PHYSICAL REVIEW E VOLUME 52, NUMBER 5 NOVEMBER 1995

Crossover integral-equation theory for the structure of simple liquid metals

S. K. Lai and H. C. Chen

Department of Physics, National Central University, Chung-li 32054, Taiwan, Republic of China
and International Centre for Theoretical Physics, Trieste, Italy

(Received 7 September 1994; revised manuscript received 2 May 1995)

The main purpose of this work is to report on a calculation that describes the role of a long-range bridge function as applied to the study of the structure of simple liquid metals. We have drawn attention to the crossover integral equation method, which, in essence, amounts to adding to the long-range bridge function a short-range correction of bridge diagrams. The suggested crossover scheme has been tested for the case of liquid metal Cs at both the elevated and the supercooled liquid temperatures. Remarkably good results for the calculated liquid structures were obtained.

PACS number(s): 61.25.Mv, 05.20.−y, 61.20.Lc

The study of the structure of liquids has become the core of integral-equation theories. Among the variants of these theories the hypernetted-chain (HNC) theory has received considerable attention due, on the one hand, to its feasibility to model a realistic system such as the Coulomb liquid and, on the other hand, to its possibility to combine with another integral-equation approximation yielding a more accurate and refined theory of fluids. The HNC approximation corresponds to solving iteratively the following set of coupled equations:

$$h(r)=c(r)+\rho\int h(|\mathbf{r}-\mathbf{r}'|)c(r')d\mathbf{r}\ , \qquad (1)$$

$$g(r)=\exp[h(r)-c(r)-\beta\phi(r)] \qquad (2)$$

for a pair correlation function $g(r)$. Here $h(r)=g(r)-1$ and $c(r)$ are the total and direct correlation functions, respectively, ρ is the number density, $\beta=1/k_BT$ is the inverse temperature, and $\phi(r)$ is the pair potential. In earlier applications, the HNC integral equation was first applied to study the liquid structure for the classical one-component plasma. In reference to the computer-simulated $g(r)$, it was realized that the HNC approximation generally underestimates the magnitudes of oscillations in the latter $g(r)$ and is inadequate for small and moderate distances especially near the first peak of $g(r)$ [1]. In the statistical mechanical theories of liquids the HNC approximation has been widely compared also with other approximate integral equations such as the Percus-Yevick, Born-Green-Yvon, mean spherical approximation, etc., to further assess its potentiality as a theoretical tool for the liquid structure study. From these comparative studies it is quite evident that the HNC scheme is generally applicable to the system with a long-range potential, but is only valid at a low density; the HNC approximation deteriorates, however, at moderate to high density states.

Various attempts have been devoted to finding a better substitution for the HNC scheme. Both the density functional formalism [2] and the diagrammatic expansion theory [3] have been advanced. It can be shown that the modified HNC approximation, which explicitly incorporates a bridge function $B(r)$ in (2), viz.,

$$g(r)=\exp[h(r)-c(r)-\beta\phi(r)-B(r)]\ , \qquad (3)$$

provides better closure than the HNC theory. As it stands, this modified HNC equation is mathematically rigorous if $B(r)$ can be obtained exactly by some means. There are two avenues to obtain $B(r)$. The first avenue resorts to some known models such as a fluid of hard spheres and derives an analytic or numerically tractable expression for $B(r)$. That this avenue is justifiable is based on the short-range universality ansatz for $B(r)$ [1]. However, to execute this method efficiently one requires the determination of the "bridge" parameters that characterize the model system. Both the thermodynamic self-consistency [4–6] and the Lado [7–9] minimized free energy criterion have been proposed and achieved varying degrees of success. The second avenue chooses to calculate the $B(r)$ directly. This has been followed by Iyetomi and Ichimaru (IS) [2] using the density functional formalism. According to IS the $B(r)$ can be written

$$B(r)=\sum_{j=3}^{\infty}\frac{\beta\rho^{j-1}}{(j-1)!}\int dr_1,\ldots,dr_{j-1}K^{(j)}(r_1,\ldots,r_{j-1},r)\times\prod_{i=1}^{j-1}h(r_i)\ , \qquad (4)$$

where $K^{(j)}$ is a j-particle correlation potential. Differing from the first approach, $B(r)$ given by (4) does not involve any adjustable parameter.

Both these methods have been applied proliferately in the literature to a variety of liquid systems. A general conclusion is that the thermodynamic self-consistency and the Lado criterion can equally produce structure data with desirable accuracy if the way to determine the bridge parameters is appropriately carried out. However, there still remains basic ambiguity in applying these approaches such as the use of Lado's criterion as pointed out recently by us [9]. In contrast, the $B(r)$ proposed by IS is theoretically founded on better physical grounds since it does not involve any fitting parameter. The only disadvantage is that the numerical evaluation of the multiparticle correlation potentials of $B(r)$ is a formidable task. In this Brief Report we devote further analysis to

IS's approach and see if the higher-order correlation potentials can be accounted for via other means.

To begin with we note that in their study of the higher-order correlation potentials on the convolution approximation IS express the ternary correlation potential as $\beta K^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=-h(r_{12})h(r_{23})h(r_{31})$, where $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$. This $K^{(3)}$ can be substituted into (4) to yield the simplest bridge diagram $B_{\rm IS}(r)$. The calculation of the static liquid structure factor $S(q)$ can now be performed if an interatomic potential $\phi(r)$ is given. For the latter we employ

$$\phi(r)=\frac{Z_{\rm eff}^2}{r}\left[1-\frac{2}{\pi}\int_0^\infty dq\, G_{EC}^N(q)\frac{\sin qr}{q}\right], \tag{5}$$

which is constructed from the generalized nonlocal model pseudopotential theory of Li, Li, and Wang [10]. We refer the interested readers to Ref. [11] for the definition of various physical quantities and Ref. [12] for a $\phi(r)$ of liquid metal Cs.

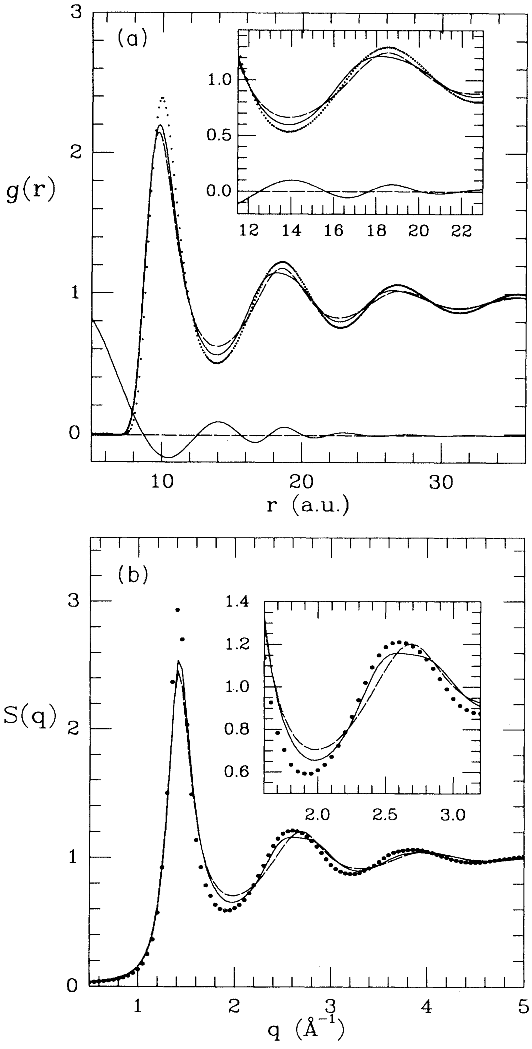

FIG. 1. (a) Pair correlation function $g(r)$ (top) for the liquid metal Cs near freezing calculated using the modified HNC with $B_{\rm IS}(r)$ (full curve) and the HNC $g(r)$ (dashed curve) compared with the MD $g(r)$ (solid circles) from [9]. The curves oscillating about the zero axis are the bridge functions $B_{\rm IS}(r)$ (full curve) and HNC $B(r)=0$ (dashed curve). The inset amplifies the $g(r)$ and $B_{\rm IS}(r)$ in the region near the second minimum and maximum. (b) Static liquid structure factor $S(q)$ for the liquid metal Cs near freezing calculated using the modified HNC with $B_{\rm IS}(r)$ (full curve) and the HNC (dashed curve) compared with the experimental data (solid circles) from Huijbin and van der Lugt [17].

Figure 1(a) displays the modified HNC and HNC $g(r)$ for the liquid metal Cs near freezing calculated iteratively using $K^{(3)}$, (1), and (3)–(5). Also included in the figure are the $g(r)$ obtained from the molecular-dynamics (MD) simulation [9] and $B_{\rm IS}(r)$ [the HNC corresponds to $B(r)=0$]. We see from the figure that $B_{\rm IS}(r)$ has a short-range part (≤ 5.3 Å) that is quite soft, shows a negative valley near the first peak of $g(r)$, changes sign to a positive peak (6.5–8.3 Å) near the principal minimum of $g(r)$, and maintains a nonzero weakly damped oscillatory behavior beyond. This distinct feature of $B_{\rm IS}(r)$ has the consequence of enhancing the principal maximum and lowering the first minimum of $g(r)$ compared with the HNC $g(r)$, where $B(r)=0$. The fact that the second maximum of the modified HNC $g(r)$ shows a broader dispersion arises mainly from the negative-positive values of $B_{\rm IS}(r)$ near the region 8.4–10.6 Å. Nevertheless, our calculated modified HNC $S(q)$, depicted in Fig. 1(b), still underestimates the measured $S(q)$, although its agreement with the latter is somewhat better compared with that of the HNC $S(q)$. It thus appears that with $K^{(3)}$ alone it is unlikely to reproduce an accurate and reliable $S(q)$. Furthermore, from the basic feature of $B_{\rm IS}(r)$, this result implies that the short-range potential is inadequately taken care of with just the ternary correlation potential $K^{(3)}$. We therefore turn to consider higher-order correlation potentials $K^{(j\geq 4)}$. Instead of proceeding to calculate the latter directly, which is numerically tedious as noted above, we draw attention to two closely related works by Foiles, Ashcroft, and Reatto [13] and Kambayashi and Hiwatari [14].

The idea behind these calculations is the following. Since $B_{\rm IS}(r)$ describes the major part of long-range interactions, one can supplement the $B_{\rm IS}(r)$ with an additional bridge function correction that hopefully accounts for the short-range potential. Surely the added correction should play the role of the omitted higher-order correlation potentials $K^{(j\geq 4)}$. On the basis of this idea, they suggested a crossover integral equation theory. The procedure consists of modifying the $j=3$ term in (4) to read

$$B(r)=f(r)B_{\rm IS}(r)+[1-f(r)]\delta B_{\rm SR}(r,\alpha)\;, \tag{6}$$

in which $\delta B_{\rm SR}(r,\alpha)$, α being the bridge parameter [1,9], is the short-range bridge function correction appropriately chosen to compensate for the part where $B_{\rm IS}(r)$ is inadequate. In (6) the continuous *mixing* function $0\leq f(r)\leq 1$ has the form $f(r)=\{1+\tanh[(r-R)/W]\}/2$, where R is the second position of $g(r)=1$; W is a parameter that restricts the r values to lie near the short-range region and may be taken to be the width extending from the position of principal peak to R. It should be noted that the choice of R is somewhat arbitrary, but its effect on $g(r)$ has been checked to be insensitive.

We have applied (6) to the liquid metal Cs near freezing by employing $\delta B_{\mathrm{SR}}(r,\alpha)\equiv B_{\mathrm{ML}}(r,\eta)$, which is an empirical hard-sphere bridge function previously proposed by Malijevský and Labík (ML) [15]. To perform our crossover (CRS) iterative calculation we determine first the bridge parameter $\alpha=\eta$, the packing ratio, by the Lado criterion [7,9]. This $B_{\mathrm{ML}}(r,\eta)$, which is substituted into (6), is used subsequently as a *fixed* bridge function correction for the CRS $B(r)$ and, in conjunction with (1) and (3), is to be solved iteratively for $g(r)$. Next, the $g(r)$ obtained is used to construct $B_{\mathrm{IS}}(r)$ and, keeping the $B_{\mathrm{ML}}(r;\eta)$ unchanged, the iterative calculation is repeated. Figures 2(a) and 2(b) depict respectively our calculated CRS $g(r)$ and its Fourier transformed $S(q)$ for the liquid metal Cs near freezing compared with those obtained from (a) $B_{\mathrm{ML}}(r,\eta)$ alone [15,16], (b) MD [16], and

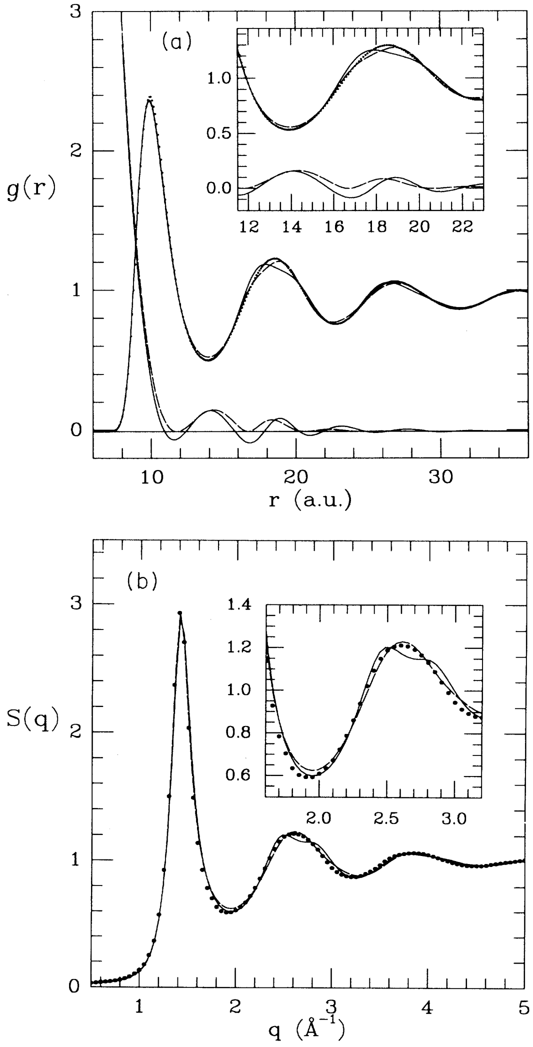

FIG. 2. (a) Same as Fig. 1(a) but for cases of the CRS $B(r)$ (full curve) and the $B_{\mathrm{ML}}(r)$ (dashed curve) compared with the MD $g(r)$ (solid circles) from [16]. (b) Same as Fig. 1(b) but for cases of the CRS $B(r)$ (full curve) and the $B_{\mathrm{ML}}(r)$ (dashed curve). The inset is enlarged to show the spurious structure of the CRS $S(q)$ (see the text).

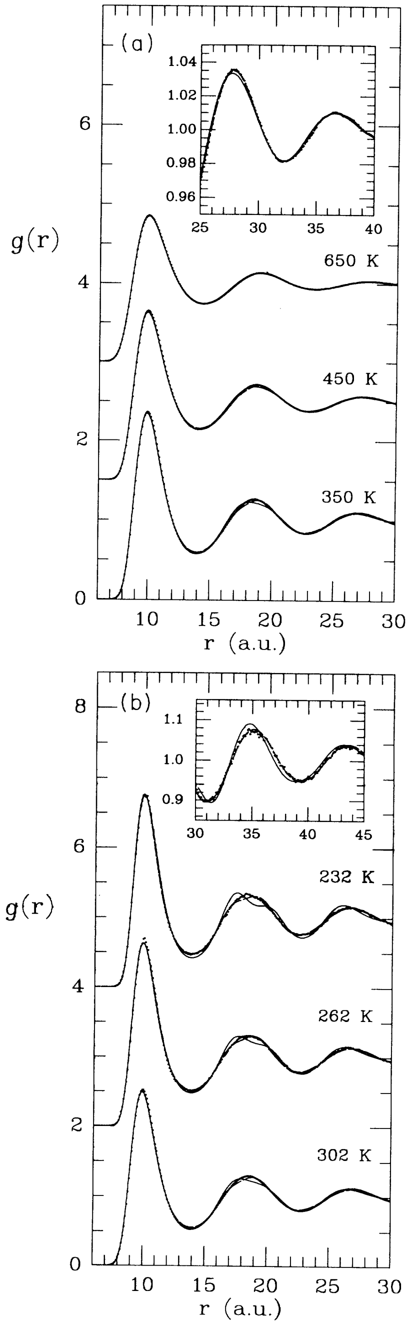

FIG. 3. (a) Pair correlation function $g(r)$ for the liquid metal Cs at higher temperatures calculated using the CRS $B(r)$ (full curve) and the $B_{\mathrm{ML}}(r)$ (dashed curve) compared with the MD simulation data (solid circles) from [21]. (b) Pair correlation function $g(r)$ for the liquid metal Cs at lower temperatures calculated using the CRS $B(r)$ (full curve) and the $B_{\mathrm{ML}}(r)$ (dashed curve) compared with the MD simulation data (solid circles) from [16].

(c) experimental $S(q)$ [17]. We stress two main features. First, relative to the MD $g(r)$, the CRS pair correlation function is found to be of equally high quality as that calculated from the $B_{\mathrm{ML}}(r,\eta)$ notably at the position of the first minimum. Second, we notice in the region of the second maximum that $S(q)$ shows a clear double peak structure whereas the measured $S(q)$ and $S_{\mathrm{ML}}(q;\eta)$ show none at all. Both the first feature and the apparent spurious structure for the CRS $S(q)$ can be explained by examining quantitatively the bridge functions $B_{\mathrm{ML}}(r,\eta)$ and CRS $B(r)$, which are plotted in Fig. 2(a). In the first place we observe that $B_{\mathrm{ML}}(r,\eta)$ has a relatively weaker *positive-definite* oscillation compared with the CRS $B(r)$, which exhibits a stronger *positive-negative* oscillation. In the region around the second minimum of $g(r)$ both the CRS $B(r)$ and $B_{\mathrm{ML}}(r,\eta)$ have the same positive peaks, but the dispersion of the former is narrower, giving rise to a slight improvement in the magnitude of the second minimum of $g(r)$. In contrast, in the vicinity of the second peak of $g(r)$, we observe a strong oscillatory behavior for the CRS $B(r)$ that varies from a negative valley (~ 8.8 Å) to a positive peak (~ 10 Å), whereas that of $B_{\mathrm{ML}}(r,\eta)$ begins with a zero valley, exhibits a broad positive value, and damps off rapidly at large r. Consequently, the structural change around the second maximum of the CRS $g(r)$ is in opposition to ML's $g(r)$ as amplified in the inset of Fig. 2(a). It is worthwhile to emphasize that the negative-positive value of the CRS $B(r)$ is necessary for explaining the moderate- to long-range part of the $S(q)$ structure. This change in sign of the $B(r)$ reminds us of a successful extraction scheme of both the long- and short-range bridge functions for studying the liquid structures of classical one-component plasmas [18,19]. It was found that the latter $B(r)$'s exhibit the same change in sign and reproduce extremely well the simulated $g(r)$. Similar structural characteristics are observed for the empirical $B(r)$ extracted also from the computer-simulated $g(r)$ for the liquid metal [20]. The relevance of these $B(r)$'s on $g(r)$ [and hence on $S(q)$] can be further deduced from several liquid structure calculations using the hard-sphere $B(r)$ [9,13,16].

The above method of calculation has been extended also to the study of liquid structure at elevated and supercooled liquid temperatures. For the liquid states at high temperatures, which are given in Fig. 3(a), there is no essential difference between the CRS $B(r)$ and $B_{\mathrm{ML}}(r,\eta)$, for the $B_{\mathrm{IS}}(r)$ will physically become less important at elevated temperatures. On the other hand, for the supercooled liquid phases, we see from Fig. 3(b) that the CRS $B(r)$ continues to delineate an equally accurate $g(r)$, although the oscillation of $B_{\mathrm{IS}}(r)$ tends to be enhanced somewhat particularly for moderate to larger r [see Fig. 2(a)]. These results suggest that the present crossover integral-equation procedure would need further embellishment for the supercooled liquid states, but the CRS theory certainly is a promising alternative to the many $B(r)$ presently available in the literature.

This work has been supported in part by the National Science Council, Taiwan, Republic of China, under Contract No. NSC83-0208-M008-056. One of the authors (S.K.L.) would like to thank Professor Abdus Salam, the International Atomic Energy Agency, and UNESCO for hospitality at the International Centre for Theoretical Physics, Trieste, Italy.

---

[1] Y. Rosenfeld and N. W. Ashcroft, Phys. Rev. A **20**, 1208 (1970).
[2] H. Iyetomi and S. Ichimaru, Phys. Rev. A **25**, 2434 (1982); **27**, 3241 (1983).
[3] J. Chihara, Prog. Theor. Phys. **59**, 76 (1978).
[4] G. Pastore and G. Kahl, J. Phys. F **17**, L267 (1987).
[5] G. Kahl and G. Pastore, Europhys. Lett. **7**, 37 (1988).
[6] S. K. Lai, Wang Li, and M. P. Tosi, Phys. Rev. A **42**, 7289 (1990).
[7] F. Lado, Phys. Lett. **89**, 196 (1982); F. Lado, S. M. Foiles, and N. W. Ashcroft, Phys. Rev. A **28**, 2374 (1983).
[8] L. E. Gonzalez, D. J. Gonzalez, and M. Silbert, Physica B **168**, 39 (1991).
[9] H. C. Chen and S. K. Lai, Phys. Rev. A **45**, 3831 (1992).
[10] D. H. Li, X. R. Li, and S. Wang, J. Phys. F **16**, 309 (1986).
[11] S. Wang and S. K. Lai, J. Phys. F **10**, 2717 (1980).
[12] S. K. Lai, J. Phys. F **18**, 1673 (1988).
[13] S. M. Foiles, N. W. Ascroft, and L. Reatto, J. Chem. Phys. **80**, 4441 (1984).
[14] S. Kambayashi and Y. Hiwatari, Phys. Rev. A **41**, 1990 (1990).
[15] A. Malijevský and S. Labík, Mol. Phys. **60**, 663 (1987).
[16] H. C. Chen and S. K. Lai, Phys. Rev. E **49**, R982 (1994).
[17] M. J. Huijbin and W. van der Lugt, Acta Crystallogr. A **35**, 431 (1979).
[18] P. D. Poll, N. W. Ashcroft, and H. E. DeWitt, Phys. Rev. A **37**, 1672 (1988).
[19] H. Iyetomi, S. Ogata, and S. Ichimaru, Phys. Rev. A **46**, 1051 (1992).
[20] E. Lomba and M. Alvarez, J. Chem. Phys. **97**, 4349 (1992).
[21] K. W. Chen, H. C. Chen, and S. K. Lai, Physica B **179**, 125 (1992).