits in fluid mechanics, see [13]. A first attempt in this direction is due to PENROSE [20]. Before rescaling the system (4.1)-(4.3) in terms of a small parameter, we first rewrite it in dimensionless form. To this end, one needs the following reference quantities and absolute constants:

$\mathcal{N}$: Avogadro number,
T: characteristic time,
M: characteristic mass,
L: characteristic length;
m_1: mass of one monomer,
M_m: molar mass of monomers: $M_m = \mathcal{N} m_1$;
C_1: characteristic value for the monomer concentration c_1,
C: characteristic value for the cluster concentration $c_i, i \geq 2$;
A: characteristic value for the coagulation coefficients $a_i, i \geq 2$,
B: characteristic value for the fragmentation coefficients $b_i, i \geq 2$,

and we consider apart A_1: characteristic value for the first coagulation coefficient a_1.

Let us set

$$\begin{cases} \overline{t}=t/T, & \overline{c}_1(\overline{t})=c_1(\overline{t}T)/C_1, \quad \overline{c}_i(\overline{t})=c_i(\overline{t}T)/C \quad \overline{\rho}=\rho/M, \\ \overline{a}_i=a_i/a, & \overline{b}_i=b_i/B \ \text{ for } i\geq 2, \quad \overline{a}_1=a_1/A_1. \end{cases}$$

When one rewrites (4.1)-(4.3) in terms of the new variables, the following dimensionless parameters appear:

$$(4.5)\begin{cases} \gamma=C/C_1, & \mu=\dfrac{M\mathcal{N}}{M_mC_1}, \\ \alpha=ATC_1, & \alpha_1=TA_1C_1^2/C=\alpha/\gamma\ A_1/A, \qquad \beta=BT. \end{cases}$$

Indeed, dropping the overlines, the system takes the following dimensionless form

$$(4.6)\quad \frac{d}{dt}c_i=\alpha(a_{i-1}c_1c_{i-1}-a_ic_1c_i)+\beta(b_{i+1}c_{i+1}-b_ic_i) \qquad \text{for } i>2,$$

$$(4.7)\quad \frac{d}{dt}c_2=\alpha_1a_1c_1^2-\alpha a_2c_1c_2+\beta(b_3c_3-b_2c_2),$$

$$(4.8)\quad \frac{dc_1}{dt}=-\gamma\left[2(a_1\alpha_1c_1^2-\beta b_2c_2)+\sum_{i=2}^{\infty}(\alpha a_ic_1c_i-\beta b_{i+1}c_{i+1})\right].$$

On the other hand, the mass conservation reads

$$(4.9)\quad c_1+\gamma\sum_{i=2}^{\infty}ic_i=\mu\rho.$$

Let us introduce a parameter $\epsilon>0$ and define a function f^ϵ by

$$f^\epsilon(x,t)=c_i^\epsilon(t) \quad \text{if} \quad t>0,\, x_i=i\epsilon\leq x<x_{i+1}=(i+1)\epsilon \quad \text{for } i\geq 2,$$

and $f^\epsilon(x,t)=0$ if $x\in[0,2\epsilon[$. Here, c_i^ϵ stands for the solution of (4.6) with a suitable scaling of the dimensionless parameters in (4.5) with respect to ϵ. We can relate the "mesh size" ϵ to a size of reference. Indeed, assuming that a $i-$particle is a perfect sphere with radius r_i, we have

$$r_i=L\overline{r}_i=\left(\frac{3V_m}{4\pi\mathcal{N}}\right)^{1/3}i^{1/3},$$

where V_m is the molar volume of a free atom and $\overline{r}_i$ appears to be without dimension. Therefore

$$i_{ref}=\frac{4\pi\mathcal{N}L^3}{3V_m}=1/\epsilon$$

which will be assumed large compared to 1.

It remains to discuss the dependence of the parameters in (4.5) with respect to ϵ. The right hand side in (4.6) would be interpreted as a a derivative, then α and β should scale as $1/\epsilon$. If the total mass (4.9) is to remain finite (and nonzero), then μ should be of order 1, whereas we would then like to view the sum over i as a Riemann sum for the integral of xf in (1.1). Hence γ should be taken of the same order as $x\,dx$, that is ϵ^2. These heuristic remarks naturally lead to the following choice

$$\gamma = \epsilon^2,\ \mu = 1,\ \alpha = \beta = 1/\epsilon,\ \alpha_1 \leq 1/\epsilon.$$

Note that we give a particular behaviour for the rate of the coagulation of two monomers A_1. Indeed, it is sometimes argued, as in [11], that attraction forces between two atoms are much smaller than between a "large" particle and a single atom. It follows that coagulation rate for single atom should be small compared to those corresponding to particles $i \geq 2$.

With this choice of the parameters, we are led to the following rescaled version of (4.6)-(4.8)

$$\frac{d}{dt}c_i^\epsilon = \frac{1}{\epsilon}(a_{i-1}c_{i-1}^\epsilon - a_i c_i^\epsilon)c_1^\epsilon + \frac{1}{\epsilon}(b_{i+1}c_{i+1}^\epsilon - b_i c_i^\epsilon) \quad \text{for} \quad i \geq 2, \tag{4.10}$$

$$\frac{d}{dt}c_2^\epsilon = \alpha_1 a_1 (c_1^\epsilon)^2 - \frac{1}{\epsilon}a_2 c_1^\epsilon c_2^\epsilon + \frac{1}{\epsilon}(b_3 c_3^\epsilon - b_2 c_2^\epsilon), \tag{4.11}$$

$$\frac{d}{dt}c_1^\epsilon = -2\epsilon^2 a_1 \alpha_1 (c_1^\epsilon)^2 + \epsilon^\epsilon b_2 c_2 - \epsilon\sum_{i=2}^{\infty}(a_i c_i^\epsilon c_1^\epsilon - b_{i+1}c_{i+1}^\epsilon). \tag{4.12}$$

Solutions to this system satisfy mass conservation:

$$c_1^\epsilon + \epsilon^2\sum_{i=2}^{\infty} i c_i^\epsilon = \rho. \tag{4.13}$$

Then, for ϵ close to zero, we recover the Lifshitz-Slyozov system in the following sense.

THEOREM 4.2. *[9] Assume the kinetic coefficients a_i, b_i satisfy:*

$$a_i, b_i \leq K, |a_{i+1} - a_i| \leq K/i, |b_{i+1} - b_i| \leq K/i$$

for some constant K. Then, there exists a subsequence, still labelled by ϵ and two functions $a, b \in W^{1,\infty}((0,\infty)) \cap L^\infty(\mathbb{R}^+)$ such that

$$\lim_{\epsilon\to 0}\sup_{i\in(r/\epsilon,R/\epsilon)}\Big(|a_i - a(i\epsilon)| + |b_i - b(i\epsilon)|\Big) = 0,$$

holds for any $0 < r < R < \infty$.

Assume there exist constants $0 < s \leq 1$, $0 < \rho, M_0, M_s < \infty$ for which

$$\forall\epsilon > 0: \quad \epsilon\sum_{i=2}^{\infty} c_i^{0,\epsilon} \leq M_0, \quad c_1^{0,\epsilon} + \epsilon^2\sum_{i=2}^{\infty} i c_i^{0,\epsilon} = \rho, \quad \epsilon\sum_{i=2}^{\infty}(\epsilon i)^{1+s}c_i^{0,\epsilon} \leq M_s.$$

Then, as $\epsilon \to 0$, up to a subsequence, we have

$$\begin{cases} f^\epsilon \rightharpoonup f \text{ weakly} * \text{ in } L^\infty_w([0,T];\mathcal{M}^1((0,\infty))) \\ \qquad\qquad \text{and in } C^0([0,T];\mathcal{M}^1((0,\infty))-weak-*), \\ c_1^\epsilon(t) \to c(t) \text{ uniformly in } C^0([0,T]), \end{cases}$$

where (c,f) is a solution to (1.1).

Note that the initial data $c_i^{0,\epsilon}$ should also be well-prepared with respect to ϵ. In particular the assumption on the zeroth moment means that

$$C/C_1 \sum_{i=2}^\infty c_i^{0,\epsilon} = \epsilon^2 \sum_{i=2}^\infty c_i^{0,\epsilon} = \frac{\text{Initial number of clusters}}{C_1}$$

(the ratio of the initial number of clusters over the characteristic concentration of monomers) is of order ϵ. We also need the extra moment of order $1+s>1$. In the spirit of our work on the continuous model [6], we can obtain compactness properties on the sequence of solutions $\left(c_1^\epsilon, f^\epsilon\right)_{\epsilon>0}$: we show that the moment properties are preserved, uniformly with respect to ϵ, while c_1^ϵ is equicontinuous. Then, we can pass to the limit without difficulties both in a discrete weak formulation of (1.1) derived from (4.4) and in the mass conservation relation (4.13).

4.2. Second-order expansion: The modified Lifshitz-Slyozov model. The connection between the discrete model (4.1-4.3) and the continuous one, as the reference size becomes large can also help us to guess a physically relevant boundary condition for the Fokker-Planck like equation presented in [10], [14]. As in the previous section, let us assume

$$\gamma = \epsilon^2,\ \nu = \epsilon,\ \mu = 1,\ \alpha = \beta = \alpha_1 = 1/\epsilon.$$

Then it can be convenient rewriting (4.4) as follows

$$\begin{aligned} \sum_{i=2}^\infty c_i^\epsilon(t)\varphi_i - \sum_{i=2}^\infty c_i^{0,\epsilon}\varphi_i &= \int_0^t \left(\frac{\varphi_2}{\epsilon} a_1 (c_1^\epsilon)^2(\tau) - \frac{\varphi_1}{\epsilon} b_2 c_2^\epsilon(\tau)\right) d\tau \\ + \int_0^t \Bigg(\sum_{i=2}^\infty a_i c_1^\epsilon c_i^\epsilon(\tau) \frac{\varphi_{i+1}-\varphi_{i-1}}{2\epsilon} &+ \sum_{i=2}^\infty a_i c_i^\epsilon(\tau)\frac{\varphi_{i+1}-2\varphi_i+\varphi_{i-1}}{2\epsilon} \\ - \sum_{i=2}^\infty b_i c_i^\epsilon(\tau)\frac{\varphi_{i+1}-\varphi_{i-1}}{2\epsilon} &+ \sum_{i=2}^\infty b_i c_i^\epsilon(\tau)\frac{\varphi_{i+1}-2\varphi_i+\varphi_{i-1}}{2\epsilon} \Bigg) d\tau. \end{aligned}$$

We now define the interpolant function by (we omit the superscript ϵ)

$$g(t,x) = c_i(t) \quad \text{for } x \in [\epsilon(i-3/2), \epsilon(i-1/2)[,\ i \geq 2$$

and $g(t,x)=0$ for $x \in [0,\epsilon/2[$. We also apply this definition for $a(x), b(x)$. We use the formula above with $\varphi_i = \varphi((i-1)\epsilon)$ for a test function φ which vanishes at the origine. This can be seen as an approximation, up to $\mathcal{O}(\epsilon^2)$ terms, of the following integral relation

$$
\begin{aligned}
\frac{d}{dt}\int_0^\infty g(t,x)\varphi(x)\,dx &= \int_0^\infty (a(x)c(t)-b(x))g(t,x)\varphi'(x)\,dx \\
&\quad +\epsilon/2\int_0^\infty (a(x)c(t)+b(x))g(t,x)\varphi''(x)\,dx \\
&\quad +\epsilon\varphi'(0)a_1c(t)^2.
\end{aligned}
\tag{4.14}
$$

We recover in this way a weak form of the following (ϵ-dependent) Fokker-Planck equation

$$
\left\{
\begin{array}{l}
\dfrac{\partial}{\partial t}g+\dfrac{\partial}{\partial x}G(g;t,x)=0,\\
G_(g;t,x)=(a(x)c(t)-b(x))g\\
\qquad\qquad -\epsilon\dfrac{\partial}{\partial x}\left(\dfrac{a(x)c(t)+b(x)}{2}\,g(t,x)\right).
\end{array}
\right.
\tag{4.15}
$$

Supplemented by the mass conservation law

$$c(t)+\int_0^\infty xg(t,x)\,dx=\rho,$$

this model appeared in [10], [14] as a variant of the Lifshitz-Slyozov model (1.1). This model is interesting in the sense that it shares more features with the discrete Beker-Döring system than the Lifshitz-Slozov equations. In particular, there exists a saturation concentration, given by $c_s=\lim_{x\to\infty} b(x)/a(x)$ (while it is $\lim_{i\to\infty} b_{i+1}/a_i$ in the discrete case). If the initial mass is greater than a critical mass $\rho(c_s)$, there is no admissible detailed equilibrium for (4.15) (i.e. an function m such that $xm\in L^1(\mathbb{R}^+)$ and $G(m)=0$). Furthermore, as we shall see below, for $\rho<\rho_s$, the equilibra ressembles those of the Beker-Döring system.

However, the connection between (4.14) and (4.15) also need the following boundary condition

$$g(t,0)=2a_1c^2(t)/(a(0)c(t)+b(0)),\tag{4.16}$$

which arises by performing the usual integration by parts. The interest of this boundary condition appears with the discussion of the detailed balance equilibrium m which are solution of

$$G(m)=0.$$

We obtain the following solutions, depending on $m(0)$ and c,

$$m(x)=m(0)\frac{a(0)c+b(0)}{a(x)c+b(x)}\exp\left(\frac{2}{\epsilon}\int_0^x\frac{a(y)c-b(y)}{a(y)c+b(y)}\,dy\right).$$

Furthermore, (4.16) relates these parameters since $G(m;0) = 0$ gives

$$m(0) = c\,\frac{2a_1 c}{a(0)c + b(0)}.$$

Therefore, we have a familly of equilibrium states parametrized only by the monomers concentration c and an easy computation proves that for a given mass $\rho > 0$, it corresponds a unique equilibrium, according to the situation known for the discrete Becker-Döring equations. Furthermore, when we perform an expansion of the formulas for the equilibrium states of both the Becker-Döring and (4.15) as $\bar{c}$ approaches the critical value $c_s = \frac{b}{a}$, we are led to the following analoguous formulae, see[10]

$$m_i = \overline{c}\ \exp\left(i\ \left(\frac{b\,\overline{c}}{a} - 1\right)\right), \quad m(z) = m(0)\ \exp\left(z\ (\frac{b\,\overline{c}}{a} - 1)\right).$$

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