The Effects of the Softness of the Interionic Pair Potential on the Liquid–Glass Transition*

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Abstract

Various forms of interionic pair potentials such as the Lennard-Jones, the soft core and the gaussian core have been adopted in the literature to characterize monatomic systems and used in computer simulation studies of the liquid–glass transition. Although the final amorphous structures have generally been produced, there is as yet no detailed account of the structural relation between these different pair potentials and the microscopic process of the liquid–glass transition. In this work, in contrast with the potentials mentioned above, we use metallic pair potentials constructed from a non-local model pseudopotential derived from first principles. By choosing pair potentials of varying softness, we present the results of Monte Carlo temperature-quench simulations for the pair distribution functions of chromium, yttrium, zirconium and alkali metal monatomic systems. We find that the softness of the interionic pair potentials of these systems exhibits an interesting correlation with the Wendt–Abraham parameter (Phys. Rev. Lett., 41 (1978) 1244) vs. temperature.

In the last few years much effort has been devoted to using computer simulations to explore the microscopic process of the liquid–glass transition. Among others, the Monte Carlo (MC) and molecular dynamics (MD) simulations are two widely used techniques and have been applied extensively to studies of problems (such as structures and thermodynamics) that provide considerable insights into our theoretical understanding of the liquid–glass transition. In a structural investigation Wendt and Abraham [1] (WA) first investigated a Lennard-Jones system and advanced an empirical criterion that relates the change in the pair correlation function with temperature to the microscopic process of the liquid–glass transition. According to their MC simulation, they discovered that the ratio \( R = \frac{g_{\text{min}}}{g_{\text{max}}} \) where \( g_{\text{min}} \) and \( g_{\text{max}} \) are the values of the pair distribution function at the first minimum and maximum positions respectively, changes in slope and varies linearly with temperature in two separate regions. The intercept of the two slopes occurs at a point \( R_{LG} \) which they defined as indicating a liquid–glass transition. At this \( R_{LG} \) value (equal to approximately 0.14) they found that the double-peak structure of the pair distribution function just begins to develop. This pioneering work of WA has subsequently been extended by Abraham [2] who not only continued the structural studies but also investigated a number of associated thermodynamic properties. Of direct relevance to the present work is that Abraham obtained \( R_{LG} = 0.11 \) in contrast with his previous result of \( R_{LG} = 0.14 \). The use of the WA parameter \( R \) vs. temperature as a probe to understand the liquid–glass transition has then received much attention. Stillinger and Weber [3], stimulated by the work of WA, adopted a gaussian core model and used the MD simulation technique to examine the possibility of the universal behaviour of \( R_{LG} \). Unfortunately the gaussian core system is unrealistically soft [4], leading to the unsuccessful prediction of an amorphous state. In the same spirit as Stillinger and Weber, Hiwatari [4] used a soft-core model and carried out MD simulations for the pair distribution function. By following the procedure of WA, he found that the WA \( R \) vs. temperature plot also changes in slope. For the soft-core liquid he obtained \( R_{LG} = 0.08 \). Some years later, the temperature dependence of \( R \) for a Lennard-Jones system was further studied by Nose and Yonezawa [5] and Tanaka [6]. Both groups of researchers reported similar variations in \( R \) with temperature and obtained \( R_{LG} = 0.1 \). Tanaka [7] has also seriously characterized a liquid metal by a real metallic potential and applied it in an MD simulation study of the liquid–glass transition. Interestingly, he found that the variation in temperature of the WA \( R \) conforms to those obtained by the above researchers and, in particular, he predicted \( R_{LG} = 0.11 \). Very recently Lai et al. [8] have applied the MC temperature-quench procedure to study the
$R$ vs. temperature curve for chromium. The changes in $R$ with temperature display the same characteristics as those discussed above.

From this brief summary it has become apparent that a subtle change in $R$ with temperature is a common feature for most of the monatomic systems. However, although the results presented by the above-mentioned researchers are interesting, there seems to be no published work that explicitly examines the interconnection between the properties of these various systems (or, more specifically, the interatomic potentials) and their corresponding relation with the $R$ vs. temperature data. In this work we present results of our MC simulations for chromium, yttrium, zirconium and rubidium monatomic systems.

The interionic pair potentials for these elements vary in softness from chromium, through yttrium and zirconium to rubidium, thus permitting us to examine the effects of the softness of interionic pair potentials on the microscopic process of the transition from a liquid to a glassy state. The calculational procedure has been described previously [8]. Here we note that for each of the elements we have considered a total of 1000 particles, and the pair potentials have been constructed using the much improved model pseudo-potential theory of Li and coworkers [9, 10].

In Fig. 1 we depict the $R$ vs. temperature results for all the monatomic elements of interest here. There are two interesting points that merit emphasis. In the first place we note that the supercooled region (between $R$ (liquid) and $R_{LG}$) is smallest for chromium and increases as rubidium is approached. Secondly, independent of the elements under study, $R_{LG}$ for any of the metals approximately satisfies $R_{LG} = 0.1 \pm 0.02$.

To understand the first point, we display in Fig. 2 the repulsive parts of the different pair potentials appropriately scaled so that the degree of softness is clearly seen. It is interesting to note that the interionic pair potential is “hardest” for chromium and becomes softer as we proceed through yttrium and zirconium to the alkali metal (see Fig. 2). This feature of the potential has a crucial effect on the liquid–glass transition because an element with a softer pair potential is structurally more susceptible to interparticle rearrangement as the temperature quench probes progressively from a liquid into the glassy region. This will result in a comparatively smaller slope and hence a larger supercooled branch. In contrast, since chromium ions have the “hardest” repulsive part, they will have less freedom to rearrange themselves as the temperature of the system is lowered, thus leading to a smaller supercooled region. Regarding the second point, such a universal constant for $R_{LG}$ has to be attributed to packing saturation because at $R_{LG}$ the ions have just undergone the transition into the glassy state and therefore will be more like a solid in behaviour, losing the ability to move about as freely as in the supercooled or liquid phase. An attempt to explain this universality will be reported elsewhere [11].

To summarize, we may stress that the pair potential used here is quite accurate (although strictly speaking even this potential only represents an approximation to real metallic bonding) and reasonable
for studying the microscopic process of the liquid–glass transition. Unfortunately the extremely high quenching rate (of the order of $10^{12}$ K s$^{-1}$) of MC simulation prevents us from making a direct comparison with laboratory glasses (typical quenching rate, $10^6$–$10^8$ K s$^{-1}$). This does not imply, however, that the present calculation is without merit. In fact, because many of the interesting features of real metallic glasses are unambiguously displayed (see Fig. 2 and Table 1 of ref. 8, for example) in our computer-simulated glasses, the present work does provide considerable insights into our theoretical understanding of the physical process involved. At least it helps us to understand why rubidium metal is less likely than chromium to form an amorphous solid.

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References