ETP

EU COST action P6 "Magnetofluiddynamics"
Working Group "Use of magnetic fields in crystal growth"
Workshop
Use of magnetic fields in crystal growth
13.-14. June 2002, University of Latvia, Riga, Latvia

Simplified kinetic models
for some growth aspects
in industrial single crystal growth

A. Muiznieks[1,2], I. Madzulis[2]
[1]Institute for Electrothermal Processes, University of Hanover, Germany
[2]Department of Physics, University of Latvia

Abstract

In the present paper the crystallisation process from melt is considered on the atomic level analytically. A new kinetic equation in mean field approximation is proposed for the averaged crystallisation occupancy of the layers of crystal lattice in the vicinity of phase interface. The latent heat per atom and the number of closest neighbours are used as parameters in this equation. The proposed equation is solved numerically and the results obtained for crystallisation process with the cubic lattice show a good qualitative and quantitative agreement with the results obtained by Monte Carlo method. Besides, the model has allowed to investigate the oscillating character of the crystallisation process and relations between the temperature, growth velocity and growth orientation. The transition from metastable state to rough growth is analysed and processes diagrams with growth, melting and metastable zones are calculated.

Melt-solid growth velocity as a function of temperature by neglecting the surface structure

Transition intensities for thermodynamic equilibrium (L – latent heat per atom, T_0 – equilibrium temperature

$$I_{L \to C} = A \exp\left[\frac{L}{2kT_0}\right], \, I_{C \to L} = B \exp\left[\frac{-L}{2kT_0}\right], \, I_{L \to C} = I_{C \to L}, \, and \, B = A \cdot \exp\left[\frac{L}{kT_0}\right]$$

Crystal growth velocity, if $T < T_0$ (H_L, H_C –entalpies per atom in liquid and crystal phase)

$$v = \xi(I_{L \to C} - I_{C \to L}) = A \exp\left[\frac{H_L(T) - H_C(T)}{2kT}\right] - A \exp\left[\frac{L}{kT_0}\right] \cdot \exp\left[-\frac{H_L(T) - H_C(T)}{2kT}\right]$$

It follows the dependency from Wilson and Frenkel theory

$$v = v_0 \left[\exp\left(\frac{H_L(T) - H_C(T)}{kT} - \frac{L}{kT_0}\right) - 1\right]$$

For small temperature differences

$$v = v_0 \left[\underbrace{\exp\left(\frac{L}{kT} - \frac{L}{kT_0}\right)}_{-----arriving\ part-----} - \underset{\substack{leaving \\ part}}{1}\right]$$

Analysis by considering the surface structure

Liquid->crystal transition intensities if s_C bonds each with an energy J are created and s_L bonds remains not realised ($s_C + s_L = s$, Js/2=L, multipliers M describe the surfase structure)

$$W_{L \to C} = A \exp\left(\frac{s_C J}{2kT}\right) = A \exp\left(\frac{L}{2kT}\right) \cdot M_{L \to C}, \quad M_{L \to C} = \left[\exp\left(+\frac{s_C J}{4kT}\right) \cdot \exp\left(-\frac{s_L J}{4kT}\right)\right]$$

$$W_{C \to L} = B \exp\left(-\frac{s_C J}{2kT}\right) = B \exp\left(-\frac{L}{2kT}\right) \cdot M_{C \to L}, \quad M_{C \to L} = \left[\exp\left(-\frac{s_C J}{4kT}\right) \cdot \exp\left(+\frac{s_L J}{4kT}\right)\right]$$

If the following dimensionless quantities are introduced $\quad l = L/(kT_0) \quad \Theta = T/T_0$

$$M_{L \to C} = \left[\exp\left(\frac{l}{2\Theta s}\right)\right]^{s_C} \cdot \left[\exp\left(-\frac{l}{2\Theta s}\right)\right]^{s_L}, \quad M_{C \to L} = \left[\exp\left(-\frac{l}{2\Theta s}\right)\right]^{s_C} \cdot \left[\exp\left(\frac{l}{2\Theta s}\right)\right]^{s_L}$$

The crystallisation front is described with an occupancy distribution in growth direction (layer by layer) and for the occupancy of the layer with number z the equation in following form are formulated (Temkin)
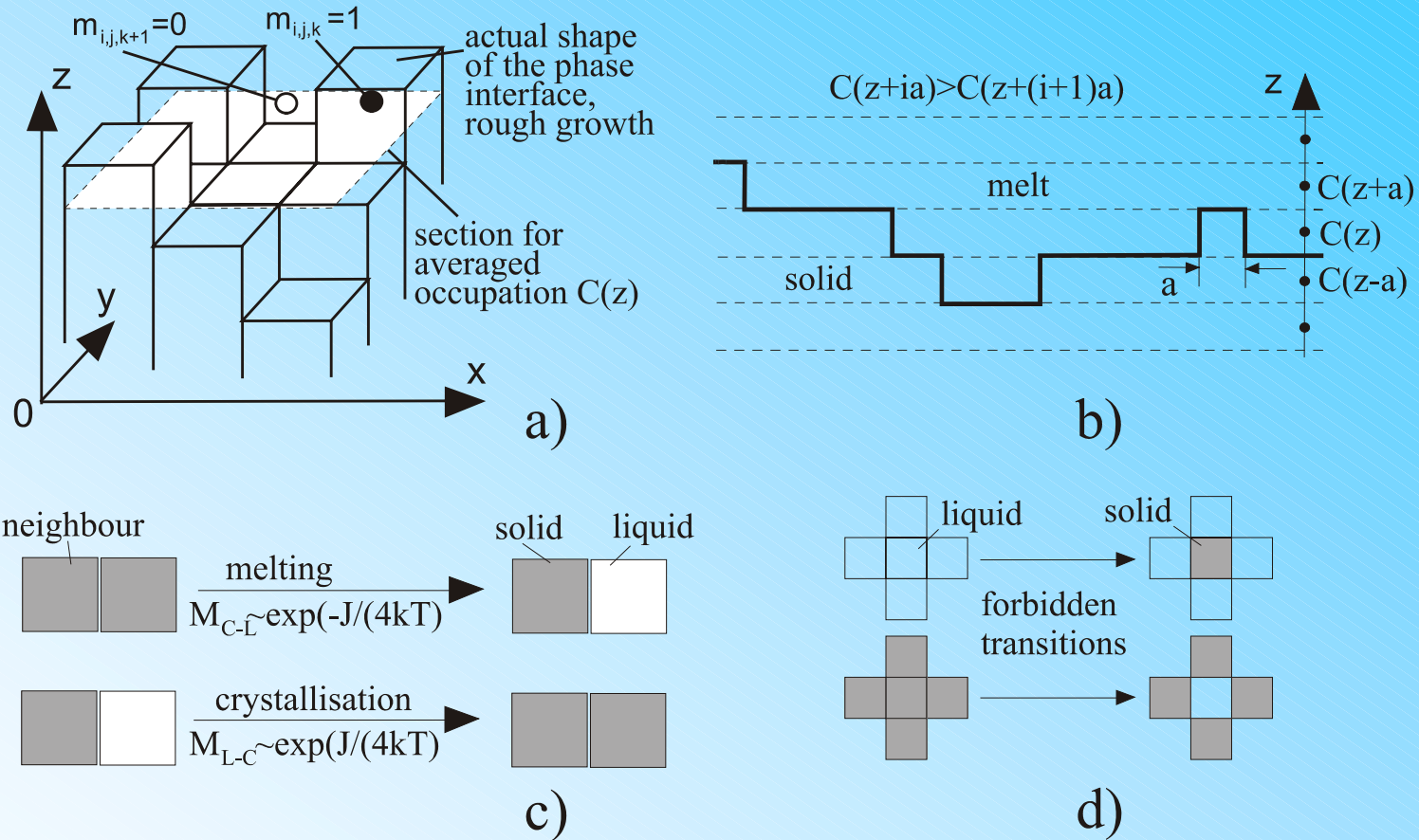
$$\partial C(z)/\partial t = f\left[C(z-a); C(z); C(z+a)\right]$$

Fig. 1. a) Occupied (*m=1*, atom belongs to the crystal) and empty (*m=0*, atom belongs to the melt) sites in the cubic lattice. b) The averaged occupancy *C(z)* of the layer with number *z*, $0<C(z)<1$. c) Changes of the bond energy in the cases of melting and crystallisation. d) Forbidden phase transitions in the model.

Proposal for multipliers M using occupancy C

$$M_{L\to C}\ \left((1-C(\mathbf{r}_m))\exp(-l/2\Theta s)+C(\mathbf{r}_m)\exp(l/2\Theta s)\right)$$

$$M_{C\to L}\ \left((1-C(\mathbf{r}_m))\exp(l/2\Theta s)+C(\mathbf{r}_m)\exp(-l/2\Theta s)\right)$$

Proposal for kinetic equation for C (index m denotes closest neighbours)

$$\frac{\partial C(\mathbf{r})}{\partial \tau}=(1-C(\mathbf{r}))\exp(l/\Theta-l)\cdot M_{L\to C}-C(\mathbf{r})\cdot M_{C\to L},$$

$$M_{L\to C}=\left[\prod_m\left((1-C(\mathbf{r}_m))\exp(-l/2\Theta s)+C(\mathbf{r}_m)\exp(l/2\Theta s)\right)-\prod_m(1-C(\mathbf{r}_m))\exp(-l/2\Theta s)\right],$$

influence of the forbidden transitions

$$M_{C\to L}=\left[\prod_m\left((1-C(\mathbf{r}_m))\exp(l/2\Theta s)+C(\mathbf{r}_m)\exp(-l/2\Theta s)\right)-\prod_m C(\mathbf{r}_m)\exp(-l/2\Theta s)\right],$$

influence of the forbidden transitions

For the cubic crystal lattice (s_0 – averaged number of closest neighbours in the actual growing layer)

$$\frac{\partial C(z)}{\partial \tau} = (1 - C(z)) \exp(l/\Theta - l) \cdot M_{L \to C} - C(z) \cdot M_{C \to L},$$

$$M_{L \to C} = \left[(1 - C(z)) \exp(-l/2\Theta s) + C(z) \exp(l/2\Theta s)\right]^{s_0} \times$$

$$\left[(1 - C(z - a)) \exp(-l/2\Theta s) + C(z - a) \exp(l/2\Theta s)\right]^{(s - s_0)/2} \times$$

$$\left[(1 - C(z + a)) \exp(-l/2\Theta s) + C(z + a) \exp(l/2\Theta s)\right]^{(s - s_0)/2}$$

$$- \left[(1 - C(z)) \exp(-l/2\Theta s)\right]^{s_0} \times \left[(1 - C(z - a)) \exp(-l/2\Theta s)\right]^{(s - s_0)/2} \times$$

$$\left[(1 - C(z + a)) \exp(-l/2\Theta s)\right]^{(s - s_0)/2},$$

$$M_{C \to L} = \left[(1 - C(z)) \exp(l/2\Theta s) + C(z) \exp(-l/2\Theta s)\right]^{s_0} \times$$

$$\left[(1 - C(z - a)) \exp(l/2\Theta s) + C(z - a) \exp(-l/2\Theta s)\right]^{(s - s_0)/2} \times$$

$$\left[(1 - C(z + a)) \exp(l/2\Theta s) + C(z + a) \exp(-l/2\Theta s)\right]^{(s - s_0)/2}$$

$$- \left[C(z) \exp(-l/2\Theta s)\right]^{s_0} \times \left[C(z - a) \exp(-l/2\Theta s)\right]^{(s - s_0)/2} \times$$

$$\left[C(z + a) \exp(-l/2\Theta s)\right]^{(s - s_0)/2},$$

a) new grown layer

L

number of neighbors in the new layer

4   a   3

α macroscopic angle

a)

b)

only one new bond per atom is created in the new layer
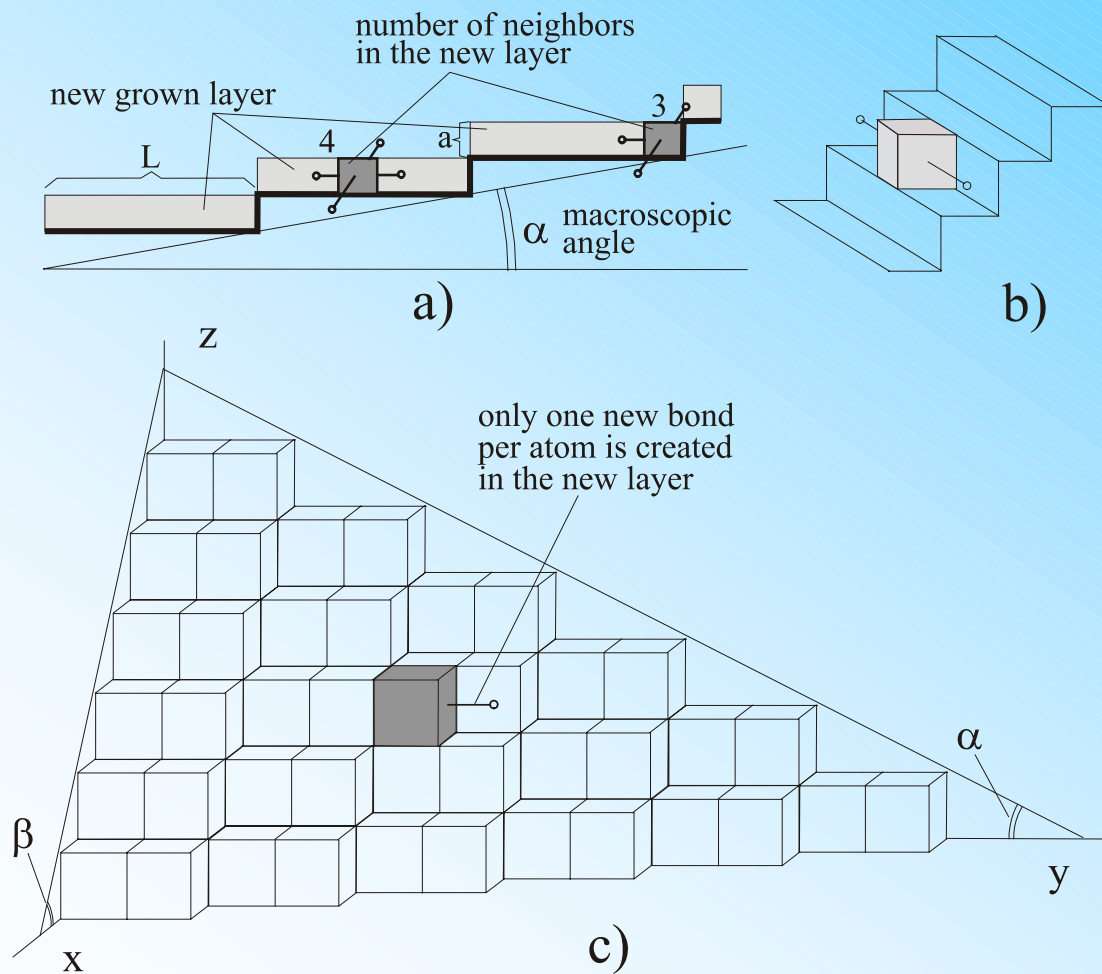
z

β

x

α

y

c)

Fig. 2. Some examples for the relation between the inclination of the crystallisation front and averaged number s_0 of neighbours in the new layer for the cubic lattice. a) An illustration to the angle α, to the shape of the new grown layer and to averaged number of neighbours in the new actual layer for the step-shaped surface structure. b) The case with α=45 and the averaged number of neighbours in the new layer s_0=2. c) An example for the relation between angles α and β describing inclination of the crystallisation front and the averaged number of the neighbours in the actual layer s_0=0.5.

Realtion between values of angles and s0 for cubic lattice

$$s_0 = \frac{l_x/a \cdot l_y/a \cdot 4 - 2 \cdot l_x/a - 2 \cdot l_y/a}{l_x/a \cdot l_y/a} = 4 - 2\mathrm{tg}\,\alpha - 2\mathrm{tg}\,\beta$$

Deffinition of dimensionless instant growth velocity

$$\upsilon = \left(\sum_z \frac{\partial C(z)}{\partial \tau} \right)$$

Dimensionless entropy of phase boundary

$$S' = S/k_B = -\sum_z \big(C(z)\ln(C(z)) + (1-C(z))\ln(1-C(z)) \big)$$

Simplified kinetic equation

$$\frac{\partial C}{\partial \tau} = (1-C)\exp(l/\Theta - l) \cdot \big[(1-C)\exp(-l/2\eta\Theta s) + C\exp(l/2\eta\Theta s)\big]^{s_0}$$

$$- C\big[(1-C)\exp(l/2\eta\Theta s) + C\exp(-l/2\eta\Theta s)\big]^{s_0}$$
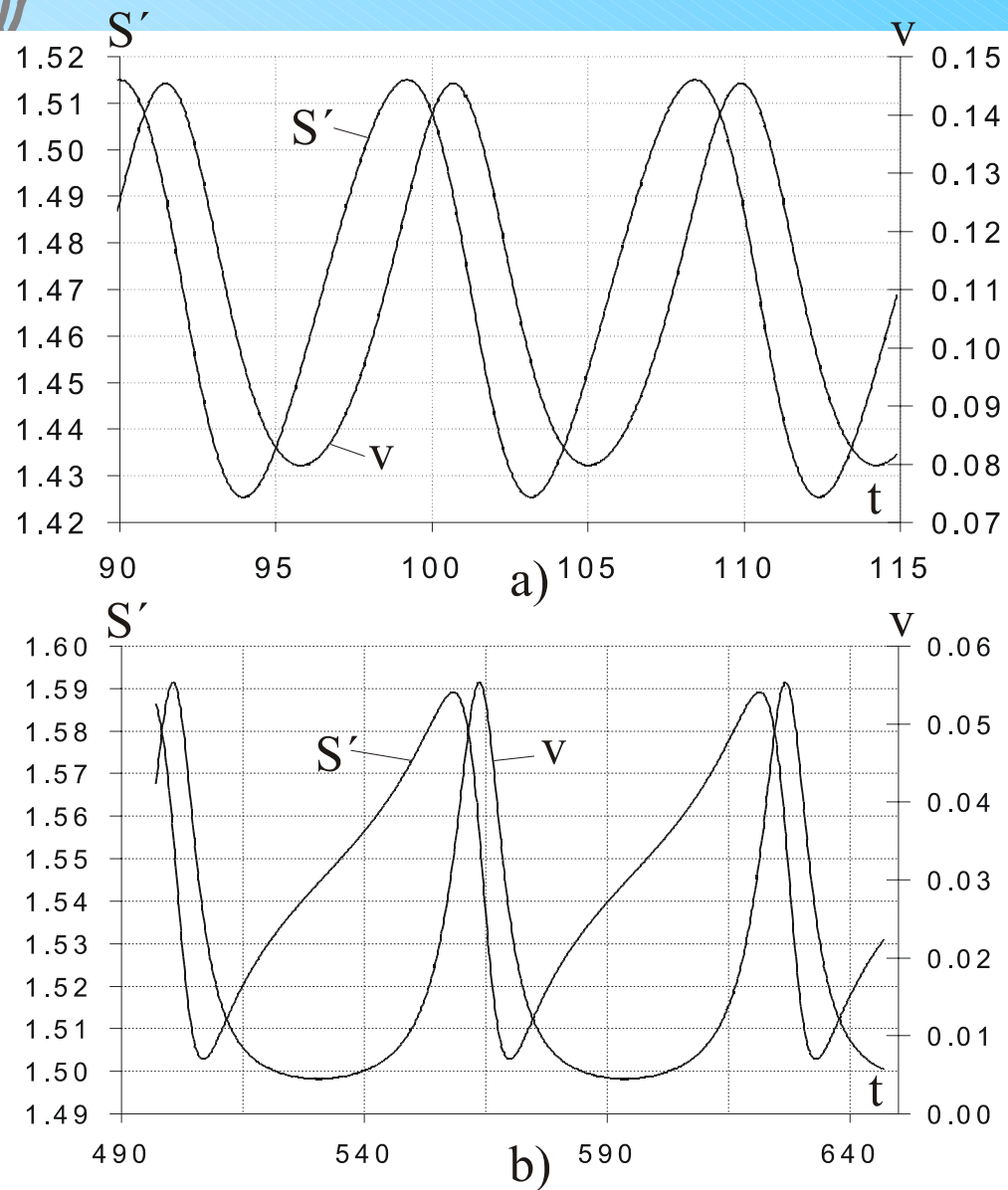
Fig. 3. Dependence of the growth velocity and entropy of the surface on time at $l=2.8$, $s=6$, $s_0=4$ and at the temperature values: a) $\Theta=0.96500$; b) $\Theta=0.99050$.
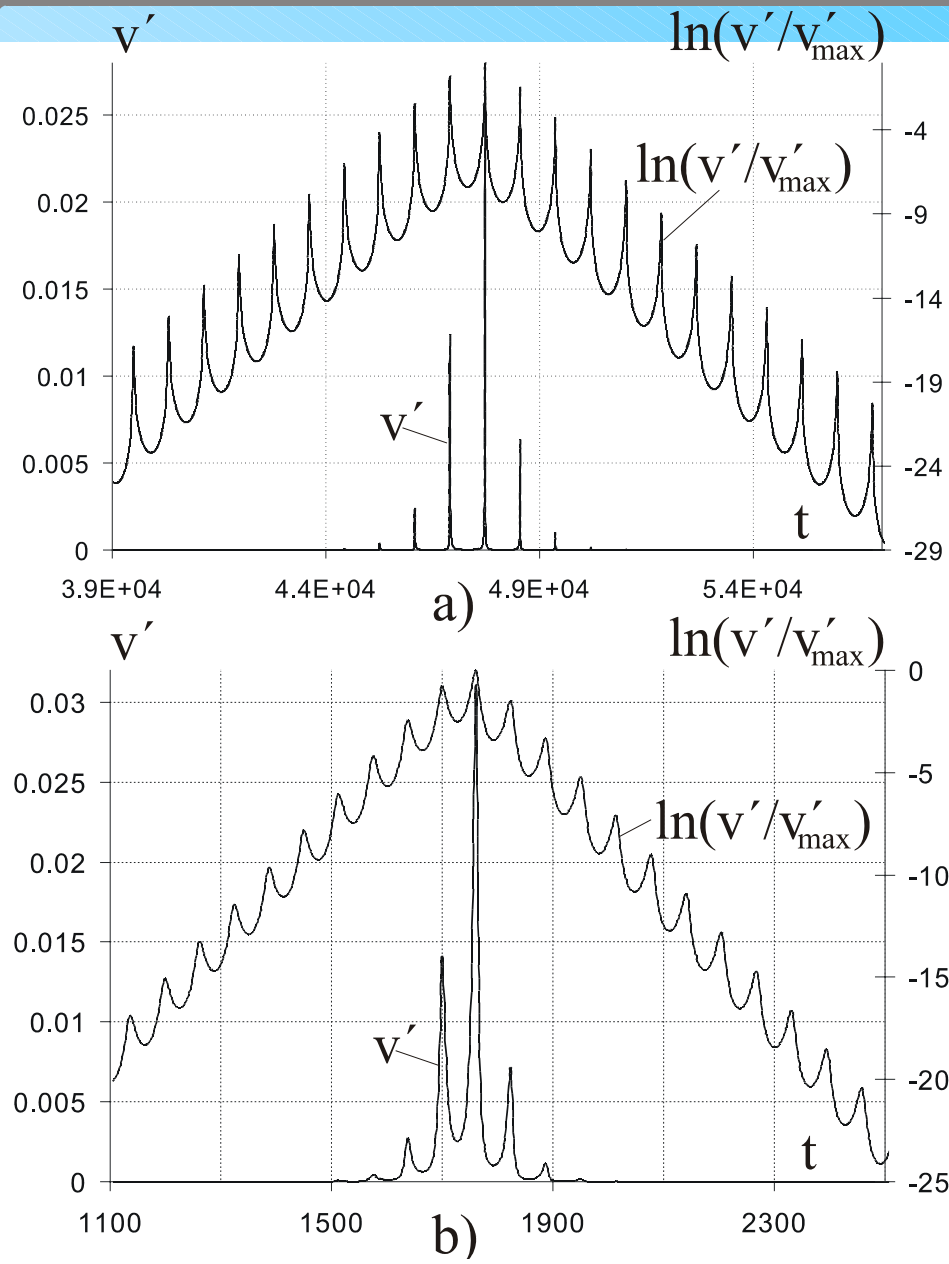
Fig. 4. Dependence of the derivative $dC(z)/dt$ and $\ln[dC(z)/dt]$ at fixed z value at $l=2.8$, $s=6$, $s_0=4$ and at the temperature values: a) $\Theta=0.99204$; b) $\Theta=0.99050$.
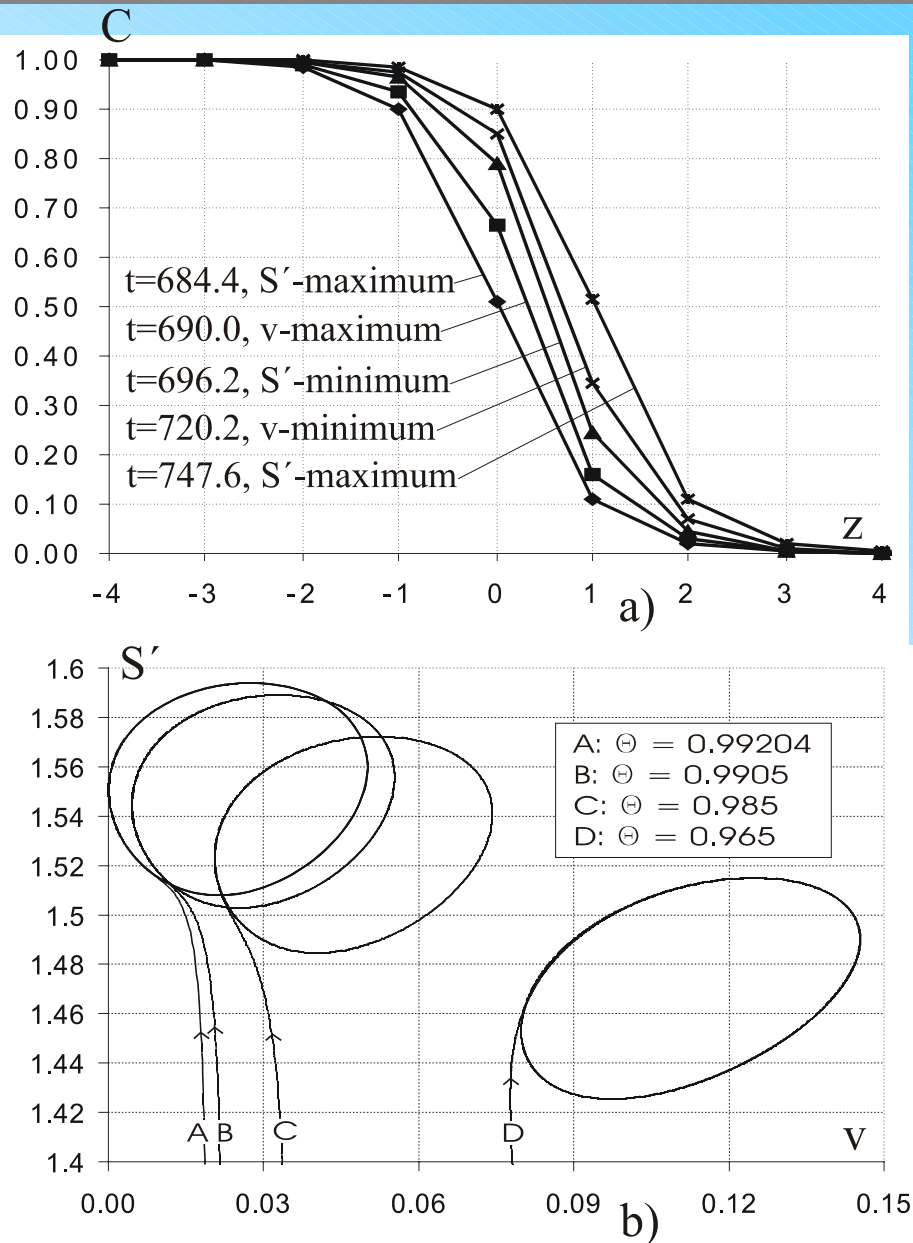
Fig. 5. a) Function C(z) for different time instants in the frame of one growth cycle at the temperature Θ=0.99050, l=2.8, s=6, s_0=4. b) Phase trajectories (relation between entropy and velocity) for 4 different temperatures. Initial condition corresponds to the absolutely smooth surface.
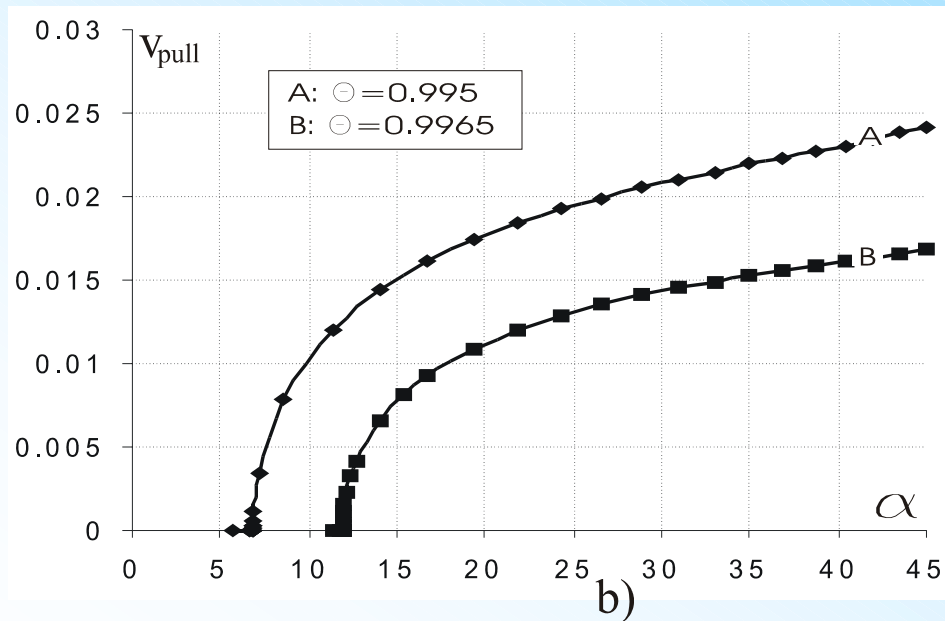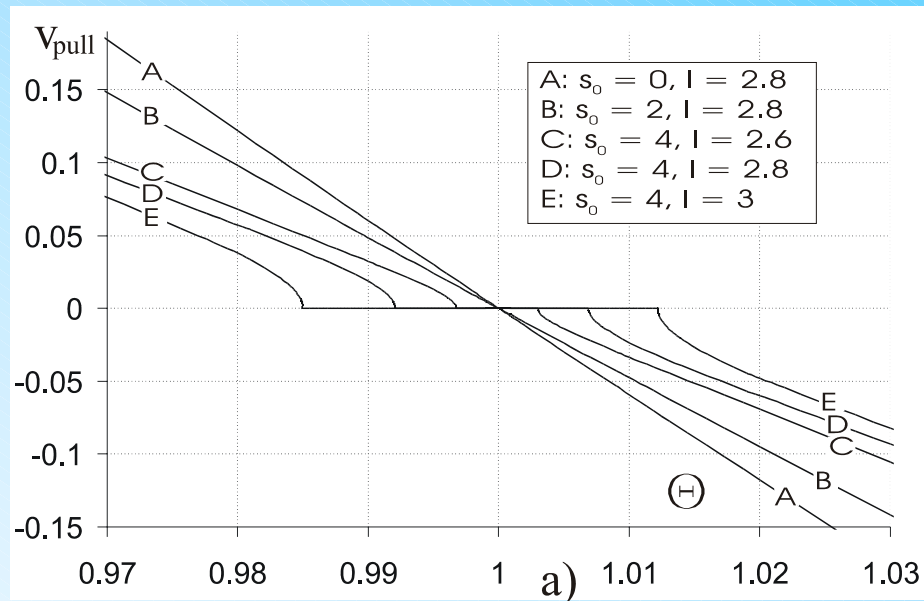
Fig. 6. a) Pulling velocity as function of temperature at *s*=6 for different values of s_0 and *l*. b) Pulling velocity as a function from angle between the crystallisation front and horizontal plane for cubic lattice at different temperature values, *l*=2.8, *s*=6.
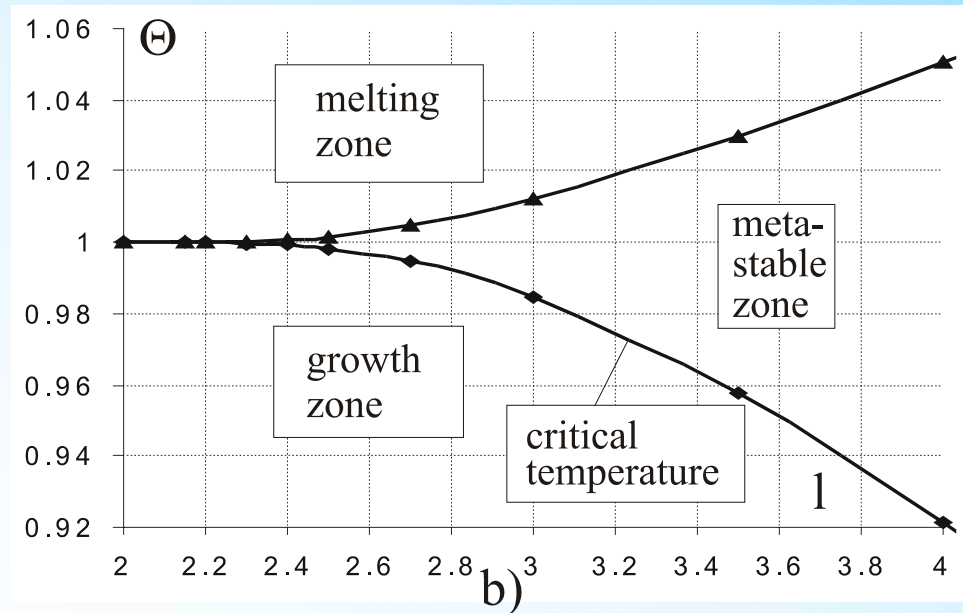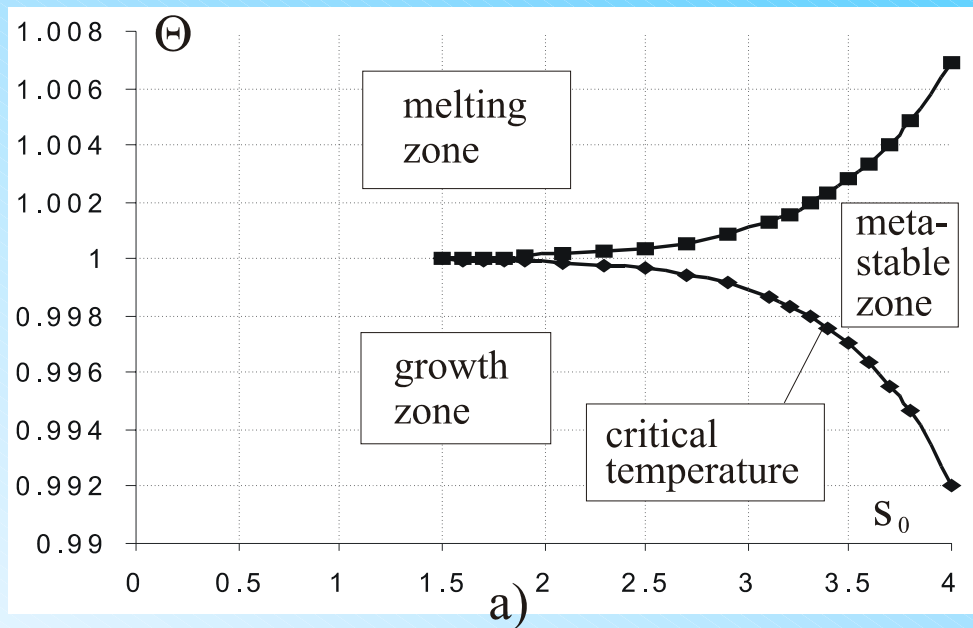
Fig. 7. Values of the critical temperature for crystal growth and melting as a function a) from s_0 at l=2.8, s=6; b) from l at s=6, s_0=4.
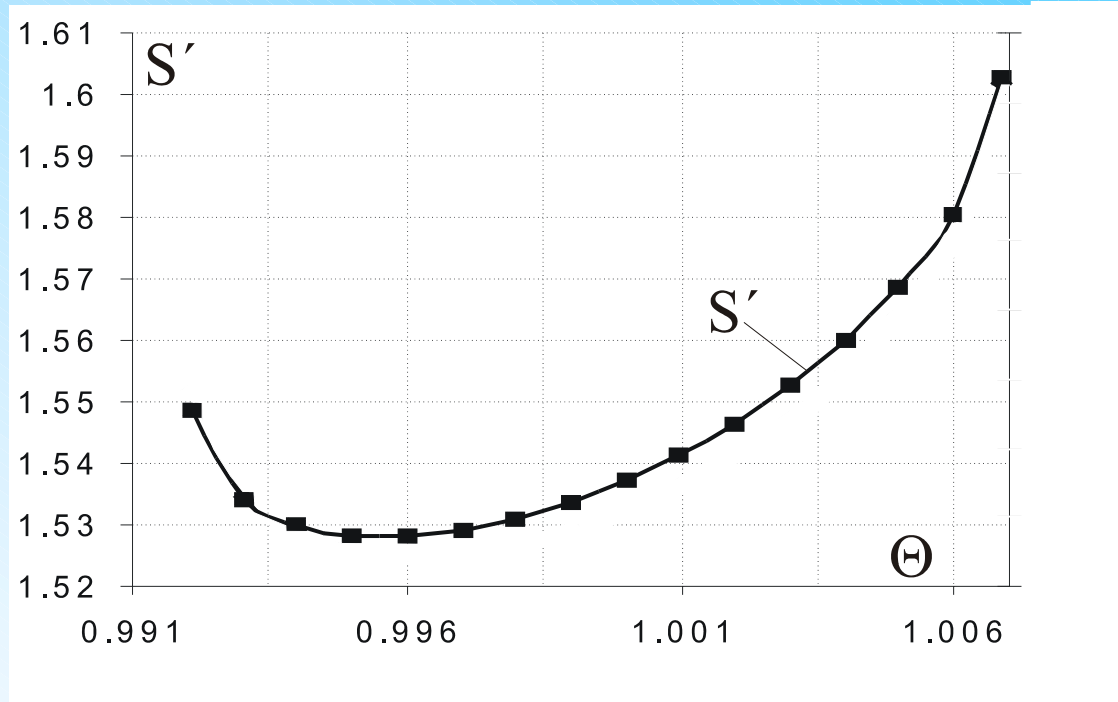
Fig. 8. Entropy of the surface in metastable zone as a function from temperature at l=2.8, s=6 and, s_0=4.
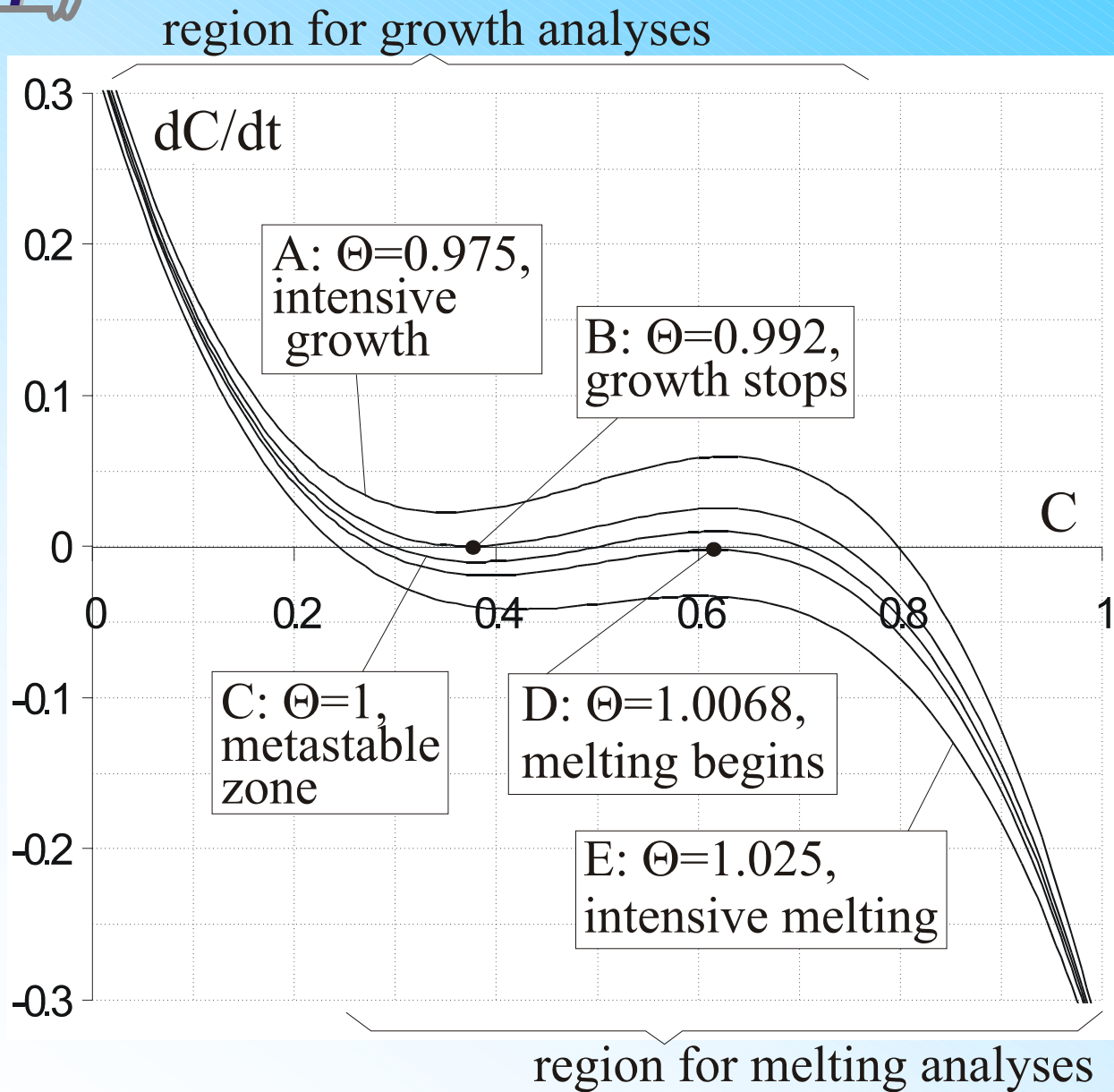
Fig. 9. Dependence of *dC/dt* on *C* for the simplified model with parameters: $l=2.8$, $s=6$, $s_0=4$, $\eta=1.725$. The value of η is chosen to fit the value of the critical growth temperature calculated from complete model.

Conclusions

The results obtained by the proposed analytical model of crystallisation process in the mean field approximation for the cubic lattice have shown a good qualitative and quantitative agreement with the Monte Carlo results obtained by other authors. Besides the model has allowed to investigate the oscillating character of the crystallisation process and relations between the temperature, growth velocity and growth orientation. The transition from metastable state to rough growth has been analysed and processes diagram with growth, melting and metastable zones has been calculated.

The proposed model offers promising possibilities for further developments and analysis: 1) The investigations in case of silicon crystallographic structure; 2) Analysis in case of macroscopic spatial temperature inhomogeneity at the phase boundary, or in case of macroscopic temperature oscillations or in case of curved crystallisation front; 3) Detailed analysis of the transition layer between solid and fluid; 4) Modelling of the facets.