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ON CELLULAR INSTABILITY IN THE SOLIDIFICATION OF A DILUTE BINARY ALLOY[1]

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Abstract

In the solidification of a dilute binary alloy, a planar solid-liquid interface is often found to be unstable, spontaneously assuming a cellular structure. If the solute rejection coefficient is close to unity, then, near the stability threshold, the characteristic cell size may significantly exceed the diffusional width of the solidification zone. This situation enables one to derive an asymptotic nonlinear equation which directly describes the dynamics of the onset and stabilization of cellular structure:

$$f_\tau + \nabla^4 f + \nabla[(2-f)\nabla f] + \alpha f = 0 .$$

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1. Introduction

Problems of linear stability in the physics of continuous media frequently lead to dispersion relations expressible as equations of the type

$$\omega = (R-R_c)k^2 - k^4 \quad , \quad k = |\vec{k}| \tag{1}$$

near the stability threshold (R_c); here ω and $\vec{k}$ are the growth rate and wave vector of a small harmonic perturbation:

$$\Phi \sim \exp(\omega t + i\vec{k}\cdot\vec{x}) \, . \tag{2}$$

Φ is a certain characteristic function, whose precise meaning depends on the problem context. Comparing (1) and (2), we obtain the following equation for the linear evolution of Φ:

$$\Phi_t + (R-R_c)\nabla^2\Phi + \nabla^4\Phi = 0 \, . \tag{3}$$

At $R > R_c$, Eq. (3) implies exponential amplification of long-wave perturbations. In real situations, this unrestricted amplification of the perturbation is usually suppressed by nonlinear effects, which may correspond to certain nonlinear terms not appearing in Eq. (3):

$$\Phi_t + (R-R_c)\nabla^2\Phi + \nabla^4\Phi + \textit{nonlinear terms} = 0 \, . \tag{4}$$

The spatial dimensionality of the characteristic function Φ is often less than that of the initial problem. Hence, the construction of the closed nonlinear equation (4) is an essential simplification of the problem. Indeed, a dimensionality-lowering procedure of this kind frequently proves technically possible because, by (1), near the stability threshold we have

$$k \sim \sqrt{R-R_c} \quad , \quad \omega \sim (R-R_c)^2 \tag{5}$$

i.e., we are dealing with a process which varies slowly both in time and in space.

The approach just described has recently found successful application in deriving equations for the nonlinear evolution of phase in certain biochemical oscillations [1,2], for propagating flame fronts [3], for the free surface of a liquid film [4], and for the plane form in Bénard-Marangoni convection [5,6]. Some of these equations were even rich enough to describe chaotic behavior in the relevant physical systems.

The asymptotic technique[5] developed in the above-cited papers has also proved effective in deriving an equation for the nonlinear evaluation of solid-liquid interfaces in crystal growth problems.

It is known (see, e.g., Langer [8]) that, under certain conditions, when a dilute binary alloy is solidifying, a planar solid-liquid interface is found to be unstable, spontaneously assuming a cellular structure. The characteristic cell size may significantly exceed the diffusional width of the solidification zone. It will be shown below that this effect becomes more prominent, near the stability threshold, as the so-called solute rejection coefficient $1-K$ comes closer to unity. Thus, structure of the interface may be not only quasi-stationary but even quasi-planar. Thanks to this, one can lower the dimensionality of the relevant mathematical problem and obtain an explicit nonlinear equation which directly describes the dynamics of the onset and crystallization of the cellular structure.

[5]The techniques employed resemble those of Newell and Whitehead [7], who studied pockets of closely related modes in Rayleigh-Bénard convection and obtained envelope equations for slow modulation. The difference is that, whereas Newell and Whitehead perturb about a finite wave number, in our case one has to perturb about zero (see (5)).

2. Mathematical Model

We start with a mathematical model originated by Mullins and Sekerka [9] to describe an experimental situation in which solidification is controlled so that the mean position of the interface ($z = 0$) moves at a constant speed V (Fig. 1). Following Wollkind and Segel [10], we assume that the thermal diffusivity D_T of the system is significantly greater than the diffusivity D of the solute. Then, if the latent heat is not too large, the heat generated on the interface may be neglected. Moreover, following Langer [8], we assume that the thermal diffusivities of the liquid and solid phases are equal. Under these simplifying assumptions, disturbances of the interface does not induce disturbance of the temperature field, which may be assumed fixed and equal to

$$T = T_0 + Gz \ . \tag{6}$$

Here z is the coordinate of the mean position of the interface (Fig. 1), T_0 the temperature corresponding to the undisturbed planar interface and G the imposed temperature gradient.

The diffusion of the solute in the liquid phase is described by an equation

$$C_t = VC_z + D\nabla^2 C \ , \quad z \geq \Phi(x,t) \tag{7}$$

where C is the concentration of the solute, $z = \Phi$ the equation of the liquid-solid interface.

The temperature at the interface depends both on the curvature of the interface ν and on the solute concentration C; on the assumption that C is small:

$$T = T_m(0) + (dT_m(0)/dC)C - T_m(0)\Gamma\nu \quad (z = \Phi) \ . \tag{8}$$

Here $T_m = T_m(C)$ is the equilibrium melting temperature of the planar interface. $C = 0$ corresponds to the pure solvent. Γ is the capillarity constant,

$$\nu = -\frac{\Phi_{xx}}{(1+\Phi_x^2)^{3/2}}. \tag{9}$$

It follows from (6) and (8) that

$$T_0 = T_m(0) + (dT_m(0)/dC)C_0 \tag{10}$$

where C_0 is the solute concentration at the planar interface.

Eliminating the temperature from (6) and (8), we obtain the following direct relationship between the solute concentration at the interface and its geometry:

$$C = C_0 + \frac{T_m(0)\Gamma\nu + G\Phi}{dT_m(0)/dC}. \tag{11}$$

Conservation of the solute at the interface yields the equation

$$V_n(K-1)C = D\,\frac{dC}{dn} \tag{12}$$

where

$$\vec{n} = \frac{(-\Phi_x, 1)}{\sqrt{1+\Phi_x^2}}$$

is the unit vector normal to the interface and

$$V_n = \frac{(V+\Phi_t)}{\sqrt{1+\Phi_x^2}}$$

is the normal speed at which the interface is moving. K is the distribution coefficient, defined as the ratio of the equilibrium concentration of solute on the solid side of the interface to that on the liquid side ($K<1$).

Thus,

$$C \to KC_0 \qquad as \qquad z \to \infty\,. \tag{13}$$

Eq. (7), together with conditions (11)-(13), fully define the mathematical problem for the unknown functions C and Φ.

The basic solution, corresponding to the undisturbed planar interface ($\Phi \equiv 0$), is

$$C^{(b)} = KC_0 + (1-K)C_0 \exp(-Vz/D) \ , \ z \geq 0 \ . \tag{14}$$

3. Linear Stability Analysis

We first transform to nondimensional variables and parameters:

$$Vz/D = \tilde{z} \ , \ Vx/D = \tilde{x} \ , \ V^2 t/D = \tilde{t} \ ,$$
$$D\nu/V = \tilde{\nu} \ , \ C/C_0 = \tilde{C} \ , \ V\Phi/D = \tilde{\Phi} \ , \tag{15}$$
$$\frac{GD}{VC_0(dT_m(0)/dC)} = W(K-1) \ , \ \frac{\Gamma V T_m(0)}{DC_0(dT_m(0)/dC)} = \beta(K-1) \ .$$

In terms of these variables, problem (11)-(13) becomes

$$\tilde{C}_{\tilde{t}} = \tilde{C}_{\tilde{z}} + \nabla^2 \tilde{C} \ , \ \tilde{z} \geq \tilde{\Phi} \ ,$$
$$\tilde{C} = 1 + \beta(K-1)\tilde{\nu} + W(K-1)\tilde{\Phi} \ , \ (1-K)(1+\tilde{\Phi}_{\tilde{t}})\tilde{C} + \tilde{C}_{\tilde{z}} - \tilde{\Phi}_{\tilde{x}}\tilde{C}_{\tilde{x}} = 0 \ , \ \tilde{z} = \tilde{\Phi} \ ; \tag{16}$$
$$\tilde{C} \to K \quad as \quad \tilde{z} \to \infty \ .$$

$$\tilde{C}^{(b)} = K + (1-K)\exp(-\tilde{z}) \ . \tag{17}$$

Linear analysis of the stability of the basic solution (17) yields the following dispersion relation (Wollkind and Segel [10]):

$$\omega = (1 - W - \beta k^2)\left[\sqrt{1/4 + k^2 + \omega} + K - 1/2\right] - K$$
$$(\tilde{\Phi} \sim \exp(\omega\tilde{\tau} + ik\tilde{x})) \ . \tag{18}$$

Fig. 2 exhibits the position of the neutral stability curves for various values of K. At small $W_c - W$ ($W_c = 1$), in the instability region:

$$k \sim \sqrt{W_c - W} \ , \ \omega \sim K \sim (W_c - W)^2 \ . \tag{19}$$

Thus, the disturbed structure of the interface turns out here to be both quasi-stationary and quasi-one-dimensional. For such values of the parameters, the dispersion relation (18) simplifies to

$$\omega \simeq (W_c - W)k^2 - \beta k^4 - K \qquad (W_c = 1)\ . \tag{20}$$

This expression highlights the role of each of the parameters (Fig. 3). At $W < W_c$, instability sets in only at sufficiently small values of the distribution coefficient K.

4. Nonlinear Asymptotic Analysis

For the sequel, it is convenient to transform to a curvilinear coordinate system attached to the disturbed interface:

$$\tilde{z} - \tilde{\Phi}(\tilde{x},\tilde{t}) \to \tilde{z}\ ,\ \tilde{x} \to \tilde{x}\ ,\ \tilde{t} \to \tilde{t}\ . \tag{21}$$

Problem (16) then becomes

$$\begin{gathered} \tilde{C}_{\tilde{t}} = (1+\tilde{\Phi}_{\tilde{t}})\tilde{C}_{\tilde{z}} + \tilde{C}_{\tilde{x}\tilde{x}} + (1+\tilde{\Phi}_{\tilde{x}}^2)\tilde{C}_{\tilde{z}\tilde{z}} - 2\tilde{\Phi}_{\tilde{x}}\tilde{C}_{\tilde{x}\tilde{z}} - \tilde{\Phi}_{\tilde{x}\tilde{x}}\tilde{C}_{\tilde{z}}\ , \\ (1-K)(1+\tilde{\Phi}_{\tilde{t}})\tilde{C}(0) + (1+\tilde{\Phi}_{\tilde{x}}^2)\tilde{C}_{\tilde{z}}(0) - \tilde{\Phi}_{\tilde{x}}\tilde{C}_{\tilde{x}}(0) = 0\ , \\ \tilde{C}(0) = 1 + \beta(1-K)\tilde{\Phi}_{\tilde{x}\tilde{x}} - (1-K)W\tilde{\Phi}\ ,\ \ \tilde{C}(\infty) = K\ . \end{gathered} \tag{22}$$

We put

$$W = W_c(1-\varepsilon) \qquad (\varepsilon \ll 1)\ . \tag{23}$$

Our previous estimates (19) now suggest the following definitions of scaled variables and parameters:

$$\xi = \tilde{x}\sqrt{\varepsilon}\ ,\ \zeta = \tilde{z}\ ,\ \tau = \varepsilon^2\tilde{t}\ ,\ K = \kappa\varepsilon^2\ . \tag{24}$$

In terms of these variables, we shall look for a solution of problem (22) in the form

$$C = \kappa\varepsilon^2 + (1-\kappa\varepsilon^2)\exp(-\zeta) + \varepsilon u(\xi,\zeta,\tau,\varepsilon)\ ,$$

$$u = u^0 + \varepsilon u^1 + \varepsilon^2 u^2 + \cdots$$

$$\tilde{\Phi} = \varepsilon F(\xi,\tau,\varepsilon) = \varepsilon(F^0 + \varepsilon F^1 + \varepsilon^2 + \cdots) . \tag{25}$$

The problem in the zeroth approximation is

$$\begin{gathered} u^0_\zeta + u^0_{\zeta\zeta} = 0 , \\ u^0(0) + u^0_\zeta(0) = 0 \ , \ u^0(0) + W_c F^0 = 0 \ , \ u^0(\infty) = 0 . \end{gathered} \tag{26}$$

Hence

$$u^0 = -W_c F^0 \exp(-\zeta) . \tag{27}$$

As this stage the zeroth approximation is defined only up to an as yet unknown factor $W_c F^0$. To determine this factor, we proceed to the next (first) approximation.

$$\begin{gathered} u^1_\zeta + u^1_{\zeta\zeta} = -u^0_{\zeta\zeta} - F^0_{\xi\xi} \exp(-\zeta) , \\ u^1(0) + u^1_\zeta(0) = 0 \ , \ u^1(0) + W_c F^1 = \beta F^0_{\xi\xi} + W_c F^0 \ , \ u^1(\infty) = 0 . \end{gathered} \tag{28}$$

The solution is

$$u^1 = (-W_c F^1 + W_c F^0 + \beta F^0_{\xi\xi})\exp(-\zeta) + (1-W_c)F^0_{\xi\xi}\zeta\exp(-\zeta) - (1-W_c)F^0_{\xi\xi} . \tag{29}$$

From boundary condition at $\zeta = \infty$

$$(1-W_c)F^0_{\xi\xi} = 0 \quad or \quad W_c = 1 . \tag{30}$$

Thus, although we have obtained a numerical value for W_c, the function F^0 is still undefined. We therefore go on to the second approximation:

$$\begin{gathered} u^2_\zeta + u^2_{\zeta\zeta} = -u^1_{\xi\xi} - F^1_{\xi\xi}\exp(-\zeta) + u^0_\tau + F^0_\tau \exp(-\zeta) - \\ -(F^0_\xi)^2 \exp(-\zeta) + 2F^0_\xi u^0_{\xi\xi} + F^0_{\xi\xi} u^0_\tau , \end{gathered} \tag{31}$$

$$\begin{gathered} u^2(0) + u^2_\tau(0) = \kappa u^0(0) - F^0_\tau + (F^0_\xi)^2 + F^0_\xi u^0_\xi(0) , \\ u^2(0) + W_c F^2 = \beta F^1_{\xi\xi} + W_c F^1 + \kappa W_c F^0 \ , \ u^2(\infty) = 0 . \end{gathered} \tag{32}$$

The solution is

$$u^2 = [-F^2+F^1+\beta F^1_{\xi\xi}+2\kappa F^0+F^0_{\xi\xi}+\beta F^0_{\xi\xi\xi\xi}-(F^0_\xi)^2-F^0F^0_{\xi\xi}]\exp(-\zeta)+$$
$$+[\beta F^0_{\xi\xi\xi\xi}+F^0_{\xi\xi}-(F^0_\xi)^2-F^0F^0_{\xi\xi}]\zeta\exp(-\zeta)- \tag{33}$$
$$F^0_\tau-\kappa F^0-F^0_{\xi\xi}-\beta F^0_{\xi\xi\xi\xi}+(F^0_\xi)^2+F^0F^0_{\xi\xi}\ .$$

Condition at $\xi=\infty$ yields the desired equation for F^0:

$$F^0_\tau+\beta F^0_{\xi\xi\xi\xi}+[(1-F^0)F^0_\xi]_\xi+\kappa F^0=0\ . \tag{34}$$

Via the transformation

$$F^0=(1/2)f\ ,\ \tau=4\beta\overline{\tau}\ ,\ \xi=\sqrt{2\beta}\,\overline{\xi}\ ,\ \kappa=(1/4\beta)\alpha \tag{35}$$

Eq. (34) can be brought to the following one-parameter form, which is more convenient for analysis:

$$f_{\overline{\tau}}+f_{\overline{\xi\xi\xi\xi}}+[(2-f)f_{\overline{\xi}}]_{\overline{\xi}}+\alpha f=0\ . \tag{36}$$

Considerations of symmetry and invariance show that, in the three-dimensional case, the equation for $f=f(\overline{\xi},\overline{\eta},\overline{\tau})$ must have the form

$$f_{\overline{\tau}}+\nabla^4 f+\nabla[(2-f)\nabla f]+\alpha f=0\ . \tag{37}$$

5. Some Basic Properties of Equation (36)

The structure of Eq. (36) immediately yields certain qualitative conclusions about the evolution of the disturbances. First, it is clear that, since $\alpha>0$, the mean position of the interface always returns to its undisturbed state. Thus, it suffices to consider the case in which, through the entire time interval,

$$\int_{-\infty}^{\infty} f(\overline{\xi},\overline{\tau})d\overline{\xi}=0\ . \tag{38}$$

The initial amplification of small disturbances is due to the positive sign of $2-f$. On sections of the interface where f is positive, the instability will become weaker as the amplitude increases. Wherever f is negative, however, the instability will become stronger. This is apparently the explanation for the characteristic profile of the experimentally observed solidification front: the sections of the front convex toward higher temperatures have considerably lower curvature than those convex toward lower temperatures (Fig. 1).

It is interesting that Eq. (36) is a limiting case of the equation

$$f_{\bar{\tau}} + f_{\bar{\xi}\bar{\xi}\bar{\xi}\bar{\xi}} + [(2 - \gamma f + f_{\bar{\xi}}^2) f_{\bar{\xi}}]_{\bar{\xi}} + \alpha f = 0 \qquad (39)$$

which describes the evolution of a plane form of the Rayleigh-Bénard convection in nearly insulated liquid layer [11]. Parameter γ is proportional to $d\mu/dT$, where $\mu = \mu(T)$ is the temperature dependent viscosity of the liquid. Eq. (39) reduces to Eq. (36) for $\gamma \gg 1$.

Fig. 4 shows the results of numerical solution of the initial-value problem for Eq. (39) with $\alpha = 1.01$ and $\gamma = 5$ [11]. The equation was solved in the interval $0 \leq \bar{\xi} \leq 11\pi$ with periodic boundary conditions. The initial condition assumed was the antisymmetric perturbation $f(0,\bar{\xi}) = (\bar{\xi} - 15)\exp[-(\bar{\xi} - 15)^2/10]$. With the passage of time, a steady cellular structure developed, quite similar to that shown in Fig. 1. It would be of interest to do some numerical experiments with the two-dimensional equation (37) and to see whether it generates hexagonal structures of the solidification front.

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Figure Captions

Fig. 1. Diagram illustrating directional-solidification experiment.

Fig. 2. Neutral stability curves for different K values. $(\partial W(k,K)/\partial K < 0)$.

Fig. 3. Rate of stability parameter ω vs. disturbance wavenumber k. $(W < W_c)$.

Fig. 4. Stationary cellular structures generated by Eq. (39).

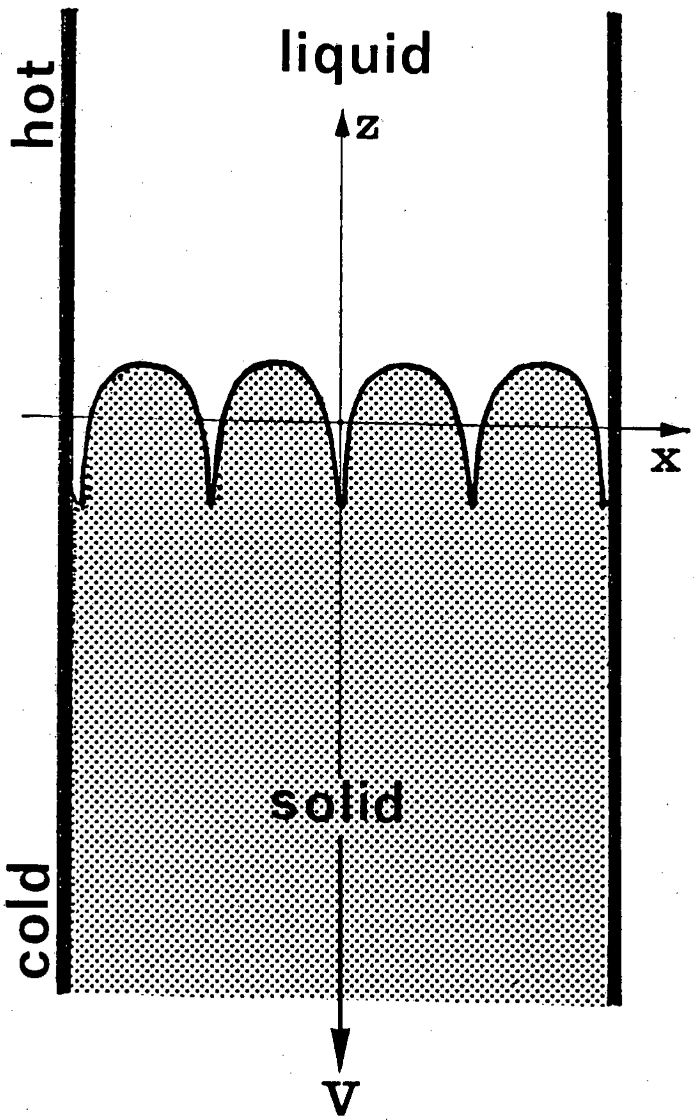

Fig. 1

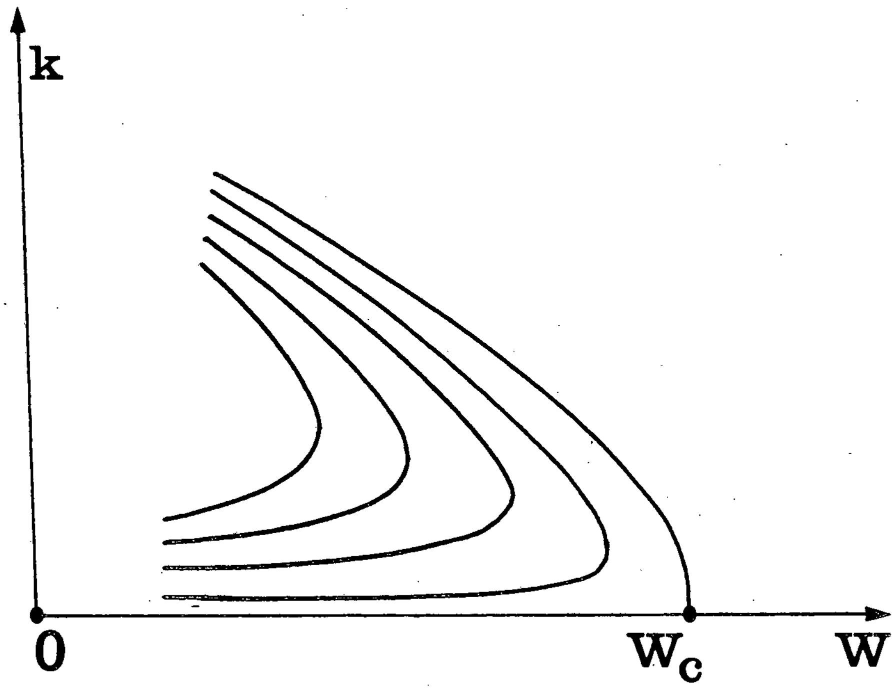

Fig. 2

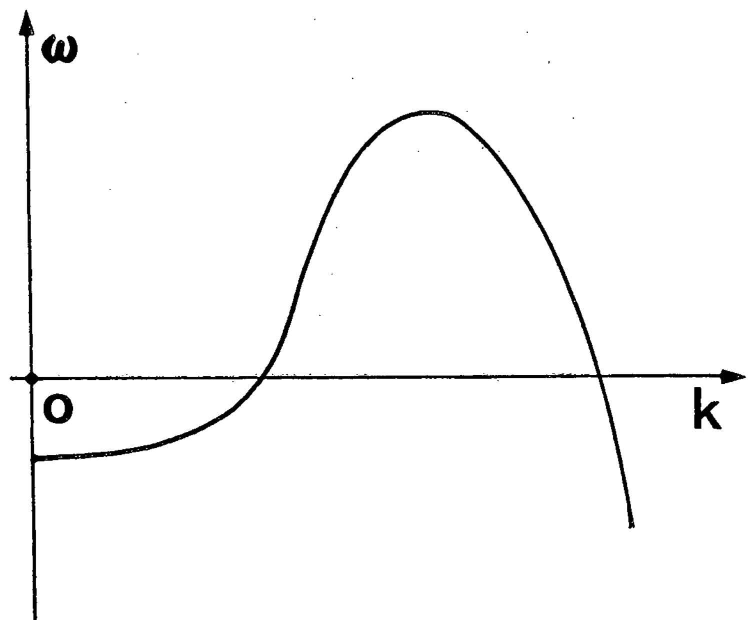

Fig. 3

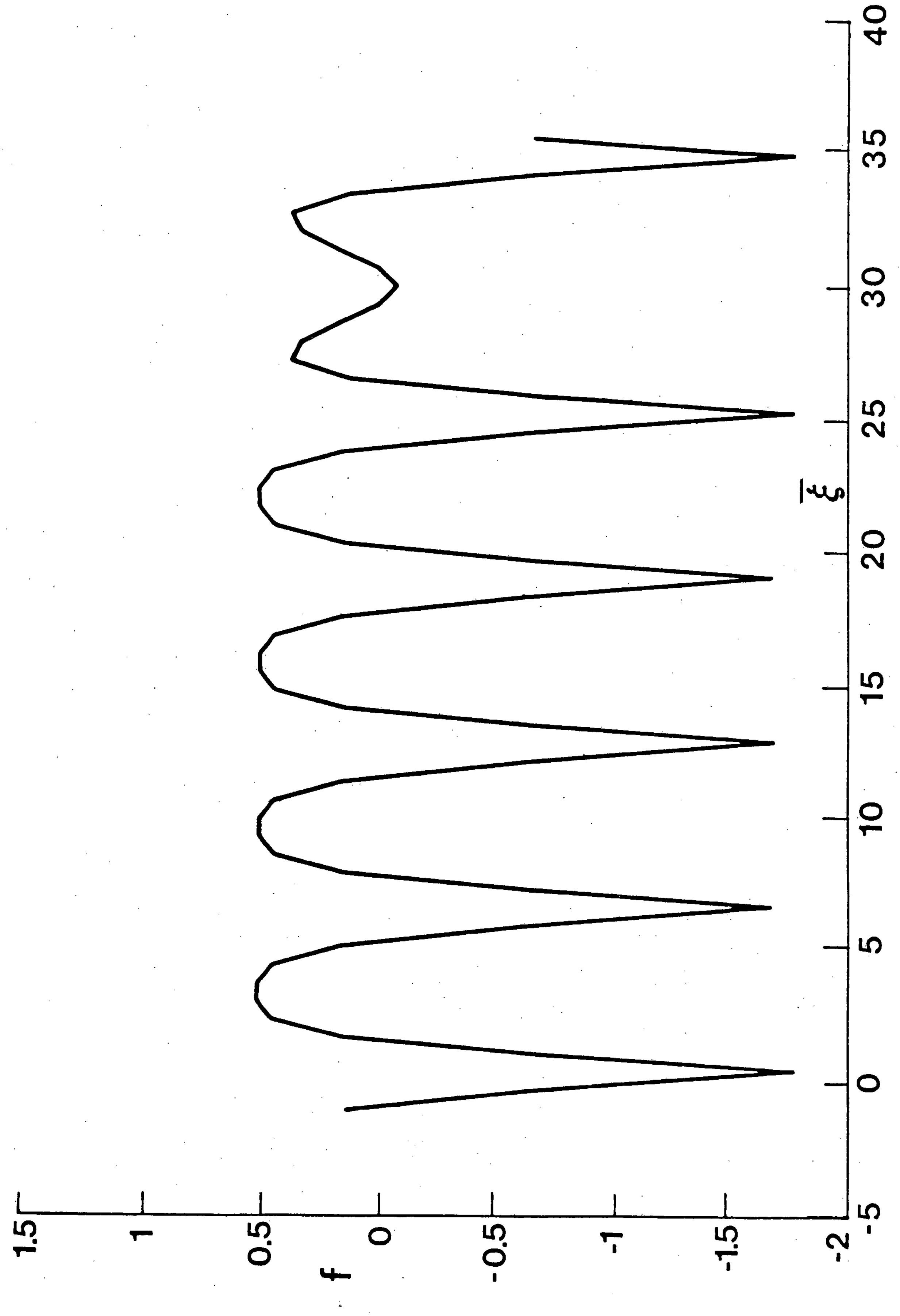

Fig. 4

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