Brief Reports

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Anomalies in the structure factor for some rapidly quenched metals

R. S. Liu*
Department of Physics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

S. Wang†
Department of Physics, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424, Republic of China
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From a molecular-dynamics simulation on the liquid-to-glass transition of 500 In atoms, it is demonstrated that the structure factor $S(q)$ has a peak on the high-q side of its principal peak not only for experimentally reported supercooled Ga liquid but also for those supercooled liquids for which the repulsive part of the interatomic pair potential has a shoulder. This appears to be due to the occurrence of particular clusters in these supercooled liquids. Thereby, an alternative possible physical origin for the presence of a shoulder on the high-q side of the principal peak of $S(q)$ for some metals at their respective melting temperatures is suggested.

It is well known experimentally[1,2] that the structure factor $S(q)$ of pure Ga liquid metal has a shoulder on the high-q side of its principal peak, when the temperature T is not significantly higher than the melting temperature Tm of pure Ga metal. Further, it has been shown experimentally[3] that this shoulder tends to become a small peak in the normal liquid to supercooled-liquid transition. Accordingly, the structure factor of rapidly quenched Ga metal differs significantly from that of a conventional rapidly quenched metal, in which a shoulder (or peak) appears on the high-q side of the second peak of $S(q)$. The main purpose of this work is twofold; (i) to demonstrate that such an anomaly as above exists for those metals, for which the repulsive part of the interatomic pair potential has a shoulder (Fig. 1); and (ii) to suggest a possible physical origin for this anomaly, this also lending additional support to our recent work[4] on the anomaly of $S(q)$ for conventional rapidly quenched metals.

For this purpose, we started with a molecular-dynamics (MD) simulation on the liquid-to-glass transition to a system of 500 In atoms, subject to periodic boundary conditions, and interacting via an interatomic pair potential, that is

$$V(r)=(Z_{\rm eff}^2/r)\left[1-(2/\pi)\int_0^\infty dq\, F(q)\sin(rq)/q\right], \quad (1)$$

with $Z_{\rm eff}$ and $F(q)$ standing, respectively, for the effective ionic-valence and the normalized energy wave-number characteristic, defined in the energy-independent nonlocal model-pseudopotential theory.[5] The pair potential given by Eq. (1) can be used immediately as an interatomic pair potential between two In atoms in the calculation of $S(q)$, as demonstrated in Ref. 2. In view of this and of the fact that pure In metal can be a laboratory glass through a vapor-quenching process as in the Ga case, the former metal is chosen in this work. The above-noted simulation is then carried out in the usual manner,[4] but using the mean atomic volume $\Omega(T)$ determined from the condition that the pressure involved in the simulation be constant at about 5 bars.[6] In order to check if the present simulation is reasonably performed, the result of $\Omega(T)$ from this simulation have been compared with those obtained from a variational thermodynamic calculation[7] (Table I). It appears from this comparison that the present (MD) simulation should not contain significant errors.

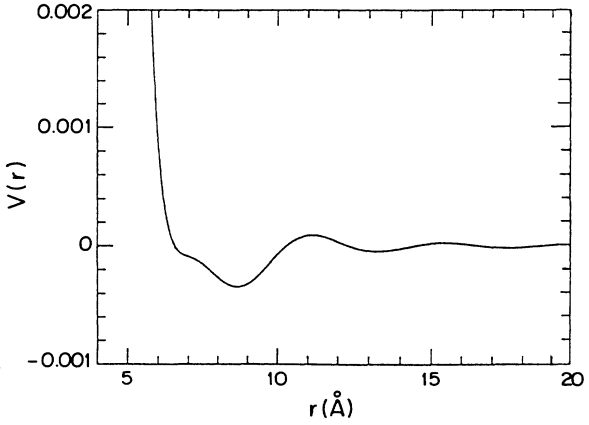

FIG. 1. The interatomic pair potential $V(r)$ in atomic units, obtained from Eq. (1) for pure In metal at Tm. The shoulder, appearing in the repulsive part of this potential, remains nearly unchanged in the liquid to supercooled-liquid transition.

TABLE I. The values of Ω(a.u.) obtained from the present simulation (PS) for rapidly quenched In metal along with those obtained from a variational calculation (VC) (Ref. 7).

T(K)	400	360	320	250	200	150	120	84
Ω(PS)	192.1	190.9	190.2	188.1	186.6	185.5	184.8	183.9
Ω(VC)	192.2	191.3	190.4	188.7	187.6	186.4	185.7	

Having obtained $\Omega(T)$, the pair distribution functions (PDF) $g(r)$ are determined in the same manner as in Ref. 4 and displayed in Fig. 2 for selected T's. These $g(r)$'s are then extended to large r as in the literature[8] and the corresponding $S(q)$'s determined, i.e.,

$$S(q)=1+\int d\mathbf{r}[g(r)-1]\exp(i\mathbf{q}\cdot\mathbf{r})/\Omega \ . \quad (2)$$

The aspects of the presently obtained $g(r)$'s (Fig. 2) and $S(q)$'s (Fig. 3) that merit emphasis are as follows. (1) The features of $g(r)$ on the right-hand side of its principal peak are quite different from those for conventional metallic glasses. (2) There is no shoulder (or peak) on the high-q side of the second peak in $S(q)$ even for amorphous In metal at $T=84$ K, which is considerably below the corresponding glass-transition temperature [$\cong 120$ K from the temperature dependence of $\Omega(T)$ presently determined (Table I)]. This is contrary to the results of conventional rapidly quenched metals, for which a shoulder (or peak) is present on the high-q side of the second peak of $S(q)$. (3) A small shoulder is present on the high-q side of the principal peak of the presently obtained $S(q)$ at 434 K (5 K higher than Tm for In) as experimentally reported,[1,2] this being consistent with the analytic work of Silbert and Young,[9] and becomes a small peak in the normal-liquid to supercooled-liquid transition (Fig. 3). This aspect is also contrary to the results of conventional rapidly quenched metals, in which the repulsive part of the interatomic pair potential does not exhibit any shoulder. Now, it appears that aspect (3) is compatible with those $V(r)$'s in which the repulsive part has a shoulder (or ledge). At any rate, the above-noted aspects are similar to those experimentally observed in the normal-liquid to supercooled-liquid transition for pure Ga metal.[3] Now, since the detailed features of $g(r)$ and $S(q)$ depend strongly upon the interatomic pair potential, it may be concluded that aspects (1), (2), and (3) are common for those metals for which the repulsive part of the interatomic pair potential between any two atoms has a shoulder (Fig. 1), which must be in the positive-energy region for the small peak to be close to the principal peak of $S(q)$, as in the Ga case.[3]

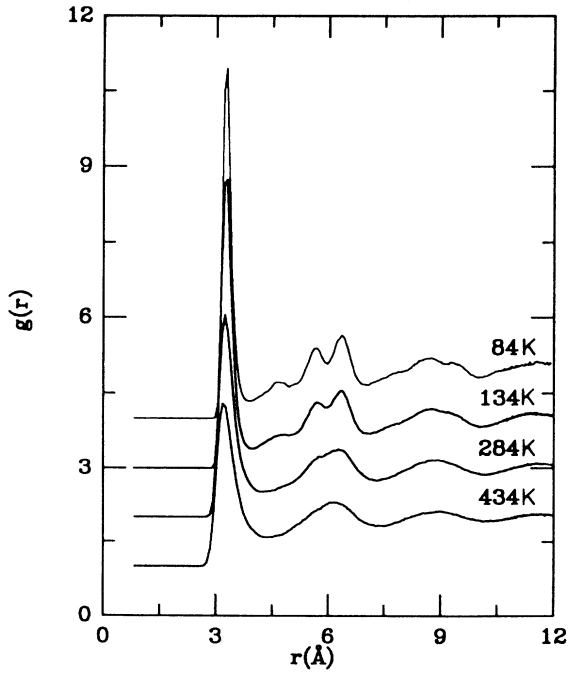

FIG. 2. Temperature-quench results for the $g(r)$'s of pure In metal ($Tm \cong 429$ K) for selected temperatures. The glass-transition temperature is about 120 K in the present MD simulation in which the quenching rate is 4×10^{13} K/s.

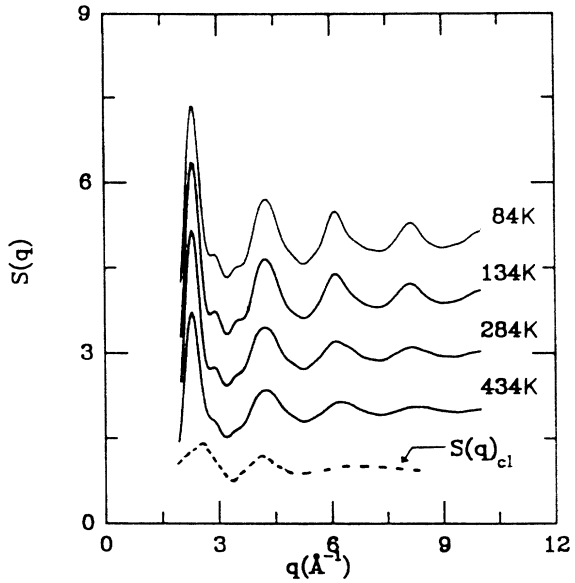

FIG. 3. The structure factors, obtained using the presently determined $g(r)$'s as in Ref. 4. Also included is the calculated $S(q)_{cl}$, denoted by the dotted line.

Now, we turn to clarify the above aspects (2) and (3). For this, the pair-analysis technique (see Ref. 10 for details) is applied to the atomic configurations obtained from the present MD simulation to determine the microstructure of the presently considered rapidly quenched In metal. The points of the obtained results that merit emphasis are as follows.

(i) The relative number of 1551 atomic bonded pairs (which are characteristic of icosahedral structure[10]) are so small that no icosahedra are present in the present MD simulation. This is contrary to the results of conventional rapidly quenched metals, each containing many icosahedra[4,11] (corresponding to a large number of 1551 atomic bonded pairs) so that a shoulder is present on the high-q side of the second peak of $S(q)$ for these metals (see Ref. 4 for justification).

(ii) Of the various atomic bonded pairs, the number of 1311 atomic bonded pairs (which appear in rhombohedral structure) are the most prevalent in the present simulation.

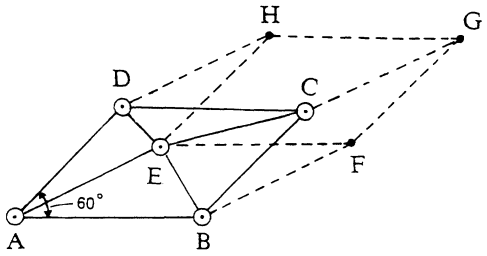

FIG. 4. A cluster consisting of five atoms, located respectively at *A*, *B*, *C*, *D*, and *E* points in a rhombohedron. The *BD*, *DE*, and *EB* bounded pairs here are 1311 like.

Now, the above-noted aspect (2) can be understood from point (i). There remains to clarify aspect (3) mentioned above. For this, we need to recall that a shoulder on the high-q side of the second peak of $S(q)$ of a conventional rapidly quenched metal can be successfully explained by considering the effects of icosahedra (each consisting of twelve 1551 atomic bonded pairs) on $S(q)$, as demonstrated in Ref. 4. In view of this, we have followed the same procedure as in Ref. 4 to calculate the structure factor of a cluster in which there are 1311 atomic bonded pairs (Fig. 4), these pairs being present in place of 1551 atomic bonded pairs in the present MD simulation in which the interatomic pair potential (Fig. 1) differs significantly from that in the conventional MD simulations. The first peak of the calculated structure factor, obtained from the equation[12]

$$S_{\rm cl}(q)=1+\frac{2}{5}\sum_{i=1}^{5}\sum_{j=1}^{5}\sin(qr_{ij})/(qr_{ij})\ , \tag{3}$$

in which the summation is taken over *ABCDE* atoms (Fig. 4) and noted by the dotted line in Fig. 3, compares favorably with the small peak of the actual $S(q)$ in position (see Fig. 3). Now it appears that the small peak on the high-q side of the principal peak of the actual $S(q)$, as noted in Fig. 3, arises from the effects of the clusters, each being similar to that shown in Fig. 4, on $S(q)$.

The above interpretation of the small peak in question may now be extended to illustrate the presence of a shoulder on the high-q side of the principal peak of $S(q)$ for the metal of interest at T's somewhat above its Tm,[1,2] because the corresponding relative number of 1311 atomic bonded pairs, N_{1311}, is found to be non-negligible ($N_{1311}\cong 0.13$, corresponding to a small number of clusters for pure In metal) even at a T somewhat above Tm. In addition, the same MD simulation has been carried out for pure In metal at 500 K, which is considerably higher than the corresponding Tm($\cong$429 K for In). It is found that the corresponding N_{1311} is negligible and that, as also demonstrated in Ref. 2, the corresponding $S(q)$ does not exhibit any shoulder, this being consistent with observation (see Fig. 3 of Ref. 2 for details). This simply implies that the shoulder in question is closely associated with those clusters, each of which consists of 1311 atomic bonded pairs such as that shown in Fig. 4.

In summary, it may be concluded that (i) the anomaly of $S(q)$, as noted in Fig. 3, is common for those rapidly quenched metals, for which the repulsive part of the interatomic pair potential has a shoulder; and (ii) the shoulder on the high-q side of the principal peak of $S(q)$, as shown in Fig. 3 for $T=434$ K, arises from the effects of the clusters just noted on $S(q)$ and becomes a small peak in the normal-liquid to supercooled-liquid transition, because more clusters of this type appear to affect $S(q)$ in this case. This is not the case at all for conventional rapidly quenched metals, for which the shoulder (or peak) appears on the high-q side of the second peak of $S(q)$, this being due to the effects of many icosahedra on the atomic structure.

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*Present address: Department of Physics, Hunan University, Changsha 410012, China.

†Permanent address: Department of Physics, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.

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[6]The pressure [$=-(\partial F/\partial\Omega)_T$] in a simple metal can now be evaluated numerically with high accuracy, because an accurate expression is available for the corresponding Helmholtz free energy F. The pressure is very sensitive to Ω so that the value of Ω at 10 bars does not differ significantly from that at 5 bars.

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