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**THERMAL BEHAVIOUR OF THE DEBYE-WALLER FACTOR  
AND THE SPECIFIC HEAT OF ANHARMONIC CRYSTALS**

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by

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## ABSTRACT

We study, within the framework of the Variational Method in Statistical Mechanics, the influence of the cubic and quartic crystalline anharmonicity on the classical and quantum thermal behaviour of the specific heat, Debye temperature  $\theta$ , Debye-Waller factor  $W$ , crystalline expansion and phonon spectrum. The systems, ~~we~~ mainly focalize are the single oscillator, ~~and~~ the monoatomic linear chain and simple cubic crystal. The trial Hamiltonian is an harmonic one, therefore the various anharmonic influences are mainly absorbed into the renormalization of  $\theta(T)$ . Several differences between the classical and quantum results are exhibited.

Satisfactory qualitative agreement with experience was obtained in the low-temperature regime, in particular in what concerns the existence of a minimum in  $\theta(T)$  which has been observed in Cu, Al, Ag, Au and Pb. For the intermediate-temperature regime the customary linear behaviour of  $W(T)$  (hence  $\theta(T)$  almost constant) is ~~re~~obtained. Finally in the high-temperature regime, the present treatment leads to a  $\sqrt{T}$  - dependence for the  $W$ -factor, which implies in the wrong curvature with respect to experimental data. A possible explanation of this disagreement might be related to the melting phenomenon, which is not covered by the present theory. (Author)

I - INTRODUCTION

After the starting-point given by the works of Debye<sup>[1]</sup> in 1914, Faxen<sup>[2]</sup> in 1918 and Waller<sup>[3]</sup> in 1923, a great quantity of theoretical and experimental work has been dedicated to the study of the thermal behaviour of the x-ray (neutron,  $\gamma$ -ray, etc) scattering by a vibrating regular lattice. Various improvements have been introduced, through different generalizations of the historical "single-atom harmonic perfect crystal", by taking into account the anharmonicity of the crystal, the presence of more than one atom per unit cell, the existence of different kind of defects (impurities, dislocations and others) in the crystalline periodicity, the quantum effects, etc.

Let us recall that the scattered intensity  $I$  we are talking about is proportional, for a single-atom crystal, to  $e^{-2W(T)}$  where  $W(T)$  is the so called (temperature dependent) Debye-Waller factor. If we call  $T_0$  a reference temperature, it obviously holds that

$$\frac{I(T)}{I(T_0)} = e^{-2[W(T) - W(T_0)]} \quad (1)$$

It is customary to introduce a quantity noted  $Y(T, T_0)$  through

$$W(T_0) - W(T) = \frac{\sin^2 \theta}{2\lambda^2} Y(T, T_0) \quad (2)$$

$$\text{or} \quad Y(T, T_0) = \frac{\lambda^2}{\sin^2 \theta} \ln \frac{I(T)}{I(T_0)} \quad (2')$$

In quite general situations,  $Y(T, T_0)$  does not depend neither on the incident wavelength  $\lambda$  nor on the scattering angle  $\theta$ . Let us also recall that, within the quantum harmonic hypothesis, we have

$$W = \frac{f(T)}{\theta_D} \quad (3)$$

where  $f(T)$  is a well known function (see for example Ref. [4] ) which tends to be constant in the limit  $T \rightarrow 0$ , and increases linearly with  $T$  in the (classical) limit  $T \rightarrow \infty$ ; the characteristic Debye temperature  $\theta_D$  separates these two regimes. We remark that expression (2') is well adapted for obtaining  $Y(T, T_0)$  directly from experience; consequently, the demand of validity of relation (3) leads in general to a temperature dependent "Debye temperature" which we shall note  $\theta_{DW}(T)$ . Furthermore, always within the quantum harmonic hypothesis, we have that the vibrational contribution to the constant volume specific heat is given by

$$C_v = g(T / \theta_D) \quad (4)$$

where  $g(x)$  is a well known function (see for example Ref. [5] ) which behaves as  $x^d$  ( $d \equiv$  space dimensionality) in the limit  $T \rightarrow 0$ , and tends to be constant in the (classical) limit  $T \rightarrow \infty$ ,

$\theta_D$  being oncemore the characteristic temperature which separates the two regimes. If we demand now the validity of relation (4) and try to fit experimental data, we obtain (quite generally) another temperature dependent "Debye temperature" which we shall note  $\theta_{SH}(T)$ . Usually  $\theta_{DW}(T)$  and  $\theta_{SH}(T)$  do not exactly coincide, hence there is no hope, for any theory which (explicitly or implicitly) adopts a quasi-harmonic framework, to simultaneously interpret with accuracy scattering and specific heat experimental data. This criticism holds for most available theories, and our own treatment does not escape from it. Nevertheless, partial success is of course not excluded, as it will become clear later on.

The W factors of copper (in the range 4-500°K<sup>[6]</sup>) and aluminium (in the range 4-400°K<sup>[7]</sup>) have been measured and interpreted within central force models. However it is known<sup>[8]</sup> that these models are inadequate for explaining, over the entire wavelength region, other vibrational properties. In what concerns copper, DeWames et al<sup>[8]</sup> calculated, by using several sets of force constants<sup>[9-11]</sup>, its W factor; they concluded that the experimental accuracy is not high enough to distinguish the most adequate among them.

The anharmonic contribution to the W factor has been taken into account in several works. For instance, Owen and Williams<sup>[12]</sup> have phenomenologically introduced the anharmonicity of a single-atom crystal through use of a characteristic temperature  $\theta(T) = \theta(T_0) \left[ 1 - \alpha\gamma(T - T_0) \right]$  where  $T_0$  is a reference temperature,  $\gamma$  is the Grüneisen constant and  $\alpha$  is the cubic thermal expansion factor.

This procedure leads to an  $\gamma$  - parameter which reasonably fits the experimental data (in range 300-900<sup>o</sup>K) for gold and copper, but not those for aluminium. Maradudin and Flinn [13] have explicitly introduced, within a classical framework, the cubic and quartic anharmonic contributions to the  $W$  factor; they obtained, besides the usual linear (in  $T$ ) harmonic term, corrections in  $T^2$  and  $T^3$ , which allow for a satisfactory fit with experimental data in what concerns the  $\gamma$  factor but not in what concerns  $\theta_{SH}(T)$  [14]. Since that period there has been a regain of interest in calculation of the  $W$  factor [15-24,29]. In particular a certain success has been obtained [15-17] in the simultaneous interpretation of the frequency spectra and  $W$  factor measurements in cubic metals.

In the present work we study, by taking into account the cubic and quartic anharmonicity, within a variational statistical framework, the thermal behaviour of the frequency spectrum, the crystalline expansion, the Debye Waller factor and finally the specific heat of single-atom crystals. In particular, this theory predicts for the  $W$  factor: a) a small temperature dependence in the limit  $T \rightarrow 0$ ; b) a linear dependence for intermediate temperatures; c) a  $\sqrt{T}$  dependence in the limit  $T \rightarrow \infty$ . Furthermore, it becomes possible to interpret the minimum of  $\theta_{SH}(T)$  observed by Horton and Schiff [14] and Flinn and McManus [7] in Cu, Al, Ag, Au, Pb.

In Section II we perform, in order to exhibit the kind of approximation we use, the classical and quantum calculation of the thermal expansion and thermally renormalized vibration frequency associated to a single anharmonic oscillator; in Section III we establish the same physical quantities for a first-neigh-

bour linear chain. In Section IV we present, for a single oscillator as well as for a one-two-and three-dimensional crystal, the results we obtain for the vibrational contribution to the constant volume specific heat; in Section V we discuss, for a three-dimensional crystal, the thermal behaviour of the Debye-Waller factor; finally in the Section VI we conclude and compare the predictions of the present theory with available experimental information.



## II- SINGLE OSCILLATOR

### II.1 INTRODUCTION

In order to present the problem and exhibit the nature of our approximation, we shall discuss in the present section a single anharmonic oscillator (with cubic and quartic contributions) within the framework of the Variational Method in both Classical and Quantum Statistical Mechanics. We shall focus the thermal behaviour of the renormalized frequency and of the expansion. We shall assume the following Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 - cx^3 + bx^4 \quad (1)$$

where  $\omega$ ,  $c$  and  $b$  are real positive quantities ( $\omega$  and  $c$  conventionally;  $b$  to ensure stability). According to the relative values of  $\omega$ ,  $b$  and  $c$  the potential energy might present one or two minima. The two-minima possibility might lead, in the case of systems of interacting oscillators, to structural phase transitions. As this eventuality lays beyond the scope of the present paper, we shall impose the existence of only one minimum, hence

$$c^2 \leq \frac{16}{9} m\omega^2 b \quad (2)$$

Furthermore, by introducing the variables

$$x = \eta + u$$

$$\eta = \langle x \rangle \equiv \text{thermal mean value}$$

the Hamiltonian (1) can be re-written in a convenient form for variational purposes with a trial Hamiltonian given by

$$H_0 = \frac{p^2}{2m} + \frac{1}{2} m\Omega^2 u^2 \quad (3)$$

The variational free energy  $\bar{F}$  (to be not confused with the exact free energy) is given by [25]

$$\bar{F} = F_0 + \langle H - H_0 \rangle_0 \quad (4)$$

where  $F_0$  and  $\langle \dots \rangle_0$  denote respectively the free energy and the canonical mean value associated to  $H_0$ .

## II.2 CLASSICAL STATISTICS

The use of (1) and (3) into (4) leads to

$$\bar{F} = F_0 + \frac{1}{2} m\omega^2 \eta^2 - c\eta^3 + b\eta^4 + \left( \frac{1}{2} m\omega^2 - 3c\eta + 6b\eta^2 - \frac{1}{2} m\Omega^2 \right) \langle u^2 \rangle_0 + 3b \langle u^2 \rangle_0^2 \quad (5)$$

where we have used that  $\langle u^4 \rangle_0 = 3 \langle u^2 \rangle_0^2$ . Next we impose the minimization equations  $\frac{\partial \bar{F}}{\partial \Omega} = 0$  and  $\frac{\partial \bar{F}}{\partial \eta} = 0$ , which lead to

$$v^2 (v^2 - 1 + 6C\lambda - 12B\lambda^2) - 12Bt = 0 \quad (6.a)$$

$$v^2 (\lambda - 3C\lambda^2 + 4B\lambda^3) - (3C - 12B\lambda)t = 0 \quad (6.b)$$

where we have used that

$$\frac{\partial F_0}{\partial \Omega} = \Omega^2 \langle u^2 \rangle_0$$

$$\frac{1}{2} m \Omega^2 \langle u^2 \rangle_0 = \frac{1}{2} k_B T \quad (\text{classical equipartition})$$

and have introduced the reduced variables

$$v \equiv \Omega / \omega \quad ; \quad \lambda \equiv \eta \sqrt{\frac{m \omega}{\hbar}} \quad ;$$

$$t \equiv \frac{k_B T}{\hbar \omega} \quad ; \quad B \equiv \frac{b \hbar}{m^2 \omega^3} \quad ; \quad C = c \sqrt{\frac{\hbar}{m^3 \omega^5}}$$

The constant  $\hbar$  has been artificially introduced in order to make easier the comparison with the quantum case. The restriction (2) becomes

$$C^2 \leq -\frac{16}{9} B \quad (2')$$

The equations (6.a) and (6.b) implicitly give  $v(t)$  and  $\lambda(t)$  (see Fig. 1), whose asymptotic behaviours are

$$v \sim 1 + (6B - 9C^2) t$$

$$\lambda \sim 3Ct$$

in the limit  $t \rightarrow 0$ ,

and

$$v \sim (12Bt)^{1/4} \left\{ 1 + \frac{(12B)^{-1/2}}{4} \left( 1 - \frac{3C^2}{4B} \right) t^{-1/2} + \frac{(12B)^{-1}}{32} \left( 1 - \frac{3C^2}{4B} \right)^2 t^{-1} + \right. \\ \left. + \left[ \frac{(12B)^{1/2}}{4} L^2 - \frac{3}{32} (12B)^{-3/2} \left( 1 - \frac{3C^2}{4B} \right) \right] t^{-3/2} \right\}$$

$$\lambda \sim \lambda_{\infty} - Lt^{-1/2} + \frac{(12B)^{1/2}}{2} \left( 1 - \frac{3C^2}{4B} \right) t^{-1} - (12B)^{-1} \left( 1 - \frac{3C^2}{4B} \right) Lt^{-3/2}$$

in the limit  $t \rightarrow \infty$

with

$$\lambda_{\infty} \equiv C/4B$$

and 
$$L \equiv \frac{C}{8\sqrt{3} B^{3/2}} \left( 1 - \frac{C^2}{2B} \right)$$

Note that within restriction (2') it is  $L > 0$ .

### II.3 QUANTUM STATISTICS

The trial Hamiltonian (3) may be rewritten in terms of boson operators

$$H_0 = \hbar\Omega (B^{\dagger} B + 1/2) \quad (3')$$

with the well known transformation

$$x = \sqrt{\frac{\hbar}{2m\Omega}} (B^{\dagger} + B)$$

$$p = i \sqrt{\frac{\hbar m\Omega}{2}} (B^{\dagger} - B)$$

which must be defined in terms of the renormalized frequency [26],

The expression (5) still holds with

$$F_0 = k_B T \ln \left[ 2 \operatorname{sh} \frac{\hbar \Omega}{2k_B T} \right]$$

and

$$\langle u^2 \rangle_0 = \frac{\hbar}{2m\Omega} \operatorname{ctgh} \left( \frac{\hbar \Omega}{2k_B T} \right)$$

The minimization equations  $\frac{\partial \bar{F}}{\partial \Omega} = 0$  and  $\frac{\partial \bar{F}}{\partial \eta} = 0$  now become

$$v^2 (v^2 - 1 + 6C\lambda - 12B\lambda^2) - 6B \operatorname{ctgh} \left( \frac{v}{2t} \right) = 0 \quad (7.a)$$

$$v (\lambda - 3C\lambda^2 + 4B\lambda^3) + \frac{1}{2} (12B\lambda - 3C) \operatorname{ctgh} \left( \frac{v}{2t} \right) = 0 \quad (7.b)$$

The  $v$  and  $\lambda$  thermal behaviours are given, in the limit  $t \rightarrow 0$ , by

$$v \sim v_0 + C_v e^{-v_0/t}$$

$$\lambda \sim \lambda_0 + C_\lambda e^{-\lambda_0/t}$$

with

$$v_0 (\lambda_0 - 3C\lambda_0^2 + 4B\lambda_0^3) + \frac{1}{2} (12B\lambda_0 - 3C) = 0$$

$$v_0^3 - v_0 + 6C\lambda_0 v_0 - 12B\lambda_0^2 v_0 - 6B = 0$$

$$C_v \equiv \frac{12Bv_0^3 - 18v_0(C - 4B\lambda_0)^2}{2v_0^5 + 6Bv_0^2 - (3C - 12B\lambda_0)^2}$$

$$C_\lambda \equiv \frac{6v_0^2(C - 4B\lambda_0)}{2v_0^3 + 6B - (3C - 12B\lambda_0)^2}$$

As expected the equations (7.a) and (7.b) reproduce (6.a) and (6.b) in the classical limit  $t \rightarrow \infty$ . Within this limit we have the following behaviours:

$$v \sim (12Bt)^{1/4} \left\{ 1 + \frac{(12B)^{-1/2}}{4} \left( 1 - \frac{3C^2}{4B} \right) t^{-1/2} + \frac{(12B)^{-1}}{32} \left( 1 - \frac{3C^2}{4B} \right)^2 t^{-1} + \left[ \frac{(12B)^{1/2}}{4} L^2 - \frac{3}{32} (12B)^{-3/2} \left( 1 - \frac{3C^2}{4B} \right)^3 + \frac{(12B)^{1/2}}{48} \right] t^{-3/2} \right\}$$

$$\lambda \sim \lambda_\infty - Lt^{-1/2} + (12B)^{-1/2} \left( 1 - \frac{3C}{4B} \right) t^{-1} - (12B)^{-1} \left( 1 - \frac{3C^2}{4B} \right)^2 Lt^{-3/2}$$

where, for  $v$ , we have exhibited the quantum correction with respect to the classical behaviour. It is remarkable that, within a high asymptotic order, classical and quantum results coincide (the same happens with  $\lambda(t)$ ).

The solutions  $v(t)$  and  $\lambda(t)$  of (7.a) and (7.b) are represented in the Fig. 2. The analysis of  $v_0$ ,  $\lambda_0$ ,  $C_v$  and  $C_\lambda$  shows that, within the restriction (2') and depending on the relative value of  $B$  and  $C$ , we have (see Fig. 3)

$$\begin{aligned} v_0 & \begin{cases} > \\ < \end{cases} 1 \\ \lambda_0 & \begin{cases} \geq \\ = \end{cases} 0 \\ C_v & \begin{cases} > \\ < \end{cases} 0 \end{aligned}$$

$$c_{\lambda} \geq 0$$

The fact that, in contrast with the classical situation, we have, at vanishing temperatures,  $v_0 \neq 1$  and  $\lambda_0 \neq 0$  is clearly a consequence of the energy of the fundamental state being  $\frac{\hbar\Omega_0}{2}$  over the bottom of the potential.

### III. LINEAR CHAIN

#### III.1 INTRODUCTION

In this section we discuss, within the variational framework, a cyclic linear chain made of  $N$  identical first-neighbour - interacting oscillators. Oncemore we shall be interested in the thermal behaviour of crystalline expansion and frequency spectrum. We shall assume the Hamiltonian

$$H = \sum_{j=1}^N \left\{ \frac{P_j^2}{2m} + \frac{1}{2} m\omega^2 (x_{j+1} - x_j)^2 - c(x_{j+1} - x_j)^3 + b(x_{j+1} - x_j)^4 \right\} \quad (8)$$

with the constants  $\omega$ ,  $c$  and  $b$  satisfying the same restrictions as for the single-oscillator case.

By introducing the new variables

$$x_j = u_j + \eta$$

the Hamiltonian becomes

$$H = \sum_{j=1}^N \frac{P_j^2}{2m} + \left( \frac{1}{2} m\omega^2 - 3c\eta + 6b\eta^2 \right) \left[ (u_{j+1} - u_j)^2 + b(u_{j+1} - u_j)^4 \right] +$$

$$+ N \left( \frac{1}{2} m\omega^2 \eta^2 - c\eta^3 + b\eta^4 \right) +$$

$$+ (\text{odd terms in } u_{j+1} - u_j) \quad (8')$$

Then, through the Fourier-transformation given by



$$u_j = \frac{1}{\sqrt{N}} \sum_q x_q e^{-iqj}$$

$$p_j = \frac{1}{\sqrt{N}} \sum_q p_q e^{-iqj}$$

(q runs all over the first Brillouin zone),

the Hamiltonian takes the following form

$$H = \sum_q \left\{ \frac{|p_q|^2}{2m} + 2 \left[ \frac{1}{2} m\omega^2 - 3c\eta + 6b\eta^2 \right] (1 - \cos q) |x_q|^2 \right\} +$$

$$+ \frac{3b}{2N} \sum_{\substack{qq' \\ q''}} \left\{ \left( e^{-iq} - 1 \right) \left( e^{-i(q+q')} - 1 \right) \left( e^{-iq''} - 1 \right) \left( e^{-i(q''-q')} - 1 \right) x_q x_{q+q'} x_{q''} x_{q''-q'} \right\}$$

$$+ N \left[ \frac{1}{2} m\omega^2 \eta^2 - c\eta^3 + b\eta^4 \right] + (\text{odd term in seq.}) \quad (8'')$$

We now introduce the following trial Hamiltonian:

$$H_0 = \sum_q \left[ \frac{|p_q|^2}{2m} + \frac{1}{2} m\Omega_q |x_q|^2 \right] \quad (9)$$

### III.2 CLASSICAL STATISTICS

The use of relations (4), (8'') and (9) lead to the following expression for the variational free energy:

$$\bar{F} = F_0 + \sum_q \left\{ \left[ (m\omega^2 - 6c\eta + 12b\eta^2) (1 - \cos q) - \frac{m\Omega_q^2}{2} \right] \langle |x_q|^2 \rangle_0 + \right.$$

$$\left. + \frac{6b}{N} (1 - \cos q)^2 \langle |x_q|^2 \rangle_0^2 \right\} + \frac{12b}{N} \sum_{qq'} (1 - \cos q)(1 - \cos q') \langle |x_q|^2 \rangle_0 \langle |x_{q'}|^2 \rangle_0 + \\
 + N \left( \frac{1}{2} m\omega^2 \eta^2 - c\eta^3 + b\eta^4 \right) \tag{10}$$

Then the minimization of  $\bar{F}$  with respect to  $\Omega_q$  and  $\eta$  leads to

$$\mu^2 (\mu^2 - 1 + 6C\lambda - 12B\lambda) - 12Et = 0 \tag{11.a}$$

$$\mu^2 (\lambda^2 - 3C\lambda^2 + 4B\lambda^3) - (3C - 12B\lambda)t = 0 \tag{11.b}$$

where we have used the classical equipartition principle and the phonon frequency spectrum

$$\Omega_q^2 = 2\omega^2 \mu^2 (1 - \cos q) \tag{12}$$

and we have introduced the same reduced variables of section II.

We remark that, by doing  $\mu \rightarrow v$ , equations (11.a) and (11.b) rigorously reproduce equations (6.a) and (6.b). However it should be clear that  $\mu$  represents the renormalized longitudinal sound velocity, while  $v$  is the renormalized frequency of a single oscillator.

### III.3 QUANTUM STATISTICS

In order to study the quantum statistics of the Hamiltonian (8''), we shall put it into a second quantization form through use of the transformation

$$x_q = \left( \frac{\hbar}{2m\Omega_q} \right)^{1/2} \left( B_{-q}^+ + B_q \right)$$

$$p_q = i \left( \frac{\hbar m \Omega_q}{2} \right)^{1/2} \left( B_q^+ - B_{-q} \right)$$

where  $[B_q, B_{q'}^+] = \delta_{qq'}$

This procedure leads to a free energy

$$\bar{F} = F_0 + \sum_q \left\{ \frac{1 - 6C\lambda + 12B\lambda^2}{\mu_q} (1 - \cos q) - \mu_q/2 \right\} Y_q +$$

$$+ \frac{12B}{N} \left\{ \sum_q (1 - \cos q) \frac{Y_q}{\mu_q} \right\}^2 + N \left\{ \frac{1}{2} \lambda^2 - C\lambda^3 + B\lambda^4 \right\} \quad (13)$$

where  $\bar{F}$  and  $F_0$  are given in  $\hbar\omega$  units and

$$\bar{F} = t \sum_q \ln (2 \text{sh} (\mu_q / 2t))$$

$$Y_q \equiv \langle B_q^+ B_q + 1/2 \rangle_0 = \frac{1}{2} \text{ctgh} (\mu_q / 2t)$$

$$\mu_q \equiv \frac{\Omega_q}{\omega}$$

From the conditions  $\frac{\partial \bar{F}}{\partial \mu_q} = 0$  and  $\frac{\partial \bar{F}}{\partial \lambda} = 0$  we obtain

$$\mu(\mu^2 - 1 + 6C\lambda - 12B\lambda^2) - \frac{12B}{N} \sum_q \text{sen} q \text{ctgh} \left( \frac{\mu \text{sen} q}{t} \right) = 0 \quad (14.a)$$

$$\mu(\lambda - 3C\lambda^2 + 4B\lambda^3) - \frac{(3C - 12B\lambda)}{N} \sum_q \text{sen} q \text{ctgh} \left( \frac{\mu \text{sen} q}{t} \right) = 0 \quad (14.b)$$

As expected, these equations reproduce (11.a) and (11.b) in the classical limit  $t \rightarrow \infty$ . On the other hand, in the limit  $t \rightarrow 0$ , we obtain

$$\mu(\mu^2 - 1 + 6C\lambda - 12B\lambda^2) \sim \frac{24B}{\Pi} + \frac{2\Pi B}{v_0^2} t^2 \quad (15.a)$$

$$\mu(\lambda - 3C\lambda^2 + 4B\lambda^3) \sim \frac{6C - 24B\lambda}{\Pi} + \frac{\Pi(C - 4B\lambda_0)}{v_0^2} t^2 \quad (15.b)$$

where we have used the quasi-continuum limit ( $N \rightarrow \infty$ ). These equations lead to

$$\begin{aligned} \mu &\sim \mu_0 + C_\mu t^2 \\ \lambda &\sim \lambda_0 + C_\lambda t^2 \end{aligned}$$

with

$$\mu_0 (\mu_0^2 - 1 + 6C\lambda_0 - 12B\lambda_0^2) = \frac{24B}{\Pi}$$

$$\mu_0 (\lambda_0 - 3C\lambda_0^2 + 4B\lambda_0^3) = \frac{6C - 24B\lambda_0}{\Pi}$$

$$C_\mu \equiv \frac{\Pi^2 [2B\mu_0^2 - 3(C - 4B\lambda_0)^2]}{2\mu_0 \left[ \Pi\mu_0^2 \left( \mu_0^2 + \frac{12B}{\Pi} \right) - 18(C - 4B\lambda_0)^2 \right]}$$

$$C_\lambda \equiv \frac{\Pi^2 (C - 4B\lambda_0)}{2 \left[ \Pi\mu_0^2 \left( \mu_0^2 + \frac{12B}{\Pi} \right) - 18(C - 4B\lambda_0)^2 \right]}$$

we remark that, through the transformations

$$\mu_0 \rightarrow v_0 \quad ; \quad C_\mu \rightarrow \frac{\Pi^2}{24v_0^2} C_v \quad ;$$

$$B \rightarrow \frac{\Pi}{4} B \quad ; \quad C_\lambda \rightarrow \frac{\Pi^{3/2}}{12v_0^2} C_\lambda \quad ;$$

$$C \rightarrow \frac{\sqrt{\Pi}}{2} C \quad ;$$

$$\lambda_0 \rightarrow \frac{2}{\sqrt{\Pi}} \lambda_0$$

the above relations exactly reproduce the ones we obtained in Section II.

#### IV. SPECIFIC HEAT

##### IV-1 INTRODUCTION

Let us now calculate the constant "volume" specific heat  $C_v$  for both the single oscillator and the linear chain cases. Within the variational approximation it is

$$C_v = \frac{\partial}{\partial T} \langle H \rangle_0 \quad (16)$$

##### IV.2 SINGLE OSCILLATOR

Within classical statistics expression (16) may be rewritten as follows

$$C_v = k_B \left( 1 - \frac{t}{v} \frac{\partial v}{\partial t} \right) \quad (17)$$

where we have used (6.a) and (6.b). Note that the thermal expansion enters only indirectly, through its influence on  $v(t)$ . Furthermore if  $v$  monotonously increases (with  $t$ ), then  $C_v$  monotonously decreases; if  $v$  presents a minimum (see Fig. 2.a), then  $C_v$  present a maximum (see Fig. 4). Its asymptotic behaviours are

$$C_v \sim \frac{3}{4} k_B \left\{ 1 + \frac{1 - \frac{3C^2}{4B}}{6 \sqrt{12B}} t^{-1/2} \right\} \quad (18)$$

in the limit  $t \rightarrow \infty$ ,

and

$$C_v \sim k_B \left[ 1 - (6B - 9C^2)t \right] \quad (18')$$

in the limit  $t \rightarrow 0$ .

The discussion of these asymptotic behaviours leads to three different cases (see Fig. 4).

Within Quantum Statistics, expression (16) becomes

$$C_v = \frac{1}{2} k_B v \frac{\partial}{\partial t} \left\{ \operatorname{ctgh} \frac{v}{2t} \right\} \quad (19)$$

where we have used (7.a) and (7.b).

The asymptotic behaviour in the limit  $t \rightarrow 0$  is given

$$C_v \sim 4v_0 \frac{e^{-v_0/t}}{t}$$

while in the limit  $t \rightarrow \infty$  it is still given by expression (18) (see Fig. 5).

### IV.3 LINEAR CHAIN

The classical specific heat for this case is given by

$$C_v = N k_B \left( 1 - \frac{t}{\mu} \frac{\partial \mu}{\partial t} \right) \quad (20)$$

which differs from the single oscillators case only by a factor N.

In the quantum case we obtain, through use of equations (14.a) and (14.b),

$$C_v = k_B \mu \frac{\partial}{\partial t} \int_0^q \operatorname{sen} \frac{q}{2} \operatorname{ctgh} \left( \frac{\mu}{t} \operatorname{sen} \frac{q}{2} \right) \quad (21)$$

Clearly expression (21) reproduces (20) in the classical limit. On the other hand, in the limit  $t \rightarrow 0$ , we have

$$C_v \sim \frac{N \mu k_B}{3 \mu_0} t \quad (22)$$

The temperature dependence of  $C_v$  is shown in the Fig. 6.

If we compare the equations (7.a) and (7.b) with (14.a) and (14.b) we observe a great similarity between them. The difference holds on the fact that, while in the first case (single oscillator) the temperature dependence appears explicitly in the unique  $\operatorname{ctgh}$ -term, in the second one (linear chain) it appears through an integral on  $\operatorname{ctgh}$ -terms. Therefore it is clear that for a d-dimensional crystal we shall obtain a d-dimensional integral on the same type of  $\operatorname{ctgh}$ -terms.

Hence, in the limit  $t \rightarrow 0$ , the asymptotic behaviour (22) will become  $C_v \propto t^d$ , as in the well known *harmonic* Debye case. At high temperature, all cases (for any value of  $d$ ) are expected to have the same type of asymptotic behaviour. Let us conclude by saying that these considerations lead to

$$\mu \sim \mu_0 + C_\mu t^{d+1} \quad (t \rightarrow 0) \quad (23.a)$$

$$\mu \propto t^{1/4} \quad (t \rightarrow \infty) \quad (23.b)$$

where  $C_\mu$  is related, for any value of  $d \geq 1$ , to  $C_v$  through a transformation similar to the one we exhibited in Section III.3.

## V. DEBYE-WALLER FACTOR

Let us recall that the scattered amplitude of x-rays (and other similar beams) is given by

$$\exp(-W) = \langle \exp [i\vec{k} \cdot (\vec{u}_j - \vec{u}_{j'})] \rangle \quad (24)$$

where  $\vec{k} = \vec{k} - \vec{k}'$  is the scattering vector,  $\vec{u}_j$  is the displacement of the  $j$ -th atom from its equilibrium position and  $\langle \dots \rangle$  denotes the thermal canonical average. In any quasi-harmonic approximation the probability distribution of the displacements is Gaussian in both classical and quantum treatments (see, for example, Ref.[27]).



Hence (see for example Ref. [28]).

$$\exp (-W) = \exp \left\{ -\frac{1}{2} \langle [\vec{k} \cdot (\vec{u}_j - \vec{u}_j')]^2 \rangle_0 \right\} \quad (24')$$

where now  $\langle \dots \rangle_0$  denotes the thermal average with a Gaussian law. Within the variational treatment we are dealing with, we obtain

$$W = \frac{1}{6} K^2 \langle (\vec{u}_j - \vec{u}_j')^2 \rangle_0 = \frac{K^2}{6} \int_{\vec{q}} \langle |u_{\vec{q}}|^2 \rangle_0$$

where we have performed a Fourier transformation. Within the quasi-continuum limit and Debye approximation, we obtain for  $d = 3$  (see also Ref. [24])

$$W = \frac{3}{2} \frac{K^2 \hbar^2 T^2}{m k_B (\Theta(T))^3} \int_0^{\frac{\Theta(T)}{T}} \left( \frac{1}{e^z - 1} + \frac{1}{2} \right) z dz \quad (25)$$

where  $m$  is the mass of the atom and  $\Theta(T)$  the thermally renormalized Debye temperature. Therefore the anharmonic influence appears exclusively through  $\Theta(T)$ , which is given by

$$\Theta(T) = \frac{\hbar \Omega_D(T)}{k_B} = 2\hbar a q_D \omega_{\mu}(T) \quad (26)$$

where  $a$  is the characteristic crystalline parameter,  $\Omega_D$  the Debye frequency and  $q_D$  the Debye wave vector. By using relations (23a), (23.b), (25) and (26) we finally obtain

$$W \sim \frac{1}{16} \frac{K^2}{a^2 q_D} \left( \frac{3 k_B}{b} \right)^{1/2} T^{1/2}$$

in the limit  $T \rightarrow \infty$ , and

$$W \sim \alpha + \beta T^2 + \gamma T^4$$

in the limit  $T \rightarrow 0$ ,

where

$$\alpha \equiv \frac{3K^2 \hbar}{16m a q_D \omega \mu_0}$$

$$\beta \equiv \frac{3\pi^2 k_B K^2}{96m \hbar a^3 q_D^3 \omega^3 \mu_0}$$

$$\gamma \equiv -C_\mu \alpha / \mu_0$$

In Fig. 7 we present typical harmonic and anharmonic Debye-Waller factors as functions, of temperature.

VI. CONCLUSION

The purpose of the present work was to study the influence of (cubic and quartic) anharmonicity of real crystals on the thermal behaviour of some relevant physical quantities (constant volume specific heat, thermally renormalized Debye temperature ( $\theta$ ), Debye-Waller factor ( $W$ ), crystalline expansion, phonon spectrum). The calculations were performed within the framework of the Variational Method in Statistical Mechanics, which in a relatively simple and unified manner provides the thermal dependence, for the whole range of temperatures, of the above quantities. In order to be clear, our methodology consisted in first presenting the single oscillator case, then the linear chain, and finally we generalized some of our results to d-dimensional monoatomic crystals. Because of our harmonic choice for the trial Hamiltonian, most of the physical quantities were given, as functions of temperature, by relations formally equal to those customary for the purely harmonic case, and the anharmonic influence was mainly absorbed into the renormalization of  $\theta(T)$ .

In what concerns the low-temperature regime, the present treatment succeeded in providing forms of  $\theta(T)$  which qualitatively fit well with experimental data. In particular was obtained (for a defined region of the space of the harmonic and anharmonic elastic constants) the minimum of  $\theta(T)$  which is typical [7, 14] of Cu, Al, Ag, Au and Pb.

For the intermediate-temperature regime, we obtained the customary [7,12,14,18,23,29] linear dependence of the W and Y-factors (in other words  $\theta(T)$  approximatively constant).

Finally, in the high-temperature regime, the present treatment leads to a  $\sqrt{T}$ -dependence for the W-factor, which implies in the wrong curvature when comparison is made with experimental results for Al<sup>[12]</sup> and Na<sup>[23,29]</sup>. Nevertheless, let us point out that the high temperature regime practically coincides with the region just below the melting point, where the phase transition effects, not included in the present treatment, are expected to be important (and in the sense of accelerating the increase of the W-factor with temperature). More precisely, the Al and Na were respectively observed [12,23,29] in the regions 300-900°K and 100-370°K (we recall that their melting points are respectively 933°K and 371°K). Furthermore it is suggestive the fact that several other substances (which were observed in regions relatively far from their melting points) did not deviate from the linear increase of W(T); namely Cu (observed in the 300-900°K region<sup>[12]</sup>; melting point 1356°K), Au (300-900°K<sup>[12]</sup>; 1336°K), Fe (200-1100°K<sup>[18,23,29]</sup>, 1809°K), Mo (100-500°K<sup>[23]</sup>; 2890°K) and Cr (100-500°K<sup>[23]</sup>; 2130°K).

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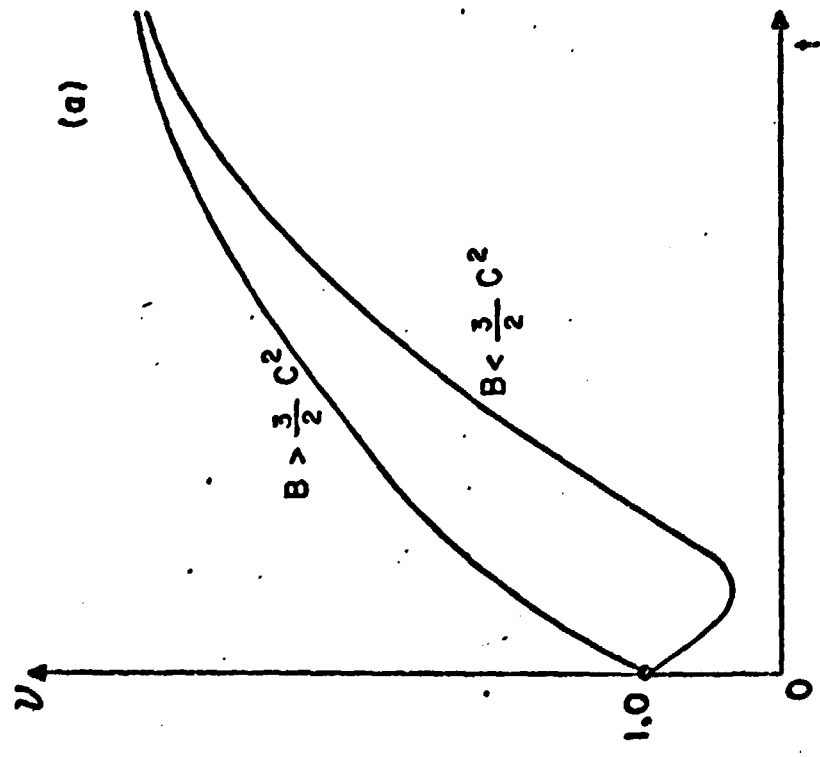
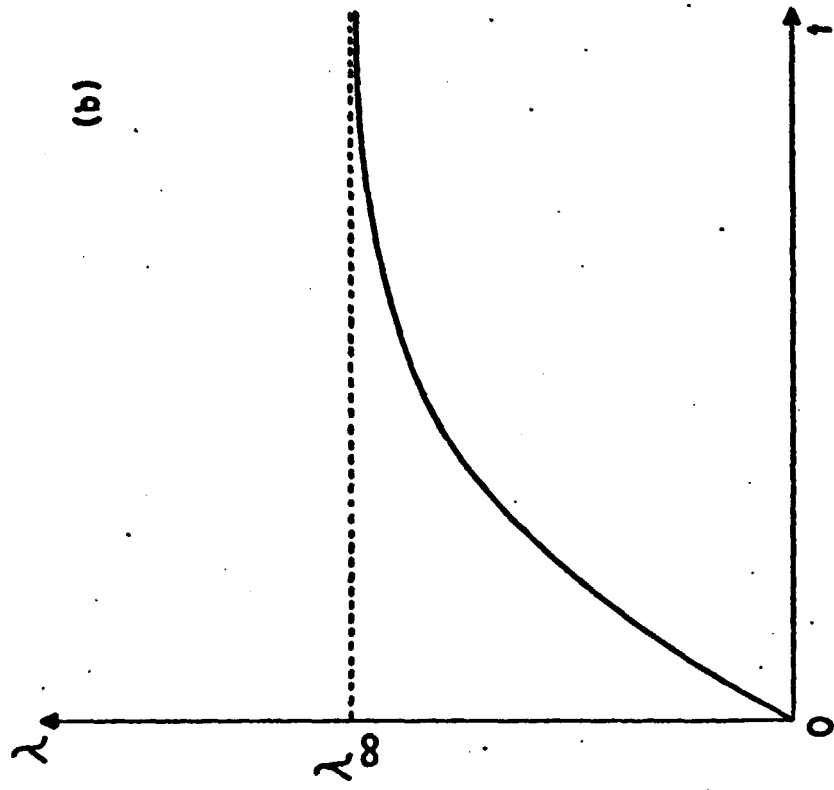
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CAPTION FOR FIGURES

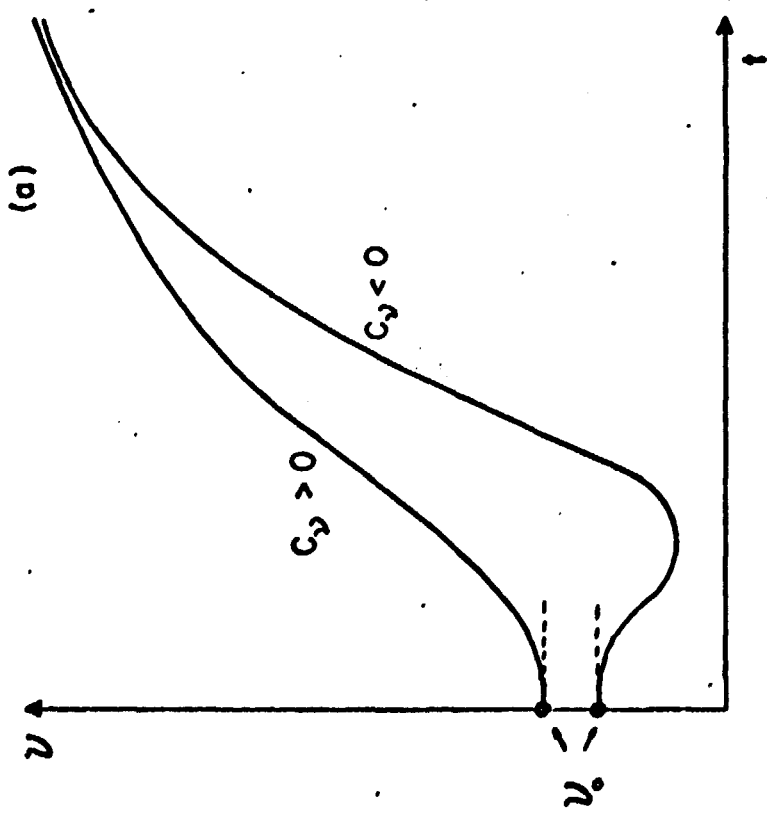
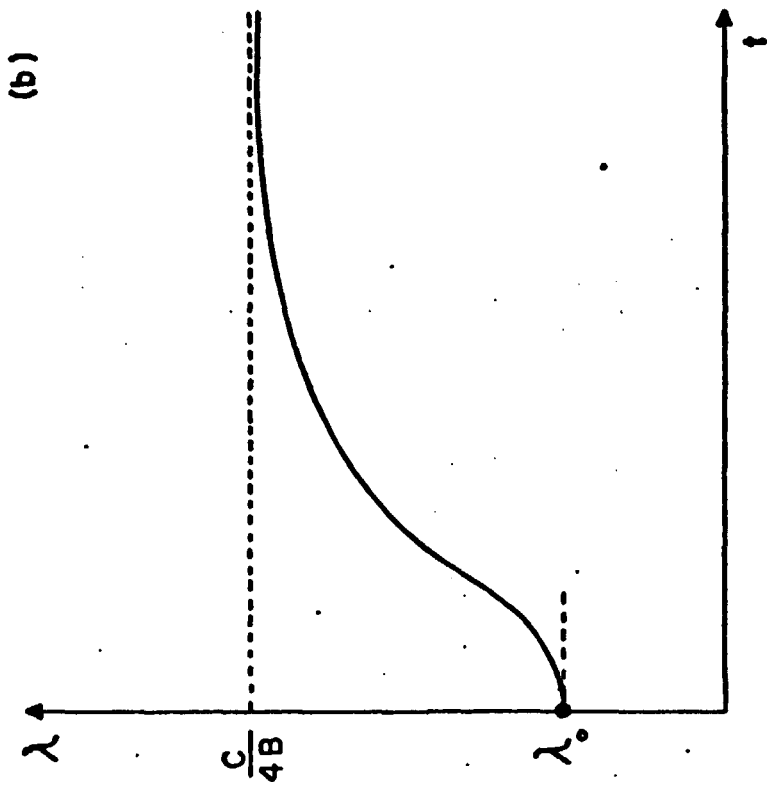
- Fig. 1 - Classical thermal behaviour of the: a) reduced renormalized frequency; and b) reduced linear expansion parameter. The saturation value denoted by  $\lambda_{\infty}$  is  $C/4B$ . In the limit  $t \rightarrow 0$  is  $\nu \sim 1 + (6B - 9C^2)t$  and  $\lambda \sim 3Ct$ ; in the limit  $t \rightarrow \infty$  it is  $\nu \sim (12bt)^{1/4}$  and  $\lambda \sim \lambda_{\infty} - Lt^{1/2}$ .
- Fig. 2 - Quantum behaviour of the: a) reduced renormalized frequency; b) linear expansion parameter. In the limit  $t \rightarrow 0$  it is  $\nu \sim \nu_0 + C_{\nu} \frac{e^{-\nu_0}}{t}$  and  $\lambda \sim \lambda_0 + C_{\lambda} \frac{e^{-\nu_0}}{t}$ ; in the limit  $t \rightarrow \infty$  the classical asymptotic behaviours are re-obtained (see Fig. 1).
- Fig. 3 - Mapping of the B-C space according the cases  $C_{\nu} \gtrless 0$  and  $\nu_0 \gtrless 1$ . The region I is forbidden by condition (2'); region II corresponds to  $C_{\nu} < 0$  and  $\nu_0 < 1$ ; region III corresponds to  $C_{\nu} > 0$  and  $\nu_0 < 1$ ; region IV corresponds to  $C_{\nu} > 0$  and  $\nu_0 > 1$ .
- Fig. 4 - Thermal behaviour of the classical specific heat.  
(a) :  $1 < \frac{9}{6} \frac{C^2}{B} < 2$  ; (b) :  $\frac{9}{6} \frac{C^2}{B} > 2$  ;  
(c) :  $\frac{9}{6} \frac{C^2}{B} < 1$

- Fig. 5 - Thermal behaviour of the quantum specific heat for both cases  $B \gtrless \frac{3}{4} C^2$ .
- Fig. 6 - Thermal behaviour of the quantum specific heat of a linear chain for both cases  $B \gtrless \frac{3}{4} C^2$ .
- Fig. 7 - Thermal behaviour of the quantum Debye-Waller factor of a three-dimensional crystal in both harmonic (dashed line) and anharmonic (continuous line) cases.  $A_0'$  might be greater than  $A_0$  (as in this figure) or not, depending on the values of  $B$  and  $C$ .

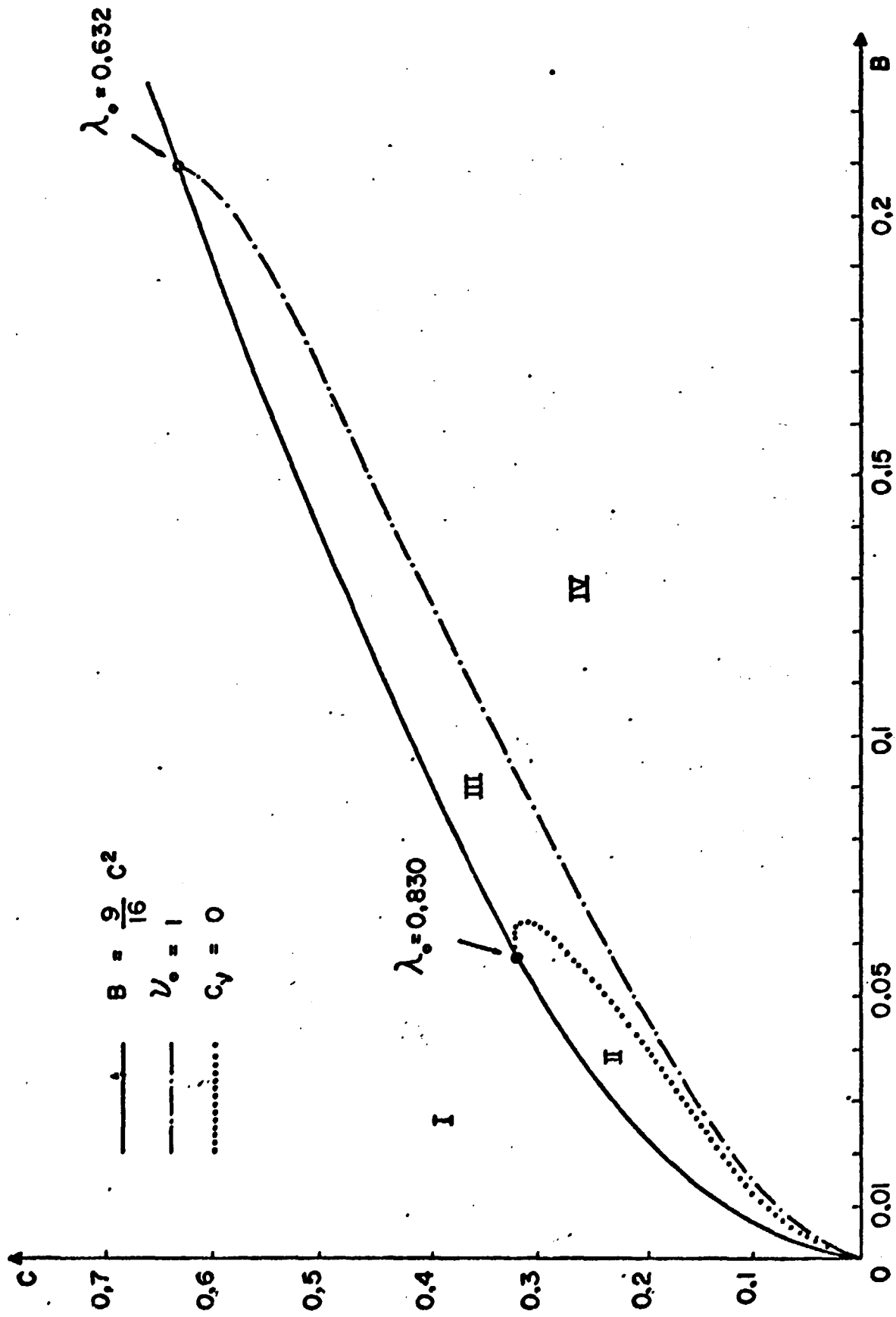




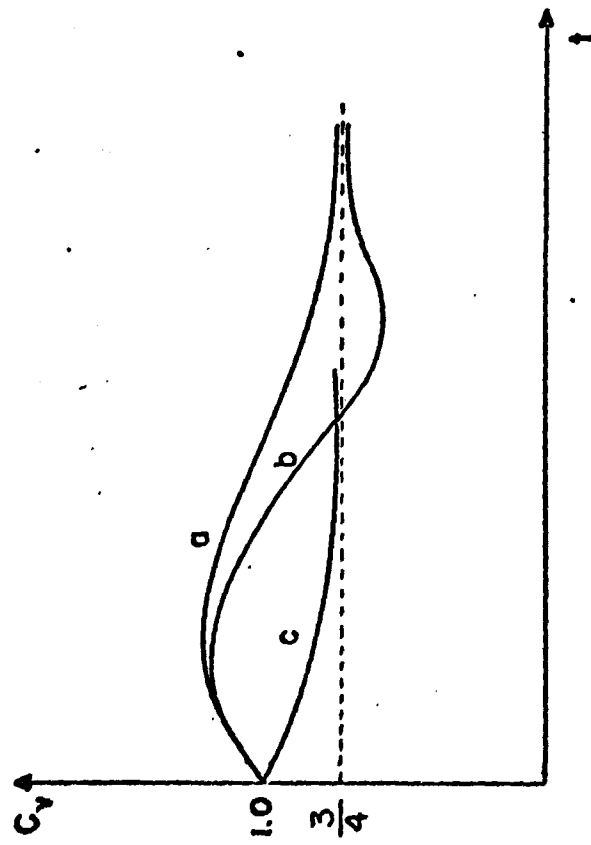
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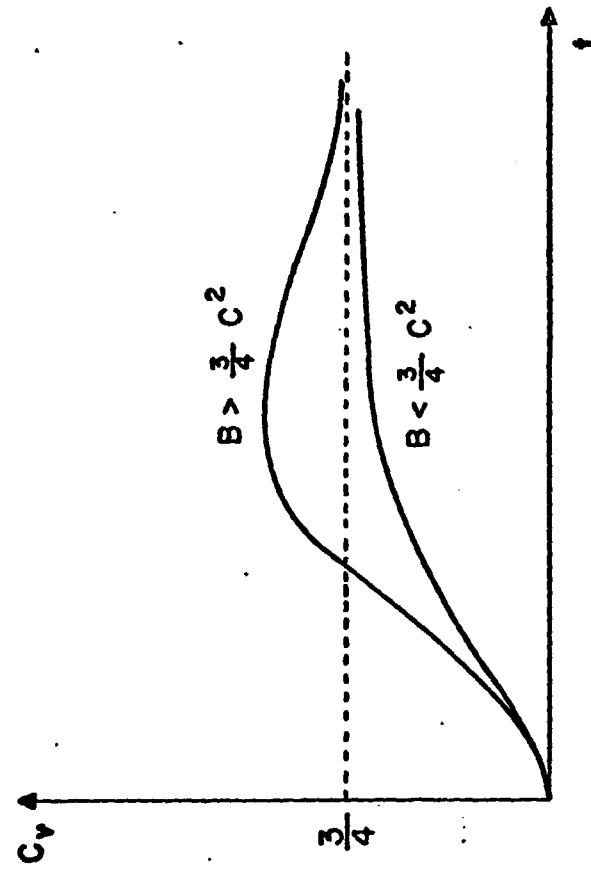
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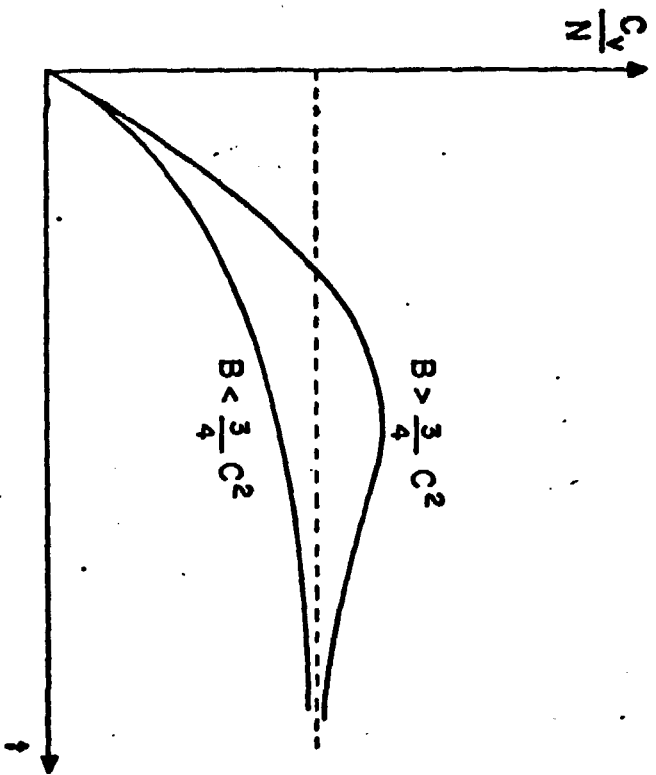
(FIG. 3)



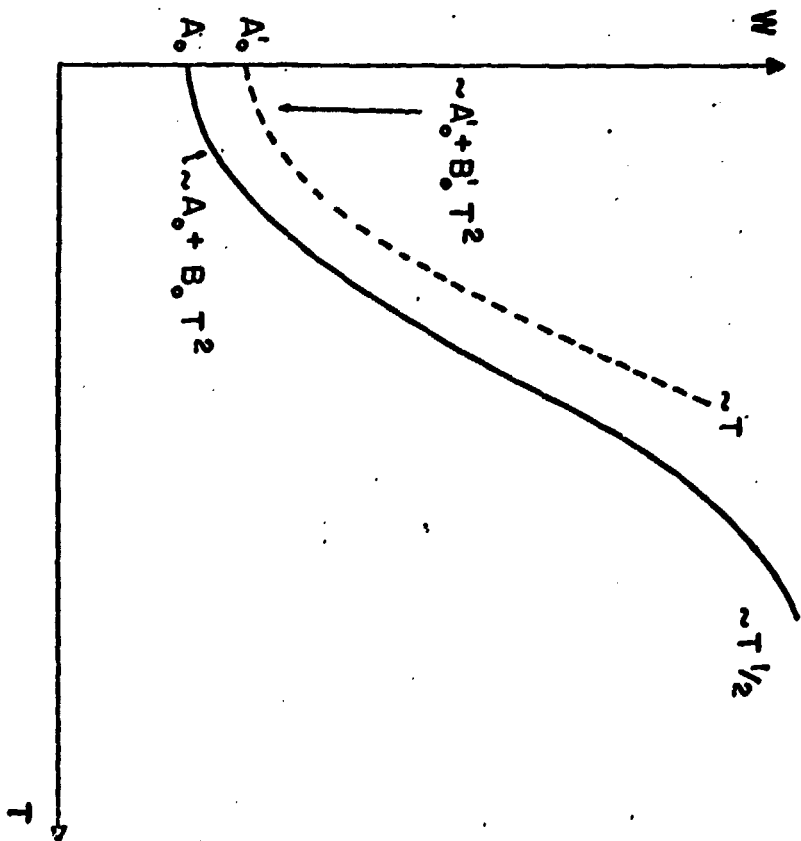
(FIG. 4)



(FIG. 5)



(FIG. 6)



(FIG. 7)

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