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THEORY OF ANHARMONIC CRYSTALS IN PSEUDOHARMONIC APPROXIMATION

I. LINEAR CHAIN

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I. Introduction

Recently a theory of anharmonic crystals was developed which allows to take into account in the lower order perturbation theory all the higher order anharmonic terms in a self-consistent manner (see [1]-[3] and the references cited in [3]). In [4]-[6] a simple model of the crystals- the linear chain with nearest neighbour interaction was investigated. Although this model is very far from the real three-dimensional crystals, its investigation permits us to discuss qualitatively some properties of the three-dimensional crystals. Also in this case we can obtain a simple solution which helps to clarify some aspects of the theory.

It was shown in [4]-[6] that the chain under small external tension becomes unstable at sufficiently high zero-point energy or at sufficiently high temperature. It was shown also in [4] that the damping of the self-consistent phonons is sufficiently small even near the instability temperature and consequently the most simple pseudoharmonic approximation [2] can be used. This allows to simplify the calculations essentially and investigate the properties of the anharmonic linear chain in a wide range of temperature and coupling constant. This investigation was made in [6] for the case of small external tensions.

In present paper we consider the properties of an anharmonic linear chain in the case of the arbitrary external tension in pseudoharmonic approximation. Some preliminary results were reported earlier in [7]. In Section 2 we obtain a self-consistent system of equations for the determination of the properties of the anharmonic chain. In Section 3 we investigate the behaviour of the self-consistent equation in the high temperature limit and we introduce the conception of the instability temperature and the critical temperature. These quantities are calculated in Section 4. In Section 5 we discuss the results.

2. Self-Consistent System of Equations in Pseudoharmonic Approximation

Let us consider a linear chain of length L which consists of $N+1$ identical atoms with the mass M. We take into account only the nearest neighbour interaction which described by the interaction potential denoted by $\varphi(R_n - R_{n-1})$. It is convenient to introduce the equilibrium separation between the neighbouring atoms and the relative displacement operators by the following definition:

$$R_n - R_{n-1} = \langle R_n - R_{n-1} \rangle + u_n - u_{n-1} \equiv l + u_n - u_{n-1} \qquad (I)$$

The equilibrium separation l in the one-dimensional case can be obtained from the equation [3] :

$$P = -\frac{1}{2} \left\langle \frac{\partial}{\partial R_n} \varphi(R_n - R_{n-1}) \right\rangle , \qquad (2)$$

which shows, that the average force acting on the arbitrary atom in the equilibrium position is equal to zero.

Applying the method which was formulated in [2] a self-consistent system of equations for the investigation of a linear chain was obtained in [6] . It was shown that the renormalized frequency of vibrations takes the form:

$$\omega_k^2 = \frac{4f(\theta,\ell)}{M}\sin^2\frac{k\ell}{2} = \frac{f(\theta,\ell)}{f}\,\omega_{ok}^2 \equiv \alpha^2\omega_{ok}^2\,, \tag{3}$$

where ω_{ok} is the harmonic frequency of the vibrations and f stands for the harmonic strength constant. The pseudoharmonic strength constant $f(\theta,\ell)$ can be written as :

$$f(\theta,\ell) = \frac{1}{2}\,\tilde{\varphi}''(\ell)\,, \tag{4}$$

where we introduce the self-consistent potential:

$$\tilde{\varphi}(\ell) = \langle \varphi(R_n - R_{n-1})\rangle = \sum_{s=0}^{\infty}\frac{1}{s!}\left(\frac{\overline{u^2}}{2}\right)^s \varphi^{(2s)}(\ell). \tag{5}$$

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

$$\overline{u^2} = \langle (u_n - u_{n-1})^2\rangle = \frac{1}{Nf}\sum_k \frac{\omega_{ok}^2}{2\omega_k}\coth\frac{\omega_k}{2\theta}\,. \tag{6}$$

In addition to the temperature $\theta = kT$ the properties of the linear chain are determined also by the length of the chain $L = N\ell$ or by the external tension P . According to (2),(5) these parameters satisfy the following equation:

$$P = -\frac{1}{2}\,\tilde{\varphi}'(\ell)\,, \tag{7}$$

which is the thermal equation of state for the linear chain.

The caloric equation of state is obtained from the internal energy which is given in our approximation by the equation [6] :

$$\frac{1}{N}E = \frac{1}{2}\left\{\tilde{\varphi}(\ell) + f(\theta,\ell)\,\overline{u^2}\right\}. \tag{8}$$

In this way we have a closed system of equations (3) - (8) which determined the properties of the anharmonic linear chain in the pseudoharmonic approximation. This self-consistent system of equations is determined by the self-consistent potential (5) which can be obtained if the potential $\varphi(R)$ is known. Let us take the Morse-potential as a model one:

$$\varphi(R) = D\left\{\left[e^{-a(R-r_0)} - 1\right]^2 - 1\right\}. \qquad (9)$$

We note here after [I], that the deviation of a Lennard - Jones (I2-6) interatomic potential from the Morse-potential with $ar_0 = 6$ in the domain of the thermal expansion of the lattice is rather small. Therefore we shall take further $ar_0 = 6$. Applying (5),(9) we get the following expression for the self-consistent potential :

$$\tilde{\varphi}(l,y) = D\left\{e^{-12\left(\frac{l}{r_0}-1\right)}e^{2y} - 2e^{-6\left(\frac{l}{r_0}-1\right)}e^{y/2}\right\}, \qquad (\mathrm{I0})$$

where $y = a^2\overline{u^2} = 36(\overline{u^2}/r_0^2)$.

Let us consider the case in which the external tension is fixed : P = const. but contrary to [5],[6] we don't suppose that P is small. The length of the chain depends on the temperature of the system if we keep the external tension fixed. The equilibrium separation of neighbouring atoms l can be written as follows:

$$l(\theta) = l_0 + \delta l = r_0\left\{1 + \frac{1}{4}y + \frac{\delta l}{r_0}\right\}, \qquad (\mathrm{II})$$

where l_0 is the equilibrium separation at $P = 0$ which can be determined using equations (7),(I0). It is convenient to introduce the reduced tension $P^* = P(r_0/D)$. (We note here, that in [4]-[6] was used the dimensionless tension $p = P^*/2$). Then the equation (7) taking into account (I0), (II) reads:

$$P^* = 6\, e^{-6\frac{\delta l}{r_0}}\, e^{y} \left(e^{-6\frac{\delta l}{r_0}} - 1 \right). \qquad \text{(I2)}$$

Using equations (I0), (II), (I2) the pseudoharmonic strength constant α according to (3), (4) can be written as follows:

$$\alpha^2 = \frac{f(\theta, l)}{f} = e^{-y}\, e^{-6\frac{\delta l}{r_0}} \left\{ 2\, e^{-6\frac{\delta l}{r_0}} - 1 \right\} =$$

$$= \frac{P^*}{3} + \frac{1}{2} \left\{ e^{-y} + \sqrt{e^{-2y} + \frac{2P^*}{3} e^{-y}} \right\}. \qquad \text{(I3)}$$

Solving the last equation for y we get:

$$y = \ln \frac{\alpha^2 - \frac{P^*}{6}}{\left(\alpha^2 - \frac{P^*}{3}\right)^2} . \qquad \text{(I4)}$$

Consequently the expressions for the self-consistent potential (I0), the equilibrium separation of neighbouring atoms (II) and the internal energy (8) can be written as follows :

$$\tilde{\varphi}(l) = -D \left\{ \alpha^2 - \frac{P^*}{2} \right\}, \qquad \text{(I5)}$$

$$l = r_0 \left\{ 1 + \frac{1}{12} \ln \frac{\alpha^2 - \frac{P^*}{6}}{\left(\alpha^2 - \frac{P^*}{3}\right)^4} \right\}, \qquad \text{(I6)}$$

$$\frac{1}{N} E = \frac{D}{2} \left\{ \alpha^2 \ln \frac{\alpha^2 - \frac{P^*}{6}}{e\left(\alpha^2 - \frac{P^*}{3}\right)^2} + \frac{P^*}{2} \right\}. \qquad \text{(I7)}$$

Let us replace the sum over k by integral over $\varphi = kl/2$ in equation (6). Taking into account (15) we can rewrite (6) as an equation for α:

$$\lambda \alpha y(\alpha) = \int_0^{\pi/2} d\varphi \sin\varphi \coth \frac{\alpha \sin\varphi}{2\tau}, \qquad (18)$$

where $\omega_{0L} = (4f/M)^{1/2}$ is the maximum value for the vibrational frequency of the chain in harmonic approximation, $\lambda = (\pi D/\omega_{0L})$ is the dimensionless coupling constant and $\tau = (\theta/\omega_{0L})$ is the dimensionless temperature.

It is worth-while to note, that the self-consistent equation (18) determines the properties of the anharmonic linear chain : when λ, τ and P^* are given, from the equation (18) we can get the renormalization of the frequency α, which according to (16), (17) determines the length of the chain and its internal energy. It is easy to see that all the equations obtained here for $P^* \ll 1$ coincide with those of paper [6].

3. Self-Consistent Equation in the High Temperature Limit

Let us consider now the self-consistent equation (18) in the high temperature limit $(\tau \gg 1)$. In this case (18) can be rewritten in the following form:

$$\alpha^2 y(\alpha) = T^* \left\{ 1 + \frac{1}{24}\left(\frac{\pi\alpha}{\lambda T^*}\right)^2 + \cdots \right\}, \qquad (19)$$

where we introduce the reduced temperature $T^* = (\theta/D) = \tau\pi/\lambda$. Taking into account only the first term in the r.h.s. of (19) and using (12), (13), (14) the self-consistent equation can be written as follows:

$$F(y) = \left(1 - \frac{P^*}{3T^*}y\right)^2 e^y - \frac{y}{T^*}\left(1 - \frac{P^*}{6T^*}y\right) = 0\,. \quad (20)$$

We point out here that (20) has different number of real solutions depending on the P^*, T^* values. The physical solution is that one, which coincides with the harmonic solution if the anharmonic terms tend to zero. The harmonic solution is given by

$$y_{harm} = \frac{T^*}{\alpha^2_{harm}} = \frac{2\,T^*}{1 + \frac{2}{3}P^* + \sqrt{1 + \frac{2}{3}P^*}} \,. \quad (21)$$

The dependence of the physical solution of equation (20) on the reduced temperature T^* and reduced tension P^* is given in Fig. I. If the tension $(P^* < P_c^*)$ and temperature $[T^* \leq T_s^*(P^*)]$ are sufficiently low the equation (20) has real solutions, the smallest is the physical one. The temperature $T_s^*(P^*)$ is determined by the coincidence of two real solutions : $y_1(T_s^*) = y_2(T_s^*)$. Consequently the instability temperature $T_s^*(P^*)$ determined by this condition can be obtained by solving the following system of equations:

$$F(y) = 0 \quad ; \quad F'(y) = 0 \,. \quad (22)$$

For $T^* > T_s^*(P^*)$ the solutions y_1 and y_2 become complex conjugate. In the region $P^* < 0$ and $T^* > T_s^*(P^*)$ the equation (20) has complex conjugate solutions only and consequently the linear chain has no stable state. The same situation is occured at all temperatures if $P^* < 0$ and $|P^*|$ sufficiently high. But when $P^* \geq 0$ in addition to complex conjugate solutions there are also real solutions $y_3 < y_4$. The smallest of them is the physical one. In this case at the temperature $T^* = T_s^*(P^*)$ the state of the chain changes by jump from the state S_1 (at $T^* \leq T_s^*$) to some new state S_2 which is stable at temperature $T^* \geq T_s^*(P^*)$. At the instability temperature $T_s^*(P^*)$ the length (I6) and the internal energy (I7) of the chain take a jump and their derivatives - the coefficient of the linear thermal expansion and the specific heat at constant pressure - tend to infinity as $T^* \to T_s^*(P^*)$.

In the region of sufficiently high tension or temperature: $P^* \geq P_c^*$ or $T^* \geq T_c^*$, the equation (20) has always two real solutions, the smallest of them is the physical one. The critical temperature T_c^* and the critical tension P_c^* are determined by the coincidence of three real solutions of the equation (20): $y_1(T_c^*, P_c^*) = y_2(T_c^*, P_c^*) = y_3(T_c^*, P_c^*)$, consequently they can be obtained from the solution of the following system of equations:

$$F(y) = 0 \quad ; \quad F'(y) = 0 \quad ; \quad F''(y) = 0 \quad . \tag{23}$$

In this region $P^* \geq P_c^*$ or $T^* \geq T_c^*$ the chain is always stable and its physical quantities - the internal energy and the length - are smooth functions of the temperature and the tension.

4. Instability Temperature and Critical Temperature

Thus, the analyse of the solutions of the self-consistent equation (20) gives a convenient method for the determination of the instability temperature $\tau_s(P^*)$ and the critical temperature τ_c. According to (22) the instability temperature is obtained as a simultaneous solution of the equation (I8) and its derivative:

$$\lambda\left\{y(\alpha)+\alpha y'(\alpha)\right\}=-\frac{1}{2\tau}\int_0^{\pi/2} d\varphi \sin^2\varphi \, sh^{-2}\left(\frac{\alpha\sin\varphi}{2\tau}\right). \qquad (24)$$

According to (23) the critical temperature is obtained as a simultaneous solution of the equations (I8), (24) and the second derivative of (I8):

$$\lambda\left\{2y'(\alpha)+\alpha y''(\alpha)\right\}=2\left(\frac{1}{2\tau}\right)^2\int_0^{\pi/2} d\varphi \sin^3\varphi \, ch\left(\frac{\alpha\sin\varphi}{2\tau}\right) sh^{-3}\left(\frac{\alpha\sin\varphi}{2\tau}\right), \qquad (25)$$

where the function $y(\alpha)$ is given by the equation (I4).

The results of numerical solutions of these **systems of** equations are given in Fig. 2, Fig. 3. In Fig. 2 the dependence of the instability temperature $\tau_s=(\Theta_s/\omega_{0L})$ on the dimensionless coupling constant λ is presented for some values of P^*. In Fig. 3 the dependence of the instability temperature on the reduced tension is presented for some values of λ. In both Figures the critical curves are denoted by dotted line. We don't consider here the case of small values of $\lambda \lesssim 2$ which demands additional calculations. It will be discussed elsewhere.

In [5] [6] we obtain the following expressions for the instability temperature *) in the case of high ($\tau \gg 1$) and low ($\tau \ll 1$) temperature :

$$\tau_s = \frac{\lambda}{\pi e}\left\{1+\frac{e}{2}P^* - \frac{e}{24}\left(\frac{\pi}{\lambda}\right)^2\right\} \qquad (26)$$

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

$$\tau_s = \frac{1}{\pi e}\sqrt{\frac{6}{e}(\lambda-\lambda_0)} \ ; \quad \lambda_0 = \frac{e}{2}\left\{1-\left(\frac{e}{2}\right)^2 P^*\right\}. \qquad (27)$$

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

The results of numerical solutions agree quite well with asymptotic expressions (26), (27) for $P^* \ll 1$.

We can also obtain the asymptotic expressions for the critical temperature in the case of high temperature ($\tau \gg 1$). In this case the equations (I8), (24), (25) read :

$$\alpha^2 \ln \frac{\alpha^2 - \frac{P^*}{6}}{\left(\alpha^2 - \frac{P^*}{3}\right)^2} = T^* + \frac{1}{24}\left(\frac{\pi}{\lambda}\right)^2 \frac{\alpha^2}{T^*} , \qquad (18a)$$

$$\ln \frac{\alpha^2 - \frac{P^*}{6}}{\left(\alpha^2 - \frac{P^*}{3}\right)^2} - \frac{\alpha^4}{\left(\alpha^2 - \frac{P^*}{6}\right)\left(\alpha^2 - \frac{P^*}{3}\right)} = \frac{1}{24}\left(\frac{\pi}{\lambda}\right)^2 \frac{1}{T^*} , \qquad (24a)$$

$$\alpha^4 - \alpha^2 P^* + \frac{(P^*)^2}{6} = 0 . \qquad (25a)$$

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*) We note here, that the instabilty temperature τ_s in[4]-[6] was called as critical temperature and denoted by τ_c .

Using (I8 a), (24 a) we obtain the instability temperature :

$$T_s^* = \frac{\alpha_s^6}{(\alpha_s^2 - \frac{P^*}{6})(\alpha_s^2 - \frac{P^*}{3})} . \qquad (28)$$

The critical value of the renormalization parameter α_c is given by the solution of (25a) which reads :

$$\alpha_c^2 = \frac{P_c^*}{2}\left(1 + \frac{\sqrt{3}}{2}\right) . \qquad (29)$$

The calculations give for the critical tension and critical temperature the following approximative expressions :

$$P_c^* \approx 0,334 \left\{1 - \frac{\sqrt{3}}{24}\left(\frac{\pi}{\lambda}\right)^2\right\} , \qquad (30)$$

$$T_c^* \approx \sqrt{3}\, P_c^* \approx 0,575 \left\{1 - \frac{\sqrt{3}}{24}\left(\frac{\pi}{\lambda}\right)^2\right\} , \qquad (3I)$$

where equations (29), (I8a) and (28) were used. The results of numerical solutions agree quite well with the asymptotic expressions (30), (3I) for $\lambda \geq 2$.

5. Discussion.

In this work the stability region of an anharmonic linear chain was investigated in the case of arbitrary external tension in a wide range of temperature. It was find out - contrary to [6]- that the instability phenomenon is vanished at critical temperature T_c^* and critical tension P_c^* .

We make some remarks about the physical meaning of the instability temperature T_s and the critical temperature T_c . It is well known, that though the fluctuation of the average position of the atoms in a linear chain is great : $\sqrt{<u_N^2>}/\ell \sim$

$\sim \sqrt{N} \gg 1$, but the relative displacement of the neighbouring atoms is small : $[\langle (u_n - u_{n-1})^2 \rangle]^{1/2} / l \ll 1$. This fact shows the existence of the short range order in a linear chain, so that it can be considered as a bound state of N atoms, where collective exitations - the phonons - can exist [8]. If the temperature increases, the number of phonons increases too which means increasing of the amplitude of the relative displacement of the neighbouring atoms. At the temperature $T > T_s$ in the self-consistent equation (I8) appear complex conjugate values of the vibrational frequency and consequently infinitive relative displacement of atoms : $[\langle (u_n - u_{n-1})^2 \rangle]^{1/2} \sim e^{\gamma t}$ $(\gamma > 0)$. This means, that the linear chain becomes unstable in respect to the propagation of collective excitations which destroy the bound state of atoms in the chain. On this ground we may consider the external tension as some external field which in the case of $P > P_c$ limits the motion of atoms in the linear chain.

The stability of the chain with fixed length found in [6] isn't meaningless from the physical point of view as in this case the tension increases rather rapidly with the temperature : at $T \sim T_s$: $P \gtrsim P_c$ and it can stabilize the lattice. We think, that the instability of the lattice at fixed volumes found in [I] is connected with the possibility of exchange of the atoms situated in the neighbouring lattice cites which we didn't take into account here. To investigate this problem the hard core part of the interatomic potential should be carefully taken into account.

The theory developed here does not take into account the damping of the phonons. Its influence on the properties of the anharmonic linear chain will be considered elsewhere.

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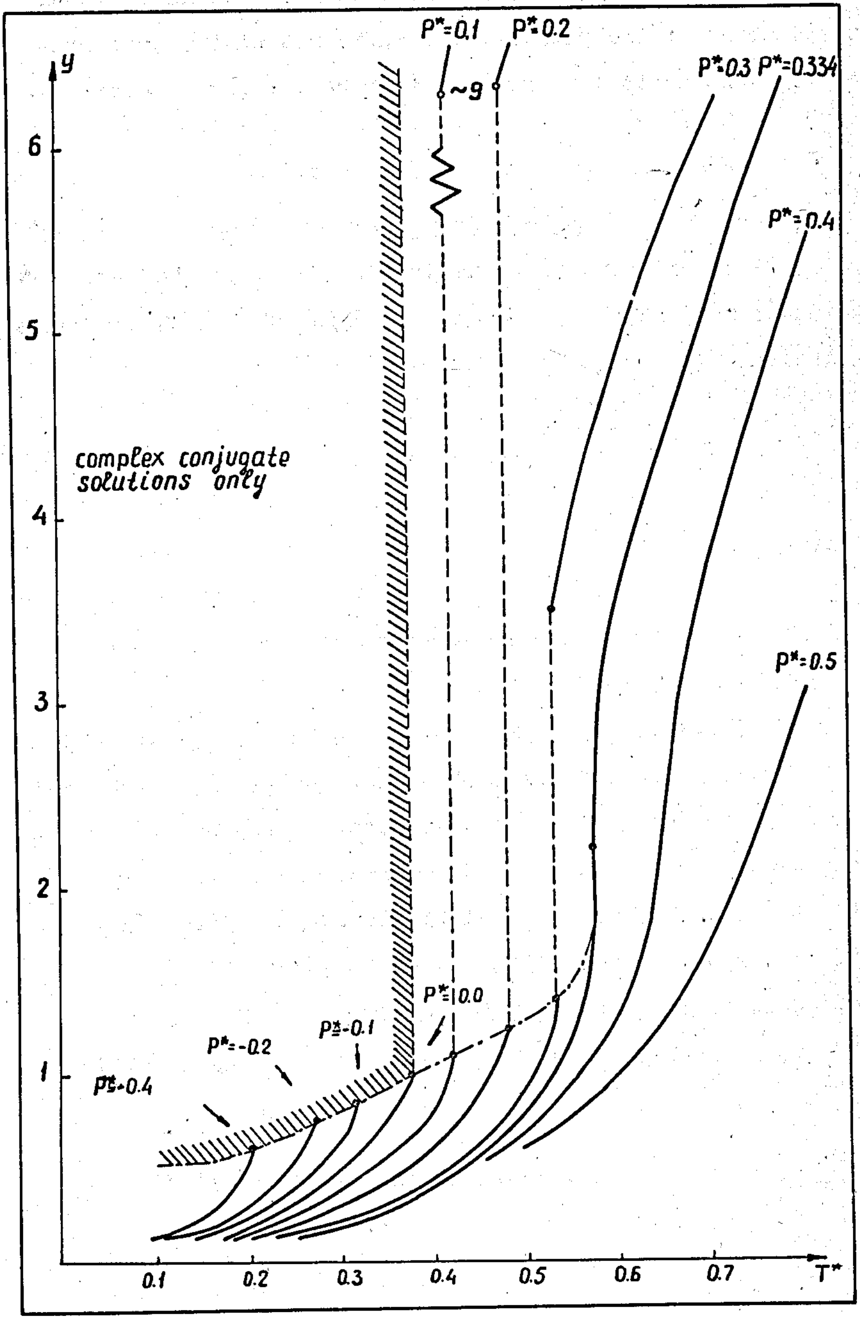

Fig. I. The physical solution of the self-consistent equation in the high temperature limit.

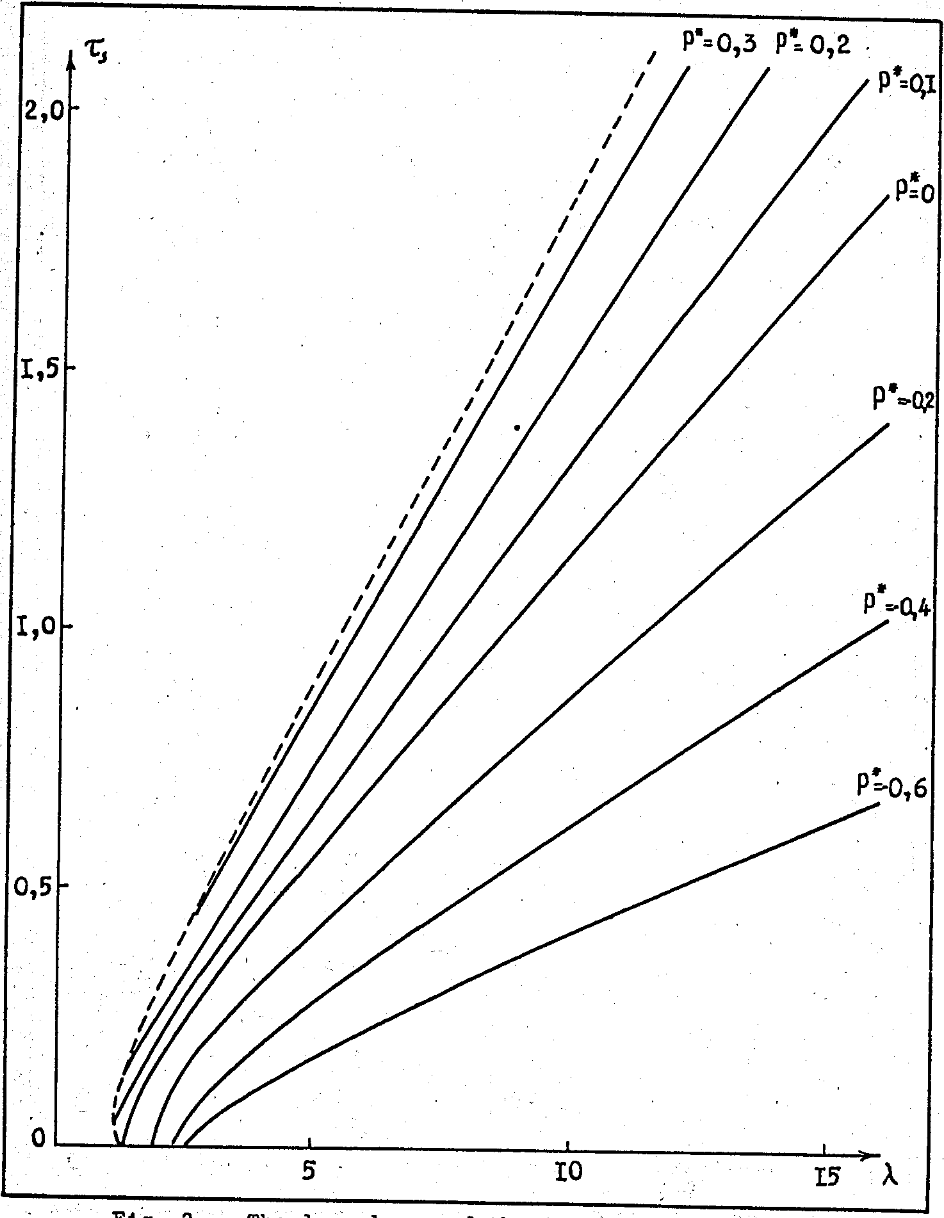

Fig. 2. The dependence of the instability temperature $\tau_s = (\Theta_s / \omega_{oL})$ on the dimensionless coupling constant $\lambda = (\pi D / \omega_{oL})$.

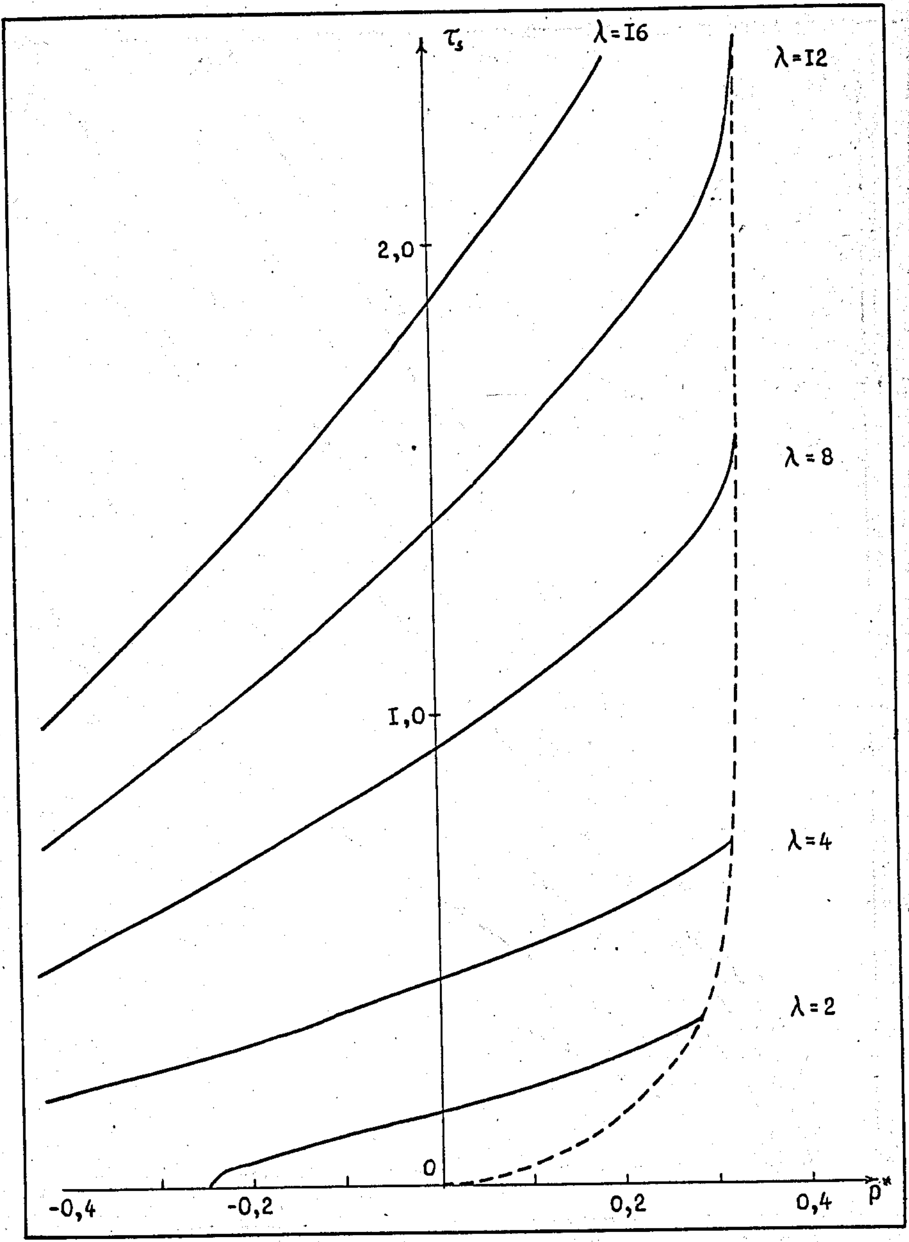

Fig. 3. The dependence of the instability temperature τ_s on the reduced tension $\mathcal{P}^*$.