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A Modified Version of the Lifshitz-Slyozov Model

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Abstract—We revisit the well-known Lifshitz-Slyozov model for precipitation, from the perspective of detailed balance equilibria and saturation density. It is shown that, in this respect, the Lifshitz-Slyozov model behaves very differently from its discrete counterpart, the Becker-Döring system; in particular it has no saturation density. We propose a modification of the Lifshitz-Slyozov model which has a saturation density, and whose detailed balance equilibria are a continuous analog of those of the Becker-Döring system. Therefore this model seems more suitable for the study of phase transitions. Mathematically, the modified system consists of a parabolic equation coupled to an integral equation.

Keywords—Phase transitions, Precipitation, Lifshitz-Slyozov system, Becker-Döring system.

1. INTRODUCTION

In this paper, we investigate phase transition models which represent the exchange of particles between clusters, and are based on the application of the law of mass action to reactions of the type

$$X_i + X_1 \rightleftharpoons X_{i+1}, \qquad i = 1, \dots \infty. \tag{1}$$

Here it is assumed that only one particle can be exchanged at a time, X_i denotes clusters containing i particles (or i-mers), and X_1 denotes free particles (or monomers). The size of the clusters i may be treated as a discrete, or a continuous variable. The description of the corresponding models may be found, respectively, in [1,2]. We will refer to these models, respectively, as the Becker-Döring and the Lifshitz-Slyozov model. The mathematical theory of the Becker-Döring system is now fairly complete (see [3–6]). As far as the authors know, the Lifshitz-Slyozov system has received little attention in the mathematical literature, and there has been no study of the relationship between these two models. Therefore it is of interest to compare their physical properties. More precisely, the Becker-Döring system has a family of detailed balance equilibria, which exist provided the total number of particles per unit volume in the system is less than a certain value, the saturation density ρ_s. In one sense, this physical property makes the Becker-Döring model a phase transition model: ρ_s is the maximal density the system can sustain without undergoing a phase transition. It therefore represents the saturated vapor density. Here we will show that this essential physical feature, the existence of a saturation density, is not present in the Lifshitz-Slyozov system. We will propose a modification of the Lifshitz-Slyozov model which incorporates the existence of ρ_s.

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The paper is organized as follows: in the second section, we recall the classical Becker-Döring and Lifshitz-Slyozov models, and some well-known properties of the Becker-Döring system. We then give a description of the detailed balance equilibria for the Lifshitz-Slyozov system and show they are monodisperse. This motivates the introduction of our new model, which we present in Section 3. We then show that this new model has a saturation density, given by a formula which is very similar to the discrete one. Finally, we show that in the vicinity of equilibrium, the detailed balance equilibria of both models have the same expression in terms of the kinetic constants.

2. THE CLASSICAL BECKER-DÖRING AND LIFSHITZ-SLYOZOV MODELS

2.1. The Models

The Becker-Döring model is obtained when one specifies the reaction rate J_i of (1) by the use of mass action kinetics

$$J_i = k_i c_i c_1 - q_{i+1} c_{i+1}, \tag{2}$$

where $c_i = c_i(t)$ denotes the concentration of i-mers at time t, and k_i, q_i are, respectively, the coagulation and fragmentation coefficients. One then obtains the system

$$\frac{dc_i}{dt} = J_{i-1}(c) - J_i(c), \qquad i \geq 2, \tag{3}$$

$$\rho(t) := c_1(t) + \sum_{i=2}^{\infty} i c_i(t) = \sum_{i=1}^{\infty} i c_i(0) := M, \tag{4}$$

in which (4) expresses the conservation of the total number ρ of particles per unit volume. For large clusters, it seems natural to treat i as a continuous variable z, which then has the physical meaning of a volume. Denoting by $f = f(t,z)$ the size density and by $c = c(t)$ the concentration of monomers at time t, system (3),(4) is replaced by the Lifshitz-Slyozov system [2]

$$\frac{\partial f(t,z)}{\partial t} + \frac{\partial G}{\partial z} = 0, \tag{5}$$

$$c(t) + \int_0^{\infty} z f(t,z)\, dz = M. \tag{6}$$

Here G denotes the growth rate of clusters of size z. An explicit expression for G is obtained in [2] by assuming the process to be diffusion-controlled. This leads to an expression of the form

$$G(z,t) = (k(z)c(t) - q(z)) f(z,t),$$

where k and q may be written explicitly.

In fact, G may be obtained directly from (2) by using the formal analogy

$$J_{i-1} - J_i = -\frac{J_i - J_{i-1}}{i-(i-1)} \to -\frac{\partial J}{\partial z}, \qquad J_i \approx (k_i c_1 - q_{i+1})\, c_i \to (kc - q) f. \tag{7}$$

This leads to equation (5). The key point here is that in the expression of J_i, the concentration c_{i+1} has been replaced by c_i. A more precise Taylor expansion would lead to diffusion in the size variable z, i.e., to a parabolic equation for f. It is this observation which provides the basis of our model. A discussion of the relevance of a diffusive term in (5) may be found in [7], but the nature of the corresponding detailed balance equilibria is not addressed.

2.2. Detailed Balance Equilibria

For the reader's convenience, we recall the following facts about detailed balance equilibria for the Becker-Döring system [4]. For a detailed balance equilibrium, the concentration m_i of i-mers is given by

$$m_i = Q_i \left(\bar{c}\right)^i, \qquad \text{where } Q_1 = 1, \quad Q_i = \prod_{r=2}^{i} \left(\frac{k_{r-1}}{q_r}\right), \qquad i \geq 2. \tag{8}$$

Here $\bar{c}$ denotes the monomer concentration. Therefore such an equilibrium is entirely determined by $\bar{c}$. If the total density is finite, then $\bar{c}$ must be less than the radius of convergence of the corresponding power series

$$\bar{c} \leq c_s := \left(\limsup_i (Q_i)^{1/i}\right)^{-1}. \tag{9}$$

The quantity c_s can be viewed as a saturation concentration, and the corresponding mass

$$\rho_s := \sum_{i=1}^{\infty} i Q_i \left(c_s\right)^i$$

(which may or may not be finite) can then be interpreted as the saturated vapor density. We first give bounds for c_s in the following proposition.

PROPOSITION 1.

$$\liminf_i \left(\frac{q_{i+1}}{k_i}\right) \leq c_s \leq \limsup_i \left(\frac{q_{i+1}}{k_i}\right).$$

PROOF. Define the following quantities:

$$u_n := \ln\left(\frac{Q_n}{Q_{n+1}}\right) = \ln\left(\frac{q_{n+1}}{k_n}\right), \qquad S_n = \frac{u_1 + \cdots + u_n}{n} = \frac{-1}{n}\left(\ln\left(Q_{n+1}\right)\right).$$

Note that from (9) we have $\ln c_s = \liminf S_n$. The result now follows from the following version of Cesaro's lemma:

$$\liminf u_n \leq \liminf S_n \leq \limsup S_n \leq \limsup u_n.$$

For the classical Lifschitz-Slyozov model, detailed balance equilibria satisfy the relation

$$(k(z)\bar{c} - q(z))m(z) = 0. \tag{10}$$

Therefore their existence and nature depends on the function $u := q/k$. If, for instance, we assume this function to be constant, we see that $\bar{c}$ is uniquely determined, whereas $m(z)$ is totally undetermined. If, on the other hand, we assume u to be strictly increasing, we obtain the following characterization of detailed balance equilibria.

LEMMA 2. *Assume u is strictly increasing. Then any detailed balance equilibrium with density M is monodisperse: $m(z) = a\delta_{z_c}$, where a and z_c satisfy*

$$u\left(z_c\right) = \bar{c}, \qquad \bar{c} + a u^{-1}\left(\bar{c}\right) = M.$$

PROOF. From (10) we must have $m(z) = 0$ for any $z \neq z_c := u^{-1}(\bar{c})$. Thus, the support of the measure m must be reduced to the point z_c. By a classical result, m is a combination of finitely many derivatives of δ_{z_c}, but since it is a positive measure, we obtain $m(z) = a\delta_{z_c}$ for some a.

REMARK 1. If the increasing function u has a finite limit, then (as in the discrete case) the saturation concentration c_s, i.e., the maximal possible value for $\bar{c}$ is equal to this limit. However, there is no saturation density, i.e., any value is possible for M. Moreover, the physical nature of the detailed balance equilibria is radically different here since they are monodisperse.

REMARK 2. Another noticeable difference between the discrete and continuous models is that here the total density M does not uniquely determine a corresponding detailed balance equilibrium.

3. THE MODIFIED MODEL

3.1. The Modified Model and Its Detailed Balance Equilibria

Replacing (7) by a second-order Taylor expansion, we obtain the system

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial z}((k(z)c(t) - q(z))f - \frac{1}{2}\frac{\partial}{\partial z}((k(z)c(t) + q(z))f)) = 0, \tag{11}$$

$$c(t) + \int_0^\infty z f(t,z)\,dz = M, \tag{12}$$

which has to be supplemented with initial and boundary data

$$c(0) = c_0 \geq 0, \quad f(0,z) = f_0(z) \geq 0, \qquad \text{for } z \in]0,\infty[, \tag{13}$$

$$f(t,0) = 0, \qquad \text{for } t > 0. \tag{14}$$

The detailed balance equilibria $(\bar{c}, m(z))$ are now obtained by solving a first-order differential equation which expresses that the flux is null. After some manipulation, one obtains

$$m(z) = m(0)\left(\frac{k(0)\bar{c} + q(0)}{k(z)\bar{c} + q(z)}\right)\exp\left(2\int_0^z \frac{k(t)\bar{c} - q(t)}{k(t)\bar{c} + q(t)}\,dt\right). \tag{15}$$

3.2. The Saturation Density and Saturation Concentration

We can now obtain the saturation density in a simple case.

PROPOSITION 3. *Assume that the kinetic coefficients satisfy*

$$q(z) \geq q^* > 0, \qquad zk^* \geq k(z) \geq k_* > 0; \qquad \alpha := \lim_{z\to\infty}\frac{q(z)}{k(z)} \tag{16}$$

exists. Then the saturation density for system (11),(12) is equal to α.

PROOF. The total density of the equilibrium (15) is given by

$$M(\bar{c}) = \bar{c} + m(0)k(0)\int_0^\infty F(z)\,dz, \tag{17}$$

where

$$F(z) = \left(\frac{z}{k(z)}\right)\left(\frac{\bar{c} + u(0)}{\bar{c} + u(z)}\right)\exp\left(2\int_0^z \frac{\bar{c} - u(t)}{\bar{c} + u(t)}\,dt\right).$$

Here we have written $u(z) = (q(z)/k(z))$; it is straightforward to check that the function F is integrable iff $\bar{c} < \alpha$.

A natural question is whether detailed balance equilibria exist for a prescribed total density M (see Remark 1 above) less than the saturation density. In the case of the discrete system, the total density, being given by a power series, is a strictly increasing function of the monomer concentration. We now show that this is also the case for our model.

PROPOSITION 4. *Assume (16) and* $u(0) \leq u(z)$, *for all* $z \geq 0$. *Then, in the range* $0 \leq \bar{c} < c_s$, *the quantity* $M(\bar{c})$ *is strictly increasing.*

PROOF. The proof just consists in differentiating (17) with respect to $\bar{c}$, and checking the convergence and sign of the corresponding integral

$$M'(\bar{c}) = 1 + m(0)k(0)\int_0^\infty \frac{z}{k(z)}H(z)\,dz,$$

where

$$H(z) = \left(\frac{u(z) - u(0)}{(\bar{c} + u(z))^2} + \frac{\bar{c} + u(0)}{\bar{c} + u(z)}\int_0^z \frac{4u(t)}{(\bar{c} + u(t))^2}\,dt\right)\exp\left(2\int_0^z \frac{\bar{c} - u(t)}{\bar{c} + u(t)}\,dt\right).$$

3.3. Comparison of the Two Models

If the expression of the saturation density is in complete analogy to the discrete case, it is, on the other hand, interesting to compare the expressions (15) and (8) of the detailed balance equilibria. Our next result shows that both expressions agree in the vicinity of saturation.

PROPOSITION 5. *Assume the discrete coefficients k_i, q_i and the functions q, k are given constants. Consider the detailed balance equilibria (15),(8) for a given total density M. Then these two quantities have the same limit value when M approaches the saturation density.*

PROOF. It follows from the previous result that M totally determines the value of c_1 and $\bar{c}$, the monomer concentration for, respectively, the Becker-Döring and our model. We may therefore perform an expansion of formulas (8) and (15) as $\bar{c}$ approaches $c_s = q/k$. These expansions, respectively, lead to the limiting values

$$m_i = \bar{c} \exp\left(i\left(\frac{k\,\bar{c}}{q} - 1\right)\right), \qquad m(z) = m(0) \exp\left(z\left(\frac{k\,\bar{c}}{q} - 1\right)\right). \tag{18}$$

It can also be shown that in this saturation asymptotics, the continuous analog of the free energy functional of the Becker-Döring system (see [4,6]) provides a Lyapunov functional for systems (11),(12). This result, together with the existence theory for (11),(12), will appear elsewhere.

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