THERMAL EXPANSION OF SOLIDS BASED ON AN ANHARMONIC OSCILLATOR APPROACH

A.I. HASHIMOVA
Sumgait State University, Sumgait, Azerbaijan
hasimovaaynur@gmail.com

The article explains the thermal expansion of solids using a harmonic oscillator model. It assumes atoms oscillate around equilibrium points in a crystal lattice. If oscillations were purely harmonic, thermal expansion would not occur; expansion arises from anharmonicity. Anharmonicity introduces an additional term in the potential energy expression, leading to a non-zero thermal expansion coefficient. The theoretical results agree with experimental data, such as the temperature dependence of copper's thermal expansion coefficient. At high temperatures, the thermal expansion coefficient becomes nearly constant. At low temperatures, it follows a T^3 dependence and approaches zero as temperature approaches absolute zero. Factors affecting thermal expansion differ between metals and semiconductors; in metals, the electron gas plays a significant role. In semiconductors, impurities, defects, and changes in the band gap also influence the expansion coefficient. The Debye temperature can be estimated from experimental values of the thermal expansion coefficient.

Keywords: Thermal expansion, solids, harmonic oscillator model, anharmonicity, potential energy
DOI:10.70784/azip.1.2026111

1. INTRODUCTION

One of the main thermodynamic properties of solids is their thermal expansion. Thermal expansion can occur under adiabatic or isothermal conditions. Thermal expansion plays a significant role in defining the physical behavior of materials under different thermal conditions and is essential for both fundamental research and practical applications.

Thermal expansion can occur under two primary thermodynamic conditions: isothermal and adiabatic. Under isothermal conditions, the material exchanges heat with the environment, and the temperature remains constant during expansion or contraction. In this case, thermal equilibrium with the surroundings is quickly restored, and the process proceeds with heat transfer.

In contrast, under adiabatic conditions, there is no heat exchange between the system and its surroundings. As a result, the expansion or contraction occurs so rapidly that the material's internal energy changes, leading to a change in temperature. This distinction is critical when studying the response of solids to thermal stimuli over different time scales and environments.

Understanding thermal expansion is crucial for predicting the behavior of materials in various fields, including electronics, construction, and energy systems, where temperature fluctuations can significantly impact performance and reliability [1].

To understand how thermal expansion occurs, let us consider a simple model. Assume that the atoms located at the lattice points of a crystalline structure perform harmonic oscillations. In this case, the restoring force of the oscillations is taken as an elastic force, and its magnitude is expressed as follows:

$$\bar{f} = -kx \tag{1}$$

Under these conditions, the potential energy of the par ticle undergoing displacement takes the following form.

$$U = \frac{k\bar{x}}{2} \tag{2}$$

In these formulas, x represents the displacement, while k stands for the spring stiffness coefficient.

2. EXPERIMENTAL SETUP

A plot of potential energy versus displacement, derived from equation (2), yields the graph shown in Figure 1.

In the figure, particles 1 and 2 are located at a distance $\boldsymbol{r_0}$, which corresponds to the minimum value of the potential energy $\boldsymbol{U(r)}$ at absolute zero temperature**.** This distance r_0 represents the interatomic spacing in the crystalline structure of the solid in its initial state.

As the temperature increases, each particle begins to oscillate around its equilibrium position. The equilibrium state between the particles is established when the repulsive force acting between them is equal in magnitude and opposite in direction to the attractive force. Let us assume that particle 1 is fixed. In this case, when the kinetic energy E_k of particle 2 reaches its maximum, the particle will pass through the equilibrium position, and at that point, it will be located above the potential well. Let us first consider the particle moving to the right.
As it moves to the left, its kinetic energy gradually transforms into potential energy due to the increasing repulsive force. The displacement to the left will continue until the kinetic energy is completely converted into potential energy. As a result, the condition $U(x) = E_k$ will be satisfied. The total potential energy in this case will be equal to $-[U_0 - U(x)]$ [2] .

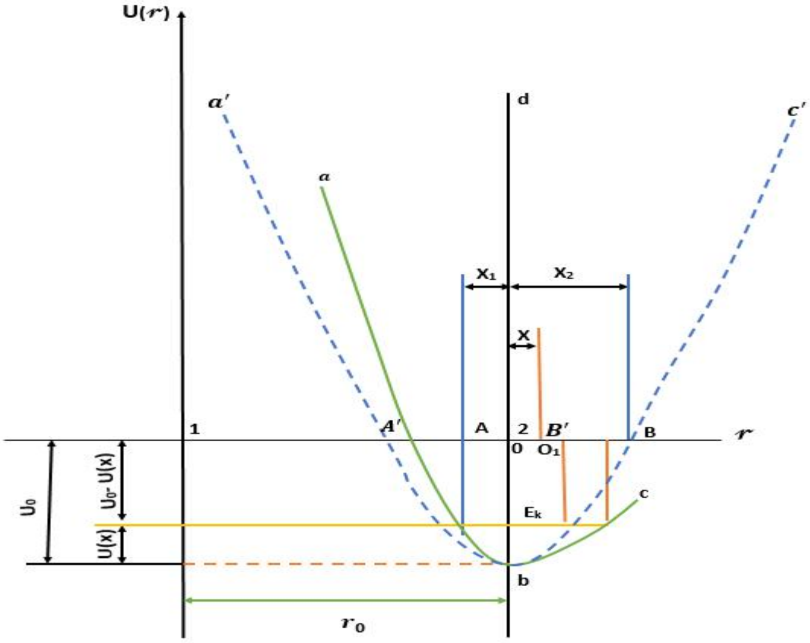

Fig 1. Distance dependence of the interatomic interaction potential energy

Thus, the second particle is displaced by a distance X_1 toward the left boundary position. After that, the second particle moves in the opposite direction, displacing by a distance X_2 from the right boundary position, and the change in potential energy remains − $[U_0 – U(x)]$. If this motion were considered as harmonic oscillation, then the displacements in both directions from the equilibrium position would be equal. Consequently, no thermal expansion would occur during the heating of the body. In this case, the increase in temperature would only cause the amplitude of the oscillation to increase, while the distances between the particles would remain unchanged. This situation is illustrated by the broken line connecting points d, b, and c' in the figure, forming a parabolic curve.

3. SYNTHESIS PROCESS AND OBTAINING THE SAMPLE

In reality, the oscillations proceed in a completely different manner and the dependence is represented by the solid line (a, b, c) in the figure. As can be seen, this line is asymmetric with respect to the bd line. The branch ba of the curve is steeper and rises more sharply compared to the bc branch. This indicates the anharmonic nature of the particle's oscillations. As a result, an additional term related to this anharmonicity appears in the expression for the potential energy, and the formula is written as follows [3]:

$$U(x) = \frac{\beta x^2}{2} - \frac{gx^3}{3} \tag{3}$$

$$F(x) = -\frac{\partial U}{\partial x} = -\beta x + gx^2 \tag{4}$$

If we take the average values for displacement x and force f(x) in expression (4) to find the value of the coefficient of thermal expansion, the expression will be as follows:

$$\overline{f}(x) = \overline{-\beta x} + \overline{gx^2} \tag{5}$$

If we take $\overline{f}(x)=0$ for free vibration, we can write:

$$\overline{x} = \frac{g\overline{x^2}}{\beta} \tag{6}$$

In this case, neglecting the $\frac{gx^3}{3}$ term in the expression for potential energy, we can write the following value for x^2:

$$x^2 = \frac{2U\overline{\omega}}{\beta} \tag{7}$$

If this value is substituted into expression (6) in place of $\overline{x^2}$, the following formula is obtained:

$$\overline{x} = \frac{2g\overline{U(x)}}{\beta^2} \tag{8}$$

It is well known that an oscillating particle possesses both potential and kinetic energy. Thus, we can write the average potential energy as equal to the kinetic energy, $\overline{U(x)}=\overline{E_k}$. Consequently, the total energy can be expressed accordingly.

$$E = \overline{E_k} + \overline{U(x)} \tag{9}$$

Thus, we obtain the following formula.

$$\overline{x} = \frac{gE}{\beta^2} \tag{10}$$

If we divide both sides of the equation by r_0 , we obtain:

$$\frac{\bar{x}}{r_0}=\frac{g}{\beta^2 r_0}E \qquad (11)$$

Thus, we obtain the following formula for the coefficient of thermal expansion.

$$\alpha=\frac{1}{r_0}\frac{d\bar{x}}{dT}=\frac{g}{\beta^2 r_0}\frac{dE}{dT}=\chi C_v \qquad (12)$$

$$\chi=\frac{g}{\beta^2 r_0} \qquad (13)$$

C_V – heat capacity per particle.

As it appears, the coefficient of thermal expansion is directly proportional to the specific heat capacity at constant volume. In the literature, the comparison of the experimental values of the temperature dependence of the thermal expansion coefficient and the specific heat capacity for copper has indeed confirmed this theoretical result.

In the high-temperature region, the energy of the vibrational motion of particles reaches approximately kT. In this case, the heat capacity per particle (C_v) becomes approximately K. Thus, the coefficient of thermal expansion is given by:

$$\alpha=\chi C_v=\frac{gk}{\beta^2 r_0} \qquad (14)$$

If the value of E is expressed based on quantum statistics ($\bar{E}=\frac{h\omega}{e^{h\omega/kT}-1}$), the coefficient of thermal expansion will depend on temperature, and as the temperature approaches absolute zero, the coefficient of thermal expansion will also approach zero.

When the new expression obtained for α is substituted with the values of g, k, β, and r_0, a value of 10^{-4} - 10^{-5} 1/K is obtained. This corresponds well with the experimental values. Experiments show that in the high-temperature region, α is practically independent of temperature [4].

Experimental results indicate that, in the high-temperature region, the coefficient of thermal expansion (α) remains practically unaffected by changes in temperature.

It should be noted that the formula determining the relationship between α and C_v for metals was first derived by Grüneisen and is as follows.

$$\alpha=\frac{\gamma\cdot\chi}{3V}C_v \qquad (15)$$

Here, χ is the Grüneisen constant. The value of this constant for metals ranges from 1.5 to 2.5.

In thermodynamics, the value of the coefficient of thermal expansion is calculated using the following formula:

$$\beta=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad (16)$$

Here, β denotes the volumetric expansion coefficient.

Numerous experiments have shown that, similar to the specific heat capacity, the coefficient of thermal expansion also depends on temperature in the low-temperature region.

According to Barron's theory, the temperature dependence of the thermal expansion coefficient in the region where T<<θ (θ is the Debye temperature) is expressed by the following formula:

$$\beta=A\frac{T^3}{v}\frac{d}{dP}\left(\frac{v}{\overline{\overline{U^3}}}\right) \qquad (17)$$

This expression is sometimes also written in the following form:

$$\beta=\frac{C_v}{V_v}\frac{d\bar{v}}{dP} \qquad (18)$$

In expression (17), $\overline{U}$ is the mean speed of sound, A is a constant, C_v is the specific heat capacity at constant volume, and v is the vibration frequency.

At very low temperatures, the thermal expansion coefficient is proportional to T^3, while at high temperatures it approaches a constant value. According to Nernst's theory, as the temperature approaches absolute zero, the expansion coefficient also approaches zero. The temperature dependence of thermal expansion differs between metals and semiconductors: in metals, the electron gas makes a noticeable contribution. This contribution can be determined by measurements near absolute zero and varies linearly with temperature.

In all solids, alongside the general character of the thermal expansion coefficient, its temperature dependence differs significantly between metals and semiconductors. In metals, the electron gas makes a considerable additional contribution to the value of the thermal expansion coefficient. This additional term can be isolated by performing measurements at temperatures close to absolute zero. Calculations show that the electronic part of thermal expansion varies linearly with temperature, being proportional to the first power of temperature.

It has also been shown in the literature that the contribution of the electron gas to the thermal expansion coefficient can be estimated as follows:

$$\beta_{el}=V^{-1}\frac{\partial\Phi}{\partial T\partial P}=\frac{\partial\rho}{\partial P}T \qquad (19)$$

Here, Φ denotes the thermodynamic potential, V is the volume, and ρ is the density of electrons at the Fermi level.

In semiconductors, the value of the thermal expansion coefficient is also influenced by dopants, defects, and changes in the magnitude of the chemical bonding forces.

Several studies have shown that in semiconductors, the temperature dependence of the band gap width arises both due to the thermal expansion coefficient and as a result of lattice vibrations. This relationship can be expressed as follows:

$$\frac{\partial E_g}{\partial T}=\left(\frac{\partial E_g}{\partial T}\right)_0+\left(\frac{\partial E_g}{\partial T}\right)_V \qquad (20)$$

$$\left(\frac{\partial E_g}{\partial T}\right)_0 = -\frac{3\alpha}{\chi}\cdot\frac{\partial E_g}{\partial P} \qquad (21)$$

In these expressions, $\left(\frac{\partial E_g}{\partial T}\right)_0$ - represents the temperature dependence of the band gap width, while $\left(\frac{\partial E_g}{\partial P}\right)_T$ - characterizes the variation of the band gap width with pressure. Here, α denotes the thermal expansion coefficient, and χ_T is the isothermal compressibility coefficient [5].

Scientific research has also shown that in semiconductors there exists a relationship between the effective mass of charge carriers and the thermal expansion coefficient. Specifically, if the effective mass is determined by the interaction between the energy bands separated by the forbidden gap, then its variation will depend on changes in the band gap width caused by thermal expansion.

Moreover, in crystals with magnetic ordering, an additional contribution to the thermal expansion value arises from the magnetic interaction forces.

$$\alpha=\alpha_{q\text{ə}f}+\alpha_{el}+\alpha_{maq} \qquad (22)$$

In crystals that possess both magnetic ordering and ferroelectric properties, certain anomalies are observed in the temperature dependence of the thermal expansion coefficient. These anomalies are associated with phase transitions.

In anisotropic crystals, due to the dependence of the frequency on pressure changes, the thermal expansion coefficient may also be negative. Thus, it has been theoretically shown that if $\frac{\partial v}{\partial P}>0$, the thermal expansion coefficient is positive, whereas if $\frac{\partial v}{\partial P}<0$, it becomes negative.

For anisotropic materials, the general character of the temperature dependence of the thermal expansion coefficient is similar to that of isotropic materials. However, in such materials, the values of the thermal expansion coefficients along different crystallographic axes can differ significantly [6].

In the existing literature, it has been shown that the temperature dependence of the thermal expansion coefficient is analogous to that of the specific heat capacity. In other words, at temperatures higher than the Debye characteristic temperature, the thermal expansion coefficient α becomes constant, similarly to C_v. Such a dependence indeed corresponds to experimental values for metals that possess a perfect cubic crystalline structure.

It has also been shown that the Debye characteristic temperature can be determined using the experimental values of the thermal expansion coefficient. For this purpose, an empirical formula is provided [7].

$$\theta=\frac{19{,}37}{\left(\bar{A}V^{2/3}\alpha\right)^{1/2}}$$

Here, α is the linear thermal expansion coefficient, $\bar{A}$ is the mean square atomic mass, and V is the atomic volume. In those studies, it was noted that the thermal expansion coefficient is an important parameter for developing theoretical models describing the temperature dependence of thermal properties in complex semiconductors with layered and chain-like crystal structures.

4. CONCLUSION

The conducted theoretical and experimental investigations confirm that thermal expansion is one of the key thermodynamic properties of solids, with significant importance for both fundamental studies and practical applications. Thermal expansion can occur under isothermal or adiabatic conditions, and the distinction between these regimes depends on whether there is an exchange of heat with the environment, which affects changes in the internal energy and temperature of the material.

In crystalline solids, atomic motion is not purely harmonic but anharmonic in nature. This anharmonicity is the primary reason for thermal expansion. As a result, the coefficient of thermal expansion (α) is directly proportional to the specific heat capacity at constant volume (Cv). At high temperatures, Cv becomes nearly constant, leading α to also become nearly temperature-independent. Conversely, in the low-temperature region, the temperature dependence of α follows the T^3 law, and as temperature approaches the Debye temperature, α tends toward zero.

There are notable differences between metals and semiconductors: in metals, the electron gas contributes an additional term to thermal expansion, which varies linearly with temperature at very low temperatures. In semiconductors, α is influenced by dopants, defects, and changes in chemical bonding strength. Moreover, the temperature dependence of the band gap width in semiconductors is closely related to both thermal expansion and lattice vibrations.

In crystals exhibiting magnetic ordering, magnetic interactions add further contributions to the thermal expansion coefficient, resulting in anomalies near phase transitions, especially in ferroelectric and magnetically ordered materials. In anisotropic crystals, the values of α along different crystallographic directions can differ significantly, and the coefficient can even become negative depending on the pressure dependence of vibrational frequencies.

Studies also show that the Debye characteristic temperature can be estimated from experimental α values, providing a useful tool in modeling temperature-dependent thermal properties of complex semiconductors, especially those with layered or chain-like structures.

Overall, the relationship between α, Cv, and other thermodynamic parameters plays a crucial role in understanding the thermal, mechanical, and electronic behavior of solids under various conditions. This understanding is fundamental for predicting material performance and reliability in applications ranging from electronics to energy systems.

[1] *C. Kittel and P. McEuen***.** Introduction to Solid State Physics 8th ed. (Wiley New York 1996) Google Scholar

[2] *D.C. Wallace*, Thermodynamics of Crystals (Wiley, 1972). Google Scholar, Crossref

[3] *J.P. Dismukes* et al., J. Phys. Chem. 68, 3021 (1964).

[4] *N.V. Hung J.J. Rehr.* Anharmonic correlated Einstein-model Debye–Waller factors. Phys Rev B. 997; https://doi.org/10.1103/PhysRevB.56.43.

[5] *J.C. Slater.* Note on Grüneisen's constant for the incompressible metals. Phys Rev. 1940; https://doi.org/10.1103/PhysRev.57.744

[6] *M.M. Kurbanov, D.D. Bayramov, N.S. Sardarova.* Thermal expansion of $TlInX_2$ (x-s, Se,Te)**.** Inorganic Materials, Moscow: -2000, № 2, -p. 183–184.

[7] *G.K. White.* Thermal Expansion at low temperatures. Nature, -1960, v. 187, № 4721, -p.927–929.

Received: 24.12.2025