

Three-phase Analytical Model for Simple Matter

Mahach Magomedov^{C, S}

Institute for Geothermal Research of Daghestan Scientific Centre RAS, Makhachkala, Daghestan, Russia

Simulating on the same basis the solid, liquid and gas states of a matter, I represent the system as a virtual structure composed of $N+N_v$ cells with identical sizes, where N_v cells in this system are vacant. In this case, let us assume that the structure composed of $N+N_v$ cells is similar to the structure of the crystal lattice of the material under consideration. This is the so-called “isostructural approximation of the lattice model”. In addition, let us assume that atoms in the system can be found in two states: the localized (L-) state and the delocalized (D-) state. In the L-state, an atom is localized in a cell of the virtual lattice and can have only vibrational degrees of freedom. In contrast, the entire volume of the system is available for an atom in the D-state; such an atom can have only translational degrees of freedom. As was shown in [1], the fraction of atoms that pass from L-state (when an atom vibrates in the cell formed by the nearest environment) into D-state (i.e., acquiring a kinetic energy that is higher than a certain threshold value E_d) is described by the incomplete gamma function of the form:

$$x = (2/\pi^{1/2}) \int_{E_d/k_b T}^{\infty} t^{1/2} \exp(-t) dt .$$

Here, k_b is the Boltzmann constant, T is the temperature, E_d is the energy of delocalization of atom. The probability of vacancy creation into the lattice model is described by expression [2]:

$$\phi = (2/\pi^{1/2}) \int_{(E_v/k_b T)^{1/2}}^{\infty} \exp(-t^2) dt ,$$

The energy E_v can be referred to as the energy of vacancy formation in a virtual lattice structure. Proceeding from the potential of interatomic interaction Mie–Lennard-Jones:

$$\varphi(r) = [D/(b-a)][a(r_o/r)^b - b(r_o/r)^a] , \quad b > a > 2 ,$$

the expression for specific (per atom) free energy of model is :

$$f(\rho, T) = f_i + f_s + f_d + f_w , \quad \rho = N/V . \quad (1)$$

Here the first item is the free energy of the translated motion of D-atoms:

$$f_i = -x k_b T \ln[(T/A_d)^{3/2} (\rho_o/\rho)] , \quad A_d = (2\pi \hbar^2 / m k_b)(\rho_o/e)^{2/3} ,$$

where \hbar is the Planck constant; m is the mass of an atom; $\rho_o = (3k_p/4\pi)(2/r_o)^3$; k_p is the packing fraction of the structure from $(N+N_v)$ spherical cells. The second item in Eq. (1) is the free energy of the “static interaction” all atoms: $f_s = (k_n/2)(1-\phi) D (a Y^{b/3} - b Y^{a/3}) / (b-a)$, $Y = (\rho/\rho_o)/(1-\phi)$,

where k_n is the first coordination number for a virtual structure composed of $N+N_v$ cells. Term f_d of Eq. (1) is the free energy of the “dynamic interaction for D-atoms:

$$f_d = x k_n (1-\phi) D [a Y^{b/3} l_3(b, \xi_p) - b Y^{a/3} l_3(a, \xi_p)] / (b-a) , \quad \xi_p = (0.5/3^{1/2})(1/k_p)^{1/3} ,$$

where $l_3(k, t) = \{[(1+t)^{k-2} - (1-t)^{k-2}] / [2(k-2)t(1-t^2)^{k-2}]\} - 1$. Item f_w is the specific free energy of the “vibrational motion for L-atoms”:

$$f_w = 3(1-x) k_b T \{0.5 y + \ln[1 - \exp(-y)]\} , \quad y = 3 \Theta / 4 T , \quad \Theta \text{ is the Debye temperature. At } x = 1 \text{ from Eq. (1)}$$

one obtains the free energy of gas, and at $x = 0$ one gets the free energy of the ideal crystal. It is shown that the model takes into account the “communal entropy”, and it satisfies both the third law of thermodynamics and the condition of thermodynamic self-consistence equations. It is shown that under corresponding choice of function E_d this model can describe solid, liquid gaseous phase and phase transition between them, including triple and critical points.

[1] *Magomedov M.N. // The Physics of Metals and Metallography. 1995. V. 80. N 4. P. 383 – 392.*

[2] *Magomedov M.N. // Semiconductors. 2008. V. 42. N 10. P. 1133 – 1145.*