

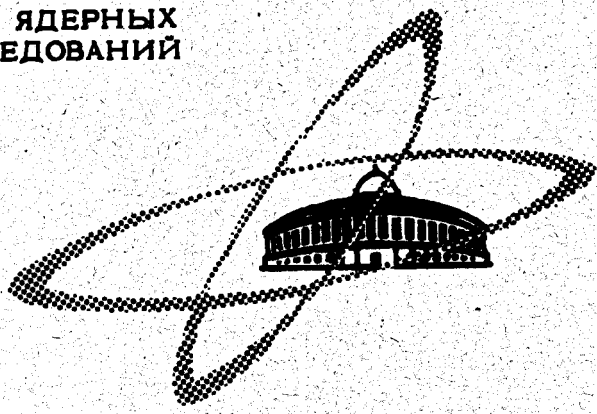
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ЛАБОРАТОРИЯ ТЕОРЕТИЧЕСКОЙ ФИЗИКИ

T. Siklós

**THEORY  
OF ANHARMONIC CRYSTALS  
IN PSEUDOHARMONIC APPROXIMATION  
II. THREE-DIMENSIONAL LATTICE**

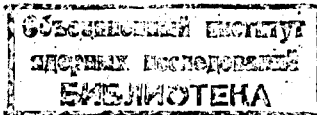
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**THEORY  
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## I. Introduction

In our previous paper [1] the simple model of a crystal - the linear chain with nearest neighbour interaction was investigated in pseudoharmonic approximation. The properties of the three-dimensional lattice, namely the facecentred cubic (f.c.c.) one with the nearest neighbour central force interaction was considered in pseudoharmonic approximation in the paper [2] in the case of small pressure. It was shown, that in this case the lattice becomes unstable at sufficiently high zero-point energy or temperature. It was shown also in [3] that the damping of the self-consistent phonons is sufficiently small even near the instability temperature and consequently the most simple pseudoharmonic approximation [4] can be used.

In present paper we consider the properties of the f.c.c. lattice with the nearest neighbour central force interaction in the case of the arbitrary external pressure in pseudoharmonic approximation. In Section 2 we obtain a self-consistent system of equations for the determination of the physical properties of the crystal. In Section 3 the instability and the critical temperature are calculated as the functions of the external pressure and the dimensionless coupling constant of the atoms. In Section 4 we discuss the results.

## 2. Self-Consistent System of Equations in Pseudoharmonic Approximation

We consider a f.c.c. lattice consisting of  $N$  identical atoms of mass  $M$ . The Hamiltonian of a crystal with nearest neighbour central force interactions reads:

$$H = \sum_l \frac{\vec{p}_l^2}{2M} + \frac{1}{2} \sum_{l \neq m}' \varphi(|\vec{R}_l - \vec{R}_m|), \quad (1)$$

where  $\vec{p}_l$  and  $\vec{R}_l$  are the momentum and the position operators for the atom in the lattice site  $l$ , respectively. The interaction potential between neighbouring atoms is denoted by  $\varphi(|\vec{R}_l - \vec{R}_m|)$ . The prime on the summation means that the second summation is performed only over the  $z$  nearest neighbours (for f.c.c.  $z = 12$ ).

We introduce the displacement operators  $u_l^\alpha$  from the equilibrium positions  $l_\alpha$  according to the definition:

$$\vec{R}_l^\alpha = \langle \vec{R}_l^\alpha \rangle + u_l^\alpha \equiv l_\alpha + u_l^\alpha. \quad (2)$$

The equilibrium lattice constant  $d = l/\sqrt{2}$  can be obtained from the equation

$$P = -\frac{1}{6V} \sum_{l \neq m}' l_\alpha \left\langle \frac{\partial}{\partial R_l^\alpha} \varphi(|\vec{R}_l^\alpha - \vec{R}_m^\alpha|) \right\rangle, \quad (3)$$

which shows, that the average force acting on each atom in the equilibrium position is equal to zero [5]. In equation (3) the external pressure is denoted by  $P$  and  $V = N\sigma = Nl^3/\sqrt{2}$  stands for the volume.

Applying the method which was formulated in [4], a self-consistent system of equations for the investigation of the f.c.c. lattice was obtained in [2]. It was shown that the renormalized frequency of vibrations takes the form:

$$\omega_{kj}^2 = \frac{f(\theta, l)}{f} \omega_{\alpha kj}^2 \equiv \alpha^2 \omega_{\alpha kj}^2, \quad (4)$$

where  $\omega_{\alpha j}$  is the harmonic frequency of the vibrations and  $f = \varphi''(r_0)$  stands for the harmonic strength constant. The pseudoharmonic strength constant  $f(\theta, l)$  can be written as:

$$f(\theta, l) = \tilde{\varphi}''(l), \quad (5)$$

where we introduce the self-consistent potential which in certain approximation can be written in the form [3]:

$$\tilde{\varphi}(l) \approx \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{1}{2} \bar{u}^2\right)^n \varphi^{(2n)}(l). \quad (6)$$

The mean square relative displacement of neighbouring atoms can be written as:

$$\bar{u}^2 = \frac{1}{l^2} \langle [\vec{l}(\vec{u}_l - \vec{u}_0)]^2 \rangle = \frac{1}{f(\theta, l) \kappa N} \sum_{\alpha j} \omega_{\alpha j} \coth \frac{\omega_{\alpha j}}{2\theta}. \quad (7)$$

In addition to the temperature  $\theta = kT$ , the properties of the crystal are determined also by the volume  $V$  of the crystal or by the external pressure. According to (3), (6) these parameters satisfy the following equation:

$$P = - \frac{\kappa l}{6v} \tilde{\varphi}'(l) = - \frac{2\sqrt{2}}{l^2} \tilde{\varphi}'(l). \quad (8)$$

The caloric equation of state is obtained from the internal energy which is given in our approximation by the equation

$$\frac{1}{N} E = \frac{\kappa}{2} \left\{ \tilde{\varphi}(l) + \frac{1}{2} f(\theta, l) \bar{u}^2 \right\}. \quad (9)$$

In this way we obtained a closed system of equations (4) - (9) which determine the properties of the anharmonic crystal in pseudoharmonic approximation. This self-consistent system of equations is determined by the self-consistent potential (6) which can be obtained if the potential  $\varphi(\bar{R})$  is known. Let us take the Morse-potential as a model one:

$$\varphi(R) = \epsilon \left\{ \left[ e^{-\alpha(R-r_0)} - 1 \right]^2 - 1 \right\}. \quad (10)$$

As in [1] we take  $\alpha r_0 = 6$ .

Let us consider the case, in which the external pressure is fixed  $P = \text{const.}$ , but contrary to [2] we don't suppose that  $P$  is small. It is convenient to introduce the reduced pressure  $P^* = P \frac{\sigma^3}{\epsilon}$ , where  $\sigma^6 = r_0^6/2$  is the parameter of the Lennard-Jones (12-6) interaction potential. Then in the same way as in [1] we get the following expressions for the pseudoharmonic renormalization of the frequency  $\alpha$ , the dimensionless mean squared relative displacement of neighbouring atoms  $y$ , the self-consistent potential  $\tilde{\varphi}(l)$ , the equilibrium separations of neighbouring atoms  $l$ , and the internal energy  $(1/N) E$ :

$$\alpha^2 = \frac{P^*}{12} \left( \frac{l}{r_0} \right)^2 + \frac{1}{2} \left\{ e^{-y} + \sqrt{e^{-2y} + \frac{P^*}{6} \left( \frac{l}{r_0} \right)^2 e^{-y}} \right\} \quad (11)$$

$$y = \alpha^2 \bar{u}^2 = 36 (\bar{u}^2 / r_0^2) = \ln \frac{\alpha^2 - \frac{P^*}{24} \left( \frac{l}{r_0} \right)^2}{\left[ \alpha^2 - \frac{P^*}{12} \left( \frac{l}{r_0} \right)^2 \right]^2} \quad (12)$$

$$\tilde{\varphi}(l) = - \epsilon \left\{ \alpha^2 - \frac{P^*}{8} \left( \frac{l}{r_0} \right)^2 \right\} \quad (13)$$

$$l = r_0 \left\{ 1 + \frac{1}{12} \ln \frac{\alpha^2 - \frac{P^* (\frac{l}{r_0})^2}{24}}{\left[ \alpha^2 - \frac{P^* (\frac{l}{r_0})^2}{12} \right]^2} \right\} \quad (I4)$$

$$\frac{1}{N} E = G E \left\{ \alpha^2 \ln \frac{\alpha^2 - \frac{P^* (\frac{l}{r_0})^2}{24}}{e \left[ \alpha^2 - \frac{P^* (\frac{l}{r_0})^2}{12} \right]^2} + \frac{P^* (\frac{l}{r_0})^2}{8} \right\} \quad (I5)$$

Let us replace the sum over  $\vec{k}_j$  by the integral over frequency  $\omega$  in equation (7) according to the formula :

$$\frac{1}{3N} \sum_{k_j} (\dots) = \int_0^{\omega_{0L}} g(\omega) d\omega (\dots) = \frac{1}{2} \int_0^2 dx G(x) (\dots),$$

where  $x = 2(\omega/\omega_{0L})$  ;  $\omega_{0L} = (\mathcal{E}_0/M)^{1/2}$  is the maximum value of the harmonical vibrational frequency,  $G(x)$  is the distribution function which was obtained in [6]..

Then equation (7) can be rewritten as an equation for  $\alpha$  :

$$\lambda \alpha y(\alpha) = \frac{3}{8 \cdot 1,02} \int_0^2 dx G(x) x \coth \frac{\alpha x}{4\tau}, \quad (I6)$$

where  $\lambda = \mathcal{E} / \mathcal{E}_0^{(v)}$  is the dimensionless coupling constant for atoms,  $\mathcal{E}_0^{(v)} \approx 1,02 \omega_{0L}$  is the zero-point energy per atom in the harmonic approximation,  $\tau = \Theta / \omega_{0L}$  is the dimensionless temperature. The function  $y(\alpha)$  is given by (I2), (I4). It is easy to see, that all the equations obtained here, for  $P^* \ll 1$  coincide with those of work [2] .

Let us compare the self-consistent equation (I6) and the expressions (II)-(I5) with those obtained in [1] for the monoatomic linear chain. It is easy to see, that they have the similar form and consequently the similar analytical behaviour.

Therefore, we don't repeat here the discussions of the Section 3 of [I] and give only the results.

### 3. Instability Temperature and Critical Temperature

According to [I] the instability temperature can be obtained as a simultaneous solution of the equation (I6) and its derivative:

$$\lambda \{ \gamma(\alpha) + \alpha \gamma'(\alpha) \} = -0,3676 \frac{1}{4\tau} \int_0^2 dx \mathcal{G}(x) x^2 s h^{-2} \left( \frac{\alpha x}{4\tau} \right) \quad (I7)$$

The critical temperature can be obtained as a simultaneous solution of the equations (I6), (I7) and the second derivative of (I6):

$$\lambda \{ 2 \gamma'(\alpha) + \alpha \gamma''(\alpha) \} = 0,3676 \left( \frac{1}{4\tau} \right)^2 \int_0^2 dx \mathcal{G}(x) x^3 c h \left( \frac{\alpha x}{4\tau} \right) s h^{-3} \left( \frac{\alpha x}{4\tau} \right), \quad (I8)$$

where the function  $\gamma(\alpha)$  is given by (I2), (I4).

The results of numerical solutions of these systems of equations are given in Fig. 1-Fig. 3. In Fig. 1 the dependence of the pseudoharmonic renormalization of the frequency  $\alpha_s = \omega_{kj} / \omega_{\omega kj}$  at the instability temperature on the reduced pressure  $P^*$  is presented for some values of  $\lambda$ . In Fig. 2 the dependence of the instability temperature  $\tau_s = \Theta_s / \omega_{\omega L}$  on the dimensionless coupling constant  $\lambda$  is given for some values of  $P^*$ . In Fig. 3 the dependence of the instability temperature on the reduced pressure is presented for some values of  $\lambda$ . In all Figures the critical curves are denoted by dot-and-dash lines. We don't consider here the case of small values of  $\lambda \leq 2$  which demands additional calculations. It will be discussed elsewhere.



For the values of  $\lambda \geq 12$  we obtain the following values for the critical temperature  $T_c^* \approx 1,56$  and the critical pressure  $P_c^* \approx 0,37$ , where  $T^* = \theta/\epsilon = 11,76 \tau/\lambda$  is the reduced temperature.

In work [2] were obtained the following expressions for the instability temperature <sup>\*)</sup> in the cases of high ( $\tau \gg 1$ ) and low ( $\tau \ll 1$ ) temperature :

$$\tau_s = \frac{1,02 \lambda}{3e} \left\{ 1 + \frac{e}{5,1} P^* - \frac{e}{24} \left( \frac{3}{1,02 \lambda} \right)^2 \right\} \quad (19)$$

$$(\tau \gg 1 ; P^* \ll 1)$$

$$\tau_s = \frac{1,05}{\pi e} \left\{ \frac{10}{3e} (\lambda - \lambda_0) \right\}^{1/4} ; \quad \lambda_0 = \frac{e}{2} \left\{ 1 - \frac{e^2}{7,12} P^* \right\} \quad (20)$$

$$(\tau \ll 1 ; P^* \ll 1)$$

The results of numerical solutions agree quite well with the asymptotic expressions (19), (20) for  $P^* \ll 1$ .

Using equations (12)-(15) and the solution  $\alpha_s$  of the equations (16), (17), the dimensionless mean squared relative displacement of the neighbouring atom  $u$ , the self-consistent potential, the equilibrium separation of neighbouring atoms and the internal energy were calculated at the instability temperature. In Fig. 4 the internal energy of the crystal  $(1/N) E/\epsilon$  at the instability temperature is presented as a function of  $\lambda$  and in Fig. 5 as a function of  $P^*$ . The results of numerical calculations agree quite well with the results of paper [2] in the case of small pressure.

<sup>\*)</sup>We note here, that the instability temperature  $\tau_s$  in [2] was called critical temperature and denoted by  $\tau_c$ .

#### 4. Discussions

In this work the behaviour of a three-dimensional f.c.c. lattice was investigated in the case of arbitrary external pressure in a wide range of temperature. It was shown, that the behaviour of three-dimensional lattice doesn't differ qualitatively from the one-dimensional lattice discussed in [1].

It is also interesting to note, that the reduced instability temperature  $T_S^* = \theta_s / \epsilon$  as a function of the reduced pressure  $P^*$  qualitatively agree with the reduced melting curves of the inert-gas solids [7]. It seems therefore that the point of dynamic instability lies close to the melting point of the crystal. The critical temperature  $T_c^*$  and the critical pressure  $P_c^*$  found here limited the instability region of the crystal. But it should be noted here that the damping of phonons ( the second order terms in the self-consistent theory [3] ) should be taken into account in order to get more rigorous results. They will be considered in a separate paper.

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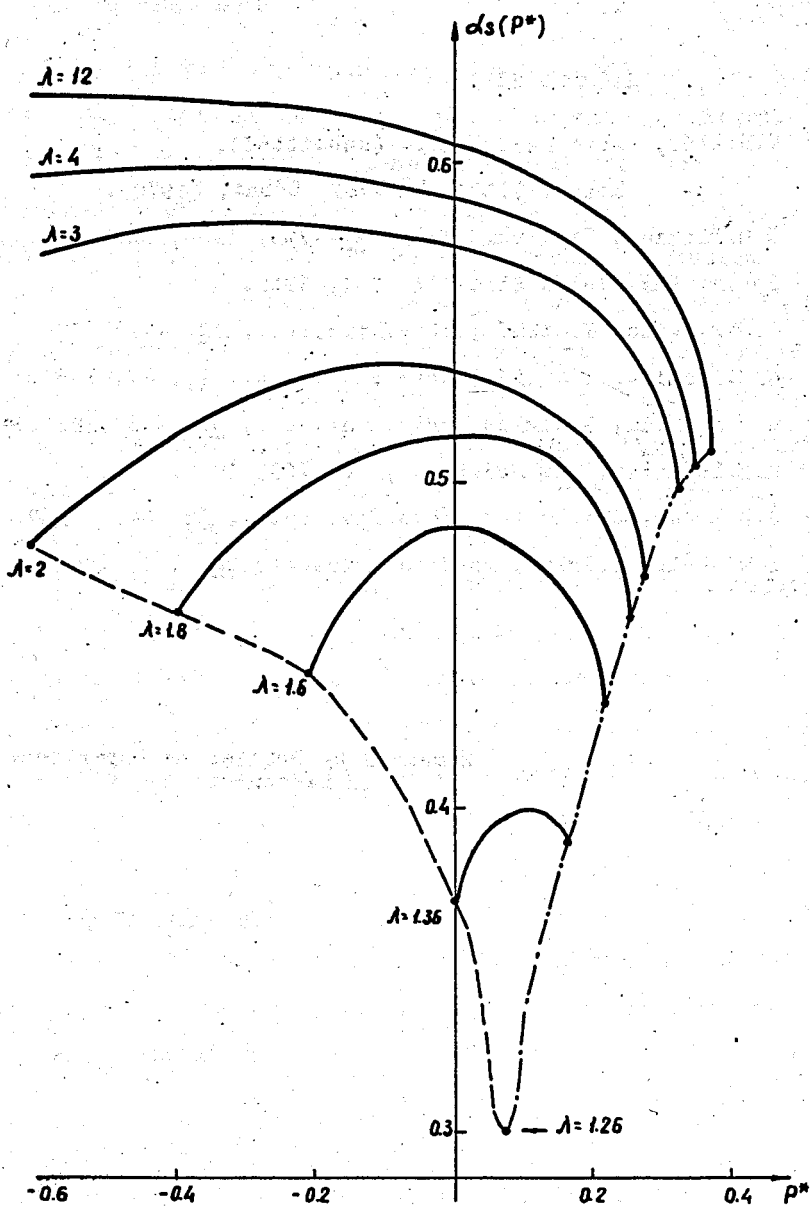


Fig. 1. The dependence of the pseudoharmonic renormalization of the frequency  $\alpha_s = \omega_{\kappa_j} / \omega_{0\kappa_j}$  at the instability temperature on the reduced pressure  $P^*$ .

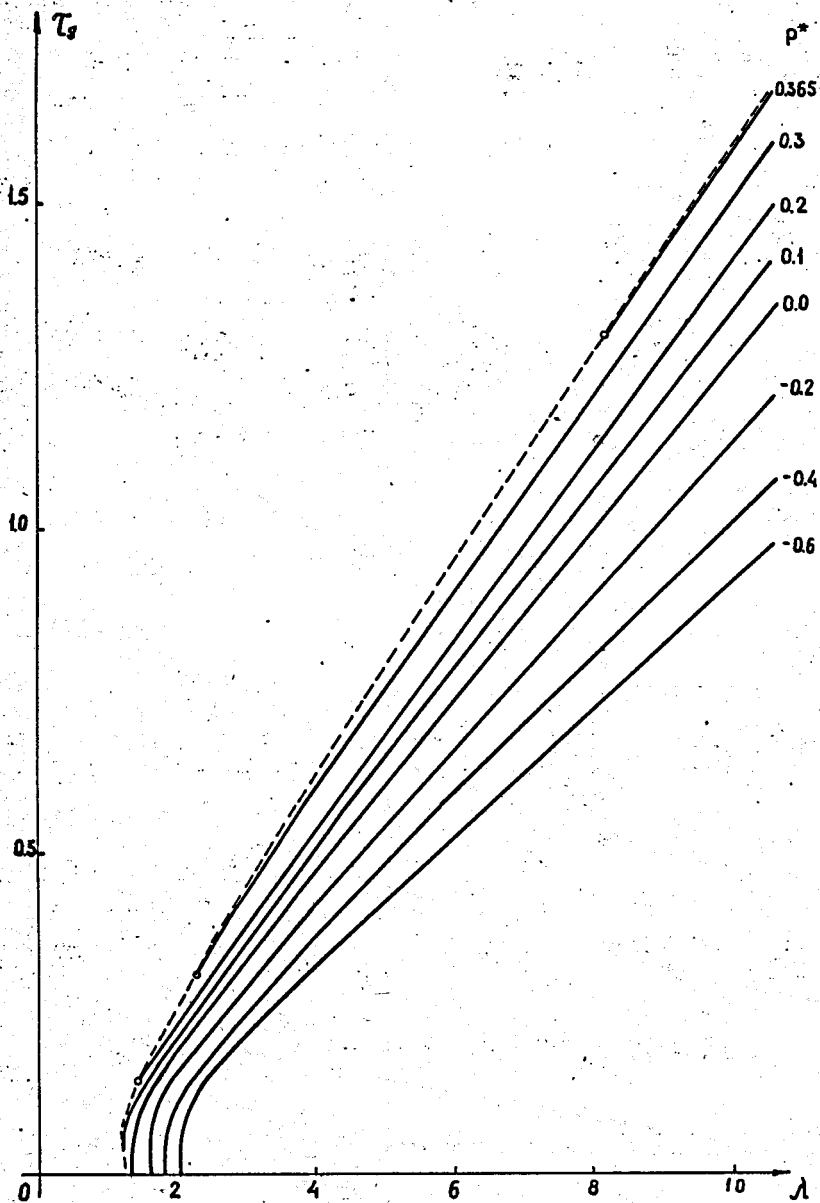


Fig. 2. The dependence of the instability temperature  $\tau_s = \theta_s / \omega_{oL}$  on the dimensionless coupling constant,  $\lambda$  of the atoms.

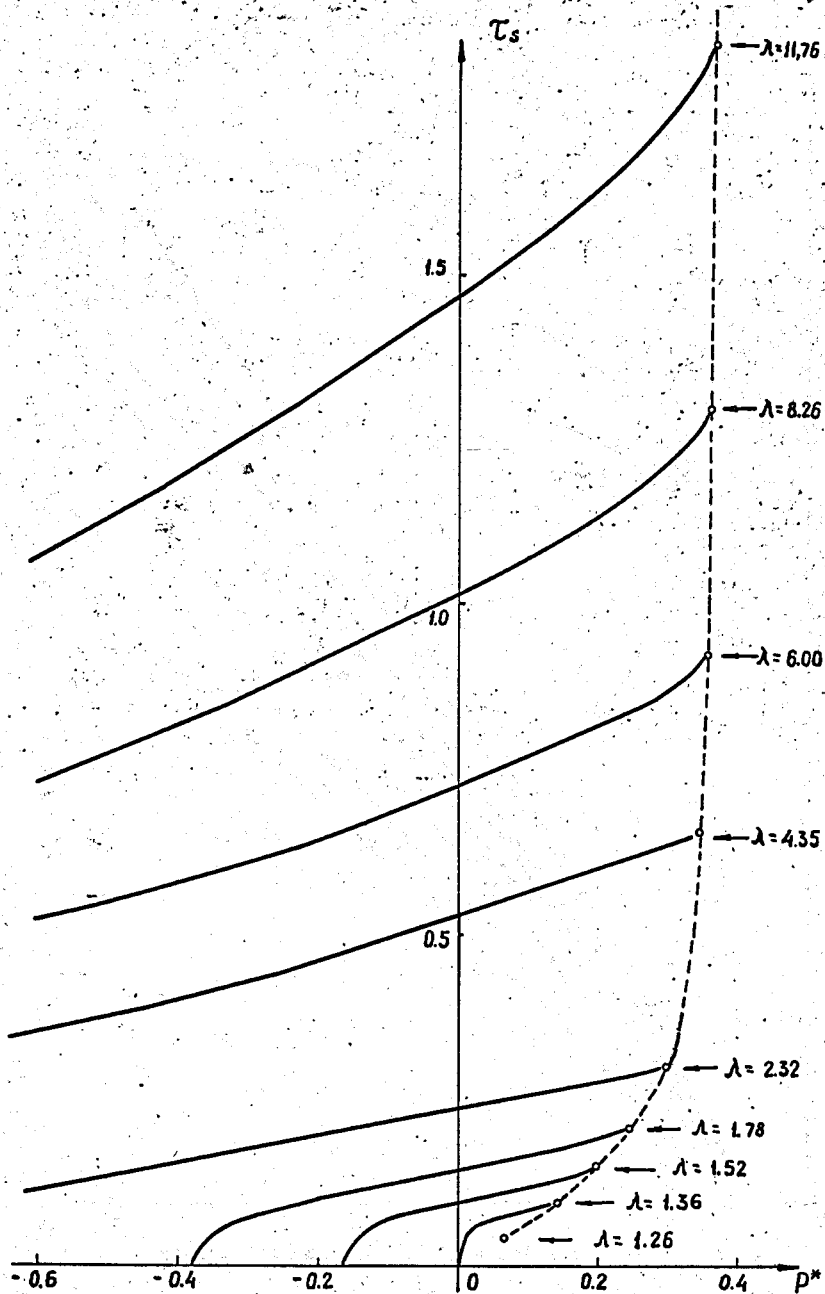


Fig. 3. The dependence of the instability temperature  $\tau_s$  on the reduced pressure  $P^*$ .

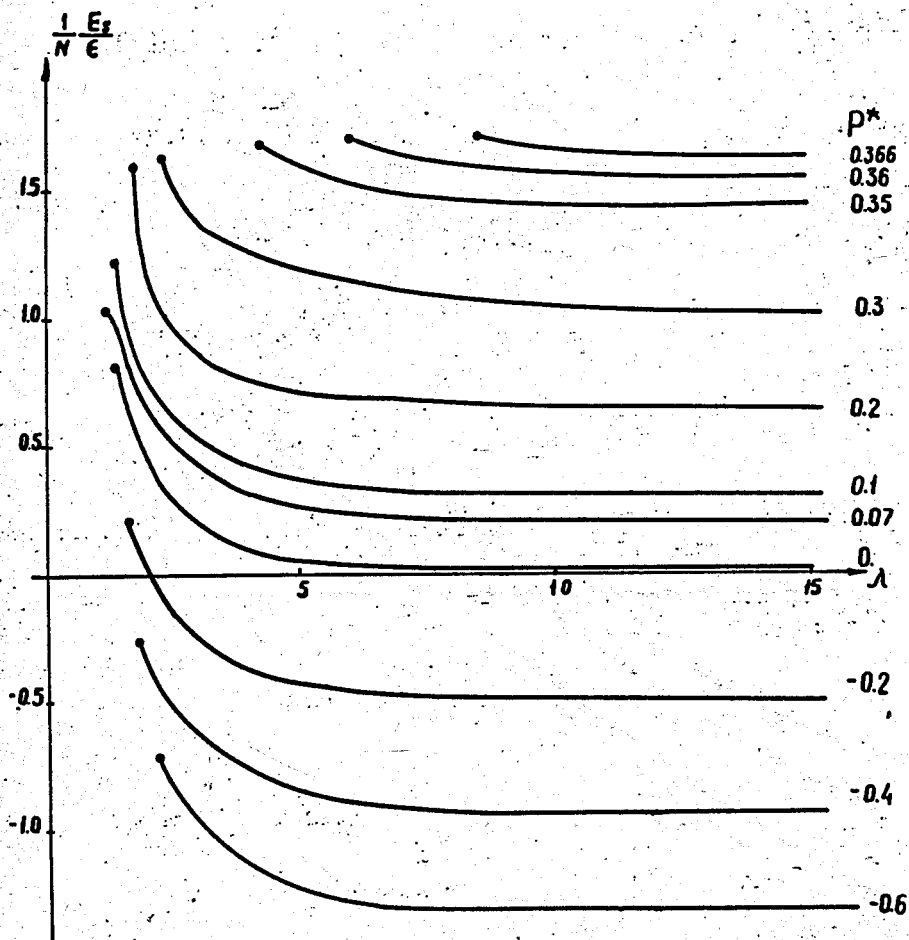


Fig. 4. The dependence of the internal energy  $(1/N) E_s / \epsilon$  at the instability temperature on the dimensionless coupling constant  $\lambda$ .

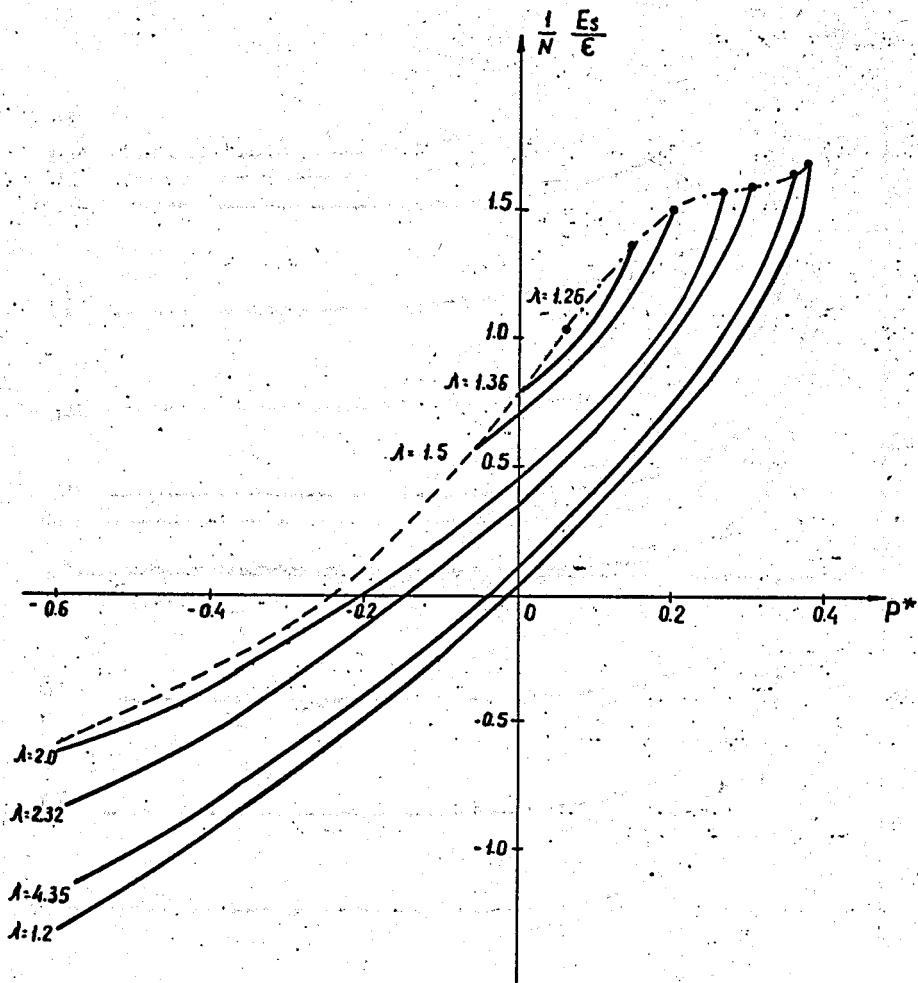


Fig. 5. The dependence of the internal energy at the instability temperature on the reduced pressure  $P^*$ .