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Testing of Frank’s hypothesis on a containerless packing of macroscopic soft spheres and comparison with mono-atomic metallic liquids

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ABSTRACT

It is well-known that metallic liquids can exist below their equilibrium melting temperature for a considerable time. To explain this, Frank [1] proposed that icosahedral ordering, incompatible with crystalline long-range order, is prevalent in the atomic structure of these liquids, stabilizing them and enabling them to be supercooled. Some studies of the atomic structures of metallic liquids using Beam-line Electrostatic Levitation (BESL; containerless melting), and other techniques, support this hypothesis [2,3]. Here we examine Frank’s hypothesis in a system of macroscopic, monodisperse deformable spheres obtained by containerless packing under the influence of centripetal force. The local structure of this packing is analyzed and compared with atomic ensembles of liquid transition metals obtained by containerless melting using the BESL method.

1. Introduction

Fahrenheit [4] was the first to demonstrate that water can be maintained in the liquid phase below its melting temperature (supercooling). Turnbull’s [5] demonstration that liquid metals can also be supercooled was surprising, given the similarity in density and coordination numbers of the liquid and crystalline phases and their simple symmetric structural units, in contrast to the complex molecular structures in water, organic compounds, proteins, etc. To explain the supercooling of metallic liquids, Frank [1] proposed that the local order in the supercooled liquid must be quite different from that in the solid, despite the similar densities and coordination numbers. He observed that there are actually three distinct close packing schemes that give a local coordination of 12 (i.e. when a central atom is surrounded by 12 neighbors). These three distinct packings are face-centered cubic (FCC), hexagonal close packed (HCP) and icosahedrons. Here, two packings are considered distinct if a transformation from one to the other is not possible without an atom losing contact with the central one. Only for icosahedral packing among these three, the surrounding atoms do not touch each other.

If the atoms are deformable (a condition which will be argued for later), the atoms can deform to form denser packing locally and reduce the overall energy of the cluster [1]. The icosahedral structure is incompatible with long-range crystalline (translational) periodicity but is locally stable, thus rearrangement to a crystal structure is energetically costly in local scale but favorable on longer length scale, giving rise to the observed barrier for nucleation of the stable crystal phase. Based on these considerations, Frank proposed that icosahedral short-range order (ISRO) is dominant in the local structures of metallic liquids. The first experimental proof of this hypothesis was obtained recently [2] during an investigation of the supercooling of a Ti–Zr–Ni alloy. To avoid heterogeneous nucleation, samples were containerlessly processed under high vacuum and simultaneous in situ synchrotron scattering measurements were performed using the Beam-line Electrostatic Levitation (BESL) technique [2,6]. A metastable quasicrystal formed directly from the melt, due to lower nucleation barrier (compared to that of the competing stable C14 crystal structure) arising from local icosahedral order. Analysis of the atomic structures of the supercooled liquid prior to quasicrystal formation also demonstrated a growth of icosahedral short-range order upon cooling, confirming Frank’s hypothesis [2].

As a first approximation, atomic interactions can be modeled using hard (rigid) spheres. While this method has been applied often for atomic liquids [7–11], hard-sphere models do not allow the compressibility commonly observed in liquid metals. Soft-sphere systems facilitate more meaningful studies which provide an attractive way to study the mechanical response of atomic ensembles and gain structural and dynamical insights. A particu-

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larly successful example is the use of bubble raft and similar models to study the atomistic nature via nanoindentation [12,13]. It is also known that the electronic interaction among atoms causes considerable distortion in electron density distribution [14,15], allowing the atoms to deform. The deformability of the atoms can lead to denser packing which reduces the local energy of the clusters in a given structure, and a soft-sphere model is more appropriate for modeling such a system. It is therefore interesting to use a soft-sphere system as a structural model for supercooled liquids, and the attempt is made in this study to develop a macroscopic model system of this type by using deformable spherical particles.

2. Methods

A so-called ‘centripetal packing’ (CP) [16] of macroscopic particles is used as a model system. It is produced by computer experiments using discrete element modeling [16–18]. Initially, 20,000 soft spherical particles of radius 1 cm are randomly distributed in a three-dimensional cubic box, each side of it measuring 75 cm. From the start of this computer experiment ($t = 0$) all the particles experience a hypothetical force, whose magnitude equals the gravitational force but in a direction towards the overall center of gravity (CG; this is calculated based on the effective mass of the ensemble). Since conventional gravity is not employed (and can be thought of as “switched off”) all the particles accelerate towards the CG under the influence of this hypothetical force, and a packing is formed. This packing is called centripetal packing (CP), as it is obtained using a force that acts towards the CG. The use of this kind of force is interesting because it allows all the particles to move towards the center of the box (because of the initial random distribution, the CG is close to the box center) and the packing can be produced without any interaction between the constituent spheres and the confining walls. As a result, the packing captures the containerless feature of a BESL experiment. Other parameters of this simulation can be found elsewhere [18].

Since CP structures will be compared with BESL results [19], a brief description of BESL is provided here for the sake of completeness; more details can be found elsewhere [2,6]. In BESL, a sample (placed in a highly evacuated chamber) is illuminated by ultraviolet light to positively charge it. By using a pair of electrodes (bottom grounded and top negative, with the potential controlled by feedback algorithm) the sample can be levitated, resulting in a containerless experiment. The stability of the sample is achieved by two additional sets of orthogonal electrodes, also using feedback control. The sample is heated by a laser and the temperature is recorded using a pyrometer. The setup is used in a high-energy synchrotron X-ray facility and the diffraction spectra are recorded at high frame rates using a state-of-the-art 2D detector. These spectra are corrected and further investigated by reverse Monte Carlo analysis (RMCA) to produce representative atomic ensembles.

The high vacuum condition of BESL is simulated in CP by the absence of any additional gas phase between the particles. The soft-sphere condition is achieved by modeling the particle-particle interaction using spring and dashpot models [20,21] for both the normal and tangential components. The normal component of the contact force is modeled by the Hertz theory and the tangential component by the Mindlin–Deresiewicz theory [16,22]. In this way, the local structures of the centripetal packing are determined and compared with those obtained experimentally for a mono-atomic liquid using BESL.

Two metrics are used for the local structure analysis. The first is the Honeycutt-Andersen (HA) index [23], which describes the local structure around a pair of atoms, called the root pair. Each HA index consists of a set of four numbers: If the root pair atoms are nearest neighbors, the first number is unity (the nearest-neighbor distance is set from the location of the first minima in the radial distribution function (RDF)). The second number denotes the number of nearest neighbors common to the root pair. The third number denotes the number of bonds among the nearest neighbors of the root pair. If the first three numbers of the HA index are the same for two local structures that are topologically distinct, they are distinguished by an arbitrary fourth index. Icosahedral (ICOS) order is thus identified by an HA index of 1551, distorted icosahedral (DICOS) order is identified by indices of 1541 and 1431, HCP and FCC order are collectively identified by 1421 and 1422, body-centered cubic (BCC) order is identified by 1661, etc.

The second metric used is the bond orientation order (BOO) parameter, originally proposed by Steinhardt et al. [24,25]. In this method a set of order parameters based on spherical harmonics is constructed for the orientation between a central atom and all of its nearest neighbors,

$$Q_{lm}(\vec{r}) = Y_{lm}(\theta(\vec{r}), \phi(\vec{r})), \tag{1}$$

where $\vec{r}$ denotes the orientation of each bond with respect to the central atom. Quadratic and third order invariants of the order parameters are then calculated by

$$Q_l = \left[\frac{4\pi}{2l+1}\sum_{m=-l}^{l}\left|\bar{Q}_{lm}\right|^2\right]^{\frac{1}{2}}, \quad \text{where} \quad \bar{Q}_{lm} = \frac{1}{N_b}\sum\nolimits_{\text{bonds}} Q_{lm}(\vec{r}). \tag{2}$$

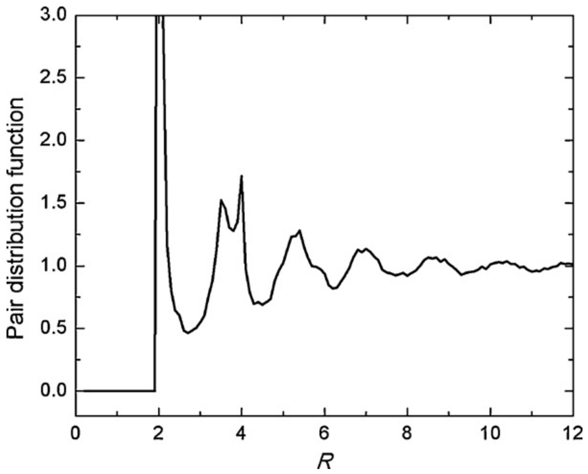

Fig. 1. The pair distribution function for centripetal packing. The distance from the atom center (R) is in dimensionless units (scaled to the sphere radius).

The rotationally invariant part (l even) of this is totaled for all the bonds and then normalized with respect to the value for random packing. This parameter provides useful information about the local structure. For example, icosahedral order is identified by a large number of Q_6 and Q_{10} values, while others remain nearly zero.

Although the HA and BOO methods both provide useful information about the local structure, there are some important distinctions. The HA analysis describes only the structure around a root pair. In terms of clusters, it would provide information on only a fraction of the distribution of atoms around a central atom. For example, an abundance of the HA index 1551 indicates that there are fragments of icosahedral clusters, but it does not indicate the presence of fully formed icosahedra. In contrast, the BOO provides a complete description of the cluster. However, it is sometimes difficult to interpret BOO results, since different clusters might share Q values. It is unclear which metric provides the best information and it often depends on the application. It could be argued, for example, that only the local structure is relevant for a discussion of the nucleation barrier. In this case, the HA index would be more appropriate. For the present study, both HA and BOO will be used to provide complementary information on the structure.

3. Results and discussion

The pair distribution function of the centripetal packing is shown in Fig. 1. A pronounced split in the second peak is observed, and this feature is more pronounced in the pair distribution function of CP than in that of the monoatomic liquids: Ti, Zr and Ni in supercooled states ($T/T_\text{m} \approx 0.8$), as shown in [19].

It is interesting to analyze the local structure in more detail in terms of the HA and BOO parameters. To avoid surface effects in the CP structure, the central part of the packing is cut out in the shape of a cube containing 4184 spheres. This shape was chosen to maintain consistency with the BESL studies of Ti, Zr and Ni liquids available in literature [19], which used 5000 atoms. The HA indices found for the RMCA structures of liquid Ti, Zr, and Ni near the melting temperature (Fig. 2(a)) and in the supercooled state (Fig. 2(b)) are compared with those for the centripetal packing in respective figures. The structure of the CP is dominated by icosahedral (ICOS) and distorted icosahedral (DICOS) order. The structures of the metallic liquids near the melting temperature contain a significant amount of DICOS order, but significantly less ICOS order and more crystal-like order such as FCC/HCP (Fig. 2(a)). Upon cooling the amount of ICOS in the liquid increases and approaches that in the CP; the amount of DICOS also increases, becoming even greater than in the CP (see Fig. 2(b)). Interestingly, the amount of crystal-like order in the liquid does not change significantly with undercooling.

The BOO parameters of the supercooled metallic liquids (corresponding to Fig. 2(b)) are compared in Fig. 3 with those of the CP. These results support the conclusions from the HA index analysis. The pronounced value of Q_6 in the CP again indicates a higher degree of icosahedral order in this packing than in the metallic liquids. The presence of other nonzero Q_l values indicates that there is