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Straightforward calculation of the WCA entropy and internal energy for liquid metals

N.E. Dubinin*, A.A. Yuryev, N.A. Vatolin

Institute of Metallurgy of the Ural Division of the Russian Academy of Sciences, Amundsen Str., 101, Ekaterinburg 620016, Russia

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ABSTRACT

The explicit expression for the reference-system entropy within the Weeks–Chandler–Andersen (WCA) approximation is derived and applied to straightforward calculation of the WCA entropy and internal energy of liquid alkali metals. It is shown that the procedure used gives the same results as a numerical differentiation of the Helmholtz free energy but with a smaller computing complexity.

1. Introduction

The Weeks–Chandler–Andersen (WCA) method [1,2] of the thermodynamic perturbation theory (TPT) [3] is widely used for the structure and thermodynamics study of different kinds of real fluids [4–12]. A number of works have analyzed accuracy and validity of the WCA approximation [13–18]. In some special cases, there are analytical formulas obtained from molecular dynamics simulations for different thermodynamic functions of the WCA fluid [4,11,18–21]. However, the explicit expression for the entropy in a general form has not been used in this approximation up to now in concrete calculations in particular for liquid metals and their alloys. It has been calculated numerically as a partial derivative of the Helmholtz free energy with respect to the temperature at the constant volume [5,6,10]. Here, we find the expression for the WCA reference-system entropy in the explicit form not exceeding the frameworks of the original WCA method [1,2] and apply it to liquid metal thermodynamics calculations.

2. WCA method

For the system with a potential energy, U, represented as the sum of pair interactions only, that in the integral form is:

$$U = 2\pi\rho \int_0^\infty \varphi(r) g(r) r^2 dr \tag{1}$$

(where ρ is the number density; $\varphi(r)$ is the pair interatomic potential; $g(r)$ is the pair correlation function), the thermodynamic perturbation theory gives the following separations [3]:

$$U = U_0 + U_1, \tag{2}$$

$$\varphi(r) = \varphi_0(r) + \varphi_1(r), \tag{3}$$

where U_0 and $\varphi_0(r)$ are the reference-system terms; U_1 and $\varphi_1(r)$ are perturbations. Hereafter, all thermodynamic functions will be written per atom.

The Helmholtz free energy, F, in the first-order TPT expansion (that denotes the high temperature approximation) is [3]:

$$F = F_0 + \left\langle U_1 \right\rangle_0, \tag{4}$$

where

$$\left\langle U_1 \right\rangle_0 = 2\pi\rho \int_0^\infty \varphi_1(r) g_0(r) r^2 dr. \tag{5}$$

The WCA approach is applicable to fluids with a soft repulsive part of the pair potential and the WCA separation of $\varphi(r)$ is written

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* Corresponding author. Tel.: +7 343 232 90 78; fax: +7 343 267 91 86.
E-mail address: ned67@mail.ru (N.E. Dubinin).

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as follows [1]:

$$\varphi_{0\mathrm{WCA}}(r)=\begin{cases}\varphi(r)-\varphi(r_m), & r<r_m\\ 0, & r\geq r_m\end{cases}, \tag{6}$$

$$\varphi_{1\mathrm{WCA}}(r)=\begin{cases}\varphi(r_m), & r<r_m\\ \varphi(r), & r\geq r_m\end{cases}, \tag{7}$$

where r_m is the position of the first minimum of $\varphi(r)$.

The main approximation in the framework of the WCA approach is [1]:

$$y_{0\mathrm{WCA}}(r)=y_{\mathrm{HS}}(r), \tag{8}$$

where "HS" denotes the hard-sphere system; $y(r)$ is the cavity correlation function:

$$y(r)=g(r)e^{\beta\varphi(r)}. \tag{9}$$

Here $\beta=1/(k_BT)$; k_B is the Boltzmann constant; T is the temperature. From Eqs. (8) and (9),

$$g_{0\mathrm{WCA}}(r)=y_{\mathrm{HS}}(r)e^{-\beta\varphi_{0\mathrm{WCA}}(r)}. \tag{10}$$

According to Eq. (9),

$$y_{\mathrm{HS}}(r)=g_{\mathrm{HS}}(r)e^{\beta\varphi_{\mathrm{HS}}(r)}, \tag{11}$$

and since $\varphi_{\mathrm{HS}}(r)=0$ at $r\geq\sigma$, where σ is the HS diameter,

$$y_{\mathrm{HS}}(r)=g_{\mathrm{HS}}(r),\quad r\geq\sigma. \tag{12}$$

The Helmholtz free energy of the WCA reference system, $F_{0\mathrm{WCA}}$, was obtained in Refs. [1,2] using Eq. (10):

$$F_{0\mathrm{WCA}}=F_{\mathrm{HS}}-2\pi\rho k_BT\int_0^\infty(g_{0\mathrm{WCA}}(r)-g_{\mathrm{HS}}(r))r^2dr, \tag{13}$$

where $F_{\mathrm{HS}}=3k_BT/2-TS_{\mathrm{HS}}$; S is the entropy.

Eqs. (4), (5), and (13) give the following expression:

$$F_{\mathrm{WCA}}=F_{\mathrm{HS}}-2\pi\rho k_BT\int_0^\infty(g_{0\mathrm{WCA}}(r)-g_{\mathrm{HS}}(r))r^2dr+2\pi\rho\times\int_0^\infty\varphi_{1\mathrm{WCA}}(r)g_{0\mathrm{WCA}}(r)r^2dr. \tag{14}$$

Taking into account Eq. (7) for all r and Eqs. (10), (6), and (12) for only distances higher than r_m, the last integral in Eq. (14) can be written as follows:

$$\int_0^\infty\varphi_{1\mathrm{WCA}}(r)g_{0\mathrm{WCA}}(r)r^2dr=\varphi(r_m)\times\int_0^{r_m}g_{0\mathrm{WCA}}(r)r^2dr+\int_{r_m}^\infty\varphi(r)g_{\mathrm{HS}}(r)r^2dr. \tag{15}$$

Then add and subtract simultaneously the term $\varphi(r_m)\int_0^{r_m}g_{\mathrm{HS}}(r)r^2dr$ to the right-hand side of Eq. (15). The subtracted term together with the first term of the right-hand side of Eq. (15) give:

$$\varphi(r_m)\int_0^{r_m}g_{0\mathrm{WCA}}(r)r^2dr-\varphi(r_m)\int_0^{r_m}g_{\mathrm{HS}}(r)r^2dr=\varphi(r_m)\times\int_0^\infty(g_{0\mathrm{WCA}}(r)-g_{\mathrm{HS}}(r))r^2dr. \tag{16}$$

Due to Eq. (6) and the property of $g_{\mathrm{HS}}(r)$ to be equal to zero at $r<\sigma$, the added term can be transformed as follows:

$$\varphi(r_m)\int_0^{r_m}g_{\mathrm{HS}}(r)r^2dr=\int_\sigma^{r_m}\varphi(r)g_{\mathrm{HS}}(r)r^2dr-\int_\sigma^{r_m}\varphi_0(r)g_{\mathrm{HS}}(r)r^2dr. \tag{17}$$

Summarizing the right-hand sides of Eqs. (16) and (17) with the last term of Eq. (15) leads to transformation of Eq. (14) to the convenient for the further calculations form:

$$F_{\mathrm{WCA}}=F_{\mathrm{HS}}+2\pi\rho\left[-k_BT\int_0^\infty(g_{0\mathrm{WCA}}(r)-g_{\mathrm{HS}}(r))r^2dr+\int_\sigma^\infty\varphi(r)g_{\mathrm{HS}}(r)r^2dr-\int_\sigma^{r_m}\varphi_{0\mathrm{WCA}}(r)g_{\mathrm{HS}}(r)r^2dr+\varphi(r_m)\times\int_0^\infty(g_{0\mathrm{WCA}}(r)-g_{\mathrm{HS}}(r))r^2dr\right]. \tag{18}$$

Note that the simplification of the WCA suggested by Ben-Amotz and Stell [22] gives Eq. (18) without its last term.

The original WCA condition for the σ-value defining is [1]:

$$\int_0^\infty(g_{0\mathrm{WCA}}(r)-g_{\mathrm{HS}}(r))r^2dr=0. \tag{19}$$

Due to condition (19), Eq. (18) becomes:

$$F_{\mathrm{WCA}}=F_{\mathrm{HS}}+2\pi\rho\int_\sigma^\infty\varphi(r)g_{\mathrm{HS}}(r)r^2dr-2\pi\rho\int_\sigma^{r_m}\varphi_{0\mathrm{WCA}}(r)g_{\mathrm{HS}}(r)r^2dr. \tag{20}$$

Another condition for the determination of the HS diameter was suggested by Lado [23]. However, it leads to the different expression for F_{WCA} and is not considered in the present work.

Earlier, the entropy and internal energy, E, from Eq. (20) were being calculated numerically [10]:

$$S_{\mathrm{WCA}}\equiv S_{0\mathrm{WCA}}=-\left(\frac{\partial F_{\mathrm{WCA}}}{\partial T}\right)_\rho, \tag{21}$$

$$E_{\mathrm{WCA}}=F_{\mathrm{WCA}}+TS_{\mathrm{WCA}}. \tag{22}$$

In the next section the explicit expressions for these thermodynamic functions will be given.

3. Derivation of the expression for the reference-system WCA entropy

Let us represent the WCA entropy as follows:

$$S_{0\mathrm{WCA}}=S_{\mathrm{HS}}+\Delta S_{0\mathrm{WCA}}, \tag{23}$$

where $\Delta S_{0\mathrm{WCA}}$ is an additional term aroused due to the difference between potentials $\varphi_{\mathrm{HS}}(r)$ and $\varphi_{0\mathrm{WCA}}(r)$.

To obtain $\Delta S_{0\mathrm{WCA}}$, we use the procedure analogous to that used in Ref. [24] for obtaining the entropy of the square-well fluid. Since the potential energy of the HS system is equal to zero and therefore the difference between the HS internal energy and the reference-system internal energy is equal to U_0, the well-known thermodynamic relation,

$$\left(\frac{\partial S}{\partial T}\right)_\rho=\frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_\rho, \tag{24}$$

taking into account Eq. (23), can be rewritten as:

$$\left(\frac{\partial(\Delta S_{0\mathrm{WCA}})}{\partial T}\right)_\rho=\frac{1}{T}\left(\frac{\partial U_{0\mathrm{WCA}}}{\partial T}\right)_\rho, \tag{25}$$

where, in accordance with Eq. (1),

$$U_{0\mathrm{WCA}}=2\pi\rho\int_0^\infty\varphi_{0\mathrm{WCA}}(r)g_{0\mathrm{WCA}}(r)r^2dr. \tag{26}$$

Then

$$\Delta S_{0\mathrm{WCA}}=\int\frac{1}{T}\left(\frac{\partial U_{0\mathrm{WCA}}}{\partial T}\right)_\rho dT. \tag{27}$$

From Eqs. (26) and (27) using Eq. (10) one obtains:

$$\Delta S_{0\mathrm{WCA}} = \frac{2\pi\rho}{k_\mathrm{B}}\left[\frac{k_\mathrm{B}}{T}\int_0^{r_m}\varphi_{0\mathrm{WCA}}(r)y_\mathrm{HS}(r)e^{-\beta\varphi_{0\mathrm{WCA}}(r)}r^2dr + k_\mathrm{B}^2 \times \int_0^{r_m} y_\mathrm{HS}(r)e^{-\beta\varphi_{0\mathrm{WCA}}(r)}r^2dr + \mathrm{Const}\right]. \quad (28)$$

To define unknown constant we use the condition $\Delta S_{0\mathrm{WCA}}=0$ at $\varphi_{0\mathrm{WCA}}(r)=\varphi_\mathrm{HS}(r)$:

$$\mathrm{Const} = -k_\mathrm{B}^2\int_\sigma^{r_m} g_\mathrm{HS}(r)r^2dr. \quad (29)$$

As a result,

$$\Delta S_{0\mathrm{WCA}} = \frac{2\pi\rho}{T}\int_0^{r_m}\varphi_{0\mathrm{WCA}}(r)g_{0\mathrm{WCA}}(r)r^2dr + 2\pi\rho k_\mathrm{B}\left(\int_0^{r_m} g_{0\mathrm{WCA}}(r)r^2dr - \int_\sigma^{r_m} g_\mathrm{HS}(r)r^2dr\right) = \frac{U_{0\mathrm{WCA}}}{T} + 2\pi\rho k_\mathrm{B}\int_0^\infty (g_{0\mathrm{WCA}}(r) - g_\mathrm{HS}(r))r^2dr, \quad (30)$$

and

$$S_\mathrm{WCA} \equiv S_{0\mathrm{WCA}} = S_\mathrm{HS} + \frac{U_{0\mathrm{WCA}}}{T} + 2\pi\rho k_\mathrm{B}\int_0^\infty (g_{0\mathrm{WCA}}(r) - g_\mathrm{HS}(r))r^2dr. \quad (31)$$

Then, from Eqs. (18) and (31),

$$E_\mathrm{WCA} = \frac{3k_\mathrm{B}T}{2} + U_{0\mathrm{WCA}} + 2\pi\rho\left[\int_\sigma^\infty \varphi(r)g_\mathrm{HS}(r)r^2dr - \int_\sigma^{r_m}\varphi_{0\mathrm{WCA}}(r)g_\mathrm{HS}(r)r^2dr + \varphi(r_m)\int_0^\infty (g_{0\mathrm{WCA}}(r) - g_\mathrm{HS}(r))r^2dr\right]. \quad (32)$$

Taking into account Eq. (19),

$$S_\mathrm{WCA} = S_\mathrm{HS} + \frac{U_{0\mathrm{WCA}}}{T}, \quad (33)$$

and

$$E_\mathrm{WCA} = \frac{3k_\mathrm{B}T}{2} + U_{0\mathrm{WCA}} + 2\pi\rho\left[\int_\sigma^\infty \varphi(r)g_\mathrm{HS}(r)r^2dr - \int_\sigma^{r_m}\varphi_{0\mathrm{WCA}}(r)g_\mathrm{HS}(r)r^2dr\right]. \quad (34)$$

Equations obtained lead to significant simplification of the WCA-calculation procedure and will be used in the next section for calculating the entropy and internal energy of liquid alkali metals.

4. Calculations for liquid alkali metals

As a rule, to construct an effective pair potential for simple metal the pseudopotential theory is used (in atomic units (a.u.)):

$$\varphi(r) = \frac{z^2}{r} + \frac{1}{8\pi^2\rho}\int_0^\infty F(q)\frac{\sin(qr)}{qr}q^2dq, \quad (35)$$

where z is the valence and $F(q)$is the energy–wavenumber characteristic:

$$F(q) = -\frac{q^2\omega^2(q)}{8\pi\rho}\left[(\varepsilon_\mathrm{H}(q)-1)^{-1} + (1-f(q))\right]^{-1}, \quad (36)$$

Table 1
The entropy and internal energy of liquid alkali metals calculated using Eqs. (33) and (34) at $T=373$ K.

	Na	K	Rb	Cs
S/k_B	8.05	9.80	11.18	12.41
E (eV)	−6.12	−5.38	−4.98	−4.79

Here $\omega(q)$ is the form-factor of the unscreened ion pseudopotential, $\omega(r)$, which is here the Animalu–Heine model pseudopotential [25] in the local approximation [26] (the corresponding pseudopotential parameters are also listed in Ref. [26]); $\varepsilon_\mathrm{H}(q)$ is the Hartree dielectric function; $f(q)$ is the exchange-correlation function, which is taken here in the Vashishta–Singwi form [27]. For simple metals the additional terms, the electron energy, U_e, and the electron entropy, $S_e = zT\left(\pi k_\mathrm{B}/k_\mathrm{F}\right)^2$ (where $k_\mathrm{F} = (3z\rho\pi^2)^{1/3}$ is the Fermi wave vector), must be added to the right-hand sides of Eqs. (34) and (33), respectively. The free-electron gas energy is calculated by us within the Nozieres–Pines approximation [28]. The contribution S_HS obtained from the compressibility equation is used [29].

For concrete calculations, one needs function $g_{0\mathrm{WCA}}(r)$ at $r<\sigma$. Since $\varphi_\mathrm{HS}(r)=\infty$ at $r<\sigma$, the function $y_\mathrm{HS}(r)$ (Eq. (11)) is not determined in this region in a general case. At all r, the exact analytical solution for $y_\mathrm{HS}(r)$ exists within the Percus–Yevick (PY) [30] approximation only:

$$y_\mathrm{HS-PY}(r) = \begin{cases} -c_\mathrm{HS-PY}(r), & r<\sigma \\ g_\mathrm{HS-PY}(r), & r\geq\sigma \end{cases}, \quad (37)$$

where $c(r)$ is the direct correlation function; $c_\mathrm{HS-PY}(r)$ and $g_\mathrm{HS-PY}(r)$ are the analytical Wertheim–Thiele expressions [31,32] being used in our work.

Results obtained for liquid Na, K, Rb, and Cs at $T=373$ K are listed in Table 1. It is found that the straightforward calculation suggested gives the same results for the WCA entropy and internal energy as ones obtained by the numerical differentiation of the WCA Helmholtz free energy (Eqs. (21) and (22)).

5. Conclusion

The explicit expression is derived for the entropy of the reference system in the WCA approximation. On the basis of this expression the straightforward calculation procedure for the WCA thermodynamics is suggested. The usefulness of this procedure is successfully shown on the example of liquid alkali metals.

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