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RELATIONSHIP BETWEEN HEAT CAPACITY AND THERMAL EXPANSION DERIVED FROM THE LENNARD–JONES POTENTIAL

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Abstract

The relationship between heat capacity (C_p) and linear thermal expansion (α) derived from the Lennard–Jones potential is $C_p=A\alpha(U_0-E)$, where U_0 is the heat of sublimation at T=0, E is the enthalpy and A is the coefficient. The values of A for different solidified inert gases coincide with one another within the limits of experimental error (±2%).

The relationship is shown to be valid for various substances: solidified rare gases, diamond, halite and copper.

Keywords: equation of state, heat capacity, thermal expansion

Introduction

Relationship between thermal expansion and heat capacity derived from thermodynamic consideration (Lewis, 1907) is

$$C_p=C_v+\beta^2K_TTV \tag{1}$$

where β is the volume thermal expansion, K_T is the bulk modulus at constant temperature (T), V is the molar volume, C_p and C_v are the heat capacities at constant pressure and volume, respectively. The values of C_p, β, K_T, T and V are measured in experiment, C_v cannot be measured but only estimated according to a model of a solid.

Another relatinship was suggested by Grueneisen in 1908:

$$C_v=\frac{1}{\gamma}\beta K_TV \tag{2}$$

where γ is the Grueneisen constant.

Considering the relation between the energy of a solid (E) and the mean interatomic distance (R), the relationship between heat capacity and thermal expansion is

$$C_p=\alpha R\frac{dE}{dR} \tag{3}$$

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The equation uses neither C_v nor K_T, but only thermal properties available after measurements. Equation (3) was tested using experimental data on thermodynamic properties of solidified inert gases [1]. The values of $R(\mathrm{d}E/\mathrm{d}R)$ were derived from Lennard–Jones potential

$$U(R)=U_0\left[-2\left(\frac{R_0}{R}\right)^6+\left(\frac{R_0}{R}\right)^{12}\right] \tag{4}$$

The mean interatomic distance was calculated using classical approach

$$R=\frac{\int_{R_1}^{R_2} r[E-U(r)]^{-1/2}\mathrm{d}r}{\int_{R_1}^{R_2}[E-U(r)]^{-1/2}\mathrm{d}r} \tag{5}$$

where R_1 and R_2 are the roots of Eq. (4):

$$R_1=R_0\left[1+\left(\frac{E}{U_0}\right)^{1/2}\right]^{-1/6} \text{ and } R_2=R_0\left[1-\left(\frac{E}{U_0}\right)^{1/2}\right]^{-1/6} \tag{6}$$

Unfortunately, such an evaluation does not allow us to analyze the relation between heat capacity and thermal expansion. The physical meaning of term $R(\mathrm{d}E/\mathrm{d}R)$ is not so evident as that of terms in Eqs (1) and (2). The objective of this work was to transform Eq. (3) into an expression with clear physical meaning and to check whether the expression can be applied to the analysis of experimental data on thermal expansion of solids.

Calculations

To simplify the procedure of averaging interatomic distance, we avoided integration of a probability density function over an interval of interatomic distance and used simple mathematical operations instead.

The arithmetical average interatomic distance is

$$R=\frac{R_1+R_2}{2} \tag{7}$$

$$R\frac{\mathrm{d}E}{\mathrm{d}R}=12U_0\varepsilon^{1/2}\frac{(1-\varepsilon^{1/2})^{-1/6}+(1+\varepsilon^{1/2})^{-1/6}}{(1-\varepsilon^{1/2})^{-7/6}-(1+\varepsilon^{1/2})^{-7/6}} \tag{8}$$

where $\varepsilon=E/U_0$.

After rearrangement

$$R\frac{\mathrm{d}E}{\mathrm{d}R}=12U_0(1-\varepsilon)\left(1+\frac{1}{6}\frac{1-\frac{55}{216}\varepsilon-\frac{21506}{155520}\varepsilon^2+\ldots}{1-\frac{5}{72}\varepsilon+\frac{935}{31104}\varepsilon^2+\ldots}\right)^{-1} \tag{9}$$

It will be shown below that for solidified inert gases, ε value does not exceed 0.3. With an accuracy of 2% near the melting point, Eq. (9) is equivalent to

$$R\frac{\mathrm{d}E}{\mathrm{d}R}=\frac{72}{7}(U_0-E) \tag{10}$$

and

$$C_\mathrm{p}=\frac{72}{7}\alpha(U_0-E) \tag{11}$$

The geometric average interatomic distance is

$$R=\sqrt{R_1R_2} \tag{12}$$

The differentiation yields exact expression

$$R\frac{\mathrm{d}E}{\mathrm{d}R}=12(U_0-E) \tag{13}$$

and

$$C_\mathrm{p}=12\alpha(U_0-E) \tag{14}$$

Equation (14) differs from Eq. (11) by a coefficient.

Testing the relationship

To test the derived relationships, the zero-point energy U_0 (enthalpy of sublimation at T=0), linear thermal expansion $\alpha(T)$, and heat capacity $C_\mathrm{p}(T)$ of crystalline Ne, Ar, and Kr were used. Solidified inert gases are known as substances obeying the Lennard–Jones potential best. All data were borrowed from literature.

The following calculations were performed. First, smoothed values of enthalpy are derived from experimental data on heat capacity (for solids, especially at low temperatures, the change of energy at heating is equivalent to the increment of enthalpy). Second, the enthalpy of a crystal is calculated for several values of ε ($H_\varepsilon=\varepsilon U_0$). The values of ε are chosen at will. Third, using the smoothed values of $H(T)$, the temperature T_ε is calculated for each value of enthalpy H_ε. Forth, the values of $\alpha(T_\varepsilon)$ and $C_\mathrm{p}(T_\varepsilon)$ are calculated using smoothed functions $\alpha(T)$ and $C_\mathrm{p}(T)$. Finally, the values of coefficient A_ε are calculated

$$A_\varepsilon=\frac{C_\mathrm{p}(T_\varepsilon)}{\alpha(T_\varepsilon)(U_0-H_\varepsilon)} \tag{15}$$

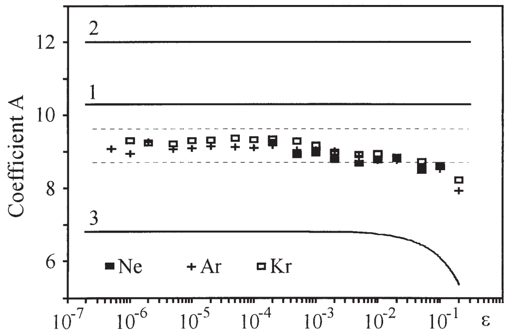

Fig. 1 Coefficient A calculated after various averaging procedures (lines) and derived from thermal properties of solidified inert gases (marks). Lines: 1 – arithmetical average; 2 – geometric average; 3 – classical density probability function. Dotted lines indicate ±5% limits

In Fig. 1, the results of calculations are shown. One can see that: i) The values of A_ε for Ne, Ar, Kr are nearly the same. The differences between them are within the limits of experimental error. ii) The values of A_ε are nearly independent of the ε values. The deflection from the constant begins near the melting point (the triple point for Ne). iii) Predicted values of A_ε are close to those derived from experimental data.

Finally, the relationship between heat capacity and thermal expansion for all solidified inert gases is

$$C_p = A\alpha(U_0 - E) \tag{16}$$

Coefficient A is not true constant but decreases slightly with increasing E/U_0 (by 15% at the melting point). At low temperatures ($E/U_0 < 10^{-3}$) $A \approx 9.17$.

Comparison between various relationships

To exclude C_v from Eq. (1), it should be combined with Eq. (2):

$$C_p = \beta K_T V\left(\frac{1}{\gamma} + \beta T\right) \tag{17}$$

The theory predicts that γ is a constant of ~1. At low temperatures $\beta T << 1/\gamma$, Eq. (17) can be written

$$C_p = \beta \frac{1}{\gamma} K_T V \tag{18}$$

At low temperatures, in turn, one can neglect E in Eq. (16), for $E << U_0$. Substituting α for β, the relationship derived from the law of interaction is

$$C_p = \beta \frac{1}{3} A U_0 \tag{19}$$

Comparing Eq. (18) and (19), one can see that they both predict similar functional relations between heat capacity and thermal expansion at low temperatures. The relationship derived from the Lennard–Jones potential has an evident advantage. It uses only the results of heat capacity and thermal expansion measurements.

The values of A_ε for Ne, Ar and Kr are the same within the limits of experimental error. The values of γ in Eq. (2) are shown in Fig. 2. The spread is much greater than that for A_ε (Fig. 1). It is as high as tens of percents.

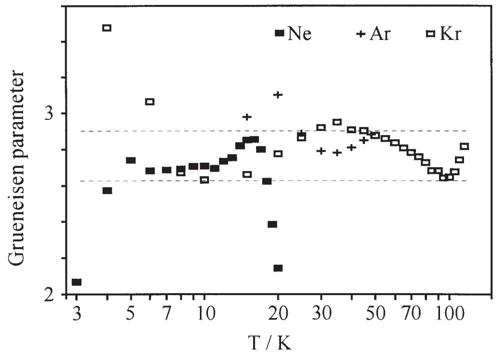

Fig. 2 The Grueneisen parameter for solidified inert gases: Ne [2], Ar [14] and Kr [10]. Dotted lines indicate ±5% limits

Substances with various types of interatomic interaction

To check how Eq. (16) is applied to the analysis of experimental data on thermal expansion of solids, three different substances were chosen: diamond (covalent, U_0=709 kJ mol^{-1}), halite (NaCl, ionic, 231 kJ mol^{-1}), and copper (metal, 337 kJ mol^{-1}). The α values were calculated using experimental data on C_p (below 298.15 K) and computer database (above 298.15 K) [2] and values of $A(\varepsilon)$ for solidified inert gases

$$\alpha(T)=\frac{C_p(T)}{A\left(\frac{E}{U_0}\right)(U_0-E)} \tag{20}$$

Diamond has the greatest energy of interaction between constituent atoms and, subsequently, very low thermal expansion. This poses great difficulties for experimental investigations of thermal expansion of diamond below room temperature. In 1961, a small negative thermal expansion between 40 and 90 K was reported [3]. Thirty years after, the X-ray measurements of synthetic diamond single crystals in the range 4.2–320 K did not confirm the negative thermal expansion [4].

The low-temperature thermal expansion coefficient of diamond was calculated using experimental data on heat capacity [5]. The results of the calculations are shown in Fig. 3, together with the experimental data. The values of $\alpha(T)$ after analysis of all experimental data available at the time were tabulated in [6]. Smoothed values

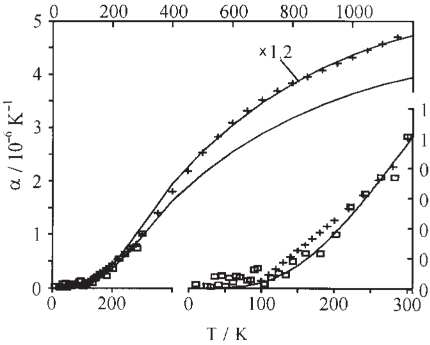

Fig. 3 The thermal expansion coefficient of diamond: smoothed tabulated values (crosses, [6]); recent experimental data (squares, [4]); calculated after Eq. (20) (line). At high temperatures the calculated values fit experimental data better if multiplied by 1.2

increase with increasing temperature as if the negative thermal expansion below 90 K really exists. The values measured in [4] increase gradually with increasing temperature but the spread is too large. At elevated temperatures, Eq. (20) predicts the values 20% lower than experimental data. Multiplied by a factor of 1.2, the calculated values fit the experimental data well. Below 300 K ($E<<U_0$), Eq. (20) can be readily integrated. The resulting formula relates the unit cell parameter to the energy at a temperature

$$a(T)=a_0\exp\left(\frac{E(T)}{AU_0}\right) \tag{21}$$

where a_0 is the unit cell parameter at T=0. Calculated values of $a(T)$ agree well with measured ones (Fig. 4).

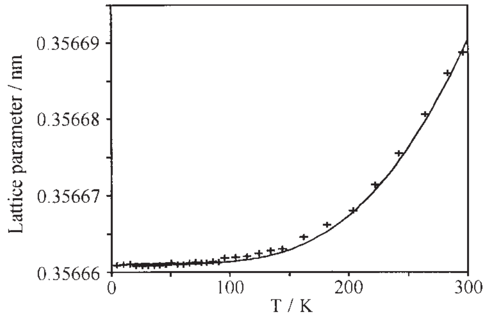

Fig. 4 The lattice parameter of diamond at low temperatures: experimental data (crosses, [4]) and calculated after Eq. (21) (line)

The results of calculations of the thermal expansion coefficient of NaCl are shown in Fig. 5, together with experimental data [7, 8]. In a temperature range of

7–22 K the difference between calculated and measured values is 1% or less. The difference increases with increasing temperature and gets as high as 33% at 800 K. Multiplied by a factor of 1.5, the calculated values fit high-temperature experimental data very well. The Grueneisen constant changes similarly. It increases from 0.89 at 6 K to 1.57 at 283 K (by 75%) [7].

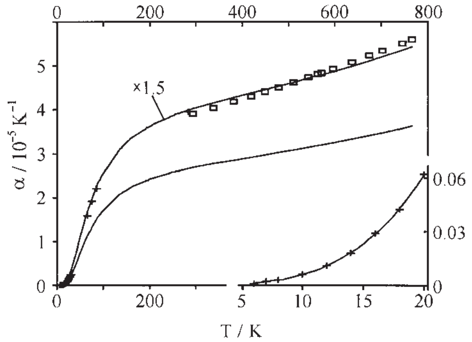

Fig. 5 The thermal expansion coefficient of NaCl: experimental data (crosses, [7] and squares [8]) and calculated after Eq. (20) (line). At high temperatures the calculated values fit experimental data better if multiplied by 1.5

For metals, low-temperature heat capacity and thermal expansion contain two contributions, electronic and lattice. The electronic-to-lattice ratio is not the same for heat capacity and thermal expansion. These are calculated by fitting the experimental data to polynomial regression $aT+bT^3$. The errors caused by the fitting are much greater than the experimental errors. To avoid the discussion of the fitting procedures, no quantitative comparison was performed below 10 K. Low-temperature heat capacity measured in [9] (below 30 K) and [10] (above 20 K) were used. Calculated using Eq. (20), the values of α for copper turned out to be systematically lower than experimental values. Multiplied by a factor of 2, these fit the experimental data well. The results of calculations after equation

$$\alpha(T)=\left(\frac{2C_\mathrm{p}(T)}{A\frac{E}{U_0}(U_0-E)}\right) \tag{22}$$

are shown in Fig. 6.

At temperatures above 200 K, experimental and calculated values differ by 1% or less. Such a difference is surprisingly small. The experimental data used for the comparison are the results of very careful investigations that were carried out in metrological institutions of the USA [11] and Japan [12]. The same sample, Standard Reference Material 736, was used in both works. The results agree with one another excellent except one point at the lowest temperature: $\alpha(20\ \mathrm{K})=0.23\cdot10^{-6}\ \mathrm{K}^{-1}$ [11], $0.28\cdot10^{-6}\ \mathrm{K}^{-1}$ [12], $0.29\cdot10^{-6}\ \mathrm{K}^{-1}$ (calculated after Eq. (22)). They are shown in Fig. 6.

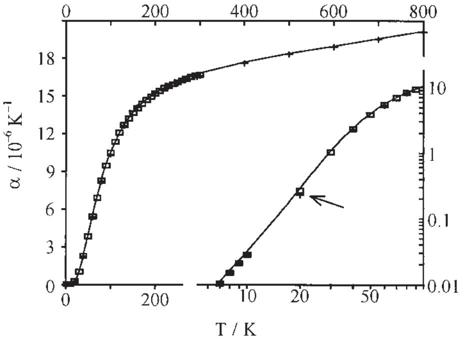

Fig. 6 The thermal expansion coefficient of copper: experimental data (crosses [11], empty squares, [12], and filled squares [13]) and calculated after Eq. (22) (line). The arrow indicates the experimental points (*T*=20 K) with the greatest discrepancy

At temperatures below the calculated values of the thermal expansion coefficient can be compared with the experimental data of Pereira *et al.* [13]. Value $0.28\cdot10^{-6}$ K^{-1} seems more preferable than $0.23\cdot10^{-6}$ K^{-1}.

Equation (22) explains the irregular behavior of thermal expansion in series Cu, Ag, Au. The α values for silver is greater than that for copper for all temperatures. α values for gold are the greatest among these metals at low temperatures but the least at high temperatures. It was shown above that Eq. (22) fits thermal expansion of copper with high accuracy. To simplify the calculations, the formula will be used in a shortened form

$$\alpha(T)=\frac{2}{AU_0}C_p(T) \tag{23}$$

where A and U_0 are used as in Eq. (21). U_0 is equal to 287 kJ mol^{-1} for Ag and 374 kJ mol^{-1} for Au [2]. Low temperature heat capacity can be estimated using the Debye model

$$C_p\approx\frac{12\pi^4}{5}R\frac{T^3}{\Theta^3} \tag{24}$$

where Θ is the Debye temperature (Cu – 315 K, Ag – 215 K, Au – 170 K) and R is the gas constant. The electronic contribution is neglected. Inserting Eq. (24) in Eq. (23), one can estimate α for the metals at T=10 K: α(Cu, 10):α(Ag, 10):α(Au, 10)= $3.2\cdot10^{-8}$:$12.3\cdot10^{-8}$: $20.3\cdot10^{-8}$ $K^{-1}\approx1:3.8:6.4$. The smoothed values derived from experiments are $3\cdot10^{-8}$: $11.1\cdot10^{-8}$:$22.8\cdot10^{-8}$ $K^{-1}\approx1:3.7:7.6$ [6]. At high temperatures, heat capacity is nearly constant

$$C_p\approx3R \tag{25}$$

and the thermal expansion coefficient depends mainly on the value of U_0. At 1000 K, the estimates of the thermal expansion coefficients are α(Cu, 1000):α(Ag, 1000):

α(Au, 1000)=$16.1\cdot10^{-6}$:$19.0\cdot10^{-6}$:$14.6\cdot10^{-6}$ $K^{-1}\approx1$:1.2:0.9. The smoothed values are $21.8\cdot10^{-6}$:$25.6\cdot10^{-6}$:$17.7\cdot10^{-6}$ $K^{-1}\approx1$:1.2:0.8 [6]. Thus, the irregular behavior of functions $\alpha(T)$ for Cu, Ag and Au is explained by different factors acting at low and high temperatures. Thermal expansion is governed by Debye temperatures at low temperatures but by energy of interaction between atoms at high temperatures.

Conclusions

The relationship between heat capacity and thermal expansion was derived from the Lennard–Jones potential. It contains only data that can be measured directly in calorimetric and dilatometric experiments. No data on elastic properties are involved. The relationship contains the coefficients that can be estimated or derived from applying the relationship to the substances. The relationship is shown to be valid not only for solidified inert gases but also for substances with other types of interaction between atoms: covalent (diamond), ionic (halite) and metal (copper).

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