Thermodynamic self-consistency in the variational thermodynamic calculation for liquid metals

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The importance of thermodynamic self-consistency imposed on a reference fluid in the Gibbs-Bogoliubov variational calculation is re-visited. Following the recent work of Bratkovsky [1 Phys Condens Matter 1 (1989) 3453], and choosing the one-component-plasma fluid as a reference, the role of thermodynamic self-consistency is investigated by comparing two sets of Monte Carlo data [G.S. Stringfellow, H.E. Dewitt and W.L. Slattery, Phys Rev. A41 (1990) 1105]. It is found that accurate computer simulation data can be used with great advantage to achieve thermodynamic self-consistency for the reference liquid and hence to account quantitatively for the thermodynamics and structure in a liquid metallic system.

1. Introduction

Recently, the importance of thermodynamic self-consistency (TSC) imposed on the reference fluid in the variational thermodynamic calculation has been revived [1-3]. The main issue addressed here is to attempt setting up a TSC reference fluid so that 'ambiguities' derived from different routes to the equation of state and hence their associated reference thermodynamic functions can be eliminated. In this connection, we have recently [2] re-examined the Gibbs-Bogoliubov inequality using the charged-hard-sphere fluid. We found that the TSC condition plays a crucial role in narrowing the controversial behavior between the excess entropy and the liquid structure factor, $S(q)$. Similar effort has been carried out by Chen and Lai [3] in the context of variational modified hypernetted-chain theory. Concentrating on the one-component-plasma (OCP) fluid and inspired by the work of Chaturvedi et al. [4], Bratkovsky [1] formulated within the generalized mean spherical approximation (GMSA) a theory that aims at reproducing an accurate OCP liquid structure. In this work, he attempted to impose the energy-compressibility TSC making use of the computer simulation data of Slattery et al. [5]. Surprisingly, Bratkovsky did not contrast his calculated liquid structure factor at different plasma parameter, $\Gamma$, directly with the Monte Carlo results of Slattery et al. [5], although the comparison was done with the simulation data of Hansen and Galam [6]. In view of the fact that at a given $\Gamma$ the difference between the $S_{\text{OCF}}(q; \Gamma)$ obtained by Slattery et al. [5] and that by Hansen and Galam [6] is still discernible, and also because a new assessment of the simulation data has been advanced recently [7] regarding the 'best' functional form to be used for the free and internal energy expressions, it is appropriate at this time to make again a thorough study of the OCP fluid, and to investigate the extent of its application to the thermodynamic calculation for liquid metals. The purpose of this paper is to incorporate the above-mentioned new simulation data into the GMSA theory and, by comparing various thermodynamic functions and liquid structure, we examine the role of imposing TSC condition on a reference system.
2. GMSA theory

In the GMSA, one begins by replacing the soft core of OCP with a hard core having a hard sphere diameter, $\sigma$. The closure to the Ornstein–Zernike equation can be written in a dimensionless form as

$$h(x) \equiv g(x) - 1 = -1, \quad x < 1,$$

$$c(x) = -\lim_{\mu \to 0} \left[ \frac{\gamma e^{(-\mu x)}}{x} - \epsilon e^{(-\lambda x)} \right], \quad x > 1. \quad (2)$$

Here $x = r/\sigma$, $g(x)$ is the pair correlation function, $c(x)$ is the direct correlation function and $\gamma = \Gamma/2\eta^{1/3}$, $\eta = \pi \sigma^3/6\Omega_0$ being the packing density. Note that $\eta$, $\epsilon$ and $\lambda$ are free parameters to be specified below. To solve the Ornstein–Zernike equation, we follow Bratkovsky [1] and express the Fourier transformed $c(k)$ in a factorized form as

$$1 - c(k) = Q(k)Q(-k), \quad (3)$$

where the function $Q(k)$ can be written from Hoye and Blum [8]:

$$Q(k) = 1 - 12\eta \int_0^\infty dx \ e^{(ikx)}q(x), \quad (4)$$

$$q(x) = F(x) + \lim_{\mu \to 0} \left[ A e^{(-\mu x)} + \epsilon e^{(-\lambda x)} \right], \quad x > 0,$$

$$F(x) = \left[ p_0 + p_1 x + p_2 x^2 + p_3 x^3 + \omega e^{(-\lambda x)} \right] \times \theta(1 - x). \quad (5)$$

In the above equations, $\theta(x)$ is the Heaviside step function and the coefficients $A$, $\omega$ and $p_i$, where $i = 0, 1, 2, 3$, can be shown [1] to be interrelated functionally through Baxter’s equation [9]

$$-q(x) + J(x) - 12\eta \int_0^1 dt q(t) J(|x - t|) = 0 \quad (7)$$

and

$$J(x) = \int_1^x dt h(t).$$

The thermodynamic energy-compressibility self-consistency can now be imposed. In the context of GMSA theory, one writes first the GMSA OCP internal energy and pressure equation of state

$$\beta U = 12\eta \gamma I, \quad (9)$$

$$P/P_{id} = 1 + 4\eta g(1) + \frac{1}{2} \beta U, \quad (10)$$

where $P_{id}$ is the ideal gas pressure and

$$I = J + \int_0^x dt h(t). \quad (11)$$

On the other hand, one can make use of the computer simulation data to impose the following TSC conditions [4,10]:

$$\beta U = 12\eta \gamma I = (\beta U)_{MC}, \quad (12)$$

$$\chi_T/\chi_T^{id} = \left[ 4p_2^2 - 2\kappa (p_1 - \kappa I) \right]^{-1} = (\chi_T/\chi_T^{id})_{MC}, \quad (13)$$

$$g(1) = p_1 + 2p_2 + 3p_3 - \lambda \omega e^{(-\lambda)} = 0, \quad (14)$$

where in the above $\kappa^2 = 24\eta \gamma$, $\chi_T$ ($\chi_T^{id}$) is the isothermal compressibility for an OCP (ideal gas) and the subscript MC denotes result from the Monte Carlo simulation. At this point it is obvious that, if one were given an accurate MC internal energy and equation of state expressions, one can impose a TSC condition in the GMSA theory. Differing from Bratkovsky, we propose to apply the most recent simulation data of Stringfellow et al. [7]:

$$(\beta U)_{MC} = a_s \Gamma + b_s \Gamma^s + c_s \Gamma^{-s} + d_s, \quad (15)$$

$$\left(\chi_T/\chi_T^{id}\right)_{MC} = \left[ 1 + \frac{4}{3} a_s \Gamma^s + \frac{3 + s}{9} b_s \Gamma^s + \frac{3 - s}{9} c_s \Gamma^{-s} + \frac{d_s}{3} \right]^{-1}. \quad (16)$$

Here the coefficients $a_s$, $b_s$, $c_s$ and $d_s$ depend on the choice of $s$. Although different values of $s$ have been investigated, we shall, however, limit our discussion to $s = \frac{1}{2}$ which is precisely the value adopted by Bratkovsky [1] and $s = \frac{1}{3}$ which is the ‘best’ functional form [7] for the internal energy expression that agrees excellently with the MC simulation. Accordingly, for $s = \frac{1}{2}$ ($\frac{1}{3}$), $a_s$, $b_s$, $c_s$ and $d_s$ are given by $-0.897744$ ($-0.899375$), $0.95043$ ($0.569333$), $0.18956$ ($-0.017875$) and
To progress further, one would have to solve tedious algebra for the coefficients mentioned above from a linear system of equations. These parametric relations coupled with eq. (13) and along with the Fourier transform of $x_\eta(x)$ would lead us to two transcendental equations for $\eta$ and $\lambda$ which are both expressed in terms of $\Gamma$. Following Bratkovsky, we first solve these linear coupled equations at each $\Gamma$ for the $\eta$ and $\lambda$ and then obtain analytic fit using Padé approximation. Our calculation yields

$$
\eta = \frac{z_{1,s} \Gamma + z_{2,s} \Gamma^{1-s} + z_{3,s} \Gamma^{1-2s} + z_{4,s}}{z_{5,s} \Gamma^{1-s} + z_{6,s} \Gamma^{1-2s} + z_{7,s}},
$$

(17)

$$
\lambda = \left[ \left( \Gamma - \Gamma_0 \right)^{1/2} \right] \times \left\{ \left( y_{1,s} \Gamma + y_{2,s} \Gamma^{1-s} + y_{3,s} \Gamma^{1-2s} + y_{4,s} \right) \right\}^{-1},
$$

(18)

where $\Gamma_0 = 19.55$ and $z_{i,s}$ and $y_{i,s}$ are coefficients depending on the choice of $s$. For $s = \frac{1}{4}$, the set of values for $z_{1,1/4} - z_{7,1/4}$ ($y_{1,1/4} - y_{7,1/4}$) are:

0.75270, -2.7731, 7.9419, -7.2442, -1.3580, 4.4468, 77.144 (-0.12625, 0.0, 7.7945, 126.43, 0.0, -11.397, 215.44). Similarly, for $s = \frac{1}{3}$, the values for $z_{1,1/3} - z_{7,1/3}$ ($y_{1,1/3} - y_{7,1/3}$) are:

0.69036, -0.2777, -9.8888, 12.109, 0.13382, 15.160, -69.611 (-8.3565, 131.56, -252.96, -484.75, 9.8926, 294.35, -1321.5). In the present work, the range of $\Gamma$ satisfies $\Gamma_0 < \Gamma < 200$. For the other coefficients in terms of which $S(q)$ is expressed, we refer the interested readers to the original paper of Bratkovsky [1] (see pp. 3455–3456) for mathematical relations.

The variational thermodynamic calculation can now be performed by substituting the above $S_{OCF}(q; \Gamma)$, free energy $F_{OCF}$ (eq. (6) in ref. [7]), eq. (12) for the OCP internal energy as well as the metallic Hamiltonian (see, for example, refs. [11,12,2]) into the Gibbs–Bogoliubov inequality. The excess entropy, $S^{ex}$, and specific heat at constant volume, $C_V$, can accordingly be derived.

### 3. Numerical results

We give in table 1 our calculated thermodynamic functions for Helmholtz energy, $F$, internal energy, $U$, excess entropy, $S^{ex}/k_B$, and specific heat at constant volume, $C_V$. It can be seen from the table that the functional form for $s = \frac{1}{3}$ is of superior quality, judging from the variation of $\eta(\Gamma)$ and $\lambda(\Gamma)$ (see fig. 1) which, for large $\Gamma$, give

<table>
<thead>
<tr>
<th>Metal</th>
<th>$s$</th>
<th>$\Gamma$</th>
<th>$F$</th>
<th>$U$</th>
<th>$- S^{ex}/k_B$</th>
<th>$C_V/k_B$</th>
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<tbody>
<tr>
<td>Li</td>
<td>$\frac{1}{4}$</td>
<td>185</td>
<td>-0.259929</td>
<td>-0.252895</td>
<td>4.24</td>
<td>3.38</td>
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<td></td>
<td>$\frac{1}{3}$</td>
<td>186</td>
<td>-0.259948</td>
<td>-0.252951</td>
<td>4.26</td>
<td>3.44</td>
</tr>
<tr>
<td></td>
<td>expt</td>
<td></td>
<td>-0.265</td>
<td>-0.257</td>
<td>3.61</td>
<td>3.44</td>
</tr>
<tr>
<td>Na</td>
<td>$\frac{1}{4}$</td>
<td>146</td>
<td>-0.235833</td>
<td>-0.227047</td>
<td>3.81</td>
<td>3.23</td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{3}$</td>
<td>148</td>
<td>-0.235845</td>
<td>-0.227089</td>
<td>3.84</td>
<td>3.28</td>
</tr>
<tr>
<td></td>
<td>expt</td>
<td></td>
<td>-0.2360</td>
<td>-0.2320</td>
<td>3.45</td>
<td>3.62</td>
</tr>
<tr>
<td>K</td>
<td>$\frac{1}{4}$</td>
<td>141</td>
<td>-0.201206</td>
<td>-0.191828</td>
<td>3.75</td>
<td>3.21</td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{3}$</td>
<td>142</td>
<td>-0.201216</td>
<td>-0.191862</td>
<td>3.77</td>
<td>3.25</td>
</tr>
<tr>
<td></td>
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<td></td>
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<td>-0.1956</td>
<td>3.45</td>
<td>3.42</td>
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<tr>
<td>Rb</td>
<td>$\frac{1}{4}$</td>
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<td>-0.192955</td>
<td>-0.182896</td>
<td>3.66</td>
<td>3.17</td>
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<tr>
<td></td>
<td>$\frac{1}{3}$</td>
<td>135</td>
<td>-0.192963</td>
<td>-0.182923</td>
<td>3.68</td>
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<tr>
<td></td>
<td>Expt</td>
<td></td>
<td>-0.1930</td>
<td>-0.1870</td>
<td>3.63</td>
<td>3.52</td>
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<tr>
<td>Cs</td>
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<td>-0.170693</td>
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<td>-0.170721</td>
<td>3.77</td>
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<td></td>
<td>expt</td>
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<td>-0.1820</td>
<td>-0.1757</td>
<td>3.56</td>
<td>3.43</td>
</tr>
</tbody>
</table>
a more hard-sphere-like behavior, from the calculated $F$ which is lower and in closer agreement with experiment, and from calculated $U$ and $C_v$ which show reasonable agreement also with observed data for the liquid alkali metals Na, K, Rb and Cs. The calculated thermodynamic functions for the liquid Li metal, on the other hand, are less satisfactory, although the strong electron–ion interaction for this metal has been taken care of by incorporating higher order perturbative corrections.

4. Conclusions

As in our recent work [13], when the possible state mixing effects [14] for the s- and p-valence electrons, whose atomic states are known to be rather close, are considered, we obtained significantly better results generally for all thermodynamic quantities and $S(q)$ (for $s = \frac{1}{3}$, $\Gamma$ is determined to be 169 and $F = -0.265878$; $U = -0.258618$; $-S^{ex}/k_B = 4.08$; $C_v/\kappa_B = 3.37$). It is worthwhile to notice that the $\Gamma$ predicted for $s = \frac{1}{3}$ and $\frac{1}{4}$ are large and virtually the same. This would lead to same quality of $S(q)$ as can be seen from fig. 2 where we compare the $S_{OCP}(q; \Gamma)$ with those obtained from both $s$. Finally, we note that the controversial issue between $S(q; \Gamma)$ and $S^{ex}$, i.e., an improved $S(q; \Gamma)$ (compared with experiment) would lead to a deterioration of $S^{ex}$ and vice versa, has not been significantly resolved even for the case $s = \frac{1}{3}$, implying the need for further consideration of the TSC.

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References


