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Calculation of Elastic Modulus and Other Thermophysical Properties for Molecular Crystals

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A mathematical model for the calculation of thermodynamic properties of solids is described. The mathematical model, based on statistical thermodynamics, is designed to assess the impact of atom vibration, the electron excitation, and the effect of binding energy between atoms in a crystal. To calculate the configuration integral, perturbation theory was used with the van der Waals model as the perturbation. The temperature-variable coefficients were introduced into the model. Finally, the model was compared with experimental data, proving a good match.

Nomenclature

A = free energy, J
A_1 = coefficient
a = coefficient, J · m^3
b = coefficient, J · m^3/K
C = constant dependent on material, Km$^{3\gamma}$
C_p = heat capacity at constant pressure per mole, J/kmol · K
C_v = heat capacity at constant volume per mole, J/kmol · K
c_{0S} = isentropic velocity of sound, m/s
c_{0T} = isothermal velocity of sound, m/s
E = energy, J
E_S = isentropic elastic modulus, N/mm^2
E_T = isothermal elastic modulus, N/mm^2
f = number of degrees of freedom
$g_{\mathrm{el}(0)}$, $g_{\mathrm{el}(1)}$ = degrees of degeneration of the basic and first excited state
H = enthalpy, J/kmol
$h, \hbar$ = Planck constant, J · s
i = imaginary number
k_B = Boltzmann constant, J/K
m = mass, kg
N = number of molecules in system
p = momentum, kg · m/s
q = charge, C
r_{ij} = intermolecular distance, m
s = number of atoms in molecule
T = temperature, K
T_F = Fermi temperature, K
t = time, s
V = volume, m^3
$W(E)$ = distribution density of the energy probability
w = probability
Z = partition function
β = volumetric expansion coefficient, K^{-1}
γ = Grüneisen constant
ε_F = Fermi energy, J
ζ_i = molar fraction of component i
θ = characteristic temperature, K
θ_D = Debye temperature, K
θ_E = Einstein temperature, K
ν = oscillation frequency, s^{-1}
σ = diameter of crystal atom, m
χ_S = isentropic compressibility, bar^{-1}
χ_T = isothermal compressibility, bar^{-1}
ψ = wave function

Superscripts and Subscripts

conf = configuration
el = influence of electron excitation
nuc = influence of nuclear excitation
pot = potential energy
vib = vibration
0 = ground state

Introduction

THE need for mathematical modeling of thermodynamic properties of state arises in various fields. Currently, a growing emphasis is placed on new materials, such as different alloys, polymers, plastic material, and ceramics.[1,2] Because of a large number of possible combinations of various components, mathematical models are frequently used to predict thermodynamic properties. Mathematical modeling is often used also in some metallurgical processes, such as sintering, corrosion, and welding. Furthermore, analytical computation of thermodynamic properties of state in solids is also of paramount importance in a number of other fields, for example, planetary physics. Another important area is the production of liquid–solid[3] and solid–gaseous phase diagrams. At higher pressure and temperature, such measurements may be very costly, which is why mathematical models are often used instead.

The bases for the motion of molecules and atoms in solids as well as of the effect of attractive and repulsive forces are intermolecular and intramolecular interactions between the electrons and nuclei.[4] For an accurate calculation, the Schrödinger equation for many particles must be solved:

$$\left(-\sum\frac{\hbar^2}{2m_i}\nabla_i^2+\sum\frac{q_iq_j}{r_{ij}}\right)\psi=\frac{\hbar}{i}\frac{\partial\psi}{\partial t} \tag{1}$$

The sum in Eq. (1) runs over all nuclei and electrons having the mass m_i and the charge q_i. The solution of such a differential equation is an extremely difficult task, although very accurate results may be obtained also through some generalizations.

Assume that each form of motion is independent of the others; thus, the energy of the system of molecules can be written as a sum

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of individual contributions, that is, decoupled forms of motion: The first contribution is vibration energy of molecules due to the relative motion of atoms inside the molecules. The second is the potential energy of a system of molecules, which occurs due to the attractive or repulsive intermolecular forces in a system of molecules. Third is the energy of electrons, which is concentrated in the electrons or in the electron shell of an atom or a molecule. Last is nuclear energy, which is concentrated in the atom nuclei.

Writing down the energy of the ground state (0) as a sum of individual contributions of energies in the ground state for a system of molecules, we obtain

$$E_0 = E_{\mathrm{vib}_0} + E_{\mathrm{el}_0} + E_{\mathrm{nuc}_0} + \cdots \tag{2}$$

The energy required to excite the system of molecules to higher energy levels is

$$E = E_0 + E_{\mathrm{vib}} + E_{\mathrm{el}} + E_{\mathrm{nuc}} + E_{\mathrm{conf}} \tag{3}$$

The potential intermolecular energy depends on the position of the nuclei in space. We neglect the influence of the orientation of a molecule in space, and we assume that the intermolecular energy of the system of molecules is an additive property. Because, in the present model, the phenomena treated are at higher temperatures, where quantum effects have very low influence, we used classical statistical thermodynamics to compute the thermodynamic properties of state of one-, two-, or multiatom molecules.

To this end, we can use the canonical partition,[5–12] which deals with a system of particles having final number of particles N, temperature T, and volume V.

Now introduce the partition function Z (Refs. 5–8), which applies to a system of particles at a certain volume V, temperature T, and particle number N. Let $\mathrm{d}w(E)$ be the probability that the system energy is in the interval from E to $E + \mathrm{d}E$. Thus, the mathematical formulation of probability is

$$\mathrm{d}w(E) = W(E)\,\mathrm{d}E \tag{4}$$

The probability that the system is in the ith quantum state is presented by the following equation:

$$w_i = A_1 \exp[-(E_i/k_B T)] \tag{5}$$

For a one-component system of indistinguishable molecules, we can write the expression for the partition function Z:

$$\sum w_i = 1 \rightarrow A = Z = \sum_i \exp\left(-\frac{E_i}{k_B T}\right) \tag{6}$$

where the sum spreads over all energy states with energy E_i. Assuming that the energy spectrum is continuous and with the preceding assumptions, we can then write the canonical partition function for a one-component system in an even easier form:

$$Z = \frac{1}{N!h^{Nf}} \int \cdots \int \exp\left(-\frac{E_{\mathrm{vib}} + E_{\mathrm{el}} + E_{\mathrm{nuc}}}{k_B T}\right) \mathrm{d}\boldsymbol{p}_1\,\mathrm{d}\boldsymbol{p}_2, \ldots, \mathrm{d}\boldsymbol{p}_N$$

$$\times \int \cdots \int \exp\left(-\frac{E_{\mathrm{pot}}}{k_B T}\right) \mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2, \ldots, \mathrm{d}\boldsymbol{r}_N \tag{7}$$

The second term on the right-hand side of Eq. (7) is called the configurational integral and f is the number of degrees of freedom of an individual molecule. Similarly, we can write the partition function Z for a multicomponent system of indistinguishable molecules:

$$Z = \frac{1}{\prod_i N_i! h^{N_i f_i}} \int \cdots \int \exp\left(-\frac{E_{\mathrm{vib}} + E_{\mathrm{el}} + E_{\mathrm{nuc}}}{k_B T}\right)$$

$$\times\, \mathrm{d}\boldsymbol{p}_1\,\mathrm{d}\boldsymbol{p}_2, \ldots, \mathrm{d}\boldsymbol{p}_N \int \cdots \int \exp\left(-\frac{E_{\mathrm{pot}}}{k_B T}\right) \mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2, \ldots, \mathrm{d}\boldsymbol{r}_N \tag{8}$$

In Eq. (8), N_i is the number of molecules of the ith component and f_i is the number of degrees of freedom of the ith molecule. On the basis of all of the indicated generalizations, we can write, using the canonical partition, the partition function Z of a one-component system as a product of partition functions:

$$Z = Z_0 Z_{\mathrm{vib}} Z_{\mathrm{el}} Z_{\mathrm{nuc}} Z_{\mathrm{conf}} \tag{9}$$

For a system of many components, the partition function Z (Refs. 1, 13, and 14) can be written as a product of partition functions for individual terms:

$$Z = \prod_i (Z_0 Z_{\mathrm{vib}} Z_{\mathrm{el}} Z_{\mathrm{nuc}})_i Z_{\mathrm{conf}} = \prod_i Z_i Z_{\mathrm{conf}} \tag{10}$$

By means of the partition function Z (Ref. 8), canonical theory allows the computation of thermodynamic properties of state. The further calculation of thermodynamic functions of state based on canonical theory using statistical thermodynamics is well known and may be found in Ref. 8.

Vibrational Properties of Solids

Our thermodynamic system consists of N particles associated by attractive forces. Atoms in a crystal lattice are not motionless, but they constantly thermally oscillate around their positions of equilibrium. At temperatures far below the melting point, the motion of atoms is approximately harmonic.[10,11] This assembly of atoms has $3N - 6$ vibrational degrees of freedom. We ignore six vibrational degrees of freedom[10] and mark the number of vibrational degrees of freedom as $3N$.

Through the knowledge of independent harmonic oscillators, the distribution function Z (Ref. 10) can be written as follows:

$$Z_{\mathrm{vib}} = \left\{\frac{\exp[-(h\nu/2k_B T)]}{1 - \exp[-(h\nu/k_B T)]}\right\}^{3N} \tag{11}$$

In Eq. (11) ν is the oscillation frequency of the crystal. The term $h\nu/k$ is the Einstein temperature. When comparison is made with the experimental data for simple crystals, a relatively good match with analytical calculations at higher temperatures is observed, whereas at lower temperatures, the discrepancies are higher. This is why Debye corrected Einstein's model by taking into account the interactions between the number of quantized oscillators.[10] The Debye approximation treats a solid as an isotropic elastic substance. When the canonical distribution is used, the partition function[11] may be written as

$$\ln Z = -\frac{9}{8} N \frac{\theta_D}{T} - 3N \ln\left[1 - \exp\left(-\frac{\theta_D}{T}\right)\right]$$

$$+ 3N \frac{T^3}{\theta_D^3} \int_0^{\theta_D/T} \frac{\xi^3}{\exp(\xi) - 1}\,\mathrm{d}\xi \tag{12}$$

In Eq. (12) θ_D is the Debye temperature: $\theta_D = \nu_{\max} h/k_B$. By developing the third term in Eq. (12) into a series for higher temperature range,[12] we can write

$$\xi^3/[\exp(\xi) - 1] = \xi^2 - \tfrac{1}{2}\xi^3 + \tfrac{1}{12}\xi^4 - \tfrac{1}{720}\xi^6 + \cdots \tag{13}$$

When Eq. (13) is used, Eq. (12) becomes

$$\ln Z = -\frac{9}{8} N \frac{\theta_D}{T} - 3N \ln\left[1 - \exp\left(-\frac{\theta_D}{T}\right)\right] + 3N\left(\frac{T}{\theta_D}\right)^3$$

$$\times \left[\frac{1}{3}\left(\frac{\theta_D}{T}\right)^3 - \frac{1}{8}\left(\frac{\theta_D}{T}\right)^4 + \frac{1}{60}\left(\frac{\theta_D}{T}\right)^5 - \frac{1}{5040}\left(\frac{\theta_D}{T}\right)^7\right.$$

$$\left. + \frac{1}{272{,}160}\left(\frac{\theta_D}{T}\right)^9 - \cdots\right] \tag{14}$$

The relation between the Einstein and the Debye temperature may be written as[12–15]

$$\theta_E = K\theta_D \tag{15}$$

where K ranges from 0.72 to 0.79. The Debye characteristic temperature was determined by means of the Grüneisen independent constant γ,

$$\theta_D = CV^{-\gamma} \tag{16}$$

where C is constant dependent on material.

We have developed a mathematical model for the calculation of thermodynamic properties of polyatomic crystals. The derivations of the Einstein and Debye equations, just outlined, apply specifically to monoatomic solids, that is, those belonging to the cubic system. However, experiments have shown that the Debye equation represents the values of specific heat and other thermophysical properties for certain other monoatomic solids, such as zinc, which crystallizes in a hexagonal system. Suppose that the crystal contains N molecules, each composed of s atoms. Because there are Ns atoms, the crystal as a whole has $3Ns$ vibrational modes. A reasonable approximation is obtained by classifying the vibration into 1) $3N$ lattice vibrations, which are the normal modes discussed in the Debye treatment (acoustical modes) and 2) independent vibrations of individual molecules in which bond angles and lengths may vary. There must be $3N(s-1)$ of these (optical modes). We express the optical modes using the Einstein model.

Influences of Electrons

Electronic Gas in Metals

We are interested in electrons capable of moving in a crystal and not belonging to any individual atoms but entirely to the crystal, such as, for example, conduction electrons in metals.[4] A number of such electrons may be called an electronic gas. When Fermi–Dirac statistics are used, the configuration integral[7,10,13] may then be calculated for temperatures lower than the Fermi temperature:

$$T_F = \varepsilon_F / k_B \tag{17}$$

For metals, the Fermi temperature is a few thousand kelvin. In Eq. (17), ε_F is Fermi energy. With help of Fermi–Dirac statistics and canonical distribution, we can express the electron part of free energy:

$$A_{\mathrm{el}} = \tfrac{3}{5}N\varepsilon_F\left[1 + (5\pi^2/12)(k_BT/\varepsilon_F)^2\right] - Nk_B(\pi^2/2)\left(k_BT^2\big/\varepsilon_F\right) \tag{18}$$

Influence of Electron Excitation

To calculate the influence of electron excitation in excited states, classical models of statistical thermodynamics may be used. The electron partition function for the technical range of temperatures and pressures can be written as follows[9]:

$$Z_{\mathrm{el}} = \{g_{\mathrm{el}(0)} + g_{\mathrm{el}(1)}\exp[-(\theta_{\mathrm{el}}/T)]\}^N \tag{19}$$

In Eq. (19) θ_{el} is electronic characteristic temperature.

Crystal Bonds

The bonds between the atoms or molecules in a crystal are of electrostatic nature. They are based upon Coulomb's law of attractive and repulsive forces. Atoms are associated into a crystal if the total energy of the system is reduced. Roughly speaking, bonds may be classified into the following types.

1) Van der Waals (VDW) bonds (see Ref. 14) result from forces between inert atoms and mostly saturated molecules (see Refs. 7, 14, and 15). VDW forces appear due to time-varying dipole moments occurring due to a rapid motion of electrons. In solids, this form of bond is rather rare. The system of molecules bound in this manner is called a molecular crystal, typical of some molecules such as CO_2, CH_4, and NH_3. The properties of substances bound by means of the VDW bond are softness, low melting point, and solubility in covalent liquids.

2) Ionic bonds[14] occur due to interactions between ions of opposite charge, which result in an arranged three-dimensional structure. In sodium chloride, each Na^+ ion is surrounded by six Cl^- ions, and each Cl^- ion is surrounded by six Na^+ ions, which means that the NaCl molecule is actually nonexistent. The ionic bond is spherically symmetrical and nondirectional. This means that the ion will be surrounded by as many ions of opposite charge as possible, whereby full electrical neutrality must obviously be preserved. Characteristics of this type of bond are high melting point, relative hardness of material, and solubility in all-polar liquids.

3) A covalent or strong bond[14] is formed if one or more electrons are shared between two atoms. These common electrons, most of the time located between the two atoms, cause attraction of the two atoms, as well as a reduction in the energy of the system. Typical of this bond is very high hardness, high melting point, and insolubility in almost all liquids.[14–16]

4) Metallic bonds[14,17] occur in metallic crystals with external valence electrons relatively weakly bound to the nucleus of the atom. In the formation of a solid substance, the atoms approach so closely that these valence electrons desert their atoms and can move freely over the entire crystal. This type of bonding is characterized by elasticity and forgeability of material, metallic glaze, and good electrical and heat conduction.

5) Hydrogen bonds play an important role in ice and hydrates of salt and are formed in polar parts of molecules where hydrogen is present.

The analytical calculation of configuration integrals in solids is a very difficult task. Most frequently, numerical procedures are applied in practical computations by means of the Monte Carlo method.[11] Nevertheless, the method requires a lot of computer time, with another serious drawback being that it does not provide a functional dependence of thermodynamic properties on temperature and volume. Empirical equations[6] are frequently used as well, although mostly without any theoretical basis on a molecular view of the world. In the paper, we used the perturbation VDW theory for solids calculated around a model of hard spheres[18–20] to calculate the thermodynamic properties of state. To calculate the properties of mixtures of atoms of hard spheres, we obtain the configuration free energy for a certain binary crystal:

$$\begin{aligned} A_{\mathrm{conf}\,0} &= Nk_BT\big\{-3\ln[(V^*-1)/V^*] + 5.124\ln V^* - 20.78V^* \\ &\quad + 9.52V^{*^2} - 1.98V^{*^3} + C_0 + \varsigma_1\ln\varsigma_1 + \varsigma_2\ln\varsigma_2\big\} \\ C_0 &= 15.022, \qquad V^* = V/V_0, \qquad V_0 = N\sigma^3\big/\sqrt{2} \end{aligned} \tag{20}$$

In the case of a crystal formed of atoms of the same type, free energy can be written as

$$\begin{aligned} A_{\mathrm{conf}\,0} &= Nk_BT\big\{-3\ln[(V^*-1)/V^*] + 5.124\ln V^* - 20.78V^* \\ &\quad + 9.52V^{*^2} - 1.98V^{*^3} + C_0\big\} \end{aligned} \tag{21}$$

To calculate the perturbation contribution, the VDW model was used. In most of the technical literature,[19,20] the VDW model is treated only in relation to atomic structure, whereas we additionally present the temperature-dependent coefficients

$$A_{\mathrm{conf}\,1} = -[a(\psi_1, \psi_2, T)/V] \tag{22}$$

The configuration integral is, thus, formed by the contribution of hard spheres and perturbation:

$$A_{\mathrm{conf}} = A_{\mathrm{conf}\,0} + A_{\mathrm{conf}\,1} \tag{23}$$

Coefficient a was determined as a temperature-dependent polynomial following a comparison between experimental data and analytical results:

$$a = a_0 + a_1T + a_2T^2 \tag{24}$$

Coefficients a_0, a_1, and a_2 are obtained by numerical approximation and the comparison with thermodynamic data:

$$\frac{\mathrm{d}A_{\mathrm{conf}}}{\mathrm{d}T} = -\frac{b(\psi_1, \psi_2, T)}{V} \tag{25}$$

Coefficient b was determined as a temperature-dependent polynomial following a comparison between experimental data and analytical results:

$$b = b_0 + b_1 T \tag{26}$$

Results and Discussion

The present mathematical model was used to calculate the thermodynamic properties of state of some solids, namely, 1) copper (Cu), as a typical representative component and with metallic bonds; 2) sodium chloride (NaCl), as a typical representative material with ionic bonds; and 3) carbon dioxide (CO_2), as a typical representative material in the form of molecular crystals.

Table 1 Primary constants for analytical calculations

Constant, Eq. no.	Cu	NaCl	CO_2
C,[a] (16)	0.28629	7.587	13.587
C[b]	——	7.587	13.587
C[b]	——	——	13.587
γ,[a] (16)	1.9	1.0	1.0
γ[b]	——	1.0	1.0
γ[b]	——	——	1.0
a_0, (24)	−2.2159E+6	0.000896E+6	1,3817.12
a_1, (24)	12,734.4	128,576	2,571.5
a_2, (24)	−6.05282	−21.4395	4.2879
b_1, (26)	2,464.2	17,904.7	5,371.2
b_2, (26)	−0.883	−25.3853	7.6149

[a] Acoustical mode. [b] Optical modes.

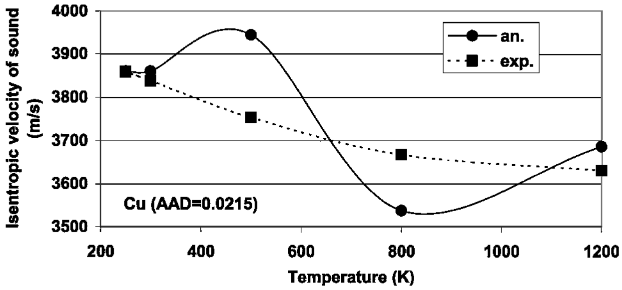

Fig. 1 Isentropic velocity of sound for Cu.

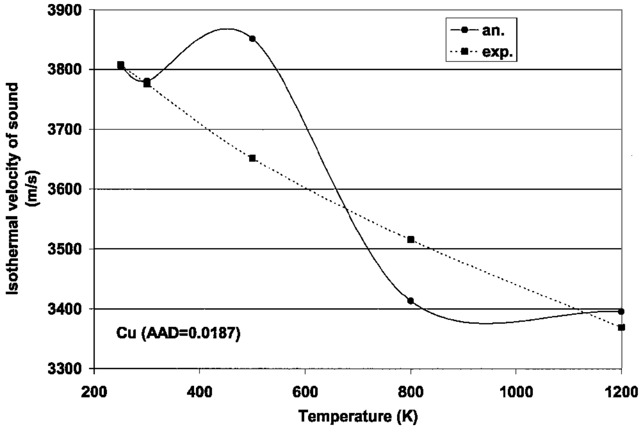

Fig. 2 Isothermal velocity of sound for Cu.

For the relation between Einstein and Debye temperatures, we used the next approximation:

$$\theta_E = 0.775\theta_D \tag{27}$$

We compared the analytical model obtained by statistical thermodynamics and experimental data. The most important data for analytical calculations are presented in Table 1. The first and second rows in Table 1 represent the fitting data important for calculation of vibrational properties. The first row for C and γ represents the data for acoustical mode, the second and third rows represent the data for optical modes.

Figures 1–7 show isentropic velocity of sound c_{0S}, isothermal velocity of sound c_{0T}, isentropic elastic modulus E_S, isothermal elastic modulus E_T, heat capacity at constant volume per mole C_V,

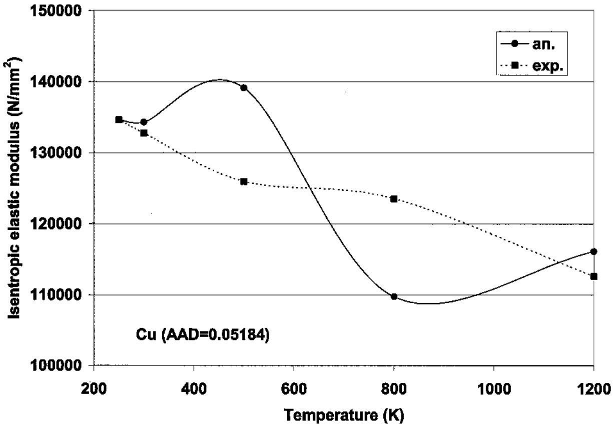

Fig. 3 Isentropic elastic modulus for Cu.

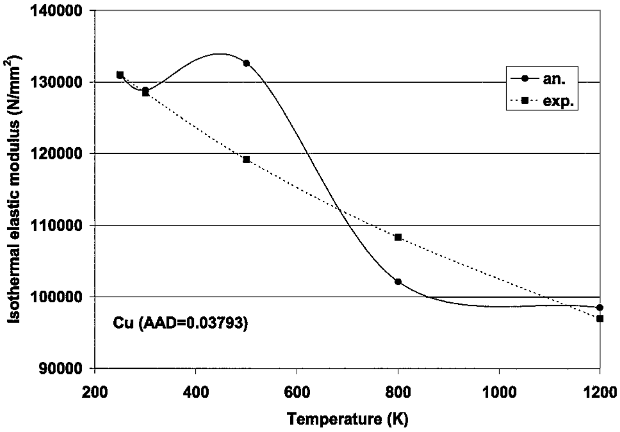

Fig. 4 Isothermal elastic modulus for Cu.

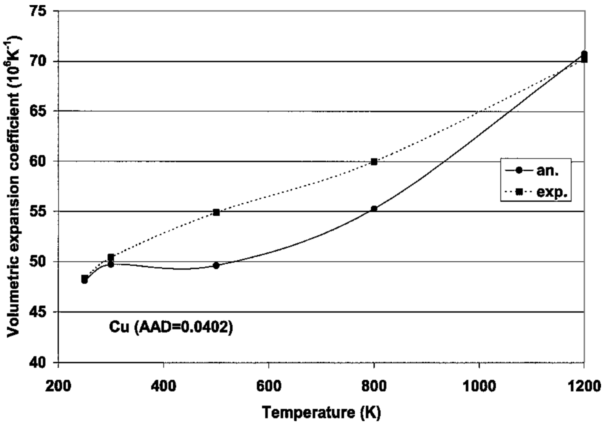

Fig. 5 Volumetric expansion coefficient for Cu.

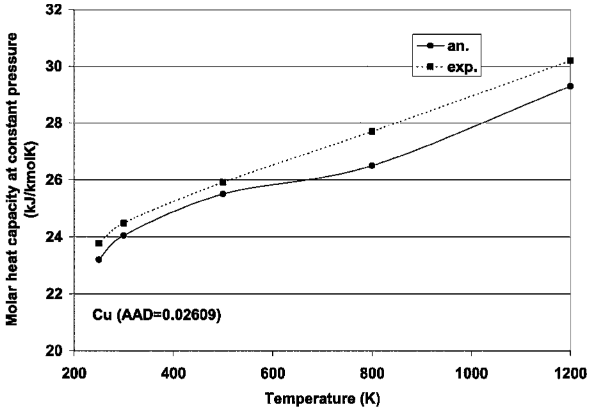

Fig. 6 Molar heat capacity at constant pressure for Cu.

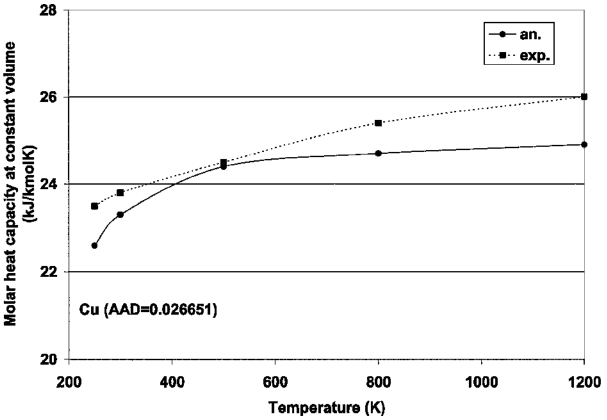

Fig. 7 Molar heat capacity at constant volume for Cu.

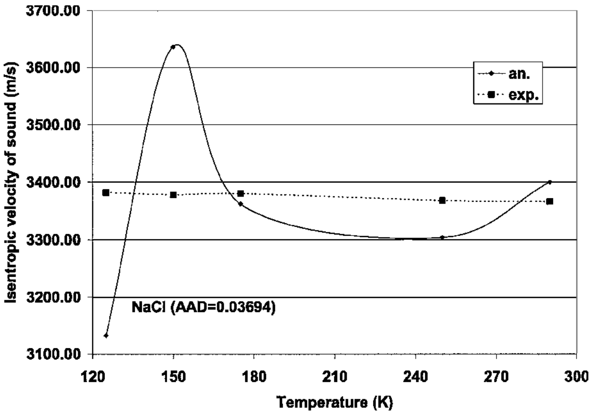

Fig. 8 Isentropic velocity of sound for NaCl.

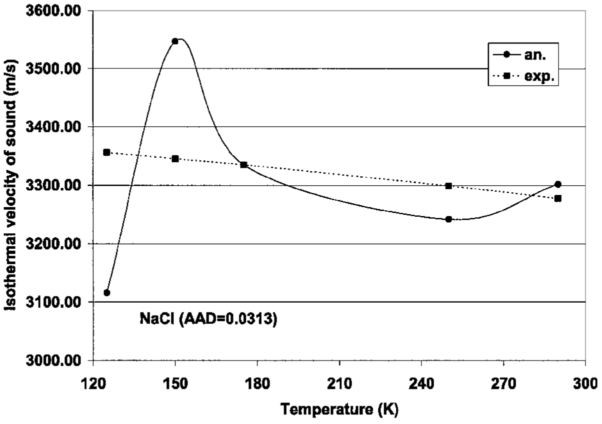

Fig. 9 Isothermal velocity of sound for NaCl.

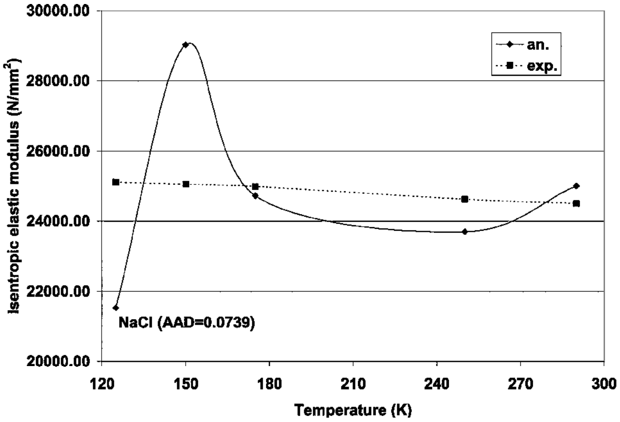

Fig. 10 Isentropic elastic modulus for NaCl.

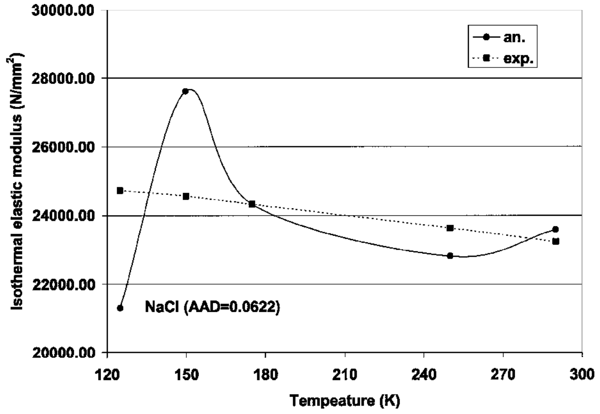

Fig. 11 Isothermal elastic modulus for NaCl.

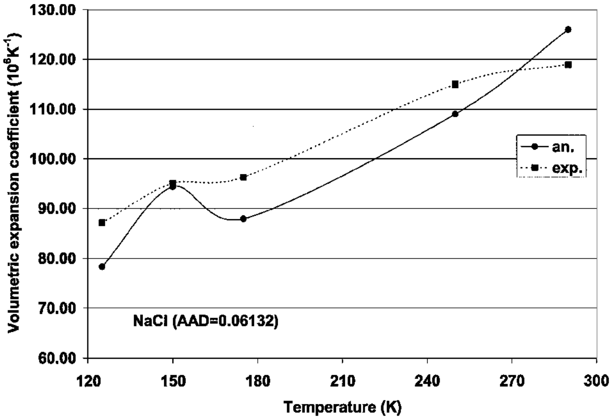

Fig. 12 Volumetric expansion coefficient for NaCl.

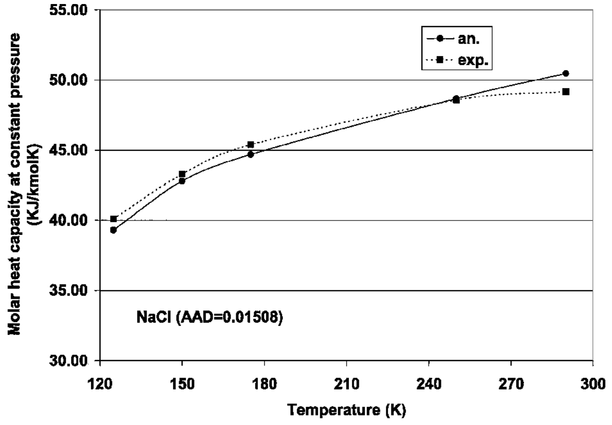

Fig. 13 Molar heat capacity at constant pressure for NaCl.

heat capacity at constant pressure per mole C_p, and volumetric expansion coefficient β for Cu. In Figs. 1–16, the analytical model is denoted an, experimental data is denoted exp, and average absolute deviation (AAD) is used as the measure of accuracy of analytical model:

$$\mathrm{ADD} = \sum \frac{|(\mathrm{data}_{\mathrm{exp}} - \mathrm{data}_{\mathrm{calc}})/\mathrm{data}_{\mathrm{exp}}|}{\text{number of points}}$$

The results obtained from the analytical model show good agreement, with the maximum AAD of 5.2% for isentropic elastic modulus.

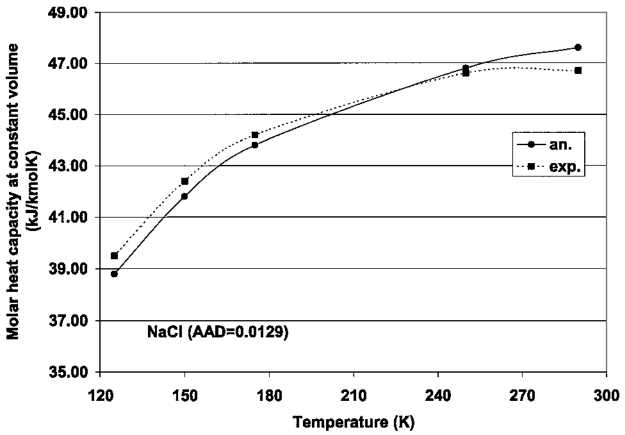

Fig. 14 Molar heat capacity at constant volume for NaCl.

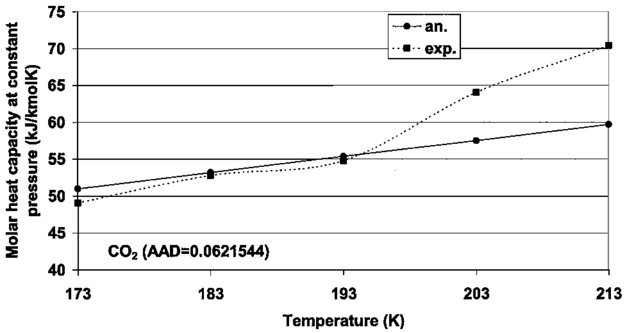

Fig. 15 Molar heat capacity at constant pressure for CO_2.

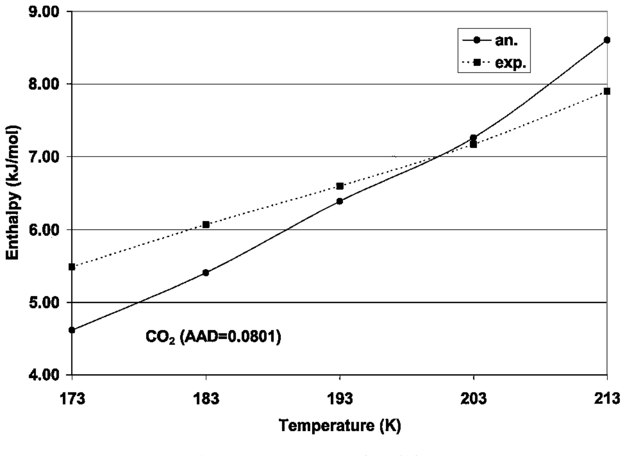

Fig. 16 Enthalpy for CO_2.

Figures 8–14 show thermophysical properties for NaCl. The results obtained by the analytical model show very good agreement with experimental data. The maximum AAD is 6.2% for isothermal elastic modulus.

Somewhat larger deviations are observed for CO_2 (Figs. 15 and 16) with maximum AAD of 8.02% for enthalpy.

Conclusions

Thermal and caloric equations of state are fundamental characteristics of matter defining thermodynamic properties over a wide range of phase diagram. The principal problem of modern powerful theories is the necessity to take into account correctly the strong collective and interparticle interaction in disordered media. Solids have been extensively studied with models based on classical thermodynamics. These models are, from a practical point of view, more accurate, and they allow simulation in wider temperature and pressure regions. Classical thermodynamics provides no insight into the microstructure of the substance. However, it allows the calculation of thermodynamic functions of state with assistance from measurements or empirical equations. Statistical thermodynamics, on the other hand, allows the calculation of the properties of state based on molecular motions in space and intermolecular interactions. This paper is one of the first attempts to determine how to calculate thermophysical properties based on statistical thermodynamics, with the help of semitheoretical models.

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