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Fluctuations of Thermal Conductivity and Morphological Stability

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Abstract

Compositional fluctuations of the binary alloy result in the corresponding fluctuations of the thermal conductivity of the material. During crystal growth, these fluctuations can significantly modify the local temperature fields at the liquid-solid interface. This , in turn, will affect the morphological stability of the growing interface. In this work, the temperature dependence of the thermal conductivity of the solid phase has been included into the Mullins-Sekerka formalism. A significant effect on the onset of the instability of planar interface has been predicted. It has been found, in particular, that for binary systems with the segregation coefficient above unity a flat interface is always unstable. The shape of the interface fluctuation should have a single harmonic character with a well defined wavelength.

Introduction

The stability of the crystal growth process is a major factor determining the structural quality of crystals used in modern technology. In fact, under unfavorable conditions small perturbations of process parameters can escalate in time and result in polycrystalline or dendritic growth. It is thus of practical importance to determine the critical conditions for the onset of instability and the wavelength of the initiating perturbation which will result in an undesirable growth regime. This knowledge can then be utilized to select the optimum range of process parameters, such as growth rate and interface temperature gradient. Control of the crystal growth process can be optimized, when the process parameters are selected correctly. Evidently, a stability criterion should be known in order to make such a choice.

The existing underlying theory can be split into a hydrodynamic stability theory, concerning bulk fluid dynamics, and the morphological stability theory, which focuses attention on the evolution of the interface shape during the solidification process. Since pioneering work by Mullins and Sekerka [1] in 1963, many refinements have been made to the morphological stability theory and many possible effects have been included in analyses. In particular, planar freezing interface stability under convection has been put forward [2], also interface stability problem during melting has been addressed [3]. Geometrical shapes other than planar have also been treated [4], eutectic solidification was studied [5]. Also, electric and magnetic effects on morphological stability have been studied [6]. The effects of anisotropy of crystal growth interface kinetic and surface diffusion have been analyzed [7]. An important extension to nonlinear theory has been attempted also [8]. The radiant heat transport effect [9] as well as diffusion dependence on concentration [10] have been considered.

In all the above analyses, a solid phase was considered as homogeneous. However, as the interface composition of the liquid phase fluctuates, so does the bulk of the growing solid phase. This, in turn, leads to perturbations in the temperature fields. As the fluctuation of the bulk composition can reach deep into a solid phase from the interface, this can create a strong fluctuation of the temperature field. This field, in turn, would modify the shape of the interface. The positive feedback of this process can create an interface breakdown, and the negative one will lead to the enhancement of the stability. In this paper we consider a binary alloy directional solidification process as a model process. We include the inhomogeneity of the thermal conductivity of the solid phase into the linear stability analysis. The buoyancy convection effect was not included at present into the analysis, so our results can only be relevant to the zero-gravity conditions. However, the interfacial fluid dynamics correction is not significant in many instances, and inclusion of it into analysis does not lead to a major modification of the Mullins-Sekerka criterion [2]. An analytic expression for the onset of instability has been derived, which is essentially a modified Mullins-Sekerka formula. The included effect can lead to enhanced stability or to instability, depending on the sign of the solutal gradient at the interface as well as on the temperature dependence of the thermal conductivity.

Morphological stability theory

We consider a unidirectional solidification process of a dilute binary alloy with the horizontal unperturbed planar liquid-solid interface moving upwards with a constant velocity v_0. It is convenient to work in the moving reference frame with the plane z=0 coinciding with the interface.

We consider thermal fields $T_{S,L}$, and solute concentration fields $C_{L,S}$, in solid and liquid, respectively. These fields can be split into unperturbed and perturbed parts as follows:

$$T_L(\mathbf{r},t)=T_{L0}(z)+t_L(z)\exp(\sigma t+i\omega x) \tag{1}$$

$$T_S(\mathbf{r},t)=T_{S0}(z)+t_S(z)\exp(\sigma t+i\omega x) \tag{2}$$

$$C_L(\mathbf{r},t)=C_{L0}(z)+c_L(z)\exp(\sigma t+i\omega x) \tag{3}$$

$$C_S(\mathbf{r},t)=C_{S0}+c_S(z)\exp(\sigma t+i\omega x) \tag{4}$$

where T_{L0}, T_{S0}, C_{L0}, C_{S0} are unperturbed components.

Following a standard approach to the linear stability theory, we take only one harmonic component in the x (horizontal to the interface) direction of all the perturbed quantities. In addition, explicit exponential time dependence exp(σt) of these perturbations is assumed. In general, the parameter σ can be complex. The basic question the stability theory has to answer is , at what conditions the parameter σ is negative, or, more precisely, its real part is negative, so that the perturbations will die out in time. In order to answer this question, a coupled system of second order differential equations with related boundary conditions has to be solved. These equations for heat conduction and solute diffusion are

$$\nabla(\kappa_S \nabla T_S)+v_0 \partial T_S/\partial z=\partial T_S/\partial t \qquad (5)$$

$$\kappa_L \nabla^2 T_L+v_0\, \rho_S/\rho_L \partial T_L/\partial z=\partial T_L/\partial t \qquad (6)$$

$$D\nabla^2 C_L+v_0\, \rho_S/\rho_L \partial C_L/\partial z =\partial C_L/\partial t \qquad (7)$$

where $\kappa_{S,L}$ are the thermal diffusivities of solid and liquid phases and D is the solute diffusion coefficient.

Boundary conditions at the solid-liquid interface can be written in the form:

$$T_S=T_L \qquad (8)$$

$$C_S=kC_L \qquad (9)$$

$$\mathbf{vn}=\mu(T_M+mC_L-T_M\Gamma K-T_L) \qquad (10)$$

$$\mathbf{vn}L_v=(-k_L\nabla T_L+k_S\nabla T_S)\mathbf{n} \tag{11}$$

$$\mathbf{vn}(C_S-C_L)=\rho_L/\rho_S D\nabla C_L\mathbf{n} \tag{12}$$

where **n** is the unit vector normal to the interface, **v** is the interface velocity in the laboratory frame, k - segregation coefficient, L_v - latent heat per unit volume of solid, $\rho_{L,S}$ - liquid, solid density, $k_{L,S}$ - thermal conductivities of liquid, solid, μ - kinetic coefficient, T_M - melting point of the pure substance, m - the slope of the liquidus line, Γ - the capillary constant, K - is the interface curvature, and C_S is solid concentration.

The time independent stationary solution on unperturbed temperature and solute fields can be written in the form:

$$T_{L0}(z)=T_0+\frac{\kappa_L G_L}{v_0}\frac{\rho_L}{\rho_S}\left[1-\exp\left(-\frac{\rho_L}{\rho_S}\frac{v_0}{\kappa_L}z\right)\right] \tag{13}$$

$$T_{S0}(z)=T_0+\frac{\kappa_S G_S}{v_0}\left[1-\exp\left(-\frac{v_0}{\kappa_S}z\right)\right] \tag{14}$$

$$C_{L0}(z)=C_\infty+\frac{1-k}{k}C_\infty\exp\left(-\frac{v_0}{D}\frac{\rho_S}{\rho_L}z\right) \tag{15}$$

where G_L, G_S denote the temperature gradients at the interface in liquid and in solid, respectively. From the boundary condition (10) follows the relationship between these gradients:

$$k_S G_S - k_L G_L = L_v v_0 \qquad (16)$$

A solute concentration in liquid far away from the interface ($z \rightarrow \infty$) is denoted in Eq. 15 by C_∞. From the boundary condition (9) one can obtain $C_{S0} = C_\infty$. In other wards, the solute concentration in growing solid is equal the concentration in the melt far away from the interface.

At this point we can proceed to the linearized equations on perturbations. In addition to the temperature and solute perturbations we have to introduce also a perturbation of the interface shape. A single Fourier component of an arbitrary interface perturbation can be taken in the form:

$$z_{SL} = \delta \exp(\sigma t + i\omega x) \qquad (17)$$

We assume the following expressions for κ_S and k_S as functions of the perturbation c_S of the solid composition:

$$\kappa_S(c_S) = \kappa_S\,(1+\gamma c_S), \quad k_S(c_S) = k_S\,(1+\gamma' c_S) \qquad (18)$$

These relations define quantities γ, γ'.

Substitution of Eqs. (1-4) into Eqs. (5-7) and retaining only linear perturbation quantities yields the following system of differential equations for the fluctuations:

$$[\kappa_S(d^2/dz^2-\omega^2)+v_0 d/dz-\sigma]t_S(z)=-\gamma\kappa_S c_S(z)d^2T_{S0}(z)/dz^2 -\gamma\kappa_S dc_S/dz\, dT_{S0}/dz \tag{19}$$

$$[\kappa_L(d^2/dz^2-\omega^2)+v_0\,\rho_S/\rho_L d/dz-\sigma]t_L(z)=0 \tag{20}$$

$$[D(d^2/dz^2-\omega^2)+v_0\,\rho_S/\rho_L d/dz-\sigma]c_L(z)=0 \tag{21}$$

We also linearize the general boundary conditions Eqs. (8-12) and obtain at z=0:

$$L_v\partial z_{SL}/\partial t=k_S(\partial t_S/\partial z+z_{SL}\partial^2T_{S0}/\partial z^2)-k_L(\partial t_L/\partial z+z_{SL}\partial^2T_{L0}/\partial z^2)+\gamma' c_S k_S\partial T_{S0}/\partial z \tag{22}$$

$$\partial z_{SL}/\partial t=\mu\{mz_{SL}\partial C_{L0}/\partial z-z_{SL}\partial T_{L0}/\partial z+mc_L-t_L+T_m\Gamma\partial^2z_{SL}/\partial x^2\} \tag{23}$$

$$\partial z_{SL}/\partial t(1-k)C_S=kv_0\partial C_{L0}/\partial z z_{SL}-(1-k)v_0c_L-\rho_L/\rho_S D\partial c_L/\partial z \tag{24}$$

We utilize now the following explicit expressions (see Eqs. (13-15)):

$$dT_{L0}/dz=G_L\exp(-v_0\rho_S/\rho_L z/\kappa_L) \tag{25}$$

$$dC_{L0}/dz=G_c\exp(-v_0\rho_S/\rho_L z/D) \tag{26}$$

$$dT_{S0}/dz=G_S\exp(-v_0 z/\kappa_S) \tag{27}$$

$$c_S(z)=kc_L(0)\exp(\sigma/v_0 z) \tag{28}$$

where $c_S(z)$ is obtained from the expression on $c_L(\mathbf{r},t)$ and Eq. (9) assuming no diffusion of solute in the solid phase.

Utilizing (25)-(28), the boundary conditions can then be rewritten in the following form:

$$(G_S-G_L)\delta+t_S(0)-t_L(0)=0 \tag{29}$$

$$L_v\sigma\delta=k_S(dt_S(0)/dz-\delta v_0/\kappa_S G_S)-k_L(dt_L(0)/dz-\delta v_0/\kappa_L G_L\rho_S/\rho_L)+G_S\gamma' k_S c_S(0) \tag{30}$$

$$\sigma\delta=\mu[m\delta G_c-\delta G_L+mc_L(0)-t_L(0)-T_m\Gamma\delta\omega^2] \tag{31}$$

$$\sigma\delta(1-k)C_{L0}=kv_0\delta G_c-(1-k)v_0c_L(0)-\rho_L/\rho_S Ddc_L(0)/dz \tag{32}$$

The solution to the equations (19,20,21) which is finite at $z \rightarrow \infty$ can be given in the form:

$$c_L(z)=A\exp(-\beta z) \tag{33}$$

$$t_L(z)=B\exp(-\alpha_L z) \tag{34}$$

$$t_S(z)=R\exp(\alpha_S z)+\zeta A\exp(\lambda z) \tag{35}$$

where

$$\beta = \frac{v_0\rho_S}{2D\rho_L}\left[1+\sqrt{1+4a^2}\right] \tag{36}$$

$$\alpha_L = \frac{v_0\rho_S}{2\kappa_L\rho_L}\left[1+\sqrt{1+4a^2\left(\frac{\kappa_L}{D}\right)^2}\right] \tag{37}$$

$$\alpha_S = \frac{v_0}{2\kappa_S}\left[-1 + \sqrt{1 + 4a^2(\frac{\kappa_S \rho_S}{D\rho_L})^2}\right] \tag{38}$$

$$\zeta = -\frac{\lambda\gamma k G_S \kappa_S}{\kappa_S(\lambda^2-\omega^2)+v_0\lambda-\sigma} \tag{39}$$

$$\lambda = \frac{\sigma}{v_0} - \frac{v_0}{\kappa_S} \tag{40}$$

and where

$$\omega = a\frac{v_0 \rho_S}{D\rho_L} \tag{41}$$

We substitute Eqs.(33,34,35) into Eqs. (29-32) and , after elimination of A,B,R,δ obtain the following condition:

$$L_v\sigma+k_S/\kappa_S v_0 G_S-k_L/\kappa_L v_0 G_L \rho_S/\rho_L-k_L\alpha_L(G_S-G_L)-(k_L\alpha_L+k_S\alpha_S)(mG_C-\sigma/\mu-G_S-T_m\Gamma\omega^2)=$$

$$[G_S\gamma k'_{-S}+k_S\zeta(\lambda-\alpha_S)+(k_L\alpha_L+k_S\alpha_S)m][\sigma(1-k)C_{L0}-kv_0G_C]/[\rho_L/\rho_S D\beta-(1-k)v_0] \tag{42}$$

We restrict our analysis to stationary modes only, for which the parameter σ is real. In case of σ>0 the perturbation grows exponentially in time, and, for σ<0 there is a stable growth condition as the fluctuation dies out. The condition σ=0 will then divide the parameters space into two regions, stable, and unstable.

We put $\sigma=0$ into Eq.(42) and obtain the stability criterion in a form given by Mullin and Sekerka, but with a correction term present:

$$(\sqrt{1+4a^2}-1+2k)(G(a)+Ba^2)-mG_c(\sqrt{1+4a^2}-1)+2kG_c\mathrm{corr}=0 \tag{43}$$

where:

$$G(a)=[G_S(v_0k_S/\kappa_S+k_S\alpha_S)+G_L(k_L\alpha_L-v_0k_L/\kappa_L\rho_S/\rho_L)]/(k_L\alpha_L+k_S\alpha_S) \tag{44}$$

and

$$B=T_m\Gamma\left(\frac{v_0\rho_S}{D\rho_L}\right)^2 \tag{45}$$

In the limit $k_{S,L}>>D$ the function $G(a)=(G_Sk_S+G_Lk_L)/(k_S+k_L)$ which is the quantity commonly used in the stability criterion.

The correction term which takes into account fluctuations of composition in solid has the form:

$$\mathrm{corr}=G_Skk_S[\gamma'+\gamma(\frac{D\rho_L}{\kappa_S\rho_Sa})^2(1+\frac{\kappa_S}{v_0}\alpha_S)]/(k_L\alpha_L+k_S\alpha_S) \tag{46}$$

DISCUSSION

We will examine the functional behavior of $G_L(a)$ with all other parameters fixed. The area above this function represents the stable condition.

We introduce nondimensional functions:

$$\bar{\alpha}_S = \kappa_S/v_0\alpha_S \tag{47}$$

$$\bar{\alpha}_L = \kappa_S/v_0\alpha_L \tag{48}$$

$$\alpha(a) = \sqrt{1+4a^2} - 1 \tag{49}$$

$$f(a) = 1 - \frac{\kappa_S\rho_S}{\kappa_L\rho_L} + \bar{\alpha}_S + \bar{\alpha}_L \tag{50}$$

$$\mathrm{eps}(a) = 2k^2G_c\kappa_S/v_0(\gamma' + \gamma(\frac{D\rho_L}{\kappa_S\rho_S a})^2(1+\bar{\alpha}_S)) \tag{51}$$

Utilizing Eq.(16) we can eliminate G_s and obtain from Eq.(43):

$$-mG_c\alpha(a)(\bar{\alpha}_L + k_S/k_L\bar{\alpha}_S) + \frac{L_v v_0}{k_L}[\mathrm{eps}(a) + (\alpha(a)+2k)(1+\bar{\alpha}_S)] + \tag{52}$$

$$+(\alpha(a)+2k)Ba^2(\bar{\alpha}_L + k_S/k_L\bar{\alpha}_S) + G_L[\mathrm{eps}(a) + f(a)(\alpha(a)+2k)] = 0$$

The above equation defines a function $G_L(a)$, which will have a pole when the denominator eps(a)+f(a)(α(a)+2k) becomes zero. Let us take a closer look at this term. In all practically interesting cases f(a) is always positive as is α(a). The function eps(a) expresses the effect of the temperature dependence of the thermal conductivity on the interface stability. In case of eps(a) > 0 we have a stabilizing correction. More interesting is the case of eps(a) < 0. It will be fulfilled when $\gamma,\gamma' > 0$ and $G_c < 0$ or $\gamma,\gamma' < 0$ and $G_c > 0$. In such cases, eps(a) tends to $-\infty$ as $a \rightarrow 0$. It is evident that [eps(a)+f(a)(α(a)+2k)] will cross zero at some small value of a. Consequently, $G_L(a)$ will have a pole at this value and no extremum in the $G_L(a)$ will exist. In conclusion, for eps(a) < 0 the planar interface is always unstable, according to the present analysis.

For semiconducting or insulating pseudobinary alloys the slope of the thermal conductivity as well as the diffusivity is always negative, as the heat conduction in these materials is predominantly by phonons, and the contribution of the alloy scattering to the phonon scattering processes is significant (see, for example [11]). For this class of materials the analyzed effect has a beneficial action of stabilization at longer wavelengths of the interface perturbation in the case where the distribution coefficient k<1 and is destabilized at k>1. Many examples of such systems can readily be found. It is more difficult to find an example of the system for which $\gamma,\gamma' > 0$ and k<1. It appears that some of metal alloys of the elements with similar valencies can serve as an example. Below, we estimate the γ, γ' for a number of metal alloys. For metals with similar valencies the thermal conductivity of the alloy is approximately a linear function of the composition. Also, the density of the composition can well be approximated with a linear dependence. The specific heat of the metallic element at high temperature follows the Dulong and Petit's law, and the specific heat of corresponding alloys can be obtained using the Kopp-Neumann law. We then obtain for the specific heat of the metallic alloy:

$$C_V(x) = x * C_{V0}/A1 + (1-x) * C_{V0}/A2 \tag{53}$$

where C_{V0} is the constant, about 6 cal g-atom^{-1} K^{-1} ; A1, A2 are the atomic weights of the alloy elements , and x is the alloy composition. We also use similar linear relations for the density and the thermal conductivity of the alloy:

$$\rho_S(x) = x * \rho 1 + (1-x) * \rho 2 \tag{54}$$

$$k_S(x) = x * k1 + (1-x) * k2 \tag{55}$$

where the thermal conductivities and the densities k1,ρ1,k2,ρ2 correspond to the constituent elements. Employing the relationship between the thermal diffusivity and the thermal conductivity of the material:

$$\kappa_S' = \frac{k_S}{C_V \rho_S} \tag{56}$$

we then obtain for small x:

$$\gamma' = (k1 - k2)/k2 \tag{57}$$

$$\gamma = \gamma' - \rho 1/\rho 2 - A2/A1 + 2 \tag{58}$$

These formulas yield the following values for specific alloys:

$Sn_xBi_{(1-x)}$: γ=6.924, γ'=7.434, k=0.0023

$In_xGa_{(1-x)}$: $\gamma=2.066$, $\gamma'=1.911$, $k=0.00001$

$Sb_xBi_{(1-x)}$: $\gamma=1.678$, $\gamma'=2.081$, $k=4.47$

$Bi_xSb_{(1-x)}$: $\gamma=-0.715$, $\gamma'=-0.675$, $k=0.26$

$Sn_xPb_{(1-x)}$: $\gamma=0.503$, $\gamma'=0.893$, $k=0.59$

$Cd_xZn_{(1-x)}$: $\gamma=0.041$, $\gamma'=-0.165$, $k=0.18$

We also included the corresponding approximate values for the distribution coefficient of the alloys. The presented approach is semi-quantitative only, especially considering the fact that most of the above alloys form eutectics.

As an illustration of the presented stability analysis, at Fig.1 we have plotted the temperature gradient G_L in the melt at the interface as a function of the wavelength of the perturbation. Also, the well known Mullin-Sekerka result (dotted curve) is plotted at this graph. The following set of parameters typical for metallic alloys has been used for this purpose:

$D=10^{-5}\text{cm}^2/\text{sec}$

$T_m\Gamma=10^{-5}$ cm K

$L_v=300$ joule/cm^3

$m=-3$

$k=0.1$

$k_L=0.15$ joule/(cm K sec)

k_S=0.3 joule/(cm K sec)

κ_L=0.1 cm^2/sec

κ_S=0.2 cm^2/sec

C_∞ =0.1

$\gamma=\gamma'=5$

$\rho_S/\rho_L=1$

$v_0=5*10^{-4}$ cm/sec

The pole position of $G_L(a)$ is at the wavelength of approximately 0.7 cm. Finally, it has been found by varying numerical values of the parameters, that the position of this pole is a sensitive function of the ratio D/v_0. The smaller the ratio, the smaller the corresponding wavelength of the pole. Practically, this instability mode can potentially be detected in case of small diffusion coefficients and high growth rates. Also, this kind of instability, if present, will lead to a well defined periodic interface shape.

CONCLUSION

In this work, we have investigated theoretically the effect of temperature dependence of the thermal conductivity on the onset of the planar interface instability during the crystal growth. The Mullins-Sekerka results have been modified and the additional correction was included into the analysis. In most of the cases with the distribution coefficient k smaller than one the considered effect yields only a small stabilizing correction to the Mullins-Sekerka formula. For k>1, however, our analysis shows that there is a wavelength at which the perturbation of the interface will always grow in time. A similar effect can be expected when the electric current is utilized as a driving force for the crystal growth (electrolytic deposition, LPEE).

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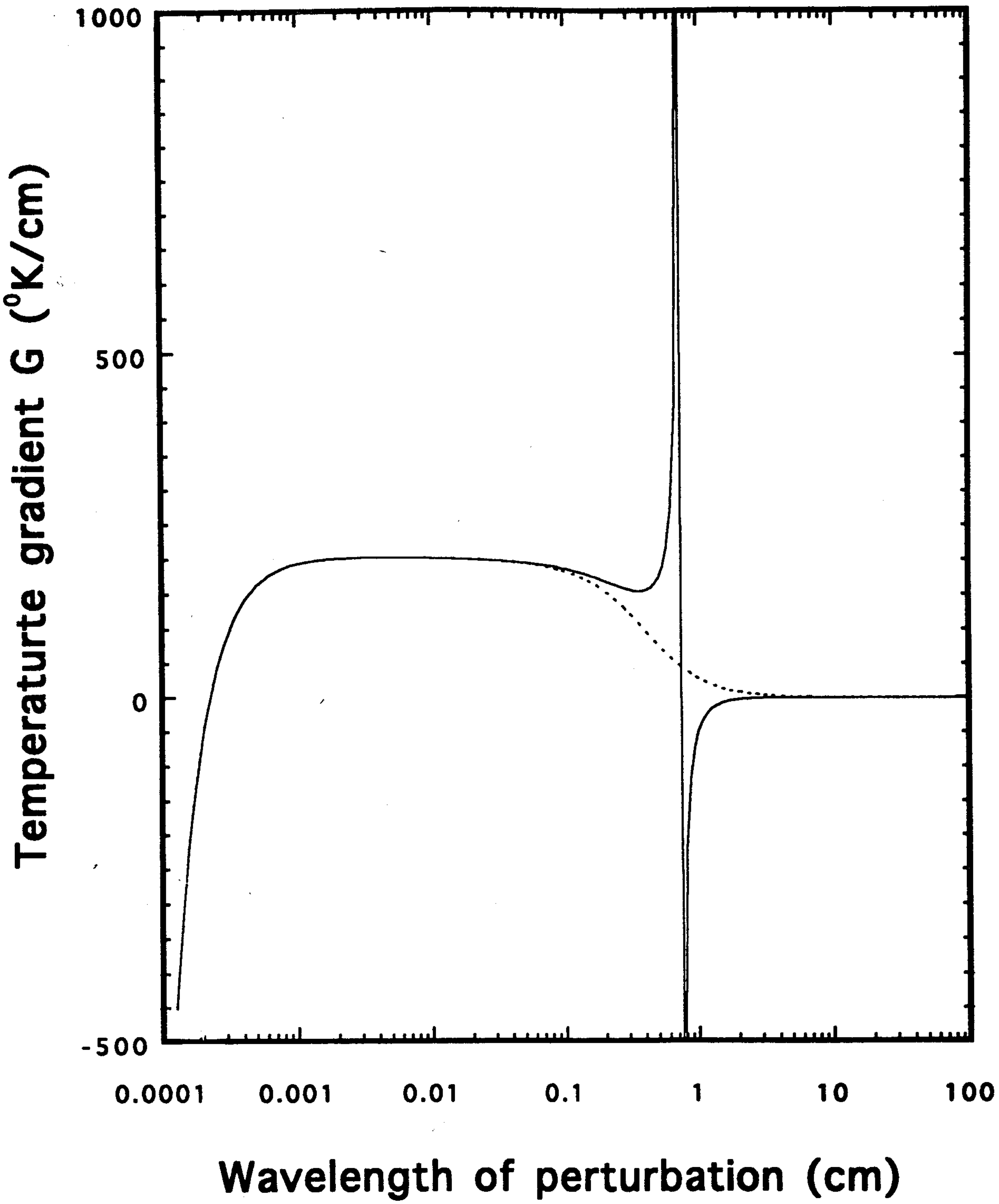

1000
500
0
-500
0.0001
0.001
0.01
0.1
1
10
100
Temperaturte gradient G (^{0}K/cm)
Wavelength of perturbation (cm)

Figure caption

Fig.1. The threshold temperature gradient Gl in the melt at the interface as a function of the wavelength of the perturbation. Solid line - this analysis; dotted line - Mullin-Sekerka result.