PHYSICS

A New Reference System in the Variational Method of Thermodynamic Perturbation Theory

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The variational method in thermodynamic perturbation theory is actively used for calculating the thermodynamic properties of metal melts. In many cases, it is the model of hard spheres (HSs) [1−5] that is most frequently used as the reference system, which makes it possible to obtain reasonably good quantitative results despite its simplicity. The use of other reference systems (the system with inverse-power potential [6], the model of single-component plasma [6], the model of charged hard spheres [7], and the system with a hard-core (HC) Yukawa potential [8]), as a rule, results in minor improvement of the results of calculation in comparison with the use of the HS reference system and, sometimes, even to their degradation [6]. It should be noted that all listed reference systems different from the HSs are systems with pure repulsive pair potentials, and the correction of the HS model occurs only due to "softening" of the repulsive part of the potential. Therefore, it is of interest to choose the reference system with the presence of attraction forces between the atoms and to analyze its applicability within the framework of the variational method.

In this work, as the reference system, we take the square-well (SW) model in which the pair potential has the attractive part:

$$\varphi_{SW}(r) = \begin{cases} \infty, & r < \sigma, \\ \varepsilon, & \sigma \leq r < \lambda\sigma, \\ 0, & r \geq \lambda\sigma, \end{cases} \tag{1}$$

where σ is the HC diameter; ε and $\sigma(\lambda - 1)$ are the depth and width of the well, respectively; $\varphi_{SW}(r)$ refers to the family of the HC potentials described by the formula

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$$\varphi_{HC}(r) = \begin{cases} \infty, & r < \sigma, \\ \phi(r), & r \geq \sigma. \end{cases} \tag{2}$$

From Eqs. (1) and (2), it follows that

$$\phi_{SW}(r) = \begin{cases} 0, & r < \sigma, \\ \varepsilon, & \sigma \leq r < \lambda\sigma, \\ 0, & r \geq \lambda\sigma. \end{cases} \tag{3}$$

The Fourier image $\phi_{SW}(r)$ is

$$\phi_{SW}(q)$$
$$= \frac{4\pi\varepsilon}{q^3}[\sin(\lambda x) - \sin x - \lambda x \cos(\lambda x) + x \cos x], \tag{4}$$

where $x = q\sigma$.

We use the SW reference system described in two different variants of the theory of fluids: in the random-phase approximation (RPA) and in the mean spherical approximation (MSA). The first approach was previously proposed in [9, 10]. The second approach is proposed in this study. The subsequent transformations are given in this study in general form for both considered variants of description of the SW model.

In the RPA, the direct correlation function $c(r)$ and its Fourier image $c(q)$ in the direct and reciprocal space, respectively, are written as follows:

$$c_{RPA}(r) = c_0(r) - \beta\varphi_1(r), \tag{5}$$
$$c_{RPA}(q) = c_0(q) - \beta\varphi_1(q), \tag{6}$$

where $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, T is the absolute temperature, $\varphi_1(r)$ is the part of the pair potential being the perturbation with respect to the pair potential of the system chosen in the framework of the RPA reference system, the accessory to which is designated by the subscript 0.

For HC potential (2), Eqs. (5) and (6) are transformed to the following form:

$$c_{\text{RPA}}(r) = \begin{cases} c_{\text{HS}}(r), & r < \sigma, \\ -\beta\phi(r), & r \geq \sigma, \end{cases} \tag{7}$$

$$c_{\text{RPA}}(q) = c_{\text{HS}}(q) - \beta\phi(q). \tag{8}$$

For describing $c_{\text{HS}}(r)$ and $c_{\text{HS}}(q)$, we use the known analytical expressions (see [9, 10]).

In the MSA case, the expressions for the structure functions are determined by the semi-analytical (SA) method developed in [11−13] within the framework of which $c(r)$ and $c(q)$ have more complex form than that in the RPA

$$c_{\text{MSA-SA}}(r) = \begin{cases} \displaystyle\sum_{m=0}^{n} b_m\left(\frac{r}{\sigma}\right)^m, & r < \sigma, \\ -\beta\phi(r), & r \geq \sigma, \end{cases} \tag{9}$$

where b_m are the coefficients determined from the condition of vanishing pair correlation function $g(r)$ inside the HC (for our purposes, it suffices to take $n = 5$)

$$c_{\text{MSA-SA}}(q) = -\beta\phi(q) + \left(\frac{4\pi}{q^3}\right)\Bigg\{ \sum_{m=1}^{n+2} x^{2-m}\frac{\partial^m \sin x}{\partial x^m} \\ \times \sum_{l=0}^{n} b_l \prod_{k=0}^{m-2}(l+1-k) \\ + \sum_{m=1}^{(n+1)/2} \frac{(-1)^{m+1}(2m)!b_{2m-1}}{x^{2m-1}} \Bigg\} \tag{10}$$

(for odd values of n).

Let us write the right-hand side of Eqs. (8) and (10) in general form as $[\Delta c(q) - \beta\phi(q)]$, where

$$\Delta c(q) = \begin{cases} c_{\text{HS}}(q), & \text{RPA}, \\ \left(\dfrac{4\pi}{q^3}\right)\Bigg\{\displaystyle\sum_{m=1}^{n+2} x^{2-m}\dfrac{\partial^m \sin x}{\partial x^m}\sum_{l=0}^{n} b_l \prod_{k=0}^{m-2}(l+1-k) \\ \quad + \displaystyle\sum_{m=1}^{(n+1)/2} \dfrac{(-1)^{m+1}(2m)!b_{2m-1}}{x^{2m-1}}, & \text{MSA-SA}. \end{cases} \tag{11}$$

For implementing the variational method, it is necessary to have convenient (desirably analytical) expressions for the structural factor $a(q)$ and the entropy S of the chosen reference system.

The structural factor of the fluid SW within the framework of the chosen approximations is written in general form as follows:

$$a_{\text{SW}}(q) = \frac{1}{1 - \rho\Delta c(q) + \beta\rho\phi_{\text{SW}}(q)}, \tag{12}$$

where ρ is the average atomic density.

For finding S_{SW}, we express the SW thermodynamic characteristics of fluid through its corresponding HS characteristics:

$$E_{\text{SW}} = E_{\text{HS}} + \Delta E_{\text{SW}}, \tag{13}$$

$$U_{\text{SW}} = U_{\text{HS}} + \Delta U_{\text{SW}}, \tag{14}$$

$$S_{\text{SW}} = S_{\text{HS}} + \Delta S_{\text{SW}}, \tag{15}$$

where E is the internal energy; U is the potential energy; and ΔE_{SW}, ΔU_{SW}, ΔS_{SW} are the additives caused by the difference between the SW and HS models.

Further, for deriving the ΔS_{SW} contribution, we use the thermodynamic relation

$$\left(\frac{\partial S}{\partial T}\right)_\rho = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_\rho, \tag{16}$$

written as

$$\left(\frac{\partial(\Delta S_{\text{SW}})}{\partial T}\right)_\rho = \frac{1}{T}\left(\frac{\partial(\Delta E_{\text{SW}})}{\partial T}\right)_\rho. \tag{17}$$

Because $U_{\text{HS}} = 0$, Eq. (14) results in $\Delta U_{\text{SW}} = U_{\text{SW}}$. On the other hand, the transition from the HS potential to the SW potential does not change the kinetic energy in the system and, hence, $\Delta E_{\text{SW}} = \Delta U_{\text{SW}}$. As a result, we come to the equality $\Delta E_{\text{SW}} = U_{\text{SW}}$, which enables us to rewrite Eq. (17) as follows:

$$\left(\frac{\partial(\Delta S_{\text{SW}})}{\partial T}\right)_\rho = \frac{1}{T}\left(\frac{\partial U_{\text{SW}}}{\partial T}\right)_\rho \tag{18}$$

(from now on, all thermodynamic values are written per atom), where

$$U_{\text{SW}} = 2\pi\rho \int_0^\infty \varphi_{\text{SW}}(r)g_{\text{SW}}(r)r^2 dr \\ = 2\pi\rho \int_\sigma^{\lambda\sigma} \phi_{\text{SW}}(r)g_{\text{SW}}(r)r^2 dr. \tag{19}$$

Using the Fourier relation between $g(r)$ and $a(q)$, we transform Eq. (19) to the form

$$U_{\text{SW}} = \frac{2}{3}\pi\rho\sigma^3\varepsilon(\lambda^3 - 1) \\ + \frac{1}{4\pi^2}\int_0^\infty [a_{\text{SW}}(q) - 1]\phi_{\text{SW}}(q)q^2 dq. \tag{20}$$

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Table 1. Values of SW parameters corresponding to a free-energy minimum of liquid Na at $T = 373$ K using various approaches to the description of the SW reference system

Approximations	σ, a.u.	λ	ε, a.u.
RPA	6.215	1.926	-0.000365
MSA	6.149	1.751	-0.000319

From Eqs. (20) and (12), we find

$$\left(\frac{\partial U_{SW}}{\partial T}\right)_\rho = \frac{\rho k_B}{4\pi^2}\int_0^\infty \frac{\phi_{SW}^2(q)q^2 dq}{[k_B T(1-\Delta c(q)) + \rho\phi_{SW}(q)]^2}. \quad (21)$$

The integration $\int \frac{dT}{T}\left(\frac{\partial U_{SW}}{\partial T}\right)_\rho$ results in the following expression:

$$\Delta S_{SW} = \frac{k_B \rho}{4\pi^2}\int_0^\infty \left[-\frac{1}{\rho^2\phi_{SW}^2(q)}\left(\ln\left|\frac{k_B}{a_{SW}(q)}\right|\right.\right.$$
$$\left.\left. + (1-\rho\Delta c(q))a_{SW}(q)\right) + C\right]\phi_{SW}^2(q)q^2 dq, \quad (22)$$

where C is the integration constant found from the condition that, at $\varepsilon = 0$ or at $\lambda = 1$, $\Delta S_{SW} = 0$:

$$C = \frac{\ln|k_B(1-\rho\Delta c(q))| + 1}{\rho^2\phi_{SW}^2(q)}. \quad (23)$$

As a result, we obtain

$$\Delta S_{SW} = \frac{k_B}{4\pi^2\rho}\int_0^\infty q^2(\ln|(1-\rho\Delta c(q))a_{SW}(q)|$$
$$ - (1-\rho\Delta c(q))a_{SW}(q) + 1)dq. \quad (24)$$

For the RPA case, a similar derivation is carried out in [9], and the following expression as a special case of Eq. (24) was obtained:

$$\Delta S_{SW-RPA}$$
$$= \frac{k_B}{4\pi^2\rho}\int_0^\infty q^2\left(\ln\left|\frac{a_{SW-RPA}(q)}{a_{HS}(q)}\right| - \frac{a_{SW-RPA}(q)}{a_{HS}(q)} + 1\right)dq. \quad (25)$$

For liquid metals, the Helmholtz energy F in the variational method with the SW reference system is determined by the inequality

$$F \leq \frac{3}{2}k_B T + U_e + \langle U\rangle_{SW} - T(S_{SW} + S_e), \quad (26)$$

where U is the sum of structure-dependent contributions to the potential energy of the system; U_e and S_e are the electron contributions to the internal energy and the entropy, respectively. A detailed description of the pseudo-potential approach used and the contributions to the right-hand side of Eq. (26) in the reciprocal space are given in [9, 10]. In the same studies, the values of the parameters of the pseudo-potential are given for Na.

The applicability of the new reference system in two approximations (RPA and MSA) is analyzed by the example of liquid Na at $T = 373$ K ($\rho = 0.0036$ a.u. [14]). In Table 1, we list the values of the SW parameters corresponding to the local minimum of the Helmholtz energy in each of the calculation variants. It should be noted that, contrary to the SW–RPA case, where the minimization was carried out on two parameters at a fixed value of λ (see [9, 10]), the use of the SW–MSA reference system enables us to carry out the minimization on all three SW parameters. The obtained thermodynamic properties corresponding to the values of parameters from Table 1 are listed in Table 2 in comparison with experimental data [15] and with the results of the HS variational method, where the minimum of the Helmholtz energy was achieved for $\sigma = 6.254$ a.u.

The analysis of the results of calculation of the thermodynamic properties shows that the use of the SW reference system in both variants of calculation (SW–RPA and SW–MSA) gives a deeper minimum of the free energy, but, at the same time, the agreement with the experimental data is worse than with using the HS reference system. The agreement with the experiment worsens in this case with increasing the depth of this minimum, i.e., when passing from SW–MSA to SW–RPA.

The best agreement with the experiment of the results of the HS variational method is related to the

Table 2. Thermodynamic properties of liquid Na at $T = 373$ K obtained by the variational method with various reference systems and the experimental data of [15]

Parameter	SW–RPA	SW–MSA	HS	(SW–MSA)	Experiment
F, eV	-6.464	-6.426	-6.397	(-6.393)	-6.399
E, eV	-6.232	-6.190	-6.156	(-6.149)	-6.149
S/k_B	7.22	7.38	7.49	(7.59)	7.79

Note: In brackets we give the result close to the Helmholtz-energy minimum with the HS reference system obtained for $\sigma = 6.10$ a.u., $\lambda = 1.751$, and $\varepsilon = -0.000236$ a.u.

fact that, under its use, we additionally applied the condition $P = 0$ (where P is the pressure in the system) for fulfilling which we minimized the free energy also on the atomic density instead of only on the parameter σ, whereas its fixed experimental value is taken within the framework of the SW variational method. In this case, in minimizing the SW−MSA reference system on the surface of the free energy $\sigma-\varepsilon$ for the fixed value of λ (1.751) to take a point close to the point of minimum F obtained in the case of the HS reference system (Table 2), the agreement with the experiment for the internal energy and the entropy is improved in comparison with the HS variational calculation. At this

point, the packing density η equal to $\dfrac{\pi\rho\sigma^3}{6}$ becomes

close to η_{HS} at the minimum point under consideration (approximately 0.43).

Thus, in this study, we principally showed the utility of using the SW model as the reference system in the variational method and that the use of the SW−MSA variant is promising. For a more complete analysis of the accuracy of the proposed approach, we further assume to carry out detailed investigation of the region of variation of parameters and an additional variation of the free energy with the melt atomic density. In addition, an increase in the number of objects of investigation (other pure metals and binary systems) can introduce greater clarity when analyzing the serviceability of the SW−MSA reference system.

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