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On the Becker/Döring theory of nucleation of liquid droplets in solids

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W I A S

Abstract

Nucleation of liquid precipitates in semi-insulating GaAs is accompanied by deviatoric stresses resulting from the liquid/solid misfit. A competition of surface tension and stress deviators at the interface determines the nucleation barrier.

The evolution of liquid precipitates in semi-insulating GaAs is due to diffusional processes in the vicinity of the droplet. The diffusion flux results from a competition of chemical and mechanical driving forces.

The size distribution of the precipitates is determined by a Becker/Döring system. The study of its properties in the presence of deviatoric stresses is the subject of this study. The main tasks of this study are: (i) We propose a new Becker/Döring model that takes thermomechanical coupling into account. (ii) We compare the current model with already existing models from the literature. Irrespective of the incorporation of mechanical stresses, the various models differ by different environments where the evolution of precipitates takes place. (iii) We determine the structure of equilibrium solutions according to the Becker/Döring model, and we compare these solutions with those that result from equilibrium thermodynamics.

1 Introduction

The appearance of a new phase in a given parent phase is an interesting problem since a long time. Its description starts with the calculation of the nucleation rate for liquid droplets in vapour in stationary process by Becker and Döring in 1935, [3]. They established the so called Becker/Döring process, whereupon droplets shrink or grow exclusively by evaporation and condensation of single molecules or atoms.

The modern version of the resulting model equations, that we will call the Becker/-Döring system has first been formulated by J. I. Frenkel in 1939 [12], see also his textbook [13]. The mathematical investigations on the dynamics of the Becker/Döring system rely on J. Burton's reformulation in 1977 [4], who, however, ignores Frenkel's studies.

Our study on the Becker/Döring model was motivated by a new important industrial application for nucleation and evolution. These phenomena regard the appearance of liquid droplets in crystalline semi-insulating Gallium Arsenide (GaAs) during necessary heat treatments at elevated temperature of GaAs wafer. Besides the classical phenomenon of surface tension, there arise deviatoric bulk stresses due to the different mass densities of liquid and solid GaAs. Moreover, semi-insulating

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GaAs posseses a complex chemical constitution, and for a proper description at least seven constituents on three crystal sublattices of the solid phase must be taken into account.

The thermodynamics of semi-insulating GaAs has been formulated and exploited in detail by the authors in [6], where in particular non-standard phase diagrams are calculated that take care for the effects of surface tension and deviatoric bulk stresses.

The most important result of [6] for the current study regards the determination of the available free energy of a liquid/solid system containing a single droplet, see Figure 6, as a function of a single variable, which may be, for example, the size of the droplet. This allows a direct application of the simple version of the Becker/Döring model, which likewise considers a single variable to describe the state of a droplet.

We have organised the study as follows:

In Chapter 2 we introduce the Becker/Döring model and we discuss in detail some aspects of its history. This is necessary, because of the occurrence of some misinterpretations of Becker and Döring's paper from 1935 in the current literature.

Chapter 3 formulates the thermodynamics to the Becker/Döring model. The main issue is the construction of a Lyapunov function to the Becker/Döring model that is compatible with Clausius version of the second law of thermodynamics. We identify this function as the available free energy for the system at hand. The mathematical literature uses a different Lyapunov function, that was proposed by J. M. Ball, J. Carr, O. Penrose in [1], which is not in accordance to the second law.

Finally, in Chapter 4 we apply the general framework to two explicit systems: Liquid droplets in semi-insulating GaAs, which has stimulated the current study, and for a comparison and illustration a liquid/vapour system containing a single substance. The latter system is the classical system, that was already treated by Becker and Döring in 1935. The most important difference between the two systems regards their possible equilibria. In fact GaAs system is able to reach an equilibrium distribution of liquid droplets in the solid phase, whereas the liquid/vapour system is driven to a state, where exclusively the liquid phase is present. However, during its passage to this final state, interesting phenomena appear. Among these are metastability of the system [1, 23] and the transition of the Becker/Döring model to the Lifshitz/Slyosov/Wagner (LSW) model [17, 34] in [21, 22, 24].

2 Formulation and discussion of the general Becker/Döring model

2.1 Formulation of the model

Relying on preliminary studies by Volmer and Weber [33], and Farkas [11], Becker and Döring [3], proposed in 1935 a simple process to model precipitation of a new phase in a given surrounding. Examples are the formation of liquid droplets in a gas, of solid precipitates in a liquid, and the appearance of liquid droplets in a crystalline solid. In the following the precipitates will be called droplets and the single molecules or atoms are often called monomers. We consider exclusively spherical droplets and describe their size by their number of molecules, α, or by their radii, r_α.

According to the proposed model, which has become known as the Bekker/Döring (BD) model, a droplet with α molecules may grow by incorporation of a monomer from the surrounding and it may shrink by emitting a monomer into the surrounding. Other processes, like the appearance of a droplet with $\alpha+\beta$ molecules by the reaction of a droplet with $\alpha > 1$ molecules with another droplet with $\beta > 1$ molecules, are not considered within the BD model.
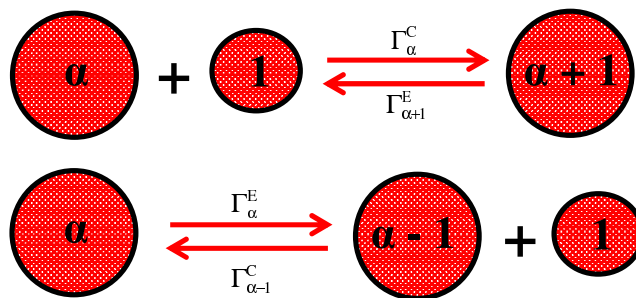

Figure 1: The Becker/Döring process

We call the two BD reactions evaporisation, E, and condensation, C, and we denote their corresponding transition rates by Γ_α^E and Γ_α^C. The transition rates give the number of reactions per second, and they must be determined by constitutive laws, whose derivation is among the objectives of this study.

2.2 The evolution equations of the Becker/Döring model

We consider a distribution of droplets with $\alpha \in \{2, ..., \nu\}$ atoms or molecules, and we introduce a set of functions $Z(t, \alpha) \geq 0$, which give at any time $t \geq 0$ the number of droplets with α atoms or molecules. The number of monomers is included here, and it is given by $Z(t, 1)$. Consequences of the introduction of a largest droplet with ν atoms or molecules and the limiting case $\nu \to \infty$ will be discussed in Section 4.1.

If ν is finite, we use the conditions

$$\Gamma_\nu^{\mathrm{C}} = 0 \quad \text{and} \quad Z(t, \nu + 1) = 0 \tag{1}$$

to terminate the system of evolution equations, which we introduce next.

The evolution of $Z(t, \alpha)$ is determined by a system of ordinary differential equations, that we call nowadays the BD system. It reads

$$\frac{\partial Z(t, \alpha)}{\partial t} = \Gamma_{\alpha-1}^{\mathrm{C}} Z(t, \alpha - 1) - \Gamma_\alpha^{\mathrm{E}} Z(t, \alpha) - \Gamma_\alpha^{\mathrm{C}} Z(t, \alpha) + \Gamma_{\alpha+1}^{\mathrm{E}} Z(t, \alpha + 1)$$
$$\text{for} \quad \alpha \in \{2, ..., \nu\}. \tag{2}$$

The right hand side of (2) represents the four possible contributions that may lead to a change of the number of droplets with α molecules.

According to Becker/Döring we introduce fluxes by

$$J_\alpha = \Gamma_\alpha^{\mathrm{C}} Z(t, \alpha) - \Gamma_{\alpha+1}^{\mathrm{E}} Z(t, \alpha + 1), \quad \text{so that} \quad \frac{\partial Z(t, \alpha)}{\partial t} = J_{\alpha-1} - J_\alpha$$
$$\text{for} \quad \alpha \in \{2, ..., \nu\}. \tag{3}$$

The evolution law for the number of monomers, i.e. of $Z(t, 1)$, depends on the chosen experimental device. For example, Becker and Döring's experimental device contained liquid droplets within vapour, and is adjusted so that a stationary state is achieved. In this state the number of monomers becomes measurable, so that no evolution law for $Z(t, 1)$ is needed. Further details of the BD device will be explained in the next section.

We are interested in another case, where the total number of molecules, N, of the considered system is kept constant. This gives rise to the side condition

$$\sum_{\beta=1}^{\nu} \beta Z(t, \beta) = N, \quad \text{which implies} \quad \frac{\partial Z(t, 1)}{\partial t} + \sum_{\beta=2}^{\nu} \beta \frac{\partial Z(t, \beta)}{\partial t} = 0. \tag{4}$$

We eliminate the time derivatives under the sum by means of the other evolution laws $(3)_2$ to obtain the evolution law for $Z(t, 1)$. There results

$$\frac{\partial Z(t, 1)}{\partial t} = -J_1 - \sum_{\beta=1}^{\nu} J_\beta. \tag{5}$$

The hierarchy of equations $(3)_2$ and (5) constitutes the BD system for a closed device. The BD system must be supplemented (i) by information on the considered experimental device, and (ii) by constitutive laws for the transition rates in order to end up with a closed system, that can be used to determine the functions $Z(t, \alpha)$.

The formulation of constitutive laws that are in accordance with the second law of thermodynamics is a most subtle problem, and it is one of the main objectives of this study. We mention already here that many treatments of this subject in the literature lead to a violation of the second law.

2.3 Historical remarks

The first studies on homogeneous nucleation, where empirical results became related to theoretical investigations date back to Volmer and Weber 1926 [33], Farkas 1927 [11] and Volmer [30]. Volmer and Weber calculated the critical radius, r_C, of a single droplet according to the Gibbs/Thomson law, [14], [29], and they determined the nucleation barrier, i.e. the work W to create isothermally a critical droplet, as $W = \sigma/3(4\pi r_C^2)$, where σ denotes the surface tension. The notion critical droplet refers to the fact, that a single droplet with radius $r < r_C$ dissolves, whereas it grows for $r > r_C$. First attempts to calculate nucleation rates can be found in [11] and [30].

In 1935 Becker and Döring studied stationary nucleation processes. The Figure 2 shows a schematic sketch of their experimental device. The process runs at constant outer pressure and constant temperature.
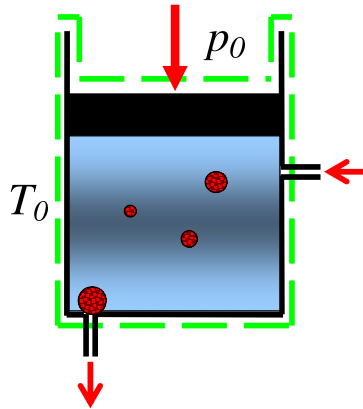

Figure 2: Schematic sketch of the Becker/Döring device

The outer pressure is adjusted so that droplets appear and grow within a gaseous phase. Stationarity of the process is achieved as follows: If the droplets have reached a certain size, i.e. if they contain $\alpha = \nu + 1$ molecules, they will be removed from the system and the same amount of matter will be supplied as single molecules to the gas. Thus there holds $Z(t, \alpha) = 0$ for $\alpha \geq \nu + 1$. According to Becker and Döring, this procedure leads to constant values (i) of the total number of molecules in the device, (ii) of all functions $Z(t, \alpha)$ for $\alpha \in \{1, 2, ..., \nu\}$, ($iii$) of the total volume of the device. Furthermore there holds (iv)

$$J_1 = J_2 = ... = J_\nu \equiv J, \tag{6}$$

where the common value J of the fluxes is called nucleation rate.

For the calculation of J, Becker and Döring had to determine the constitutive laws for the transition rates. To this end they considered a closed system containing a single liquid droplet in contact with its vapour. In Section 2.4.4 we will show that the transition rates cannot be calculated in this manner, because a contradiction

to the second law of thermodynamics will follow as a consequence. However, the resulting nucleation rates fit quite well to experimental data.

The theory of stationary processes was upgraded in 1939 in Volmer's textbook [31]. We mention that in all these treatments the instationary system (2) was never written down explicitly.

Although there is good agreement between Becker and Dörings modelling and experimental data, their model gave reasons to critisims, because the BD model ignores Brownian motion of small droplets in a gas. In other words: In the BD model, the droplets are considered to be at rest, whereas one should expect, that in particular small droplets have translational and rotational degrees of freedom, so that they take part in the thermal motion. It was Kuhrt, [15, 16], stimulated by Becker, who has studied these phenomena for the first time in 1952. During 1960 –1970, a polemic debate on the correct consideration of thermal motion of the droplets was started between various scientific groups, see for example [18] and [28]. We will not enter into this discussion here, because later on we will mainly be interested in the evolution of liquid droplets in a solid matrix, where the phenomenon obviously does not occur.

In 1939 Frenkel, [12], considered a closed device under constant outer pressure and constant temperature, and he prescribed the total number of molecules, N, and the size ν of the largest droplets in the system, see also [13]. For this system Frenkel developed at first the thermodynamic theory. In particular he calculated the available free energy for a many droplet system, where he uses information from the single droplet system, see Section 2.4 for details. Minimisation of the free energy leads to equilibrium values $Z_{\mathrm{eq}}(\alpha)$ of the function $Z(t, \alpha)$. Hereafter, Frenkel wrote down for the first time the instationary system (2), (4) and (2.2). In 1939 Frenkel, [12], and also Band, [2], concluded from this system that equilibrium is reached for

$$J_1 = J_2 = ... = J_\nu = 0, \tag{7}$$

which implies

$$\frac{\Gamma_\alpha^C}{\Gamma_{\alpha+1}^V} = \frac{Z_{\mathrm{eq}}(\alpha+1)}{Z_{\mathrm{eq}}(\alpha)}. \tag{8}$$

This gives a first hint, that the ratio of the two transition rates is restricted. Thus the constitutive laws for the transition rates must be correspondingly restricted.

In 1977 J. Burton, [4], reconsidered the BD process without any reference to Frenkel. The importance of Burton's contribution is due to the fact, that mathematical studies on the BD model refers exclusively to Burton's treatment of the subject. However, Burton changed the interpretation of the variables of the original model, that seems of minor importance at the very first moment, but a careful study of this change reveals tremendous implications.

Recall that according to Becker and Döring, the central quantity $Z(t, \alpha)$ gives at time t the number(!) of droplets with α molecules. However, in order to compare their theoretical results with experimental data from Volmer and Flood [32], Becker

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and Döring introduced on page 729 of [3] number densities and flux densities, by dividing $Z(t, \alpha)$ and J_α by the total volume $V = V_L + V_V$ of the liquid/vapour system, without changing, however, the notation. Since V is a constant in a stationary process, which was exclusively considered by Becker and Döring, the introduction of number densities and flux densities makes sense. However, in the treatment of instationary processes it makes no sense at all. Here only the droplet numbers, or the concentrations $\frac{Z(t,\alpha)}{N_0}$ where N_0 is the total number of molecules in the system, can be balanced in (3), because there is a drastic change of the total volume with time in a dynamical process that runs at constant temperature and constant external outer pressure. In fact the needed volume of an molecule in the gas phase is enlarged by a factor 1000 times with respect to the needed space in the liquid phase.
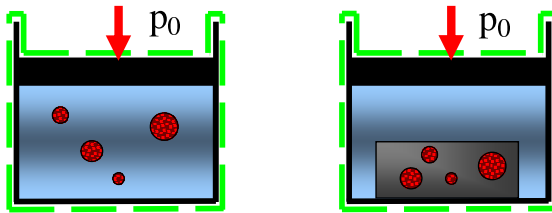

Figure 3: Many-droplet systems

Burton probably overlooked these facts, and he proposed the system (3) and (5) but with volume densities $c_\alpha(t)$ instead of the numbers $Z(t, \alpha)$.

$$j_\alpha = \gamma_\alpha^C c(t, \alpha) - \gamma_{\alpha+1}^E c(t, \alpha+1), \quad \text{so that} \quad \frac{\partial c(t, \alpha)}{\partial t} = j_\alpha - j_{\alpha-1}$$
$$\text{for} \quad \alpha \in \{2, ..., \nu\}, \quad (9)$$

and the evolution equation for $c(t, 1)$ reads

$$\frac{\partial c(t, 1)}{\partial t} = -j_1 - \sum_{\beta=1}^{\nu} j_\beta \quad \text{and} \quad \sum_{\beta=1}^{\nu} \beta c(t, \beta) = \rho. \quad (10)$$

O. Penrose *et al* accepted this change of interpretation in the seminal mathematical studies on Burton's version of the BD model, see [26, 25, 27, 1, 23, 24], where mainly the limiting case $\nu \to \infty$ is studied. Now we discuss a most important consequence of this approach.

Burton and Penrose proposed a special form of the constitutive laws for the transition rates, viz.

$$\gamma_\alpha^C = a_\alpha c_1(t) \quad \text{and} \quad \gamma_\alpha^E = b_\alpha, \quad (11)$$

where a_α and b_α should be independent of the droplet distributions. The ansatz $(11)_1$ results by a second misinterpretation of Becker and Döring's reasoning: Becker and Döring considered a single droplet with radius r_α in a gaseous phase, and they argued that every encounter of the incoming gas particles with the droplet sphere

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leads to a condensation, see Figure 1. According to the kinetic theory of gases, the number of impinging particles per second on a surface $4\pi r_\alpha^2$ by gas particles of mass m and at the temperature T is given by

$$\Gamma_\alpha^{\mathrm{C}} = 4\pi r_\alpha^2 \frac{Z(t,1)}{V_{\mathrm{V}}(t)} \sqrt{\frac{kT}{2\pi m}}. \tag{12}$$

Here k denotes Boltzmann's constant and $V_{\mathrm{V}}(t)$ is the Volume of the gas phase, which depends on time in a instationary process at constant temperature and constant outer pressure. However, the ratio $Z(t,1)/V_{\mathrm{V}}(t)$ is independent of time, because there holds the thermal equation of state for an ideal gas, which reads in the current notation

$$p_0 = \frac{Z(t,1)}{V_{\mathrm{V}}(t)} kT. \tag{13}$$

We conclude that in fact $\Gamma_\alpha^{\mathrm{C}}$ depends on a volume density involving $Z(t,1)$, however, it is related to the gas volume but not to the total volume, as it is indicated in $(11)_1$.

Although we criticise a BD model which relies on (9) and (10) but not on (3) and (5), Ball, Carr and Penrose constituted many most important mathematical results, that can easily be transferred to the current BD system (3),(5) along their strategy. We mention here only Penrose's study, [24], on the long time behaviour of a many droplet system and its approach to the Lifshitz/Slyosov/Wagner (LSW) theory [17], [34] in a certain scaling limit. Penrose reasonings were rigorously proved by B. Niethammer in 2002, see the habilitation [21] and its short version [22].

2.4 Thermodynamics of the Becker/Döring system

We proceed with a study of the properties of the BD system (3) and (5). In this chapter we investigate the approach of the droplet distribution to equilibrium from a thermodynamic point of view.

Recall that within the framework of the BD system, equilibrium is defined by

$$J_1 = J_2 = ... = J_\nu = 0, \quad \text{which implies} \quad \frac{\Gamma_\alpha^{\mathrm{C}}}{\Gamma_{\alpha+1}^{\mathrm{E}}} = \frac{Z_{\mathrm{eq}}(\alpha+1)}{Z_{\mathrm{eq}}(\alpha)}. \tag{14}$$

At first sight, there are two possibilities to get information from $(14)_2$:

1. For given transition rates one could calculate the equilibria $Z_{\mathrm{eq}}(\alpha)$ in terms of $Z_{\mathrm{eq}}(1)$, which hereafter might be determined by the conservation law $(4)_1$.

2. The other possibility results by assuming that the ratio $Z_{\mathrm{eq}}(\alpha+1)/Z_{\mathrm{eq}}(\alpha)$ follows from another source. In this case, the ratio of transition rates is fixed. For example, the evaporisation rate cannot be given independently from the condensation rate.

Thermodynamics, however, rules out the first possibility, because it is capable to determine the equilibria $Z_{\mathrm{eq}}(\alpha)$ without any reference to transition rates. This task is the subject of the next sections.

2.4.1 The second law of thermodynamics for processes at constant temperature and constant external pressure

We consider at first the system which is shown on the left hand side of Figure 3 on page 7. The following theory is also valid for the circumstances which are shown on the right hand side of Figure 3, where liquid droplets evolve in a solid GaAs matrix which is in contact with an inert gas.

Let us apply now the basic laws of thermodynamics to the control volume of the cylinder/piston system, which is indicated in Figure 3 by the dashed line.

The interior of the cylinder is denoted by B, which consists of a vapour phase B_V and a liquid phase $B_\mathrm{L} = \bigcup_{\alpha=1}^{\nu} B_\alpha$, which is decomposed into separated liquid droplets of a given distribution. B_α indicates the union of droplets with α molecules.

We study exclusively processes at constant outer pressure p_0 and constant outer temperature T_0. Furthermore we assume that the temperature T within B is constant with $T = T_0$.

The global balance laws of total energy E and entropy S to the system B reads

$$\frac{dE}{dt} = \dot{Q} + \oint_{\partial B} \sigma^{ij} v^j da^i, \quad \text{and} \quad \frac{dS}{dt} \geq \frac{\dot{Q}}{T_0}. \tag{15}$$

The quantity $\dot{Q}$ denotes the heat power, that may flow in or out so that a constant temperature T_0 is guaranteed. The surface integral gives the mechanical power due to stresses σ^{ij} acting on ∂B, which moves with the velocity v^j.

The equality sign in $(15)_2$ holds in equilibrium, whereas in non-equilibrium, the growth of entropy is greater than the ratio of supplied heat and temperature. This statement expresses Clausius version of the second law of thermodynamics, [5].

According to our assumption, there is a constant outer pressure p_0 acting on ∂B. Note that only the piston may move. In this case the mechanical power reduces to

$$\oint_{\partial B} \sigma^{ij} v^j da^i = -p_0 \frac{dV}{dt}. \tag{16}$$

Elimination of the heat power in $(15)_2$ by means of $(15)_1$ leads to the thermodynamic inequality

$$\frac{d\mathcal{A}}{dt} \leq 0, \quad \text{with the definition} \quad \mathcal{A} = E - T_0 S + p_0 V. \tag{17}$$

The newly defined quantity $\mathcal{A}$ is called the available free energy or availability. We conclude that for arbitrary thermodynamic processes that run at constant outer pressure, constant temperature and constant total mass, the availability must always decrease and assumes its minimum in thermodynamic equilibrium.

The total energy E is given by the sum of internal energy, U, and kinetic energy, K: $E=U+K$. The combination $\Psi = U - T_0 S$. gives the free energy. In the following we

will neglect the kinetic energy, so that we may write the availability as $\mathcal{A} = \Psi + p_0 V$
.

The thermodynamic inequality can now be written

$$\frac{d\mathcal{A}}{dt} = \frac{d}{dt}\left(\Psi + p_0 V\right) \leq 0. \tag{18}$$

Recall that the inequality is valid for arbitrary thermodynamic processes in B, that are, however, subjected to (i) constant temperature in B, (ii) constant outer pressure on ∂B, and (iii) constant number of molecules in B.

2.4.2 The available free energy for a many droplet system

We denote the available free energy of a system that contains only a single droplet with α molecules by $\mathcal{A}_\alpha$. Furthermore we introduce the convention $\mathcal{A}_1 = 0$. The explicit calculation of $\mathcal{A}_\alpha$ will be postponed to Section 3.2, where we consider two special cases: These concern a liquid/vapour system with liquid droplets in a vapour phase. This represents the classical Becker/Döring application, and it is revisited here for an illustration. The other example is a liquid/solid system with liquid droplets in a crystalline solid, and this case represents the main focus of this study.

For both cases we assume that the droplets have radii on the nanometer scale, whereas their distances are between 1 and 2 μm.

Relying on this assumption we may present the available free energy of the many droplet system by

$$\mathfrak{A} = \sum_{\alpha=1}^{\nu} Z(t,\alpha)\mathcal{A}_\alpha + kT\sum_{\alpha=1}^{\nu} Z(t,\alpha)\ln\left(\frac{Z(t,\alpha)}{N_{\mathrm{D}}(t)}\right) \quad \text{with} \quad N_{\mathrm{D}}(t) = \sum_{\alpha=1}^{\nu} Z(t,\alpha). \tag{19}$$

The function $N_{\mathrm{D}}(t)$ gives at any time t the total number of droplets including the monomers.

The first contribution to the available free energy of the many droplet system is the sum of the free energies of single droplet systems, thus ignoring energetic interactions between the droplets because they are assumed far apart from each other. The second contribution in (19) takes care for the *entropy of mixing* of a system consisting of ν *chemically* different species.

Note that it is due to the entropic contribution, that a system which has initial only monomers can produce droplets with $\alpha > 1$ under certain circumstances.

The representation (19) provides a basis for the further development of the theory. A more detailed motivation of (19) for the two mentioned special cases will be given in Section 3.3.

2.4.3 Equilibrium of a many droplet system

According to the thermodynamic inequality (18), the available free energy assumes a minimum, $\mathfrak{A}^{\mathrm{eq}}$, in equilibrium that is approached at constant temperature, constant external pressure and constant number of molecules, thus

$$\mathfrak{A}^{\mathrm{eq}} = \mathrm{Min!} \quad \text{under the side condition} \quad N = \sum_{\alpha=1}^{\nu} \alpha Z(t, \alpha). \tag{20}$$

The extrema of the problem (20) may be written as

$$Z_{\mathrm{eq}}(\alpha) = \lambda_{\mathrm{eq}}^{\alpha-1} Z_{\mathrm{eq}}(1) \exp\left(-\frac{\mathcal{A}_{\alpha}}{kT}\right) \quad \text{with} \quad \lambda_{\mathrm{eq}} = \frac{Z_{\mathrm{eq}}(1)}{N_D^{\mathrm{eq}}}, \tag{21}$$

where $Z_{\mathrm{eq}}(1)$ and the parameter $\lambda_{\mathrm{eq}} \leq 1$ are determined as follows: At first we calculate λ_{eq} from $(19)_2$, which can be brought into the form

$$\sum_{\alpha=1}^{\nu} \lambda_{\mathrm{eq}}^{\alpha} \exp\left(-\frac{\mathcal{A}_{\alpha}}{kT}\right) = 1. \tag{22}$$

Next we determine the equilibrium number of monomers, $Z_{\mathrm{eq}}(1)$, from $(20)_2$, i.e.

$$Z_{\mathrm{eq}}(1) = \frac{N}{\displaystyle\sum_{\alpha=1}^{\nu} \alpha \lambda_{\mathrm{eq}}^{\alpha-1} \exp(-\frac{\mathcal{A}_{\alpha}}{kT})}. \tag{23}$$

The evaluation of $(22)_2$ and (23) needs information on the α dependence of the available free energies $\mathcal{A}_{\alpha}$. With this information a detailed discussion of possible solutions of (22) becomes possible. We postpone this discussion to Section 4.1, where we consider two explicit cases.

2.4.4 The approach of a many droplet system to equilibrium

In this section we study the evolution of a many droplet system to equilibrium according to the BD model. To this end we rewrite the available free energy $(19)_1$ to obtain

$$\mathfrak{A} = kT \sum_{\alpha=1}^{\nu} Z(t, \alpha) \ln\left(\frac{Z(t, \alpha)}{q_{\alpha} N_{\mathrm{D}}(t)}\right) \quad \text{with} \quad q_{\alpha} = \exp\left(-\frac{\mathcal{A}_{\alpha}}{kT}\right). \tag{24}$$

Next we calculate the time derivative of (24). There results

$$\frac{d\mathfrak{A}}{dt} = kT \sum_{\alpha=1}^{\nu} \frac{\partial Z(t, \alpha)}{\partial t} \ln\left(\frac{Z(t, \alpha)}{q_{\alpha} N_{\mathrm{D}}(t)}\right). \tag{25}$$

The time derivatives in (25) will now be eliminated by the BD system $(3)_2$ for $\alpha \geq 2$, and by the conservation law (5) for $\alpha = 1$. After some simple rearrangements of the resulting expression, we obtain

$$\frac{d\mathfrak{A}}{dt} = kT \sum_{\alpha=1}^{\nu} J_\alpha \log\left(\frac{Z(t, \alpha+1)}{Z(t, \alpha)} \frac{N_{\mathrm{D}}(t)q_\alpha}{Z(t, 1)q_{\alpha+1}}\right), \quad \text{or with} \quad (3)_1,$$

$$= kT \sum_{\alpha=1}^{\nu} \left(\Gamma_\alpha^{\mathrm{C}} Z(t, \alpha) - \Gamma_{\alpha+1}^{\mathrm{E}} Z(t, \alpha+1)\right) \ln\left(\frac{Z(t, \alpha+1)}{Z(t, \alpha)} \frac{N_D(t)q_\alpha}{Z(t, 1)q_{\alpha+1}}\right) \quad (26)$$

The second law of thermodynamics requires $d\mathfrak{A}/dt \leq 0$. Thus we conclude that

$$\frac{N_{\mathrm{D}}(t)q_\alpha}{Z(t, 1)q_{\alpha+1}} = \frac{\Gamma_{\alpha+1}^{\mathrm{E}}}{\Gamma_\alpha^{\mathrm{C}}} \quad (27)$$

is a sufficient condition to guarantee that $\mathfrak{A}$ cannot increase during a process of a many droplet system at constant temperature and constant external pressure.

Note that the expression $(x - y)\ln(y/x)$ is always smaller than zero if $x \neq y$ and equal to zero only if $x = y$.

We consider (27) as a constitutive law for the determination of the ratio of transition rates $\Gamma_{\alpha+1}^{\mathrm{E}}$ and $\Gamma_\alpha^{\mathrm{C}}$, that is compatible with the second law of thermodynamics.

If we utilise now, for example, the expression (12) as a second constitutive law for the determination of the condensation rate $\Gamma_\alpha^{\mathrm{C}}$, both transition rates are explicitly known, and we end up with a closed BD system, which is non-linear, because the evaporation rates $\Gamma_{\alpha+1}^{\mathrm{E}}$ depend on the distribution functions $Z(t, \alpha)$ according to (27). We call this case the evolution of droplets by kinetic controlled transition rates, because $\Gamma_\alpha^{\mathrm{C}}$ results from the kinetic theory of gases.

There is another interesting case, that leads to so called diffusion controlled transition rates, where the stationary diffusion problem of a single droplet is used to calculate the difference $\Gamma_\alpha^{\mathrm{C}} - \Gamma_\alpha^{\mathrm{E}}$.

We summarise the main results of this section:

We have evaluated the available free energy $\mathfrak{A}$ of a many droplet system. From a purely thermodynamic point of view, we have determined the distribution function $Z_{\mathrm{eq}}(\alpha)$ for equilibrium, which corresponds to the minimum of the available free energy. In a second step we have calculated the time derivative of $\mathfrak{A}$, and by means of the BD system we have found (27) as a sufficient condition that guarantees $d\mathfrak{A}/dt \leq 0$. In mathematical terms: We have identified the Lyapunov function, viz. $\mathfrak{A}$, to the BD system.

2.4.5 The Lyapunov function to the BD system as proposed by J. M. Ball, J. Carr and O. Penrose

We compare now an important study to the dynamics of the BD system by J. M. Ball, J. Carr and O. Penrose (BCP), [1, 23, 24], with the results of the last section. Our discussion will rely on the BCP version (9) and (10), where the distribution function is a volume density, $c(t, \alpha)$ instead of the number density $Z(t, \alpha)/N_0$. Our criticism on this from Section 2.3, page 8, is not important for a moment. Furthermore we mention that Ball, Carr and Penrose consider exclusively the limiting case $\nu \to \infty$.

At first, Ball, Carr and Penrose represent the equilibria of (9) and (10), i.e. the solution of $j_\alpha = a_\alpha c_{\text{eq}}(1) c_{\text{eq}}(\alpha) - b_{\alpha+1} c_{\text{eq}}(\alpha + 1) = 0$ by writing

$$c_{\text{eq}}(\alpha) = Q_\alpha c_{\text{eq}}^\alpha(1) \quad \text{with the definition} \quad Q_{\alpha+1} = \frac{a_\alpha}{b_{\alpha+1}} Q_\alpha, \quad Q_1 = 1. \qquad (28)$$

Next they define the Lyapunov function

$$L(t) = \sum_{\alpha=1}^{\infty} c(t, \alpha) \left(\ln \left(\frac{c(t, \alpha)}{Q_\alpha} \right) - 1 \right), \qquad (29)$$

and conclude by means of the BD system (9), (10) and the ansatz (11) that

$$\frac{dL(t)}{dt} \leq 0. \qquad (30)$$

A comparison of (29) with the available free energy (24) reveals that the two Lyapunov functions differ from each other in a nontrivial manner.

In fact both quantities are Lyapunov functions to the BD system, however, only the available free energy (24) is in accordance to the second law of thermodynamics. For this reason we reject the Lyapunov function (29).

3 The available free energies for special cases

The BD model will now further be exploited for two special cases. The first case regards a system that contains a single substance, where liquid droplets of a pure substance nucleate and evolve in a vapour phase. This is Becker and Döring's classical example, which will be revisited here in order to explain the strategy in detail. Furthermore, it serves for a comparison with a much more complicated and subtle example, where we consider a modern application of the BD model to semi-insulating GaAs. At elevated temperatures, unwanted liquid droplets appear and evolve in a solid matrix. Here the concurrent processes are strongly affected by mechanical bulk stresses, which arise because the liquid phase has a lower mass density than the solid phase.

3.1 Single droplet systems

The evaluation of the available free energy (24) for a many droplet system needs a preliminary calculation of the available free energy for a single droplet system. This is the subject of the next section. To this end we consider the two systems, which are shown in Figure 4.
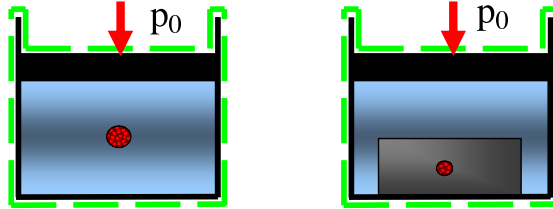

Figure 4: Single droplet systems

The pressure vessel on the left contains vapour, which is in contact with a single liquid droplet. The system on the right hand side contains a single liquid droplet within a crystalline solid, which is surrounded by an inert gas.

3.2 Available free energy for single droplet systems

3.2.1 A liquid droplet within vapour

We choose the gaseous and liquid phases of water as an example to describe the evolution of liquid droplets in a gas. The vapour should behave like an ideal gas, and in comparison to this, we assume the liquid to be incompressible. Furthermore we assume that the liquid ought to exist within the vapour phase in the form of spherical droplets at rest.

As already stated, we consider processes at constant temperature T and constant outer pressure p_0. The variables are (i) the volume V_V of the gaseous phase, (ii) the volume V_L of the liquid phase and (iii) the number α of molecules in the liquid phase. The number of vapour molecules is $N_0 - \alpha$, where N_0 denotes the fixed total number of molecules in the system.

We exploit the available free energy $\mathcal{A} = \Psi + p_0 V$, and we write at first

$$\mathcal{A} = \Psi_V + \Psi_L + \Psi_I + p_0(V_V + V_L), \tag{31}$$

in order to indicate the three contributions to the free energy that describe vapour, liquid and the interface.

The free energies for vapour and liquid are given by their general constitutive laws

$$\Psi_V = m(N_0 - \alpha)\, \psi_V\left(T, \frac{V_V}{m(N_0 - \alpha)}\right) \quad \text{and} \quad \Psi_V = m\,\alpha\,\psi_L\left(T, \frac{V_L}{m\alpha}\right). \tag{32}$$

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The functions ψ_V and ψ_L are the specific free energies of vapour and liquid, respectively, and m denotes the atomic mass.

The interfacial free energy is proportional to the surface of the interface:

$$\Psi_I = \sigma O_I = 4\pi\sigma \, r_\alpha^2. \tag{33}$$

The temperature dependent quantity σ is called surface tension.

The derivatives of the available free energy $\mathcal{A}(T, V_V, V_L, \alpha)$ with respect to the volumes yield

$$\frac{\partial\mathcal{A}}{\partial V_V} = p_V - p_0, \quad \frac{\partial\mathcal{A}}{\partial V_L} = p_L + \frac{2\sigma}{r_\alpha} - p_0. \tag{34}$$

Recall that the pressure is the derivative of the specific free energy with respect to the specific volume: $p = -\partial\psi(T, v)/\partial v$, see [19]. Thus p_V and p_L are the pressures of the gaseous and the liquid phase, respectively.

The necessary conditions for mechanical equilibrium are given by $\partial\mathcal{A}/\partial V_V = 0$ and $\partial\mathcal{A}/\partial V_L = 0$, implying

$$p_V = p_0 \quad \text{and} \quad p_L - p_V = \frac{2\sigma}{r_\alpha}. \tag{35}$$

The condition $(35)_2$ has at first been derived by Laplace and is called Laplace law. We will assume that mechanical equilibrium is much faster established than phase equilibrium, so that the conditions (35) are satisfied during the process of an evolving droplet. Consequently, the available free energy becomes a function of the single variable α.

Next we introduce the Gibbs free energies $G_V = \Psi_V + p_V \, V_V$ and $G_L = \Psi_L + p_L \, V_L$ and obtain by means of (32), (33)

$$\mathcal{A} = G_V + G_L + \frac{1}{3}\sigma O_I. \tag{36}$$

We introduce the specific Gibbs free energy of vapour and liquid as functions of temperature and pressure by $G_V = m(N_0 - \alpha)g_V(T, p_V)$ and $G_L = m\alpha g_L(T, p_L) = m\alpha g_L(T, p_0 + 2\sigma/r_\alpha)$. In the liquid there holds $4\pi/3r_\alpha^3 \, \rho_L = m\alpha$. Due to the assumption of an incompressible liquid, the liquid mass density ρ_L is a constant. We thus obtain $\mathcal{A}$ as a function of the parameters T and p_0 and of the variable α:

$$\mathcal{A}(T, p_0; \alpha) = mN_0 g_V(T, p_0) + m\alpha \left(g_L\left(T, p_0 + \frac{2\sigma}{r_\alpha}\right) - g_V(T, p_0) \right) + \frac{1}{3}4\pi\sigma \, r_\alpha^2. \tag{37}$$

The incompressibility of the liquid allows a further simplification

$$g_L\left(T, p_0 + \frac{2\sigma}{r_\alpha}\right) - g_V(T, p_0) = g_L(T, p_0) - g_V(T, p_0) + \frac{1}{\rho_L}\frac{2\sigma}{r_\alpha}. \tag{38}$$

The sign of the difference $g_L(T, p_0) - g_V(T, p_0)$ is essential for the bahaviour of the liquid/vapour system. Its determination is a simple matter due to the assumption that the vapour behaves like an ideal gas. In this case

$$g_V(T, p_0) = g_V\left(T, \bar{p}(T)\right) + \frac{kT}{m} \ln\left(\frac{p_0}{\bar{p}(T)}\right). \tag{39}$$

The quantity $k > 0$ is Boltzmann's constant, and the reference pressure $\bar{p}(T)$ is defined as a solution of the equation $g_L(T, \bar{p}) - g_V(T, \bar{p}) = 0$, which can be read off from tables, e.g. for water.

The incompressibility of the liquid can be used once more to simplify

$$g_L(T, p_0) = g_L\left(T, \bar{p}(T) + \left(p_0 - \bar{p}(T)\right)\right) = g_L\left(T, \bar{p}(T)\right) + \frac{1}{\rho_L}\left(p_0 - \bar{p}(T)\right), \tag{40}$$

so that we may write

$$g_L(T, p_0) - g_V(T, p_0) = \frac{\bar{p}(T)}{\rho_L}\left(\frac{p_0}{\bar{p}(T)} - 1\right) - \frac{kT}{m} \ln\left(\frac{p_0}{\bar{p}(T)}\right). \tag{41}$$

The first contribution in (41) can be neglected, because the specific volume of the gas is by a factor 1000 larger than the specific volume of the liquid.

Finally we introduce the positive constant $\gamma = 8\pi\sigma(3/4\pi)^{2/3}(m/\rho_L)^{2/3}$ and obtain finally an explicit representation of the available free energy for vapour containing a single liquid droplet at rest:

$$\mathcal{A}(T, p_0; \alpha) = mN_0 g_V(T, p_0) - kT \ln\left(\frac{p_0}{\bar{p}(T)}\right)\alpha + \gamma\alpha^{2/3}. \tag{42}$$

If $p_0 < \bar{p}(T)$, the free energy $\mathcal{A}(T, p_0; \alpha)$ assumes its minimum exclusively at $\alpha = 0$, so that only the vapour phase survive in equilibrium. The Figure 5 illustrates the behaviour of $\mathcal{A}(T, p_0; \alpha)$ for $p_0 > \bar{p}(T)$. There are two minima at $\alpha = 0$ and $\alpha \to \infty$. These are separated by a maximum at $\alpha = \alpha_C$, which is determined by

$$\alpha_C = \left(\frac{2\gamma}{3kT \ln\left(\frac{p_0}{\bar{p}(T)}\right)}\right)^{1/3}. \tag{43}$$

This is the classical Thomson (Lord Kelvin) [29] formula for the critical droplet number as a function of the vapour pressure, which is here controlled by the external pressure p_0. This formula serves as the basic law in the classical nucleation theory, because it may be interpreted as follows: If a droplet with α atoms occurs by fluctuation, it will further grow for $\alpha > \alpha_C$, whereas it will disappear again for $\alpha > \alpha_C$.

Recall that our treatment regards processes with fixed external pressure, which implies for a single substance, that there is no equilibrium for finite droplet size. If the volume of the container were fixed, we may find even for a single substance a stable droplet at finite size.
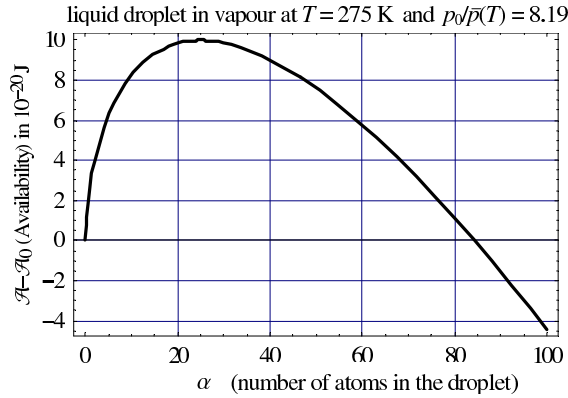
liquid droplet in vapour at $T = 275$ K and $p_0/\bar{p}(T) = 8.19$

Figure 5: Available free energy for vapour containing a single liquid droplet

3.2.2   A liquid droplet within a crystalline matrix

Our second example regards the evolution of liquid droplets in semi-insulating Gallium Arsenide (GaAs). Its constitution is described in detail in [6].

We consider the liquid as a compressible binary mixture with the constituents arsenic (As) and gallium (Ga). Furthermore we assume that the liquid behaves like a so called real mixture, so that the chemical part of the free energy contains entropic and energetic contributions.

The crystal of the solid phase consists of three face centered cubic sublattices with a common lattice constant. The sublattices are denoted by α, β and γ, and they are occupied by Ga, As and vacancies (V). Do not confuse the index of the sublattice α with the number of atoms in the liquid phase.

The Ga atoms only live on sublattice α, where they are the dominant constituent, whereas As and V are the dominant constituents on sublattices β and γ, respectively. Thus we describe the solid phase of GaAs by seven constituents. Its constitutive laws will be given, due to lack of other data, for an ideal mixture, so that the chemical part of the free energy contains only entropic contributions. From a mechanical point of view, the solid is a thermo-elastic body. The cubic anisotropy of GaAs is small, see [10, 9], and will be ignored in this study. In particular we assume that the liquid droplets have spherical shape. Thus their size is equivalently described by their radii or by the number of atoms. The distances between droplets are assumed to be much larger than their radii. Consequently there result stress components in the solid that exclusively depend on the radius r, which originates in the droplet center.

The concurrent thermodynamic processes are due to (i) chemical reactions, which determine the transfer of constituents between the sublattices of the solid, (ii) diffusional processes within the sublattices and in the liquid, (iii) interfacial processes, which determine the motion of the interfaces, and (iv) mechanical processes, which

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determine the stress components in the solid, σ^{ij}, the pressure in the liquid, p_{L}, and the total mole densities of solid, n_{S}, and liquid, n_{L}.

As before we assume that mechanical equilibrium is immediately established. Due to the high temperature range we are considering, it is reasonable to assume furthermore that chemical and diffusional equilibrium in the bulk are likewise established, so that the dynamics is driven exclusively by the motion of the interface.

The evaluation of the equations of quasi-static mechanical equilibrium has been carried out in detail in [6] and [8]. A misfitting spherical liquid droplet generates a homogeneous pressure p_{L} in the liquid and stresses that have radial symmetry in the solid surrounding of the droplet:

$$
\sigma^{rr} = -p_{\mathrm{R}} + K_{\mathrm{S}}a - 4G_{\mathrm{S}}b_\alpha \left(\frac{r_\alpha}{r}\right)^3, \quad \sigma^{\vartheta\vartheta} = \sigma^{\varphi\varphi} = -p_{\mathrm{R}} + K_{\mathrm{S}}a + 2G_{\mathrm{S}}b_\alpha \left(\frac{r_\alpha}{r}\right)^3, \ (44)
$$

and $\sigma^{ij} = 0$ for $i \neq j$. K_{S} and G_{S} denote the bulk and the shear modulus, respectively. p_{R} is the reference pressure, and a and b_α are the integration constants of the mechanical boundary problem. Due to $\lim_{r\to\infty} \sigma^{rr} = -p_0$, we have $a = (p_0 - p_{\mathrm{R}})/3K_{\mathrm{S}}$. The other integration constant b_α depends on the interfacial radius r_α and on the composition of solid and liquid. b_α is determined by Laplace's law. It reads

$$
p_{\mathrm{L}} + \sigma^{rr}_{r_\alpha} = \frac{2\sigma}{r_\alpha}, \quad \text{which can be written as} \quad p_{\mathrm{L}} - p_{\mathrm{S}} = \frac{2\sigma}{r_\alpha} - \sigma^{\langle rr\rangle}_{r_\alpha}. \tag{45}
$$

Here $p_{\mathrm{S}} = -\sigma^{ii}/3$ is the solid pressure, and $\sigma^{\langle ij\rangle}_{r_\alpha}$ denotes the traceless part of the stress at $r = r_\alpha$.

The calculation of the available free energy for the liquid/solid system starts from the decomposition

$$
\mathcal{A} = \Psi_{\mathrm{S}} + \Psi_{\mathrm{L}} + \Psi_{\mathrm{I}} + p_0(V_{\mathrm{S}} + V_{\mathrm{L}}). \tag{46}
$$

Ψ_{S} and V_{S} denote the free energy and the volume, respectively, of the solid phase. Recall that the solid is in contact with an inert gas, whereby we only indicate that the solid is subjected to an external hydrostatic pressure. The gas does not contribute to changes of $\mathcal{A}$. The important case that the gas can cross the solid/gas interface is treated in [8] on diffusion in the vicinity of an evolving droplet, and in a forthcoming paper [7] on the dynamics of a thermodynamic consistent Becker/Döring model.

As before, we introduce the Gibbs free energies $G_{\mathrm{S}} = \Psi_{\mathrm{S}} + p_{\mathrm{S}}V_{\mathrm{S}}$ and $G_{\mathrm{L}} = \Psi_{\mathrm{L}} + p_{\mathrm{L}}V_{\mathrm{L}}$ of the solid and the liquid, respectively, and obtain by means of (45)

$$
\mathcal{A} = G_{\mathrm{S}} + G_{\mathrm{L}} + \frac{1}{3}\sigma O_\alpha + \sigma^{\langle rr\rangle}_{r_\alpha} V_{\mathrm{L}}. \tag{47}
$$

The appearance of the radial component of the deviatoric stress exhibit an apparent difference to the corresponding representation (36) for the liquid/vapour system. However, note that stresses appear now even implicitly in G_{S}.

We denote the mean atomic masses of the liquid and the solid by m_α^{L} and m_α^{S}. The index α indicates a droplet with α liquid atoms, whose surrounding contains $N_0 - \alpha$

solid atoms. The available free energy can thus be written as

$$\mathcal{A} = (N_0 - \alpha)m_\alpha^S g_\alpha^S + \alpha m_\alpha^L g_\alpha^L + \omega_\alpha^I \quad \text{with} \quad \omega_\alpha^I = \frac{4\pi}{3}\sigma r_\alpha^2 + \sigma_{r_\alpha}^{\langle rr \rangle}\frac{4\pi}{3}r_\alpha^3 \qquad (48)$$

where g_α^L and g_α^S denote the specific Gibbs free energies.

For later use it is convenient to introduce the Gibbs free energy $G_0^S = N_0 \, m_0^S g_0^S$, which corresponds to a pure solid with N_0 atoms of mean atomic mass m_0^S, which is subjected to a hydrostatic pressure p_0. We rewrite (48) as

$$\mathcal{A} = N_0 m_0^S g_0^S + N_0(m_\alpha^S g_\alpha^S - m_0^S g_0^S) + \alpha(m_\alpha^L g_\alpha^L - m_\alpha^S g_\alpha^S) + \omega_\alpha^I. \qquad (49)$$

The reduction of the available free energy (49) to a function of a single variable, viz. the total number α of atoms in the droplet, is much more involved as in the former case, and for the most subtle details, we refer the reader to [6]. The reduction to a single variable relies on the assumption from above, whereupon mechanical, chemical and diffusional equilibrium are already established, so that the approach of the system to phase equilibrium is the only thermodynamic process that drives the evolution.

Finally we end up with a function $\mathcal{A}(T, p_0, N_0, X_0; \alpha)$, whose dependence on α, however, is not explicit, because the elimination of the other variables relies on a transcendental algebraic system, see [6].

There are important differences with respect to the former case of a single substance that consists of a liquid droplet in vapour. (i) The dependence of $\mathcal{A}$ on the total number of atoms in the system, N_0, and on the mean arsenic concentration of the solid X_0, is nontrivial. Their values have, in contrast to the former case, a significant influence on the evolution of the droplet. (ii) Accordingly to the former case, a critical α_C may exist, where $\mathcal{A}$ assumes a maximum. However, in contrast to the the former case, the maximum is followed by a minimum for a finite number of atoms, $\alpha_C < \alpha_E < \infty$, in the droplet. In other words: Stable droplets of finite size may appear in the solid phase.

In the liquid/vapour system, large droplets are energetically much more favourable than smaller droplets in the regime, $p_0 > \bar{p}(T)$, because they have a smaller surface energy than smaller droplets, and this is the only mechanism to reduce the available free energy. In the liquid/solid case, there are two new phenomena: Large droplets produce larger elastic energy than smaller droplets do, and the annihilation of vacancies during the growth of a liquid droplet leads to a decrease of the entropy. Both phenomena stabilize droplets of finite size.

3.3 Available free energy for many droplet systems

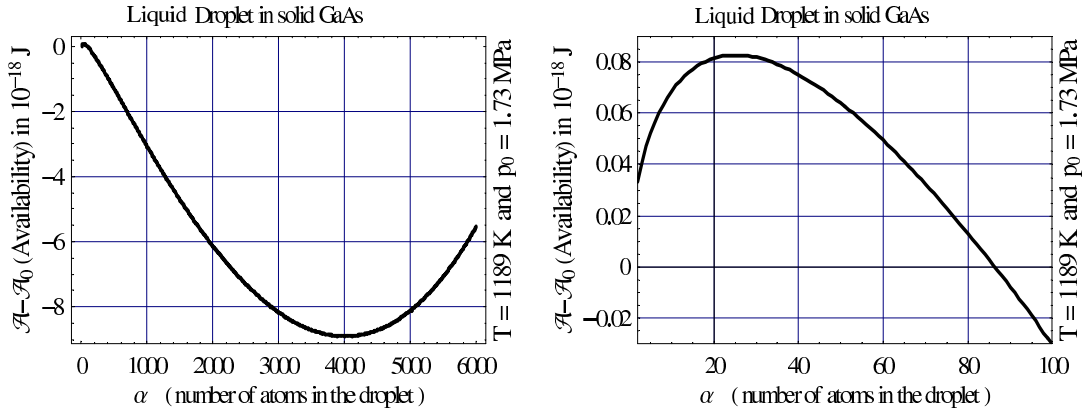In this section we derive the representation (19) of the available free energy of many droplet systems, $\mathfrak{A}$.

Figure 6: Available free energy for solid GaAs containing a single arsenic-rich liquid droplet

3.3.1 The liquid/solid system

To this end we consider at first the available free energy for the liquid/solid case, because it is the more general case. Hereafter the liquid/vapour case will follow as a simplification. Recall that we deal with situations where the distances between droplets are much larger than their radii. This fact enables the following reasoning:
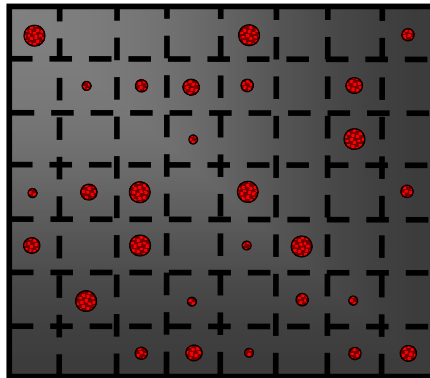

Figure 7: Ensemble of single droplet systems

We consider an ensemble of ν subsystems. Each of them contains the same number of atoms, N_0, has the same mean composition, X_0, and is under the same external pressure, p_0. At time t, for $2 \leq \alpha \leq \nu$ there are $Z(t, \alpha)$ subsystems with a single droplet containing α liquid atoms and $(N_0 - \alpha)$ solid atoms, and there are $Z_0(t)$ subsystems without droplets. The total number of solid atoms will be denoted by $Z(t, 1)$, so that there holds

$$Z(t, 1) = N_0 Z_0(t) + \sum_{\alpha=2}^{\nu} (N_0 - \alpha) Z(t, \alpha). \tag{50}$$

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Let us now denote the total number of liquid and solid atoms, which is fixed by N. Thus there holds

$$N_0 Z_0(t) = N - \sum_{\alpha=2}^{\nu} \alpha Z(t, \alpha) - \sum_{\alpha=2}^{\nu} (N_0 - \alpha) Z(t, \alpha). \tag{51}$$

Next we decompose the Gibbs free energies. For $2 \le \alpha \le \nu$, we denote the mean masses of the liquid and solid atoms of subsystems by m_α^{L}, m_α^{S}. The index α indicates that the subsystem contains a droplet with α liquid and $N_0 - \alpha$ solid atoms. m_0^{S} is the mean atomic mass of the pure solid subsystems. The Gibbs free energies can then be written as

$$G^{\mathrm{L}} = \sum_{\alpha=2}^{\nu} Z(t, \alpha)\, \alpha\, m_\alpha^{\mathrm{L}}\, g_\alpha^{\mathrm{L}} \quad \text{and} \tag{52}$$

$$G^{\mathrm{S}} = Z_0(t) N_0\, m_0^{\mathrm{S}}\, g_0^{\mathrm{S}} + \sum_{\alpha=2}^{\nu} Z(t, \alpha)\, (N_0 - \alpha)\, m_\alpha^{\mathrm{S}}\, g_\alpha^{\mathrm{S}},$$

where g_α^{L} and g_α^{S} denote the specific Gibbs free energies.

Furthermore we denote the sum of surface free energies and bulk stresses by Ω^{I}, see (47), and write

$$\Omega^{\mathrm{I}} = \sum_{\alpha=1}^{\nu} Z(t, \alpha) \omega_\alpha^{\mathrm{I}} \quad \text{with} \quad \omega_\alpha^{\mathrm{I}} = \begin{cases} 0 & \alpha = 1 \\ \frac{4\pi}{3}\sigma r_\alpha^2 + \sigma_{r_\alpha}^{\langle rr \rangle} \frac{4\pi}{3} r_\alpha^3 & \alpha \ge 2 \end{cases} \quad \text{for} \quad . \tag{53}$$

We have set $\omega_1^{\mathrm{I}} = 0$, because it refers to to a pure solid under hydrostatic pressure p_0. Furthermore, surface tension appears by definition exclusively for $\alpha \ge 2$.

G^{S}, G^{L} and Ω^{I} contribute additively to the available free energy $\mathfrak{A}$ of the total ensemble. However, there is an additional contribution, which arises because there are ν different constituents in the ensemble: solid atoms and droplets with $\nu - 1$ different sizes. We consider the processes between these constituents as chemical reactions, and consequently, according to chemical thermodynamics there is the mixing entropy, see [12, 13, 20],

$$S_{\mathrm{mix}} = -k \sum_{\alpha=1}^{\nu} Z(t, \alpha) \ln\left(\frac{Z(t, \alpha)}{N_{\mathrm{D}}}\right), \tag{54}$$

which likewise contributes additively to $\mathfrak{A}$ by $-T S_{\mathrm{mix}}$.

The available free energy of a many droplet system consisting of liquid droplets in a crystalline solid is thus represented by

$$\mathfrak{A} = G^{\mathrm{S}} + G^{\mathrm{L}} + \Omega^{\mathrm{I}} - T S_{\mathrm{mix}}. \tag{55}$$

A representation that reveals the dependence of $\mathfrak{A}$ on the distribution functions $Z(t, \alpha)$, results by virtue of (51)/ (54):

$$\mathfrak{A} = N m_0^{\mathrm{S}} g_0^{\mathrm{S}} + \sum_{\alpha=1}^{\nu} Z(t, \alpha) \left(\mathcal{A}_\alpha + kT \ln \left(\frac{Z(t, \alpha)}{N_{\mathrm{D}}(t)} \right) \right) . \tag{56}$$

The newly introduced quantity

$$\mathcal{A}_\alpha = N_0 (m_\alpha^{\mathrm{S}} g_\alpha^{\mathrm{S}} - m_0^{\mathrm{S}} g_0^{\mathrm{S}}) + \alpha (m_\alpha^{\mathrm{L}} g_\alpha^{\mathrm{L}} - m_\alpha^{\mathrm{S}} g_\alpha^{\mathrm{S}}) + \omega_\alpha^{\mathrm{I}} \quad \text{with} \quad \mathcal{A}_1 = 0 \tag{57}$$

may be now identified, up to a constant, with the available free energy (49) of a single droplet system. Note that $\alpha = 1$ indicates the ensemble members that contain no droplet at all. We thus set $m_1^{\mathrm{S}} g_1^{\mathrm{S}} = m_0^{\mathrm{S}} g_0^{\mathrm{S}}$, $m_1^{\mathrm{L}} g_1^{\mathrm{L}} = m_1^{\mathrm{S}} g_1^{\mathrm{S}}$ and $\omega_1^{\mathrm{I}} = 0$.

3.3.2 The liquid/vapour system

The available free energy for a many droplet system consisting of liquid droplets in a gas can be read of from the representation (56) and (57) by changing the subscript S that refers to the solid to a subscript V which indicates the vapour.

Furthermore, there are three simplifications: (i) the liquid/vapour case regards a single substance, so that the mean atomic masses in (57) become independent of the number of molecules in the droplet, and furthermore $m^{\mathrm{L}} = m^{\mathrm{V}} = m$, ($ii$) the specific Gibbs free energies of the vapour do not depend on how many molecules are contained in the droplet, so that the first term in (57) does not appear. (iii) there are no deviatoric stresses in $\omega_\alpha^{\mathrm{I}}$.

Thus, up to a constant, the available free energy for a many droplet system reads

$$\mathfrak{A} = \sum_{\alpha=1}^{\nu} Z(t, \alpha) \left(\mathcal{A}_\alpha + kT \ln \left(\frac{Z(t, \alpha)}{N_{\mathrm{D}}(t)} \right) \right) , \tag{58}$$

where $\mathcal{A}_\alpha$ is now defined by

$$\mathcal{A}_1 = 0, \quad \text{and} \quad \mathcal{A}_\alpha = -kT \ln \left(\frac{p_0}{\bar{p}(T)} \right) \alpha + \gamma \alpha^{2/3} \quad \text{for} \quad \alpha \geq 2. \tag{59}$$

4 Determination of equilibria

The objective of this chapter is the determination of possible equilibria according to the equations (21), (22) and (23) for the two considered many droplet systems. An important aspect will be a study on the influence of the arbitrary restriction, that there is largest droplet with ν atoms or molecules. In particular, we will consider the limiting case $\nu \to \infty$

4.1 The ν dependence of $\lambda_{\mathbf{eq}} = \frac{Z_{\mathbf{eq}}(1)}{N_{\mathbf{D}}^{\mathbf{eq}}}$

The dependence of the equilibrium distribution $Z_{eq}(\alpha)$ on the number ν of atoms or molecules in the largest droplet, results from the ν dependence of the parameter λ_{eq}, which solves the equation (22):

$$\sum_{\alpha=1}^{\nu} \lambda_{eq}^{\alpha} \exp\left(-\frac{\mathcal{A}_{\alpha}}{kT}\right) = 1. \qquad (60)$$

Recall that by definition λ_{eq} satisfies $0 < \lambda_{eq} \leq 1$. Let us denote, for a given list of increasing ν, the sequence of the solutions to (60) by λ_{ν}. The result of a numerical calculation of the sequence is shown in Figure 8 for the liquid/vapour system and in Figure 9 for the liquid/solid system.
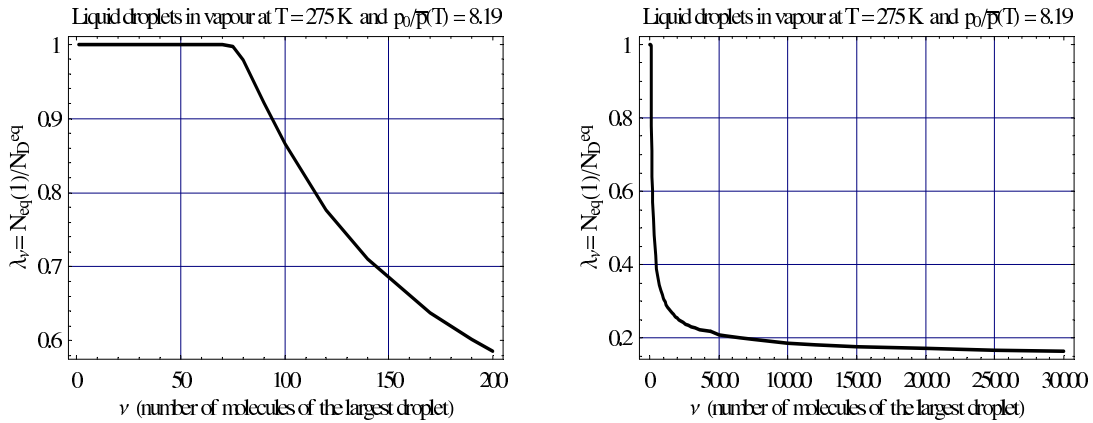

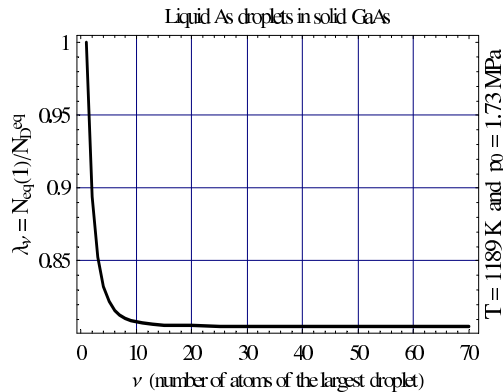Figure 8: The liquid/vapour system (H_2O)

Figure 9: The liquid/solid system (GaAs)

In the liquid/vapour system, λ_{ν} remains near to 1 for small and moderate values of ν. This is in contrast to the liquid/solid system, where λ_{ν} decreases rapidly for values

of ν in the range of the critical droplet and it converges to 0.8 for further increasing ν. The liquid/vapour system exhibits a further difference to the liquid/solid system for large ν: A limiting value, which turns out as $\bar{p}(T)/p_0$ according to the following discussion, will never be achieved.

These differences between the two systems result from the different properties of their available free energies $\mathcal{A}_\alpha$. The liquid/vapour system, see Figure 5, has a single droplet available free energy $\mathcal{A}_\alpha$, that is unbounded from below for increasing α, whereas the corresponding available free energy of the liquid/solid system, see Figure 6, exhibits a local minimum on the right hand side of the nucleation barrier and grows with further increasing α.

Regarding the liquid/solid system we conclude that λ_ν becomes independent of ν for sufficient large ν. Thus a ν independent equilibrium distribution $Z_{\mathrm{eq}}(\alpha)$ exists, see Figure 11 in the next Section.

Next we study the behaviour of λ_ν for the liquid/vapour system. Note at first that its available free energy $\mathcal{A}_\alpha$ depends on the saturation parameter $s = p_0/\bar{p}(T) > 1$. Let us define the function

$$F_\nu(s;\lambda) = \sum_{\alpha=1}^{\nu} \lambda^\alpha \exp\left(-\frac{\mathcal{A}_\alpha}{kT}\right), \tag{61}$$

which can be written by virtue of (59) and with the positive constant $a = \gamma/kT$ as

$$F_\nu(s;\lambda) = \lambda + \sum_{\alpha=2}^{\nu} (\lambda s)^\alpha \exp(-a\alpha^{2/3}). \tag{62}$$

In the following we list the properties of $F_\nu(s;\lambda)$.

1. The radius of convergence of the series

$$S(\lambda s) = \sum_{\alpha=2}^{\infty} (\lambda s)^\alpha \exp(-a\alpha^{2/3}) \tag{63}$$

   is given by $\lambda s = 1$. Moreover, the series converges also for $\lambda s = 1$, because

$$S(1) \leq \int_1^\infty \exp(-a\alpha^{2/3})d\alpha = \frac{3}{2a}\left(\exp(-a) + \sqrt{\frac{\pi}{4a}}\left(1 - \mathrm{erf}(\sqrt{a})\right)\right). \tag{64}$$

2. We denote the sum $S(1)$ by ε. For $a = 9.2223$, which is a typical value for water at $T = 275.2\mathrm{K}$, we obtain $\varepsilon = 4.43431 \times 10^{-7}$.

3. $\lim_{\nu\to\infty} F_\nu(s;\lambda)$ is estimated according to

$$F_\nu(s;\lambda) < \lim_{\nu\to\infty} F_\nu(s;\lambda) \leq \lim_{\nu\to\infty} F_\nu(s;1/s) = 1/s + \varepsilon. \tag{65}$$

   Note that the right hand side of the inequality is independent of λ.

4. For fixed $s > 1/(1 - \varepsilon)$ and each finite ν, the sequence of equations

$$F_\nu(s; \lambda) = 1. \tag{66}$$

implies a sequence of solutions λ_ν whose members have the properties

$$0 < \lambda_\nu \leq 1 \quad \text{and} \quad \lambda_\nu s > 1. \tag{67}$$

Consequently, for finite ν and $s > 1/(1 - \varepsilon)$, these solutions are outside the radius of convergence of the series (63).

5. For $\nu \to \infty$, $\lambda_\nu s$ tends slowly to 1 from above. However, due to $F_\nu(s; \lambda_\nu) > F_{\nu+1}(s; \lambda_{\nu+1}) > 1$ for each finite ν, this limiting value cannot be reached.

6. We conclude that in the limit $\nu \to \infty$, the equations $F_\nu(s; \lambda) = 1$ can only be solved, if the fixed but free parameter s is restricted by $s \leq 1/(1 - \varepsilon)$. However, there is no physical reason to restrict the parameter s in this way. For example, Becker and Döring have $4 < s < 6$ in their devices.

In summary the final conclusion is stated as follows: There is no solution of (60) in the limiting case $\nu \to \infty$. For finite ν, a unique solution of (60) exists. However, due to the arbitrarily choice of a largest droplet, it generates an artificial ν dependence of the resulting equilibrium distribution $Z_{\text{eq}}(\alpha)$. The physical reason of the phenomenon is the simplicity of the liquid/vapour system containing a single substance. The only possibility to reduce its available free energy is given by the reduction of the interfacial free energy, which drives a system with vapour and liquid droplets finally into a pure liquid phase, so that there is no coexistence of vapour and a droplet distribution with various sizes in equilibrium.

Recall once more the differences of the liquid/vapour system to the liquid/solid system containing semi-insulating GaAs. This liquid/solid system has a single droplet free energy with a local minimum at finite droplet size. The very large droplets are prevented here due to two mechanisms that are absent in the former case: The appearance of large droplets is accompanied by large deviatoric stresses, which lead to an increase of the energetic contribution to the available free energy. Secondly, the entropic contribution decreases, because the growth process of a liquid droplet in the GaAs solid is accompanied by annihilation of vacancies at the liquid/solid interface.

4.2 Equilibrium distributions

Finally we discuss the equilibrium size distributions of the droplets. These are determined by the equations (21), (22) and (23).

We consider at first the liquid/vapour system. According to the results of our study in Section 4.1, an equilibrium size distribution of droplets is only possible, if we terminate the size $\nu < \infty$ of the largest droplet. Figure 10 shows three

distributions for $\nu = 25, 50, 75, 100$, left hand side, and for $\nu = 100, 800$ on the right hand side. There is no convergence if we increase ν: In the limiting case $\nu \to \infty$, the liquid/vapour system drives into a single liquid phase.
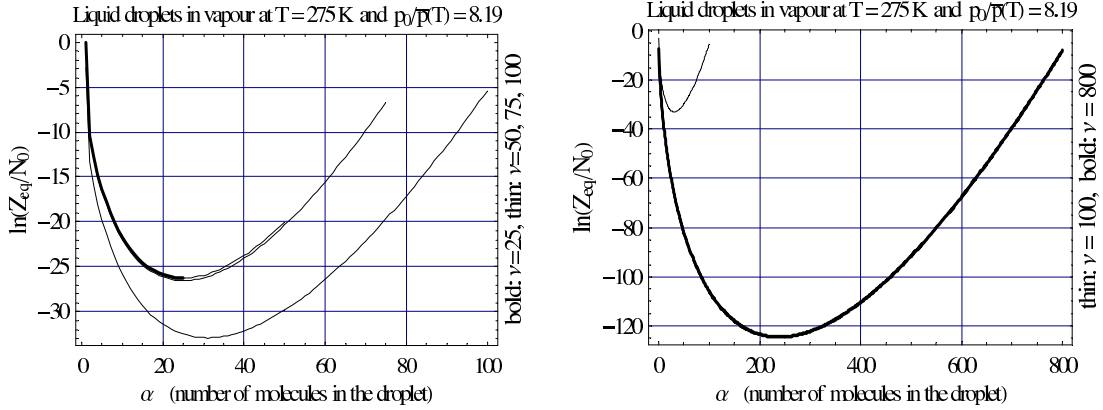

Figure 10: The liquid/vapour system (H_2O)

The liquid/solid system reveals a different behaviour. Here the results do not depend on ν for $\nu > \alpha_C = 25$. Figure 11 shows size distributions for various fixed ν, with $\alpha_C < \nu \le 5000$. On the left hand side, the size distribution is plotted in the range $1 \le \alpha \le \nu$, and in $420 \le \alpha \le 900$ on the right hand side. A ν dependence is not visible. We conclude that the limiting case $\nu \to \infty$ exists in this case. An equilibrium with a size distribution of droplets is thus attainable.
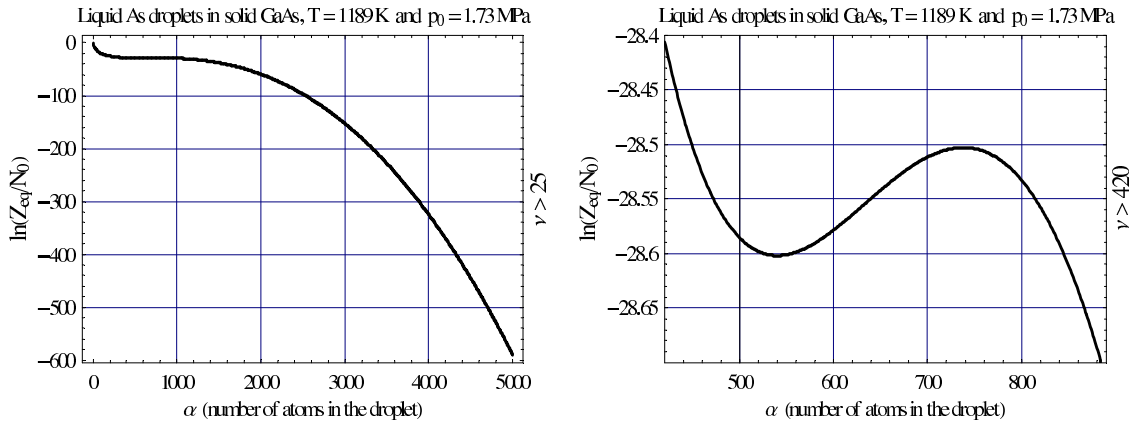

Figure 11: The liquid/solid system (GaAs)

5 Summary and outlook

In order to model the appearance of liquid droplets in solid GaAs, we have revisited the classical BD model as it is described in the literature. Originally, the exclusive

objective was the incorporation of deviatoric bulk stresses, which arise during the liquid/solid phase transition, into the existing model.

However, we found that there is no BD model in the literature, that is in accordance with the second law of thermodynamics. In particular, the possible equilibria, if there are any, contradict the equilibria resulting from a purely thermodynamic point of view. This failure has its source in the constitutive laws that are used for the determination of the transition rates. Thus the formulation of a BD model which is consistent with the second law became the first objective of this study.

Next we have applied the modified BD model with thermodynamic consistent transition rates to two explicit cases: These are the classical liquid/vapour system for a pure substance, and the liquid/solid system for semi-insulating GaAs. The main difference of the two systems regards the available free energies for the corresponding single droplet systems.

Assuming that the processes in both systems are isothermal and pressure controlled, we have studied the resulting equilibria. It turns out, that the liquid/solid system may assume an equilibrium distribution of droplets of various sizes, which is in contrast to the well known behaviour of the liquid/vapour system, which tends to form a single liquid phase.

The next studies, which we have already started, regard

(i) Experimental devices, which are volume controlled. In this case, even the simple liquid/vapour system may assume an equilibrium with a distribution of droplet sizes.

(ii) A study on the dynamics of the thermodynamic consistent BD model.

(iii) The formulation of a BD model for an open liquid/solid system (GaAs), which is embedded in an arsenic gas atmosphere, so that the arsenic can enter or leave the solid phase.

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