Bulk Modulus Calculations of Liquid Alkali Metal Alloys

Mehmet YILMAZ, Seyfeddin KARAGÖZLÜ, İdris GÜMÜŞ
Department of Physics, Yıldız Technical University,
80270 Şişli, İstanbul - TURKEY

Abstract

In this work, the bulk modulus values for liquid alkali metal alloys near melting point are studied in the framework of the Gibbs-Bogoliubov method. We use the local Heine-Abarenkov pseudopotential and Ichimaru-Utsumi screening function in these alloys. The results are compared with experimental and theoretical results.

1. Introduction

In the last two decades a number of theoretical studies have been performed on various properties of metals in liquid state [1,2]. Advances in these studies has been made possible due to the combination of the pseudopotential theory [3] with thermodynamic perturbation theories.

In this study, we use a variational method based on the Gibbs-Bogoliubov (GB) inequality [4] with a hard-sphere mixture as a reference system to calculate properties of alkali metal allyos near melting point. Hard-sphere diameters are determined by minimizing the Helmholtz free energy of the system. The pseudopotential method, the GB method and bulk modulus calculations of liquid alkali metal alloys are discussed in section 2, after which the results and conclusions are given in section 3.

2. Theory

2.1. Pseudopotential Method

The pseudopotential theory enables one to formulate the energy in terms of the pseudopotential and the structure factor. Pseudopotentials have been introduced with the

intention of simplifying the calculation of the electronic structure by eliminating the necessity to include the tightly bound electrons forming the ionic core and the strongly attractive potential responsible for binding them.

In the present work, we use the local Heine-Abarenkov pseudopotential [5] as the electron-ion pseudopotential. This model potential is written as

$$u(r) = \begin{cases} -Ze^2 A/R_M & r < R_M \\ -\frac{Ze^2}{r} & r > R_M \end{cases} \tag{1}$$

for which the Fourier transform of this potential becomes

$$u(q) = -\frac{4\pi e^2 A}{\Omega q^3}[\sin(qR_M) - qR_M\cos(qR_M)] - \frac{4\pi Ze^2}{\Omega q^2}\cos(R_M), \tag{2}$$

where Ω is the atomic volume, Z the valence charge, and A and R_M are the model potential parameters.

The bare electron-ion pseudopotential (2) should be screened since there are electrons along as well as ions in the system. The dielectric function $\varepsilon(q)$ relates the bare potential $u(q)$ to the screened potential through the relation

$$U(q) = \frac{U_{ei}(q)}{\varepsilon(q)}. \tag{3}$$

The general form of $\varepsilon(q)$ including the local-field correction $G(q)$ is expressed as

$$\varepsilon(q) = 1 + (1 - G(q))\left[\frac{4\pi Ze^2}{\Omega q^2}\frac{3}{2E_F}\right]f_0(x) \qquad (x = \frac{q}{2q_F}), \tag{4}$$

where $q_F = (3\pi^2 Z/\Omega)^{1/3}$ is the Fermi wawe vector, E_F is the Fermi energy and the Linhard function $f_0(x)$ [6] is

$$f_0(x) = \frac{1}{2} + \frac{1 - x^2}{4x}\ln\left|\frac{1 + x}{1 - x}\right|. \tag{5}$$

There are many forms proposed for the local-field correction $G(q)$. We used the local-field correction $G(q)$ of Ichimaru and Utsumi [7].

2.2. Gibbs-Bogoliubov(GB) Method

The simplest possible thermodynamic perturbation theory is a variational method based on the GB inequality. This inequality can be stated as follows. The free energy is expressed in terms of the free energy F_0 of a reference system plus a perturbation term $< V >_0$ which represents the difference between the Hamiltonians of the real and reference systems evaluated with respect to the distribution functions of the latter; the sum $F_0 + < V >_0$ is then an upper bound of F:

$$F \leq F_0 + < V >_0 . \tag{6}$$

In the present work, we use the hard-sphere system as a reference system. The best diameter and free energy are given by

$$\left(\frac{\partial F}{\partial \sigma_1}\right)_{\Omega,T,\sigma_2} = \left(\frac{\partial F}{\partial \sigma_2}\right)_{\Omega,T,\sigma_1} = 0. \tag{7}$$

2.3. The bulk modulus calculations of liquid alkali metal alloys

We consider a liquid binary mixture of $c_1 N$ hard-spheres with diameter σ_1 and $c_2 N$ with diameter σ_2, all in a volume Ω. The number densities of the ion species are $n_1 = c_1 n, n_2 = c_2 n$, where $n = N/\Omega$. If Z_1 and Z_2 are valencies, then the mean average valence electron density is $\bar{Z}n = Z_1 n_1 + Z_2 n_2$.

The Helmholtz free energy per ion of the alloy [8] is

$$F = F_{hs} + F_{ps}, \tag{8}$$

where F_{hs} is the Helmholtz free energy of the hard-sphere system and F_{ps} is the appropriate expectation value of the effective potential energy for the ion system. F_{hs} is written down as follows:

$$F_{hs} = \frac{3}{2}k_B T - TS_{hs} \tag{9}$$

$$S_{hs} = S_{gas} + S_c + S_\eta + S_\sigma \tag{10}$$

$$\frac{S_{gas}}{k_B} = \ln\left[\frac{e}{n}\left(\frac{emk_BT}{2\pi\hbar^2}\right)^{3/2}\right] \quad (m = m_1^{c_1}m_2^{c_2}) \tag{11}$$

$$\frac{S_\eta}{k_B} = \ln(1-\eta) + \frac{3}{2}\left[1 - \frac{1}{(1-\eta)^2}\right] \tag{12}$$

$$\frac{S_c}{k_B} = -(c_1 \ln c_1 + c_2 \ln c_2) \tag{13}$$

$$\frac{S_\sigma}{k_B} = \frac{\pi c_1 c_2 n(\sigma_1 - \sigma_2)^2[12(\sigma_1 + \sigma_2) - \pi n(c_1\sigma_1^4 + c_2\sigma_2^4)]}{24(1-\eta)^2} \tag{14}$$

$$\eta = \frac{1}{6}\pi(n_1\sigma_1^3 + n_2\sigma_2^3), \tag{15}$$

where S_{gas} is the ideal gas entropy, S_c is the ideal entropy of mixing and S_η depends only on the packing density η. S_σ corresponds to the mismatch between hard-spheres with different radii. F_{ps} in Eqn. (8) is given by

$$F_{ps} = F_{eg} + F_1 + F_2 + F_M, \tag{16}$$

1021

where F_{eg} arises due to free electron-gas:

$$F_{eg} = \frac{1.105}{r_s^2}\bar{Z} - \frac{0.458}{r_s}\bar{Z} - (0.0575 - 0.0155\ln r_s)\bar{Z}, \tag{17}$$

with

$$r_s = (3/4\pi n)^{1/3}. \tag{18}$$

The first two terms in Eqn.(17) are the Hartre-fock energy of the free electrons. The last term is correlation energy.

F_1 and F_2 is defined via first and second order pseudopotential perturbation theory:

$$F_1 = (c_1\alpha_1 + c_2\alpha_2)\bar{Z}n, \tag{19}$$

where

$$\alpha_i = \lim_{q\to 0}\left(u_i(q) + \frac{4\pi Z_i}{q^2}\right) \tag{20}$$

$$F_2 = \frac{1}{16\pi^3}\int_0^\infty [c_1c_2(u_1 - u_2)^2 + c_1^2u_1^2a_{11} + 2c_1c_2u_1u_2a_{12}$$
$$+ c_2^2u_2^2a_{22}]\left(\frac{1}{\varepsilon(q)} - 1\right)q^4 dq. \tag{21}$$

The Madelung contribution for the ion-ion interaction F_M is given by

$$F_M = \frac{1}{\pi}\int_0^\infty [c_1^2Z_1^2(a_{11} - 1) + 2c_1c_2Z_1Z_2(a_{12} - 1)$$
$$+ c_2^2Z_2^2(a_{22} - 1)]dq, \tag{22}$$

where $a_{ij}(q)$ is the partial structure factor defined and used by Faber. The pressure P and bulk modulus B is defined by

$$P = n^2\left(\frac{\partial F}{\partial n}\right)_T \tag{23}$$

and

$$B = n\left(\frac{\partial P}{\partial n}\right)_T. \tag{24}$$

Thus substituttion of Eqn.(23) into Eqn.(24) yields

$$B = nk_BT + B_{kin} + B_{ex-c} + B_M + B^{(1)} + B^{(2)}, \tag{25}$$

1022

where B_{kin} and B_{ex-c} show the contributions from the kinetic and exchange-correlation energies of the electron gas, respectively:

$$B_{kin} = NZ\Omega\frac{d^2F_{kin}}{d\Omega^2} = \frac{1}{4\pi r_s^2}\left(\frac{2.21 \times 5}{3r_s^2}\right) \tag{26}$$

$$B_{ex-c} = NZ\Omega\frac{d^2Fe_{ex-c}}{d\Omega^2} = -\frac{1}{4\pi r_s^2}\left(\frac{0.458 \times 4}{3r_s^2} - \frac{0.0155}{r_s}\right). \tag{27}$$

B_M takes into account the direct coulomb interaction and is given by

$$B_M = \frac{4n}{9\pi}\int_0^\infty [c_1^2 Z_1^2(a_{11} - 1) + 2c_1 c_2 Z_1 Z_2(a_{12} - 1)$$
$$+ c_2^2 Z_2^2(a_{22} - 1)]dq. \tag{28}$$

The terms $B^{(1)}$ and $B^{(2)}$ are

$$B^{(1)} = 4\pi\bar{Z}n^2\left[c_1 Z_1 R_{M1}^2\left(1 - \frac{2A_1}{3}\right) + c_2 Z_2 R_{M2}^2\left(1 - \frac{2A_2}{3}\right)\right] \tag{29}$$

$$B^{(2)} = \frac{n}{2\pi^2}\int_0^\infty \left\{c_1 c_2\left[\left(1 + \frac{5q}{9}\frac{\partial}{\partial q} + 2n\frac{\partial}{\partial n} + \frac{q^2}{18}\frac{\partial^2}{\partial q^2} + \frac{nq}{3}\frac{\partial^2}{\partial n\partial q} + \frac{n^2}{2}\frac{\partial^2}{\partial n^2}\right)\right.\right.$$
$$\times (\phi_{11}(q,n) - 2\phi_{12}(q,n) + \phi_{22}(q,n))\right]$$
$$+ \sum_{ij} c_i c_j\left[\left(1 + \frac{5q}{9}\frac{\partial}{\partial q} + 2n\frac{\partial}{\partial n} + \frac{q^2}{18}\frac{\partial^2}{\partial q^2} + \frac{nq}{3}\frac{\partial^2}{\partial n\partial q} + \frac{n^2}{2}\frac{\partial^2}{\partial n^2}\right)\right.$$
$$\left.\left.\times \phi_{ij}(q,n)\right]a_{ij}\right\}q^2 dq. \tag{30}$$

3. Results and Conclusion

Table 1 shows the input data employed in our calculations. The potential parameters A_1 and A_2 of Table 1 are obtained by fitting the internal energy to the experimental values which are shown in Table 4. Experimental internal energy values F_{int}^{exp} are from Gschneider [9]. The model potential parameters R_{M1} and R_{M2} and atomic volume values Ω_1 and Ω_2 are also taken from Animalu and Heine [10], and from the compilation of Young [11], respectively.

Table 1. Input parameters

Alloy	$\Omega_1(au)^3$	$\Omega_2(au)^3$	$R_{M1}(au)$	$R_{M2}(au)$	A_1	A_2	$T(°K)$
Li-Na	152	278	2.8	3.4	1.131	1.118	453
K-Na	527	278	4.2	3.4	1.072	1.118	373
Rb-Na	651	278	4.4	3.4	1.055	1.118	373
Cs-Na	809	278	4.8	3.4	1.044	1.118	373

For liquid binary alloys the effective hard-sphere diameters are calculated by minimizing the Helmholtz free energy (Table 2).

Table 2. Calculated diameters and packing fractions. The diameters are calculated at 50-50 concentration.

Alloy	$\sigma_1(au)$	$\sigma_2(au)$	η
Li-Na	3.615	5.808	0.427
K-Na	7.327	5.937	0.432
Rb-Na	7.679	5.914	0.441
Cs-Na	8.124	5.870	0.465

The calculated bulk modulus B values for liquid binary alloys are given in Table 3. We have included the values calculated by Dalgıç(D) [12] and Hafner(H) [13] in the same Table for comparison. Dalgıç calculated the bulk modulus values in the real space formalism using an analytic pair potential proposed by Pettifor and Ward. Hafner obtained the bulk modulus values of liquid metals and alloys using an orthogonalised plane wave-based first-principle pseudopotential. Also given in Table 4 are the bulk modulus values of liquid alkali metalas calculated by Hasegawa-Watabe (HW) [16], Hafner(H)[13], and Seyfettin Dalgıç and M. Tomak(DT) [17]. Hasegawa-Watabe use the ordinary perturbation scheme, Kleinman's screening function and the local Ashcroft pseudopotential. Dalgıç and Tomak use an analytic pair potential proposed by Pettifor and Ward, the Heine-Abarenkov pseudopotential and experimental radial distribution function.

Table 3. Experimental and calculated bulk modulus $B(10^{10}dyn/cm^2)$ values at 50-50 concentration.

Alloy	B^D	B^H	B	B_{exp}
Li-Na	23.292	–	13.109	–
K-Na	9.011	2.600	5.067	3.300[a]
Cs-Na	6.695	1.700	5.207	2.000[b]
Rb-Na	–	–	4.804	–

[a] Abowitz and Gordon [4]
[b] Kim and Letcher [15]

Table 4. Experimental internal energy $F_{int}^{\exp}(au)$ and calculated bulk modulus $B(10^{10}dyn/cm^2)$ values of liquid alkali metals.

	Li	Na	K	Cs	Rb
$F_{int}(au)$	0.262	0.232	0.195	0.174	0.186
$F_{int}^{exp}(au)$	0.262	0.232	0.195	0.174	0.186
B	17.198	5.833	2,648	1.439	1.844
B^{HW}	7.856	5.870	2.490	1.550	1.670
B^H	9.300	3.800	1.800	1.500	1.100
B^{DT}	28.010	5.271	1.764	0.875	0.821
B_{exp}	11.500	5.380	2.600	2.000	1.400

The general assumptions employed in the calculations of the bulk modulus presented here can be summarized as follows: (a) The pseudopotential theory is valid for liquid metals. (b) A system of hard-spheres represents a convenient reference system. Gibbs-Bogoliubov inequality provides the basis for a variational determination of effective hard-sphere diameters.

Comparison reveals that the calculated values of the bulk modulus are generally in good agreement with the experiments and other theoretical results. More exact calculations are, of course, possible by using a better pseudopotential and a better approximation for the screening function.

References

[1] M. Shimoji, Liquid Metals (Academic Press, New York, 1977).

[2] J. P. Hansen, Theory of Simple Liquids (Academic Press, London, 1986).

[3] W. A. Harrison, Pseudopotentials in the Theory of Metals (Benjanin, New York, 1966).

[4] D. Stroud and N. W. Ashcroft, *Phys. Rev.,* **B 5** (1968) 371.

[5] V. Heine and I. Abarenkov, *Phil. Mag.,* **8** (1964) 2055.

[6] K. S. Singwi and M. P. Tosi, *Sol. State Phys.,* **36** (1981) 177.

[7] S. Ichimaru and K. Utsumi, *Phys. Rev.,* **B 24** (1981) 7385.

[8] I. H. Umar, A. Meyer, M. Watabe and W. H. Young, *J. Phys.,* **F 4** (1974) 1691.

[9] K. Gschneider, Solid State Physics (Academic Press, New York, 1964).

[10] A. O. E. Animalu and V. Heine, *Phil. Mag.,* **12** (1965) 1249.

[11] W. H. Young, Structural and Thermodynamic Properties of NFE liquid Metals and Binary Alloys, *Rep. Prog. Phys.,* **55** (1992) 1769.

[12] S. Dalgıç , Ph. D. Thesis, Department of Physics, University of Trakya, Edirne, Turkey, 1992.

[13] J. Hafner, *Phys. Rev.,* **A 16** (1977) 351.

[14] G. Abowitz and R. B. Gordon, *J. Chem. Phys.,* **37** (1962) 125.

[15] M. G. Kim and S. V. letcher, *J. Chem. Phys.,* **55** (1971) 1164.

[16] M. Hasegawa and M. Watabe, *J. Phys. Soc. Jpn.,* **32** (1972) 14.

[17] S. Dalgıç and M. Tomak, *Turk, J. Phys.,* **18** (1994) 72.