Collineations of particles in the Kob-Andersen system

V.A. Levashov

Technological Design Institute of Scientific Instrument Engineering, 630055, Novosibirsk, Russia. E-mail: valentin.a.levashov@gmail.com

Numerous indications suggest that subtle changes occurring in the structures of liquids on supercooling are connected to the phenomenon of the glass transition and that detailed understanding of these changes is crucial for the development of new glasses with desired properties. J.D. Bernal in his 1962 Bakerian lecture, in particular, reported about an observation of approximately linear chains of several particles, referred to as collineations. He found that in the studied hard sphere system, these collineations can contain up to eight particles. Since then, the collineations of three particles have been discussed in many papers in the context of the splitting of the second peak in pair density functions of supercooled liquids and glasses. However, it appears that longer collineations involving more than three particles have not been systematically studied. Here, we report on our study of such collineations for the Kob-Andersen system of particles on cooling for the parent and inherent structures. Contrary to intuition, our findings reveal that below the potential energy landscape crossover temperature, the number of collineations in the parent structures can exceed that of the corresponding inherent structures. We also introduce a model that connects long collineations with the pair density and angular density distribution functions and demonstrate that this model describes long collineations quite well. The second part of the paper explores potential connections between collineations and: 1) the disclination lines associated with the geometric frustration approach, 2) low-energy clusters from the topological cluster classification approach, 3) chain-like cooperative motion of particles in low-temperature supercooled liquids. For the studied system, according to the used methods, no clear connection was found between collineations and these phenomena.

I. INTRODUCTION

The investigations of the structural organization of supercooled liquids and glasses continue to garner significant attention despite decades of studies [1–7]. Understanding of structures of such non-crystalline materials is important for unraveling the nature of the glass transition (GT) and developing new glasses with desired properties [8, 11].

It is generally recognized that structural changes occurring in liquids on supercooling and approach of the GT are subtle while changes in the dynamical properties are tremendous [11, 7]. Nevertheless, some relatively minor structural changes clearly correlate with the GT. For example, from a macroscopic perspective, there is a change in the slope at the GT in the temperature dependence of the liquid’s volume at constant pressure [11]. Additionally, from an average microscopic standpoint, there is a change in the slope of the ratio of the depth of the first minimum to the height of the first maximum in the pair density function (PDF) [8].

Another microscopic feature often considered as a signature of the glass state is the splitting of the second peak in the PDF [5–8, 11, 12, 17]. The development of this feature indicates that ordering on medium-range length scales is relevant to the GT [11, 16]. The structural organization associated with the splitting of the second peak is directly related to the phenomenon studied in this paper, as we discuss later.

Observations of the aforementioned features in different systems have led to extensive efforts to interpret them in terms of structural changes. Of particular importance is the observation that, in many liquids upon supercooling, icosahedral ordering develops. It is often assumed that icosahedral ordering prevents crystallization due to its five-fold symmetry, which is incompatible with crystalline periodic order [5, 13–27]. Furthermore, it has been demonstrated that icosahedra in such liquids have a tendency to agglomerate into domains [28–30]. This indicates that in liquids upon supercooling, structural heterogeneities develop with characteristic length scales larger than interparticle distances. The development of icosahedral ordering on the length scales associated with a central particle and its nearest neighbors does not occur in all liquids. This is because, in some liquids, the lowest energy local structure is not an icosahedron [2, 5, 30]. However, recent studies have demonstrated that in such liquids, five-fold structural symmetry may still be present on the length scales associated with the second and further neighbors [31–32]. This once again underscores the importance of structural medium-range order for the GT.

While the importance of medium-range order has been discussed in many publications, the structural descriptors commonly employed to address the evolution of the structure are typically local. For instance, Voronoi polyhedra, bond orientational order parameters, and the numbers of common neighbors for neighbor pairs are frequently used [5, 22, 23, 30, 33–36]. Subsequently, in addressing structural changes upon supercooling, the ways in which these units combine are often considered [2, 5, 10, 30, 31, 37].
Due to the absence of periodicity in liquids, structural changes occurring during supercooling cannot be observed using conventional crystallographic techniques \[1,6\]. Consequently, the PDF, which is experimentally accessible for liquids, often serves as the standard data for structural analysis. However, the PDF measures the angular average of the structural information, and this information is also averaged over a length scale significantly larger than the interatomic distance. On the other hand, simulations of liquid structures and studies of other systems, such as hard spheres, clearly indicate that the structures of liquids are inhomogeneous at the atomic scale. For these reasons, accurate interpretations of the PDF require careful modeling. It is worth noting in this context that the average PDF for some glasses can be modeled with relatively complex crystal structures \[38, 39\], notwithstanding the structural heterogeneities mentioned earlier.

As we already noted previously, a particular feature of the PDF that has attracted significant attention is the splitting of the second peak. This phenomenon has been observed in various systems, including hard-sphere, soft-sphere, Lennard-Jones systems, metallic glasses, and colloidal systems \[9, 17–20, 44\]. The prominence of the second peak splitting increases below the GT, and historically, this feature has been utilized as a structural indicator of the glass state \[6, 8\]. Additionally, it has been observed that the relative heights of the two peaks vary depending on the specific system and the method of preparation \[6, 13–15, 17\].

In the early studies, it was observed that the two sub-peaks of the second peak in the PDF occur at distances of approximately \( \sim 1.7a \) and \( \sim 2a \), where \( a \) represents the position of the first peak in the PDF, i.e., the nearest neighbor distance. The distance \( 1.7a \) is roughly equivalent to twice the height of an equilateral triangle with side \( a \). Consequently, this distance has been associated with the in-plane arrangement of four particles into two equilateral triangles with a common edge (distance \( \sqrt{3}a \approx 1.73a \)). Another potential geometry corresponding to the first part of the split second peak involves two regular tetrahedra with a common face (distance \( 2\sqrt{2/3}a \approx 1.63a \)). The position of the second part of the split second peak occurs at a distance of \( \sim 2a \), which is clearly associated with the collinearities of triplets of particles \[9\]. In later studies it was suggested that the splitting of the second peak is a signature of formation tetrahedral or crystal-like domains Ref. \[11–13\].

Recent investigations into the structural origin of the splitting of the second peak in the PDF have typically focused on studying the types of nearest neighbor clusters for the second neighbors, with particular emphasis on the number of their common neighbors \[14, 16\]. For the case of the Kob-Andersen (KA) system studied in this paper, such investigation had been conducted in Ref. \[14\]. An alternative approach to addressing the splitting of the second PDF peak, based on the consideration of rings of particles, has been explored in Ref. \[15\].

In 1962, J.D. Bernal in his Bakerian lecture reported about observation of collinearities involving more than three particles \[15\]. Clearly, such collinearities are associated with the splitting of the second peak in the PDF are related to the nature of intermediate range order. Bernal, in particular, noticed collinearities involving up to 8 particles, while the average length of such collinearities was estimated as 4. Bernal also noted that the existence of collinearities seems to align with the shape of the angular distribution function (ADF) presented in Ref. \[46\]. Furthermore, Bernal suggested that collinearities might play a role in the diffusion process. It was proposed that if there is a sufficiently large hole at one end of a collineation, then the entire collineation can move collectively. Thus, a hole at one end of the collineation would reappear at another end. This suggestion bears resemblance to later observations of string-like cooperative motion \[47\]. However, as we demonstrate below, these two phenomena do not appear to be related.

Since 1962, Bernal’s findings regarding collinearities of multiple particles have been mentioned in more than just a few publications, including Ref. \[9, 10, 13, 48–52\]. For instance, in Ref. \[48\], there is a suggestion that collinearities might be connected to the disclination lines in the Frank-Kasper and geometrical frustration approaches. It is also reasonable to mention Ref. \[44\] in the context of collinearities. It has been suggested in Ref. \[44\] that structural organization of metallic glasses on the intermediate range can be considered as a combination of spherical periodic order and local translational symmetry. Further, it was argued that local translational symmetry may be one-dimensional. It is possible that collinearities of particles might represent this one-dimensional local translational symmetry. However, to the best of our search efforts, long collinearities do not appear to have been systematically studied.

In our investigation of the binary (80% : 20%) KA system of particles, we observed the formation of long collinearities formed by the larger particles (80%) and decided to explore this phenomenon.

This paper effectively is divided into two parts. In the first part, we present our statistical investigations of collinearities on both the parent and inherent structures \[53–54\] and describe how to relate the PDF and the ADF to the collinearities and demonstrate that the suggested relation works quite well. In the second part, we describe our investigations of possible connections of the collinearities with some other phenomena. In particular, our study investigated whether collinearities are associated with: 1) the major skeleton of the Frank-Kasper structure or the disclination lines associated with the geometric frustration approach, 2) some clusters identified by the topological cluster classification approach, 3) strings composed of the most mobile particles. Across all considered cases, our findings, based on the applied methods, indicate that particles forming collinearities are not associated with any of the considered groups. In the aforementioned considerations, we compared the av-
verage diffusion rate of particles forming the collineations with those of all large particles. Our findings show that, on average, particles forming the collineations exhibit a slightly slower diffusion rate compared to the average large particle.

In recent years, the role of developing intermediate range order in dynamic slowdown and the GT has captured significant attention. Collineations can also be considered as a manifestation of developing intermediate range order. It is evident that average short-range order should geometrically align with the average intermediate range order and beyond. Thus, it challenging to determine which structural changes are the cause and which are the consequence. Yet, from our perspective, a specific feature observed in the behavior of the ADF suggests that the development of intermediate range order and beyond is the driver for certain changes in the short-range order.

The paper is structured as follows.

In Section II, we provide a brief overview of the simulation procedure and data analysis, with more detailed information available in the supplemental materials (SM).

Sections III and IV define and describe the observed collineations. In Sections V and VI we delve into the behaviors of the PDF and ADF. We then propose a relation that connects these functions with the collineations, demonstrating its effectiveness in describing the data. Then, in Sections VII, VIII, and IX, we explore potential connections of the collineations with the geometrical frustration approach, selected clusters from the topological cluster classification method, and the stringlike cooperative motion. We provide our concluding remarks in Section X.

II. THE USED POTENTIAL AND SIMULATIONS DETAILS

In this paper, we studied the KA model system has been extensively investigated previously [29, 30, 32, 36, 47, 53, 61–68]. In particular, there were studies of the short and medium range order in this system [29, 30, 32, 36, 47, 53, 61, 67, 69].

In our computer simulations, we used the modified forms [70] of the KA potentials [61, 62]. The unmodified KA potentials are the shifted Lennard-Jones potentials with the parameters of length, $\sigma_{ab}$, and energy, $\epsilon_{ab}$, chosen in a particular way. The modified potentials go to zero at the cutoff distances $r_{ab} = 2.5\sigma_{ab}$ with zero derivatives (forces). The same modified potentials have been used, for example, in Ref. [29, 53, 61]. We provide more details on the used potentials and the simulation procedure in the supplemental materials (SM).

The average density of the particles was $\rho_o = 1.2\sigma^{-3}$. We also performed some of the simulations on the system containing $64 \cdot 10^3$ particles.

We used the LAMMPS molecular dynamics (MD) program [74, 75]. The used value of the time step, $dt$, varied from 0.0005 in $T = 6.0c$ up to 0.005 in $T < 0.5c$.

At every considered temperature we performed (10 for the systems of 8000 particles)/(6 for the system of $64 \cdot 10^3$ particles) simulations starting from high-$T = 6.0c$ independent structures. In each of these independent simulations, we accumulated (100 for the systems of 8000 particles)/(20 for the system of $64 \cdot 10^3$ particles) configurations.

The final configurations of particles from the previous higher temperature (after the relaxation) were used as initial configurations for relaxation at the next lower temperature. The initial relaxation time for all $T > 0.46c$ was larger than 10$\tau_o (T)$ at each studied temperature. $\tau_o (T)$ is the relaxation time of the intermediate self-scattering function at temperature $T$. Then, the configurations were saved consequently with time intervals that were at least several $\tau_o$ for all $T > 0.46c$.

For $T < 0.46c$ the relaxation is already quite slow. At these temperatures, we used even longer initial relaxation times. We also used larger time-intervals between the saved configurations. We provide more details on these technical details in the SM. Thus, we estimate that for temperatures $T > 0.42c$ the structures that were used for data analysis can be considered as independent and well-relaxed. At even lower temperatures, while we still were using the relaxation procedures, the structures that were used for analysis cannot be considered as strictly independent. Actually, to have structures which are more independent at low temperatures we were producing the structures from 10 independent runs (with 100 structures in each run for 8000 particles system).

The above details, expressed in terms of the $\tau_o$ can also be reformulated approximately in terms of the mean square displacement (MSD). Thus, for $T > 0.46c$, the MSD, $<(\Delta r)^2>$, which corresponded to the time interval between the two consecutively saved structures was always larger than 0.1$\sigma^2$ for the $A$-particles. See Fig. 1a).

In summary, we believe that for $T > 0.46c$ all saved structures can be considered as independent. Then, in the temperature interval $0.42c \leq T \leq 0.46c$, the saved structures, obtained in the same simulation run, can also be considered as approximately independent. For $T \leq 0.42c$ it is reasonable to assume that the structures obtained in the same simulation run are not independent. In any case, at all studied temperatures, we analyzed all of the obtained structures (1000 for the systems of 8000 particles)/(120 for the system of $64 \cdot 10^3$ particles), as independent.

The ISs were produced using the FIRE algorithm [74, 75] within the LAMMPS program Refs. [71, 73]. The criterion for the convergence of the minimization process was: the change in the total potential energy in the cur-
rent MD step has to be smaller than $10^{-4}$ of the energy value. A maximum number of $10^4$ steps was allowed. The value of the time step used was $dt = 0.002\tau$. The recommended time step for the FIRE algorithm is the same as the time step used in MD simulations [73]. More details can be found in the SM.

III. DEFINITION OF COLLINEATIONS

We say that there is a link or a bond between two large $A$-particles if the distance between them is smaller than the cutoff distance, $r_{AAC}$, corresponding to the position of the 1st minimum in the partial PDF of $AA$ particles, i.e., $r_{AAC} = 1.43\sigma$.

We say that $N$ large $A$-particles form a $C(N, \alpha_{\text{max}})$ collineation if all nearest links in the collineation intersect at angles $\alpha > 180^\circ - \alpha_{\text{max}}$.

In the SM, we describe the algorithm that has been used to find the collineations in the system.

IV. OBSERVATION OF COLLINEATIONS ON THE PARENT AND INHERENT STRUCTURES

Two upper rows in Fig.1 show the snapshots of $C(7, 15^\circ)$ collineations formed by $A$-particles in the 8000-particles system at selected temperatures. Only particles forming the $C(7, 15^\circ)$ collineations are shown. It is clear that statistically at lower temperatures there are more collineations than at higher temperatures.

We note that it does not follow from the shown data that the collineations at lower temperatures agglomerate into some more complex structures.

Panels (a,b,c) in the 3rd row of Fig.1 show the probability distributions for the numbers of particles involved in all collineations of a particular type in instantaneous configurations. Here, in the counting procedure, we adopted the rule that if some particle belongs to more than one collineation it is counted only once. As the temperature decreases the probability distributions shift to the right. Thus, the numbers of particles in the collineations statistically increase. The shown data originate from 1000 instantaneous configurations of 8000 particles produced in 10 independent runs.

In Fig.2 the red curves and the red solid circles show how the average numbers of particles in all collineations of a particular type depend on the temperature. In every panel, there are three red curves that show the average value and the average value $\pm \sigma_{\text{mean}}$. We see that the average numbers of particles involved in the collineations monotonically increase, as the temperature of the liquid decreases. There is a more abrupt rise in the numbers of collineations in the temperature range $0.3 < T < 0.5$. In view of Ref. [76,77], this behavior might be related to the proximity of the temperatures at which the crystallization process has been observed $T \sim 0.41 \pm 0.02$ [77]. In the considered system, the crystallization process manifests itself, by the appearance of the regions containing FCC-crystals of $A$ particles.

At this stage, we will not address the origin of an abrupt rise in the number of collineations at $T \sim 0.41 \pm 0.02$ in more details. In general, the hypothesis that collineations might represent a feature that is related to the formation of the crystal nuclei deserves a consideration.

The blue curves in Fig.2 correspond to the results obtained on the inherent structures (ISs). Practically, all shown blue curves exhibit an abrupt crossover at the potential energy landscape (PEL) crossover (PELC) temperature (PELCT). Originally, the PELCT was observed by consideration of the potential energies of the ISs [53]. As far as we know, there is still no complete understanding of the structural changes that underlie the PELC. For example, in Ref. [27] it has been shown that the instantaneous values of the inherent potential energy are related to the number of the Frank-Kasper bonds (major ligands) in the system. On the other hand, as we demonstrate below, there is no a clear relation between the collineations and the major ligands. Thus, there appear to be several structural changes that can be connected to the PELC. Another example of this situation is associated with the temperature dependence of the number of some clusters that have been introduced in the topological cluster classification approach [30,36,78]. We will discuss this situation below.

Of particular interest is the relation between the red and blue curves corresponding to the collineations $C(6, 15^\circ)$, $C(6, 20^\circ)$, $C(7, 15^\circ)$, $C(7, 20^\circ)$, $C(8, 15^\circ)$, $C(8, 20^\circ)$, and $C(9, 20^\circ)$. For these collineations, in the supercooled liquid range of temperatures, $0.4 \lesssim T \lesssim 1.0$, we observe that the average number of collineations in the ISs is smaller than the number of collineations in the parent structures (PS). This is a counter-intuitive behavior. Indeed, since the ISs are more relaxed than the PSs, it is natural to expect that there always should be more collineations in the ISs. In our view, the obtained results suggest that in the parent supercooled liquid there might develop some delicate, beyond medium-range, order that is destroyed by a “rough” relaxation procedure by which the ISs are produced from the PSs. The linear collineations should be related to this order. It is also possible that the decrease in the number of collineations in the transition from the PS to IS is related to the fact that the pressure of the IS becomes negative when the temperature of the parent structures is reduced below $T \approx 0.8$. The pressure of the IS becomes even more negative as the temperature of the PS further decreases. See the SM and, for example, Ref. [79,81]. We note that in Ref. [79] it has been shown that at $\rho_o = 1.2$, that we study in this paper, the ISs (under the negative pressure) remain globally homogeneous. However, it is possible that in the process of relaxation from the PS into the IS in the system develop some local heterogeneities which can lead to the decrease in the number of collineation in the
FIG. 1. In a particular configuration of particles, at a given temperature, there are \( A \)-particles that form \( C(7,15^\circ) \) collineations. In two upper rows, only such \( A \)-particles are shown. Different panels show the results from selected configurations at selected temperatures. In the SM we provide several structure files, containing the coordinates of \( A \)-particles forming the collineations that can be examined with practically any structure-view program. In the lower row, we show the probability distributions for the numbers of \( A \)-particles forming different collineations at different temperatures. Panels (a), (b), and (c) correspond to the collineations \( C(6,15^\circ) \), \( C(6,20^\circ) \), and \( C(7,20^\circ) \) correspondingly. The abscissa-axes in these plots show the fraction of \( A \)-particles in the collineations relative to all \( A \)-particles in the system. Different curves – from the left to the right – correspond to the temperatures \( T = 3.0, 2.0, 1.5, 1.0, 0.7, 0.5, 0.39, 0.20, 0.05 \).

IS in comparison to the PS.

V. ANALYSIS OF THE PARTIAL PAIR DENSITY AND ANGULAR DISTRIBUTION FUNCTIONS

We use the following probabilistic model to connect the behaviors of the PDF and ADF, as the functions of temperature, with the numbers of particles in the collineations.

We assume that the number of nearest neighbors, \( \bar{N}_c \), is the same for all \( A \)-particles. We also assume that \( \bar{N}_c \) depends on the system’s temperature and that it corresponds to the integral over the first peak of the partial PDF (PPDF) (until the first minimum). In Fig. 3(a), we show the \( AA \)-PPDFs for selected temperatures (shown in the inset). In the inset, we show the PPDF calculated on the inherent structures. The cutoff distance \( r = 1.43\sigma \) was used in the calculations of \( \bar{N}_c \). The curves in Fig. 3(a,b) were obtained from averaging over 10 independent runs with 100 structures in each run. For \( T > 0.46 \) all structures in each run are separated by time intervals which are several times larger than the \( \alpha \)-relaxation time.

Further, we assume that the ADF for nearest neighbors is also known and that it depends on the temperature. It is convenient to use the ADF in the form suggested by G.D. Scott et. al. \[15, 40\], i.e., consider the ADF as a function of the parameter \( \omega \equiv (1/2)|1 - \cos(\theta)| \), where
FIG. 2. The dependencies of the average percentage of $A$-particles in all collineations of a particular type on the system’s temperature. The percentage is relative to the total number of $A$-particles in the system. The panels in the same row correspond to the collineations with the same number of particles, but the limiting inclusion angles are different in different columns. The red solid circles connected by the red lines show the results from the parent structures obtained on the system of 8000 particles. There are the average curves and also the average curves plus/minus the sigma of the mean (magenta). The light green open circles correspond to the results obtained on the system of 64000 particles. The error bars are not shown. The black solid circles correspond to the results obtained on the inherent structures on the system of 8000 particles. The blue curves show the errors of the mean for the inherent structures. The cyan open circles correspond to the results obtained on the system of 64000 particles. The results from the systems of 8000 and 64000 particles were obtained from 1000 and 120 configurations correspondingly.

$\theta$ is the angle between two bonds that start on a chosen particle. With this choice of the argument to the same intervals of $\Delta \omega$ correspond the same areas of the surface formed by the nearest neighbors. In Fig. 3(b) we show several AAAA-partial ADFs (PADF) at selected temperatures. In the inset, the PADFs calculated on two sets of inherent structures are shown. All curves were calculated on the same structures that were used for producing Fig. 3(a). The shown PADFs are normalized to unity. Thus, if there were only one particle in the first-neighbor shell which were homogeneously distributed over this shell then the PADF would be equal.
FIG. 3. (a) Partial radial distribution function, $g_{AA}(r)$, for AA particles at temperatures shown in the inset (a-i). In the inset, the $g_{AA}(r)$ calculated on the inherent structures are shown. Note that the first minimum of $g_{AA}(r)$ is located at $r \approx 1.43\sigma$. (b) The angular density functions (ADFs) for the triplets of A particles which are nearest neighbors at the same temperatures as in panel (a). In the inset (b-i), the ADFs calculated on the inherent structures are shown. The temperatures of the corresponding parent structures are the same as in (a) and (a-i). We are interested in the behavior of the ADFs at $\omega \approx 1$, i.e., at $\theta \approx 180^\circ$. Thus, in panels (e) and (f) we show the ADFs in the vicinity of $\omega \approx 1$ for the parent and inherent structures correspondingly. In panels (e,f), each curve corresponding to the next lower temperature is shifted upward by 0.5 with respect to the previous higher temperature for clarity. The dashed horizontal lines correspond to the hypothetical homogeneous distribution of the $\bar{N}$ nearest neighbor particles over the surface of the sphere (if the normalization is to unity). In panel (c), we show how the number of A-particles within the first minimum of $g_{AA}(r)$ depends on the temperature. The results for two different cutoff values of $r_\text{c}$ are shown. In the legends of (c), the letters “P” and “I” correspond to the results obtained on the parent and inherent structures. Panel (d) shows how the integral of the ADF over the range $\omega \in [0.983, 1]$ depends on the temperature. In the plot, the values of these integrals were multiplied by 100. The results for the parent and inherent ADFs are shown.

to unity in the whole range of $\omega$. According to the considered model, there are $\bar{N}_c(T)$ particles in the shell. Thus, the actual PADFs for these $\bar{N}_c(T)$ particles are $\bar{N}_c(T)$ times larger than those shown in Fig. 3(b).

Further, we focus on those collineations in which all angles $\theta$ between the collineations-forming bonds are in the interval $[180^\circ - 15^\circ; 180^\circ]$. This interval approximately corresponds to the interval $\omega \in [0.983; 1.0]$. In Fig. 3(c,f), we show the PADFs for the parent and inherent structures on a larger scale which includes this interval of $\omega$. This interval is on the right with respect to the vertical dashed line.

Note, in Fig. 3(c,f), that all curves obtained from the simulations are above the horizontal dashed lines corresponding to the case of homogeneous distribution of neighbors. Note also that in the cases of parent and inherent structures, the separations between the curves from the simulations and the corresponding horizontal dashed lines increase as the temperature decreases.

The most interesting feature of the shown PADF curves arises when the liquid on cooling turns into a glass (approximately when $T < 0.40$). In the glassy state, there develops a pronounced increase of the PADF towards $\omega = 1$, i.e., towards $\theta = 180^\circ$. This increase is seen in the interval $0.994 < \omega \leq 1$. In the PADFs obtained on the IS this increase towards $\omega = 1$ is present for all temperatures of the original PS. However, the increase is larger for the IS obtained from the PS at lower temperatures and especially from the PS which are below the GT temperature. This behavior, in our view, indicates that the rise of the PADF towards $\omega = 1$ is associated with development of a structural organization in the low-temperature supercooled liquid and the glass states which is not properly captured by the quick relaxation procedures by which the IS are obtained from the PS. This increase poses two questions: 1) Can this increase be considered as a characteristic structural feature of the glassy state? 2) Is the origin of this effect local or non-local? We will discuss this issue in the context of Fig. 4(b,c,d,e,f).
It is obvious that the increase in the ADF at \( \theta \approx 180^\circ \) is related to the development of the splitting of the second peak in the PDF. In particular, to the observation that this peak is split in the glass state, but not in the liquid state [3, 5, 8–17].

Further, we assume that the probability for a chosen central \( A \)-particle and one of its \( A \)-neighbors that there is another \( A \)-neighbor which is located approximately opposite to the first neighbor is:

\[
p_3 \equiv (\bar{N}_c - 1) p_{\omega} \equiv (\bar{N}_c - 1) \int_{\omega=0.983}^{\omega=1} f_{P,\text{ADF}}(\omega)d\omega. \tag{1}
\]

In (1), we put \((\bar{N}_c - 1)\) in front of the integral because we consider the probability for the second neighbor to be located oppositely enough to the first neighbor which was already chosen. The notation \(p_3\) is used because (1) addresses the case of three particles.

In Fig.3(d), we show the temperature dependence of the integral from (1) (without the \((\bar{N}_c - 1)\) prefactor). The first thing to notice is that the value of this integral calculated on the IS clearly indicates existence of the crossover temperature \(T_x\). Note that here, contrary to the standard considerations [3,4,6,11], we see this behavior in a quantity which is directly related to a particular structural property. In the standard considerations, it is not clear what structural changes cause the crossover at \(T_x\) in the PEL [3,4,11].

Another feature to notice in Fig.3(d) is that in the interval of temperatures \(0.5 < T < 3.0\) the red curve calculated on the PS is above the blue curve calculated on the IS. This again indicates, in our view, that in the liquid there develops some structural order that is being destroyed by the quick relaxation procedure leading to the IS.

In Fig.3(c), we show, for the PS and IS, how the average \( A \)-partial coordination number of \( A \)-particles, depends on the temperature for two values of the cutoff distance. The curves in Fig.3(c) were obtained by integration of the curves like those in Fig.3(a). It is of interest that the curves calculated on the PS clearly indicate the GT temperature while the curves calculated on the IS in addition exhibit the crossover temperature \(T_x\).

VI. CONNECTION OF THE PDF AND ADF WITH THE NUMBER OF PARTICLES IN COLLINEATIONS

In the discussions of collineations, the most natural question to ask is what is the number of particles in the collineations of a particular type? We addressed this question in Fig.12. However, to understand the connection between the PDF, ADF, and collineations it is more convenient to ask a different closely related question. That is: What is the probability for a randomly chosen \( A \)-particle to be located at the end (start) of any collination with \( N_c \) particles in it? Actually, the answer is quite obvious:

\[
W(N_c) = \bar{N}_c \cdot [(\bar{N}_c - 1)p_{\omega}]^{\bar{N}_c - 2}. \tag{2}
\]

In [2], the first \(\bar{N}_c\) on the rhs is the number of directions in which the collination can be directed if it starts on a chosen particle. Then, \([(\bar{N}_c - 1)p_{\omega}]\) with \(p_{\omega}\) from (1) is the probability that there is a third particle in the collination that is located at the proper angle with respect to the bond that joins the chosen start particle and its already chosen neighbor, i.e., the second particle in the collination. Then, another factor \([(\bar{N}_c - 1)p_{\omega}]\) comes from the second angle in the collination. Since there are \((N_c - 2)\) angles in the collination of \(N_c\) particles we arrive to the expression (2). Of course, we assumed that the probabilities for all angles are independent.

Note that \(W(N_c)\) can be larger than unity. In this case, \(W(N_c)\), effectively becomes equal to the average number of collineations that start on a chosen start particle.

In Fig.3(b,c,d,e,f), we show how \(W(N_c)\) depends on the temperature for the collineations with different \( N_c \) (3,4,5,6,7). In Fig.3(b,c,d,e,f), the red curves show the results directly calculated on the parent structures. The orange curves show the results calculated according to Eq. (12). Again, we note that in these calculations we take into account that \(N_c\) and \(p_{\omega}\) depend on the temperature through the temperature dependencies of the PDF and ADF, as shown in Fig.3. Similarly, the blue curves in Fig.3(b,c,d,e,f) show the results directly calculated on the inherent structure, while the black curves show the results derived from the PDFs and ADFs according to Eq. (12).

Note in Fig.4(b) that \(W(N_c)\) for the particles in \(C(3,15^\circ)\) collineations is larger than two. Thus, in Fig.4(a) we plot, for the parent structures, the probability distributions for the particles to have different \(N_c\) (for the \(C(3,15^\circ)\) collineations). These results were obtained from the direct analysis of the structures. In expression (2), in the square brackets, we have an expression \((\bar{N}_c - 1)p_{\omega}\). We explained above why we use \((\bar{N}_c - 1)\) instead of simply \(\bar{N}_c\). Yet, it is of interest to have a better understanding of how the choice of \((\bar{N}_c - 1)\) instead of \(\bar{N}_c\) affects the curves in Fig.4(b,c,d,e,f). In Fig.4(d), we address this point by presenting also the curves for \((N_c - 0.8)\), \((N_c - 0.7)\), and \((N_c - 0.5)\). These curves are marked as \((PM - 0.8)\), \((PM - 0.7)\), and \((PM - 0.5)\). We see that the curves are quite sensitive to the choice of \((\bar{N}_c - 1)\) instead of \(\bar{N}_c\).

VII. DISCUSSION OF THE POSSIBLE CONNECTION WITH THE FRANK-KASPER AND GEOMETRICAL FUSION APPROACHES

As we already mentioned in the introduction, the collineations may be related to several other phenomena previously discussed in the context of supercooled...
FIG. 4. The temperature dependencies of the percentage of the number of particles located at the ends of some collineations. The percentage is with respect to the total number of \( A \)-particles in the system. In the panels, the results of direct calculations on the parent and inherent structures are shown together with the results from the model based on the analysis of the PDFs and ADFs. In the legends of panel (b), PD-stands for “Parent Direct”, PM-stands for “Parent Model”, ID-stands for “Inherent Direct”, and IM-stands for “Inherent Model”. These notations are related to panels (b,c,d,e,f). In the legends of panel (d) the notation “PM-0.5” corresponds to the model curve in calculations of which we used \((\bar{N}_c - 0.5)\) in Eq.(2) instead of \((\bar{N}_c - 1)\).

Note that in certain ranges of temperatures there are more particles forming the collineations in the parent structures than in the inherent structures.

liquids and glasses. One of these is the concept of major skeleton introduced by Frank and Kasper in Ref. [18]. Another is the concept of “disclination lines” that is important in the geometrical frustration approach [19–21, 24, 25]. These two concepts are closely related [21, 24, 29, 27]. Investigation of a possible relation between the collineations and the major skeleton or the disclination lines will also allow us to address the local structure near the collineations.

In the basis of the Frank-Kasper and geometrical frustration approaches lies the observation that four particles can be ideally packed into the tetrahedron [18–21, 24]. Then, still from the local perspective, it is recognized that twenty tetrahedra, if slightly distorted, can be packed into the icosahedron which locally provides more dense packing than the FCC or HCP lattices. Also, since the surface edges of the icosahedron are 5% longer than the distance from the center of icosahedron to its vertices, the packings into icosahedra provide more flexibility in the packings of particles [18]. However, it is impossible to fill the whole space with tetrahedra or icosahedra alone. Thus, it is necessary to understand the nature of defects in the packings of tetrahedra (or icosahedra).

The nature of the defects in the FK and geometrical frustration approaches is analyzed from two different perspectives, though practical conclusions, in many respects, are similar.

In the FK approach [18], under the assumption that the distortions of the tetrahedra should be relatively small, it is argued that besides the particles at the centers
of the icosahedron environments (“minor sites”), with coordination of the central particle being 12, there are also “major sites” with coordinations of the central particle being 14, 15, 16, but not 13. The connection between the major sites is labeled as a major ligand. The number of major ligands for a particle with the coordination number \(Z\) is \((Z - 12)\). Thus, the number of major ligands is 2 for \(Z = 14\), 3 for \(Z = 15\), and 4 for \(Z = 16\). Correspondingly, if there is one major site, then between its nearest neighbors there should be at least two other major sites. Thus, it was argued that the major sites form the “major skeleton” of the structure. It was also concluded that two nearest major sites should have at least 6 neighbors in common, while nearest minor sites have 5 neighbors in common. The links between the major and minor sites also should have 5 neighbors in common. Further, it was argued that, like in certain transition metals and alloys, the major skeleton should have a tendency to be linear, while minor sites, i.e., the sites with coordination 12 should have a tendency to be located in the pseudo-planar, approximately orthogonal to the lines of the major skeleton.

In the geometrical frustration approach [19, 21, 24, 25], the connectivity and geometry of defects (disclination lines) is introduced through initial considerations of the packing of hard particles on the three-dimensional surface of a four-dimensional sphere. This surface is a curved three-dimensional space of finite size. It was demonstrated that it is possible to pack 120 particles on this surface in a crystal-like structure in which every particle is surrounded by twelve other particles in the (curved) icosahedral geometry. Then, it is assumed that if this structure is “projected” into 3D Euclidean space, then the resulting structure is a good approximation to the structure of some glasses and liquids. In order to perform the operation of “projection”, it is necessary for some pairs of neighbor particles, that initially have 5 neighbors in common, to introduce an additional particle into the set of common neighbors. For other pairs it may be necessary to remove some of the common neighbors. In this way, the system is introduced negative and positive disclination lines. The particles that form negative/positive (-72°/+72°) disclination lines should have coordinations more/less than twelve. Also, the number of the common neighbors of the neighbor pairs of particles that form negative/positive disclination lines should be larger/smaller than five.

Thus, in order to address a possible relation between the collineations and the major skeleton or between the collineations and the disclinations lines it should be sufficient, at least as the first step, to compare statistically the coordinates of the \(A\)-particles that form collineations with the coordinates of all \(A\)-particles [24, 25]. It is also reasonable to compare statistically the number of the common neighbors for the pairs of \(A\)-particles that form collineations with all pairs of \(A\)-particles that are nearest neighbors.

### A. Nearest Neighbor Analysis

In general, there are two major approaches for determining neighbors of a particle. In one approach, the neighbors are defined according to a chosen cutoff distance(s) [6, 33, 35, 82]. In another approach, the neighbors are defined according to a Voronoi-type tessellation [33, 35, 83]. In both of these approaches there arise ambiguities with respect to the neighbor counting [24, 35, 84]. Here, we present the results of the neighbor analysis performed in both ways.

In the chosen cutoff approach, the neighbor cutoff distance for the pairs of \(A\) particles was \(r_c(AA) = 1.43\sigma\) and for the pairs of \(A\) and \(B\) particles the cutoff was \(r_c(AB) = 1.25\sigma\). For the KA system, the shape of the partial PDF for the pairs of \(B\) particles is such that it is not quite clear how to define two particles as neighbors [61, 62]. For our present considerations, the case of two \(B\)-particles which are neighbors is irrelevant.

As the Voronoi-type analysis we used the modified radical Voronoi (modRV) tessellation as it has been described in [23, 33, 83, 86]. The radical Voronoi tessellation can be used if the studied system consists of particles of different sizes [33]. The modification used in the approach eliminates from the consideration some short edges of the Voronoi cells [24]. This leads to better results for the number of common neighbors for some pairs of particles and eliminates from the consideration some strongly distorted tetrahedra [24].

Let \(l_{AA} = 1.43\sigma\) and \(l_{AB} = 1.25\sigma\) be the distances at which the first minimums in the partial \(g_{AA}(r)\) and \(g_{AB}(r)\) are located. In our analysis with modRV [24], we used the following values for the radii of \(A\) and \(B\) particles \(R_A = l_{AA}/2 = 0.715\sigma\) and \(R_B = l_{AB} - R_A = 0.535\sigma\).

In Ref. [24, 25], the structural analysis of the inherent structures was performed to evaluate the applicability of the Frank-Kasper and geometric frustration considerations to the studied system. For this reason, we also present in Fig. 5(a1,a2) the results of the nearest neighbor and common neighbor analyses performed on the inherent structures. However, we also analyzed the parent structures. The results from the parent structures are very similar to those in Fig. 5(a1,a2), not only from the qualitative perspective but also from the quantitative point of view. The results from the parent structures are shown in Fig. 3.4 in the supplemental materials.

The results of the nearest neighbor analysis of the inherent structures produced from the parent structures at \(T = 0.5e\) are shown in Fig. 5. In this figure, the histograms of different colors correspond to different locations of the \(A\) particles in the collineations (or not in collineations at all).

The first thing to note from Fig. 5(a1,a2) is that the coordination of the majority of \(A\) particles is larger than 12. This situation is markedly different from the situation in Ref. [25] (see, in particular, Table 1) or in Ref. [24] (see, in particular, Fig. 3) where a very significant frac-
FIG. 5. Results of statistical investigations of local environments of \(A\) particles in the \(C(5, 15^\circ)\) collineations according to the chosen cutoff distances \((a_1, b_1, c_1)\) and according to the modified radical Voronoi (modRV) tessellation \((a_2, b_2, c_2)\). In panels \((a_1, a_2)\), the results for the coordination due to \(A\) and \(B\) particles together are shown. In panels \((b_1, b_2)/(c_1, c_2)\), the results for the partial coordinations due to \(A/B\) particles only are shown. The blue/red/green/orange histograms (from the left to the right) marked in the legends of \((b_1)\) as \(A_{\text{ALL}}/A_{\text{CE}}/A_{\text{C}}/A_{\text{CC}}\) correspond to the data obtained on (all \(A\) particles in the system)/(particles located at the ends of \(C(5, 15^\circ)\) collineations)/(all particles in the \(C(5, 15^\circ)\) collineations)/(from the triplets of particles in the centers of \(C(5, 15^\circ)\) collineations).

The comparison of Fig. 5(a1) with Fig. 5(a2) shows that the modRV method leads to larger total coordination numbers than the cutoff approach. Further, the comparison of \((b_1)\) with \((b_2)\) and \((c_1)\) with \((c_2)\) shows that the difference arises from how the pairs of \(A\)-particles are counted as neighbors. Indeed, the results in \((b_1)\) and \((b_2)\) are noticeably different. On the other hand, the results for the pairs of \(A\) and \(B\) particles in \((c_1)\) and \((c_2)\) are quite similar. This is a surprising result because there is some degree of ambiguity in how to define the radius of the \(B\)-particles in the modRV approach. Yet, the results in \((c_1)\) and \((c_2)\) are similar.
FIG. 6. Results of the common neighbors analysis for all AA-bonds and those AA-bonds that form C(5, 15°) collineations (NCN-Number of Common Neighbors). In panels (a1,b1,c1) the neighbors of each particle are defined according to the chosen cutoff distances while in (a2,b2,c2) the neighbors are defined according to the modRV analysis. In (a1,a2) we show the PDs for the number of common neighbors of the AA-pairs if the neighbors of both types are counted. In (b1,b2)/(c1,c2) only the common neighbors of type A/B were counted. We note that the neighbor particles in the collineations were always defined according to the cutoff distance. The most left (blue) bars in all panels correspond to the PDs calculated on all AA-bonds. The second-left (red) bars were obtained from the analysis of neighbors of two AA-bonds that are located at the ends of the C(5, 15°) collineations. Then, the third from the left (green) bars were obtained by averaging over all bonds in the collineations. Finally, the most right (orange) bars were obtained by averaging over two bonds in the collineations which are at the centers of the collineations. The legends in panel (b1) are for all panels. Note that if a particular C(5, 15°) collineation belongs to some longer collineation then some bonds in it can be counted in different roles. In such cases, every count was considered as independent.

We now turn attention to the major question of interest. Do particles forming collineations have environments different from other particles? We see from Fig. 5 that different locations of the particles in collineations weakly affect the probability distributions. Note also that the probability distributions for the particles in collineations are not that different from the probability distribution for all A-particles. The largest difference can be observed in Fig. 5(b1). In general, it follows from the distributions that particles that belong to the collineations tend to have larger numbers of A-neighbors and smaller numbers of B-neighbors. This effect can be considered as a possible indication of the relation of collineations to the tendency of the system for components separation.

The general conclusion from Fig. 5 is that statistically the average environments of the A-particles forming the collineations are slightly different than the average environment of all A-particles. Thus, it is possible to say that statistically the environments of the A-particles forming the collineations exhibit some tendency for some specific orderings. However, we clearly cannot claim from these results that the A-particles forming the collineations have some fixed geometry.

B. Common Neighbor Analysis

Another way to address the differences in the environments of the particles forming the collineations and other particles is to perform the common neighbor analysis (CNA) for the pairs of the nearest neighbors particles \[23, 34\]. Thus, in Fig. 6 we show the results of the CNA for the four sets of particles as described in the caption of the figure.

The results in Fig. 6(a1,a2) show that the majority of the bonds are the 5-fold bonds, supporting the point of view that the icosahedral ordering plays very important role in supercooled liquids and glasses \[15, 21, 23, 26\]. On the other hand, the total amount of the 4-fold and 6-fold bonds together is approximately the same as the number of 5-fold bonds. Thus, in our view, it is not quite clear if these 4-fold and 6-fold bonds should be considered as
excitations. It is of interest that in panel (a1) the number of 4-fold bonds is larger than the number of 6-fold bonds while in panel (a2) the number of 6-fold bonds is larger than the number of 4-fold bonds. In the frame of the geometric frustration approach, in Euclidean flat space the number of 6-fold bonds should be larger than the number of 4-fold bonds [21].

As far as it concerns the dependence of the bonds’ coordination on the location of the bonds in collineations, we do not observe a significant dependence in panels (a1,a2). This dependence is more pronounced in (b1,b2) and in (c1,c2). The differences have a statistical character. The major tendency that we observe is that bonds in the collineations tend to have larger number of A-neighbors and smaller number of B-neighbors. This situation is in agreement with the results from the analysis of the coordination number.

We summarize our results with respect to the relation of collineations to the disclinations lines as follows. If it is possible to speak about the disclination lines in the KA system, then it is unlikely that there is a connection between the collineations and the disclination lines.

**VIII. DISCUSSION OF THE POSSIBLE CONNECTION WITH SOME CLUSTERS STUDIED WITHIN THE TOPOLOGICAL CLUSTER CLASSIFICATION APPROACH**

Relatively recently the structures of the KA and Wahnostöm model liquids were studied using the topological cluster classification (TCC) method [30, 36, 78]. The method is based on the idea that the geometries of local configurations that occur in supercooled liquids should be closely related to the geometries of isolated clusters of particles with low potential energies.

For the KA liquid, one of the low energy configurations is the bicapped square antiprism or 11A clusters. It was demonstrated that these clusters in supercooled liquid agglomerate into large domains [30]. In this context, for example, see also Ref. [28, 37, 88].

Thus, there is a possibility that the collineations might be related to some of such domains. In order to investigate this possibility, we studied the non-randomness of the overlap between the particles forming the collineations and the particles forming some clusters from the TCC approach. Below we describe the adopted method.

Let us suppose that we have two groups of particles. In the first group, i.e., the collineations-group, there are particles that form the collineations of a particular type. In the second group, i.e., the clusters-group, there are particles that form the TCC clusters of a particular type. Further, let us assume that the probability, for a particular particle that is already in the collineations-group to belong also to the clusters-group does not depend on whether this particle belongs to the collineations-group or not. Then, the probability for an average A-particle to be in the group that represents the overlap between the two groups is:

\[ P_{\text{ovrl}} = P_{\text{coll}} \cdot P_{\text{TCC}}, \]

where

\[ P_{\text{coll}} \equiv \left(\frac{N_{\text{coll}}}{N_A}\right), \quad P_{\text{TCC}} \equiv \left(\frac{N_{\text{TCC}}}{N_A}\right) \]

are the probabilities for A-particle to be in the collineations and in the clusters groups. In [4], \( N_A \) is the total number of A-particles in the system.

Let us now assume that the overlap is not random and that the particles which are already in one of these two groups have a higher probability to be in another. In this case, \( P_{\text{ovrl}} > P_{\text{coll}} \cdot P_{\text{TCC}} \).

For example, let us assume that \( P_{\text{coll}} < P_{\text{TCC}} \) and that all particles in the collineations, \( N_{\text{coll}} \), also belong to the considered TCC clusters. In this case, \( P_{\text{ovrl}} = P_{\text{coll}} \). On the other hand, if \( P_{\text{coll}} > P_{\text{TCC}} \) then \( P_{\text{ovrl}} = P_{\text{TCC}} \). In both cases \( P_{\text{ovrl}} > P_{\text{coll}} \cdot P_{\text{TCC}} \). An opposite extreme example is given by the situation when particles in one group simply cannot be in another, i.e., \( P_{\text{ovrl}} = 0 < P_{\text{coll}} \cdot P_{\text{TCC}} \). In general, if particles in one group avoid being in another group then \( P_{\text{ovrl}} < P_{\text{coll}} \cdot P_{\text{TCC}} \).

Thus, at every temperature, we can consider the probability distribution of the quantity:

\[ \xi_{\text{ov}}(t) \equiv \frac{(N_{\text{ov}}/N_A)}{(N_{\text{coll}}/N_A) \cdot (N_{\text{TCC}}/N_A)} \sim \frac{P_{\text{ov}}}{P_{\text{coll}} \cdot P_{\text{TCC}}}, \]

where \( t \) is the time and \( N_{\text{ov}}, N_{\text{coll}}, N_{\text{TCC}} \) change with time. By definition \( \xi_{\text{ov}}(t) \), can be larger or smaller than 1. If the distribution of this quantity (with its average value) tends to be larger than 1 then it means that the particles in the collineation-group have a tendency to belong also to a TCC - group. If this quantity tends to be smaller than 1 then the particles avoid being in the collineations and TCC groups simultaneously.

In Fig. 7(a) we show the probability distributions for the fractions of A-particles in 11A-TCC clusters and in C(5,15°) collineations. In Fig. 7(b) the probability distribution for the particles in the overlap is shown. In Fig. 7(c) we show the probability distribution for the parameter \( \xi_{\text{ov}}(t) \). The shown data suggest that there is a slight avoidance for particles in collineations to be also in 11A-TCC-clusters. However, according to panel (b), the number of particles in the overlap is rather small. Thus, it is not clear how much significance can be assigned to this avoidance.

We also studied the overlap between the C(5,15°) collineations and several other TCC clusters. The results are summarized in Table I. It follows from the data that the overlap between the collineations and the studied TCC-clusters is nearly random.
FIG. 7. Addressing the non-randomness of the overlap between the $C(5,15^\circ)$ collineations and the 11A-TCC clusters at $T = 0.5$. (a) The probability distributions (PDs) for the total numbers of particles (as the fractions of $N_A$) in $C(5,15^\circ)$ collineations and the 11A-TCC clusters at $T = 0.5$. The squares and circles are the results from the simulations and the curves are the Gaussian fits. The data were obtained from 1000 configurations produced in 10 independent simulation runs. (b) The PD for the particles in the $C(5,15^\circ)$ collineations and the 11A-TCC clusters simultaneously. Note that the number of particles in the overlap is rather small: the peak of the PD is located at $\approx 2.8\%$ of $N_A$. (c) The PD for the overlap non-randomness parameter $\xi_{ov}(t)$. Since the peak of the PD is located at $\xi_{ov}(t) \approx 0.92$ we can say that there is slight avoidance for the particles in the collineations to be also in 11A-TCC clusters.

FIG. 8. The dependencies of the average percentage of both types of particles in the clusters of the selected types on the system's temperature. The percentage is with respect to the total number of particles in the system. The results from the inherent structures are also shown. In panels (b,c) the results from the inherent structures are also shown on different scales with the black curves. The scales corresponding to the black curves are shown on the right $y$-axes. The results have been obtained using the topological cluster classification analysis applied to the system containing 8000 particles. The results from three independent simulations are shown with the three curves. From each simulation 100 configurations were used for data analysis.

A. Potential Energy Landscape crossover in the number of particles in selected TCC clusters

In Fig. 2(b,c,d) it was demonstrated that the numbers of particles in collineations and certain parameters associated with the PDF and ADF exhibit crossovers clearly associated with the crossover in the PEL. In this context, it is reasonable to note that these are not the only structural parameters exhibiting this crossover. For example, in Fig. 2(b) of Ref. 28, similar crossover was observed in the number of icosahedral clusters.

In Fig. 8 we show that this crossover can also be observed in the numbers of particles in several TCC clusters. It follows from the data that the PELC is observable for all studied clusters, while it is significant only for the 11A clusters. The case of 11A clusters is also of special interest because for these clusters the presence of the crossover is quite obvious even from the analysis of the
In view of the results shown in Fig. 5 and Fig. 6, it can be expected that small differences in the diffusion rates for all particles and the particles in the collineations are caused by small statistical differences in the local environments.

The data shown in Fig. 5 for each temperature, were accumulated in several simulation runs of different lengths. The averaging was done over 1000 initial configurations in each run.

### IX. DISCUSSION OF THE POSSIBLE CONNECTION WITH THE STRINGLIKE COOPERATIVE MOTION

We also investigated if there is a relation between the collineations and the stringlike cooperative motion [47]. In Ref. [47], the attention was focused on 5% of the most mobile particles at time $t^*$, which corresponds to the maximum of the non-Gaussian parameter $\alpha_2(t) = (3 < r^4(t) > / 5 < r^2(t) >)^2 - 1$ [63]. It was demonstrated that in these 5% there are some particles that move in a stringlike fashion and that, in the studied range of temperatures, the amount of such particles changes from approximately 50% to 75% out of these 5% of the most mobile particles.

The system that was studied in Ref. [47] is the same as the system that we study here. Thus, to address the relation between the collineations and the mobile strings, we studied the overlap between the particles that form the collineations and the particles that form strings. The collineations were determined from the static structures at the initial times. The particles that form strings at the initial time were determined from the consideration of the particles’ displacements in the time window $t \approx t^*$ that started at the initial time. In total, we considered approximately 1200 initial configurations.

As benchmarks, we considered the overlaps between the 5% of the most mobile particles and the particles that formed the 11A-TCC clusters. Besides, we considered the overlaps between the collineations and TCC clusters with the least mobile 5% of the particles.

The results are shown in Fig. 5(d,e). In Fig. 5(d), the cyan curve, corresponding to the PD for the displacements of the particles in $C(6, 15^\circ)$ collineations, nearly coincides with the blue-displacement curve for all particles. The small difference is visible near the peak. This difference can be observed also in the inset, in the behavior of the blue curve at $\Delta r \approx 0.1$. Thus, in Fig. 5(d) we do not observe significant differences in the behaviors of the particles in the collineations from the behavior of all $A$-particles.

In Fig. 5(e), the PDs for several overlap parameters are shown (see Eq. 5). It follows from the data that the overlap between the 11A-clusters and the mobile particles is clearly non-random, i.e., as expected, the particles in 11A clusters avoid being mobile. Results for the $C(6, 15^\circ)$ collineations show that the overlap between the

| Cluster | 11A | 11E | FCC | 12B | 12D | 12E | 12K | BCC(9) |
|---------|-----|-----|-----|-----|-----|-----|-----|--------|
| $P_{\text{coll}}$ | 0.21 | 0.21 | 0.21 | 0.21 | 0.21 | 0.21 | 0.21 | 0.21 |
| $P_{\text{TCC}}$ | 0.145 | 0.99 | 0.88 | 0.44 | 0.91 | 0.74 | 0.24 | 0.82 |
| $\xi_{\text{ov}}$ | 0.95 | 1.01 | 1.01 | 1.03 | 1.05 | 1.03 | 0.98 | 1.00 |

TABLE I. Addressing the overlap between the $C(5, 15^\circ)$ collineations and selected TCC clusters at $T = 0.5$. We see that for all considered clusters there is no clear evidence for the presence of correlations between the particles that form clusters and the particles that form collineations.

parent structures. This is in agreement with Ref. [30] in which it has been suggested that 11A clusters play a special role in the dynamic slowdown. Thus, the crossover in the number of collineations is only one example of the development of structural organization in liquids below the PEL crossover.

### B. Diffusion

One basic question, which is of interest in the context of the observed collineations, concerns the rate of diffusion of the particles that form the collineations and how this rate compares to the rate of diffusion of other particles. In the context of the clusters of particles, for the Wahnström system, this question has been addressed in Fig. 5(c) of Ref. [78]. Here, we follow the same approach for the KA system and compare the results for the collineations with the results for the 11A clusters [30]. In Fig. 9(a) we show the time-dependencies of the MSDs of the particles that belong to the 11A and those that do not belong to the 11A clusters. As the temperature decreases, the differences between the curves corresponding to the same temperature increase. The differences are the largest at the late $\beta$-relaxation time, i.e., when the particles, on average, leave their cages. This behavior can also be observed in panel (b) that shows the normalized differences between the curves of the same color in panel (a). Notably, the difference-curves exhibit well-defined minimums that, as the temperature decreases, shift to larger times, as expected. Note also that, at the lowest temperature, at the minimum, the normalized difference is approximately 23% of the MSD calculated by averaging over all particles. In panel (c), we show the results, analogous to those in panel (b), but for the particles that belong and do not belong to the $C(6, 15^\circ)$ collineations. For the clarity of presentation, the results for lower temperatures (shown in legends of panel (a)) were shifted downwards. The comparison of the data in (c) with (b) shows that the slow-down effect for the particles in collineations is approximately five times smaller than for the particles in 11A clusters. The smallness of the effect is the reason why we did not plot the MSDs corresponding to the collineations in panel (a)—it would be difficult to distinguish between the collineations-related curves. Nevertheless, panel (c) clearly shows that the slowdown-effect is there.

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The data shown in Fig. 9 for each temperature, were accumulated in several simulation runs of different lengths. The averaging was done over 1000 initial configurations in each run.
FIG. 9. (a) The two blue curves show the dependencies of the mean square displacements (MSDs) of the particles that belong to the 11A clusters and those that do not belong to the 11A clusters at \((T/\epsilon) = 0.46\). The particles that belong to the 11A clusters diffuse slower, i.e., to them corresponds the lower blue curve. The other curves in panel (a) show similar results at the other selected temperatures. If the results for the particles that belong and do not belong to the collineations were plotted in panel (a) they would be very close, to the results for the particles that do not belong to the 11A clusters. For this reason, we do not show these data in panel (a). (b) The normalized differences between the MSDs for the particles that belong to the 11A clusters and the MSDs for the particles that do not belong to the 11A clusters. The normalization is to the MSDs of all particles, i.e., we plot \(\left\{\frac{\text{MSD}(\text{in}) - \text{MSD}(\text{out})}{\text{MSD}(\text{all})}\right\}\). (c) The results shown in this panel are analogous to those in panel (b). However, these results are for the C(6, 15°) collineations. The curves corresponding to the lower temperatures were displaced downwards. The horizontal lines of the same color as the data correspond to zeros for the displaced curves. Note that the “dynamic heterogeneity” effect for the C(6, 15°) collineations is approximately five times smaller than the “dynamic heterogeneity” effect for the 11A clusters at all temperatures. (d) The PDs of the particles’ displacements (these PDs are also the self-parts of the van Hove correlation function [82]) at time \(t^*\) approximately corresponding to the maximum of the non-Gaussian parameter \(\alpha_2(t)\), i.e., at \(t^*\) occurs the maximum of the dynamic heterogeneity effect [63]. The red curve in the inset of (d) shows the difference between the PDs for the A-particles that belong to the 11A clusters and the PD for all A-particles. The blue curve shows the difference between the PDs of the particles in C(6, 15°) collineations and the PDs of all particles. This difference for the collineations is really small. In panel (e), the green data show the PD for the overlap parameter \(\xi_{ov}(5)\) between the top 5% of the mobile particles (T5) and the A-particles in the TCC clusters. The maximum of the Gaussian fit curve is close to 0.6. This clearly shows that the particles forming the TCC clusters avoid being mobile. The blue curve shows the overlap between the bottom 5% of the mobile particles and the TCC clusters. The maximum value around 1.1 shows that A-particles in TCC clusters tend to be slower. The results for the overlap between the C(6, 15°) collineations and top/bottom 5% of the mobile particles are shown as red/orange curves. It is clear that the overlap is essentially random.

collineations and the mobile particles is almost random.

Thus, from Fig. 9(d,e) we conclude that collineations are not related to the mobility strings.

X. CONCLUSION

We studied the collineations of more than three particles in the KA model system. Though the observation of long collineations was first reported by Bernal in 1962, it appears that since then long collineations have never been studied systematically.

We found that the average number of particles in the collineations increases as the temperature of the liquid decreases. Below the GT, the increase in the number of collineations nearly vanishes.

We also studied collineations in the inherent structures. We found that the average number of particles in the collineations observed on the inherent structures nearly does not depend on the temperature of the parent liquid if it is above the potential energy landscape crossover temperature, \(T_x\). As the temperature of the parent liquid decrease below \(T_x\), the number of particles in the collineations observed on the inherent structures starts to increase. Thus, the potential energy crossover is reflected also in the collineations.

Counterintuitively, we found that the average number of particles in the collineations observed on the parent structures can be larger than the average number of particles in the collineations observed on the corresponding inherent structures. It is unclear what is the origin of this situation. It is possible that this is associated with the fact that the pressure of the inherent structures becomes negative when the temperature of the corresponding parent liquid is lower than a certain value. In any case, it appears that the relaxation from the parent to inherent
structures destroys some ordering that develops in the KA model liquid during supercooling.

We also suggested a model that connects the numbers of particles in the collineations with the PDF and ADF. The model performs rather well. From this good agreement it could be argued that the developments of some features in the ADF and PDF are caused by the developments in the intermediate range order (and beyond).

We also investigated possible connections of the collineations with several other phenomena studied in the context of supercooled liquids. In particular, we studied if there are connections with: 1) the disclinations lines from the geometric frustration approach, 2) selected clusters from the topological cluster classification method of describing the structural changes, and 3) the stringlike cooperative motion. We did not find a connection with any of these phenomena.

Here we did not study a possible connection of the collineations with the nucleation and crystallization processes. The KA system is not well-suited for this investigation. Yet, in our view, the possibility of such a connection deserves separate considerations.

XI. ACKNOWLEDGEMENTS

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Supplemental Materials for the Paper:
Collineations of particles in the Kob-Andersen system

V.A. Levashov

Technological Design Institute of Scientific Instrument Engineering,
630055, Novosibirsk, Russia. E-mail: valentin.a.levashov@gmail.com

In these supplemental materials (SM), we describe the interaction potentials used in our simulations of the Kob-Andersen system (KAS) and provide the details of our simulation procedure. We also describe the algorithm used for the chain-search. Besides, we show the data on the pressure of inherent structures and how it depends on the temperature of the parent structures. Finally, these SM contain the figures analogous to Fig.5,6 in the main text, but calculated on the parent structures.

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XII. THE USED POTENTIAL

In our simulations, we used the Kob-Andersen binary model system of particles [61, 62]. This system consists of 80% of larger A particles and 20% of smaller B particles. The masses, $m$, of all particles are the same. The particles interact via the modified Lennard-Jones potentials [53, 64, 70, 89]. The modifications guarantee that the interactions between the particles of types $a$ and $b$ become zero at $2.5 \sigma_{ab}$ [70]. The continuities of the derivatives of the potentials (the forces) at $2.5 \sigma_{ab}$ are also guaranteed.

The precise forms of the potentials are given by [64, 70]:

$$U_{ab}(r) = 4\epsilon_{ab} \left( \phi_{ab}^L(r) + \phi_{ab}^D(r) + C_{ab} \right),$$

where

$$\phi_{ab}^L(r) = \left( \frac{\sigma_{ab}}{r} \right)^{12} - \left( \frac{\sigma_{ab}}{r} \right)^6,$$

$$\phi_{ab}^D(r) = \left[ 6 \left( \frac{\sigma_{ab}}{r_{abc}} \right)^{12} - 3 \left( \frac{\sigma_{ab}}{r_{abc}} \right)^6 \right] \left( \frac{r}{r_{abc}} \right)^2,$$

$$C_{ab} = \left[ 7 \left( \frac{\sigma_{ab}}{r_{abc}} \right)^{12} - 4 \left( \frac{\sigma_{ab}}{r_{abc}} \right)^6 \right],$$

where $\phi_{ab}^L(r)$ are the Lennard-Jones parts of the potentials. The terms $\phi_{ab}^D(r)$ guarantee the continuities of the derivatives of the potentials at the cutoff distance $r = r_{abc} = 2.5\sigma_{ab}$ (the subscript “c” in $r_{abc}$ stands for “cutoff”). The constants $C_{ab}$ guarantee the continuities of the potentials at $r = r_{abc}$. 
reduced the temperature down to the starting configuration for the next lower temperature. This was done for each of the 10 independent runs. In this way, we studied those temperatures that we studied.

During the same time interval between two consecutively saved structures is such that the mean square displacement of the 2nd column shows the values of the time step used at the corresponding temperatures. We generated 1000 configurations of 8000 particles in 10 independent runs at each used at the corresponding temperatures. We generated 1000 configurations of 8000 particles in 10 independent runs at each studied temperature. Thus, in each independent run, we generated 100 independent configurations, we, starting from the very high temperatures, utilized 10 independent simulation runs. In this way, we reduced the temperature down to \( T = 0.05\epsilon \). For the larger system of 64'000 particles, we followed the same procedure for the larger system of 64'000 particles, we followed the same procedure for those temperatures that we studied.

The length scales of the interactions between the particles of different types are: \( \sigma_{AA} = 1.0\sigma \), \( \sigma_{BB} = 0.88\sigma \), and \( \sigma_{AB} = 0.80\sigma \). Note that \( \sigma_{AB} \neq (\sigma_{AA} + \sigma_{BB})/2 = 0.90 \). Though, the difference between 0.88 and 0.90 is quite small. The energy scales are: \( \epsilon_{AA} = \epsilon = 1.0\epsilon \), \( \epsilon_{BB} = 0.5\epsilon \), and \( \epsilon_{AB} = 1.5\epsilon \) The units of length and energy/temperature are \( \sigma \) and \( \epsilon \). The unit of pressure is \( \epsilon/\sigma^2 \). The unit of time is \( \tau = \sqrt{m\sigma^2}/\epsilon \).

We note that in Ref. [61, 62] a rescaled (a smaller) unit of time has been used \( \tau_{KA} = (1/\sqrt{48})\tau \). On the other
FIG. 10. Different panels show the same data on different scales. In all panels, the red curves show how the total average potential energy of the system per particle depends on the temperature. In every panel there are 3 red curves— the average and the average ±σ, where σ = σ(T) is the width of the distribution of the potential energies of individual structures (it is not the σ of the mean). The black curves in all panels show the temperature dependence of the average inherent structures’ potential energy. The blue curves correspond to the black curves ±σ of the distribution of the inherent energy values of individual structures (it is not the σ of the mean).

hand, the unit of time used, for example, in Ref. [53, 64, 89] is the same as the one used in our work.

XIII. DETAILS OF THE SIMULATION PROCEDURE

In our simulations, we used the NVT ensemble within the LAMMPS program [71, 73]. The very initial structure, from which we started all simulations, was the simple cubic lattice with the average density of all particles ρ₀ = 1.2. In this lattice, 4 planes of A particles alternated with 1 plane of B particles. Then, we “melted” this artificially created lattice within LAMMPS at temperature T = 7.0. At this high temperature, the particles are mobile and it does not take much time to achieve the mean square displacement of particles corresponding to dozens of interatomic distances. We performed several of such initial consecutive equilibration runs. Then, still at T = 7.0, we performed several consecutive runs in which the final structures for the restart files were separated from each other by time intervals corresponding to the MSDs corresponding to several dozens of interatomic distances. Thus, we assume that we produced several sufficiently different structures at T = 7.0. For the system of 8000 particles, we produced 10 structurally different restart files for further use. For the system of 64000 particles, we produced 6 independent restart files.

Then, concerning the systems of 8000 particles, for each of the created 10 configurations, we abruptly decreased the temperature down to T = 6.0. Then, each of these 10 configurations was equilibrated, at T = 6.0, for the time corresponding to the mean average displacement of particles equal to approximately 25 interatomic distances, i.e., (t ≈ 500τ), where τ = √mσ²/ε. The used value of the time step was dt = 0.0005τ. Then, starting from 10 structures equilibrated at T = 6.0, we generated 100 configurations for each of the initially equilibrated structures. Below, we address the time intervals between the saved structures in details. Thus, in total, we had
FIG. 11. Different panels show the same data on different scales. In all panels, the red curves show how the average pressure of the parent systems depends on the temperature. In fact, in every panel there are 3 red curves—the average and the average \( \pm \sigma \), where \( \sigma = \sigma(T) \) is the width of the pressure distribution of individual structures (it is not the \( \sigma \) of the mean). The black curves in all panels show the temperature dependence of the inherent structures’ average pressures. The blue curves correspond to the black curves \( \pm \sigma \) of the distribution of the energy values from individual structures (it is not the \( \sigma \) of the mean).

1000 configurations for the analysis. Further, the procedure described above for \( T = 6.0 \) was used to obtain the structures at lower temperatures. The transition to a lower temperature was performed by reducing the temperature from the available previous higher temperature just above.

This procedure allows to achieve a further configurational divergence of the structures obtained from the 10 initial independent structures at \( T = 7.0 \) (in practice, it does not matter because these initial 10 structures at \( T = 7.0 \) are already very different). For the temperatures \( T > 1.0 \), the diffusion process is fast – the particles leave their cages within times \( t < 0.5\tau \). Thus, for \( T > 1.0 \), it is not difficult to produce the equilibrated systems and then to produce the particles’ configurations “separated” by mean particle displacement of several \( \sigma \), i.e., presumably, quite different configurations. Note, the displacement of several \( \sigma \) guarantees that the “separation” time is larger than the \( \alpha \)-relaxation time.

In the temperature interval between \( T = 5.0 \) and \( T = 1.0 \) the used value of the time step was \( dt = 0.001\tau \). In the temperature interval between \( T = 1.0 \) and \( T = 0.5 \) we increased the time step from \( dt = 0.001\tau \) to \( dt = 0.005\tau \). For \( T \leq 0.5 \) the time step was \( dt = 0.005 \). Further information, concerning the details of the simulation procedure, we provide in Table II.

An insight into the degree of the system relaxation can also be gained from Fig. 10,11.

XIV. ALGORITHM FOR THE CHAIN-SEARCH

To find the collineations of \( A \)-particles, we used the following algorithm:

1) In the most external cycle (zero-order cycle) over all particles in the system we chose a particle “A” and label it as \( A_o \).

2) We determine nearest neighbors of \( A_o \) according to the cutoff distance (the 1st minimum in the \( AA \)-partial PDF). It is convenient, in a preliminary analysis, to determine the lists of neighbors of all \( A \)-particles.
3) We run the 1st order internal cycle over the neighbors of $A_o$.
4) A particular chosen $A$-neighbor of $A_o$ we label as $A_1$.
5) For the chosen $A_o$ and $A_1$ we run again the cycle over the neighbors of $A_o$ (the 2nd order internal cycle). Another (different from $A_1$) particular chosen $A$-neighbor of $A_o$ we label as $A_2$.
6) For the selected $A_o$, $A_1$, and $A_2$, we check the value of the angle $\angle(A_1 A_o A_2)$. If this angle is sufficiently close to $180^\circ$, according to a chosen angular cutoff, we say that there is a chain of the 3rd order.
7) If we are interested in chains of the 4th order, then the particle $A_1$ is used as the particle $A_o$ previously. In particular, then there is a cycle over the 1st neighbors of $A_1$ (we label them as $A_3$) and we check the angles $\angle(A_o A_1 A_3)$.
8) If we are interested in the chains of 5th order, then, after the step 7) of this algorithm is completed, the particle $A_2$ is used as the particle $A_o$ previously. In particular, then there is a cycle over the 1st neighbors of $A_2$ (label them as $A_4$) and the angle $\angle(A_o A_2 A_4)$ is checked for the angle-cutoff condition.
9) If we are interested in the chains of higher order then we introduce more cycles over the neighbors of the particles at the ends of already determined chains of lower order.

XV. POTENTIAL ENERGIES AND PRESSURES OF THE PARENT AND INHERENT STRUCTURES

In Fig. 10, we show how the potential energies per particle of the parent and inherent structures depend on the temperature. In all panels, the same data are presented, but on different scales. The results shown in this figure can be compared, for example, with the data in Fig. 1 of Ref. [53].

To produce the inherent structures we used the FIRE algorithm [22, 26] within the LAMMPS program [71, 73]. The criterion for convergence of the minimization process was: the change in the total potential energy in a particular step has to be smaller than $10^{-4}$ of the energy value. A maximum number of $10^4$ steps was allowed. The value of the time step used was $dt = 0.002$. The recommended time step for the FIRE algorithm is the same as the time step used in MD simulations [22].

Every point in the shown plots originates from 1000 configurations of 8000 particles. These 1000 configurations originate from 10 independent runs, as described in this SM in the section on simulation procedure.

In Fig. 10 as in Fig. 1 of Ref. [53], we see that for $T > 1.5$ the average energies of the inherent structures, essentially, do not depend on the temperature. Then, as the temperature of the parent system decreases, at $T \approx 1.0$, there occurs a crossover to the potential energy landscape (PEL) influenced regime.

Then, the figure shows that, at $T \approx 0.36$, the timescale of our relaxation procedure of the parent structures is not sufficient to capture the structural relaxation of the system.

In Fig. 11 we show the temperature dependencies of the pressure of parent and inherent structures. In principle, the behavior of all shown curves is similar to the behavior of the curves shown in Fig. 10. Note, that the pressure of the inherent structures becomes negative at $T \approx 0.8\epsilon$.

Thus, at $T < 0.8\epsilon$, the inherent structures may exhibit a tendency for the formation of cavities. The issue about the cavities and inhomogeneities in the inherent structures has been discussed in the past. See, for example, Ref. [79, 81, 90, 92]. In particular, for the Kob-Andersen system, it has been shown that, for the reduced densities $\rho\sigma^3 > 1.08$, the inherent structures remain homogeneous even when the pressure in these structures is negative (tensile). Thus, the crossover in the number of chains that we observe on the inherent structures may not be associated with the formation of cavities.

XVI. NEAREST NEIGHBOR AND COMMON NEIGHBOR ANALYSES OF THE PARENT STRUCTURES

In Fig. 12 we show the results of the nearest neighbor analysis conducted on the parent structures at $T = 0.5\epsilon$. These results are completely analogous to the results presented in Fig. 5 of the paper.

In Fig. 13 we show the results of the common neighbor analysis conducted on the parent structures at $T = 0.5\epsilon$. These results are completely analogous to the results presented in Fig. 6 of the paper.

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FIG. 12. Nearest neighbor analysis of $A$-particles in the collineations. This figure is completely analogous to Fig. 5 of the paper. However, the data in it have been produced from the parent structures at $T = 0.5\epsilon$.

FIG. 13. Common neighbor analysis of AA-bonds in the collineations. This figure is completely analogous to Fig. 6 in the paper. However, the data in it have been produced from the parent structures at $T = 0.5\epsilon$.

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