The Influence of Depletion Effects
on Homogeneous Nucleation Rates

The influence of depletion effects on nucleation is investigated. It is shown that starting only with monomers in a very short first stage of phase transition a primary distribution in cluster size evolves, which reduces the initial supersaturation and results in a lower nucleation rate compared with the value predicted by the classical nucleation theory.

Der Einfluß von Aufzehrungseffekten auf die Keimbildung wird untersucht. Es wird gezeigt, daß, ausgehend von einem Zustand mit ausschließlich Monomeren im System, sich bereits nach sehr kurzer Zeit eine Clustergrößenverteilung entwickelt, die die Anfangssättigung reduziert und zu einer, verglichen mit der klassischen Keimbildungstheorie, niedrigeren Keimbildungsrate führt.

1. Introduction

Despite its long history the classical nucleation theory remains till now a widely applied tool for the description of nucleation processes. Hereby it is assumed usually that the state of the medium, where the transition occures, is not changed in the period of nucleation. This additional assumption results in the possibility of the establishment of a steady-state nucleation rate after some transient period characterized by a time-lag τ.

This steady-state nucleation rate I_s can be expressed, generally, as

$$I_s = w^+(l_{cr}) \cdot N_1 \cdot Z \cdot \exp\left\{ -\frac{\Delta G(l_{cr})}{kT} \right\} \tag{1}$$

where $\Delta G(l_{cr})$ is the work of formation of a critical cluster with size l_{cr}, k is the Boltzmann constant, T the Kelvin temperature, N_1 the number of monomers in the system, Z the Zeldovich factor and $w^+(l_{cr})$ the rate of attachment of monomers to the critical nucleus [1, 2].
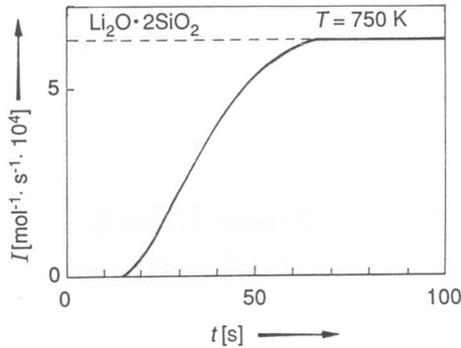
Fig. 1. Time-dependent nucleation rate I for Lithiumdisilicate under constant thermodynamic constraints $I_s = 6.3 \cdot 10^4 \, \mathrm{mol}^{-1} \, \mathrm{s}^{-1}$, $T = 750 \, \mathrm{K}$ (parameters after [6]).

It was shown in preceding papers that depletion effects affect the work of formation of critical clusters and thus the nucleation rate. Moreover, they determine qualitatively the whole course of the transition [3 – 5].

However, there exists another type of depletion connected with the formation of a primary cluster distribution consisting of aggregates of small undercritical cluster sizes. We want to remark that this effect differs from the effect on supersaturation investigated by Katz *et al.* [6] caused by stable undercritical complexes. The analysis of the influence of this effect on the value of the nucleation rate is the aim of the present communication.

2. Nucleation under time-independent conditions

The typical curve for the time-dependence of the nucleation rate I, defined as the number of supercritical clusters, formed in the system per unit time for time-independent conditions, is illustrated in Fig. 1 for the case of isoconcentration crystallization in a Lithiumdisilicate melt at constant temperature. It can be seen that after some time-lag τ the nucleation rate I approaches the classical value, given by Eq. (1).

Nucleation is described here in terms of a system of rate equations discussed in detail elsewhere [7 – 9].

3. Influence of depletion effects on the nucleation rate

If constancy of concentration is replaced by constancy of the total particle number of the system, then the process of cluster formation leads to a change of the density of monomers in a condensed system. The results of numerical calculations of the size distribution for the case of a quasi-binary melt are shown in Fig. 2.
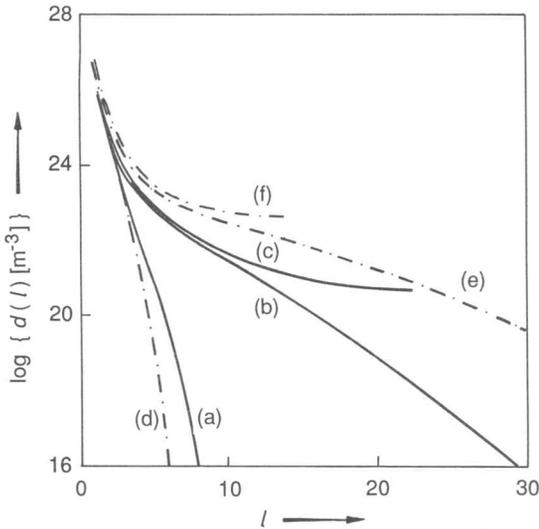
Fig. 2. Initial stage of the evolution of cluster size distribution $d(l)$ for AgCl-segregation from a sodiumborate melt. l denotes the number of particles in the cluster. Full lines: initial AgCl-concentration c_1 $(t = 0) = 3.2 \cdot 10^{26}$ m^{-3} (a) $t = 1.1 \cdot 10^{-4}$ s; (b) $t = 1.1 \cdot 10^{-2}$ s; (c) equilibrium distribution. Dashed-dotted lines: c_1 $(t = 0) = 4.2 \cdot 10^{26}$ m^{-3}; (d) $t = 8.5 \cdot 10^{-6}$ s; (e) $t = 1.9 \cdot 10^{-2}$ s; (f) equilibrium distribution (parameters after [12].

Starting with an initial distribution consisting only of monomers, this initial state of the system relaxes in a very short first stage of the transition into a primary distribution, consisting of undercritical clusters with a relatively low number of particles. Because of the use of the principle of detailed balance [7, 10] in the numerical solution of the rate equation system which involves the equilibrium distribution N^0 with

$$N^0 = N_1 \cdot \exp\left\{-\frac{\Delta G(l)}{kT}\right\} \tag{2}$$

the cluster size distribution for small undercritical clusters relaxes towards this equilibrium distribution in the very initial stage. As a result, the nucleation rate cannot reach the theoretical upper limit, given by Eq. (1).

Moreover, a calculation of the nucleation rate for different initial supersaturations shows, that the importance of this effect depends on the supersaturation itself (Table 1).

In addition, it can be obtained from Fig. 3, that a stationary state of the system, that means also a stationary nucleation rate, is established for longer periods of time only, if the initial supersaturation is relatively low (compare [4]).

Table 1. Decrease of the relative supersaturation, $\Delta g/kT$, and of the classical nucleation rate I_{class} [Eq. (1)] after initial relaxation for different c_1 ($t = 0$) (parameters see Fig. 2).

$t = 0$			After initial relaxation	
c_1 [m^{-3} 10^{26}]	$\Delta g/kT$	I_{class} [s^{-1} m^{-3}]	$\Delta g/kT$	I_{class} [s^{-1} m^{-3}]
4.2	1.07	$2.0 \cdot 10^{24}$	0.96	$1.4 \cdot 10^{23}$
5.5	1.31	$1.1 \cdot 10^{26}$	1.15	$1.0 \cdot 10^{25}$
6.5	1.46	$6.4 \cdot 10^{26}$	1.24	$4.7 \cdot 10^{25}$
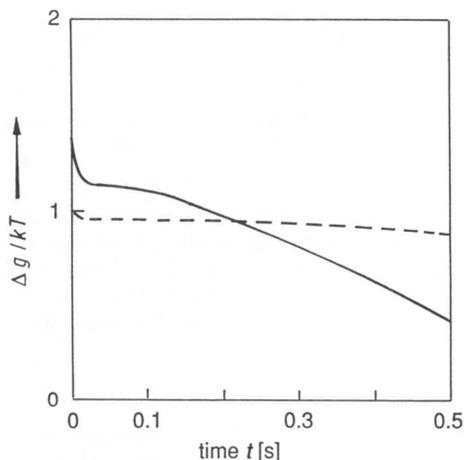
Fig. 3. Relaxation of the effective supersaturation, $\Delta g/kT$, for AgCl segregation from a sodiumborate melt in dependence on the initial AgCl concentration. Full line: c_1 ($t = 0$) $= 4.2 \cdot 10^{26}$ m^{-3}. Dashed line: $c_1(t = 0) = 3.2 \cdot 10^{28}$ m^{-3} (parameters after [12]).

4. Discussion

It was shown in the preceding paragraphs that for the case, that depletion effects have to be taken into account in the course of the transition, the supersaturation cannot be adequately expressed via the total number of monomers in the system. Instead of this expression an effective supersaturation can be introduced, where the total number of monomers is replaced by a smaller number which remains after a substraction of the monomers belonging to the primary distribution. The effect on the nucleation rate is, in general, significant and depends, as it was shown, on the value of the initial supersaturation.

To some extent this effect resembles the "heat of reaction effect" on nucleation discussed by Strey *et al.* [11] for condensation processes in

adiabatically closed systems. However, the effect mentioned here is some-what more general, since it is of importance already for isothermal con-ditions. Of course, it has to be taken into account also for adiabatically closed systems.

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