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Nucleus growth in liquid crystals

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The phase ordering kinetics of various liquid crystalline materials from well known series (PCH, CCH, nO. m, BCH and CB) when turning from a disordered to an ordered phase induced by a rapid temperature quench have been investigated. The process of phase ordering can generally be described by the growth of a characteristic length L. The exponents n of the theoretically predicted universal growth law $L(t) \sim t^n$ have been determined. In this paper we present in particular the results for the kinetics of phase formation which takes place under the mechanism of nucleus growth. As characteristic length we chose the diameter of the nuclei. We obtained values for n between 0·5 and 1 dependent on the depth of the temperature quench. These results for mainly spherical shaped nematic and smectic germs are discussed in terms of the Allen–Cahn theory for the movement of an antiphase boundary (APB). As a lower limiting value, 0·5 confirms the classical theory, while 1 as an upper limiting value can be explained by the introduction of a volume driving force.

1. Introduction

During the last two decades there has been a growing interest in the theory of phase ordering processes. Obviously, the most suitable way to describe the kinetics of ordering is to follow the growth of a characteristic length L [1]. L may be the correlation length of order, a germ radius or an average domain size. Often a universal growth law

$$L(t) \sim t^n \tag{1}$$

is obtained where t is the time after a temperature quench which has induced a phase transition and n is the universal growth exponent. This quantity is not a specific one, so it is assumed to be independent of the temperature and the nature of molecular interactions inside the system. The information implied in n is related to the order parameter Φ of the system. One of the most common theories of phase ordering describes the coarsening process by the movement of antiphase boundaries (APBs) [2]. An antiphase boundary separates two homogeneous areas which exhibit different values of the order parameter. The APB's velocity v can be understood as the growth of the characteristic length L. It turns out to be due only to the mean curvature K of the APB:

$$v \equiv \frac{dL}{dt} = MK \tag{2}$$

where M is a constant.

In the most simple case of a non-conserved, scalar order parameter, Bray obtained an exponent 0·5 by integrating equation (2) [3]. This value is valid only for spherical shaped domains where the mean curvature can be defined as the reciprocal radius or diameter of the nuclei which is formally the same.

In this paper we will focus attention on the conditions described above which were quite easy to realize in experiments on liquid crystals. Nevertheless, some other conservation laws for the order parameter are possible. For a conserved, scalar order parameter a value of 0·333 is predicted [4]. Considering a multi-component order parameter there is no change in n for a non-conserved quantity, but the prediction for the conserved order parameter is 0·25 [5]. However, these latter cases do not fit with the liquid crystalline systems we are presenting in the following.

Liquid crystals have been found to be suitable model systems to investigate these growth laws [6]. We have determined the exponents for nematic germs growing out of the isotropic phase and for smectic germs growing out of the nematic phase. Additionally, we have

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investigated the evolution of germs of Blue Phase II growing out of Blue Phase III.

In §2 we present the experimental set-up and the results obtained for the growth exponents. In §3 we discuss these results in terms of the Allen–Cahn theory. Deviations from theoretical prediction are explained by an extension of the theory.

2. Experimental

2.1. *Experimental set-up*

The nucleus growth was observed by the use of a polarizing microscope and video-recorded by a CCD-camera. The germ radii (diameters) were determined by means of digital image processing or direct on-screen measurement. Temperature control for carrying out the quenches was ensured by a common hot stage (Mettler) with an accuracy of 0·01°C. For the Blue Phases we used a home-mode hot stage based on Peltier elements which worked with an accuracy five times higher compared with the Mettler hot stage in the low temperature region (≪35°C). In performing the quench experiments we had to focus on the fact that the quench itself was carried out quite rapidly. When the germs began to nucleate, it was necessary that the system again fulfilled isothermal conditions. The quench led to supercooling, but the observed growth had to be isothermal.

The liquid crystals were mounted between glass plates. The cell thickness was 30 µm for the BPs (Blue Phases) and 12 µm for the other systems. In the case of observation of smectic germ growth, the glass plates were coated with lecithin in order to achieve homeotropic orientation.

The substances under investigation were common liquid crystalline compounds from well known homologous series. Table 1 gives a survey of the compounds used.

2.2. *Results*

2.2.1. *The phase transition nematic ← isotropic*

One can image that the I–N phase transition occurs under the mechanism of spinodal decomposition [11], but this has not been observed for low molecular mass liquid crystals so far [12]. The phase formation in such systems can usually be observed as the growth of germs which arise from nucleation. However, these germs must have reached a critical size in order to grow further. For an isotropic phase turning into a nematic phase, the formation of spherical shaped germs can usually be observed. Figure 1 shows the growth of such spheres in PCH5. We did not choose the radius of the germs as the characteristic length L, but the diameter, because this quantity formally obeys the same universal growth law of equation (1). Moreover, the diameter can be determined with higher accuracy than the radius.

The evolution of the diameter with time for different quench depths ΔT is shown in figure 2. The starting temperature T_{start} was the same for each measurement. It is approximately equal to the thermodynamic phase transition temperature T_{C}.

Obviously the determined growth exponent n is dependent on ΔT. For a small value of ΔT the resulting exponent is about 0·5 and for a large value of ΔT it equals approximately 1. The results were obtained by investigating the growth of nematic germs in other compounds. Table 2 gives an overview of different results.

2.2.2. *The phase transition smectic ← nematic*

For a smectic phase forming from a nematic phase, the shape of the growing germs will be spherical if the liquid crystal is homeotropically oriented in the cell, i.e. the director is aligned parallel to the normal to the cell surface. Otherwise one can observe the growth of dendrites [13].

In figure 3 a pictorial series is presented which shows the evolution in the growth of SmA germs in 4O.4. The pictures are presented in digitized form in order to achieve a better contrast. The homeotropic alignment leads to pseudo-isotropic optical behaviour for both the nematic phase and the smectic phase. This means that both phases appear black between crossed polarizers. Thus the phase boundary between them is hard to locate. By digital processing of the video-recorded images, the contrast could be improved. In the early stage of the growth the shape of the germs is spherical, so as the

Table 1. List of liquid crystalline compounds investigated, their chemical formulae and phase sequences. The phase transitions of interest here are printed in *italics*; transition temperatures are given in °C (Cy = cyclohexyl; Ph = phenyl).

Compound	Chemical structure	Phase sequence	Ref.
PCH5	$H_{11}C_5$–Cy–Ph–CN	Cr 31 *N 54·5 I*	[7]
PCH7	$H_{15}C_7$–Cy–Ph–CN	Cr 30 *N 57·5 I*	[7]
CCH7	$H_{15}C_7$–Cy–Cy–CN	Cr 71 *N 83·5 I*	[8]
6O.4	$H_{13}C_6O$–Ph–CH=N–Ph–C_4H_9	Cr 30 G 57 SmB 59 SmA 69·7 *N 77·3 I*	[9]
4O.4	H_9C_4O–Ph–CH=N–Ph–C_4H_9	Cr 38 G 41 SmB 44·7 *SmA 44·9 N* 73 I	[9]
BCH70	$H_{15}C_7$–Cy–Ph–Ph	Cr 74 *SmB 76·7 N* 77·3 I	[10]
CB15 (63%)/E9	chiral nematic mixture	*BPII 18·7 BPIII*	[15]

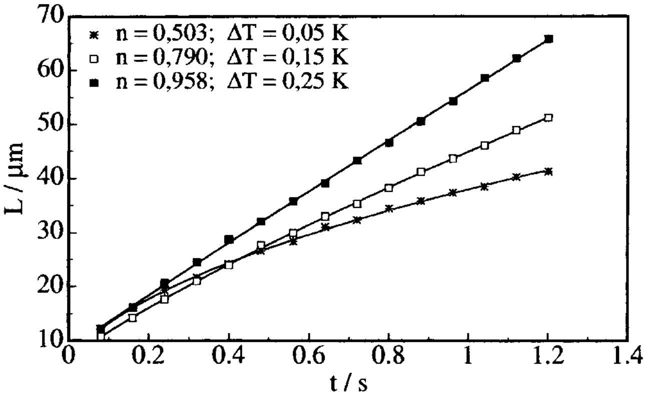

Figure 2. Evolution of the diameter of nematic germs in PCH5 for different quench depths. The values for L are average values over several germs growing under the same conditions in one single experiment.

Table 2. Average growth exponents n for spherical nematic germs in various systems at different quench depths. The highest quench depth (best supercooling) was realized for PCH7. The phase transitions should always occur under isothermal conditions.

	ΔT/K			
Compound	0·05	0·15	0·25	0·35
PCH5	0·50	0·78	1·04	—
PCH7	0·43	0·52	0·66	0·86
CCH7	0·62	0·91	1·01	—
6O.4	0·63	0·90	1·08	—

characteristic length the diameter was chosen by analogy with the nematic germs. Later the germs lose their spherical shape and the structure becomes bulbous. The evolution of the characteristic length was only pursued in the early stages where L could be defined clearly. Figure 4 shows the growth of L for different quench depths.

We also investigated the growth of SmB germs and obtained similar results. Table 3 gives a comparative survey.

2.2.3. *The phase transition BPII ← BPIII*

Blue Phase II monocrystallites exhibit a quadratic shape [14]. But due to interfacial tensions the germs do not show a regular shape, but have rounded corners and edges. Figure 5 illustrates the growth process of BPII germs growing out of the amorphous BPIII in a chiral nematic mixture of CB15 and E9, where E9 is

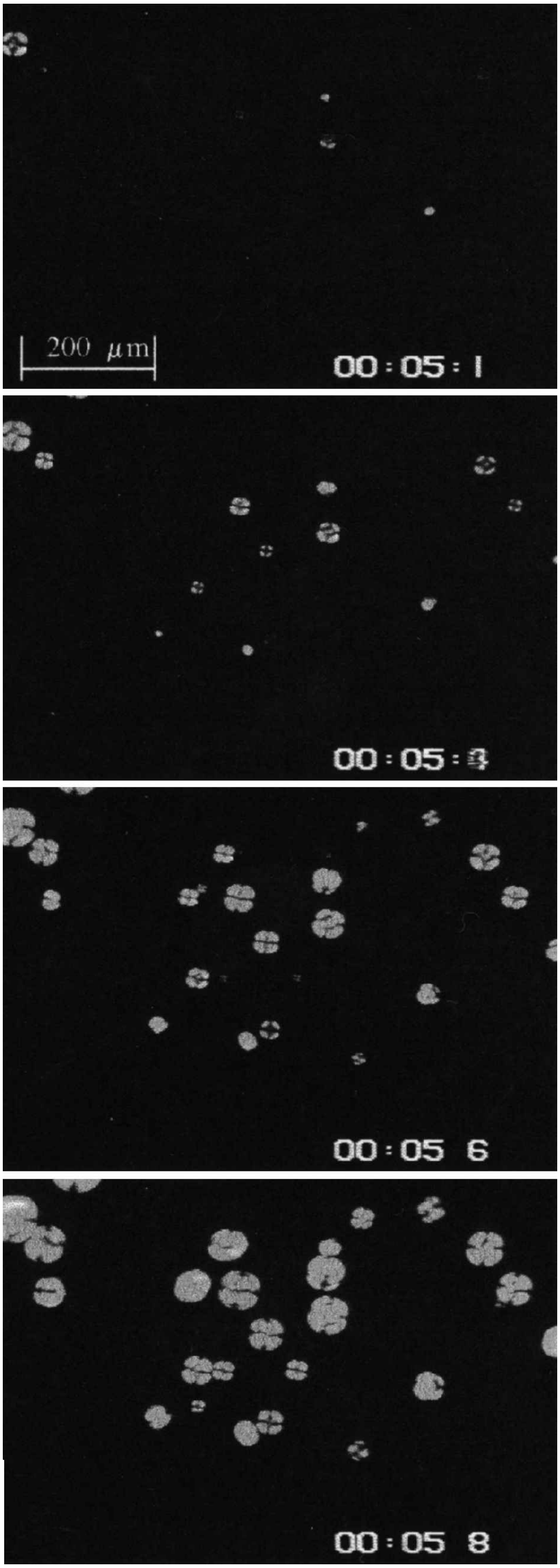

Figure 1. Nematic germs of PCH5 growing out of the isotropic phase. In the lower right corner of each picture the time after the temperature quench is given. The quench depth $\Delta T = T_{\text{start}} - T_{\text{end}}$ is 0·15 K.

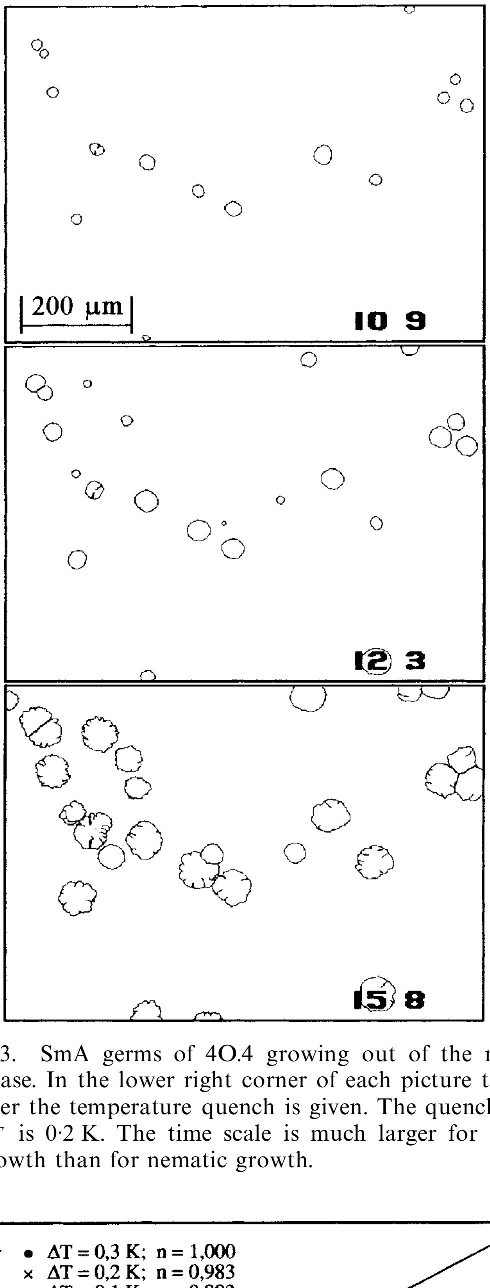

Figure 3. SmA germs of 4O.4 growing out of the nematic phase. In the lower right corner of each picture the time after the temperature quench is given. The quench depth ΔT is 0·2 K. The time scale is much larger for smectic growth than for nematic growth.

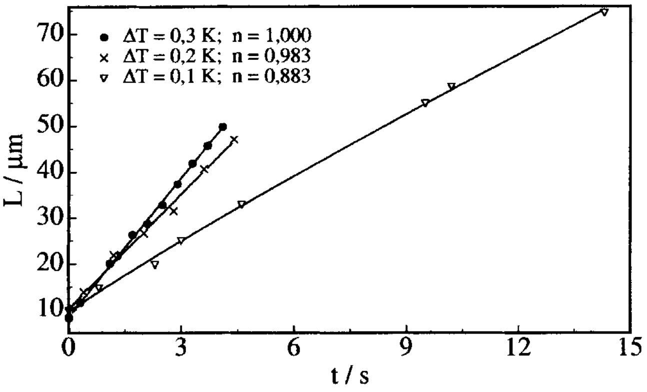

Figure 4. Evolution of the diameter of SmA germs in 4O.4 for different quench depths. The values for L are average values over several germs growing under the same conditions in one single experiment.

Table 3. Average growth exponents n for spherical smectic germs in various systems at different quench depths. The highest quench depth (best supercooling) was realized for BCH70; for low quench depths we could not observe any nucleation.

Quench depth ΔT/K	Average growth exponent n	
	4O.4 (SmA ← N)	BCH 70 (SmB ← N)
0·1	0·88	
0·2	0·98	
0·3	1·00	
0·4		0·68
0·5		0·69
0·6		0·92

itself a eutectic nematic mixture. In contrast to some pure compounds where the phase transition BPII/BPIII also occurs, the selective reflection wavelength of circularly polarized light in our mixture was about 450 nm, i.e. in the visible region of light. Consequently, it was possible to exploit video images of the coloured BPII monocrystals.

The characteristic length L of these germs was also defined by the diameter. But here we chose the diameter parallel to the edges of the crystallites. Figure 6 shows the evolution of L for the BPII germs. The average growth exponent increases from 0·75 for a small quench depth to nearly 1 for a large ΔT as one can see in table 4.

3. Discussion

The results of § 2 can easily be summarized. For small quench depths, i.e. near the phase transition temperature T_C, we obtained growth exponents scaling like the theoretical prediction of the Allen–Cahn theory. The values are in the region of 0·5. They increase with larger quench depths, i.e. larger supercooling, and they reach an upper limit of approximately 1. We could not observe a significantly higher growth exponent for spherical shaped germs.

The Allen–Cahn theory for the movement of interfaces [2] does not forecast a temperature dependence of the characteristic growth exponent. This assumption is justified by the profile of the free energy density function versus the order parameter. This profile is regarded as symmetric, i.e. the phases on both sides of the interface are equivalent in energy, although they are characterized by different order parameters. The assumption of such a profile will be correct if the temperature of the system equals T_C. But if the end temperature is below T_C, the newly formed phase will be energetically more stable than the former phase. However, the descending phase still exhibits a local minimum of the free energy. Figure 7 shows the conditions for such a case. The

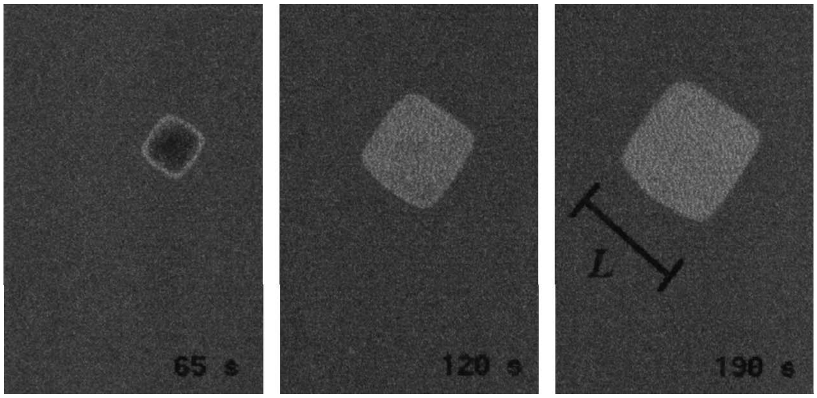

Figure 5. Photographic series of BPII germs in a mixture of CB15 (63 wt %) and E9 growing out of Blue Phase III. In the lower right corner of each picture the time after the temperature quench is given. The quench depth ΔT is 0·05 K. The time scale is much larger than for nematic and even smectic growth.

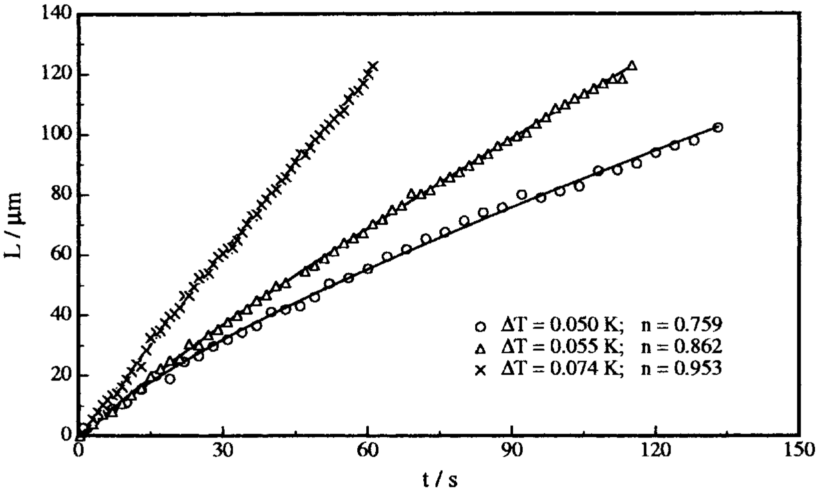

Figure 6. Evolution of the characteristic length L of BPII germs in a mixture of CB15 and E9 for different quench depths.

Table 4. Average growth exponents n for BPII germs growing out of BPIII at different quench depths. The system under investigation was a mixture of 63 wt % of chiral CB15 and nematic E9.

Quench depth ΔT/K	Average growth exponent n
0·050	0·75
0·055	0·87
0·074	0·96

difference in the free energy density between both phases is indicated by ΔF. This quantity must not be neglected when describing the velocity of the interface motion. Equation (2) has to be extended by a volume driving force β.

$$\frac{dL}{dt} = MK + \beta \tag{3}$$

where β is proportional to ΔF which is dependent on the degree of supercooling

$$\beta = \text{const}\ \Delta F(\Delta T). \tag{4}$$

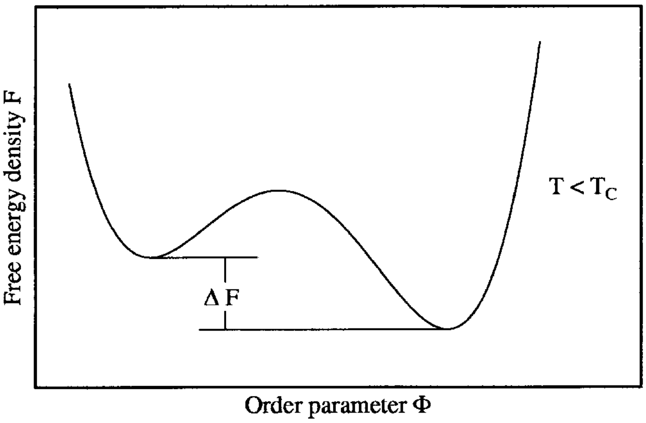

Figure 7. Profile of the free energy density versus the order parameter (see text for details).

So β describes the dependence of the growth velocity on the quench depth. Such an ansatz has already been suggested by Bray [16] for the coarsening of an Ising ferromagnet in the presence of a weak magnetic field.

In the following we will perform some detailed calculations in order to specify the dependence of the growth exponent on ΔT. Besides the volume driving force, there is also the curvature K of the phase boundary which influences the growth velocity. For spherical germs one can use the reciprocal radius or diameter in order to express the curvature. As the diameter is the characteristic length, one obtains from equation (3)

$$\frac{\mathrm{d}L}{\mathrm{d}t} = M\frac{1}{L} + \beta \tag{5}$$

where the constant M is a quantitative measure for the velocity depending on the curvature.

Separation of variables leads to

$$\frac{L}{M + \beta L}\,\mathrm{d}L = \mathrm{d}t. \tag{6}$$

Before integrating equation (6) we perform linear substitution with $u = M + \beta L$ and $\mathrm{d}L = 1/\beta\,\mathrm{d}u$. After transformation of integration limits we obtain

$$\int_M^u \frac{u - M}{\beta^2 u}\,\mathrm{d}u = \int_0^t \mathrm{d}t. \tag{7}$$

Eventually integration leads to

$$\frac{1}{\beta^2}\left(u - M + M\ln\frac{M}{u}\right) = t. \tag{8}$$

Resubstitution leads to the final equation

$$\frac{L}{\beta} + \frac{M}{\beta^2}\ln\frac{M}{M + \beta L} = t. \tag{9}$$

Equation (9) cannot be transformed into a growth law $L = f(t)$ by analytical means. Nevertheless, it is possible to define different values for the ratio β/M and to calculate corresponding L, t data. Such data can very easily be adapted to a power law $L = At^n$ which is of the form of the universal growth law of equation (1). For different ratios β/M one obtains different growth exponents n. This is shown in figure 8 in dimensionless presentation.

If the ratio β/M is very small or tends to zero, ΔF and ΔT will be very small as well, and the interface curvature will be the main driving force for the velocity of the phase boundary. The exponent equals 0·5, which is in agreement with the classical Allen–Cahn theory. If β/M becomes very large, the influence of the curvature will be negligible and the exponent approximates to 1. M is assumed to be independent of temperature. Thus a variation of the quench depth should only affect the value of β.

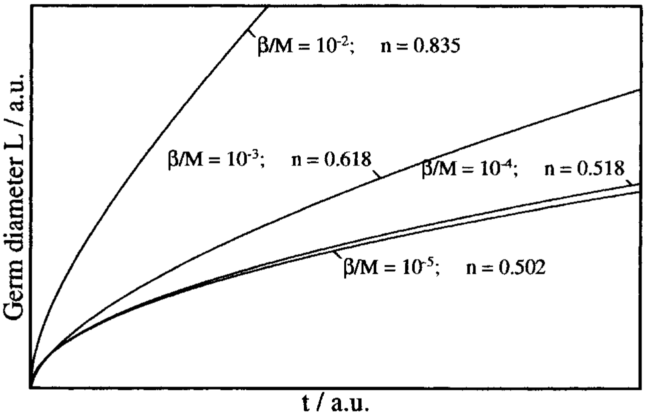

Figure 8. Evolution of the characteristic length; the transition from the curvature driven to the ΔF driven process is visualized by the increase of linearity.

Table 5. Evolution of the growth exponent by variation of the ratio β/M (dimensionless variables).

Ratio β/h	Growth exponent n
≈ 0	0·500
10^{-5}	0·502
10^{-4}	0·518
10^{-3}	0·618
10^{-2}	0·835
$\gg 1$	1·000

Table 5 again illustrates the influence of β/M on the growth exponent. An increase of β/M means an increase of the quench depth, and this leads to an eventual increase of the exponent from 0·5 to 1. This is in agreement with our experimental results. Even the growth of the non-spherical BPII crystallites can be explained, although the curvature is not exactly $1/L$. But we can approximate the curvature to the reciprocal characteristic length because the quadratic shape is not ideal. We observe strongly rounded corners and edges, so it is justifiable to consider the BPII germs as spheres as a first approximation.

Finally it can be concluded that the introduction of the volume driving force into the Allen–Cahn theory leads to a very good description of the growth of spherical shaped germs. The experimental determination of temperature dependent growth exponents has revealed the necessity to extend the theory which predicted a behaviour independent of temperature.

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