

THE THERMAL EXPANSION OF AN ALMOST LINEAR CHAIN

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[Manuscript received December 7, 1962]

Summary

A linear chain model of a close-packed line of atoms in a solid has been constructed. The model differs from usual linear chain models in that the chain is not strictly one-dimensional, the individual atoms being free to move in three dimensions. To account for the interaction of the chain with its surroundings an effective potential has been introduced. When the thermal expansion of solid argon is calculated, satisfactory agreement with experiment is obtained in the classical region.

I. INTRODUCTION

The influence of the anharmonic terms of the interatomic potential on the specific heat, compressibility, and thermal expansion of atomic solids has been studied by several authors using a linear chain model. If the model is of any validity, then the results derived should apply well to solid argon for which the interatomic potential is accurately known.

Damköhler (1935) evaluated the constant-volume partition function numerically, while Dugdale and MacDonald (1954) and MacDonald and Roy (1955) have evaluated the constant-pressure partition function analytically. Later Leibfried (1955) evaluated the constant-volume partition function analytically. However, when the thermal expansion of solid argon is evaluated on the linear chain model with the known interparticle potential (see Dobbs and Jones 1957, p. 553) the result does not agree well with experiment. More recently, linear chains have only been used as mathematical abstractions on which to illustrate the appropriate method for a three-dimensional model.

The purpose of this paper is to show that the linear chain will give reasonable results if two modifications are made to make the model more realistic. The first modification to be made is that the chain of atoms is allowed to relax sideways, i.e. it is situated in three dimensions. The chain will then correspond more closely to a close-packed line of atoms in a solid.

In order to represent the effect of the rest of the solid, inasmuch as it constrains the chain of atoms to an almost linear form, harmonic binding forces have been postulated. These forces act between the atom and the equilibrium line. With the introduction of these additional forces the classical partition function cannot be separated into a product of single integrals. The evaluation of the partition function can, however, be reduced to the solution of an eigenvalue problem, as has been discussed by Barker (1962). While strictly one-dimensional anharmonic chains have been discussed quantum mechanically by Leibfried and Ludwig (1961) and Maradudin, Flinn, and Coldwell-Horsfall (1961), the treatment here is classical.

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The second modification is to use an effective potential between members of the chain instead of the interatomic potential between two free atoms. The effective potential is used to take account of the fact that the close-packed line of atoms is in the centre of a solid and hence interacts with its surroundings.

The effective potential in the chain is constructed from the interatomic potential of two free atoms by summation over lattice sites. The energy of an atom in the close-packed line due to half the solid has been taken as the effective potential in the chain. This method of constructing an effective potential has been suggested for an Einstein model by Foreman (1962), but it is more logical to use such a construction to obtain an interparticle potential in a chain rather than the potential in which an atom moves.

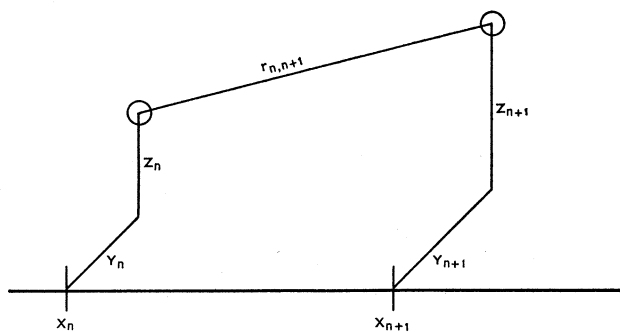


Fig. 1.—Diagram of notation for a displacement of the chain.

The result of the model is applied to the calculation of the expansion of the close-packed line of atoms for argon. The interatomic force is known for argon and accurate measurements of the thermal expansion have been made (cf. Dobbs and Jones 1957). Since the model has been constructed with a view to giving correct properties in the direction of the chain, it may be accurate for thermal expansion and compressibility but cannot be expected to give such non-directional properties as the anharmonic correction to the specific heat.

II. THE MODEL

The model chosen is that of a chain of atoms in three dimensions with nearest-neighbour interaction. This chain of atoms represents a close-packed line inside a solid. To simulate the constraining effect of the rest of the solid the chain is harmonically bound to a straight line. Figure 1 shows a diagram of the model.

It is assumed that an effective potential $\Phi(r)$ has a single minimum at $r = a$. For convenience the zero of energy is taken so that $\Phi(a) = 0$. The potential will later be expanded about $r = a$ and we let

$$\Phi(r) = Ba^2 \left[\frac{1}{2} \left(\frac{r-a}{a} \right)^2 + \frac{1}{3!} \Phi_3 \left(\frac{r-a}{a} \right)^3 + \frac{1}{4!} \Phi_4 \left(\frac{r-a}{a} \right)^4 + \dots \right]. \quad (1)$$

Here the Φ_n are dimensionless and are given by

$$\Phi_n = \frac{a^{n-2}}{B} \left. \frac{d^n}{dr^n} \Phi \right|_{r=a}, \quad (2)$$

and

$$B = \left. \frac{d^2 \Phi}{dr^2} \right|_{r=a} \quad (3)$$

is the harmonic constant of the potential.

Letting (X_n, Y_n, Z_n) denote the positions of the n th atom in the chain, where X_n is measured parallel to the line and Y_n, Z_n perpendicular to the line, then the total configuration energy of the chain is

$$U = \sum_n \left\{ \frac{1}{2} B \frac{1}{\chi_1} Y_n^2 + \frac{1}{2} B \frac{1}{\chi_2} Z_n^2 + \Phi(r_{n,n+1}) \right\}, \quad (4)$$

where

$$r_{n,n+1}^2 = (X_{n+1} - X_n)^2 + (Y_{n+1} - Y_n)^2 + (Z_{n+1} - Z_n)^2. \quad (5)$$

The harmonic terms which bind the atoms to the line are taken, for generality, as different in the Y and Z directions. The quantities χ_1 and χ_2 are two dimensionless parameters representing the ratio of the strength of the harmonic part of the interparticle potential to the strength of the sideways harmonic binding.

III. THE PARTITION FUNCTION

In order to evaluate the thermodynamic properties of the model a constant-force partition function has been studied. The classical constant-force partition function is defined by

$$e^{-G/kT} = h^{-s} \int d^s p \int d^s q \exp -\frac{1}{kT} \left\{ \mathcal{H}(p, q) + FL \right\}, \quad (6)$$

where

- G is the Gibbs energy,
- $\mathcal{H}(p, q)$ is the Hamiltonian,
- F is the applied force,
- L is the length of the chain.

For the model we are studying the Hamiltonian is given by

$$\mathcal{H} = \sum_{(n)} \frac{1}{2m} p_n^2 + U, \quad (7)$$

where m is the mass of an atom in the chain and U is given by equation (4).

The length of the chain is

$$L = X_N - X_0, \quad (8)$$

where N is the number of atoms in the chain.

The partition function cannot be separated into the product of a set of integrals as was done by Dugdale and MacDonald (1954); however, the evaluation of the

partition function can be reduced to the problem of finding the largest eigenvalue of a matrix. The reduction of a partition function to an eigenvalue problem was used by Kramers and Wannier (1941) in discussion of the Ising model of ferromagnetism. More recently, Longuet-Higgins (1958) has reduced the partition function of a multicomponent one-dimensional fluid to an eigenvalue problem, and Barker (1962) has given a comprehensive discussion of the method. For the purpose of this paper we need only note that if the partition function can be written as

$$Z = K^N \int d^N q \prod_i M(q_i; q_{i+1}), \quad (9)$$

then

$$\begin{aligned} Z &= K^N \text{Trace}\{M^N\} \\ &= K^N \lambda^N \end{aligned} \quad (10)$$

in the limit of large N . Here M^N is the N th matrix power of M and λ is the largest eigenvalue of M , i.e. λ satisfies

$$\lambda \Psi(q_i) = \int M(q_i, q_{i+1}) \Psi(q_{i+1}) dq_{i+1}. \quad (11)$$

The partition function (6) can be written in the form (9) by the identification

$$K = \left\{ \sqrt{\left(\frac{m^3 (kT)^6}{\hbar^6 B^3} \chi_1 \chi_2 \right)} \right\} e^{-Fa/kT}, \quad (12)$$

$$\begin{aligned} M = \sqrt{\left(\frac{B^3}{(2\pi)^3 \chi_1 \chi_2} \right)} e^{Fa/kT} \int \exp - \frac{1}{kT} \left\{ \frac{1}{4} B \frac{1}{\chi_1} (Y_i^2 + Y_{i+1}^2) + \frac{1}{4} B \frac{1}{\chi_2} (Z_i^2 + Z_{i+1}^2) + \Phi(r_{i,i+1}) \right. \\ \left. + F(X_{i+1} - X_i) \right\} d(X_{i+1} - X_i), \end{aligned} \quad (13)$$

and

$$q_i = (Y_i, Z_i),$$

$$q_{i+1} = (Y_{i+1}, Z_{i+1}).$$

Here the integral over the momentum coordinates has been taken and the factor K has been separated, as it is the purely harmonic contribution to the partition function.

In order to expand the anharmonic correction to the partition function in powers of the temperature and the force, the variables X , Y , Z are changed to

$$\left. \begin{aligned} x_n &= \sqrt{(B/kT)} (X_{n+1} - X_n - a), \\ y_n &= \sqrt{(B/\chi_1 kT)} Y_n, \\ z_n &= \sqrt{(B/\chi_2 kT)} Z_n, \end{aligned} \right\} \quad (14)$$

after which the matrix (13) is expanded in powers of the temperature and the force. It is convenient at this stage to reduce all quantities to dimensionless quantities

$$\left. \begin{aligned} Ng &= G/Ba^2, \\ t &= kT/Ba^2, \\ f &= F/Ba. \end{aligned} \right\} \quad (15)$$

The matrix (13) then becomes

$$M(y_n, z_n; y_{n+1}, z_{n+1}) = \{1/\sqrt{(2\pi)}\} \exp - [\frac{1}{4}(y_n^2 + y_{n+1}^2) + \frac{1}{4}(z_n^2 + z_{n+1}^2)] \int \exp - [\Phi/kT + fx] dx. \quad (16)$$

In terms of the reduced variables (15), the potential can be expanded in powers of the temperature as

$$\Phi/kT = \frac{1}{2}x^2 + \sum_{r,s} k_{rs} x^r R^s t^{\frac{1}{2}(s+r-2)}, \quad (17)$$

where

$$R^2 = \chi_1(y_{n+1} - y_n)^2 + \chi_2(z_{n+1} - z_n)^2,$$

and

$$\left. \begin{aligned} k_{30} &= \frac{1}{6} \Phi_3, & k_{12} &= \frac{1}{2}, \\ k_{40} &= \frac{1}{24} \Phi_4, & k_{22} &= \frac{1}{4} \Phi_3 - \frac{1}{2}, & k_{04} &= \frac{1}{8}, \\ k_{50} &= \frac{1}{120} \Phi_5, & k_{32} &= \frac{1}{12} \Phi_4 - \frac{1}{4} \Phi_3 + \frac{1}{2}, & k_{14} &= \frac{1}{8} \Phi_3 - \frac{3}{8}. \end{aligned} \right\} \quad (18)$$

Using (16), (17), and (18), the matrix can be expanded in powers of t and f . After the integral over x is taken, the matrix can be expanded in the form

$$M = H + V, \quad (19)$$

where

$$H = \{1/\sqrt{(2\pi)}\}^2 \exp - \{\frac{1}{4}(y_n^2 + y_{n+1}^2) + \frac{1}{4}(z_n^2 + z_{n+1}^2)\},$$

and

$$V = (1/2\pi) [\exp - \frac{1}{4}(y_n^2 + y_{n+1}^2 + z_n^2 + z_{n+1}^2)] [K_0 + K_2 R^2 + K_4 R^4 + \dots], \quad (20)$$

with

$$\left. \begin{aligned} K_0 &= \{-3k_{40} + \frac{1}{2}k_{30}^2\}t + \dots \\ &\quad + 3k_{30}f + \{15k_{50} - 105k_{30}k_{40} + \frac{3}{2}k_{30}^3\}ft + \dots \\ &\quad + \frac{1}{2}f^2/t + \{-\frac{1}{2}k_{40} + \frac{1}{4}k_{30}^2\}f^2 + \dots \\ &\quad + \dots, \\ K_2 &= \{-k_{22} + 3k_{30}k_{12}\}t + \dots \\ &\quad + \{k_{12}\}f + \{3k_{32} - 15k_{30}k_{22} - 15k_{12}k_{40} + \frac{1}{2}k_{30}^2k_{12}\}ft + \dots \\ &\quad + \{-\frac{3}{2}k_{22} + \frac{1}{2}k_{30}k_{12}\}f^2 + \dots \\ &\quad + \dots, \\ K_4 &= \{-k_{04} + \frac{1}{2}k_{12}^2\}t + \dots \\ &\quad + \{k_{14} - 3k_{30}k_{04} - 3k_{12}k_{22} + \frac{1}{2}k_{30}k_{12}^2\}ft + \dots \\ &\quad + \{-\frac{1}{2}k_{04} + \frac{3}{4}k_{12}^2\}f^2 + \dots \\ &\quad + \dots. \end{aligned} \right\} \quad (21)$$

The eigenvalue of the matrix can now be found using perturbation theory where in equation (19) V is considered as a perturbation to H .

The eigenfunctions of H can be divided into two classes. The first class is that of the eigenfunctions orthogonal to $\exp - \frac{1}{4}[y_{n+1}^2 + z_{n+1}^2]$. All such eigenfunctions are degenerate with a zero eigenvalue. If the eigenfunction is not orthogonal to

$\exp -\frac{1}{4}[y_{n+1}^2 + z_{n+1}^2]$ then substitution shows that there is only one such eigenfunction. The normalized eigenfunction is

$$\Psi_0(y_n, z_n) = \{1/\sqrt{(2\pi)}\}\exp -\frac{1}{4}[y_n^2 + z_n^2]. \quad (22)$$

The eigenvalue of this eigenfunction is one and is then the largest eigenvalue of H . The eigenvalue spectrum is then given by

$$\lambda_n = \left\{ \begin{array}{ll} 1, & n = 0, \\ 0, & n \neq 0. \end{array} \right\} \quad (23)$$

The eigenvalue λ of M can now be expanded in powers of t and f by using perturbation theory. Hence

$$\lambda = \lambda_0 + \langle 0|V|0\rangle + \sum'_n \frac{\langle 0|V|n\rangle \langle n|V|0\rangle}{\lambda_0 - \lambda_n},$$

(cf. Landau and Lifschitz 1959, p. 133) when taken to second order. Using the result of (23) this takes the very simple form

$$\begin{aligned} \lambda &= 1 + \langle 0|V|0\rangle + \sum'_n \langle 0|V|n\rangle \langle n|V|0\rangle \\ &= 1 + \langle V \rangle + \langle V \times V \rangle - \langle V \rangle^2. \end{aligned} \quad (24)$$

In this last equation the symbol 0 has been dropped, the eigenfunction involved being given by (22), and the \times symbol denotes matrix multiplication. As we shall require $\ln \lambda$, this is given to the required order by

$$\ln \lambda = \langle V \rangle + \langle V \times V \rangle - \frac{3}{2} \langle V \rangle^2. \quad (25)$$

On substituting (9) into (12)

$$\begin{aligned} \ln \lambda &= K_0 + K_2 \langle R^2 \rangle + K_4 \langle R^4 \rangle - \frac{1}{2} K_0^2 - K_0 K_2 \langle R^2 \rangle - K_0 K_4 \langle R^4 \rangle \\ &\quad + \frac{1}{2} K_2^2 \{2 \langle R^2 \times R^2 \rangle - 3 \langle R^2 \rangle^2\}. \end{aligned} \quad (26)$$

The terms involving R can be evaluated by integration.

The Gibbs energy is then given by (4) which may be written as

$$g = -t \ln K - t \ln \lambda.$$

Substituting,

$$\begin{aligned} g &= -t \ln K - \frac{1}{2} f^2 \\ &\quad + \left\{ \frac{1}{8} \Phi_4 - \frac{5}{24} \Phi_3^2 - (\chi_1 + \chi_2) \right\} t^2 \\ &\quad + \left\{ -\frac{1}{2} \Phi_3 - (\chi_1 + \chi_2) \right\} f t \\ &\quad + \left\{ -\frac{1}{8} \Phi_5 + \frac{3}{8} \Phi_3 \Phi_4 - \frac{5}{8} \Phi_3^3 + \left(-\frac{1}{2} \Phi_3 - 3 \right) (\chi_1 + \chi_2) - \frac{9}{2} (\chi_1^2 + \frac{2}{3} \chi_1 \chi_2 + \chi_2^2) \right\} f t^2 \\ &\quad + \left\{ \frac{1}{4} \Phi_4 - \frac{1}{2} \Phi_3^2 - (\chi_1 + \chi_2) - \frac{3}{2} (\chi_1^2 + \chi_2^2) \right\} f^2 t \\ &\quad + \dots \end{aligned} \quad (27)$$

From the Gibbs energy the thermal expansion of the chain is found as

$$\alpha = \frac{k}{Ba^2} \left[\left\{ -\frac{1}{2}\Phi_3 - (\chi_1 + \chi_2) \right\} \right. \\ + \left\{ \left(-\frac{1}{4}\Phi_5 + \frac{1}{3}\Phi_3\Phi_4 - \frac{5}{4}\Phi_3^2 \right) + (-\Phi_3 - 6)(\chi_1 + \chi_2) - 9(\chi_1^2 + \frac{2}{3}\chi_1\chi_2 + \chi_2^2) \right\} t \\ + \left\{ \left(\frac{1}{2}\Phi_4 - \Phi_3^2 \right) - 2(\chi_1 + \chi_2) - 3(\chi_1^2 + \chi_2^2) \right\} f \\ \left. + \dots \right]. \quad (28)$$

IV. APPLICATION TO SOLID ARGON

Because of the constraining effect of the surrounding atoms, a close-packed line of atoms inside a crystal will act as if its interparticle potential is considerably stronger than the potential between two free atoms. Hence it is necessary to calculate the effective potential which exists between the members of the chain when it is *in situ*. This effective potential is calculated by summing the free interparticle potential over the lattice sites surrounding the chain in an appropriate manner.

Before calculating the effective interparticle potential of the chain in the solid, consider an isolated one-dimensional chain maintained so that all atoms are stationary and at their equilibrium positions. Then the potential well that any one atom finds itself in, is not the interparticle potential. It will be seen that the potential well is symmetric and equal to the sum of two interparticle potentials oppositely directed. The correct way to find the effective potential in the chain is to neglect the effect of the atom to one side of the one which is being considered.

To find the effective potential in the chain representing a close-packed line in a solid a similar procedure is used. A schematic diagram of the situation is shown in Figure 2. The effective potential on the chain is taken as the potential on one atom due to half the solid. In Figure 2 the potential due to atom 4 together with half the potential due to atoms 1 and 2 would be counted if only nearest-neighbour interactions are considered.

The harmonic binding energy of the atoms to the line is found by displacing an atom perpendicularly to the line and summing the contributions due to the atoms surrounding the line. In this case, however, the summation is over all nearest neighbours.

If the interatomic potential between two isolated atoms can be expanded about the equilibrium position as

$$\phi(r) = ba^2 \left[\frac{1}{2} \left(\frac{r-a}{a} \right)^2 + \frac{1}{3!} \gamma_3 \left(\frac{r-a}{a} \right)^3 + \frac{1}{4!} \gamma_4 \left(\frac{r-a}{a} \right)^4 + \dots \right], \quad (29)$$

then for the case of a face-centred cubic crystal an easy summation over lattice sites gives for the coefficients of equation (1)

$$\left. \begin{aligned} B &= 2b, \\ \Phi_3 &= \frac{2}{3}\gamma_3, \\ \Phi_4 &= \frac{5}{8}\gamma_4, \\ \Phi_5 &= \frac{9}{16}\gamma_5. \end{aligned} \right\} \quad (30)$$

Similarly the sideways harmonic binding can be evaluated as

$$\chi_1 = \chi_2 = \frac{1}{2}. \quad (31)$$

For the face-centred cubic crystal, then, the thermal expansion is given by substituting (30) and (31) into equation (28). This gives the result

$$\alpha = \frac{k}{ba^2} \left[\left\{ -\frac{3}{16}\gamma_3 - \frac{1}{2} \right\} + \left\{ \left(-\frac{9}{256}\gamma_5 + \frac{9}{64}\gamma_3\gamma_4 - \frac{135}{1024}\gamma_3^3 \right) + \left(-\frac{3}{8}\gamma_3 - \frac{11}{4} \right) \right\} \frac{kT}{ba^2} + \dots \right], \quad (32)$$

at zero external force.

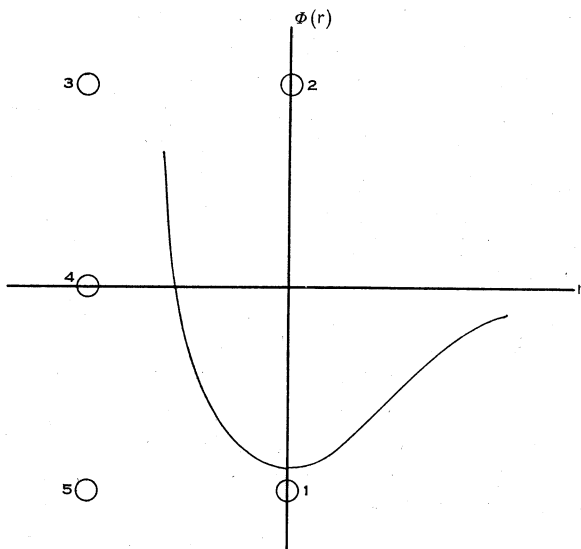


Fig. 2.—Diagram illustrating the method of finding the effective potential.

When this result is applied to argon, using the potential

$$\phi(r) = 4\epsilon\{(\sigma/r)^{12} - (\sigma/r)^6\}, \quad (33)$$

with

$$\epsilon = 169 \times 10^{-16} \text{ erg},$$

$$\sigma = 3.402 \text{ \AA},$$

as is given by Dobbs and Jones (1957), the following results are obtained:

$$\left. \begin{aligned} k/ba^2 &= 1.133 \times 10^{-4} \text{ (degK)}^{-1}, \\ \gamma_3 &= -21, \\ \gamma_4 &= 371, \\ \gamma_5 &= -6440. \end{aligned} \right\} \quad (34)$$

This may be substituted into the equation (32) to give

$$\alpha = [3.89 + 0.0297T] \times 10^{-4} \text{ (degK)}^{-1}.$$

Argon can only be considered as a classical solid at higher temperatures. The Debye temperature of argon is 80°K and evaluating the thermal expansion at this temperature gives

$$\alpha = 6.27 \times 10^{-4} \text{ (degK)}^{-1}.$$

This may be compared with the measured value (Dobbs and Jones (1957)) of

$$\alpha = [6.0 \pm 0.3] \times 10^{-4} \text{ (degK)}^{-1}.$$

Analysis of the calculations shows that, of the two modifications introduced, that of providing an effective potential plays a much more decisive role in determining the results for solid argon than the permitted slight non-linearity of the chain. This is not unexpected when one considers that a sideways displacement which is small to first order produces only a second-order change in the length of the chain. Thus, for the permitted non-linearity to be significant, large sideways displacements must occur which would require large values of $(\chi_1 + \chi_2)$ of equation (28). In fact, since Φ_3 is always negative, (28) shows that negative thermal expansion would be obtained at sufficiently low temperatures if

$$2(\chi_1 + \chi_2) > |\Phi_3|. \quad (35)$$

Comparing with (30), (31), and (34), we see that such an effect could be anticipated only for extremely anisotropic solids, i.e. close-packed linear chains which are far from their neighbours in at least one of the Y and Z directions. Such an effect has been observed in anisotropic metals (cf. Childs 1953, p. 665), but we consider application of the linear chain results would not, in this case, be of any quantitative significance.

Turning now to the question of the compressibility, two difficulties arise, the first of which is of a general nature. Since the interatomic potential is determined partly from compressibility data, a certain circularity of argument arises if the potential (33) is used to predict compressibility. It can, however, be argued that the calculation should be made since it provides a test of the self-consistency of the method used in this paper.

The second difficulty is then encountered, which is that of relating the applied force on the solid to the force in the chain, which latter is determined from an effective potential whose "cross section of influence" may not always be very clear. For the special case of a face-centred cubic crystal with purely harmonic interactions between stationary atoms, the calculation is easily made to give for the isothermal compressibility

$$\begin{aligned} K_T &= -\frac{3}{L} \left(\frac{\partial L}{\partial p} \right)_T \\ &= -3 \frac{\partial^2 g}{\partial f^2} \frac{a}{2\sqrt{2}b}, \end{aligned} \quad (36)$$

where a is the separation between nearest neighbours, and b is the strength of the harmonic interaction. (The factor 3 is to convert to volumetric compressibility.)

Assuming that (36) holds in the anharmonic case also, and using (27), (30), and (34) in (36) we have

$$K_T = 0.486\{1 + 0.00768T\} \times 10^{-10} \text{ cm}^2\text{dyne}^{-1},$$

giving the result $K_T = 0.784 \times 10^{-10} \text{ cm}^2\text{dyne}^{-1}$ at 80°K compared with the experimental value of $K_T = 0.781 \times 10^{-10} \text{ cm}^2\text{dyne}^{-1}$. The consistency check is thus satisfactory in the classical region.

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