Structural study and its relation to liquid–glass transition

S K Lai
Department of Physics, National Central University, Chung-li 32054, Taiwan, Republic of China

Received 4 November 1987

Abstract. Starting with real metallic potentials constructed from a full non-local model pseudopotential theory, we carry out two computer simulation studies for yttrium and zirconium monatomic glasses. By comparing the Wendt–Abraham parameter, \( R_{LG} \), at the liquid–glass transition point obtained in this work with (i) our previous results for chromium and (ii) various other, seemingly different monatomic glasses such as the Lennard-Jones, the soft core, etc. we find that the Wendt–Abraham criterion satisfies \( R_{LG} = 0.1 \pm 0.02 \) and may well be a universal constant. The physical indication of this \( R_{LG} \) value is interpreted and various ubiquitous structural features related to liquid–glass transition are also presented.

1. Introduction

A theoretical investigation of the microscopic process of liquid–glass transition is a challenging but interesting problem. Modelling techniques (Waseda 1981, Boudreaux 1983, Luborsky 1983), computer simulations (Kimura and Yonezawa 1983, Luborsky 1983, Jäckle 1986) and various microscopic theories (Leuthensser 1984, Bengzelius 1986) have all produced considerable insights into our understanding of this phenomenon. Despite these various efforts, there is still controversy regarding the criterion proposed for the investigation of the microscopic process of liquid–glass transition.

Wendt and Abraham (WA, 1978) first advanced an empirical criterion for the study of liquid–glass transition. According to their Monte Carlo (MC) simulation results for a Lennard-Jones system, WA asserted that when a Lennard-Jones liquid system is quenched at successive temperatures the ratio \( R = g_{\text{min}} / g_{\text{max}} \), where \( g_{\text{min}} \) and \( g_{\text{max}} \) respectively stand for the pair correlation function at its first minimum and maximum positions, varies linearly with temperature and undergoes a change in slope. They referred to the slopes in these regions as supercooled and glassy branches. They further defined the intersection of these respective slopes to be the point signalling the onset of liquid–glass transition. For the Lennard-Jones system they hypothesised that the liquid–glass transition point \( R_{LG} = 0.14 \).

In an attempt to show the universal nature of this \( R_{LG} \) value, this empirical criterion for liquid–glass transition has subsequently been examined by Stillinger and Weber (1979) using a gaussian core system. Based on this model, they obtained a WA parameter \( R_{LG} = 0.14 \). In the following year the universal nature of \( R_{LG} \) was re-examined by Hiwatari (1979, 1980) using a molecular dynamics (MD) simulation for a soft-core liquid. In contrast to the value obtained by the previous authors, Hiwatari
found $R_{LG} = 0.08$, which is substantially smaller. Since then there have been several
computer simulation calculations presenting results in close relation to structural
properties. In the first place Abraham (1980) considerably extended the work of WA
and reported $R_{LG} = 0.11$ for a Lennard-Jones liquid (in contrast to his previous result
$R_{LG} = 0.14$, see Wendt and Abraham (1978)). Nose and Yonezawa (1985) started a
series of computer simulation studies for a similar Lennard-Jones system to Abraham,
and by following the recipe proposed by WA they gave $R_{LG} = 0.1$ for their MD
simulation results on 864 particles. A rather thorough and extensive MD investigation
on real liquid Rb metal has been initiated by Hsu and Rahman (1979a, b) and
Mountain (1982, 1983). These authors have quantitatively studied the nucleation
problem and have attempted to examine various criteria (kinetically) leading to the
development of metastable equilibrium states. These studies, while not yielding direct
information about the WA parameter of interest in this paper, do provide profound
insights into our understanding of computer glasses.

The work by Tanaka (1983, 1986a), also for Rb but using a different pairwise
potential constructed from the pseudopotential of Shaw (1970), is perhaps worthy of
mention. Using MD simulation techniques like Hsu and Rahman (1979a, b) and
Mountain (1982, 1983) Tanaka determined the pair correlation function against
temperature and found the WA parameter to be 0.11. Recently (Tanaka 1986b), he
also presented a detailed comparison of his MD simulation studies for monatomic
argon and Rb glasses. Besides finding many similar features between these systems,
he found $R_{LG} = 0.094$ for argon. The present author (Lai et al 1987) has also carried
out a MC simulation calculation for monatomic Cr and the ratio $R_{LG}$ was calculated to
be 0.101. From this brief summary it appears appropriate at this time to recheck the
possibility of this universal property of the empirical criterion of WA because all the
recent computer simulation studies for various seemingly different monatomic
systems mentioned above tends to indicate the same $R_{LG} = 0.1$.

In this paper we present two further MC simulation calculations for Y and Zr
monatomic glasses for which reasonable interatomic potentials are now available. We
hope to convey our proposition that the WA parameter $R_{LG}$, irrespective of the
material under study, may well be a universal constant for all monatomic glasses. To
allow for possible numerical fluctuation due, for example, to the number of particles
used in the simulation, we propose $R_{LG} = 0.1 \pm 0.02$. In addition to examining this
universal criterion we shall present the change in the pair distribution functions
(denoted also by $g(r)$ hereafter) of each element at their respective temperature
quench. We show that the liquid–glass transition is characterised, at the proposed
$R_{LG} = 0.1 \pm 0.02$, by the flattening of the second $g_{max}$. The characteristic features of the
amorphous states of both elements will also be displayed.

The presentation of the paper is briefly as follows. In the next section, we
summarise the method used in the present computation. This is followed in §3 by a
discussion of our numerical results; we compare and analyse these results in relation
to our previous work and work done recently by other researchers.

2. Calculational procedure

For any computer simulation study (MC or MD) to be carried out, one first of all
requires an interatomic potential as a prime input. For this we adopt the potential
function theoretically constructed from the generalised non-local model potential
theory of Li et al. (1986a, b, c), which has been shown by them to be reasonable in terms of calculated thermodynamic quantities. Mathematically this interatomic potential is given by (Wang and Lai 1980)

\[ V(r) = \frac{Z_{\text{eff}}^2}{r} \left( 1 - \frac{2}{\pi} \int_0^\infty dq \, G_{\text{EC}}(q) \frac{\sin(qr)}{q} \right) \]

where \( Z_{\text{eff}} = Z^2 - \rho_d^2 \), \( \rho_d \) being the depletion charge, and \( G_{\text{EC}}(q) \) is the normalised energy wavenumber characteristics.

For the MC calculation, we utilise \( N = 1000 \) particles confined to a cubic cell and apply standard periodic boundary conditions to simulate the bulk properties. In order to simulate the different stationary or metastable states, we follow Abraham (1980) and prepare these states by instantaneously quenching the metallic liquid. In each of these simulations we first equilibrate the system through at least \( 3 \times 10^5 \) MC steps and adjust the displacement vector to give an acceptance ratio of \( \sim 50\% \). When the system has reached equilibrium, we carry out \( 6 \times 10^5 \times 10^1 \) further MC steps to obtain the pair correlation functions. For each temperature-quenched state, we therefore start with the last fluid configuration of a well-equilibrated state and the suddenly quenched state of the system is obtained by simply setting the desired temperature in the usual MC method. This procedure is repeated for each temperature (altogether we divided between the liquid and amorphous states into ten equal steps) and in each metastable state we proceed (a) with an acceptance ratio of \( \sim 50\% \) and (b), after equilibration, for at least \( 6 \times 10^5 \times 10^1 \) further MC steps. By applying this procedure and using the pair potential (see Li et al. (1986b, c) for plotted \( V(r) \)) given just above, we obtain the pair distribution functions. We note that the densities for liquid Zr and Y are respectively taken from Li et al. (1986b, c) and Kononenko et al. (1984) and the densities of the intermediate states are estimated by interpolating linearly between

![Figure 1. Theoretical pair distribution function (full curve) of Zr calculated using MC simulation and compared with the experimental data (\( \bullet \)) of Waseda (1980). The system is at the melting temperature.](image-url)

\[ \dagger \] The quenching rate corresponding to the present procedure is thus expected to be much larger than the standard MC simulation method (see remark 7 of Wendt and Abraham 1978).
liquid and solid state data. As far as our structure statistics show and within the approximations of the procedure made here, there is no indication in our results of any instability initiated by the nucleation process. Our theoretical \( g(r) \) for Zr at its melting temperature is displayed in figure 1 and this is compared with the experimental \( g(r) \) of Waseda (1980) (the experimental \( g(r) \) for Y is unfortunately not available). The results of calculations for the \( g(r) \) as a function of temperature are shown in figures 2 and 3.

3. Discussion and comments

We examine first of all the pair correlation function of Zr given in figure 1. The first thing that one notices from this figure is that our MC \( g(r) \) has a slightly higher first peak maximum. However, in contrast to the \( g(r) \) for Cr, the position of the first peak of \( g(r) \) compares favourably with the experiment. Overall the comparison between theory and experiment for liquid Zr metal has been much improved. Such an improvement, however, is by no means fortuitous and is to be attributed to the fact that for Zr (and also for Y) there is a complete 3d closed shell which allows it to be orthogonal by the d-type valence electronic state. Accordingly, the model pseudopotential approach is more appropriate to Zr and Y than to Cr. Bearing in mind further the simplicity of the present model potential, such a fair agreement is not unexpected and should be considered as quite reasonable.

We now discuss the WA parameter \( R_{1G} \). In table 1 we present our theoretical \( R_{1G} \) (determined from figures 2 and 3) for Y and Zr and these are found, respectively, to be 0.100 and 0.098 at \( T = 1020 \text{ K} \) and \( T = 1350 \text{ K} \). By considering our previously obtained \( R_{1G} \) for Cr, we now propose a universal \( R_{1G} = 0.1 \pm 0.02 \) for all the monatomic glasses. As a first check on our conjecture we compare the present \( R_{1G} \) results with those obtained independently by Hiwatari (1979, 1980) for a soft-core liquid.

<table>
<thead>
<tr>
<th>System</th>
<th>Method</th>
<th>( N )</th>
<th>( R_{1G} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>MC</td>
<td>1000</td>
<td>0.100</td>
</tr>
<tr>
<td>Zr</td>
<td>MC</td>
<td>1000</td>
<td>0.098</td>
</tr>
<tr>
<td>Cr</td>
<td>MC</td>
<td>1000</td>
<td>0.101</td>
</tr>
<tr>
<td>Rb</td>
<td>MD</td>
<td>864</td>
<td>0.110</td>
</tr>
<tr>
<td>lJ</td>
<td>MC</td>
<td>108</td>
<td>0.110</td>
</tr>
<tr>
<td>lJ</td>
<td>MD</td>
<td>864</td>
<td>0.100</td>
</tr>
<tr>
<td>lJ</td>
<td>MD</td>
<td>864</td>
<td>0.094</td>
</tr>
<tr>
<td>SC</td>
<td>MD</td>
<td>256</td>
<td>0.080</td>
</tr>
<tr>
<td>GC</td>
<td>MD</td>
<td>432</td>
<td>0.140</td>
</tr>
</tbody>
</table>

\(^a\) Lai et al (1987)  
\(^c\) Abraham (1980).  
\(^d\) Nose and Yonezawa (1985).  
\(^e\) Tanaka (1986b).  
\(^f\) Hiwatari (1980).  
\(^g\) Stillinger and Weber (1979).
Tanaka (1983, 1986a) for metallic Rb, and Abraham (1980), Tanaka (1986b) and Nose and Yonezawa (1985) for a Lennard-Jones system. It is interesting to note from this table that despite their seemingly different metallic or non-metallic properties, i.e., irrespective of the monatomic systems being studied, all of the predicted $R_{LG}$ (see table 1) lie well within our hypothesised value of $R_{LG} = 0.1 \pm 0.02$. The result $R_{LG} = 0.14$ obtained by Stillinger and Weber (1979) is the only exception but this is not to be considered too seriously because the change in the respective slopes of their gaussian core model is not as clear-cut as others (compare figure 5 of Stillinger and Weber (1979) with the corresponding figures of Hiwatari (1979, 1980), Abraham (1980), Nose and Yonezawa (1985) and Tanaka (1983, 1986a, b)) and, moreover, there is no sign of amorphous structure (the usual double peak splitting) in the glassy state reported by them. The failure of the simulation studied of Stillinger and Weber in giving a $R_{LG}$ that lies within the presently proposed value is now believed to be due to the unrealistic softness of the gaussian core model, as criticised by Hiwatari (1980).

An immediate question of interest is: Why is it that $R_{LG} = 0.1 \pm 0.02$ is a universal constant? Is there any physical indication or precursor pertaining to it? Before pursuing the answers to these questions, it is perhaps of interest to digress a moment and examine figures 2 and 3 closely. There are three interesting features that merit emphasis. In the first place we note that all the general structural characteristics of an amorphous state are contained in our present results. Secondly, we find that as the temperature is progressively reduced from the liquid phase, the second maximum of $g(r)$ changes subtly from a single peak, flattens, and rapidly develops into a clear, well

![Figure 2](image1.png)

**Figure 2.** Temperature-quench results of the pair distribution function of Y. The amorphous state Y is calculated at room temperature.

![Figure 3](image2.png)

**Figure 3.** Temperature-quench results of the pair distribution function of Zr. The amorphous state Zr is calculated at room temperature.
resolved, double-peak splitting (of which the first is higher than the second). Accompanying these changes in the second peak maximum, it is easy to see that the dispersion of the first peak of \( g(r) \) becomes narrower and increases in height (see also figure 4 below). In particular we stress that the flattening† of \( g(r) \) for both elements considered here correlates quite well with the liquid–glass transition point (see figures 2 and 3). Thirdly, we observe that as the temperature is lowered, the amplitudes of oscillations beyond the second peaks increase, as was first pointed out by Abraham (1980)‡. Apart from these general features, it is also worth emphasising that our calculated ratios \( r_2/r_1, r_3/r_1, \) and \( r_2/r_1 \), where \( r_1, r_2, r_3 \) and \( r_1 \) are respectively the positions of the first, second and third maxima of \( g(r) \), are consistent with measurements on laboratory amorphous metals (Leung and Wright 1974, Cargill 1975, see table 2).

We may now return to the questions raised just above. A clue to the understanding of the universality of \( R_{1,G} \) may be sought by exploring further the variation in temperature of the spatial ionic correlation in supercooled and glassy regions. In their original paper, Wendt and Abraham (1978) interpret the striking feature of \( R_{1,G} \) to be associated with the packing saturation of the first shell of nearest neighbours. The onset of liquid–glass transition, proposed in this work to be at \( R_{1,G} = 0.1 \pm 0.02 \), is found to be intimately related to this hypothesis. Specifically we note that \( R_{1,G} \) signals a critical point where the ions, on further temperature quenching, make a transition into the glassy region and therefore begin to lose their ability to wander about as freely as in a liquid system. That this begins at \( R_{1,G} = 0.1 \pm 0.02 \) is conjectured to be connected to the fact that the ionic positions (and hence their motion) from hereon are being confined by their nearest neighbours to lie within a certain restricted region (some authors call it a cage or a cell). Thus, when making the transition into the glassy region, all the ions are expected to have a greater tendency to be almost ‘localised’ (compared with the larger mobility of ionic motions in a liquid or supercooled region) until the eventual amorphous structure is reached.

Such a picture of a solid-like transition can be readily inferred by recalling the well known Lindemann relation (Lindemann 1910) for the melting phenomenon. According to Lindemann, melting occurs when the root mean square amplitude of an ionic vibration approaches one tenth of the nearest-neighbour distance. In an attempt to understand the universality of \( R_{1,G} \), and as a qualitative measure of an analogue of the Lindemann criterion, we have displayed in figure 4 the variation of \( \hbox{HWHM}/r_1 \)§ (\( \hbox{HWHM} \) being the half-width at half-maximum and \( r_1 \) the position of the first nearest-neighbour of \( g(r) \)) with temperature. It is remarkable to see that the curve of \( \hbox{HWHM}/r_1 \)

### Table 2. Ratios of first \( (r_1) \), second \( (r_2, r'_2) \) and third \( (r_3) \) position maxima of the pair distribution function for solid amorphous Y and Zr at room temperature.

<table>
<thead>
<tr>
<th>Element</th>
<th>( r_2/r_1 )</th>
<th>( r'_2/r_1 )</th>
<th>( r_3/r_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>1.75</td>
<td>1.98</td>
<td>2.59</td>
</tr>
<tr>
<td>Zr</td>
<td>1.73</td>
<td>1.95</td>
<td>2.58</td>
</tr>
</tbody>
</table>

† The same criterion has been found by Hiwatari (1980).
‡ Such a feature has also been observed by Mountain (1982).
§ This quantity was first applied by Hiwatari (1980) to discuss the glass transition point for a soft-core system.
against temperature also displays a change in slope, and, interestingly, at the intersection of the slopes we obtain \( \text{HWHM}/r_1 \) equals 0.091 for Y and 0.085 for Zr at nearly the same liquid–glass transition temperatures (\( T(Y) = 1040 \) K and \( T(Zr) = 1380 \) K). Although these results cannot constitute a quantitative explanation for the \( R_{LG} \), they nevertheless provide valuable information for our theoretical understanding of such a possible universal constant.

Certainly it is also true that such a universal \( R_{LG} \) is intimately connected to the ubiquitous observation that the microscopic structure of any amorphous state is basically the same, that is, a first nearest-neighbour peak, at virtually the same position as its liquid counterpart, and an increased probability of atomic or ionic neighbours at \( r = \sqrt[3]{3} r \), and \( r = 2 r_1 \). When the \( R_{LG} = 0.1 \pm 0.02 \) point is reached, we would expect all the ions in the system to have been arrested in a disordered state and, in general, to be approaching the characteristic type of vibrational motion as we understand it in crystalline solids. This solid-like behaviour of ionic motion will be more apparent as the temperature is lowered further (decreasing of the first \( g_{\text{min}} \) and a corresponding increase of the first \( g_{\text{max}} \)) until a glassy or amorphous state is formed. The change in slopes\( ^{\dagger} \) from higher \( (R > R_{LG}) \) to smaller \( (R < R_{LG}) \) values (see, for example, figure 1 of Lai 1987) in the Wendt–Abraham curve of \( R \) against temperature therefore describes a physical situation in which the motion of ions with large mobility (in the sense of a liquid disordered system) makes a transition into another disordered state where the ionic mobility is much reduced and restricted. This explains the existence of two linear \( R-T \) regions, called supercooled and glassy branches by WA. This proposed universal constant \( R_{LG} \), defined as a point of liquid–glass transition irrespective of the material, is quite similar to the (liquid–crystal transition) \( R_{LC} \).
0.2 ± 0.02, taken to be the molecular criterion along the freezing curve by Raveche et al (1974).

4. Conclusion

We summarise the main results of this work as follows. We have carried out detailed computer simulations for Y and Zr in an attempt to recheck the universality of the WA criterion. By first comparing the MC pair distribution function of Zr with available experimental data we arrive at the conclusion that the present interionic pair potentials for Y and Zr, constructed from a first-principles generalised non-local model pseudopotential, are reasonable for use in the structural studies. These pair potentials, in conjunction with the MC technique, are applied to calculate the g(r) at each instantaneous temperature quench. The results of the changes of g(r) with temperature allow us to explore the variation of R with temperature for Y and Zr. From these latter curves we obtain the R_LG for Y and Zr and these are further compared with (i) the R_LG for Cr (Lai et al 1987) and (ii) other monatomic systems published recently. We find that the critical WA parameter satisfies R_LG = 0.1 ± 0.02 and may well be a universal constant for all monatomic systems. In order to explain this constant R_LG value we draw an analogy between this critical point and Lindemann's criterion of the melting phenomenon. By plotting the $I_{WHM}/r_1$ (corresponding qualitatively to the ratio of root mean square amplitude of vibration to mean ion–ion distance) against temperature we discover that $I_{WHM}/r_1$ also changes in slope and the intersection is at nearly the same liquid–glass transition temperature. But although the present work has been confined to a discussion of monatomic glasses, the similarities in the final glassy states of any laboratory amorphous solids make it interesting to see whether the findings reported here remain valid in amorphous alloys where chemical or concentration dependence may have a dominant influence.

Acknowledgments

This work has been supported in part by the National Science Council, Taiwan, Republic of China under contract No NSC76-0208-M008-19. The author would also like to express his appreciation to the Computer Center of the Ministry of Education, Taiwan for providing computing facilities.

Note added in proof. Very recently Watanabe and Tsumuraya (1988 J. Chem. Phys. 88 1991) have reported a molecular dynamics simulation for liquid sodium. The value of R_LG obtained by them is 0.08, thus providing further support for the work presented here.

References

Hsu C S and Rahman A 1979a J. Chem. Phys. 70 5234
--- 1979b J. Chem. Phys. 71 4974
Lai S K 1987 J. Mater. Sci. Eng. 6th Int. Conf. on Rapidly Quenched Metals, Montreal to be published
Leung P K and Wright J G 1974 Phil. Mag. 30 995
--- 1986c Can. J. Phys. 64 852
--- 1987 J. Chem. Phys. to be published
Lindemann F A 1910 Phys. Z. 11 609
--- 1983 J. Chem. Phys. 78 7318
Nose S and Yonezawa F 1985 Solid State Commun. 56 1005
Stillinger F H and Weber T A 1979 J. Chem. Phys. 70 4879
--- 1981 Prog. Mater. Sci. 26 1