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Quantum concentration for the liquid phase of elements

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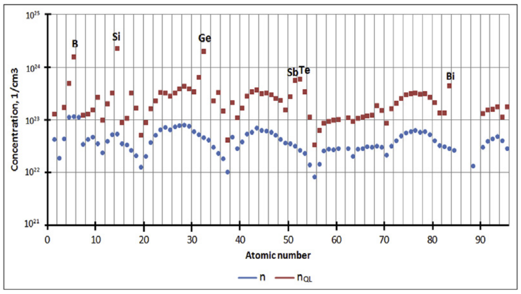
HIGHLIGHTS

- The novel concept of quantum concentration (QC) for the liquid phase was presented.
- Metalloids exhibited a highest value of QC compared with other elements.
- The size dependence of melting temperatures of metals was calculated by using QC.

GRAPHICAL ABSTRACT



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ABSTRACT

The novel concept of quantum concentration for the liquid phase of elements was introduced which indicates the number of possible states of atoms per unit volume. A simplified thermodynamic energy model for a solid–liquid phase transition is used to define the quantum concentration for the liquids. Values of quantum concentration for liquid phase of most of elements were calculated and analyzed. It was revealed that the metalloids such as boron, silicon, germanium, antimony, tellurium and bismuth exhibited a highest value of quantum concentrations compared with other elements. Several physical and chemical properties of substances (such as melting temperature and free energy) can be calculated using these data. The size dependence of melting temperatures of Au, Pb and Sn spherically symmetric nanoparticles were calculated and compared well with experimental data and theoretical model based on generalized Gibbs–Thomson predictions.

1. Introduction

For the past century quantum theory has been an essential part of the modern physics and quantized energy levels, spin, the geometry of electronic orbitals, and the Pauli Principle can all be applied to understand the behavior of the single atom, extending to atom clusters, small molecules, and finally to the properties of matter [1]. This provides a substantial useful framework for various features of the modern elements including the behavior of atoms during chemical bonding and has played a significant role in the development of numerous modern technologies. For example, the application of the *quantum concentration* concept in an ideal gas as pioneered by Kittel and Kroemer [2] has made quantum states “countable” and therefore accessible for a statistical calculation of entropies. The quantum concentration (number of states per volume) of an ideal gas is determined by the following equation:

$$\rho_Q = \left(\frac{2\pi MkT}{h^2}\right)^{3/2} \tag{1}$$

where M is the particle mass, T is the absolute temperature, k is the

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Boltzmann constant and h is Planck constant. Since the quantum concentration of the ideal gas is limited, it would be contradictory if the concentration of available states in a liquid would be infinite, therefore it should be countable as well and can be treated statistically. Let consider a system with one kind of particles with the particle number n that can be distributed over available sites with the number N. The number of particles per one available site is $c = n/N$.

The identical average particle energy W_n and the entropy of distribution (mixing over available states) S^M the free energy can be expressed by using Helmholtz free energy (F) approximation:

$$F = n \cdot W_n - T \cdot S^M \tag{2}$$

Using typical permutation statistics as described in several textbooks on thermodynamics and materials science [1–4] and solid state electronics [5–8] using Equation (2), we define the entropy of distribution per particle the following equations:

$$S = S^M(N, n) = +k \cdot \{N \ln N - (N - n)\ln(N - n)\} \tag{3}$$

$$\Rightarrow S^M(N, c) = -k \cdot N \cdot \{c \ln c + (1 - c)\ln(1 - c)\} \tag{4}$$

This formalism can be effectively used in materials science as well as in condensed matter physics. While in standard theory the entropy of distribution is used for the mixing of n impurity atoms in a matrix of N atoms we consider here the distribution of n atoms of one kind over $\boldsymbol{N_Q}$ quantum states that the particles can occupy:

$$c = \frac{n}{N_Q} \tag{5}$$

Here c means the number of n atoms per N_Q quantum states.

In this work we introduce a novel concept for a statistical interpretation of the entropy of melting using the quantum concentration for the liquid phase n_{QL}, which allows for a statistical calculation of the free energy in the liquid. The quantum concentration of liquids can be determined using a geometrical relation derived from the thermodynamic energy model for a solid–liquid phase transition. The thermodynamic energy model to calculate the size dependence of the melting temperature of spherically symmetric nanoparticles is considered. The relation between the results and limited experimental observations is also discussed.

2. Thermodynamic energy model for a solid–liquid phase transition

The diagram of the thermodynamic energy model for a solid–liquid phase transition is a simplification of the standard thermodynamic model for alloys [1–4] that is valid for systems without phase separation presented in Fig. 1. According to the considered model the free energy per atom for solid and liquid phases are expressed through the following relations:

$$F^{liqu}(n,n_Q) = n \cdot (W_s + W_{lat.heat}) + kT \cdot n_Q \cdot \{c_l \ln c_l + (1-c_l)\ln(1-c_l)\}$$
$$\Rightarrow f^{liqu}(n,n_Q) := \frac{F^{liqu}}{n} = W_s + W_{lat.heat} + \frac{kT}{c_l}\{c_l \ln c_l + (1-c_l)\ln(1-c_l)\} \tag{6}$$

where $f^{solid} := \frac{F^{solid}}{n} = W_s$, $W_{lat.\ heat}$ is latent heat of fusion per atom, W_s is energy per atom in the solid phase, and $c_l = \frac{n}{n_{QL}}$ is the number of atoms of the pure phase divided by the number of available states in the liquid phase with the physical meaning of an occupation rate.

At the melting point T_m the free energies in solid and liquid phases are equal to each other:

$$f^{solid} = f^{liquid} \tag{7}$$

thus from Equation (6) it follows:

$$W_{lat.heat} = -\frac{kT_m}{c_l}\{c_l \ln c_l + (1 - c_l)\ln(1 - c_l)\} \tag{8}$$

The thermodynamic energy model for a solid–liquid phase transition has an important geometrical interpretation, since the curve representing the free energy per atom of the liquid phase is fixed at the temperature $T = 0$ (it has the value of W_s plus $W_{lat.heat}$) and at the melting temperature T_m. According to Equation (3) the slope is corresponding to the negative entropy per atom S^M/n. Decreasing entropy per atom lead to increase c_l that expends a fewer additional occupational states in the liquid phase as compared to the solid phase.

3. Quantum concentration of the liquid

Since the quantum concentration of an ideal gas is limited, the quantum concentration of the liquid similarly has to be limited and

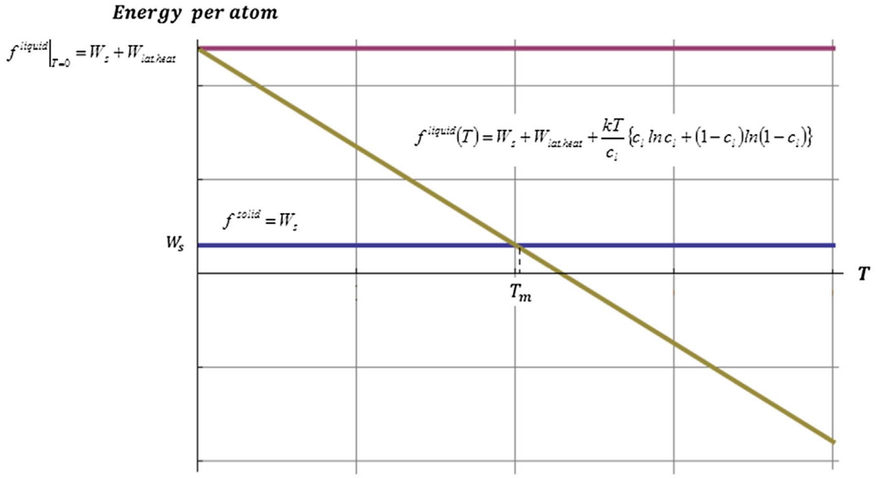

Fig. 1. Diagram of the thermodynamic energy model for a solid–liquid phase transition.