A simple thermodynamic description of the combined Einstein and elastic models

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Abstract

A simple application of the Einstein model combined with an elastic description of the solid state is developed. The frequency of quantum oscillators has been assumed as volume dependent and elastic energy terms with a static character have been included to complete the description. Such an extension enables us to construct the complete thermodynamics. In particular, the model yields a practical equation of state and describes the thermal expansion coefficient as well as the isothermal compressibility of solids. The thermodynamic properties resulting from the Gibbs free-energy analysis have been calculated and are illustrated in figures. Some comparisons of the theoretical results with experimental data for solid argon have been made.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The Einstein model of the solid state has been known for many years as the first model able to describe qualitatively the low-temperature behaviour of the specific heat [1–3]. This model often serves as an approximation for studies of optical phonons or soft modes in some intermetallic compounds [4] and is also found suitable to describe thermal properties of some modern low-dimensional structures [5]. It is also referred to as the prototype which led to the development of the more sophisticated Debye model [6]. Nonetheless, it has been shown that in many cases the Einstein model provides better results than the Debye model [7]. It is known that in spite of its usefulness and simplicity, the pure Einstein model lacks the ability to describe fully the thermodynamic properties of the solid state. For instance, neither the proper equation of state nor the thermal expansion or compressibility can be obtained. Thus, apart from the celebrated specific heat behaviour, which is an important consequence of the quantum nature of harmonic oscillators, other thermodynamic properties have not successfully been described within this model.

There have been numerous attempts in the literature to improve the pure Einstein model [8–12]. For instance, a ‘variational Einstein model’ was developed in [8] to describe low-temperature solids from the Feynman path integral perspective. The formalism was applied to a specific system, consisting of solid hydrogen with lithium impurities. However, one of the theoretical results of [8] seems to be controversial, namely the dependence of the free energy, which is presented there as an increasing function of temperature (see figure 16 of [8]), giving the indication that the corresponding entropy is negative. Cankurtaran and Askerov [9] introduced the so-called Einstein–Debye model, with which calculations of the thermal expansion coefficient were possible by introducing the Grüneneisen parameter. However, neither the Gibbs free energy nor the compressibility could be calculated within that approach. Thus, a complete thermodynamic description was not achieved. In [10] the ‘nonlocal Einstein crystal’ was considered, for which the thermodynamic functions have been constructed. The considerations presented in [10] seem to be of a purely theoretical character, the Einstein crystal being replaced by a harmonic sublattice with a size that is coupled to the total volume. Additionally, the Mie–Grüneisen approach has been developed by Holzapfel et al for the description of simple metals [11] as well as some simple solids, such as NaCl and MgO [12]. The optimized pseudo-Debye–Einstein model was been used in that work, and good agreement with the experimental data was achieved. However, the method
presented in [11, 12] does not seem to be straightforward enough to use since it requires the introduction of many fitting parameters for calculations of the free energy.

On the other hand, there exists a rich literature on the description of solid state properties within the elastic models [13–22]. These studies are supported by experimental measurements [23, 24]. For instance, Birch [19] considers single crystal and polycrystalline NaCl at high pressure using the finite strain (Eulerian) theory. In this approach, the equation of state contains coefficients which have to be fitted at each particular temperature. Despite the usefulness of the model for studies of isothermal compression, it does not involve the thermal (vibrational) energy and therefore is not suitable for description of the specific heat. Similarly, in the paper of Vinet et al [20, 21] the universal form of the equation of state has been found based on a scaling argument. The results obtained there have been discussed in the context of the Birch–Murnaghan equation of state [18] and show very good agreement with the experimental data. However, the Gibbs free energy was not derived in [20, 21], so that a full thermodynamic description of the system has not been constructed. As a matter of fact, the same deficiency is found in some other papers devoted to the application of the equation of state based on elastic models. A comparative review of the experimental equations of state existing in the literature is given in [25, 26].

Among other modern methods one should mention the first-principles computations within the density-functional theory (DFT). This includes, for instance, the equation of state, elastic constants and calculations of the phonon dispersion relation [27]. On the other hand, using the first-principles molecular dynamics simulation (FPMD) method the thermal expansivity and the specific heat have been calculated [28]. Good agreement with the experimental data is often achieved. However, an analytic description remains desirable from the point of view of understanding the physics behind the model.

Such a situation motivated us to combine the Einstein and elastic models and to complete them in a way that enabled us to overcome the above-mentioned problems. Looking in the literature, such an idea could already be found in some papers [29, 30]; however, only particular thermodynamic characteristics were studied there. Thus, our aim is to construct a self-consistent and full thermodynamic description. In order to make this possible, the following aspects should be taken into account. Firstly, the common frequency of quantum oscillators should not be treated as a constant value but should be volume (and, in consequence, temperature) dependent. Obviously, such an idea is not new, having emerged for the first time in the paper of Grüneisen [31] where a specific frequency/volume dependence was assumed as a hypothesis. This assumption is supported by the argument that the wavelength of collective excitations (phonons) depends on the crystal size. Secondly, the vibrational Einstein Hamiltonian necessarily needs to be completed by the static, elastic part [32]. The elastic energy accounts for the mutual interactions of the atoms even if they are not in a thermal vibrating state [18, 22]. It is known that the static energy is responsible for crystal compressibility [18], and owing to its magnitude and nature, cannot be inferred from the model of independent oscillators. It turns out that for the purpose of the combined model the elastic free energy should also be modified by taking into account the linear term (which is normally neglected in the elastic theory) as well as the static entropy. The details of this modification will be explained in section 2. For reasons of analytical simplicity we will neglect the electronic excitation term. It is argued that this term is generally a small correction to the solid equation of state [30].

Taking this into account, we propose to improve the model and construct the Gibbs energy of the system from the beginning. We assume that the balance between the internal and external pressures keeps the system in mechanical equilibrium. According to our knowledge, the detailed balance between the expanding pressure of quantum oscillators and the compressive elastic pressure has not been discussed in the literature. Having obtained an expression for the Gibbs energy, a full thermodynamic description of the crystal can be achieved. The main parameters of the theory, which can be extracted from experiment, are the Einstein frequency in the ground state (or the Einstein temperature), the volume elastic modulus in the ground state—supplemented by the structural space-filling coefficient—and the Grüneisen parameter. We will show that these parameters, in principle, allow us to calculate other properties within a reasonable range of experimental values.

The paper is organized as follows: in section 2 the outline of the model is given and the method of derivation the Gibbs energy is presented. In particular, for the combined model the new equation of state is obtained. In section 3 some representative numerical results concerning the thermodynamic properties are illustrated in figures. These calculations are compared with the experimental data for solid argon. A critical discussion of the presented approach is also included.

2. Theoretical model

2.1. The model Hamiltonian

The Hamiltonian is assumed in the form of:

\[ \mathcal{H} = \mathcal{H}_e + \mathcal{H}_\omega, \]  

where the elastic, volume-dependent part, \( \mathcal{H}_e \), can be written as:

\[ \mathcal{H}_e = N A e + \frac{1}{2} N B e^2 - \frac{1}{3!} N C e^3 + \frac{1}{4!} N D e^4, \]  

whereas the oscillatory part, \( \mathcal{H}_\omega \), is given in the form:

\[ \mathcal{H}_\omega = \sum_{i=1}^{N} \hbar \omega (\hat{n}_i + \frac{1}{2}). \]  

In (2) and (3) \( N \) is the number of atoms which are treated as the three-dimensional oscillators and \( \hat{n}_i \) is the excitation number operator connected with the \( i \)th oscillator. The form of the elastic Hamiltonian (2) assumed in this paper is different (much simpler) from that presented in [29] or [30]. The
elastic Hamiltonian, \( H_e \), consists of several terms. The most important is the harmonic term \((\omega \epsilon^2)\), where the \( B \) constant is the volume elastic modulus in the ground state. We found that the linear term \((\epsilon)\) is also necessary, where the \( A \) constant is responsible for the internal (compressive) pressure. Although the linear, anharmonic part is assumed to be very small in comparison with the harmonic one \((A \ll B)\), its role is very important in balancing the internal (expanding) pressure produced by the anharmonic oscillators, i.e. by the \( H_{\omega} \) part. A certain requirement for \( A \)-values is imposed as the equilibrium condition for the total energy, which is discussed later. The relative elastic deformation \( \epsilon \) is defined by the relation:

\[
V = V_0(1 + \epsilon),
\]

where \( V \) is the crystal volume in a current thermodynamic state, and \( V_0 \) is the volume at external pressure \( p = 0 \) (vacuum) and temperature \( T = 0 \). Equation (4) indicates that a non-zero value of volume deformation \( \epsilon \) occurs when the external pressure \( p \neq 0 \) and/or the temperature \( T > 0 \) is applied. Thus, the possibility of introducing the isothermal compressibility and thermal expansion coefficient has been opened within the presented approach.

A composition of the Hamiltonian (1) consisting of the classical \((H_c)\) and quantum \((H_{\omega})\) parts is justified for the purpose of constructing the thermodynamics [22]. Obtaining the free energy of the full system is one of the main goals, and can be conveniently done by summing up the free energies corresponding to those two parts. A similar *modus operandi* has also been presented in [32], albeit for a different approach. It should be stressed that by introducing the elastic Hamiltonian, \( H_e \), the static non-vibrational energy has been taken into account, which is crucial for the equation of state. It is worth mentioning that the method can be further generalized by also introducing the electronic part of the free energy [22].

### 2.2. The elastic free energy

In order to calculate the elastic (Helmholtz) free energy, one has to evaluate the static internal energy and the static entropy. The static internal energy \( U_e \) can be immediately found from the classical part of the Hamiltonian:

\[
U_e = H_c.
\]

From equation (2) it is seen that this energy is explicitly volume dependent. On the other hand, the static entropy \( S_e \) is connected with filling up the volume of the system in the absence of thermal movement. Let us denote by \( V_{ex} \) the volume occupied by \( N \) atoms in the crystal state. For a given crystallographic lattice we can introduce the space-filling coefficient \( q = V_{ex}/V_0 \). For instance, for FCC and HCP structures and the model of hard spheres \( q \approx 0.74 \). Thus, inside each primitive cell \( q = \rho_1 \) is the probability of finding an atom, whereas \( 1 - q = \rho_2 \) is the probability of not finding one. The static entropy connected with the bimodal distribution \( \rho_i \) (where \( i = 1, 2 \)) can be calculated from the mean value of \( \ln \rho_i \), using the general formula for the exact differential of entropy [33]:

\[
dS_e = -Nk_B d(\ln \rho).
\]

Hence, in our case:

\[
S_e = -Nk_B[q \ln q + (1 - q) \ln(1 - q)] - Nk_B c \quad (7)
\]

where \( c \) is a constant of integration. Since \( c \) is arbitrary, as a matter of convenience we can choose \( c = 0 \). This arbitrariness is due to the fact that only changes in entropy are experimentally measurable and have thermodynamic significance [33, 34].

The entropy is additive with respect to the number of primitive cells \( N \). For the purpose of this paper it is assumed in the first approximation that the space-filling coefficient \( q \) is volume independent and, in consequence, the corresponding entropy \( S_e \) is constant. Thus, the static entropy (for \( c = 0 \)) results in the residual entropy of the crystal for \( T \to 0 \), which is due to the fact that the whole volume is not perfectly filled. Moreover, the important role of \( S_e \) (being dependent on \( q \)) may manifest itself in the structural (first order) phase transitions [22].

The elastic, Helmholtz free energy can now be found from the formula:

\[
F_e = U_e - T S_e. \quad (8)
\]

Hence, we finally obtain:

\[
F_e = NA \epsilon + \frac{1}{2} NB \epsilon^2 - \frac{1}{3!} NC \epsilon^3 + \frac{1}{4!} ND \epsilon^4 + Nk_B T[q \ln q + (1 - q) \ln(1 - q)]. \quad (9)
\]

For the full thermodynamic description this energy should be completed by the vibrational, Einstein part.

#### 2.3. The vibrational free energy

For the Hamiltonian (3) it is convenient to employ the canonical ensemble. The Helmholz free energy can be found from the formula:

\[
F_v = -k_B T \ln Z_v \quad (10)
\]

where the statistical sum \( Z_v \) can be calculated exactly as:

\[
Z_v = \text{Tr} e^{-\beta H_v} = [2 \sinh(\frac{\beta \hbar \omega}{2})]^{-2N}. \quad (11)
\]

where \( \beta = 1/k_B T \). Thus we obtain:

\[
F_v = 3Nk_B T \ln[2 \sinh(\frac{\beta \hbar \omega}{2})]. \quad (12)
\]

On the other hand, the vibrational internal energy \( U_v \) is given by the statistical mean value of the corresponding Hamiltonian:

\[
U_v = \langle H_v \rangle = 3N \hbar \omega \left( \langle \hat{n} \rangle + \frac{1}{2} \right) = \frac{3}{2} N \frac{\hbar \omega}{\tanh(\frac{\beta \hbar \omega}{2})}. \quad (13)
\]

Hence, the vibrational entropy \( S_v \) can be found from the relationship:

\[
S_v = \frac{U_v - F_v}{T} = \frac{3N \hbar \omega}{2T \tanh(\frac{\beta \hbar \omega}{2})} - 3Nk_B \ln \left( 2 \sinh \left( \frac{1}{2} \beta \hbar \omega \right) \right). \quad (14)
\]
The specific heat at constant $V$ is given by the well-known formula:

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V = \frac{\partial U}{\partial T}$$

$$= 3Nk_B \left( \frac{\Theta}{2T} \right)^2 \sinh^2 \left( \frac{\Theta}{2T} \right)$$

where $\Theta = h\omega/k_B$.

Further, in order to improve the Einstein model it is assumed that $\omega$ is not a constant but is volume dependent according to the Gr"{u}neisen assumption [31]:

$$\omega \propto \frac{1}{V^\gamma}$$

where $\gamma$ is the Gr"{u}neisen constant. Thus, we can write:

$$\omega = \frac{\alpha_0}{(1 + \varepsilon)^\gamma},$$

where we made use of the relation (4), and $\alpha_0$ in (17) is the Einstein frequency in the ground state (i.e. at $p = 0, T = 0$, and $\varepsilon = 0$). Then, the variable $\Theta = h\omega/k_B$ can be presented in the form of:

$$\Theta = \frac{\Theta_0}{(1 + \varepsilon)^\gamma}$$

where

$$\Theta_0 = \frac{h\omega_0}{k_B}.$$  \hspace{1cm} (18)

$\Theta_0$ is the so-called Einstein temperature. The correction of the Einstein model presented by equation (18) implies that all the thermodynamic potentials will depend on the volume via elastic deformation $\varepsilon$.

### 2.4. Thermodynamic functions of the combined model

The total Helmholtz free energy is given by the sum of expressions (9) and (12), with the help of (16)–(19):

$$F = NA\varepsilon + \frac{1}{2}NB\varepsilon^2 - \frac{1}{3!}NC\varepsilon^3 + \frac{1}{4!}ND\varepsilon^4$$

$$+ Nk_B T[q \ln q + (1 - q) \ln(1 - q)]$$

$$+ 3Nk_B T \ln \left\{ 2 \sinh \left( \frac{\Theta_0}{2T} \left( 1 + \varepsilon \right)^\gamma \right) \right\}. \hspace{1cm} (20)$$

The total Gibbs energy is then given by:

$$G(p, T) = F + pV. \hspace{1cm} (21)$$

The equation of state can be obtained from the variational principle:

$$\left( \frac{\partial G}{\partial \varepsilon} \right)_{p, T} = 0$$

which, from (21), is equivalent to:

$$pV_0 = - \left( \frac{\partial F}{\partial \varepsilon} \right)_T$$

where $F$ is given by (20). From (23), after differentiation of (20), we obtain:

$$pV_0 = -NA - NB\varepsilon + \frac{1}{2}NC\varepsilon^2 - \frac{1}{3!}ND\varepsilon^3$$

$$+ \frac{3}{2} \gamma \left( \frac{nk_B \Theta_0}{2T} \right) \sinh \left( \frac{\Theta}{2T} \right) \left( 1 + \varepsilon \right)^\gamma.$$  \hspace{1cm} (24)

For the high-temperature limit equation (24) takes the form:

$$p = \frac{\partial F}{\partial V} + \frac{3Nk_B T}{V} \gamma$$

which is the classical lattice dynamics pressure [22]. On the other hand, in the low-temperature limit ($T \rightarrow 0$) and for small pressure the deformation $\varepsilon$ is small too, and equation (24) can be linearized as:

$$pV_0 \approx -NA - NB\varepsilon + \frac{1}{2} \gamma Nk_B \Theta_0 [1 - (1 + \gamma)\varepsilon]. \hspace{1cm} (26)$$

Normally, when $p = 0$ then in the ground state $\varepsilon = 0$ as well. Consequently, we have to demand that the internal pressure of oscillators, which is then equal to $\frac{1}{2} \gamma Nk_B \Theta_0$, cancels out the pressure arising from the anharmonic, linear term, i.e. $-NA$.

Then the system is in equilibrium without any external force. The condition for this demand leads to the specific choice for the anharmonic constant $A$, namely:

$$A = 3\gamma A_0$$ \hspace{1cm} (27)

where

$$A_0 = \frac{h\omega_0}{k_B}. \hspace{1cm} (28)$$

The energy constant $A_0$ presents a convenient unit for introduction of the dimensionless external pressure $\pi$ defined by:

$$\pi = \frac{V_0}{NA_0} p$$ \hspace{1cm} (29)

and the dimensionless temperature $\tau$:

$$\tau = \frac{k_B T}{A_0}. \hspace{1cm} (30)$$

With the above quantities, and equations (27) and (28), the equation of state (24) takes the simple form:

$$\pi + 3\gamma + \frac{B}{A_0} \varepsilon - \frac{C}{2A_0} \varepsilon^2 + \frac{1}{3!} \frac{D}{A_0^3} \varepsilon^3$$

$$\approx 3\gamma \frac{1}{(1 + \varepsilon)^{\gamma + 1}} \tanh^{-1} \left[ \frac{1}{\tau (1 + \varepsilon)^{\gamma}} \right]. \hspace{1cm} (31)$$

Equation (31), obtained within the approximations assumed in this paper, presents a dimensionless equation of state from which the elastic deformation $\varepsilon(\pi, \tau)$ can be calculated for arbitrary temperature $\tau$ and external pressure $\pi$.

The Gibbs free energy (21) in the dimensionless form can be written as follows:

$$\frac{G(p, T)}{NA_0} = 3\gamma \varepsilon + \frac{B}{2A_0} \varepsilon^2 - \frac{1}{3!} \frac{C}{A_0} \varepsilon^3 + \frac{1}{4!} \frac{D}{A_0^4} \varepsilon^4$$

$$+ \tau [q \ln q + (1 - q) \ln(1 - q)]$$

$$+ 3\gamma \ln \left\{ 2 \sinh \left[ \frac{1}{\tau (1 + \varepsilon)^{\gamma}} \right] \right\} + \pi (1 + \varepsilon), \hspace{1cm} (32)$$

where $\varepsilon = \varepsilon(\pi, \tau)$ is given by (31). It is easy to show that from the formula (32) all thermodynamic properties can be derived self-consistently. For instance, the total entropy fulfils the relationship

$$S = - \left( \frac{\partial G}{\partial T} \right)_p = \frac{k_B}{A_0} \left( \frac{\partial G}{\partial \tau} \right)_{\pi} \hspace{1cm} (33)$$
and, with the use of (31), it can be obtained in the dimensionless form:

\[
\frac{S}{Nk_B} = -q \ln q - (1 - q) \ln(1 - q) + \frac{3}{\tau(1 + \epsilon)^\gamma} \tan^{-1} \left( \frac{1}{\tau(1 + \epsilon)^\gamma} \right) - 3 \ln \left( 2 \sinh \left( \frac{1}{\tau(1 + \epsilon)^\gamma} \right) \right) .
\]  

(34)

On the other hand, the volume of the sample satisfies the equation

\[
V = \left( \frac{\partial G}{\partial p} \right)_T = \frac{V_0}{N_A} \left( \frac{\partial G}{\partial \pi} \right)_\tau ,
\]  

(35)

which again leads to the equation of state (31). Other thermodynamic properties follow from the second derivatives of the Gibbs energy. For instance, the heat capacity at constant \( p \) is given by

\[
C_p = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_p = -k_B \left( \frac{\partial A}{\partial T} \right)_p ,
\]  

(36)

whereas the heat capacity at constant \( V \) can be calculated from the relationship

\[
C_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{k_B}{A_0} \left( \frac{\partial U}{\partial \tau} \right)_\pi .
\]  

(37)

On the other hand, the internal energy, \( U \), can be written in the dimensionless form:

\[
\frac{U}{N_A} = 3 \gamma \epsilon + \frac{1}{2} B / A_0 \epsilon^2 - \frac{1}{3} C / A_0 \epsilon^3 + \frac{1}{4} D / A_0 \epsilon^4 + \frac{3}{(1 + \epsilon)^\gamma} \tan^{-1} \left( \frac{1}{\tau(1 + \epsilon)^\gamma} \right) .
\]  

(38)

Application of (38) in (37) leads to the dimensionless expression for \( C_V \):

\[
\frac{C_V}{Nk_B} = 3 \left( \frac{1}{\tau(1 + \epsilon)^\gamma} \right)^2 \sinh^{-2} \left( \frac{1}{\tau(1 + \epsilon)^\gamma} \right) .
\]  

(39)

It should be noted that for the particular case, when \( \epsilon = 0 \), equation (39) is equivalent to formula (15). However, in general, a non-zero \( \epsilon \) should be determined from the equation of state (31).

Among other response functions which can be calculated either from the Gibbs free energy or from the equation of state is, for example, the thermal expansion coefficient

\[
\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{k_B}{A_0} \frac{1}{1 + \epsilon} \left( \frac{\partial \epsilon}{\partial \tau} \right)_\pi ,
\]  

(40)

and the isothermal compressibility

\[
\kappa_T = -\frac{1}{V} \left( \frac{\partial p}{\partial V} \right)_T = -\frac{V_0}{N_A} \frac{1}{1 + \epsilon} \left( \frac{\partial \epsilon}{\partial \pi} \right)_\tau .
\]  

(41)

In particular, for \( p = 0 \) and \( T = 0 \), i.e. in the ground state, these response functions can be obtained from the approximate equation of state (26). For this purpose, equation (26) can be rewritten in the form

\[
\epsilon \approx -\frac{V_0}{N_A} \frac{1}{3\gamma(\gamma + 1) + B/A_0} .
\]  

(42)

It can be observed that equation (42) for \( p < 0 \) presents Hooke’s law at \( T = 0 \). Further, we can formally make use of the linear expansion of volume, namely

\[
V(p, T) \approx V_0 + \left( \frac{\partial V}{\partial \pi} \right)_\tau T + \left( \frac{\partial V}{\partial p} \right)_\tau p .
\]  

(43)

It can be noticed that equation (43) can equivalently be written as:

\[
\epsilon \approx \alpha_0 T - \kappa_0 p
\]  

(44)

where \( \alpha_0 \) and \( \kappa_0 \) are the response functions (40) and (41), respectively, and these functions are taken in the ground state. Now, by comparison of equations (42) and (44), we obtain the result

\[
\alpha_0 \equiv \frac{1}{V_0} \left( \frac{\partial V}{\partial T} \right)_\tau = 0
\]  

(45)

and

\[
\kappa_0 \equiv -\frac{1}{V_0} \left( \frac{\partial V}{\partial p} \right)_\tau = \frac{V_0}{N_A} \frac{1}{3\gamma(\gamma + 1) + B/A_0} .
\]  

(46)

It is apparent that both the elastic coefficients, \( A(=3\gamma A_0) \) and \( B \), are important for the determination of isothermal compressibility at \( T = 0 \). Since \( B \gg A_0 \), where \( A_0 \) is the zero-point energy of Einstein oscillators, it is obvious that for this compressibility an elastic energy plays a dominant role. Finally, let us note that the equation of state derived by Vinet et al [21] for \( T = 0 \) reduces for small \( p \) to the form:

\[
\epsilon \approx (1/B_0)p ,
\]  

which agrees with our equation (42) in the limit \( A_0 \rightarrow 0 \).

2.5. A note on the Grüneisen equation

The Grüneisen parameter \( \gamma \) is introduced by the definition [2, 3]

\[
\gamma \equiv \frac{\partial \ln V}{\partial \ln \omega} = -\frac{V}{\omega} \frac{d \omega}{dV} ,
\]  

(47)

which is equivalent to our relation (16). Typical experimental values of the Grüneisen parameter are in the range \( 1 \leq \gamma \leq 3 \) [3]. Some particular definitions of that parameter, depending on the model, have been discussed in [35]. The experimental determination of \( \gamma \) is connected with the so-called Grüneisen equation:

\[
\frac{\alpha_p}{\kappa_T} = \gamma \frac{C_V}{V} ,
\]  

(48)

which has been tested extensively, especially in the low-temperature region. It is worth noticing that the derivation of (48) can be based on the exact thermodynamic identity

\[
\frac{\alpha_p}{\kappa_T} = \left( \frac{\partial \pi}{\partial T} \right)_V .
\]  

(49)

In the case in hand, in order to calculate \( (\partial p/\partial V)_V \), the equation of state \( p = p(T, V) \) should be taken in the form
of (24). It can easily be checked that after the calculation of the derivative in (49), equation (48) is satisfied. It should also be noted that the calculations of all quantities in (48) using the present method require prior solution of the equation of state (31). In particular, for the low-temperature region, where \(C_v\) tends to zero according to the third law of thermodynamics, we obtain from equation (48) that \(\alpha_p \to 0\). This limit is in agreement with the previous result (45).

3. Numerical results and discussion

3.1. Exemplary calculations for the model

In order to perform the numerical calculations, based on the formulae from section 2, it is necessary to estimate the energy constants, of which \(A_0\) and \(B\) are the most important. The volume elastic modulus in the ground state, \(10^{-19}\)–\(10^{-18}\) J. In turn, the coefficient \(A_0\) is given by equation (28), where \(\Theta_0\) is the Einstein temperature. Assuming that \(\Theta_0\) is typically of the order \(10^{-21}\)–\(10^{-20}\) J. Thus, the \(A\) constant (\(A = 3\gamma A_0\)) is about two orders smaller than the elastic bulk modulus \(B\), and the linear anharmonic term in the Hamiltonian (2) can be considered as a small correction to the harmonic one. This confirms the fact that such quantities as the thermal expansion coefficient \(\alpha_p\) (equation (40)) or the isothermal compressibility \(k_T\) (equation (41)) are mainly determined by the \(B\) constant, not by \(A_0\). The above estimations of \(A\) and \(B\) constants, together with the assumed \(C = D = 0\), yield from equation (40) \(\alpha_p \sim (10^{-6} - 10^{-8}) K^{-1}\) for temperatures near the Einstein temperature, which is a physically reasonable order of value. In the same token assuming a realistic amount of volume per atom, i.e. \(V_0/N \sim 10^{-29} - 10^{-28} m^3\), we obtain on the basis of equation (41) \(k_T \sim 10^{-11} - 10^{-10} Pa^{-1}\), which is also a correct order for the isothermal compressibility.

Although the anharmonic elastic energy \(\propto A\) is a small correction in comparison to the harmonic one, it can be of the same order of magnitude as the vibrational energy resulting from Einstein oscillators. Therefore, this anharmonic term is vital in balancing the expanding pressure resulting from oscillators in the case when the frequency is volume dependent (17). The expanding pressure arises owing to the decrease of the energy (frequency) of oscillators when they experience collective excitations in increasing volume. The total equilibrium of the system requires balancing of the internal (stretching) forces resulting from expanding quantum oscillators, internal compressive forces of the elastic medium and the external pressure \(p\). The resulting deformation \(\varepsilon\) is temperature and pressure dependent and can be calculated from the equation of state (31). The other energy constants, \(C\) and \(D\), play merely a correcting role in modelling the static potential, and are important for high temperatures where the elastic deformation \(\varepsilon\) is significant. The exemplary numerical results, presented in this section in figures 1–8, are obtained for the following set of parameters: \(B/A_0 = 10^2\), \(D = 0\) and \(q = 0.74\).

In figure 1 we present the dependence of \(\varepsilon\) upon \(\pi\) for different reduced temperatures \(\tau = 0\), 0.5 and 1, as well as for two selected Grüneisen parameters: \(\gamma = 1\) and 2. The
Figure 4. The dimensionless isothermal compressibility coefficient \( \frac{N_0}{A_0} \kappa_T = -\frac{1}{V_0} \left( \frac{\partial V_0}{\partial \pi} \right)_T \) versus dimensionless temperature \( \tau \). The parameters are the same as in figure 3.

Figure 5. The dependence of Gibbs free energy per lattice site in \( A_0 \) units upon dimensionless temperature \( \tau \). Three values of the dimensionless pressure, \( \pi = 0, 0.5 \) and 1, are assumed. The Grüneisen parameter is \( \gamma = 2 \) and the elastic energy parameters are \( B/A_0 = 100, C/A_0 = D/A_0 = 0 \).

Figure 6. Dependence of entropy per lattice site in Boltzmann constant units upon dimensionless temperature \( \tau \). The dashed and solid lines correspond to \( \gamma = 1 \) and \( \gamma = 2 \), respectively, whereas \( B/A_0 = 100, C/A_0 = D/A_0 = 0 \) and \( \pi = 0 \). The dashed-dotted line is plotted under constraint \( \varepsilon = 0 \), i.e. for the ideal Einstein model.

Figure 7. Entropy for the dimensionless pressure \( \pi (\pi = 0, 0.5 \) and 1) normalized to the entropy for \( \pi = 0 \) versus dimensionless temperature \( \tau \). The dashed and solid lines correspond to \( \gamma = 1 \) and \( \gamma = 2 \), respectively. The elastic energy parameters are the same as in figure 6.

Figure 8. Specific heat \( C_V \) at constant \( V \) per lattice site in \( k_B \) units versus dimensionless temperature \( \tau \). The elastic energy parameters are the same as in figures 6 and 7. In the main plot the parameters \( \pi = 0 \) and \( \gamma = 2 \) are assumed. In the inset the difference \( C_V(\pi) - C_V(\varepsilon = 0) \) is plotted for \( \pi = 0 \) and 1, as well as for \( \gamma = 1 \) (dashed line) and \( \gamma = 2 \) (solid line).

calculations are based on the equation of state (31) for \( C/A_0 = D/A_0 = 0 \). It is seen that these dependences are almost linear in character, and the slopes of the curves correspond to the isothermal compressibility. It can be deduced from figure 1 that the isothermal compressibility coefficient should be weakly dependent on pressure in a wide range of temperatures. This observation is in accordance with the analogous assumption in the Murnaghan theory of the equation of state [18]. At higher temperatures (for \( \tau = 1 \)) the Grüneisen parameter has a remarkable influence on the magnitude of elastic deformation, leading to the increase of \( \varepsilon \) when \( \gamma \) increases.

In figure 2 the dependence of \( \varepsilon \) upon \( \tau \) for various external pressures (\( \pi = 0, 0.5 \) and 1) is presented. The rest of the parameters are the same as in figure 1. In this case the dependences are not linear and their local slopes are attributed to the thermal expansion coefficient. It is remarkable that by increasing the Grüneisen parameter \( \gamma \) the relative deformation \( \varepsilon \) increases, which is evidently pronounced at high temperatures. Such behaviour is in agreement with the previous figure (figure 1). The dependence presented in this figure is qualitatively similar to the dependence of the lattice constant on temperature, as can be seen in the [36] for the case of AlN. The effect of external pressure on the temperature dependence of relative deformation in figure 2 resembles, for example, the results obtained in [26].
In figure 3 the dimensionless thermal expansion coefficient (see equation (40)) is plotted versus temperature \(\tau\) for external pressure \(\pi = 0\) and Grüneisen parameter \(\gamma = 2\). Different curves correspond to various \(C/A_0\) parameters. It is seen that \(C/A_0\) has influence mainly at high temperatures, where it causes an increase of the thermal expansion coefficient. Let us note, on the basis of equations (28) and (30), that \(\tau = 2\) corresponds to the Einstein temperature. In the low-temperature region the thermal expansion coefficient tends to zero independently on \(C/A_0\), which is in agreement with the Grüneisen equation (48). A qualitatively similar behaviour for the thermal expansivity has been found in [12] for the case of MnO, in [18] for Ti, Al, NaCl and Na, or in [36] for AlN. The conclusion that the anharmonic term becomes important only in the high-temperature region is in agreement with the free energy calculations from first principles [28]. A similar conclusion can be drawn from [37] where the influence of intrinsic anharmonicity on the thermodynamic functions has been studied.

The dimensionless isothermal compressibility (see equation (41)) is plotted in figure 4 versus \(\tau\) for the external pressure \(\pi = 0\) and Grüneisen parameter \(\gamma = 2\). As in figure 3, different curves correspond to various \(C/A_0\) parameters. A remarkable influence of \(C/A_0\) values on the compressibility is seen for the temperatures \(\tau > 1/2\). On the other hand, for \(\tau \to 0\) the compressibility tends to some non-zero value, \(\kappa_0\), being in agreement with equation (46). Qualitatively similar experimental results have been obtained for Pb and NaCl [18]. The dependence of isothermal compressibility on temperature corresponds to the fact that the elastic constants are temperature dependent (the exemplary studies can be found in [32, 38]).

In figure 5 the Gibbs free energy per atom is presented in \(A_0\) units versus reduced temperature \(\tau\). The three curves in figure 5 correspond to different external pressures, \(\pi = 0\), 0.5 and 1, and are plotted by the solid, dashed and dashed-dotted lines, respectively. In this case \(C/A_0 = 0\) and \(\gamma = 2\). We see that application of external pressure causes an increase in the Gibbs energy. It is demonstrated in figure 5 that the Gibbs energy is a concave function of temperature with a monotonous decrease versus \(\tau\). Such behaviour indicates a thermodynamically stable solution when the entropy (defined by equation (33)) is positive. Let us note that the initial slope of the Gibbs energy, at \(\tau \to 0\), corresponds to the residual entropy.

The entropy is illustrated in figures 6 and 7 as a function of temperature \(\tau\). In both figures \(C/A_0 = 0\). In figure 6 we plotted entropy per lattice site in the Boltzmann constant units, for external pressure \(\pi = 0\). The solid and dashed curves, which are for \(\gamma = 1\) and \(\gamma = 2\), respectively, correspond to our model, where \(\pi\) is a function of temperature and is calculated from the equation of state (31). Due to our choice of integration constant \((c = 0\) in equation (7)) we see that the residual (configurational) entropy is present, which does not depend on the Grüneisen parameter \(\gamma\). Moreover, one can notice that for \(T \to 0\) the entropy change versus temperature tends to zero \((\Delta S \to 0)\), which is in accordance with the third law of thermodynamics. On the other hand, the increase of \(\gamma\) causes some small increase of entropy at high temperatures. For comparison, the dashed-dotted curve presents the entropy for the pure Einstein model, where \(\pi\) is put equal to zero for all temperatures. As stated before, the condition \(\pi = 0\) is equivalent to the assumption that the frequency of oscillators is kept constant and does not depend on volume. For the pure Einstein model there is no residual entropy in the ground state, since the configurational ordering of atoms is not taken into account.

It turned out that the entropy is very weakly sensitive to the external pressure, and in figure 7 we want to study this property in more detail. The relative changes of the entropy \(S(\pi)/S(\pi = 0)\) are plotted versus \(\tau\) for \(\pi = 0.5\) and 1. The dashed and solid lines are for \(\gamma = 1\) and \(\gamma = 2\), respectively. We note that the sensitivity of \(S\) on \(\pi\) is greater for higher Grüneisen parameters \(\gamma\). It is also seen that the influence of high external pressure on the ratio \(S(\pi)/S(\pi = 0)\) is most remarkable for some intermediate temperatures \((\tau \approx 0.6)\), whereas for \(\tau \to 0\) the influence of \(\pi\) becomes negligible. Again, the behaviour of \(S\) near \(T = 0\) is in agreement with the third law of thermodynamics. The lowering of entropy for \(T > 0\), when the external pressure is applied, corresponds to the positive thermal expansion coefficient, in accordance with the Maxwell relation \((\partial S/\partial V)_{\pi} = -(\partial V/\partial T)_{\pi}\).

The specific heat per lattice site in Boltzmann constant units and at constant volume is plotted versus temperature \(\tau\) in figure 8. The anharmonic parameters are \(C/A_0 = D/A_0 = 0\). The main plot has been obtained for \(\pi = 0\) and \(\gamma = 2\). We note that the value of \(\tau = 2\) corresponds to the Einstein temperature. The low-temperature behaviour of the specific heat is typical for the Einstein oscillators, being in agreement with the third law of thermodynamics. On the other hand, the high-temperature part of the curve is classical. In order to see the difference between the present model and the classical Einstein result in more detail, in the inset we plot this difference for \(\pi = 0\) and 1, as well as for two Grüneisen parameters \(\gamma = 1\) (dashed line) and \(\gamma = 2\) (solid). \(C_V(\pi)\) corresponds to the specific heat of the present model, whereas \(C_V(\pi = 0)\) is the Einstein result, when \(\omega\) does not depend on \(V\). It is worth noticing that for \(\pi = 0\) some small increase in the specific heat occurs for temperatures \(T > 0\). Similar to the entropy, the specific heat is only weakly sensitive to the external pressure \(\pi\). In particular, one can see that a pressure of \(\pi = 1\) causes a small decrease in \(C_V\) at some restricted range of low temperatures. When the Grüneisen parameter increases all the above changes become enhanced.

### 3.2. A comparison with experimental data for solid argon

For solid argon, which forms a FCC structure below the melting temperature of 84 K, the Debye temperature is \(\Theta_D = 85\) K. From the approximate formula \(\Theta_D = (2\pi/\beta^3)\), which can be derived on the basis of [2], the Einstein temperature, \(\Theta_E = 68.51\) K, can be estimated. Hence, on the basis of equation (28) we find that the \(A_0\) constant amounts to \(A_0 = 0.04729 \times 10^{-20}\) J. On the other hand, the isothermal compressibility at zero temperature, \(\kappa_0\), can be found from the experiment [39], and for polycrystalline samples it amounts to
Figure 9. Elastic deformation $\varepsilon$ versus absolute temperature $T$ for solid argon. Solid line, our calculation; dashed line, smoothed experimental data after [40]; open symbols, experimental data after [39].

Figure 10. Isothermal compressibility coefficient $\kappa_T$ versus absolute temperature $T$ for solid argon. Solid line, our calculation; open symbols, experimental data after [39].

Figure 11. Volume thermal expansion coefficient $\alpha_p$ at constant pressure $p = 0$ versus absolute temperature $T$ for solid argon. Solid line, our calculation; dashed line, smoothed experimental data after [40]; open symbols, experimental data after [39]; filled symbols, experimental data after [42].

$\kappa_0 = 4.1 \times 10^{-10}$ Pa$^{-1}$. The volume per atom can be estimated as $V_0/N = 36.383 \times 10^{-30}$ m$^3$. The Gr"uneisen parameter can be taken as a mean value of the experimental data from various temperature ranges [39], which yields $\gamma = 2.5$. Having obtained the data given above, on the basis of equation (46) the ratio $B/A_0$ can be estimated, yielding $B/A_0 = 160$. The other elastic energy constants, which are of higher order, i.e. $C$ and $D$, can be treated as the theoretical fitting parameters. We found that the optimal fit to the experimental data (taken from table III, p. 561 of [39]) is obtained for $C/A_0 = 1250$ and $D/A_0 = 5000$, valid for $\varepsilon > 0$. Taking into account the above set of parameters, we have calculated $\varepsilon$, $\kappa_T$, $\alpha_p$, and $C_T$ for solid argon in the full temperature range $0$ K $< T < 84$ K. To complete the comparison, we supplemented the results with two example isotherms. Since the isotherms cover the range of both positive and negative deformation $\varepsilon$, we decided to allow some asymmetry in our model elastic potential. Thus, for $\varepsilon < 0$ we adopted the anharmonic parameter value of $C/A_0 = 3000$, i.e. the potential is steeper in this range. The results are presented in figures 9–13 by the solid lines, whereas the experimental data [39] are shown by the open symbols. In addition, the figures have been supplemented with the smoothed experimental data from [40–42].

Figure 12. Molar specific heat $C_V$ at constant $V$ versus absolute temperature $T$ for solid argon. Solid line, our calculation; dashed line, smoothed experimental data after [40]; open symbols, experimental data after [39]. The dashed-dotted line correspond to the calculation with constraint $\varepsilon = 0$, i.e. for the pure Einstein model.

Figure 13. Isotherms for solid argon (dependence of elastic deformation on external pressure) for two selected temperatures. Solid lines, our calculation; dashed lines, smoothed experimental data after [41].
In figure 9 the calculation of elastic deformation $\varepsilon$ versus absolute temperature $T$ is presented. The derivative of elastic deformation over the pressure, i.e. the isothermal compressibility coefficient $\kappa_T$, is plotted versus $T$ in figure 10. It can be noted that in both figures 9 and 10 the experimental dependences are nonlinear, in agreement with the present theory. In turn, the thermal expansion coefficient, $\alpha_0$, at constant pressure ($p = 0$) is plotted in figure 11 for the same temperature range as in figures 9 and 10. Finally, the molar specific heat $C_V$ at constant $V$ is presented in figure 12. For comparison, in figure 12 the dashed line is plotted for the pure Einstein model when we impose the constraint $\varepsilon = 0$.

Our calculated isothermal compressibility, $\kappa_T$, can be related to the adiabatic compressibility, $\kappa_S$, via the formula

$$\kappa_T = \kappa_S (1 + \alpha_p \gamma T).$$

(50)

It can be checked that the above formula is equivalent to the Grüneisen equation (48) which is also satisfied in our case. As pointed out in [39], the values of $\kappa_S$ and $\kappa_T$ can be measured independently; $\kappa_T$ by the ultrasonic method from isentropic sound velocity and $\kappa_T$ by the piston-displacement method of Bridgman. Using the formula (50) a satisfactory agreement between those two measurements was obtained in [39]. Such consistency directly transfers to our calculations; therefore in figure 10 only the $\kappa_T$ curve has been presented.

Regarding the isothermal compressibility $\kappa_0$ (at $p = 0$, $T = 0$) we adopted here the value $\kappa_0 = 4.1 \times 10^{-10}$ Pa$^{-1}$ for polycrystalline samples after [39]. On this basis the classical (atomic volume) bulk modulus, $B'$, can be estimated at $T = 0$ K: $B' = 1/\kappa_0 = 0.244 \times 10^{10}$ N m$^{-2}$. On the other hand, for single cubic crystals the bulk modulus can be obtained from the formula [2] $B' = (C_{11} + 2C_{12})/3$, if the elastic constants $C_{11}$ and $C_{12}$ are known. These constants for argon single crystals have been deduced from the measured isentropic sound velocity [43]. The values extrapolated to $T = 0$ K are: $C_{11} = 4.39$ and $C_{12} = 1.83$ in units of $10^8$ N m$^{-2}$. Hence, the bulk modulus $B'$ obtained on this basis is $B' = 0.268 \times 10^{10}$ N m$^{-2}$. It can be concluded that this value of $B'$ for single crystals is about 10% larger than for polycrystalline samples given in [39].

In figure 13 two selected isotherms are shown (the low- and high-temperature ones), presenting elastic deformation $\varepsilon$ as a function of external pressure $p$. It is visible that using a model asymmetric potential, a good fit to experimental data in the whole pressure range studied is obtained, both for high- and low-temperature results. This emphasizes the pronounced importance of the exact form of the static lattice potential for pressure studies, since the deformations here exceed 10%. The selected potential provides a reliable description for pressures up to 10 kbar. In light of the assumption that our static elastic potential originates from the expansion at the point $T = 0$ and $p = 0$, further adjusting the potential would improve the consistency between calculations and experimental data for higher pressures.

It can be concluded, on the basis of figures 9–13, that the agreement between calculated curves and the experimental data is quite satisfactory. One should take into account that all these curves have been calculated self-consistently for the same set of parameters, as described above in this subsection. It can be supposed that the fitting could be even better if we would allow the Grüneisen parameter to vary with temperature and pressure, as has been suggested from the experimental measurements [39, 44]. As far as the specific heat is concerned, the new result (solid line) differs only insignificantly from the Einstein result (dashed), and the difference is mainly noteworthy at high temperatures. However, it should be noted that the dashed line in figure 12 is the only result of the pure Einstein model which can be compared with all these experimental data. The full description of the temperature dependences of remaining quantities, such as $\varepsilon$, $\kappa_T$ and $\alpha_p$, has been possible in the improved approach to the Einstein model, when the equation of state (31) is taken into account.

3.3. Final remarks

In the present paper a simple combination of the Einstein and elastic models of the solid state is presented. First of all, the dependence of the frequency of quantum oscillators on the volume has been introduced in a simplified way via the Grüneisen assumption. Simultaneously, the elastic properties of the crystal have been taken into account via a classical Hamiltonian, containing anharmonic terms.

The idea that the free energy is a sum of several components has been presented, for instance, in the book by Wallace [22]. However, we have shown that exploitation of this idea led us to a new form of the equation of state (31). Contrary to the Birch–Murnaghan equation of state, which presents only an isothermal description [22], in our equation the temperature $T$ plays a role equivalent to the rest of the variables, i.e. $p$ and $V$. In particular, the thermal expansion coefficient and the isothermal compressibility have simultaneously been derived from this new equation of state. It is well known that these quantities could not be inferred from the sole Einstein model. On the other hand, our equation of state also includes the pressure resulting from expanding quantum oscillators. Moreover, comparing our method with the papers based on the Wallace approach, one should notice that one of our anharmonic parameters in the static potential, namely $A$, is not independent but has been related to the Einstein temperature (via equations (29) and (30)). As we pointed out, such a relationship ensures that the equilibrium condition for the total free energy at $p = 0$ and $T = 0$ is satisfied and the system of quantum oscillators becomes stable. When this point is not discussed, the functional form of the static lattice energy can also be adopted in the form given in [30] (after Vinet et al). That form is much more complicated than our polynomial approach; nevertheless it has successfully been applied for very high pressures.

The present method requires several constant parameters, such as the Einstein temperature and isothermal compressibility (or the volume elastic modulus) at the absolute zero temperature, as well as the Grüneisen parameter, which should be taken from experiment.

The region of applicability of the model (its temperature and pressure range of validity) is mainly connected with the number of terms which are taken into account in the
polynomial form of the elastic Hamiltonian (2). This form is based on the assumption that the equilibrium central point is $\varepsilon = 0$ for $T = 0$ and $p = 0$. Thus, the theory is most applicable for expansion around this equilibrium. However, as we have seen on the example of solid argon, merely the density of states function requires a separate Grüneisen parameter, which makes the method much more complicated. The free energy should also be included [30]. However, such a description of the system in a relatively wide range of external pressures, involving also the Poisson coefficient. The approach for anisotropic deformations and anisotropic elastic deformation. However, it seems possible to generalize the quasistatic processes. Therefore, shock-wave experiments cannot be described within this model.

It should be noted that the method is relatively simple, gives an analytical form of the equation of state, and can therefore serve as a first approximation for more advanced approaches. For instance, in the prototype calculations we have used only a single variable $\varepsilon$ for description of the volume elastic deformation. However, it seems possible to generalize the approach for anisotropic deformations and anisotropic external pressures, involving also the Poisson coefficient. The presented method can be potentially extended based on the Debye approximation, in which the linear dispersion relation for collective excitations together with the proper density of states are taken into consideration. For instance, in [30] the vibrational free energy has been taken into account in the high-temperature Debye model. In that approach each moment of the density of states function requires a separate Grüneisen parameter, which makes the method much more complicated. On the other hand, for metallic systems the electronic part of the free energy should also be included [30]. However, such extensions of the method need further studies and should be a subject of separate assignment.

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