Theoretical analysis of Growth Shape Evolution of Crystal Grown with Pulling

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Received zzz, revised zzz, accepted zzz
Published online zzz

Key words Crystal shape, Geometric model, Effects, Kyropoulos method, SAPMAC method
PACS 61.50.Aj, 81.10.-h, 81.10.Fq

This paper constructed a geometric model of crystal growth with pulling. On the basis of the model, effects of processes on crystal shape evolution were clarified. The results shown some effects always used to control the crystal diameter in practice. Some unusual effects also be shown. Crystal could have a self-stable diameter and decreasing the convex extent of solid liquid interface could enhance the increase rate of crystal diameter or reduce the decrease rate of crystal diameter.

1 Introduction

Shape control is, no doubt, one of the most important goal in the crystal-pulling process[1, 2], espeically in Kyropoulos method and SAPMAC method, a recently developed method on the basis of Kyropoulos method and Czochralski method. They grow large size crystals through advancing of a big growth bubble and with tiny pulling rate [3-5], which would result in the crystal growth rate in the crystal radial direction is relatively large. As a consequence the crystal diameter is more sensitive to the variation of processes and the shape control is more difficult as compare with Czochralski method. In that context, an convenient approach for theoretical analyzing the effect of processes on the shape evolution of crystal is valuable.

Actually, some relations for Czochralski method have been founded through simplified energy conservation analysis in the past. The crystal diameter was believed to can positive feedback to its increase in shoulder-expanding procedure when the expanding angle kept constant and increase faster with larger expanding angle [6]. In equal-diameter procedure, the sensitivity of crystal diameter to temperature variation, normally named as diameter inertia, is determined by the properties of crystal, melt and growth atmosphere as well as by the crystal size. For a given growth system, measures including decreasing temperature, decreasing crystal diameter, reducing rotate rate and enhancing heat exchange ability can enhance the diameter inertia so depress the sensitivity of crystal diameter[6].

G. Singh[7] *et.al* constructed a shape model of Kyropoulos method according to a simple mass transfer approach. It was concluded that the shape of the crystal is not affected obviously by the shape of the solid liquid interface but affected by the curvature of the interface. It was also shown that the crystal takes a upper limit diameter which could be approximately expressed as $\sqrt{\rho_m/\rho_c}D$, where ρ_m and ρ_c are respetively the density of melt and crystal, D is the diameter of crucible.

Above literatures did not give out a relative full view of the effects of various factors on the shape evolution of crystal grown with pulling. This paper discussed in detail the effects of several parameters on the crystal shape on the basis of a geometric model constructed for the growth based on the quasi-stationary approximation and the results obtained in the study of the shape of sapphire crystals grown by the SAPMAC method.

2 Model Construction

Similar to Kyropoulos method, there exists a crystal bubble during SAPMAC process(schematically shown in Fig.1a). This crystal bubble penetrates into melt deeply so can move its solid liquid interface in three dimensions but not just in one dimension a mode used by Czochralski method[8]. Thus, the bubble would have an obvious growth rate component in the crucible radial direction, which results in the shoulder-expanding angle of SAPMAC method could be quite large (≥140°).

We also observed many growth layers in the sapphire crystals grown by SAMPAC method (see Fig.2). The layers not only exhibit on surfaces but also penetrate into the crystals. They implied the crystal is grown layer by layer even through under confined growth conditions and the shape of crystal is a surface constructed by the edges of growth layers. A similar idea has been used to construct the kinetic-geometric model for the morphology prediction of free growth crystal[9]. Besides, the crystal is always pulled up along the crystal axis direction during SAPMAC process, the pulling is carried out some times continuously and some times intermittently with very short interval. Therefore, if we suppose the solid liquid interface does not advance ahead in the moment of pulling is reasonable. The height between the top surfaces of two adjacent layers (Fig.1c) could be expressed as $h=u\Delta t+\delta$, where Δt is the time of every pulling, u is the pulling speed and δ is the height of the melt level drop caused by every pulling. The thick of the layer along the melt level could be expressed as $l= v_{//}(r, y_e)\Delta t'$, where $\Delta t'$ is the time of every interval and $v_{//}(r, y_e)$ is the rate component the endpoint (r, y_e) of solid liquid interface moves in the crucible radial direction. When $\Delta t\to 0$ and $\Delta t'\to 0$, h could bear a relation as follow with l, see Fig.1c,

$$\frac{h}{l}=\frac{h}{\frac{h}{\dot{S}\big|_r}-\frac{h}{\dot{f}\big|_r}} \tag{1}$$

where $S(x)$ and $f(x)$ are respectively the shape function of the crystal and every growth layer, $\dot{S}\big|_r \equiv \left(dS/dx\right)_{x=r}$ $\dot{f}\big|_r \equiv \left(df/dx\right)_{x=r}$. Then when neglecting the density difference of melt and crystal, the relation of u and $v_{//}(r, y_e)$ can be obtained as below by integrating a formula $\delta= ur^2\Delta t /(R^2-r^2)$ which has been shown in [10] with a similar format.

$$\frac{u\Delta t}{v_{\|}\Delta t'}=\frac{1}{\frac{1}{\dot{S}\big|_r}-\frac{1}{\dot{f}\big|_r}}\left(1-\frac{r^2}{R^2}\right) \tag{2}$$

Because $\Delta t\to 0$ and $\Delta t'\to 0$, they could be considered to be equal, therefore Eq.2 can be simplified into

$$\frac{u}{v_{\|}}=\frac{1}{\frac{1}{\dot{S}\big|_r}-\frac{1}{\dot{f}\big|_r}}\left(1-\frac{r^2}{R^2}\right) \tag{3}$$

If taking the density difference of melt and crystal into account, two effects could lead the melt level drop: 1) the volume decrease caused by the crystallization shrinkage; 2) the pulling. For the first effect, the crystallization shrinkage volume could be expressed as

$$V=\pi r^2 v_{\|}\,\dot{f}\big|_r\,\Delta t\left(1-\frac{\rho_c}{\rho_m}\right) \tag{4}$$

. Therefore, the melt level drop caused by crystallization shrinkage could be shown as

$$\delta_s = \frac{r^2}{R^2 - r^2} v_{\parallel} \dot{f}\Big|_r \Delta t \left(1 - \frac{\rho_c}{\rho_m}\right) \tag{5}$$

For the second effect, we pull a part of the crystal out from melt and then the melt will compensate the space originally taken by the part pulled out, so this course is irrelevant to density difference. It just requires that the volume of the space originally taken by the part pulled out equals to the volume of the compensating melt, so the relation $\delta_p = ur^2\Delta t/(R^2-r^2)$ is yet valid. Summing the drop caused by the two effects, the totle drop of melt level can be expressed as

$$\delta = \frac{r^2}{R^2 - r^2} \Delta t \left[v_{\parallel} \dot{f}\Big|_r \left(1 - \frac{\rho_c}{\rho_m}\right) + u \right] \tag{6}$$

As a consequence, we have

$$\frac{u}{v_{\parallel}} = \frac{1}{\frac{1}{\dot{S}\Big|_r} - \frac{1}{\dot{f}\Big|_r}} \left(1 - \frac{r^2}{R^2}\right) + \frac{r^2}{R^2} \dot{f}\Big|_r \left(\frac{\rho_c}{\rho_m} - 1\right) \tag{7}$$

It is obvious this relation could be simplified into Eq.(3) when neglecting the density difference between melt and crystal. Next, a expression of crystal shape evolution can be obtained as

$$\dot{S}(r) = \frac{\left[\frac{u}{v_{//}} + \left(1 - \frac{\rho_c}{\rho_m}\right)\frac{r^2}{R^2}\dot{f}\Big|_r\right]\dot{f}\Big|_r}{\frac{u}{v_{//}} + \left(1 - \frac{r^2\rho_c}{R^2\rho_m}\right)\dot{f}\Big|_r} \tag{8}$$

3 Effects of processes on the crystal shape evolution

It is evident according to Fig1.c that the sign of $\dot{S}$ indicates the vatiation trend of crystal diameter, $\dot{S} > 0$ implies the diameter increases, $\dot{S} < 0$ implies the diameter decreases and $\dot{S} = \infty$ means the diameter does not change. The magnitude of $\dot{S}$ is samller, the diameter changes faster. Fig.3 depicted the realtion between $\dot{S}$ and $\eta \equiv r^2/R^2$, where $\tau \equiv u/v_{//}$. It was shown that $\dot{S}$ is positive and gradually increases to infinite value with the of crystal radius increasing before r exceeding a certain value $\eta_c R$. That implies that the crystal radius would initially increase to $\eta_c R$, and then r would keep constant since if r exceeds $\eta_c R$, it would next decrease until to $\eta_c R$. As a consequence, the crystal radius would fluctuate around $r = \eta_c R$. That means the crystal radius is self-stable. The self-stable radius could obtained by setting the denominator of Eq.8 as zero, that is

$$r = R\sqrt{\left(1 + \frac{u}{v_{//}\dot{f}\Big|_r}\right)\frac{\rho_m}{\rho_c}} \tag{9}$$

We also should note that this self-stabl radius is also the limiting radius of crystal grown under determined processes and Eq.9 is similar to the expression of limiting radius poiinted out by G. Singh[7].

From Fig.3, we can also see the curve gradually moves left with the increase of τ, which will result in the part corresponding to $\dot{S} > 0$ fully locates in the region $\eta \leq 0$ when the pulling rate is enough large, so the crystal

can not grow if the pulling rate in the shoulder-expanding procedure is higher than a certain value, this value could be obtained as $-\dot{f}|_{\tau=0} v_{//}$ by calculating η_c>0. For Kyropoulos method and SAPMAC method, the solid liquid interface is always taper and its cone angle is about 90°[11], so their $\dot{f}|_{\tau=0}$ is about -1, the pulling rate in the shoulder-expanding procedure of Kyropoulos method or SAPMAC method can not exceed the radial growth rate of crystal.

Existence of the self-stable radius suggests the controlling stability of crystal diameter can be enhanced by designing the crucible radius as $r_n\eta_c^{-1}$ in equal-diamter procedure, where r_n represents the desired crystal radius. That needs to adjust the cruccible radius accoring to each desired crystal, which is obviously unconvenient in many cases. In practice, crystal shape is always controlled by adjusting the pulling rate and the heat power, the latter is relevant to $v_{//}$ and $\dot{f}|_r$. Eq.10 gives out the differential of $\dot{S}$ to $\tau \equiv u/v_{//}$. It is evident positive in most cases, which implies that $\dot{S}$ is a monotone increase function ofτ, increasing the pulling rate or reducing the radial growth rate of crystal would depress the rate of crystal radius increase during the shoulder-expanding procedure and equal-diameter procedure but accelerate the decrease of crystal radius during the tailing procedure. This rule has been naturally used in practice where enhancing the pulling rate is taken temporarily to adjust crystal diameter. The experiments of sapphire crystal growth through SAPMAC method have shown that the crystal would grow slower along the radial direction at a smaller heat power decrease rate so the shoulder-expanding angle became smaller.

$$\frac{\partial \dot{S}}{\partial \tau} = (1-\eta)\left(\frac{\dot{f}|_r}{\tau + \left(1 - \frac{\rho_c}{\rho_m}\eta\right)\dot{f}|_r} \right)^2 \tag{10}$$

Now we consider the effect of solid liquid interface curvature on the crystal shape evolution. Eq.11 is the differential of $\dot{S}$ to $\dot{f}|_r$. Its sign is same as that of the numerator. By noting the numerator as a function $g(\dot{f}|_r)$, we have its function plot in the region $\dot{f}|_r < 0$ as Fig.4. g is always positive when $\rho_m/\rho_c < r^2/R^2 < 1$. According to the analysis above, $\dot{S}$ should be negative under that condition since $\eta_c^2 \le \rho_m/\rho_c$. Therefore, decreasing the convex extent of solid liquid interface would accelerate the decrease of the crystal diameter. When $r^2/R^2 < \rho_m/\rho_c$, there is a zero point here denoted as κ and shown as Eq.12. If the convex extent of interface is relatively small namely $\dot{f}|_r < \kappa$, g is positive so $\dot{S}$ is a increase function of $\dot{f}|_r$, indicating that the decrease in the convex extent of interface would reduce the increase rate of crystal diameter (when $\dot{S} > 0$) or enhance the decrease rate of crystal diameter (when $\dot{S} < 0$); If the convex extent of interface is relatively larger namely $\dot{f}|_r > \kappa$, g is negative so $\dot{S}$ is a decrease function of $\dot{f}|_r$, indicating that the decrease in the convex extent of interface would enhance the increase rate of crystal diameter (when $\dot{S} > 0$) or reduce the decrease rate of crystal diameter (when $\dot{S} < 0$).

$$\frac{\partial \dot{S}}{\partial \dot{f}|_r} = \frac{\tau^2 + 2\tau\eta\left(1 - \frac{\rho_c}{\rho_m}\right)\dot{f}|_r + \eta\left(1 - \frac{\rho_c}{\rho_m}\right)\left(1 - \frac{\rho_c}{\rho_m}\eta\right)\left(\dot{f}|_r\right)^2}{\left[\tau + \left(1 - \frac{\rho_c}{\rho_m}\eta\right)\dot{f}|_r\right]^2} \tag{11}$$

$$\kappa = -\frac{\tau}{1-\frac{\rho_c}{\rho_m}\eta}\left[1+\sqrt{\frac{\eta-1}{\eta\left(1-\frac{\rho_c}{\rho_m}\right)}}\right] \tag{12}$$

The third case above is not intuitionistic. Further analysis shown that the effect of interface convex extent on the crystal shape evolution would be much simpler if ignoring the difference between the crystal density and the melt density. In that case the the differential of $\dot{S}$ to $\dot{f}|_r$ is positive when the pulling rate is not zero, which implies, under any conditions, decreasing the convex extent of interface would reduce the increase rate of crystal diameter (when $\dot{S}>0$) or enhance the decrease rate of crystal diameter (when $\dot{S}<0$). Therefore, the intuitionistic case pointed before is a result of the density difference.

Section 2 indicates that δ_s is the only factors affected by $\dot{f}|_r$ when considering the density difference. That is to say there is no difference in the δ_s for different interface when neglecting the density difference, and the δ_s of low convex extent interface is smaller than that of high convex extent interface when considering the density difference. Fig.5 shows the growth of different interfaces in the cases of $\rho_m=\rho_c$ and $\rho_m<\rho_c$. In the case of $\rho_m=\rho_c$, the growth start points G and G′ of different interfaces are on same melt level since their melt level drop δ is same, but G′ of lower convex extent interface more approaches the crystal axis than G, leading the growth endpoint of lower convex extent interface more approaches the crystal axis after same growth distance $l= v_{//}\Delta t$, thus the increase rate of crystal diameter of lower convex extent interface is smaller. In the case of $\rho_m<\rho_c$, the growth start points G′ of lower convex extent interface is on a higher level, which makes G′ move right as compare with the case of $\rho_m=\rho_c$. When the distance G′ moves right is larger than Δd , the growth endpoint of lower convex extent interface would more departs from the crystal axis after same growth distance $l= v_{//}\Delta t$, resulting in the crystal diameter has a higher increase rate.

4 Conclusion

We have discussed the effects of processes on the crystal shape evolutin by constructing a geometric model of the crystal growth with pulling. Some of the results are common in practice and may have been realised by crystal engineers for a long time, but some for example the existence of self-stable diameter would have not been realised up to now. If all the process factors could be controled to be fixed during the growth, obtaining a crystal with constant diameter would be easy, however, that is too difficult to keep all the process factors fixed in the present.

It should be pointed out that the model here is a phenomenological model. It is valuable for clarifying the roles of various process factors paly in the adjusting the crystal shape. Actually, the factors $\dot{f}|_r$ and $v_{//}$ are relevant. They are determined by the normal rate of solid liquid interface which is determined by the heat diffusion, the pulling rate, the crystal size and the physical properties of crystal, this is just the basic task of numerical simulation, so $\dot{f}|_r$ and $v_{//}$ should be regarded as indirect process factors. Here our point is that if $\dot{f}|_r$ and $v_{//}$ could be written as functions of all the direct process factors such as the pulling rate, the heat power and the cooled power, the crystal shape could be predicted by calculating Eq.8.

Acknowledgements Great thanks should be given to Dr V.M. Mamedov for his review for the manuscript and his valuable remarks

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Figures

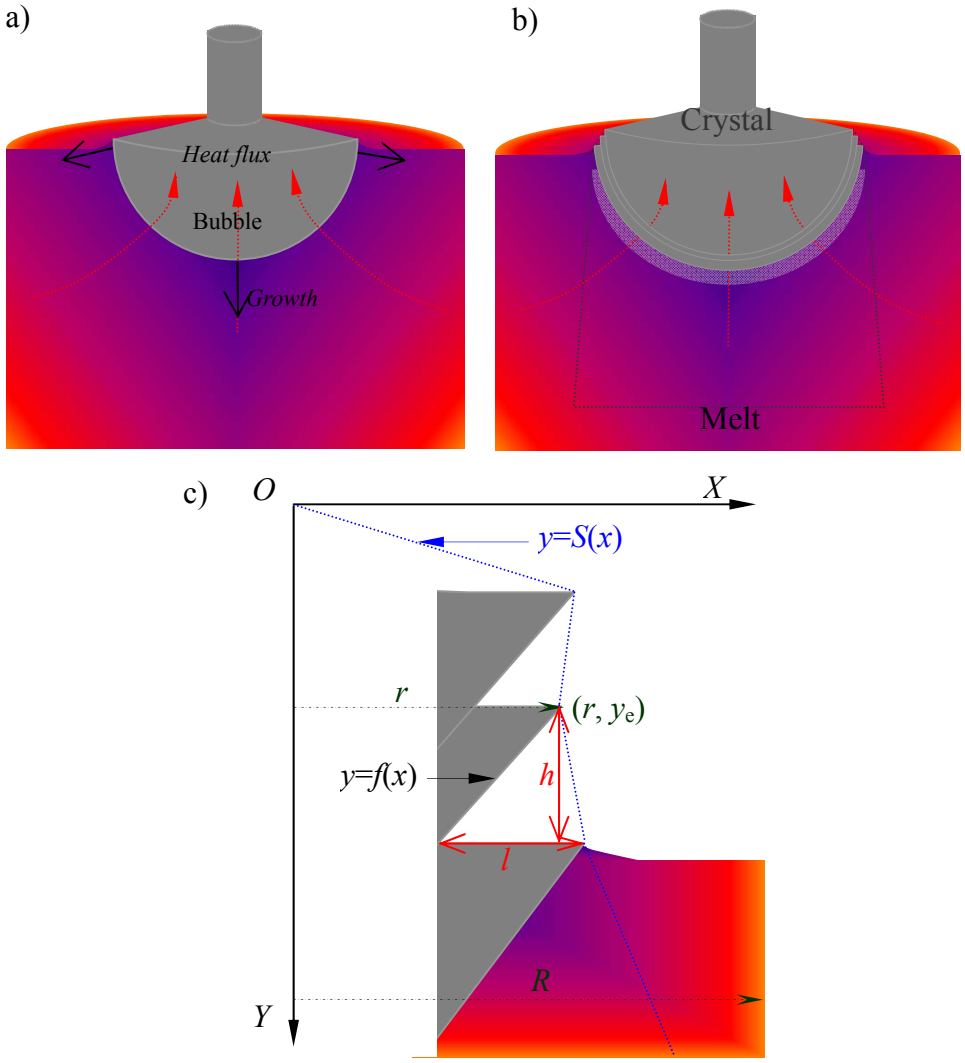

Fig.1 Geometric model for crystal growth of the SAPMAC method. a) shows the bubble, b) shows the layer growth course and c) shows the geometric relation between the crystal shape, the layer extending and the pulling

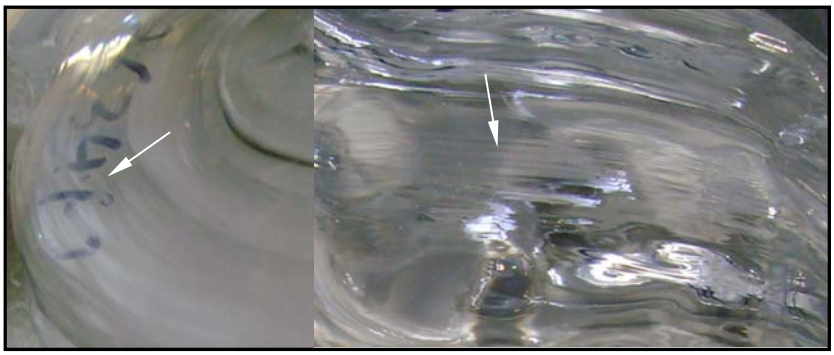

Fig.2 Layers pattern on the crystal (arrows)

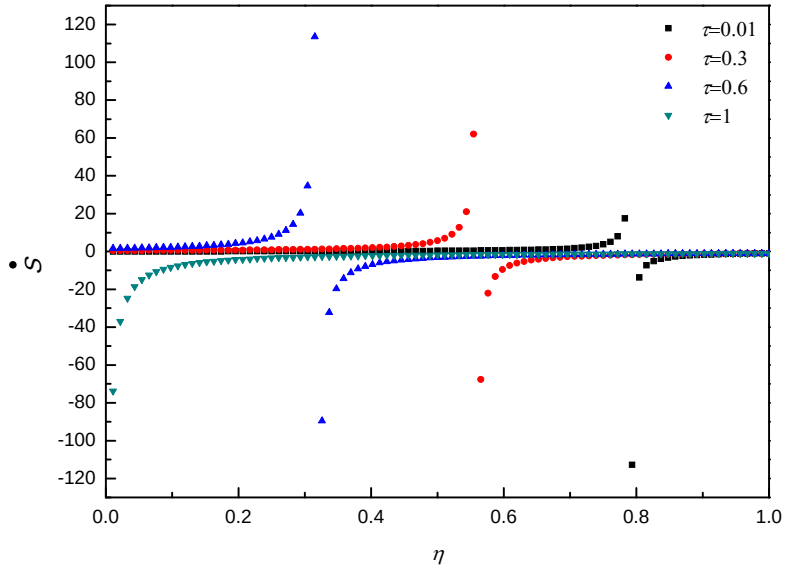

Fig.3 Plot showing the relation between $\dot{S}$ and $\eta \equiv r^2/R^2$

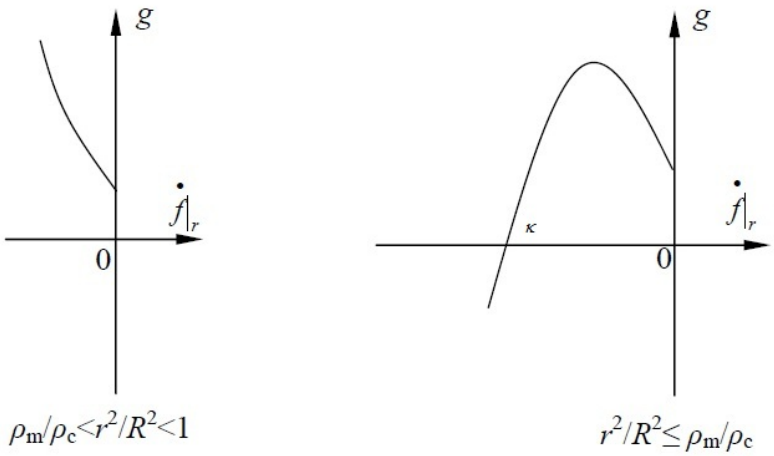

Fig.4 Schematic showing the numerator function of Eq.11, $g(\dot{f}|_r)$

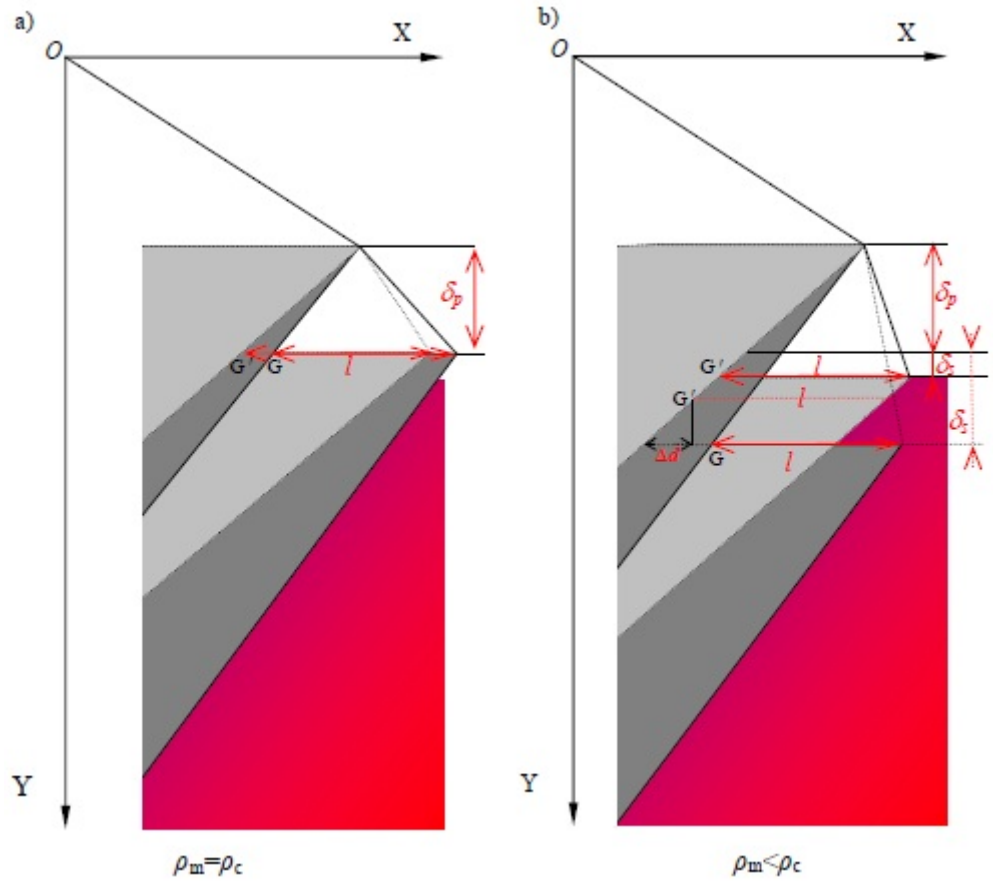

Fig.5 Schematic showing the effect of the convex extent of solid liquid interface on the crystal diameter variation