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THE THEORY OF INHOMOGENEOUS CRYSTAL ORDER

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Abstract

The inhomogeneous crystal order is studied in terms of a tensor crystal-order theory. The local crystal order parameter is represented by the cubic nonor. The correlation length r_c near the temperature of absolute instability of a crystal phase is found within the mean-field small-fluctuations approximation: $r_c \sim r_0 (\tau^*)^{-1/4}$; $r_c(T_c) \approx 2.4\, r_0$. The crystal order in a semi infinite (flat surface) crystal is investigated. The effects, due to a few surface layers are treated phenomenologically. The possibility of an anomalous behaviour of temperature derivates of the surface characteristics of a crystal is exhibited.

1. Introduction

The theory of crystal order, [1] - [3] , describes the crystal in terms of the field $\hat{\Lambda}(\vec{r})$ of local crystal order. For all, but hexagonal crystals, the field $\hat{\Lambda}(\vec{r})$ is an irreducible rank-4 tensor. It represents the sixteenth-pole moment of the density-function in a small volume δV of a crystal. As follows from experimental data, δV contains $\sim 10^2$ atoms. The investigation of different model hamiltonians, carried out in [1] - [3] , showed that in the vincinity of the melting temperature T_c the main physical characteristics are practically model-independent. The mean-field approximation (MFA) used in [1] - [3] describes the system with relative error ~ 0.1. In these papers only the case of a homogeneous crystal order was studied. The aim of present work is to give the description of an inhomogeneous crystal order, based on ideas developed in previous papers. For example, the crystal surface gives rise to inhomogeneities in crystal structure. If not very close to the melting temperature $((T_c-T)/T_c > 0.1)$, the correlation length is small. The correlation length is equal to, in the meanfield small-fluctuations approximation, the correlation radius r_c of the influence of a point inhomogeneity on the crystal structure. While $T \rightarrow T_c$, r_c increases and becomes infinite in the temperature T^* of the crystal's instability.

2. The MFA equations of inhomogeneous order

Suppose the hamiltonian of the crystal arrangement is [1]

$$H\{\hat{\Lambda}\} = -\int \left[J(|\vec{r}-\vec{r}\,'|) \operatorname{Tr} \hat{\Lambda}(\vec{r}) \hat{\Lambda}(\vec{r}\,') + \operatorname{Tr} \hat{h}_e(\vec{r}) \hat{\Lambda}(\vec{r}\,') \right] dV\, dV', \qquad (1)$$

where $\hat{h}_e$ is an external field. In MFA $\hat{\Lambda}(\vec{r})$ equals to the average $\langle \hat{\Lambda}(\vec{r}) \rangle = \hat{T}$ for all points $\vec{r}$ but the one under consideration, for which the probability distribution of $\hat{\Lambda}$ is

$$dW\{\hat{\Lambda}\} = Z^{-1} \exp\left\{- \frac{H\{\hat{\Lambda}\}}{T}\right\},$$

$$Z = \int d\hat{\Lambda} \exp\left\{- \frac{H\{\hat{\Lambda}\}}{T}\right\}. \qquad (2)$$

(2)

The MFA hamiltonian $H\{\hat{\Lambda}\}$ takes the form

$$H\{\hat{\Lambda}\} = -\mathrm{Tr}\,\hat{h}\hat{\Lambda}\ ;\ \hat{h}(\vec{r}) = \hat{h}_e(\vec{r}) + \hat{h}_s(\vec{r}),$$

$$\hat{h}_s(\vec{r}) = \int J(|\vec{r}-\vec{r}\,'|)\hat{T}(\vec{r}\,')\,dV'. \tag{3}$$

One obtains the average value $\hat{T}$ of the parameter $\hat{\Lambda}$ from (2)

$$\hat{T} \equiv \langle\hat{\Lambda}\rangle = Z^{-1}\int\hat{\Lambda}\exp\left\{-\frac{H\{\hat{\Lambda}\}}{T}\right\}d\hat{\Lambda}. \tag{4}$$

Eqs. (3),(4) were solved in [1] - [3], in the case of $\hat{h}_e = 0$, when the integration over the space of configurations $\{\hat{\Lambda}\}$ reduced to 1) the integration over all rotations $\hat{q}$ of the SO(3) group: $\hat{\Lambda} = \hat{q}\hat{\Lambda}_0$ (continuous model [2]) and II) summing up over discrete rotations forming a discrete subgroup of SO(3). In the vincinity of T_c, $\hat{T}(\hat{h})$ is practically model-independent.

Consider the system with cubic local crystal-order parameter. All the irreducible tensors $\hat{T},\hat{h},\hat{h}_e,\hat{\Lambda}$ are proportional to the standard tensor $\Pi_{\alpha\beta\gamma\delta}$ (nonor). $\Pi_{\alpha\beta\gamma\delta}$ is the irreducible part of $\Pi_{\alpha\beta\gamma\delta}$, where

$$\Pi_{\alpha\beta\gamma\delta} = \sum_{i=1}^{3} n_\alpha^{(i)} n_\beta^{(i)} n_\gamma^{(i)} n_\delta^{(i)}\ , \tag{5}$$

with $\vec{n}^{(1)},\vec{n}^{(2)},\vec{n}^{(3)}$ - three orthonormal vectors. Let's define invariant amplitudes

$$\hat{T}(\vec{r}) = a(\vec{r})\Pi,\ \ \hat{h}_s(\vec{r}) = h_s(\vec{r})\Pi,\ \hat{h}_e(\vec{r}) = h_e(\vec{r})\Pi, \tag{6}$$

then eqs. (3),(4) look as follows

$$a(\vec{r}) = a[h(\vec{r}),T]$$

$$h(\vec{r}) = h_e(\vec{r}) + \int J(|\vec{r}-\vec{r}\,'|)a(\vec{r}\,')\,dV'. \tag{7}$$

The dependence of a on h is, in the discrete 4-state model o paper [1]

$$a(h) = \frac{8}{9}\,\frac{e^{\frac{224}{27}\frac{h}{T}} - 1}{e^{\frac{224}{27}\frac{h}{T}} + 3}\ . \tag{8}$$

In eq. (8) the temperature T is measured in units $T_0 = \int J(|\vec{r}|)\,dV$. Eq. (7) with proper boundary conditions forms the equation of inhomogeneous crystal order.

Let's solve this nonlinear equation in the case of small inhomogeneities. Denoting by h_0, a_0 the values of h and a in an infinite, homogeneous crystal with no external fields ($h_e = 0$), one has

$$h(\vec{r}) = h_0 + \delta h(\vec{r})\ ;$$

$$a(\vec{r}) = a_0 + \delta a(\vec{r}) = a_0 + \alpha\,\delta h(\vec{r});\quad \alpha = \left(\frac{da}{dh}\right)_{h=h_0}; \tag{9}$$

$$\delta h(\vec{r}) = h_e(\vec{r}) + \alpha\int J(|\vec{r}-\vec{r}\,'|)\,\delta h(\vec{r}\,')\,dV'. \tag{10}$$

To solve the linear eq. (10) it's convenient to use the Fourier harmonics

$$\delta h(\vec{r}) = \sum_k \delta h_k e^{i\vec{k}\vec{r}}\ ;\ h_e(\vec{r}) = \sum_k h_{ek} e^{i\vec{k}\vec{r}}\ ,$$

$$J(\vec{r}) = \sum_k J_k e^{i\vec{k}\vec{r}}\ .$$

One obtains from (10)

$$\delta h_k = \frac{h_{ek}}{1-\alpha J_k}\ . \tag{11}$$

The solution of eq. (10) with $h_e(\vec{r}) \sim \delta(\vec{r})$ (point inhomogeneity) is the Green's function of eq. (10) and coincides (to a multiplicative factor) with the correlation function calculated in the mean-field small-fluctuations approximation. In this case $h_{ek} = \mathrm{const}$, and one has to find the solutions $\vec{k}_c$ of the following equation

$$1 - \alpha(T)\,J_k = 0. \tag{12}$$

At temperature T^* of an absolute instability of crystal structure the line $h = J_0 a$ is tangent to $a = a\left(\frac{h}{T}\right)$ in point a_0; hence $\alpha(T^*) = \frac{da}{dh}\Big|_{h_0,T^*} = J_0^{-1}$ and the only solution of eq. (12) at T^* is $\vec{k}_c = 0$. In small neighbourhood of T^* ($\tau^* = (T^* - T)/T^* \ll 1$)

only small $\vec{k}$ are important, and

$$J_K \approx J_0\left(1-\frac{k^2}{k_0^2}\right), \qquad (13)$$

where $r_0 \sim k_0^{-1}$ is the interaction radius of the order parameter. The point $a=a_0$ at $T=T^*$ is a regular one for eq. (12) and in its vincinity one has

$$\alpha(a)\approx\alpha(a_0)\left[1-\gamma(a-a_0)\right]. \qquad (14)$$

In the vincinity of T^* (see [1])

$$a(T)-a_0=\left(\frac{\tau^*}{d}\right)^{1/2}. \qquad (15)$$

Taking into account that $\alpha(a_0)=J_0^{-1}$ one obtains the solution k_c of eq. (12) near T^*

$$k_c^2=-k_0^2\gamma\left(\frac{\tau^*}{d}\right)^{1/2}. \qquad (16)$$

The Green's function $G(r)$ is

$$G(r)\sim\frac{1}{r}e^{-r/r_c}, \qquad r_c=\frac{1}{|k_c|}=r_0\left(\frac{d}{\gamma^2\tau^*}\right)^{1/4}. \qquad (17)$$

r_c is the correlation length. For the 4-state model, (8), one obtains at T_c

$$r_c(T_c)\approx 2.4\, r_0 . \qquad (18)$$

The formulas (14),(15) are applicable in the small neighbourhood of T^*, with $\tau^*\sim 10^{-2}$. For $\tau^* > 10^{-1}$ $r_c\approx r_0$.

One expects r_0 to be close to a cluster's characteristic length. For such r_0 the nearest-neighbour crystal-order parameter interactions play the central role. The experimental data show that $r_0\sim 4\div7$ crystal lattice sizes. Far from T_c the lattice deffects with such a characteristic length are local, while close to the temperature T^* the changed crystal order due to a local defect has the size r_c of many interatomic distances.

3. I-D inhomogeneity. The semi-infinite crystal case

Let's study the case, when the crystal order depends on x only. Eq. (7) takes the form

$$h(x)=h_e(x)+\int\tilde{J}(|x-x'|)\,a(x')\,dx', \qquad (19)$$

where

$$\tilde{J}(|x|)=\int J(|\vec{r}|)\,dy\,dz . \qquad (20)$$

One expects the solutions of eq. (19) to be practically $\tilde{J}$-independent, for $\tilde{J}(|x|)$ slowly changing for $x<x_0$ and quickly tending to 0 for $x>x_0$. We choose

$$\tilde{J}(|x|)=\frac{1}{2}e^{-|x|}, \qquad (21)$$

the temperature and length units are $T_0 = 1$ and $x_0 = 1$. Taking the second derivate of (19) one obtains, for $h_e = 0$

$$\frac{d^2h}{dx^2}=h(x)-a\left[h(x)\right]. \qquad (22)$$

Eq. (22) has the form of the Newtonian equation, that describes the dynamics of a material particle with unit mass and "coordinate" h that depends on "time" x. The potential energy $U(h)$ is

$$U(h)=-\int_0^h\left[y-a(y)\right]dy . \qquad (23)$$

The solution of eq. (22) takes the form

$$x-x_0=\int_{h(x_0)}^{h(x)}\frac{dy}{\sqrt{2(E-U(y))}}, \qquad (24)$$

where E - constant. $U(h)$ is intimately connected with the thermodynamic potential $\phi(h)$. For the 4-state model

$$U(h)=-\frac{1}{7}\phi(h)-\frac{1}{7}T\ln 4 . \qquad (25)$$

The plots $U(h)$ for $T=T_c$ and $T_L<T<T_c$, T_L being the temperature of the liquid phase absolute instability, are given in Fig. 1.

The behaviour of the system depends on I) the value of E, II) boundary conditions and III) temperature T. The simplest solutions are 1) the "domain wall" between the liquid and the crystal at $T=T_c$, II) periodic oscillations of crystal order, III) flat nuclei of phases, IV) small inhomogeneities.

Consider the domain-wall case at $T=T_c$. The boundary conditions $h\to h_B (x\to+\infty)$, $h\to 0 (x\to-\infty)$, where h_B is the value of the homogeneous order in an infinite crystal, imply that $E = 0$. The solution (24) describes 3 phases. For $|x-x_0|>L$ there are two different phases (crystal and liquid) tending exponentially to their boundary-condition values. The area $|x-x_0|<L$ is the domain wall. The calculations show that $L\sim 1$. The plot $h(x)$ is given in Fig. 2.

In what follows the semi-infinite crystal will be examined. It is located at $x>0$ and the plane $x = 0$ is the surface of the crystal:

$$a=0 \quad \text{for} \quad x<0 \ . \tag{26}$$

The physical surface properties (e.g. the density) are, in general, different from the volume ones. It implies that eq. (19) can't be applied in the small vincinity of the surface. Suppose, for the beginning, that the change of the form of this equation is small enough to be neglected. Differentiating (19) at $x = 0$ one obtains, in this approximation, the boundary condition for $h(0)$:

$$h'(0)=h(0) \ . \tag{27}$$

The first integral of eq. (22),

$$\frac{1}{2}\left(\frac{dh}{dx}\right)^2+U(h)=E \tag{28}$$

at $x = 0$ gives, with the help of (27),

$$E-\frac{1}{2}h^2(0)=U(h(0)) \ . \tag{29}$$

Eq. (29) can be easily solved graphically, Fig. 3, and yields $h(0)$ at different temperatures.

In the vincinity of T_c, $T<T_c$, $E=U(h_B,T)$ can be expanded into powers of $\tau=(T-T_c)/T_c$. For h and $|\tau|$ small enough $U(h,\tau)\approx U(h,0)$. One obtains from (29)

$$h(0)\sim(Q\tau)^{1/2} \ , \tag{30}$$

with Q proportional to the latent heat. The solution of eq. (19) is, for $\tau\to 0$, $h\ll 1$

$$h(x)=h(0)\,e^{2.38x} \ . \tag{31}$$

Eqs. (30),(31) state that at temperatures close to T_c the crystal surface layer is liquid with very small anisotropy ($a\approx 0$). The width $\lambda(\tau)$ of this layer is

$$\lambda(\tau)=|\ln h(0)|\sim|\ln|\tau|| \ . \tag{32}$$

If $|\tau|$ isn't small enough, i.e. $|\tau|\geqslant 10^{-1}$, then $h(0)$ and $a(0)$ are close to their bulk values. In this case the small changes of structure in the surface layer (i.e. the boundary conditions) result in a small change of solutions of eq. 19. Close to the melting point T_c, at $\tau\to 0$, a small change of boundary conditions lead to important change of solutions. The specific properties of the surface layer will be treated phenomenologically by means of the extra field δh. δh acts on the surface of the crystal and represents the influence of the surface inhomogeneities on the cubic order parameter. Instead of (27) one has the boundary condition

$$h'(0)=h(0)+C \ . \tag{33}$$

For such a boundary condition the crystal order $h(x)$, near the surface is given, at $\tau\to 0$, $h\ll 1$, by the formula (31), where

$$h(0)=1.2C+0.36\sqrt{2.04C^2-\tau} \ . \tag{34}$$

Close to T_c $(|\tau|\ll C^2)$ $\lambda(\tau)\sim-\ln C$; for $C^2\ll|\tau|\ll 1$ $\lambda(\tau)\sim-\ln|\tau|$.

The important characteristic is the quantity

$$\frac{\partial\lambda}{\partial\tau}=1.2\,\frac{1}{\sqrt{204C^2-\tau}\,\left(3.4C+\sqrt{2.04C^2-\tau}\right)} \ . \tag{35}$$

Fig. 4 shows the behaviour of $\partial\lambda/\partial|\tau|$ for $C = 0.1$ and $C = 0.01$. For $C \leqslant 0.01$ at $T \approx T_c$ ($|\tau| \leqslant 10^{-3}$) the crystal order changes drastically with temperature.

At temperatures, where the crystal phase becomes metastable, the square-root operand in (34)-(35) tends to 0 when $\tau \longrightarrow 2.04C^2$ (if C is small enough). Taking into account that [1] $(T^*-T_c)/T^* \approx 0.02$ one finds the crucial value of C: $C_g \approx 0.1$. When $C > C_g$, the metastable-crystal surface is stable; the instability of the crystal structure at T^* is associated with volume effects. When $C < C_g$, the crystal surface becomes unstable at $\tau_1 < 0.02$. In this case it's the surface or deffects that give rise to the instability. Fig. 5 shows the plot of $h(0)$ vs. τ for different C.

The analytic formulas (34)-(35) are applicable at $C \leqslant C_M \sim 0.1$ ($C_M \approx \frac{1}{6} h_B(T_c)$). Experimental data (see the next section) exhibit the possibility that the behaviour of surface characteristics of some crystals is due to the small value of C.

In general, the strength of the influence of field δh on crystal-surface properties and the value of C depend on relative orientation of the surface and the crystal axes. The change of this orientation results in the change of $U(h)$, i.e. (see (25)) ϕ. The constant C is connected with the strength of crystal-surface tension.

4. The surface effects

The surface of the crystal is described in terms of the surface characteristics. The simplest ones are: the black-body coefficient, the work of exit, the coefficient of microrigidity. Each one contains an integral information about the crystal structure in the surface layer of width R. At low temperatures the crystal is nearly homogeneous and no strong surface anomalies occur. Close to T_c the behaviour of the system depends on the ratio $\lambda(\tau)/R$. The characteristics with $\lambda(0)/R \ll 1$ don't exhibit any strong surface anomalies. If, however, $\lambda(0)/R \gg 1$, the crystal order in the layer connected with a surface characteristic W differs strongly from an ideal (volume) one. In

this case, the temperature dependence of W can be obtained from the following simple arguments. Denote by $\Delta W(\tau)$ the difference between $W(\tau)$ and $W(\tau, a = a_B)$, where a_B describes the homogeneous order in an infinite crystal. At temperatures such that $\lambda(\tau)/R \ll 1$ $\Delta W(\tau) \sim \delta W(\tau) \cdot \lambda(\tau)$, where $\delta W(\tau)$ is the change of the density of W. If $\lambda(\tau)/R \gg 1$ then $W(\tau) \sim \delta W(\tau) \cdot R$. If C is small enough then $\partial\lambda/\partial\tau \gg \partial\delta W/\partial\tau \sim -da/d\tau$ for τ - small. As the result, the derivate $dW/d\tau$ has the maximum at $\tau \sim \tau_0 (\lambda(\tau_0) \sim R)$. Its height M_0 depends on C; the smaller C the bigger M_0. The plot of W and $dW/d\tau$ vs. temperature is given (quantitatively) in Fig. 6.

One can suggest that the anomalies found in [4], [5] are due to the small value of C in materials examined and are reflecting the effects described above (eqs. (34),(35)).

We thank Ya.A.Kraftmakher for helpful discussion on experimental data.

References

[1] A.C.Mitus, A.Z.Patashinskii, ZhETF, 80, 1554, 1981.

[2] A.C.Mitus, A.Z.Patashinskii, The theory cf crystal order. Novosibirsk, preprint 81-20, INP.

[3] A.C.Mitus, A.Z.Patashinskii, Theory of Crystal Order, II, The rhombic symmetry case. Novosibirsk, preprint 81-36, INP.

[4] J.Bezemer, R.T.Jonget, Physica, 83 B+C, 338, 1976.

[5] Ya.A.Kraftmakher, VI Europ. Conf. Thermophysical Properties of Materials-Research and Applic., June 26-30, 1978. Dubrovnik, Yugoslavia.

The figure captions

Fig. 1. Plot $U(h)$ for $T=T_c$ (line 1) and $T_L<T<T_c$ (line 2).

Fig. 2. Flat "domain wall" between the crystal and the liquid at $T=T_c$.

Fig. 3. The graphical solution of eq. (29) for $h(0)$.

Fig. 4. Plot $\partial\lambda/\partial|\tau|$ for $C = 0.1$ and $C = 0.01$.

Fig. 5. $h(0)$, eq. (34) vs. τ.

Fig. 6. The qualitative plot of the surface characteristic W and $dW/d\tau$ vs. τ.

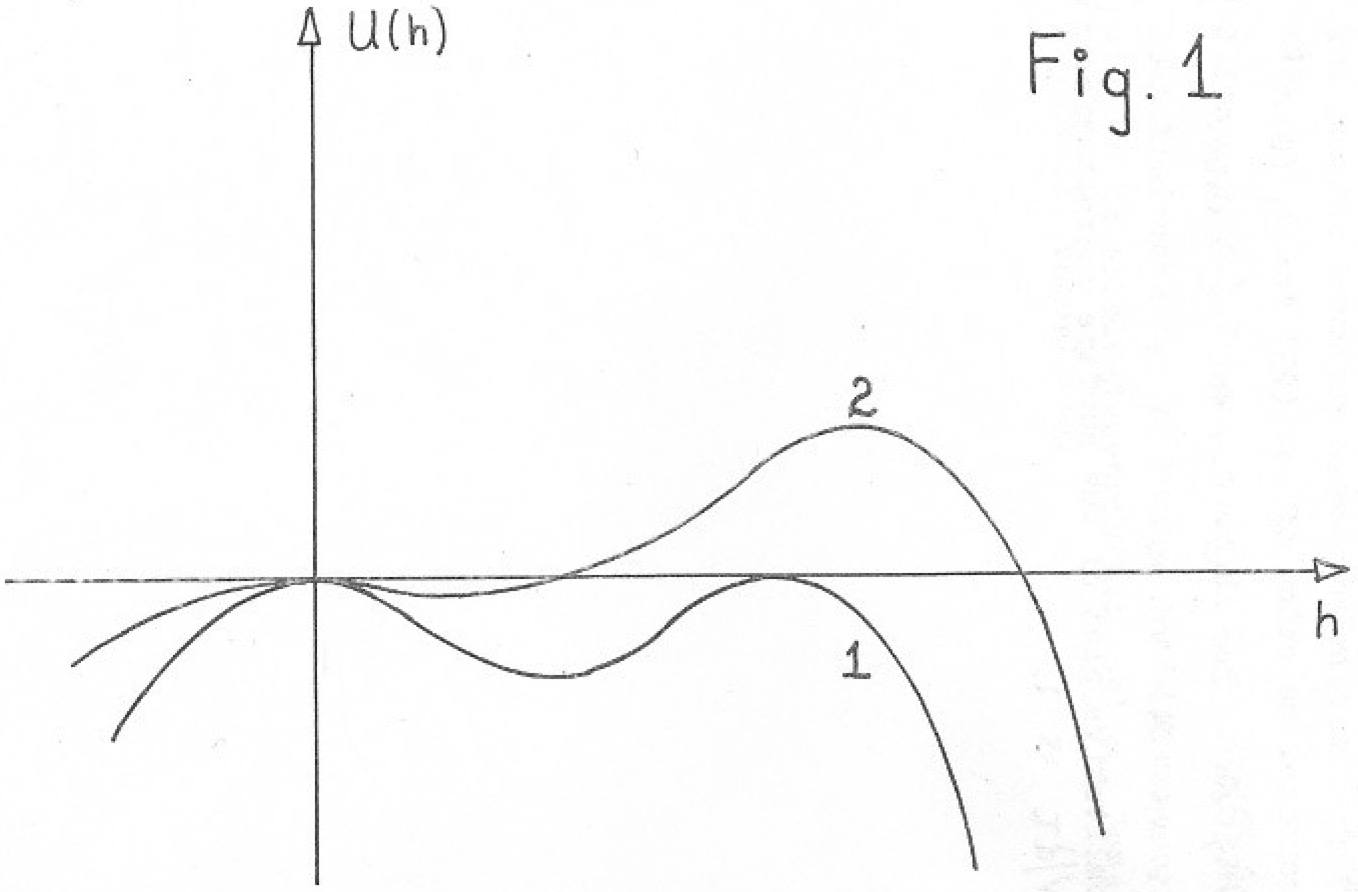


Fig. 1

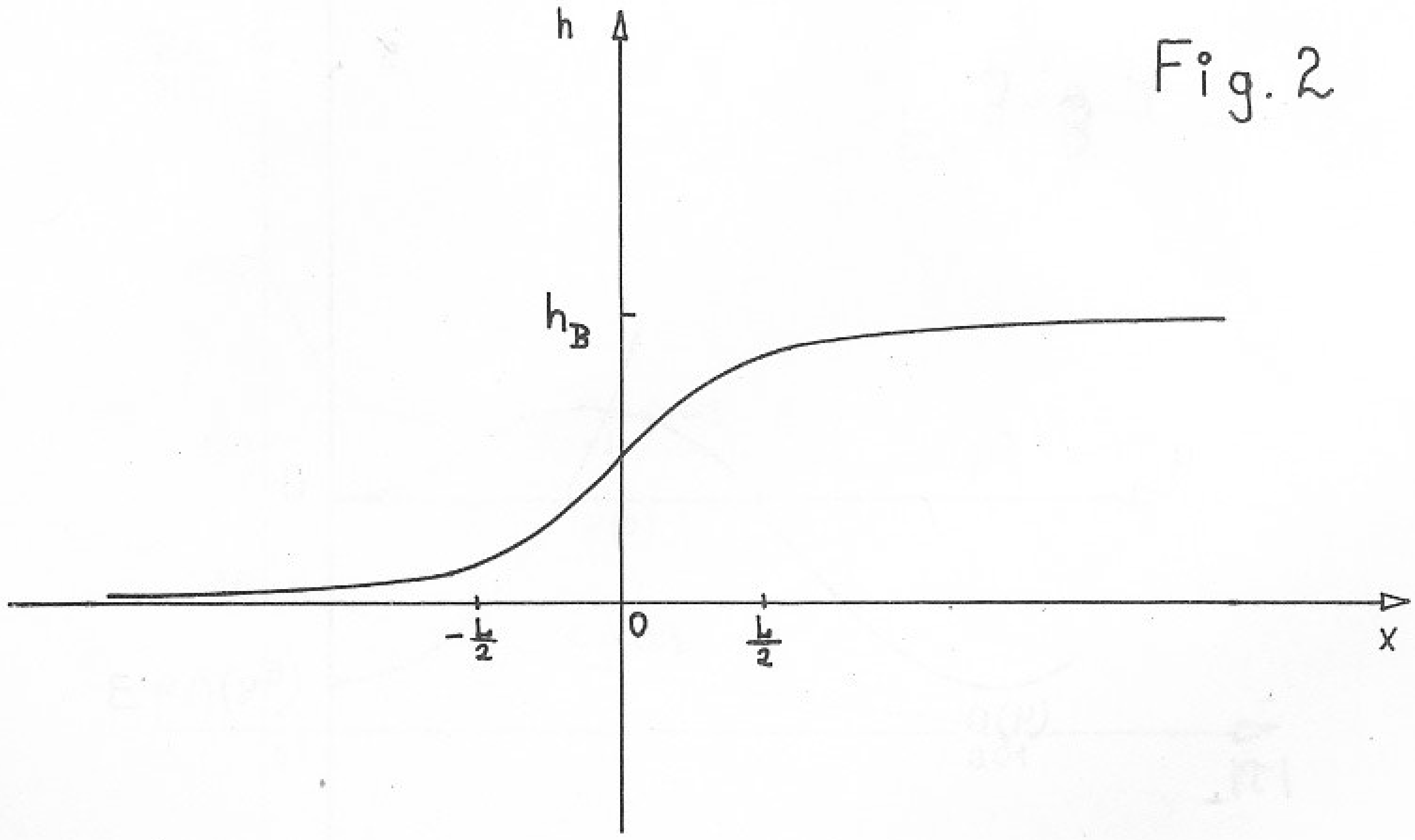
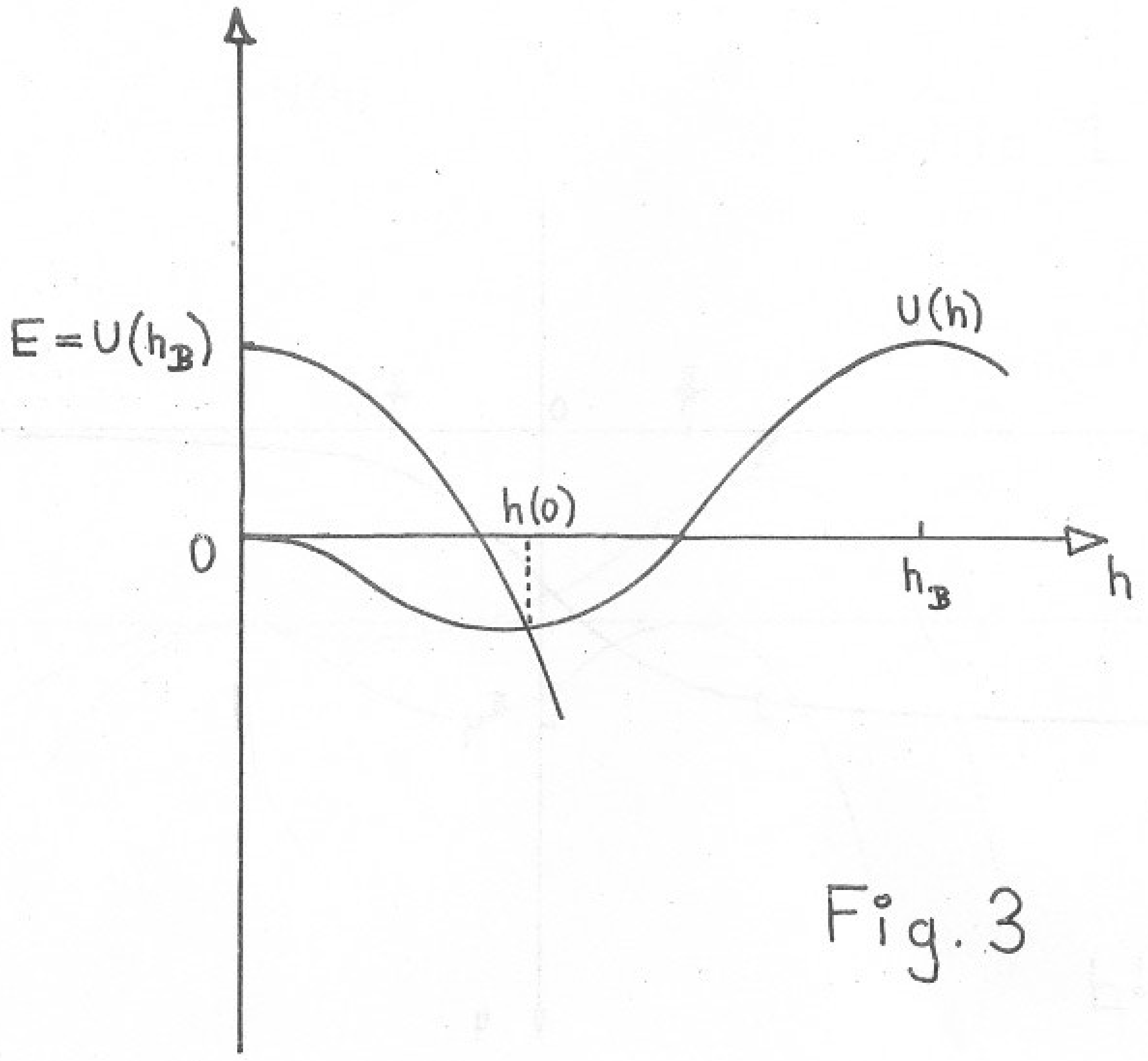


Fig. 2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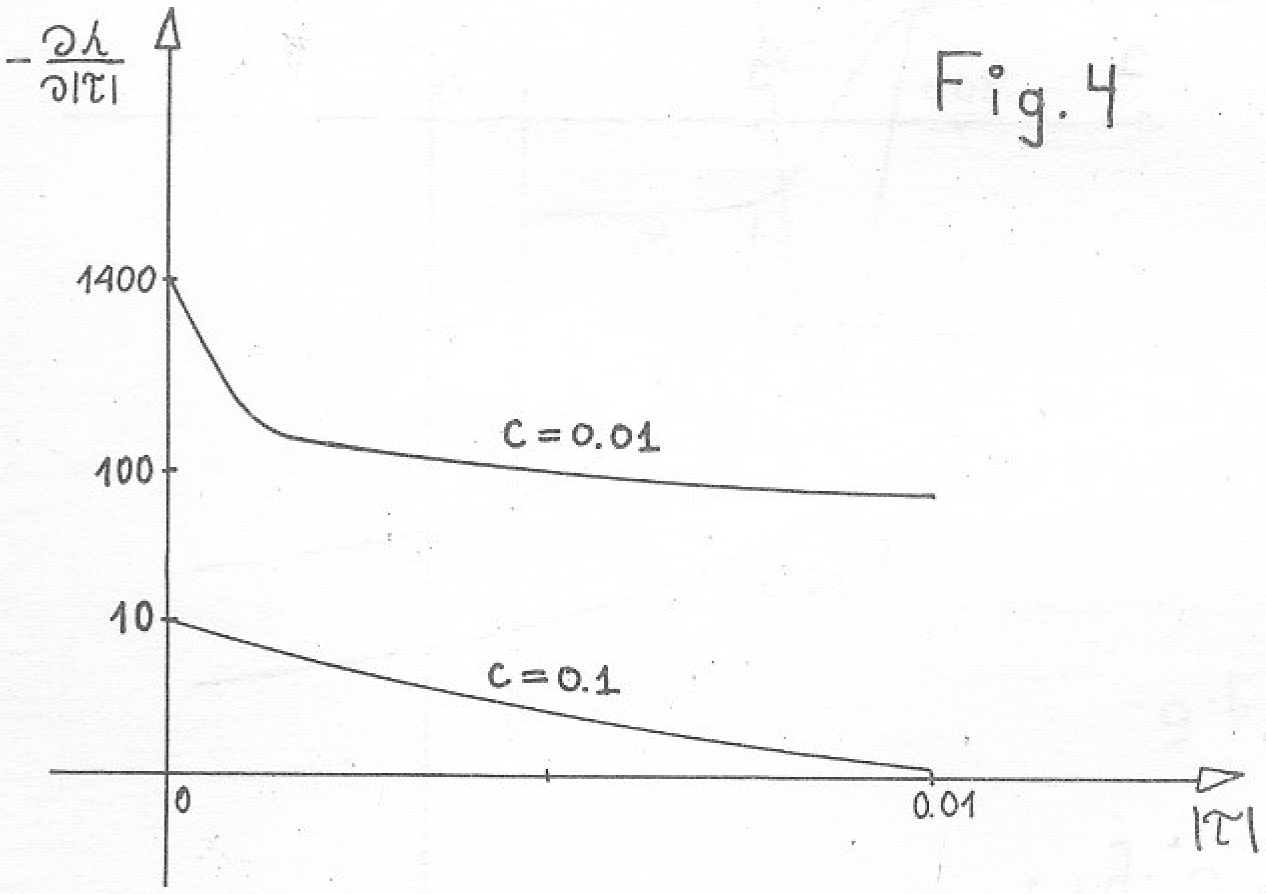
0
$h(0)$
h_B
h

Fig. 3


$-\frac{\partial \lambda}{\partial |\tau|}$
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$c = 0.1$
0
0.01
$|\tau|$

Fig. 4

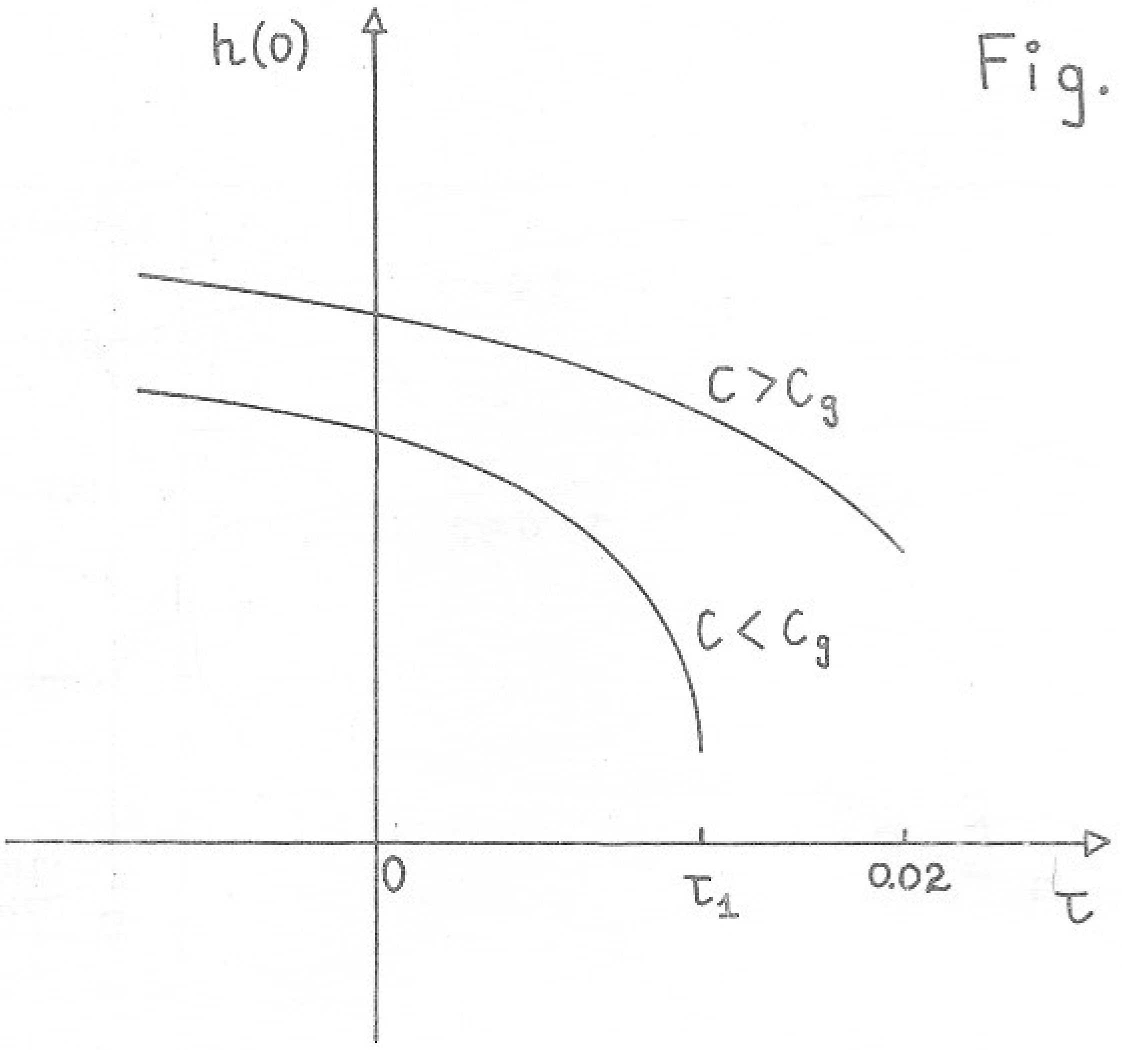

Fig. 5

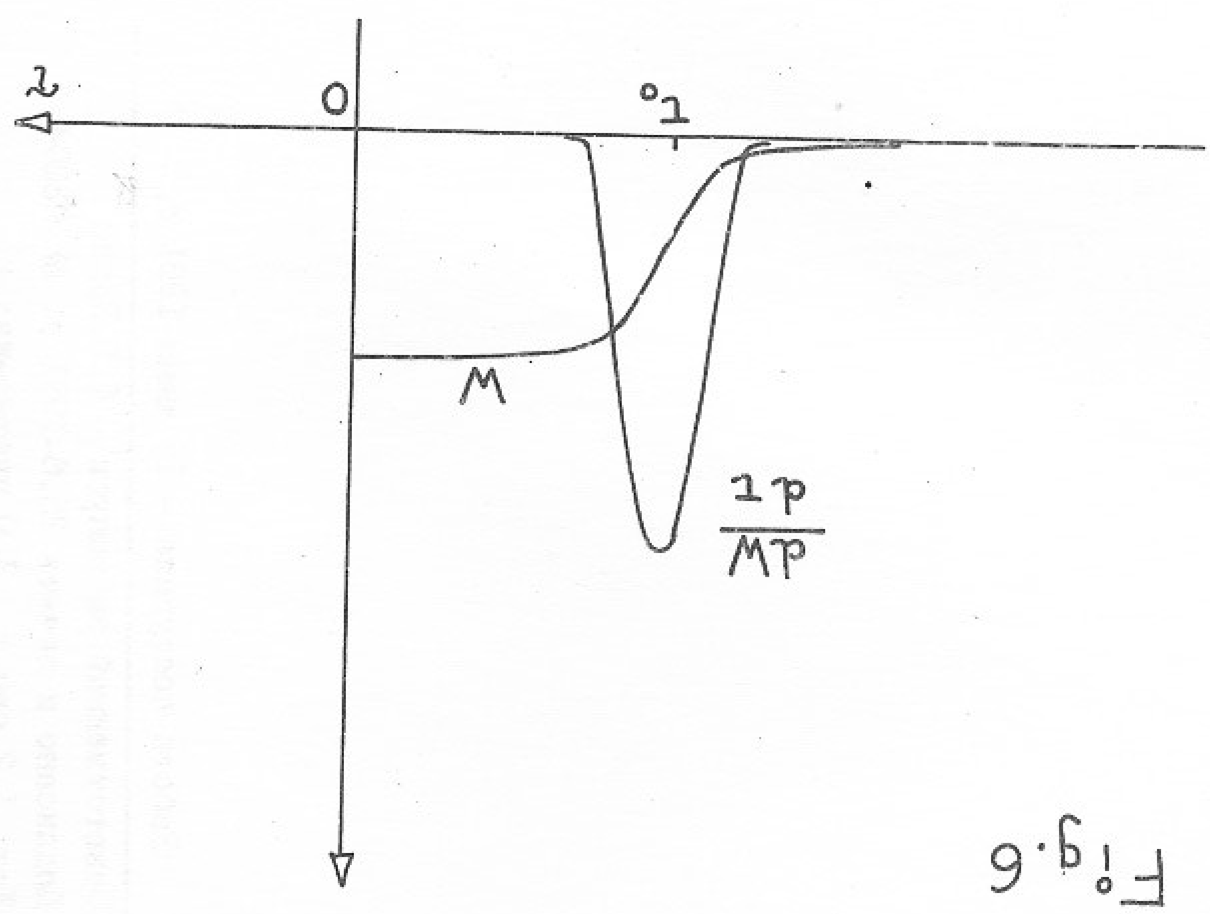

Fig. 6

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