Gibbs–Bogoliubov variational procedure with the square-well reference system

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Abstract

For the first time, the square-well (SW) model is used as a reference system in the thermodynamic variational calculations for liquids. The SW system is taken within the random phase approximation. To apply this approach to simple metals, the local Animalu–Heine model pseudopotential, the Vashishta–Singwi exchange-correlation function, and the Nozieres–Pines exchange-correlation energy are used. Thermodynamics and structure of liquid Na at $T = 373$ K are studied. We found that there are several areas of the SW parameters where the solution is stable. We chose the best of such areas in which the calculated structure factor is in good agreement with the experimental one. Then the Helmholtz free energy is minimized in this area with respect to the hard-core diameter and the SW depth at the fixed SW width. It was found that the SW variational procedure gives an upper bound of the Helmholtz free energy which is lower than that in the hard-sphere variational procedure, and that the obtained thermodynamic properties are in reasonable agreement with the experiment.

1 Introduction

The variational method [1] based on the Gibbs–Bogoliubov inequality is widely applied for thermodynamic calculations of the liquid metal state. Usually, the hard-sphere (HS) model is used as a reference system in such calculations [2–7]. Nevertheless, there have been a number of attempts to use other reference systems for these purposes: the one-component plasma (OCP) model [8], the charged HS (CHS) model [9–11], and the HS Yukawa (HSY) one [12, 13]. In [8], the numerical solution of the hypernetted chain approximation for the structure factor, $a(q)$, was used. For the CHS and

HSY, the exact solutions of the mean spherical approximation obtained by Palmer and Weeks [14] and by Waisman [15], respectively, have been used.

Here, the square-well (SW) model is suggested for the first time as a reference system in the thermodynamic variational calculations for simple liquid metals. We take the SW model in the framework of the random phase approximation (RPA) [16], because only in the RPA does the analytical expression for the structure factor of the SW fluid exist [17]. The expression for the SW fluid entropy corresponding to the RPA structure factor is obtained in the present work.

This method is applied to calculate the structure factor, the Helmholtz free energy, the internal energy, and the entropy of liquid Na at 373 K.

2 The random phase approximation for hard-core pair potentials

An arbitrary hard-core (HC)-based pair potential, $V_{HC}(r)$, can be written as

$$V_{HC}(r) = \begin{cases} \infty, & r < \sigma \\ \phi(r), & r \geq \sigma \end{cases}, \tag{1}$$

where σ is the HC diameter.

The direct correlation function, $c(r)$, in the RPA for the potential expressed by eq. (1) is

$$c_{RPA}(r) = \begin{cases} c_{HS}(r), & r < \sigma \\ -\beta\phi(r), & r \geq \sigma \end{cases}, \tag{2}$$

where $c_{HS}(r)$ is the direct correlation function of the HS fluid. We use the analytical form of $c_{HS}(r)$ obtained by Wertheim [18] and Thiele [19] in the Percus–Yevick approximation.

In this case the structure factor is

$$a_{RPA}(q) = \frac{1}{1 - \rho c_{HS}(q) + \beta\rho\phi(q)}, \tag{3}$$

where $c_{HS}(q)$ and $\phi(q)$ are Fourier transforms of $c_{HS}(r)$ and $\phi(r)$, respectively; ρ is the mean atomic density; $\beta = (k_B T)^{-1}$; k_B, the Boltzmann constant; T, temperature.

3 The square-well fluid

The SW pair potential is

$$V_{SW}(r) = \begin{cases} \infty, & r < \sigma \\ \varepsilon, & \sigma \le r < \lambda\sigma \\ 0, & r \ge \lambda\sigma \end{cases} \tag{4}$$

where ε and $\sigma(\lambda - 1)$ are the SW depth and SW width, respectively.
Thus,

$$\phi_{SW}(r) = \begin{cases} \varepsilon, & r < \lambda\sigma \\ 0, & r \ge \lambda\sigma \end{cases}. \tag{5}$$

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

$$\phi_{SW}(q) = 4\pi\varepsilon[\sin(\lambda x) - \sin(x) - \lambda x \cos(\lambda x) + x \cos(x)]/q^3, \tag{6}$$

where $x = q\sigma$, and in the long-wave limit

$$\phi_{SW}(q = 0) = \frac{4}{3}\pi\sigma^3\varepsilon(\lambda^3 - 1). \tag{7}$$

The potential energy of the SW fluid per atom, U_{SW}, can be found as follows:

$$U_{SW} = 2\pi\rho \int_0^\infty V_{SW}(r)g_{SW}(r)r^2 dr = 2\pi\rho \int_\sigma^{\lambda\sigma} \phi_{SW}(r)g_{SW}(r)r^2 dr, \tag{8}$$

where $g(r)$ is the pair correlation function.
Using the relation between $g(r)$ and $a(q)$,

$$g(r) = 1 + \frac{1}{2\pi^2\rho} \int_0^\infty [a(q) - 1]\frac{\sin(qr)}{qr}q^2 dq, \tag{9}$$

eq. (8) can be transformed into

$$U_{SW} = \frac{1}{2}\rho\phi_{SW}(q = 0) + \frac{1}{4\pi^2} \int_0^\infty [a_{SW}(q) - 1]\,\phi_{SW}(q)q^2 dq. \tag{10}$$

The entropy of the SW fluid per atom, S_{SW}, consists of three parts:

$$S_{SW} = S_{HS} + \Delta S_{SW} = S_{IG} + \Delta S_{HS} + \Delta S_{SW}, \tag{11}$$

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where S_{HS} is the entropy of the HS fluid; S_{IG} is the ideal gas entropy in atomic units (a.u.),

$$S_{IG} = k_B \left[\frac{5}{2} + \ln \left(\frac{1}{\rho} \left[\frac{k_B T m}{2\pi} \right]^{\frac{3}{2}} \right) \right]; \tag{12}$$

ΔS_{HS} and ΔS_{SW} are the additional terms derived from HS repulsion and SW attraction, respectively; m is the atomic mass. Here, ΔS_{HS} obtained from the compressibility equation is used [2]:

$$\Delta S_{HS} = k_B \left[\ln(1 - \eta) + \frac{3}{2} \left(1 - \frac{1}{(1 - \eta)^2} \right) \right], \tag{13}$$

where $\eta = (\pi \rho \sigma^3 / 6)$ is the packing fraction.

To obtain the contribution ΔS_{SW} we use the well-known relation

$$\left(\frac{\partial S}{\partial T} \right)_\rho = \frac{1}{T} \left(\frac{\partial E}{\partial T} \right)_\rho, \tag{14}$$

where E is the internal energy.

Since $E_{SW} = E_{HS} + U_{SW}$, eq. (14) can be rewritten as follows:

$$\left(\frac{\partial (\Delta S_{SW})}{\partial T} \right)_\rho = \frac{1}{T} \left(\frac{\partial U_{SW}}{\partial T} \right)_\rho. \tag{15}$$

Equation (3) for the SW potential is

$$a_{\text{SW-RPA}}(q) = \frac{1}{1 - \rho c_{HS}(q) + \beta \rho \phi_{SW}(q)}. \tag{16}$$

From eqs. (10) and (16) one gets

$$\left(\frac{\partial U_{SW}}{\partial T} \right)_\rho^{\text{RPA}} = \frac{\rho k_B}{4\pi^2} \int_0^\infty \frac{\phi_{SW}^2(q) q^2 dq}{[k_B T (1 - \rho c_{HS}(q)) + \rho \phi_{SW}(q)]^2}. \tag{17}$$

Integration $\int \frac{dT}{T} \left(\frac{\partial U_{SW}}{\partial T} \right)_\rho^{\text{RPA}}$ leads to the following expression for ΔS_{SW} within the RPA:

$$\Delta S_{\text{SW-RPA}} = \frac{k_B \rho}{4\pi^2} \int_0^\infty \left[-\frac{1}{\rho^2 \phi_{SW}^2(q)} \left(\ln \left| \frac{k_B}{a_{\text{SW-RPA}}(q)} \right| \right. \right.$$
$$\left. \left. + (1 - \rho c_{HS}(q)) a_{\text{SW-RPA}}(q) \right) + C \right] \phi_{SW}^2(q) q^2 dq, \tag{18}$$

where constant C is defined so as to satisfy the condition $\Delta S_{\text{SW-RPA}} = 0$ at $\varepsilon = 0$ or at $\lambda = 1$:

$$C = \frac{\ln |k_{\text{B}}(1 - \rho c_{\text{HS}}(q))| + 1}{\rho^2 \phi_{\text{SW}}^2(q)}. \tag{19}$$

As a result,

$$\Delta S_{\text{SW-RPA}} = \frac{k_B}{4\pi^2 \rho} \int_0^\infty q^2 (\ln |(1 - \rho c_{\text{HS}}(q)) a_{\text{SW-RPA}}(q)|$$
$$- (1 - \rho c_{\text{HS}}(q)) a_{\text{SW-RPA}}(q) + 1) \mathrm{d}q \tag{20}$$

and

$$S_{\text{SW-RPA}} = S_{\text{IG}} + \Delta S_{\text{HS}} + \Delta S_{\text{SW-RPA}}. \tag{21}$$

4 The Gibbs–Bogoliubov inequality for simple liquid metals with the SW reference system

The Gibbs–Bogoliubov inequality is (hereafter all terms are written per atom)

$$F \leq F_0 + \langle U_1 \rangle_0, \tag{22}$$

where F is the true Helmholtz free energy of the system; F_0 is the Helmholtz free energy of the reference system; U_1 is the perturbation:

$$U_1 = U - U_0, \tag{23}$$

where U is the potential energy of the whole system; U_0, the potential energy of the reference system.

The Helmholtz free energy of the reference system is

$$F_0 = \frac{3}{2} k_{\text{B}} T + U_0 - T S_0, \tag{24}$$

where S_0 is the entropy of the reference system.

Taking into account that as a reference system we use the SW model within the RPA, and using eqs. (22) and (24), the inequality (22) can be rewritten as follows:

$$F \leq \frac{3}{2} k_{\text{B}} T + \langle U \rangle_{\text{SW-RPA}} - T S_{\text{SW-RPA}}. \tag{25}$$

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For simple metals, the structure-independent electron gas contributions to the internal energy and entropy, U_e and S_e, respectively, should be added to the right side of the Gibbs–Bogoliubov inequality [2]:

$$F \leq \frac{3}{2}k_\mathrm{B}T + U_e + \langle U \rangle_\text{SW-RPA} - T(S_\text{SW−RPA} + S_e). \qquad (26)$$

It is convenient to transform the right side of eq. (26), F_var, to the wave space:

$$F_\text{var} = \frac{3}{2}k_\mathrm{B}T + E_0 + E_1 + E_2 + E_3 - T(S_\text{SW−RPA} + S_e), \qquad (27)$$

where E_0 is the free-electron gas energy; E_1 is the first-order pseudopotential term; E_2 is the band structure energy; E_3 is the Madelung energy.

The free-electron gas contributions to the internal energy and entropy, respectively, are (hereafter all characteristics are given in a.u.)

$$E_0 = \frac{3}{10}z k_\mathrm{F}^2 - \frac{z}{2}\left(\frac{\pi k_\mathrm{B}T}{k_\mathrm{F}}\right)^2 + E_\text{EC}, \qquad (28)$$

$$S_e = zT\left(\frac{\pi k_\mathrm{B}}{k_\mathrm{F}}\right)^2, \qquad (29)$$

where z is the valence; $k_\mathrm{F} = (3z\rho\pi^2)^{1/3}$ is the Fermi wave vector; E_EC is the exchange-correlation energy taken here in the Nozieres–Pines approach [20].

The pseudopotential-dependent terms in eq. (27) are expressed as follows:

$$E_1 = z \lim_{q \to 0}\left(\omega(q) + \frac{4\pi\rho z}{q^2}\right), \qquad (30)$$

$$E_2 = \frac{1}{2\pi^2\rho}\int_0^\infty a_\text{SW−RPA}(q)F(q)q^2\mathrm{d}q, \qquad (31)$$

where $\omega(q) = \rho\int \omega(r)e^{-i\vec{q}\vec{r}}\mathrm{d}^3\vec{r}$ is the form factor of the unscreened ion pseudopotential, $\omega(r)$; $F(q)$ is the energy wavenumber characteristic:

$$F(q) = -\frac{q^2}{8\pi\rho}\omega^2(q)[(\varepsilon_\mathrm{H}(q) - 1)^{-1} + (1 - f(q))]^{-1}. \qquad (32)$$

Here, $\varepsilon_\mathrm{H}(q)$ is the Hartree dielectric function and $f(q)$ is the exchange-correlation function. We use $f(q)$ suggested by Vashishta and Singwi [21].

In the present work, the Animalu–Heine model pseudopotential [22] in the local approximation [23], $\omega_{\mathrm{LAH}}(r)$, with the following form factor is used:

$$\omega_{\mathrm{LAH}}(q) = -\frac{4\pi\rho}{q^2}\left[(z - AR_{\mathrm{M}})\cos(qR_{\mathrm{M}}) + \frac{AR_{\mathrm{M}}\sin(qR_{\mathrm{M}})}{qR_{\mathrm{M}}}\right]$$
$$\times \exp\left[-0.03\left(\frac{q}{2k_{\mathrm{F}}}\right)^4\right], \tag{33}$$

where A and R_{M} are the pseudopotential parameters – well depth and model radius, respectively.

The Madelung energy depends only on the structure and is expressed as follows:

$$E_3 = \frac{z^2}{\pi}\int_0^\infty (a_{\mathrm{SW-RPA}}(q) - 1)\mathrm{d}q. \tag{34}$$

In principle, the Helmholtz free energy should be minimized with respect to the core diameter, the SW width, and the SW depth.

5 Results and discussion

We apply the formalism under consideration to calculate the structure factor and thermodynamic properties of liquid Na at $T = 373$K. Input data are listed in Table 1. The values of the pseudopotential parameters are taken from the work [23]. The experimental value of the mean atomic density was obtained in [24].

Table 1. Input data for the calculation (in a.u.).

R_{M}	A	ρ	λ
2.174	−0.2136	0.003602	1.926

Since the SW-RPA solution leads to unphysical behavior of the structure factor at some sets of the SW parameters, it is not possible to minimize the Helmholtz free energy with respect to all three SW parameters in a wide range of their values. Therefore, we perform minimization with respect to two parameters (HC diameter and SW depth) at fixed SW width. To do so, the region of the SW width values (1.85–1.93) where $a(q)$ is physically reasonable has been found. In this region we take λ (see Table 1) at which the best agreement between calculated and experimental [25] structure factors has been achieved (see Figure 1, where the structure factor obtained by
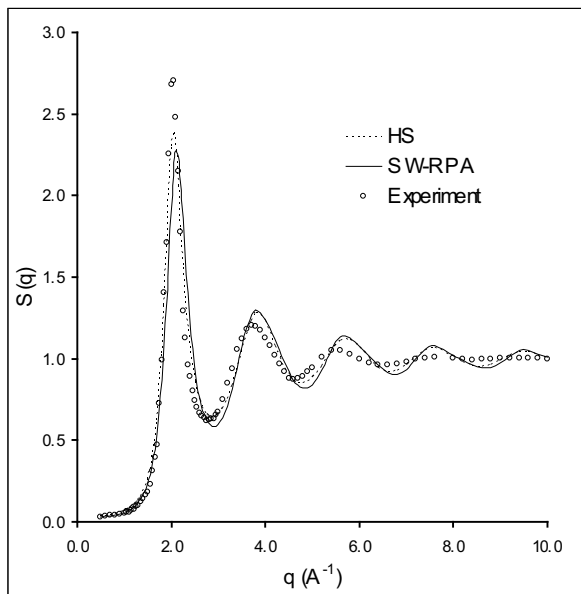
Figure 1. The structure factor obtained with the SW-RPA reference system in comparison with one obtained with the HS reference system and experimental data.

means of the traditional variational method with the HS reference system at $\sigma = 6.2544$ a.u. and $\rho = 0.0034$ a.u. is shown also).

Tables 2 and 3 list the obtained thermodynamic properties and values of the varying SW parameters. The total internal energy is $E = 3k_BT/2 + E_0 + E_1 + E_2 + E_3$ and total entropy is $S = S_{SW-RPA} + S_e$. The HS reference system results are obtained at the same σ and ρ as the corresponding structure factor.

It is obvious from Tables 2 and 3 that the SW variational procedure gives a lower upper bound of the Helmholtz free energy than the HS variational procedure and that the results obtained are in reasonable agreement with the experiment [26].

Table 2. Obtained values of the SW parameters and structure-dependent contributions to the free energy.

σ (a.u.)	ε (a.u.)	E_2 (eV)	E_3 (eV)	$\Delta S_{HS}/k_B$	$\Delta S_{SW\text{-}RPA}/k_B$
6.2149	-0.000365	-0.2053	-5.8652	-0.1511	0.0022

Table 3. The SW-RPA results for the Helmholtz free energy, internal energy and entropy in comparison with the HS results and experiment.

	SW-RPA	HS	Experiment
F (eV)	-6.464	-6.397	-6.158
E (eV)	-6.232	-6.156	-6.149
S/k_{B}	7.22	7.49	7.79

6 Conclusion

The performed work shows that the SW model in principle can be used as a reference system within the variational method of the thermodynamic perturbation theory. However, the roughness of the RPA leads to difficulties when one uses the SW-RPA reference system in practical calculations for liquid metal state. Progress in this area of investigation can be achieved by using theories of liquids that are more accurate than the RPA, such as the mean spherical approximation, by which the semi-analytical solution for the SW fluid has been recently obtained [27, 28].

Acknowledgments

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