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Consistent Description of Thermodynamic Properties of Liquid Non-Transition Metals[1]

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ABSTRACT

Traditional approach of combining the method of pseudopotentials (in electron theory of metals) and methods of statistical physics (of liquid state) has been used for the consistent description of thermodynamic properties of liquid non-transition metals. New version of thermodynamic perturbation theory (related to the base system of hard spheres) has been developed for ionic subsystem of metal. Application of the theory has resulted in obtaining simple equation of state for Helmholtz free energy and achieving the consistent description of thermodynamic properties. Comparison of obtained results with experimental data for liquid alkali metals and lead, bismuth, magnesium in the range of temperature from melting points to 2000 K suggests the effectiveness of developed equations.

KEY WORDS: liquid non-transition metal; method of pseudopotentials; perturbation theory; thermodynamic properties.

1. INTRODUCTION

Electron theory of metals combined with the methods of statistical physics gives clear and complete explanation of different types of interparticle interactions (electron-electron, ion-electron, effective ion-ion), their energies and contributions into bulk thermodynamic (and other properties) of metals. For the majority of alkali metals satisfactory agreement of predicted values and experimental data can be achieved in third order of perturbation of ion-electron interaction pseudopotential [1 - 3]. However, sufficiently correct description of particular contributions into the interactions has not been achieved yet. Compensation of the different contributions of opposite signs takes place in free energy expression and its derivatives. Satisfactory agreement can be achieved with experimental data on energy, capacity, and density for given temperature and pressure. Nevertheless, satisfactory agreement with isothermal compressibility and sound velocity cannot be achieved yet. General reasons behind this are known. The unsolved problem is that of refinement of exchange-correlated contributions into energy, compressibility, and static relative dielectric constant of moderately dense electron gas. Despite of extensive research in this direction [4 - 7], simple interpolating expressions [4] still remain the best. These expressions provide characteristics of effective potential of interionic interactions which are in satisfactory agreement with experimental data on structure factor of liquid metals [2, 3]. On the other side, further development of thermodynamic perturbation theory is needed for calculation of the contributions into free energy of ionic subsystem of metal. Barker-Henderson theory [8] is the most successful version of such development. However even in this version effective diameter of hard spheres (as the base system) is overestimated by $0.05 - 0.15\ \mathring{A}$. This leads to the higher packing of particles.

It appeared that screening of paired interionic interactions in liquid metal is significantly different from the nature of screening of paired interparticle interactions in molecular liquid. That is why present authors have developed the modification of thermodynamic perturbation theory based on the integral equation [9, 10] which is more specific for metallic liquids. It has allowed to

obtain comparatively simple equation of state for free energy of liquid non-transition metals. This equation has provided better and consistent agreement with all thermodynamic properties.

2. BASIC RELATIONS

2.1 Thermodynamic Perturbation Theory

Introduction of perturbing part $\Phi_1(R)$, relative to intermolecular potential $\Phi_0(R)$ of the base system of hard sphere particles, with the help of dimensionless coefficient λ:

$$\Phi(R,\lambda) = \Phi_0(R) + \lambda\Phi_1(R), \quad 0 \le \lambda \le 1 \tag{1}$$

yields the following expression for Helmholtz free energy:

$$\frac{F}{Nk_BT} = \frac{F_0}{Nk_BT} + \frac{2\pi n}{k_BT}\int_0^1 d\lambda \int_0^\infty g(R,\lambda)\,\Phi_1(R)\,R^2\,dR\,. \tag{2}$$

In equation (2), F_0 is Helmholtz free energy of hard sphere system of the same density, $g(R,\lambda)$ - particle radial distribution function, N - number of particle in the system, n - particle density, T - temperature, k_B - Boltzman constant, R - distance between particles in liquid.

Relation between $\Phi(R)$ and $g(R)$ has been selected in the form of the integral equation [9, 10] with the use of structure factor $S(q)$:

$$\frac{\Phi(R)}{k_BT} = -\ln[g(R)] + K(R)\,, \tag{3}$$

where $$K(R) = \frac{1}{2\pi^2 n}\int_0^\infty h^2(q)\,\frac{\sin(qR)}{qR}\,q^2\,dq\,, \qquad h(q) = S(q) - 1.$$

Substitution of (1) into (3) with subsequent differentiation with respect to λ yields

$$\frac{\Phi_1(R)}{k_BT}\,g(R,\lambda) = h(q,\lambda)\frac{\partial K(R,\lambda)}{\partial\lambda} - \frac{\partial h(q,\lambda)}{\partial\lambda} + \frac{\partial K(R,\lambda)}{\partial\lambda} \tag{4}$$

and substitution of (4) into (2) with subsequent integration over λ and Fourier-transformation yields expression (in Fourier space of variable q):

$$\frac{F - F_0}{Nk_BT} = -\frac{1}{2}\Delta h(q=0) + \frac{1}{2}\Delta K(q=0) + \frac{1}{4\pi^2 n}\frac{2}{3}\int_0^\infty \left[h^3(q) - h_0^3(q)\right] q^2\, dq\,. \tag{5}$$

In $\Delta h(q=0) \equiv S(q=0) - S_0(q=0)$, $\Delta K(q=0) = h^2(q=0) - h_0^2(q=0)$ subscript " $_0$ " refers to the base system of hard spheres.

Taking into account that the base system of hard spheres is considered to be of the same density as the perturbed system, it is possible to require the conditions [2] be satisfied

$$\int_0^\infty [h(q) - h_0(q)]\, q^2\, dq = 0\,,$$

$$\int_0^\infty \left\{ [h(q) - h_0(q)] - \frac{1}{2}\left[h^2(q) - h_0^2(q)\right] + \frac{1}{3}\left[h^3(q) - h_0^3(q)\right] + \ldots \right\} q^2\, dq = 0\,. \tag{6}$$

Now equation (5) with the help of conditions (6) can be cast into the form:

$$\frac{F - F_0}{Nk_BT} \cong -\frac{1}{2}[S(q=0) - S_0(q=0)] + \frac{1}{2}\left[h^2(q=0) - h_0^2(q=0)\right]. \tag{7}$$

Using the relation between structure factor $S(q)$ and direct correlation function $C(q)$

$$S(q) = \frac{1}{1 - nC(q)}$$

estimation of thermodynamic perturbation theory series can be obtained:

$$\frac{F - F_0}{Nk_BT} = -\frac{1}{2} S_0^2\, nC_1(q=0) + \ldots\,, \tag{8}$$

where $C_1 = C - C_0$.

In low-temperature liquid metal $S_0(q=0)$ is of order $10^{-3} - 10^{-2}$, and order of $nC_1(q = 0)$ in chaos phase approach ($nC_1 = -\Phi_1 / k_BT$) is 10^1 . Thus first term of series (8) has order of $10^{-5} - 10^{-3}$. These estimations (according to (9)) verify known fact of closeness of macroscopic properties of liquid metals in melting point region and properties of corresponding system of hard spheres. For example, for non-transition metals at temperature near melting point heat capacity is $(3.4 - 4.0)\cdot k_B$, and excess entropy is $(1.8 - 4.6)\cdot k_B$. For the system of hard spheres of the same density the corresponding values are $(3.4 - 4.1)\cdot k_B$ and $(3.1 - 5.0)\cdot k_B$.

2.2 Free Energy of Liquid Non-Transition Metal

According to the results obtained by applying the method of pseudopotentials in electron theory of metals and statistical theory of liquid state, free energy per particle $F(\rho,T)$ at temperature T and density ρ can be presented

$$F(\rho,T) = F_e + nzb(0) + \Delta E + F_i \ . \tag{9}$$

Here, F_e - energy of homogenous electron gas which can be expressed be Nozieres-Pines interpolation relation [1]

$$F_e = \frac{3}{5} k_F^2 - \frac{3}{2\pi} k_F - 0.1156 + 0.0315 \ln\left[\left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{k_F}\right] , \tag{10}$$

where k_F - Fermi's wave vector, z - valence of metal. $b(0)$ is non-coulomb part of ion-electron pseudopotential $\omega(q)$ in metal:

$$b(0) = \lim_{q \to 0} \left[\omega(q) + \frac{4\pi z e^2}{q^2} \right] . \tag{11}$$

In equation (9), ΔE also depends on mean density of metal only and can be expressed as

$$\Delta E = \frac{4\pi z e^2}{q^2} \int_0^\infty F(x)\, dx - nzb(0) - \frac{z}{2} v^2 \frac{\partial^2 F_e}{\partial v^2} , \tag{12}$$

where $x = \frac{q}{2k_F}$, $F(x) = H^2 [\varepsilon(x) - 1] / \varepsilon(x)$, $H = q^2\omega(q) / 4\pi z e^2$,

v - volume per ion, $\varepsilon(q)$ - static dielectric constant of electron gas.

The contribution F_i is considered to be structure-dependent free energy of the system of classical particles (ions) of effective paired interionic potential $\Phi(R)$. For non-transition liquid metals this potential can be expressed as

$$\Phi(R) = \Phi_c(R) + \Phi_e(R) , \tag{13}$$

where $\Phi_c(R) = \frac{z^2 e^2}{R}$ - direct Coulomb interionic interation, and $\Phi_e(R)$ - indirect interaction among ions through electrons of conductivity:

$$\Phi_e(R) = \frac{1}{2\pi^2 n} \int_0^\infty \Phi_e(R) \frac{\sin(qR)}{qR} q^2 \, dq$$

defined in terms $\omega(q)$ and $\varepsilon(q)$ by well-known equations [1, 2]. Using introduced notation, equation (9) can be rewritten

$$F(\rho, T) = F_e + nzb(0) + \frac{1}{2} \Phi_e(R = 0) - \frac{1}{2} \Phi(R = 0) + F_i \ , \tag{14}$$

where $\Phi(q = 0) = 2nzb(0) + zv^2 \frac{\partial^2 F_e}{\partial v^2}$, $\quad \Phi_e(R = 0) = -\frac{8z^2 k_F}{\pi} \int_0^\infty F(x) \, dx$.

Taking into account the orders of quantitative estimations in (8), it can be assumed that $F_i \cong F_0$. Thus, equation (14) for free energy is a function weakly depending on the form of interionic potential, and pseudopotential $\omega(q)$, and dielectric constant $\varepsilon(q)$. Hence, it is possible to avoid the problems of detailed description of dielectric constant $\varepsilon(q)$ and exact calculation of integrals the following types

$$\int_0^\infty \Phi(R) R^2 \, dR \ , \qquad \int_0^\infty \Phi(R) g_0(R) R^2 \, dR \ .$$

It is important that selected $\varepsilon(q)$ satisfies the summation rule for compressibility of electron gas, and correct asymptotic behavior for $q \to 0$ and $q \to \infty$. These requirements can be satisfied by the following mathematical expression

$$\frac{\varepsilon(q) - 1}{\varepsilon(q)} = \exp\left[- q^2 \beta^2(k_F) \right] \ . \tag{15}$$

If model pseudopotential is selected to be

$$\omega(q) = -\frac{4\pi z e^2}{q^2} \cos(qR_c) \tag{16}$$

then

$$\Phi_e(R = 0) = -\frac{z^2}{\beta\sqrt{\pi}} \left\{ 1 + \exp\left[-\left(\frac{R_c}{\beta}\right)^2 \right] \right\}, \tag{17}$$

$$\beta^2 = R_c^2 + \frac{3}{8}\frac{\pi}{zk_F^3} z v^2 \frac{\partial^2 F_e}{\partial v^2} . \tag{18}$$

Finally, as a results of (14), the appropriate equation for free energy:

$$F \cong F_e - \frac{1}{2}\frac{z^2}{\beta\sqrt{\pi}}\left\{ 1 + \exp\left[-\left(\frac{R_c}{\beta}\right)^2 \right]\right\} - \frac{1}{2} z v^2 \frac{\partial^2 F_e}{\partial v^2} + F_0 . \tag{19}$$

Equation (19) is two-fold parametric: R_c from (16), and hard spheres packing parameter $\eta = \frac{\pi}{6} nd^3$ from F_0 .

Exactly as it took place in Barker-Henderson theory, as well as in the general case of weak repelling, hard sphere diameter d is a function of temperature. For example, in the case of (n,m) Lennard-Jones potential, such dependence can be presented by

$$d(T) = a - bT^{1/n} , \tag{20}$$

where a , $b = \text{Const}$, and n depends on the specifics of repulsion and attraction. If parameters a , b , n in equation (20) are selected from the conditions describing thermodynamic properties in melting point region of metal, then all thermodynamic properties can be obtained from (19).

3. RESULTS

In previous publications [2, 3] authors calculated thermodynamic properties of liquid alkali metals (Na, K, Rb, Cs) with the use of equation (9), values of dielectric constant $\varepsilon(q)$ in the approximation [4] and model pseudopotential of ion-electron interactions [1]:

$$\omega(R) = \begin{cases} ze^2 U/R_c, & \forall\ R < R_c \\ ze^2/R, & \forall\ R < R_c \end{cases} \tag{21}$$

$$\omega(R) = ze^2 \left\{ \frac{\exp(-R/R_c) - 1}{R} + \frac{a}{R_c}\exp\left(\frac{R}{R_c}\right) \right\} . \tag{22}$$

For alkali metals second and third orders of perturbation of the pseudopotential have been applied. For Pb, Bi, Mg only third order of perturbation of the pseudopotential has yielded satisfactory results. In order to determine contribution associated with F_i Barker-Henderson perturbation theory [8] has been used. The results of such calculation for the case of Na and Pb are presented

in Tables I, II. Analysis of these results shows that it is very difficult problem of consistent selection of the energy approximation of electron gas, dielectric constant of electron gas, and the perturbation theory for determined effective interionic interaction. The addressed issue was a development of new approach which would allow to avoid above mentioned problems at least partly.

Obtained equations (8), (14), (19) have been applied for new calculations of thermodynamic properties of above mentioned metals. Satisfactory agreement of predicted values and experimental data has been achieved. Comparison in Tables I, II represents better agreement for isobaric capacity and isothermal compressibility. Unfortunately, values on isothermal compressibility still contain high errors. Obtained results for liquid lead are illustrated in Table III. These results are obtained for the following values of the parameters in equations (16 - 20):

$$a = 4.36 , \qquad b = 0.356 , \qquad n = 6 , \qquad R_c = 0.647 \cdot a_B ,$$

where a_B - Bohr radius.

Obtained results showed that obtained modification of thermodynamic perturbation theory is successful in applying at least to liquid non-transition metal. The simplifying assumptions regarding analysis and conclusions about static dielectric of electron gas have been confirmed. Comparison of obtained results with experimental data suggests that developed method can be used for standardization procedure of thermodynamic data on the properties of liquid non-transition metals.

REFERENCES

1. N.P. Kovalenko, Y.P. Krasny, S.A. Triger, *Statistical Theory of Liquid Metals*. - Moscow: Nauka, 1990. - 204p.
2. V.P. Onistchenko, O.F. Kutirkin, A.Y. Bickov. *Proc. of 14-th European Conference on Thermophysical Properties*, Lyon - Villeurbanne, France, 1996. - p.301.
3. V.P Onistchenko, V.P. Zhelezny, O.F. Kutirkin, A.Y. Bickov, *Ukr. J. of Phys.* **41**: 1070 (1996).
4. D.J.V. Geldart, S.H. Vosko, *Can. J. Phys.* **44**, N2: 2137 (1996).
5. R. Vashishta, K.S. Singwi, *Phys. Rev.* **B1**, N3: 875 (1972).
6. S. Ichimary, K. Utsumi, *Phys. Rev.* **B24**, N12: 7385 (1981).
7. M.V. Vavrukh, V.B. Solovyan, *Ukr. J. of Phys.* **38**: 948 (1993).
8. J.A. Barker, D. Henderson, *J. Chem. Phys.* **47**: 2856 (1967).
9. U. De Angelis, N.H. March, *Phys. Lett.* **A56**, N4: 287 (1976).
10. N.H. March, *Can. J. Phys.* **65**: 219 (1987).
11. P.I. Bistrov, D.H. Kagan, G.A. Krechetov, E.E. Shpilrain. *Liquid-metal heat transfer media for heat tubes and heat machines* . - Moscow: Nauka, 1998. - 263 p.
12. B.I. Zinovyev. *Thermophysical properties of metals at high temperature (Handbook).* - Moscow: Metallurgia, 1989. - 383 p.
13. B.G. Markov, *High temperature thermophysics* (Moscow) **13**: 1108 (1975).
14. E. Babic, M.A. Howson, G.J. Morgon, *Phil. Mag.* **B59**: 331 (1989).

Table I. Comparison of Predicted Values and Experimental Data on Properties of Liquid Sodium

(1 - calculation with the use of pseudopotential in equation (22),

2 - calculation with the use of pseudopotential in equation (21))

Temperature K	Density ($kg \cdot m^{-3}$)			Isobaric heat capacity ($J \cdot kg^{-1} \cdot K^{-1}$)			Isothermal compressibility, (MPa^{-1}) $\beta_T \cdot 10^5$		
	1	2	[11]	1	2	[11]	1	2	[11]
400	911.5	919.3	920.2	1672.4	1710.7	1371.0	9.5	11.7	18.7
600	864.1	864.6	877.4	1514.7	1518.0	1301.0	12.2	14.9	24.2
800	824.2	818.2	831.0	1415.0	1392.6	1260.4	14.9	18.3	30.5
1000	787.6	776.2	783.0	1327.9	1332.0	1252.8	18.0	21.8	38.3
1200	753.2	737.6	737.7	1301.6	1289.7	1279.9	21.5	26.6	48.3
1400	720.0	700.7	682.1	1265.3	1261.3	1342.5	25.1	31.3	62.1
1600	689.4	666.2	629.1	1241.1	1235.5	1440.5	29.2	35.7	82.4
1800	659.2	633.9	574.0	1237.9	1215.5	1574.3	33.0	40.0	116.0
2000	630.0	602.9	519.0	1190.0	1214.1	1743.9	38.4	47.3	182.5

Table II. Comparison of Predicted Values with Experimental Data on Properties of Liquid Lead

(1 - calculation with the use of pseudopotential in equation (22))

Temperature K	Density ($kg \cdot m^{-3}$)		Isothermal heat capacity ($J \cdot kg^{-1} \cdot K^{-1}$)		Isothermal compressibility $\beta_T \cdot 10^5$ (MPa^{-1})	
	1	[12]	1	[12]	1	[13, 14]
601	10672	10686	145.3	146.4	2.7	1
800	10428	10430	140.4	143.3	2.8	3.7
1000	10198	10198	136.4	140.1	2.9	4.2
1200	9982	-	133.4	-	3.0	
1400	9781	-	132.1	-	3.2	
1600	9594	-	132.6	-	3.4	
1800	9421	-	135.1	-	3.7	
2000	9263	-	140.1	-	4.1	

Table III. Comparison of Predicted Values with Experimental Data on Properties of Liquid Lead

(1 - calculation with the use of pseudopotential in equation (19))

Temperature K	Density ρ ($kg \cdot m^{-3}$)		Isothermal heat capacity ($J \cdot kg^{-1} \cdot K^{-1}$)		Isothermal compressibility $\beta_T \cdot 10^5$ (MPa^{-1})	
	1	[12]	1	[12]	1	[13, 14]
600	10689	10686	146.3	146.4	3.7	3.5 - 3.2
700	10573	-	144.4	143.3	4.1	-
800	10453	10430	142.8	140.1	4.5	3.7
900	10329	-	141.5	-	5.0	-
1000	10203	10198	140.7	-	5.6	4.2
1100	10073		140.2		6.2	
1200	9938		140.1		6.9	
1300	9799		140.6		7.8	
1400	6952		141.8		8.9	
1500	9497		143.9		10.2	
1600	9330		147.5		12.13	
1700	9145		153.6		14.9	
1800	8931		165.6		19.7	
1900	8652		201.5		32.2	