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Wave-Space Representation for the Variational Upper Bound of the Helmholtz Free Energy in the Tight-Binding Approximation

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Abstract

The wave-space expression is obtained for the variational upper bound of the Helmholtz free energy described in the framework of the tight-binding model.

Keywords: Variational method, tight-binding model, transition metal, Helmholtz free energy, wave space

In the work [1] was suggested to calculate thermodynamic properties of liquid transition metals using the Gibbs-Bogoliubov(GB)-inequality-based variational method in conjunction with the tight-binding (TB) model of Ducastelle [2]. The aforementioned formalism was developed in the real space. For simplification of the calculation procedure it is convenient to write the Helmholtz free energy, *F*, in the wave space. Our work is devoted to the realization of this task.

In the variational method with the hard-sphere (HS) reference system *F* is determined from the following form of the GB inequality (per atom):

$$F \le \frac{3}{2}k_b T + \langle U \rangle_{HS} - TS_{HS} \quad , \tag{1}$$

where k_b is the Boltzmann constant, *T* - temperature, U - potential energy, S - entropy.

The potential energy in the TB model [2] is written as follows:

$$U = \int_{-\infty}^{\varepsilon_F} \mathrm{d}\varepsilon\varepsilon \sum_{m=1}^{N} n_m(\varepsilon) + \sum_{m=1}^{N-1} \sum_{l=m+1}^{N} \varphi(|\mathbf{r}_{ml}|) \quad , \tag{2}$$

where ε is the *d*-electron energy, ε_F - Fermi energy, $n_m(\varepsilon)$ - density of *d*-electron states in site *m*, *N* - number of atoms in the system, $\varphi(r)$ - pair interatomic potential responsible for all non-*d* contributions into U :

$$\varphi(r) = A\exp(-ar) \quad , \tag{3}$$

where A and a are the parameters. The Gaussian form is used for $n_m(\varepsilon)$:

$$n_m(\varepsilon) = 10\sqrt{1/(2\pi\mu_m)}\; e^{-\frac{\varepsilon^2}{2\mu_m}} \quad . \tag{4}$$

Here, μ_m is the second moment of $n_m(\varepsilon)$:

$$\mu_m = \sum_{l=1, l\neq m}^{N} \beta^2\left(\left|\mathbf{r}_{ml}\right|\right) \quad , \tag{5}$$

where

$$\beta(r) = B\exp(-br) \quad , \tag{6}$$

B and *b* are the parameters.

The first term in the right-side part of Eq. (2) is the *d*-electron contribution to the potential energy, U_d . Using Eq. (4) , it can be written as

$$U_d = -10\sum_{m=1}^{N}\sqrt{\frac{\mu_m}{2\pi}}e^{-\frac{\varepsilon_F^2}{2\mu_m}} \tag{7}$$

The average of *U* with respect to the HS system per atom is given by

$$\langle U\rangle_{HS} = \langle U_d\rangle_{HS} + 2\pi\rho\int_0^\infty \varphi(r)g_{HS}(r)r^2\mathrm{d}r \quad , \tag{8}$$

where $g(r)$ is the radial distribution function, ρ - mean atomic density,

$$\langle U_d\rangle_{HS} = -10\sqrt{\frac{\langle\mu_m\rangle_{HS}}{2\pi}}e^{-\frac{\varepsilon_F^2}{2\langle\mu_m\rangle_{HS}}} \quad . \tag{9}$$

Here,

$$\langle\mu_m\rangle_{HS} = 4\pi\rho\int_0^\infty \beta^2(r)g_{HS}(r)r^2\mathrm{d}r \quad . \tag{10}$$

In [1] was found that the magnitude of $e^{-\frac{\varepsilon_F^2}{2\langle\mu_m\rangle_{HS}}}$ is a constant for each metal since it depends on the number of *d* electrons per atom, N_d , only. As a result, Eq. (9) can be rewritten by the following way:

$$\langle U_d\rangle_{HS} = -10 f\left(N_d\right)\sqrt{\frac{\langle\mu_m\rangle_{HS}}{2\pi}} \quad . \tag{11}$$

Thus, the right-side part of inequality (1) per atom, F_{var} , becomes the following:

$$F_{\mathrm{var}} = \frac{3}{2}k_bT - \frac{10}{\sqrt{2\pi}}\, f\left(N_d\right)\sqrt{\langle\mu_m\rangle_{HS}} + 2\pi\rho\int_0^\infty \varphi(r)g_{HS}(r)r^2\mathrm{d}r - TS_{HS} \,. \tag{12}$$

To convert Eq. (12) to the wave space we use the relation

$$g(r) = 1 + \frac{1}{2\rho\pi^2}\int_0^\infty [S(q)-1]\frac{\sin(qr)}{qr}q^2 \mathrm{d}q \quad . \tag{13}$$

As a result,

$$F_{\mathrm{var}} = \frac{3}{2}k_b T - \frac{10 f(N_d)}{\sqrt{2\pi}}\sqrt{\tilde{\mu}_{HS}} + \frac{2Aa}{\pi}\int_0^\infty (S_{HS}(q)-1)\left[\frac{q}{(a^2+q^2)}\right]^2 \mathrm{d}q + \frac{4\pi\rho A}{a^3} - TS_{HS} \tag{14}$$

where

$$\tilde{\mu}_{HS} = \frac{\pi\rho B^2}{b^3} + \frac{8bB^2}{\pi}\int_0^\infty (S_{HS}(q)-1)\left[\frac{q}{(4b^2+q^2)}\right]^2 \mathrm{d}q \quad . \tag{15}$$

The Wertheim-Thiele [3, 4] exact $S_{HS}(q)$ obtained in the Percus-Yevick approximation [5] can be used for actual calculations.

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