Surface Tensions for Liquid Polyvalent Metals

S. K. Lai (黎昌強), M. L. Huang (黃敏郎) and S. Wang (王瑞卿)†
Department of Physics, National Central University
Chung-Li 32054, R. O. C.
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The Gibbs-Bogoliubov variational perturbation method has been
generalised and applied to the study of surface tensions of liquid poly-
valent metals. The calculation is made tractable by combining the
above variational theory with the Generalised Nonlocal Model Pseudo-
potential of Li et al recently developed for the calculations of the
energetics of liquid polyvalent metals. An important feature in the
present work is that it allows us to go beyond the linear screening
approximation albeit in a somewhat average way. The results of com-
putations show that the surface tensions of liquid polyvalent metals
can be reasonably accounted for provided an accurate
Helmholtz free
energy, higher-than-second order corrections and a more realistic
approximation on the interionic terms are all properly considered.

I. INTRODUCTION

Recently there has been a great theoretical interest in the understanding of the surface
tension (ST) of simple liquid metals. Various theoretical models, such as the pseudoatom
model, the density functional approach, the variational perturbation method etc.
have subsequently been proposed in the literature and although each involves approxima-
tions in one form or another, our knowledge of ST has been considerably improved. From
the calculations of these different models it has become increasingly evident that the surface
properties of a liquid metal are quite different from those in the solid metal surface. For
example, for a solid metal surface the jellium model with a first-order pseudopotential
theory can be successfully used to account for the surface energy of a number of
metals. However the same theory, when generalised to the calculation of ST of a liquid metal
surface, fails completely even for liquid alkali metals. This explains the upsurge of
theoretical interest in developing higher-order corrections to the first-order theory as
mentioned above. Among these Hasegawa and Watabe (HW), Chacon et al., Foiles
† On leave from Guelph-Waterloo program in Physics, University of Waterloo, Waterloo, Ontario, Canada N2L
2W7.
and Ashcroft\textsuperscript{15} and Lai\textsuperscript{14} have attempted to examine the effects of second-order pseudo-potential perturbation corrections on the calculated ST. Despite these various efforts the theoretical prediction of surface properties has not progressed very quickly. This is particularly true for liquid polyvalent metals where, to the best of our knowledge, only HW and Chacon et al seem to have obtained satisfactory ST results for a number of simple liquid metals. Unfortunately the uncertainties in their input data (such as the choice of an Ashcroft empty core parameter, the use of an unjustified packing fraction fitted to experiments etc.) and the high sensitivity of the calculation to them, have made their calculations to ST to some extent fortuitous. This point has recently been criticized by Lai\textsuperscript{14} (hereafter referred to as I). In order to remove these uncertainties, Lai has proposed a full nonlocal pseudopotential approach to the study of ST and found that calculated ST is dramatically different from those obtained by the latter authors. By examining various possible sources of errors, it was concluded in I that the electron density response function $\chi_0(r,\vec{f})$ is one of the most probable causes for the discrepancies in ST found between theories and experiments. Therefore in a recent communication\textsuperscript{17} we have advanced higher-order corrections to the usual second order pseudopotential perturbation theory. The results of computations do show significant improvement over the corresponding ones computed using the second order theory. However, because in the latter work various physical entities, such as the indirect ion-ion terms (Eq. (21) below), are approximated by bulk liquid quantities, the calculated ST are not quantitatively predicted.

In this paper we carry out a full calculation and adopt as in HW, a more realistic approximation on the indirect interactions in which the electron density at the metallic surface is taken to be an average of the local electron densities at the ion positions; the effects of the inhomogeneity of the electron density on $\chi_0(r,\vec{f})$ are then treated by considering nonlinear contributions to the pseudo-wavefunction (hence the charge density). To test our theory we apply our formalism to the study of ST for liquid polyvalent metals. Within the approximation made in this work, we show that the ST for liquid polyvalent metals can be satisfactorily accounted for only in those metals where the theoretical equilibrium metallic densities are predicted to be at the minima of Helmholtz free energies. In addition we have found that a considerable amount of ST resides in the position dependent self-energy term $\delta \sigma_{2\rho\rho}^2$ (Eq. (22) below) in accordance with the conclusion reached by Foiles and Ashcroft\textsuperscript{15}. The presentation of our paper is briefly as follows. In Sec. 2, we review the mathematical formalism of high-order corrections to the usual second order pseudopotential perturbation theory. The calculated energy and pseudo-wavefunctions in conjunction with the variational thermodynamic perturbation theory will then be used to derive tractable expressions for the ST. Sec. 3 presents the results of ST for liquid polyvalent metals. The importance of various contributions to the ST will be examined and discussed.
II. MATHEMATICAL FORMALISM

In this section, we present the essentials of our variational perturbation theory to the calculation of ST. We first discuss the method of incorporating higher-order corrections to the usual second order pseudopotential perturbation theory and then outline how this theory is adapted to derive tractable expressions for the ST.

2.1 High-order Corrections

According to Li et al.\textsuperscript{18} the usual second order pseudopotential perturbation theory starts with a one-electron energy and pseudo wavefunction given by

$$E_k = <k|H|k> + \sum_{k'} \frac{<k|H|k'><k'|H|k>}{E_k^{(0)} - E_k^{(0)}}$$

(1)

$$\chi_k = |k> + \sum_{k'} \frac{<k'|H|k>}{E_k^{(0)} - E_k^{(0)}} |k'>$$

(2)

in which $H$ is the hamiltonian customarily written as

$$H = \frac{p^2}{2} + W$$

(3)

where $p$ is the kinetic energy operator and $W$, which is the single electron model-potential, is mathematically written

$$W(r) = \sum_{\lambda} w_{el}(r - R_{\lambda}) + V_{ee}$$

(4)

Here, $w_{el}$ represents a model-potential describing the interaction of an electron at $r$ and an ion at $R_{\lambda}$. The last term on the right-hand side of Eq. (4) denotes the electronic potential arising from the rest of the valence electrons. In the usual second order pseudopotential perturbation theory one generally determines the potential $W$ self-consistently using the Poisson equation with a charge density constructed from Eq. (2). The resulting $V_{ee}$ can accordingly be differentiated into two contributions, viz, one originating from the electronic screening potential and the other potential, due to the depletion charge density, stems from the difference between the true and pseudo wavefunctions. In the application to sp-metals like Na, one generally assumes that $W$ is weak and hence the expansion of $E_k$ and $\chi_k$ in terms of lowest order plane-waves $|k>$ is sufficient. For a polyvalent metal, Eqs. (1) and (2) may be inadequate because of the increasingly strong electron-ion interaction. Thus in order to make the calculation tractable, Li et al.\textsuperscript{18} replace the $|k>$ in Eqs. (1) and (2) by...
which are also one-electron states but ones more appropriate than \( |k> \) and are chosen to-form a complete orthonormal set. In the context of model-potential theory such a procedure is allowable, as has been demonstrated by Ho et al.\(^{19}\). Now, by exploiting the non-uniqueness property of a model potential and by carrying out suitable unitary transformation so that all the nonlinear effects are being transferred to the model potential, Li et al. are able to cast the forms of Eqs. (1) and (2) into

\[
E_k = \frac{k^2}{2} + \frac{\sum' q}{q} \frac{<k | W^m | k + q> - <k + q | W^m | k>}{E_k^{(0)} - E_{k+q}^{(0)}}
\]

(5)

\[
\chi_k = Q \left[ |k>, \sum' q \frac{<k + q | W^m | k>}{E_k^{(0)} - E_{k+q}^{(0)}} |k+q> \right]
\]

(6)

where \( Q \) is a unitary transformation operator, \( W^m \) is a modified electron-ion model potential similar in form to Eq. (4) but now contains an additional parameter, i.e., \( \beta \) introduced to include higher-order pseudopotential perturbation effects. The procedure for the determination of this parameter has been described in detail by Li et al.\(^{18}\) and interested readers should consult their works for more details.

### 2.2 Derivation of Surface Tension Expression

Having outlined the method of calculation of the one electron energy and pseudowavefunction, we may apply Eqs. (5) and (6) to the calculation of ST. To this end, we follow I and start by considering that a liquid metal surface is a semi-infinite system for which the coupling between an electron and an ion is assumed to be adequately described by a weak nonlocal model potential, \( W^m \). The Hamiltonian for such a system can be written in atomic units (\( e = h = m = 1 \)) as

\[
H = H_e + H_i + H_{ei}
\]

(7)

and

\[
H_e = \frac{1}{2} \int \frac{E_{i}^2}{|r_i - r'_i|} - \sum_{i,j} \frac{1}{|r_i - r_j|} - \frac{1}{2} \int \frac{\sum' Q n^+(Q)}{|r_i - r'_i|} + \frac{1}{2} \int \frac{\sum' \int dr' \frac{n^+(r) n^+(r')}{|r - r'|}}{|r - r'|} ,
\]

(8)

\[
H_i = \sum_{Q} \frac{Z^2}{2M} \frac{P_q^2}{|Q|} + \sum_{e} \frac{Z^2}{2m} \frac{R_q^2 - R_{q'}^2}{|r_i - r_j|} \frac{Z}{Q} \frac{\int dr \frac{Z_{n}(r)}{|r - r'|} + \frac{1}{2} \int dr \int dr' \frac{\sum' P_q n^+(r')}{|r - r'|}}{|r - r'|} ,
\]

(9)
Here $\mathbf{H}_{ei}$ is the hamiltonian of the electron gas (ionic) system to which is added a positive (negative) neutralizing background, $n^+ (r)$ ($-n^+(r)$), in order to handle the ill-behaved, long-range Coulombic interaction. The last term in Eq. (7) $\mathbf{H}_{ei}$ represents the interactions between electrons and ions. Now, in the present variational perturbation theory, our unperturbed electronic system is taken to be the jellium, $\mathbf{H}_{e}$, plus $\sum <\delta v(r)>_+$ in which

$$\delta v(r) = \sum \delta v^M_b \left( |r-R_b| \right) + \int \frac{d^3r'}{4\pi |r-r'|} n^+_+(r').$$

where the subscript $b$ above and in Eq. (10) refer to bare ion, $\Delta W^M_b$ is the nonlocal part of the bare ion pseudopotential, and $\delta v$, by itself, is the external potential felt by an electron in the jellium. Such a choice for the unperturbed electronic system has previously been emphasized by HW$^{10,11}$ Chacon et al.$^{12,13}$ and I. Eq. (11) then has to be ensemble averaged over an ion distribution which can be chosen arbitrarily (see Eq. (19)).

Having decided on this unperturbed electronic system we may now proceed to apply adiabatic approximation and reduce the two component nature of a metal into an effective one component classical ionic system. The corresponding effective hamiltonian can be written

$$\mathbf{H}_{eff} = \mathbf{F}_i + \mathbf{H}_{z},$$

in which the electronic Helmholtz free energy is given by

$$F' (R_1, R_2, \ldots, R_N) = -k_B T \ln \text{Tr} (\mathbf{e}) \exp \left\{ -\left( H_e + H_{el} \right)/k_B T \right\}$$

where $k_B$ and $T$ are respectively the Boltzmann constant and temperature. The notation $R_1, R_2, \ldots, R_N$ corresponds to a specific ionic configuration with respect to which the electronic degree of freedom, denoted by $\text{Tr} (\mathbf{e})$, is to be evaluated. To make further progress, we rewrite Eq. (13) as

$$F_i \left( R_1, R_2, \ldots, R_N \right) = -k_B T \ln \text{Tr} (\mathbf{e}) \exp \left\{ -\left( H_e + \sum _+ <\delta v(r)>_+ \right)/k_B T \right\} + H_{z} - \sum _+ <\delta v(r)>_+ /k_B T$$

and, by treating $H_e + \sum _+ <\delta v(r)>_+$ as an unperturbed electronic system as emphasized above, the calculation can be carried out by using perturbation expansion in terms of the expansion parameter $\delta v(r) - <\delta v(r)>_+$. This procedure can be easily done (see for example, Hasegawa and Watabe$^{11}$) and the resulting Eq. (14) becomes
\[ H_{\text{eff}} = \sum_{q} \frac{P_{q}}{2M} + F_0 + F_1 + F_2 + F_M \]  

(15)

where \( P_{q} \) and \( M \) are respectively the momentum operator and mass of an ion. \( F_0, F_1, F_2 \) and \( F_M \) are respectively given by Eqs. (16), (18) and (19) in the work of HW. The last term on the right-hand side of Eq. (15) is the familiar Madelung term. It is important to note at this point that although mathematically the method of calculation is similar to that of our previous work, the details of the model-potential are not the same. We have in fact incorporated high-order corrections (through \( \beta \) parameter) and for application to Ca, Sr, and Ba, the early transition-metal series, an additional sd-mixing interaction (denoted by \( \delta \) parameter in the work of Li et al\(^\text{18}\)) by working with Eqs. (5) and (6).

The next step in our derivation of a ST expression is to apply the Gibbs-Bogoliubov inequality. According to this inequality the Helmholtz free energy is bounded above and given by

\[ F \approx F_{\text{ref}} + <H_{\text{eff}} + H_{\text{ref}},>_{\text{ref}} \]  

(16)

where \(<\ldots,>_{\text{ref}}\) means an ensemble average over an ionic distribution of the reference system. As a convenient reference system applicable to polyvalent metals, we choose a system of hard spheres in the presence of an external potential, \( V_{\text{ex}}(r) \). The introduction of this latter potential is necessary since the hard sphere system does not form a free surface. However in this work we continue to assume its contribution to the surface tension to be insignificant (see Ref. 14 for reasons). Substituting Eq. (15) into Eq. (16) we obtain

\[ F \approx F_{\text{ref}} + F_0 + <F_1>_{\text{ref}} + <F_2>_{\text{ref}} + <F_M>_{\text{ref}} \]  

(17)

The calculation from hereon parallels that of I. In the first place we assume and approximate that the thermal average is to be expressed in terms of a one-body, \( \rho_{\text{ref}}(R), \) and a two-body, \( \rho_{\text{ref}}(R, R') \) distribution function with the latter being selected to be

\[ \rho_{\text{ref}}(R, R') = \rho_{\text{ref}}(R) \rho_{\text{ref}}(R') g_{\text{ref}}(|R - R'|) \]  

(18)

where \( g_{\text{ref}}(|R - R'|) \) refers to the bulk radial distribution function. By arbitrarily setting

\[ n_+(r) = Z \rho_{\text{ref}}(r) \]  

(19)

making use of Eq. (18), parametrizing the electron density profile (similar monatomic form is assumed for ions with \( L \rightarrow M \)) to be

\[ n_+(r) = \begin{cases} \frac{1}{n} & x < 0 \\ \frac{1}{2} \frac{1}{n} \exp \left( \frac{-x}{L} \right) & x > 0 \end{cases} \]  

(20)
and taking a realistic approximation on the indirect ion-ion term to be

$$\Phi_{\text{ind}} (R, R') \approx \Phi_{\text{ind}} (R, R')_{1}$$

where $$n' = \left( \frac{n(R) + n(R')}{2} \right)$$, being an average of the electron densities at the ion positions $$R$$ and $$R'$$, we obtain finally

$$\gamma = \frac{\rho_{1}^{(0)}}{2} + \sigma_{0} + \sigma_{1} + \sigma_{2,\text{pair}} + \sigma_{M} + \delta \sigma_{2,\text{self}} + \delta \sigma_{2,\text{pair}}$$.

The detailed expressions for the first five terms on the right-hand side of Eq. (22) can be found in I if the relevant physical quantities are substituted by ones constructed from the Generalised Nonlocal Model Pseudopotential (GNMP) theory. The last two terms are just the same as those in HW except that the nominal valence, $$Z$$, and the energy wavenumber characteristic, $$F$$, there are respectively replaced by those in the GNMP. We also remark that in the present variational perturbation theory the parameter $$L$$ is determined by first minimizing $$\sigma_{0}(L, M) + \sigma_{1}(L, M)$$ for a given $$M$$ and then the minimum value of $$\gamma$$ is searched for by varying $$M$$. If we let $$\sigma$$ be that minimum value, then, our theoretical ST would be $$\sigma = [\gamma]_{\text{min}}$$.

### III. NUMERICAL RESULTS AND DISCUSSIONS

We have applied Eq. (22) to the calculations of ST for liquid polyvalent metals. For most contributions in $$\sigma$$ the numerical procedures for their evaluation have been given in I. Here we only mention that a special numerical technique called B-spline function has been used in the computation of $$\sigma_{ij}(q_{j})/\partial \mathbf{n}$$ appearing in all of the $$\sigma_{ij}^{(0)}$$ integrals. The results of calculations displaying various contributions in $$\sigma$$ are documented in Table 1.

#### TABLE 1.
The electronic density profile $$L$$, the high-order correction parameter $$\beta$$, and the various contributions to the calculated surface tension $$\sigma$$ (in units of dyn cm$$^{-1}$$) at their respective melting temperature. The bracketed entries for Ca, Sr, and Ba refer to the sd-mixing parameter $$\delta$$ (see Ref. 18). Experimental data are taken from Ref. 22.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$$L$$</th>
<th>$$\beta$$</th>
<th>$$(\delta)$$</th>
<th>$$\sigma_{0}$$</th>
<th>$$\sigma_{2,\text{pair}}$$</th>
<th>$$\sigma_{M}$$</th>
<th>$$\delta \sigma_{2,\text{self}}$$</th>
<th>$$\delta \sigma_{2,\text{pair}}$$</th>
<th>$$\sigma$$</th>
<th>$$\sigma_{\text{expt.}}$$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>1.317</td>
<td>0.89</td>
<td>-256</td>
<td>-1204</td>
<td>2643</td>
<td>4445</td>
<td>226</td>
<td></td>
<td>1.0</td>
<td>5.15</td>
</tr>
<tr>
<td>Cd</td>
<td>1.220</td>
<td>0.95</td>
<td>-156</td>
<td>-1274</td>
<td>-3214</td>
<td>4843</td>
<td>231</td>
<td></td>
<td>1.40</td>
<td>144.70</td>
</tr>
<tr>
<td>Zn</td>
<td>1.241</td>
<td>0.94</td>
<td>-137</td>
<td>-2413</td>
<td>-5331</td>
<td>6976</td>
<td>235</td>
<td></td>
<td>1.38</td>
<td>147.56</td>
</tr>
<tr>
<td>Ca</td>
<td>1.544</td>
<td>0.94</td>
<td>-175</td>
<td>-894</td>
<td>-1861</td>
<td>2592</td>
<td>101</td>
<td></td>
<td>1.20</td>
<td>220.41</td>
</tr>
<tr>
<td>Sn</td>
<td>1.125</td>
<td>0.85</td>
<td>-150</td>
<td>-1274</td>
<td>-4673</td>
<td>6756</td>
<td>601</td>
<td></td>
<td>1.41</td>
<td>184.78</td>
</tr>
<tr>
<td>Al</td>
<td>1.192</td>
<td>0.82</td>
<td>-174</td>
<td>-4228</td>
<td>-9277</td>
<td>13553</td>
<td>1245</td>
<td></td>
<td>1.55</td>
<td>103.93</td>
</tr>
<tr>
<td>Sr</td>
<td>1.659</td>
<td>0.74</td>
<td>-152</td>
<td>-627</td>
<td>-868</td>
<td>1642</td>
<td>69</td>
<td></td>
<td>1.24</td>
<td>173.20</td>
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<td>Be</td>
<td>-</td>
<td>0.96</td>
<td>-123</td>
<td>493</td>
<td>-919</td>
<td>1452</td>
<td>64</td>
<td></td>
<td>1.18</td>
<td>150.27</td>
</tr>
</tbody>
</table>
Before discussing the significances of them, one relevant remark is in order. In the present calculation despite our effort to adopt a more realistic approximation for Eq. (21) and incorporate, in some average way, the inhomogeneity of the electron gas (through Eq. (6)), our calculated ionic density profile remains a step function ($M = 0$) for all of the liquid elements considered in this work. This result, in common with the findings of Hafner and Chacon et al.\textsuperscript{13} ($M < 0.8$ a.u.), implies that the present approximations for the pair correlation function $g(R, R')$ and $\Phi_{md}(R, R')$ are still not sufficiently accurate to explain the ion density profile at the liquid surface.\textsuperscript{21} In the following we have therefore presented our theoretical $\sigma$ determined for the case $M = 0$. Generally we see from Table 1 that our calculated $\sigma$ agree to within 15% -- 50% of the measured values. In almost all of the polyvalent metals, the contribution from the self-energy term, $\delta a_{2\text{self}}$, is quite dominant accounting from approximately 40% -- 80% (for the Ba, Sr, Mg, Cd, In, Ca and Zn), to more than 100% (Al) the experimental data.\textsuperscript{22} Contrary to the results obtained in the local pseudopotential theory, the contribution from $\delta a_{2\text{pair}}$ turns out to be somewhat larger compensating to about 40% (compare to $\sim 30\%$ in the local potential theory) of the theoretical $\delta a_{2\text{self}}$. Both these results, however, indicate further the important role played by the electronic screening effects. We note that when we terminated our calculation at the second order perturbation theory (corresponding to $\beta = 0$), the $\sigma$ for the polyvalent metals were either predicted to be significantly smaller or became unphysical as has been previously demonstrated for Mg and Al.\textsuperscript{17} Even when the high-order correction ($\beta \neq 0$) is included, it is only when we adopt a more realistic approximation of Eq. (21) that we will be able to obtain a more physical $\sigma$.\textsuperscript{23} In particular, it is perhaps noteworthy to emphasize at this point that for all of the polyvalent metals of interest here, the incorporation of high-order correction has led successfully to the calculations of bulk equilibrium liquid metallic densities at the minima of Helmholtz free energies to an accuracy of about 5% to 18% without introducing any ad hoc parameter such as those which appeared in the works of Umar et al.\textsuperscript{12} This point, which has often been ignored, is crucial in the calculation of ST because the latter is essentially a difference between Helmholtz free energies in the bulk and at the surface. This is one main reason for the present successful prediction of ST for Mg, Cd, Al, and In, where the equilibrium metallic density of each is theoretically determined to an accuracy of about 5% the measured value (see Li et al.\textsuperscript{18}). For the other polyvalent metals, the calculations of equilibrium atomic volumes at the minima of Helmholtz free energies deteriorate somewhat and range from 15% to 18%. This explains the comparatively larger deviations from experiments of ST found for Ca, Sr, Zn and Ba.

To summarize, we may conclude that the variational method based on the Gibbs-Bogoliubov inequality can be used to calculate the ST for polyvalent metals provided the perturbation theory used (i) includes higher-than-second order correction, (ii) adopts a more realistic approximation for the interionic terms such as that given by Eq. (21), and (iii) a highly accurate Helmholtz free energy is used throughout. To obtain a realistic ion density profile, it appears that much effort has still to be devoted to a more accurate description of the transition zone at the surface specifically for the evaluation of $g(R, R')$ and $\Phi_{md}(R, R')$.\textsuperscript{23}
which are found to be of crucial importance.

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REFERENCES

17. S. K. Lai and S. Wang, Sixth Int. Conf. on Liquid and Amorphous Metals, West Germany, 156 45 1456 (1988).
21. For the calculation of ST insofar as most important interactions are on the liquid side of the interface, these approximations are of course relatively well justified.
23. The reader can easily check on this by adding up the first five terms on the right-hand side of Eq. (22).