Anomalies in the liquid structure of Ga metal

Shiow-Fon Tsay and S. Wang*

Department of Physics, National Sun Yat-sen University, Kaohsiung, Taiwan 80424, Republic of China
(Received 30 July 1993; revised manuscript received 30 December 1993)

Molecular-dynamics simulations on the structures of 500 Ga atoms in liquid states are carried out at constant pressure for different high temperatures. Thereby, it is demonstrated that such anomalies as those present in the observed structure factors for the Ga liquids at high temperatures are due primarily to the effect of the occurrence of particular clusters (or local-ordering units) on the states of pure Ga liquid.

I. INTRODUCTION

Since the work of Ashcroft and Lekner,[1] the uniform distribution of the hard spheres (HS), having an appropriate diameter, is well recognized as a basis for atomic distribution in liquid metals. However, one has also found the experimental results[2,3] indicating some deviations from the completely uniform distribution of HS, such as those shown in Ref. 3 and those in Fig. 1. Such deviation produces (i) an asymmetry of the principal peak in the structure factor $S(q)$ for pure Zn, Cd, and other liquid metals at high temperature and (ii) not only an asymmetry of the principal peak but also a shoulder on the high-q of the principal peak in $S(q)$ for some metals, such as Bi and Ga (Fig. 1). Theoretically, the anomalous features, such as the shoulders for Ga and the other metals at their respective melting temperatures and the asymmetric principal peak for Zn- and Cd-type metals[3] have been reproduced in the literature[4-10] by using those

interatomic pair potentials, in which the repulsive part is equivalent to hard core together with an adjacent ledge (Fig. 2 from Ref. 11), which arises from the electronic contribution to those potentials and which is not present in the interatomic pair potentials for those liquid metals, for which the HS model can be applied with high accuracy. In addition, using the relation between the pair potential and the pair-distribution function (PDF), Hafner and co-workers[7,10] attempted to interpret the anomalous features just noted. They ascribed the anomalous structure of liquid Ga to the change of the curvature of the pair potential around the nearest-neighbor distance. Nevertheless, the physical origin for the above-noted deviation is still not fully understood and deserves quantitative study. This study is presented in the next section. Some conclusions are drawn in the last section.

II. CALCULATION AND RESULTS

First, the molecular-dynamics (MD) simulation on an equilibrium liquid state of a system of 500 Ga atoms, using the Verlet algorithm with a time step equal to
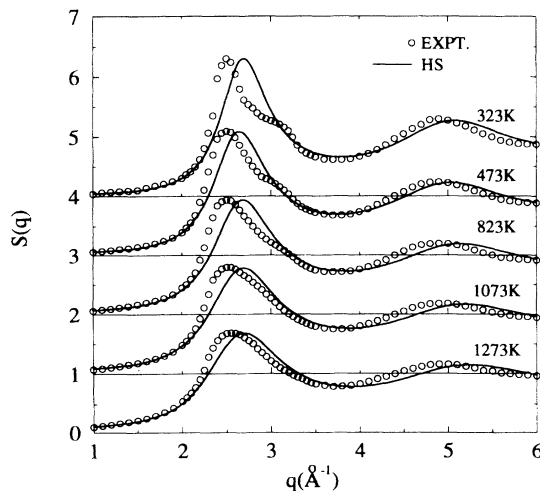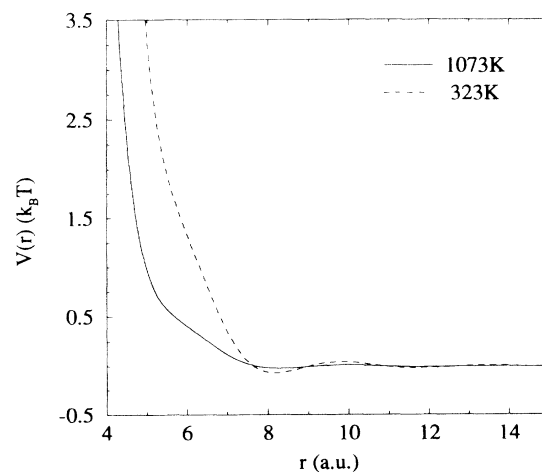

FIG. 1. The observed $S(q)$'s (Ref. 2) for Ga liquids, compared with the corresponding $S_{HS}(q)$'s, obtained from the HS model (Ref. 1) using (i) the observed mean atomic volumes (Table I) and (ii) the most appropriate parking density $\eta = 0.34$, 0.36, 0.385, 0.405, 0.430, for $T = 1273$, 1073, 823, 473, 323 K, respectively.

FIG. 2. The theoretical interatomic pair potential, $V(r)$, obtained as described in Ref. 11, for pure Ga metal at $T = 323$ K, which is slightly above the melting temperature of Ga metal and that at $T = 1073$ K. The mean atomic volumes used for these two T's are just those listed in Table I.

<u>50</u>   108

TABLE I. The values of Ω (a.u.) obtained from the present MD simulation at different temperatures. Also included are the corresponding experimental values (Ref. 2).

T (K)	1273	1073	823	473	323
Ω_{cal}	150.14	146.79	144.63	138.43	135.12
Expt.	142.23	139.28	135.87	130.82	128.45

1.5×10^{-15} sec, is carried out at constant pressure (about 1 bar) in the same manner as in Ref. 11 for selected high temperatures. From this, the mean atomic volume Ω, the PDF, denoted by $g(r)$, and the corresponding $S(q)$, i.e.,

$$S(q) = 1 + \int d\mathbf{r}[g(r) - 1]\exp(i\mathbf{q}\cdot\mathbf{r})/\Omega , \qquad (1)$$

are determined as in Ref. 11 for the system under consideration. The values of Ω thus determined for use in the present MD calculation are noted in Table I. These values are in good agreement with the corresponding experimental results, this implying that the presently used first-principles atomic potential (Fig. 2 from Ref. 11) is highly accurate for the present type study, just as previously demonstrated by the results in Table I of Ref. 8. The corresponding calculated $S(q)$'s are displayed in Fig. 3 along with the corresponding experimental $S(q)$'s. Apparently, the presently obtained $S(q)$'s exhibit the same anomalous features as those present in the experimental $S(q)$'s for all the high temperatures considered here (Fig. 3). At this point, it is worth noting that the increase of the number of the particles presently used (500) has no significant effect on $S(q)$ for $q > 1$ Å (dashed line in Fig. 3).

Now, we turn to find the physical origin for the anomalous features in the $S(q)$'s displayed in Fig. 3. For this, the structures of the atomic configuration in the present MD simulation are analyzed as in Ref. 12 by characterizing the pairs of atoms with four indices. The first index is
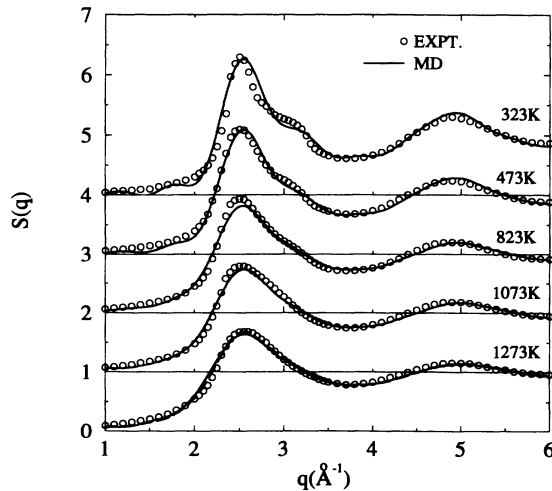
1 if the pair of atoms (expressed by the open circles in Fig. 4) is bonded (denoted by solid line in Fig. 4) and 2 otherwise. The second index represents the number of near-neighbors common to the two atoms in the pair of interest. The third index is the number of bonds between the common neighbors. These three numbers are not sufficient to characterize a diagram uniquely as pointed out in Ref. 12, so a fourth index is added to resolve ambiguity about the arrangement of the atomic bonds[12] (as shown in Fig. 4). Of the results obtained for the different atomic bonded pairs, those that merit emphasis are summarized in Table II. It now appears that the most prevalent atomic bonded pairs in the Ga liquids under consideration are the 1311-type rather than the 1551-type atomic bonded pairs, which are prevalent in the usual metals, in which the repulsive part of the interatomic pair potential does not exhibit such a ledge as that shown in Fig. 2. The atomic clusters (or say, local-ordering units), associated with the just noted atomic bonded pairs and found from the present pair analysis, are shown in Fig. 4. To go further, we notice that a shoulder on the high-q side of the second peak of $S(q)$ for the conventional rapidly quenched metallic liquids can be interpreted by con-

FIG. 3. Comparison of the presently simulated $S(q)$'s (corresponding to Ω_{cal} in Table I) with the corresponding observed $S(q)$'s (Ref. 2) for Ga liquids. Also included is the simulated structure factor of 1000 Ga atoms at 1273 K, denoted by the dashed line.
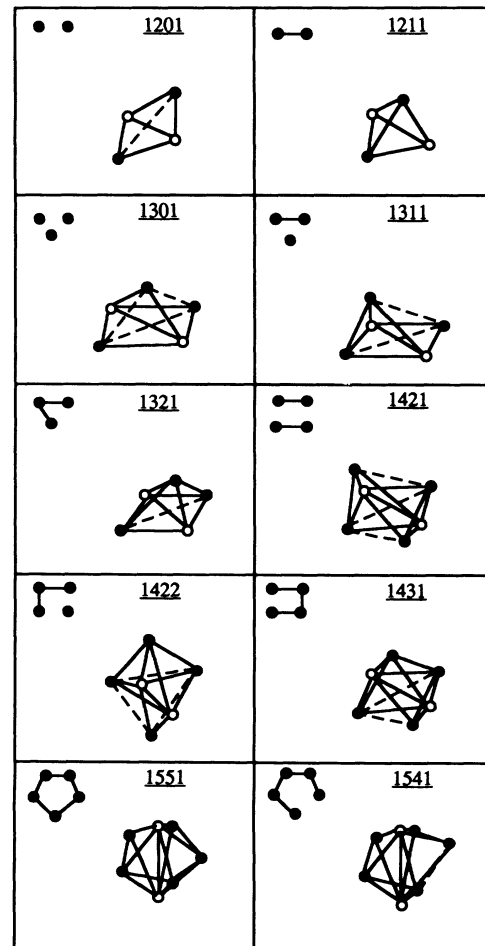

FIG. 4. The clusters associated with the atomic bonded pairs noted in Table II. Nearest-neighbors (defined in Ref. 12) are connected by solid lines ("bonds").

TABLE II. The values of the relative numbers of the essential atomic bonded pairs, N_{ijkl}, appearing the present MD simulation on the structure of 500 Ga atoms in the liquid states at different high temperatures.

T (K)	N_{1201}	N_{1211}	N_{1301}	N_{1311}	N_{1321}	N_{1421}	N_{1422}	N_{1431}	N_{1541}	N_{1551}
1273	0.064	0.040	0.038	0.165	0.106	0.050	0.096	0.140	0.073	0.031
1073	0.062	0.037	0.040	0.166	0.098	0.052	0.103	0.148	0.077	0.031
823	0.061	0.031	0.044	0.171	0.094	0.056	0.109	0.149	0.080	0.033
473	0.145	0.046	0.105	0.246	0.072	0.049	0.105	0.090	0.029	0.010
323	0.188	0.045	0.133	0.251	0.061	0.040	0.094	0.065	0.018	0.005

sidering the effects of icosahedronlike clusters (each consisting of twelve 1551 atomic bonds pairs) on $S(q)$.[13] The icosahedronlike clusters do not appear in the rapidly quenched Ga liquid[11] and hence, experimentally, no shoulder is present on the high-q side of the second peak of $S(q)$ for the supercooled Ga liquids or Ga glass.[14] Accordingly, the $S(q)$ of interest appears to be a mixture of the structure factors of the HS and those atomic clusters, which contribute little to the structure factor of the HS, such as those shown in Fig. 4. In view of this, we now rewrite Eq. (1) in the form

$$S(q)=C_{HS}S_{HS}(q)+ \sum_{\alpha} C_{\alpha}S_{\alpha}(q) , \tag{2}$$

where C_{HS} and C_{α} stand, respectively, for the weighting factors for the HS structure factor, $S_{HS}(q)$, and the structure factor of the αth cluster, that is,

$$S_{\alpha}=1+ \int d\mathbf{r}[g_{\alpha}(r)-1]e^{i\mathbf{q}\cdot\mathbf{r}}/\Omega . \tag{3}$$

Herein, the C's and g_{α} satisfy

$$C_{HS}+ \sum_{\alpha}C_{\alpha} \equiv C_{HS}+C_{cl}\sum_{\alpha}N_{\alpha}=1 \tag{4}$$

and

$$g(r)=C_{HS}g_{HS}(r)+ \sum_{\alpha}C_{\alpha}g_{\alpha}(r) , \tag{5}$$

respectively, N_{α} referring to N_{ijkl} in Table II. In this work, $g_{\alpha}(r)$ is the PDF for the case, in which the atomic configuration is similar to that of the αth cluster (Fig. 4). The involved atoms have a probability to form each of the clusters noted in Fig. 4, as indicated by the relative numbers in Table II, so Eqs. (5) and (2) follow for the present study. Having written Eq. (2), $S_{\alpha}(q)$ for the clusters can be easily estimated using (i) the equation[15]

$$S_{cl}=1+ \frac{2}{N} \sum_{i=1}^{N}{}' \sum_{j=1}^{N} \frac{\sin(q|\mathbf{r}_i-\mathbf{r}_j|)}{(q|\mathbf{r}_i-\mathbf{r}_j|)} , \tag{6}$$

for q significantly greater than zero and (ii) the atomic position vectors obtained from the present MD simulation for the $\mathbf{r}_i$'s of N atoms involved in the cluster under consideration. Of the estimated results, those estimated for the present prevalent clusters at $T=473$ K are displayed in Fig. 5. It is found that the first peaks of the displayed structure factors deviate from that of the HS's $S(q)$. Thereby, the structure factors, obtained from Eq. (2) using the appropriate values for C_{HS} and η (the packing density of the HS), may exhibit such anomalous features as those noted in the Introduction. Indeed, this is the case (Fig. 6) if C_{HS} and η are chosen to be as those
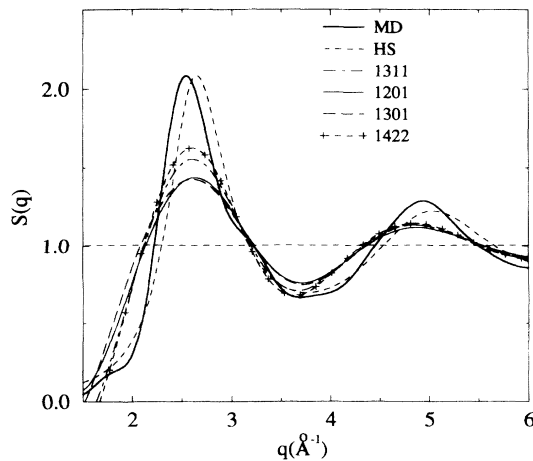
FIG. 5. The structure factors of the 1311, 1201, 1301, and 1422 clusters (Fig. 4) along with the structure factors of MD and that of HS (from Fig. 1) at $T=473$ K.
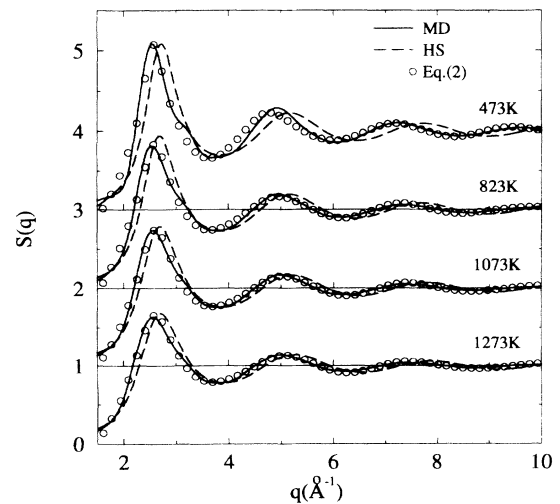
FIG. 6. The structure factors obtained from Eq. (2) using the theoretical volume, Ω_{cal} in Table I, for $T=473$ K ($C_{HS}=0.4263$, $\eta=0.47$), 823 K ($C_{HS}=0.446$, $\eta=0.425$), 1073 K ($C_{HS}=0.5513$, $\eta=0.39$) and 1273 K ($C_{HS}=0.5546$, $\eta=0.37$). Also included are the results of the present MD and the HS (Fig. 1).
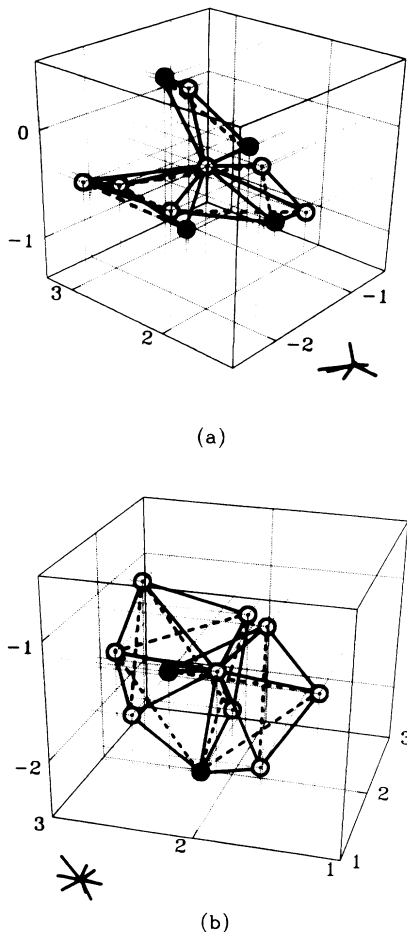
(a)

(b)

FIG. 7. The clusters consist, respectively, of six and eight 1201-type small clusters in pure Ga liquid at 473 K.

given in Fig. 6. The other aspects of the displayed results (Fig. 6) that merit emphasis are as follows. (1) The agreement of the structure factor deduced from Eq. (2) with the present MD calculation is excellent for (i) larger q at $T \leq 823$ K and (ii) the q's > 1.5 Å^{-1} at higher T's. This occurs primarily because of the use of Eq. (6), which is less accurate for small q. (2) From the values of C_{HS}, used in the calculation of $S(q)$ from Eq. (2) and given in Fig. 6, the HS contribution to the $S(q)$ decreases with decreasing T, because the number of the clusters increases with decreasing T (Table II). Accordingly, in the pure Ga liquid at 473 K the large clusters, corresponding to the icosahedra in the conventional rapidly quenched liquids, may be formed. Indeed, such large clusters are found from the present simulation at 473 K (Fig. 7). Their structure factors, obtained from Eq. (6), have a shoulder or small peaks on the high-q side of its principal peak (dot-dashed line in Fig. 8). When using the struc-
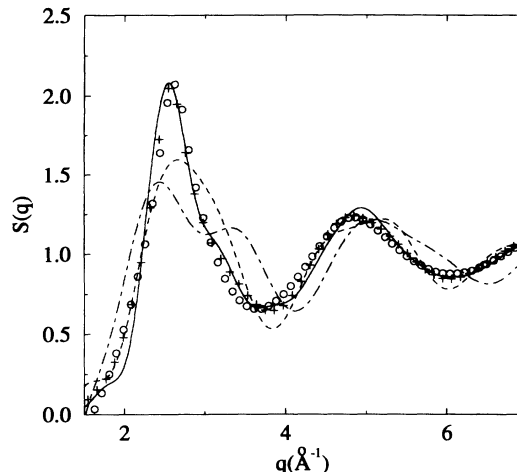

FIG. 8. The structure factors obtained from Eq. (6) for a large cluster [$- - -$ for Fig. 7(a) and $-\cdot-\cdot-\cdot$ for Fig. 7(b)] and from Eq. (2) for pure Ga liquid ($+ + +$), containing the large clusters of 1201 type, at 473 K. Also included are present MD results (solid line) and the result of Eq. (2) displayed in Fig. 6 (O O O) for the purpose of comparison.

ture factors of the large clusters of this type instead of those of the 1201-type small clusters, the structure factor deduced from Eq. (2) (denoted as the plus in Fig. 8) exhibits clearly such a shoulder as noted in the Introduction.

III. CONCLUSION

The anomalous features of the experimentally observed structure factors for pure Ga liquids at high temperatures are reproduced by the present MD calculation, using the same first-principles interatomic pair potential as that used in Ref. 11. These anomalous features can also be reproduced by using Eq. (2). Now, it may be concluded that the asymmetry of the principal peak and the shoulder on the high-q side of this peak in the structure factor of pure Ga liquid at high T is due primarily to the effect of the occurrence of the particular type clusters (such as 1311 and 1201 types) on its liquid state. A similar interpretation may be applicable for the anomalies in the structures of the other liquid metals mentioned in the Introduction.

ACKNOWLEDGMENTS

---

*Permanent address: University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

[1]N. W. Ashcroft and J. Lekner, Phys. Rev. 145, 83 (1966).

[2]Y. Waseda, The Structure of Non-crystalline Materials (McGraw-Hill, New York, 1980).

[3]Y. Waseda and S. Takeda, Chin. J. Phys. 31, 225 (1993).

[4]M. Silbert and W. H. Young, Phys. Lett. A 58, 469 (1976).

[5]K. K. Mon, N. W. Ashcroft, and G. V. Chester, Phys. Rev. B

19, 5103 (1979).

[6]C. Regnaut, J. P. Badiali, and M. Dupont, Phys. Lett. **74A**, 245 (1979); **75A**, 516(E) (1979).

[7]J. Hafner and G. Kahl, J. Phys. F **14**, 2259 (1984).

[8]D. H. Li, J. Gryko, and S. Wang, Phys. Lett. **112A**, 40 (1985).

[9]S. K. Lai, Wang Li, and M. P. Tosi, Phys. Rev. A **42**, 7289 (1990).

[10]J. Hafner and W. Jank, Phys. Rev. B **42**, 11 530 (1990).

[11]S. F. Tsay, Phys. Rev. B **48**, 5945 (1993); preceding paper, **50**, 103 (1994).

[12]D. Honeycutt and H. C. Andersen, J. Phys. Chem. **91**, 4950 (1987).

[13]R. S. Liu, D. W. Qi, and S. Wang, Phys. Rev. B **45**, 451 (1992).

[14]A. Bererhi, A. Bizid, L. Bosio, R. Cortes, A. Defrzin, and C. Segaud, J. Phys. (Paris) Colloq. **41**, C8-218 (1980).

[15]C. W. B. Grigson and E. Barton, Br. J. Appl. Phys. **18**, 175 (1967).