Decagonal quasicrystal-like mesoscopic order in three-dimensional purely repulsive simple fluid

R.E. Ryltsev
Institute of Metallurgy, Ural Division of Russian Academy of Sciences, Yekaterinburg 620016, Russia and L.D. Landau Institute for Theoretical Physics, Russian Academy of Sciences, 117940 Moscow, Russia

B.A. Klumov
High Temperature Institute, Russian Academy of Sciences, 125412, Izhorskaya 13/2, Russia and L.D. Landau Institute for Theoretical Physics, Russian Academy of Sciences, 117940 Moscow, Russia

N.M. Chchelkatchev
Department of Physics and Astronomy, California State University Northridge, Northridge, CA 91330, USA
L.D. Landau Institute for Theoretical Physics, Russian Academy of Sciences, 117940 Moscow, Russia
Moscow Institute of Physics and Technology, 141700 Moscow, Russia
Institute for High Pressure Physics, Russian Academy of Sciences, 142190 Troitsk, Russia and Institute of Metallurgy, Ural Division of Russian Academy of Sciences, Yekaterinburg 620016, Russia

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We show that strongly interacting molecular or nanoparticle system can be driven to three-dimensional quasicrystalline state rather than to liquid, glass or “ordinary” crystal just by purely repulsive, isotropic and monotonic interaction pair potential. It should have two characteristic length scales describing the repulsion strength. Molecular dynamic simulations show at certain density-temperature domain the phase with three-dimensional decagonal quasicrystalline order at both the local and the medium scales. It is self-assembled from liquid through the first order phase transition. We suggest that the underlined mechanism of decagonal order formation is the stabilization of large icosahedral-like clusters due to the existence of two effective interparticle distances.

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Since their discovery in the 1980s [1], the quasicrystals (QC) have demanded increasing attention due to their remarkable physical properties. QCs have been observed experimentally and in simulations not only in metallic alloys [2], but also in molecular systems [3, 4] and soft-matter nanoparticle solutions [5–7]. One the most important open issue in this field is understanding microscopic physical mechanism that drives the particular strongly interacting molecular or nanoparticle system to choose the quasicrystal state rather than to convert into liquid, glass or “ordinary” crystal. Here we address the problem from the other side: How simple the particle system can be to show the quasicrystal order?

Intuitively for a given strongly interacting molecular or nanoparticle system the interaction potential should be quite unusual to produce the quasicrystal. It has been shown by molecular dynamic simulations that the quasicrystalline order does not require an extraordinary interaction between particles but it can be obtained within the simple-fluid model with one sort of particles interacting only with the isotropic pair potential [8–10]. However most of these investigations have been restricted to quite special case, namely, to the two-dimensional particle systems. To the best of our knowledge, there is the only example of self-assembling of the quasicrystal during the simulation of three-dimensional (3D) monatomic system with isotropic potential [9]. This potential has two attractive wells separated by pronounced maximum and has been specially constructed to encourage formation of icosahedral local order. We show that strongly interacting particle system can be driven to three-dimensional quasicrystal state just by purely repulsive, isotropic and monotonic interaction pair potential. But it should have two characteristic length scales describing the repulsion strength.

The existence of several interparticle scales is the typical feature of effective interactions constructed for different condensed matter 3D-systems including molecular liquids [20, 21], soft matter systems [22, 23] and metallic alloys [24–27]. Simple fluid models based on such interactions can well explain and reproduce liquid-liquid phase transitions [28, 30], water-like anomalies [31–36], glassy dynamics [37, 38] and polymorphism [36, 39]. Here we observe within such simple fluid model at certain density-temperature domain the phase with three-dimensional decagonal quasicrystalline order at both the local and the medium scales. This phase is self-assembled from liquid through first order phase transition. We suggest that the underlined mechanism of decagonal order formation is the stabilization of large icosahedral clusters due to the existence of two effective interparticle distances.

We investigate by the molecular dynamic simulation three-dimensional system of particles interacting via repulsive two-length scale potential: \( U(r) = \varepsilon (d/r)^\eta + \varepsilon n_r [2\kappa_0 (r - \sigma)] \), where \( n_r(x) = 1/(1 + \exp(x)) \), \( \varepsilon - \) is the unit of energy, \( d \) and \( \sigma \) are “hard”-core and “soft”-
core diameters. We take here \( n = 14, k_0 = 10, \) and \( \sigma = 1.35 \). We focus on these parameters because they reveal complex system behavior: the phase diagram with polymorphous transitions [39], water-like anomalies [34] and glassy dynamics [37]. In the remainder of this paper we use the dimensionless quantities: \( \bar{r} \equiv r/d, \bar{U} = U/\epsilon, \) temperature \( \bar{T} = T/\epsilon, \) density \( \bar{\rho} \equiv N d^3/V, \) and time \( \bar{t} = t/(d \sqrt{m/\epsilon}) \), where \( m \) and \( V \) is the molecular mass and system volume correspondingly. As we will only use these reduced variables, we omit the tildes. For MD simulations, we have used DL_POLY Molecular Simulation Package [40], for more simulation details see [41].

Recently, it was reported [37] that the system demonstrates excellent glass-forming ability in the density range \( 0.52 \lesssim \rho < 0.74 \). Inside this region, one can equilibrate supercooled liquid without crystallization down to temperatures at which relaxation time becomes too large for simulation. At \( \rho > 0.74 \) and \( \rho < 0.46 \) the system spontaneously crystalizes whereupon supercooling below the melting line. But within \( 0.46 < \rho \lesssim 0.54 \) situation is more complicated: system undergoes phase transition into some ordered but non-crystalline state. It is also important that the narrow density region \( \rho \in (0.51 - 0.53) \) is the intersection of both areas: at intermediate cooling rates, system falls into glassy state but, at slower ones, it undergoes the phase transition. Below we will study the features of this transition for \( \rho = 0.5 \).

First we focus on the thermodynamic origin of the transition. Fig. 1(a) shows the time dependence of configurational energy \( E_{\text{cfg}} \) at \( T = 0.1 \) and \( \rho = 0.5 \). We see that the transition is attended by the sharp jump of average \( E_{\text{cfg}} \) which occurs spontaneously at certain time. So there is release of heat at the transition. In Fig. 1(b), temperature dependencies of \( E_{\text{cfg}} \) for both the high-temperature (liquid) and low-temperature (QC) phases are respectively presented at cooling and heating. We see pronounced hysteresis demonstrating strong supercooling and (or) overheating effects in the transition. Simulation in NPT ensemble reveals spontaneous decrease of system particle density taking place during the transition (see Fig. 1(c)). All of the features mentioned are the clear evidences that the transition under consideration is a first order phase transition.

This transition is also accompanied by the strong changes of the structural properties. Fig. 2 shows the radial distribution function (RDF) \( g(r) \) and its cumulant \( N(< r) = 4 \pi \rho \int_0^r \xi^2 g(\xi) d\xi \), the structure factor \( S(q) \) and the bond angle distribution function \( P(\varphi) \) at \( \rho = 0.5 \) and two temperatures which are slightly higher and slightly lower than the transition temperature. The cumulative RDF is practically the same for both phases (Fig. 2a). It means that the average numbers of neighbors in the first and the second coordination shells change only slightly during the transition. On the other hand, we see from evolution \( g(r) \), \( S(q) \) and \( P(\varphi) \) that structure properties change considerably when we go in parameter space from one phase to the other. Notice in particular that the low-temperature phase is essentially ordered and so its structure is obviously not the liquid-like one.

In order to understand better the structural changes in the vicinity of the transition, we have performed the detailed orientational local order analysis based on bond order parameters \( q_i \) and \( w_i \) [42,43]. Within the method the rotational invariants (RIs) of rank \( k \) of both second \( q_i(i) \) and third \( w_i(i) \) order are calculated for each particle \( i \) in the system from the vectors (bonds) connecting its center with the centers of its nearest neighboring particles. The values of the order parameters \( q_i \) and \( w_i \) are explicitly determined for any ideal geometrical figure and they do not depend on particular spatial cluster orientation. That allows using them as local structure indicators which can be particulary used to quantify freezing and melting of different systems (e.g. [40,49]).

We investigate the local structure using the probabil-
The transition is accompanied by the strong increase of the self-diffusion coefficient \( D \) and estimated the abundance of particles involved in the formation of icosahedral-like clusters \( n_{ico} \). We have performed such calculations for icosahedral local order and estimated the abundance of particles involved in the formation of ico-like clusters \( n_{ico} \). In Fig. 2 we show \( n_{ico}(T) \) near transition temperature \( (T_{tr}) \) at \( \rho = 0.5 \). The transition is accompanied by the strong increase of \( n_{ico} \) that agrees with the results of qualitative analysis of \( q_4 - q_6 \) PDF (Fig. 3). In Fig. 4 the temperature dependency of the self-diffusion coefficient \( D \) is also shown.

We see that \( D \) decreases drastically than the transition happens. Both the mean square displacement and the intermediate scattering function of the system demonstrate pronounced plateau at \( T < T_{tr} \) (see insert in Fig. 4 for intermediate scattering function). So we see that low-temperature phase has “solid-like” dynamics.

Thus we see that, below the transition temperature...
FIG. 5. (Color online) Typical snapshots of the particle system at $\rho = 0.5 T = 0.1$ demonstrating decagonal order. (a,b): Mesoscopic structure of single quasicrystallite in the plane perpendicular (a) and parallel (b) to axes of the decagonal tubes made of face-shared icosahedra. The particles located at the centers of these tubes are colored yellow. These particles form dimers with bond length corresponding to hard core of $U(r)$ which is about $d/\sigma \approx 0.74$ of the interparticle distance corresponding to soft core (see the locations of two maxima of first RDF peak in Fig. 2a). (c): Decagonal tube made of the face shared icosahedra; (d,e) The structure of the double icosahedron (the two face-shared icosahedra) — the building block of the decagonal tubes. Particles belonging to common face are colored blue. (f,g): Junction mechanism of decagonal tubes. The red particles as well as yellow ones are short-bonded. These pictures show that certain fraction of particles involved in tubes formation must be located at shorter distances in comparison to others.

For $T_{tr}$, the system is essentially ordered (Fig. 2) and its local structure is strongly icosahedral. In this connection, it is important to understand how the icosahedral clusters are distributed in space. Analysis of the snapshots reveals that structure of low-temperature icosahedral phase is “polyquasicrystal”. It consists of nanosized quasicrystallites randomly oriented relative each other. The structure of each quasicrystallite has pronounced decagonal (10-fold) symmetry (Fig. 5a,b). What we see in Fig. 5a as decagons are in fact spatial “tubes” made of face-shared icosahedra (Fig. 5i). The building block of such tubes — so called double icosahedron — is shown in Fig. 5f, i.e. As it is seen from the Fig. 5i, icosahedral tubes tend to connect to each other and form quasicrystal-like mosaic in the plane perpendicular to tube axes. The mechanism of this connection is illustrated in Fig. 5g.

MD produces the “polycrystal” QC with rather small (quasi)crystallites, see Fig. 5a,b. Frankly speaking, it is hard here to distinguish the QC from the corresponding approximant at local and mesoscopic levels without growing larger (quasi)crystallites and building of the diffraction pattern to determine the global order. Poly-QC with large enough (quasi)crystallites can be grown beyond MD by, e.g., doing Monte-Carlo relaxation with additional healing out topological defects separating (quasi)crystallites [15]. This procedure and the diffraction pattern we leave for the forthcoming paper. Here we show that standard and straightforward MD in simple system already shows without additional artificial efforts the possibility of QC-order in 3D.

The presence of the two characteristic interparticle distances plays the key role in the formation of the decagonal order. To show it we color by red and yellow in Fig. 5 the short-bonded nearest-neighbor particles located at distances corresponding to “hard” core of the interaction potential (see also the slitted first RDF peak in Fig. 2a). These particles are grouped in pairs along the axes of the icosahedral tubes (yellow) and at the centers of the pentagons belonging to adjacent icosahedra (red). Without such short-bonded particles it hardly possible to construct spatial decagonal clusters (like in Fig. 5).

We can now formulate the two conditions necessary for formation of the ideal three-dimensional quasicrystal structure: 1) there should be optimal ratio between the length of short and long nearest-neighbor bonds to minimise the icosahedral distortion and 2) the concentration of short and long bonds should be optimal. These conditions can be only realized in relatively small domain of system parameters. This is the reason why quasicrystals are relatively rare. We repeat again that our results suggest that proposed mechanism of decagonal order stabilisation is rather general and does not depend on any morphological anomalies.

FIG. 6. (Color online) Density dependence of the icosahedral order fraction $n_{ico}$ at $T = 0.08$. Abundance of ico-like particles 

$\rho$

Abundance of ico-like particles

0.06

0.08

0.1

0.47 0.49 0.5 0.52 0.53
peculiarities of system interaction except the existence of two characteristic length scales of the interaction.

In our case, the ratio between the short and the long bond lengths between nearest-neighbor particles is determined by the width of the potential shoulder $\sigma$ whereas the “concentration” of the short-bonds depends mainly on density $\rho$. So we suggest that there is small area in $\rho - \sigma$ plain where the icosahedral order is favored and so quasicrystal formation is possible. To check it we calculate density dependence of the fraction $n_{ico}$ of icosahedral order within the range where the phase transition takes place. To support our conclusion we show in Fig. 5 that dependence for $T = 0.08$ (below $T_{tr}$) for a number of densities. We see that $n_{ico}(\rho)$ has pronounced narrow peak in the vicinity of $\rho = 0.5$. Outside the density region corresponding to the transition $n_{ico}$ is almost zero.

To conclude, we show by molecular dynamic simulation that simple one component three-dimensional particle system with purely repulsive interaction demonstrates self-assembling of decagonal quasicrystalline-like mesoscopic order. We demonstrate that the underlined mechanism of decagonal order formation is the stabilization of large tube-like clusters made of face-shared icosahedra due to the existence of two effective interparticle interactions. The proposed mechanism is universal and may be applicable to any system with two-scale interaction such as metallic alloys, network forming systems and soft-matter systems.

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