The Single Step VMHNC Calculations for Liquid Alkali Metals in the Inverse Problem

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Abstract

An effective pair potential $\phi(r)$ for liquid alkali metals close to their melting points is extracted from an experimental structure factor using the inverse method based on the variational modified hypernetted-chain integral equation theory of liquids (VMHNC). The first order pair potential according to the procedure suggested by de Angelis and March is also presented for comparison. It has been found that the inverted pair potentials of liquid alkali metals scale well.

Key Words: liquid metals, inverse potentials, VMHNC theory

1. Introduction

As is well known, the effective pair potential plays an important role to explain the properties of liquid metals. The assumption of a pair potential implies that n-body contributions to the potentials with $n > 2$ are negligible or can be successfully averaged into effective pair potential. The effective pair potential of the liquid alkali metals can be obtained by the pseudopotential perturbation theory based on the nearly-free electron (NFE) model at their melting points and its applicability is limited. Another approximate procedure, the so-called inverse problem for deriving the pair potentials from experimental liquid structure factor has been proposed by Johnson and March [1,2]. The accuracy of the inverse method has been improved to obtain a reliable pair potential of the system [3-6]. One of the routes applied to derive the effective pair potentials from measured structural data has been utilized by a number of workers [7,8], which is based on the formalism developed by de Angelis and March from the Born-Green-Yvon hierarchy. This is the so-called approximate inversion formula [3]. Some integral equation theories, the Percus-Yevick (PY), Hypernetted Chain (HNC), Mean Spherical approximation (MSA) and Modified Hypernetted Chain (MHNC) equation [9] are studied for solving the inverse problem. The molecular-dynamics simulation for model fluids has provided a testing ground for these theoretical methods [10-14]. Related to this, other integral equation theories successfully applied to the metallic systems can be found in the literature [15,17]. Researchers show that the variational hypernetted chain theory (VMHNC) is widely used to predict static structure factors and thermodynamic properties of liquid metals in direct calculations [17]. It is for these reasons that we choose the VMHNC integral-equation method based on the Ornstein-Zernike equation for our inverse calculations.

The inversion schemes that rely on such rearrangements of the closure equation are often called "single-step" inversions. Our first aim in this paper is to apply the single-step VMHNC inversion to extract the pair potential. For this purpose, the MHNC equation is solved for a fluid of particles interacting through the inverse potential using the variational criterion. This is the so-called VMHNC approximation [17]. At the

level used in the present work, the VMHNC has accuracy comparable to the local MHNC procedure proposed by Lado et al. (LFA) [18]. The deficiency of LFA comes from the analytic behaviour of the hard sphere parametrized bridge functions used. Our second aim is to extract the pair potentials from experimental structure data using the approximate inversion formula of de Angelis and March [3], which is used for some liquid metals [7,8]. In this paper, it is to be used as a test case to check our results using VMHNC.

In practice the inverted potentials depends on the quality of the data and on the method for its handling. The smoothing and iterative transform techniques are often used for inversion of experimental structure factor data. The origin of the difficulty in single-step inversions is that the fourier transform of the experimental data S(k) is available only in a limited k region. This produces truncation oscillations in transforming S(k) directly to pair distribution function g(r). However the systematic errors in measuring S(k) affects g(r) and superimposed truncation oscillations at all r, and the repulsive core part of $\beta\phi(r)$ is rather insensitive to these errors in S(k). We have used the iterative transform technique and a linear q expansion in the small k region. It is shown that the accuracy of the single-step VMHNC approach is good in comparison with the predicted inverse potentials $\beta\phi(r)$ for liquid alkali metals obtained employing molecular dynamics (MD)[19]. We have also compared our results with those obtained from the neutral-pseudoatom method (NPA)[20]. It has been found that the single-step VMHNC inversion method yields more agreeable results for the inverse potential. This work and other calculations in the inverse problem has indicated that the structure of simple liquid metals near their melting point is mainly determined by the repulsive part of the pair potential and the attractive part has only a small effect on the structure [11,21,22]. The inverted potentials and radial distribution functions obtained in this work scale very well. The calculated scaled values $S^\star(0)$ of liquid alkali metals are in good agreement with others [23,24]. Hence, the validity of the proposed inversion scheme for liquid alkali metals, which is based on the single-step VMHNC approach in the inverse problem, has been confirmed.

The organization of this paper is as follows. We review the theoretical methods applied in this work in section 2. In section 3 we present the results of our calculations. First, we give a brief discussion of our inversion procedure using experimental structural data to extract the pair potentials. The scaled pair potentials of liquid alkali metals obtained by the VMHNC and approximate inversion formula are compared with the ab initio potentials, namely the neutral pseudoatom calculations (NPA), and MD potentials when these are available. The scaled single-step VMHNC potentials for liquid alkali metals show that as we progress down the column of the alkali metals we find the expected trends.

2.   The Inverse Problem

The distribution function g(r) completely characterizes the static correlations in a fluid at the pair level. It is related to the measured structure factor S(k) by

$$g(r) = 1 + \frac{1}{2\pi^2\rho r} \int (S(k) - 1)k\sin(kr)dk, \tag{1}$$

where ρ is the number density of ions. The solution of the inverse problem, i.e. g(r)→$\phi(r)$, is based on certain approximations.

2.1.   Integral equations

In the integral equation approach, the effective pair potential $\phi(r)$ has beeen obtained using the closure relations in terms of the pair distribution function g(r) and the direct correlation function c(r) which can be obtained from $S(k)$ by

$$c(r) = \frac{1}{2\pi^2\rho r} \int (1 - \frac{1}{S(k)})k\sin(kr)dk. \tag{2}$$

Then using the Ornstein-Zernike relation,

$$g(r) - 1 - c(r) = \rho \int (g(|r - r'|) - 1)c(r')dr'. \tag{3}$$

For convenience we list the approximate theories and relevant equations below.

2.1.1. Modified Hypernetted Chain (MHNC) Equation:

The exact MHNC equation has the form:

$$\beta\phi_{\text{MHNC}} = g(r) - c(r) - \ln g(r) - 1 + B(r), \tag{4}$$

where $B(r)$ denotes the bridge function, for which some approximation must be made. When the bridge function is ignored, B(r)=0, we have the hypernetted-chain (HNC) approximation. The universality hypothesis of the bridge functions, as first pointed out by Rosenfeld and Ashcroft [9], is the usual approach for choosing the bridge function. Several approximate bridge functions [25,26] for hard sphere fluids have been proposed in parametrized form to be used in Equation (4). In this work, we follow Rosenfeld and Ashcroft in assuming the universality of the bridge function, B(r), as described by the Percus-Yevick (PY) approximation for the hard spheres (HS) system with packing fraction η; that is, $B(r) = B_{\text{PY}}(r, \eta)$ is given by

$$B_{\text{PY}}(r, \eta) = y_{\text{PY}}(r, \eta) - 1 - \ln y_{\text{PY}}(r, \eta), \tag{5}$$

where $\eta = \pi\rho\sigma^3/6$ with σ denoting the hard sphere diameter. The procedure to determine the parameter η has led to different though closely interwoven approaches [26,9].

2.1.2. Variational Modified Hypernetted Chain (VMHNC) Theory:

The VMHNC belongs to a class of integral equation theories of liquids. This approach, proposed by Rosenfeld [17], determines $\eta = \eta(\beta, \rho)$ so as to minimize the helmholtz free energy functional $f^{\text{VMHNC}}(\beta, \rho, \eta)$ by the variational condition

$$\frac{\partial f^{\text{VMHNC}}(\beta, \rho, \eta)}{\partial \eta} = 0. \tag{6}$$

In the above equation

$$f^{\text{VMHNC}}(\beta, \rho, \eta) = f^{MHNC}(\beta, \rho, \eta) - \Delta_\phi(\eta), \tag{7}$$

where $f^{MHNC}(\beta, \rho, \eta)$ is the MHNC free energy functional [17], and Δ_ϕ is given by

$$\Delta_\phi = \frac{1}{2}\rho \int_0^\eta d\eta' \int dr g_{\text{PY}}(r, \eta') \frac{\partial B_{\text{PY}}(r, \eta')}{\partial \eta'} - \delta_\phi(\eta), \tag{8}$$

with δ_ϕ chosen so as to obtain the virial/compressiblity consistency. Following Rosenfeld [17], we have used

$$\delta_\phi = f_{\text{CS}}(\eta) - f_{\text{PYV}}(\eta), \tag{9}$$

where f_{PYV} and f_{CS} are the hard-sphere expressions for the reduced Helmholtz free energies derived from the Percus-Yevick virial and the Carnahan-Starling equations of state, respectively [22]. The choice $\delta_\phi = 0$ recovers the approach proposed by Lado [18].

2.2. The Approximate Inversion Formula

This procedure is based on the formalism developed by de Angelis and March [3] in order to obtain the higher correlation functions for a liquid metal from the Born-Green-Yvon hierarchy. It provides a systematic iterative approach to derivation of an effective pair potential by

$$\phi(r) = \phi(r)_0 + \phi(r)_{\mathrm{I}} + \phi(r)_{\mathrm{II}} \tag{10}$$

with the potential of mean force $\phi(r)_0$,

$$\phi(r)_0 = -k_B T \ln(g(r)), \tag{11}$$

where $k_B T$ is the Boltzman constant and

$$\phi(r)_{\mathrm{I}} = \frac{k_B T}{8\pi^3 \rho} \int (S(k) - 1)^2 \exp(ikr) dk. \tag{12}$$

The second order term $\phi(r)_{\mathrm{II}}$ is also possible to express in terms of S(k) by a very complicated way and it will not be included below in discussion for s-p bonded liquid metals. This route has been used by a number of workers [7,8,27]. It represents an explicit solution of the inverse problem. de Angelis and March [3] has pointed out that the Born-Green, Percus-Yevick (PY) and Hypernetted Chain (HNC) equations lead to the same results for the first order approximate formula.

3. Results and Discussion

We choose the neutron diffraction results of Olbrich et al. [28] for liquid Li at 470 K and high quality x-ray diffraction data of Greenfield et al. [29] for liquid Na and K. The experimental structure factor $S_{\mathrm{expt}}(k)$ x-ray diffraction data of Waseda [21] and Hujiben et al. [23] for liquid Rb and Cs close to their melting points, repectively, are used as input data to extract the inverse potentials for these metals. Thermodynamic states studied in this work are given in Table 1.

Table 1. Thermodynamic states studied in this work. Scaled values of $S^\star(0)$ of liquid alkali metals, as obtained from the extrapolated experimental data and $S^\star_{\mathrm{expt}}(0)$ from Ref. [23,24].

Metal	T (K)	ρ (Å^{-3})	$S^\star(0)$	$S^\star_{\mathrm{expt}}(0)$
Li	470	0.04451	0.450	0.443
Na	373	0.02426	0.461	0.461
K	338	0.01275	0.458	0.468
Rb	313	0.01030	0.478	0.469
Cs	303	0.00834	0.482	0.463

(i) Inversion of experimental structural data: The experimental data $S_{\mathrm{expt}}(k)$ are available only in a limited k region. The pair distribution function $g_{\mathrm{expt}}(r)$ obtained by Fourier transforming the original experimental data of $S_{\mathrm{expt}}(k)$ is nonzero in the small-r region, where the $g_{\mathrm{expt}}(r)$ should be zero physically. Therefore we extrapolated $S_{\mathrm{expt}}(k)$ in both larger and smaller k regions given in the Appendix. In order to obtain the revised effective potentials accurately we removed the unphysical structure of $g_{\mathrm{expt}}(r)$ in the small-r region. The iterative transform was continued until the direct transform of the experimental $S_{\mathrm{expt}}(k)$ leads to a $g_{\mathrm{expt}}(r)$ that is very flat below r_0, determined by the closest approach of two atoms. The extrapolated liquid structure factors of alkali metals scale when they are plotted against k/k_m, where k_m refers to the first peak of the structure factor for each system are shown in Figure 1. It is also seen clearly that the extrapolated structure factors also scale well, except Cs. This is related with the original experimental data of Hujiben et al. Further, in the long wave limit scaled values of $S^\star(0) = 24(2)^{1/2} \int (g_{\mathrm{expt}}(r^\star) - 1) r^{\star^2} dr^\star$, where $r^\star = r/r_m$,

r_m refers to the position of the first $g_{\text{expt}}(r)$ peak. Due to the good scaling behaviour of $g_{\text{expt}}(r)$, we expect that $S^{\star}(0)$ is constant for all members of alkali metals. In Table 1, we show the scaled values of $S^{\star}(0)$ and compare them with those obtained by different methods [23,24]. It is mentioned that the calculated $S^{\star}(0)$ values are in good agreement with others. The average value of $S^{\star}(0)$ from proposed inversion procedure is 0.466, that is, higher than the value of 0.461 from [23,24]. It is expected that the effective pair potentials of these metals should also scale reasonably.
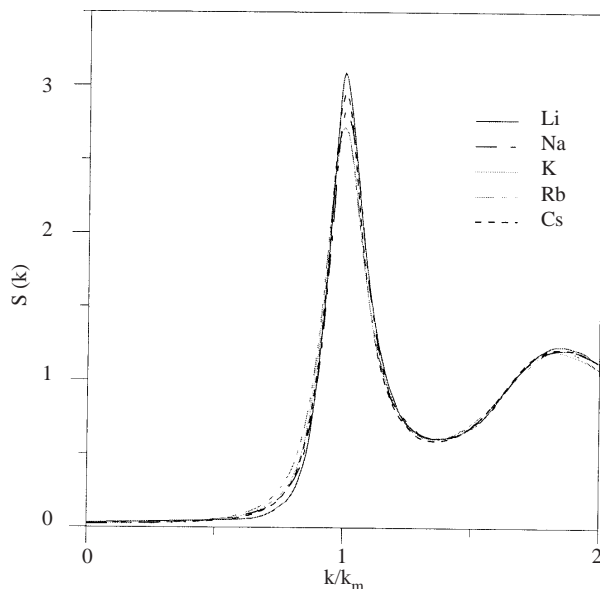

Figure 1. Extrapolated S(k) vs. k/k_m of liquid alkali metals near their melting points.

Effective Pair Potentials: The inverted potentials are extracted from the experimental data by the MHNC equation (2.4) with the bridge function which is found by the variational condition that minimizes the free energy. The calculated η values are 0.43, 0.446, 0.458, 0.463, 0.467 for Li, Na, K, Rb and Cs, respectively. Figure 2 shows our calculated scaled potentials $\beta\phi(r)$ from the data of Olbrich et al. for lithium at 470 K , along with the corresponding experimental pair distribution $g_{\text{expt}}(r)$ obtained by the fourier transform (FT) of the experimental structure factor $S_{\text{expt}}(k)$. The predicted inverse potentials for liquid Na from the data of Greenfield et al. at 373 K are shown in Figure 3. We also compare these effective potentials with those obtained by Gonzalez et al. from NPA theory and inverse potential derived from the multistep MHNC-MD calculations by Reatto et al.[10]. The potential derived from approximate inversion formula show less damped Friedel oscillations than the oscillations of VMHNC and others. We have noted that the height of the main peak of g(r) is unimportant for determining $\beta\phi(r)$. The feature of $\phi(r)$ is sensitive to errors in $S(k)$. The repulsive core is clearly related to the steepness with which $g(r)$ goes to zero as r decreases toward the atomic diameter. This must be related to the behaviour of $S(k)$ at large k, because of the Fourier transform relation between $g(r) - 1$ and $S(k) - 1$. We have examined the sensitivity of the repulsive core of $\phi(r)$ to the large k region of $S(k)$. We chose for liquid potassium at 338K, the k values from 1 to 8.45 (Å^{-1}, and r values from 0.74 Å to 6.283 Å. We find that the position of the minima is at 4.45 Å for the potential derived from approximate inversion formula. The minimum for potentials from the HNC and MHNC equations is at 4.414 Å. The difference between HNC and VMHNC potentials is related with PY-HS bridge function. In Figure 4, the scaled VMHNC and approximate inversion potentials of liquid Cs at 303 K are shown by comparing with the NPA potential. It is observed that, as we go down column Ia of the Periodic Table, the extracted potential becomes harder, the width increases, and the position of the principal maximum is displaced to larger values of $r/r_{\min}$ where $r_{\min}$ is the position of the potential minumum. As for the long-range behaviour, it is observed that the Friedel oscillations are rather marked in Cs, slighty damped for Rb, and very similar for K and Na, although they increase in magnitude as the atomic number increases. The variations within this group follow rather well trends suggested by others [30].
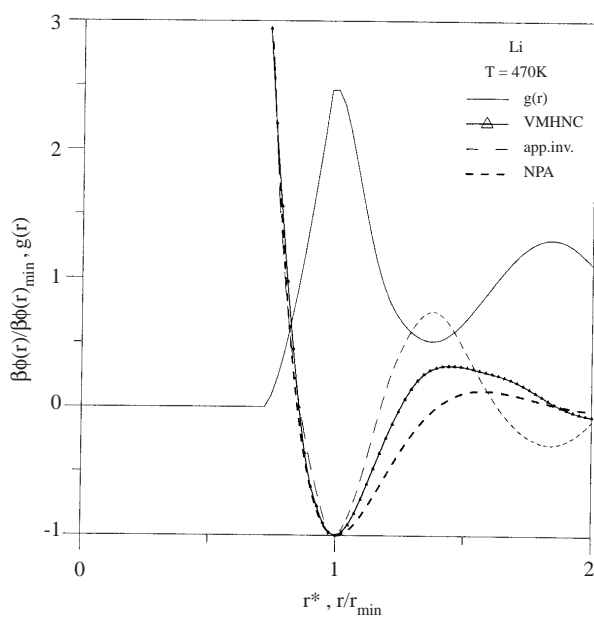
Figure 2. Scaled effective pair potentials for liquid Li near its melting along with the corresponding scaled experimental pair distribution $g_{\text{expt}}(r)$ obtained by the FT of the experimental structure factor .
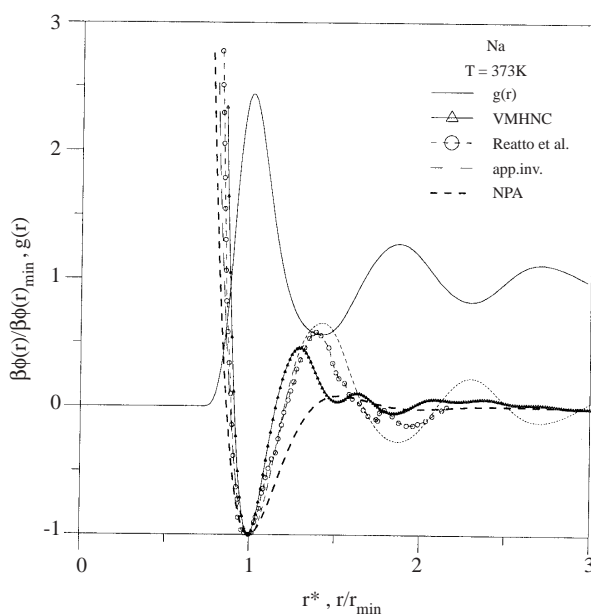

Figure 3. Scaled effective pair potentials for liquid Na at 373 K along with the corresponding scaled experimental pair distribution $g_{\text{expt}}(r)$.

VMHNC approximation yields also reasonably good results for Alkalis of low atomic number but starts to yield unreliable results for elements of higher atomic numbers like Rb and Cs. The extracted potentials within the limit of experimental accuracy, including the longwavelength region of the structure factor are more reliable than previously obtained from experimental data.
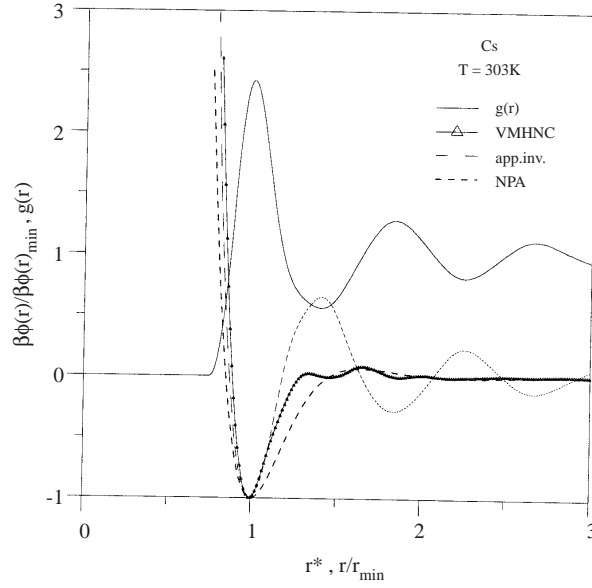
Figure 4. Scaled effective pair potentials for liquid Cs near its melting point.

Finally, it is safe to say that the inversion formula of the Angelis and March is working rather well in giving the correct trends as far as the position and the depth of the pair potential is concerned. The Friedel oscillations, on the other hand, still poses problems.

4.   Appendix

The details of the calculation of $g_{\mathrm{expt}}(r)$ by FT of $S_{\mathrm{expt}}(k)$ are given below.
(i) For the smaller-k region, the experimental data that has been extrapolated smoothly using

$$S_{\mathrm{calc}}(k_i) = S_{\mathrm{expt}}(0) + \exp(\lambda_1 k_i - \lambda_2)\sqrt{k_i}. \tag{13}$$

The sum of differences between the calculated structure factor $S_{\mathrm{calc}}(k)$ and experimental structure factor $S_{\mathrm{expt}}(k)$ were weighted as follows to obtain a function F which was minimized

$$F = \sum_{i=1}^{N} f_i, \tag{14}$$

$$f_i = |(S_{\mathrm{calc}}(k_i) - S_{\mathrm{expt}}(k_i)|, \tag{15}$$

where $S_{\mathrm{expt}}(0)$ is the long-wave length limit of the experimental structure factor obtained from the isothermal compressibility. λ_1 and λ_2 are constants. N is the number of data points in small-k region of $S_{\mathrm{expt}}(k)$ which depends on the experimental structure data of simple metal used.
(ii)As for the large-k region, $S_{\mathrm{expt}}(k)$ has been extrapolated to $80\mathrm{A}^0$ using spline functions to accurately obtain $g_{\mathrm{expt}}(r)$ in the small-r region. We have used the fast fourier transform method. The number of grid points and step size used in numerical integrations are 4096 points and $\delta r = 0.041a$, respectively.

Acknowledgments

References

[1] M. D. Johnson, N. H. March, *Phys. Lett.,* **3** (1963) 313.

[2] M. D. Johnson, P. Hutchinson, N. H. March, *Proc. R. Soc. London* **A 282** (1964) 283.

[3] U. de Angelis, N. H. March, *Phys. Lett.* **A 56** (1976) 287.

[4] W. Schommers, *Phys. Rev.***A 28** (1983) 3599.

[5] D. Levesque , J. J. Weis and L. Reatto, *Phys. Rev. Letters* **54** (1985) 451.

[6] M. W. C. Dharma-Wardana, G. C. Aers , *Phys.Rev.* **B 30** (1984) 5367.

[7] D. I. Page , U. de Angelis, and N.H. March, *Phys. Cem. Liq.* **12**,(1982) 53.

[8] U. Dahlborg, M. Davidovic, *Phys. Chem. Liq.* **15** (1986) 243, N. H. March, Physics of Simple Liquids, vol. 15 (Amesterdam: North-Holland) p 645.

[9] Y. Rosenfeld, N. W. Ashcroft, *Phys. Rev.* **A 20** (1979) 1208.

[10] L. Reatto, D. Levesque and J. J. Weis, *Phys. Rev.* **A 33** (1986) 3451, G. C..Aers, M. W. C. Dharma-wardana, *Phys. Rev.* **A 29** (1984) 2734.

[11] L. Reatto, M. Tau, *J. Chem. Phys.* **86** (1987) 6474, F. Barrocchi, P. Chieux, R. Magli, L. Reatto and M. Tau, *J. Phys.:Condens. Matter* **5** (1993) 4299.

[12] S. Munejiri, F. Shimojo, K. Hoshino and M. Watabe, *J. Phys. Condens. Matter* **9** (1997) 3303.

[13] M. C. Bellisent-Funel, P. Chieux, D. Levesque and J. J. Weis, *Phys. Rev.* **A 39** (1989) 6310.

[14] G. Kahl, M. Kristufek, *Phys. Rev.* E **49** (1994) 3568, G. Kahl, B. Bildstein and Y. Rosenfeld, *Phys. Rev.* **E 54** (1996) 5391

[15] Y. Rosenfeld, G. Kahl, *J. Phys.:Condens. Matter* **9** (1997) L89.

[16] G. Zerah and J.P. Hansen,*J. Chem. Phys.* **84** (1986) 2336, J-F. Wax, N. Jakse, and J-L, Bretonnet, *Phys. Rev.* **B 55** (1997) 12099, H. S. Kang, *Phys. Rev.* **B 60** (1999) 6362.

[17] Y. Rosenfeld, *J. Stat. Phys.* **42** (1986) 437; L. E. Gonzalez, D. J. Gonzalez and M. Silbert, *Physica* **B 168** (1991) 39, *Phys. Rev.* **A 45** (1992) 3803.

[18] F. Lado, S. M. Foiles and N. W. Ashcroft *Phys. Rev.* **A 28** 2374, F. Lado *Phys. Lett.* **A 89** (1982) 196.

[19] S. S. Dalgic, S. Dalgic, M. Tomak (to be submitted)

[20] L. E. Gonzalez, A. Meyer, M. P. Iniguez, D. J. Gonzalez, M. Silbert *Phys. Rev.* **E 47** (1993) 4120.

[21] Y. Waseda, The Structure of Non-Crystalline Materials (New York: McGraw-Hill, 1980)

[22] M. Shimoji, Liquid Metals (London: Academic Press, 1977)

[23] M. J. Huijben and W. van der Lugt, Acta Cryst **A 35** (1979) 431.

[24] N. Matsuda, H. Mori, K. Hoshino, and M. Watabe, *J. Phys.: Condens. Matter* **3** (1991) 827, A. Bari, P. Pal, and R. N. Joarder, *Pramana (India)* **42** (1994) 395.

[25] L. Verlet, J. J. Weis *Phys. Rev.* **45** (1972) 939, M. S. Smith, D. Henderson, *Mol. Phys.* **67** (1989) 431.

[26] D. Henderson, E. W. Grunduke, *J. Chem. Phys.* **69** (1975) 601.

[27] N. H. March, *Can. J. Phys.* **65** (1987) 219.

[28] H. Olbrich, H. Ruppersberg and S. Steeb, *Z. Naturforsch.* **38A** (1983) 1328.

[29] A. J. Greenfield, J. Wellendorf, *Phys. Rev.* **A 4** (1971) 1607.

[30] J. Hafner, From Hamiltonians to Phase Diagrams (Berlin: Springer, 1987)