Particles population splitting and density fluctuation equivalence of overdamped and supercooled simple liquid

E. B. Postnikov
Department of Theoretical Physics, Kursk State University, Radishcheva st., 33, 305000 Kursk, Russia

It is shown that even the simplest liquid of particles interacting via the Lennard-Jones potential, which corresponds to liquid argon, can exhibit non-trivial properties of the self-diffusive motion under high pressures and the temperature around the boiling point. Molecular dynamics simulations reveal effects of population splitting, slowing down ballistic flights to superdiffusion, and change of the velocity fluctuations from continual to point process during short times. For large times, analytical calculations based on the fluctuation theory provides an explicit expression reproducing isothermal change of the self-diffusion coefficient in liquid argon corresponding to the experimental data. These results lead to the conclusion that such behavior is based on the reduced mobility of particles reflected in their density fluctuations that can be equivalently achieved in the cases either low temperatures and pressures (supercooling) or moderate temperatures and high pressures (overdamping).

I. INTRODUCTION

In principle, numerical simulations of simple liquids by the method of molecular dynamics (MD) is a quite old topic, for example, quite accurate estimations of details of molecular motion and the self-diffusion coefficient in comparison with the actual experimental data for liquid argon are dated back to the seminal work by A. Rahman [1]; a review of further developing of such simulations and their results can be found in Ref. [2]. However, their majority is limited by the vicinity of the liquid-vapor coexistence curve and moderately high supercritical pressures at low temperatures as well as smallest time intervals corresponding to the stable normal diffusive regime. This fact may be conditioned by a limited number of experimental data available for simulations testing and discussion, especially liquified noble gases [3, 4] as well as techniques for their obtaining. Thus, recent model studies utilizing MD simulations are shifted to the region of supercritical and supercooled fluid states, where specific structure conditions lead to a variety of anomalous effects reflected in the transport coefficients even for relatively large characteristic times, and phase transitions [5–8].

At the same time the Lennard-Jones simple liquid can play a role of a model system even for discussing anomalous diffusion in more complex media mimicking the problems, which arises in biophysical systems [9, 10]. In this case, extremely short-time range dynamics may be crucial since it strongly depends on the microscopic surrounding of a moving particle leading to different effects as particle population splitting, non-ergodicity, etc. [11]. Due to an existence of inter-particle interactions, such walking processes and structural features should be taken into account not only in the context of trapping but also reaction binding, see e.g. [12] including such a hot topic as the direct MD simulation of forming mesoscopic objects like viruses [13].

As a complement to the areas of study mentioned above, this work addresses in its MD part another range of liquid states: within the temperature range between the triple and critical points (sufficiently far from the latter) but for high pressures. It is focused on the relatively unexplored in details short-time range of processes, where an influence of liquid’s microscopic structure is sufficient.

Respectively, changes in microstructure should be unavoidably reflected in as thermodynamic quantity as the excess entropy, which determines the behavior of the macroscopic coefficient of self-diffusion [14]. Thus, the second part of this work deals with the large-time counterpart of the problem: an analytic predictive calculation of the self-diffusion coefficient in liquid argon for the same pressure-density-temperature conditions basing on an interplay between the density fluctuations and measurable thermodynamic quantities, the density and the isothermal compressibility. To assure physical relevance, the actual experimental information on thermodynamic and transport properties known in reference literature and databases are used for the direct comparison of calculated and measured data.

Due to a usage of fluctuation approach, the final part consists of discussion of probabilistic character of MD number density fluctuations and the velocity steps sequence at different time scales and their correspondence to physical situations of local trapping in amorphous media.

II. SELF-DIFFUSION: SIMULATIONS

A. Method and parameters

The free available Python code [15] was used for simulations. It realizes the molecular dynamics algorithm for 864 particles interacting via the Lennard-Jones potential

\[ U(r) = 4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6}, \]

*postnicov@gmail.com
with parameters $\epsilon/k_B = 120$ K, $\sigma = 3.4$ Å ($k_B$ is Boltzmann’s constant) that corresponds to the classic Rahman’s system. Periodic boundary conditions were applied to the box of the side $L_{\text{box}}$, which was fixed and chosen in such a way that the mean density of particles within the box corresponded to the actual density of liquid argon at 90 K, i.e. $L_{\text{box}} = 10.229\sigma$ respectively to the density $\rho_{\text{sat}} = 1378.6$ kg · m$^{-3}$ on the saturation curve, and $L_{\text{box}} = 10.034\sigma$ respectively to the density $\rho_{20} = 1432.1$ kg · m$^{-3}$ at 20 MPa on the isotherm. Note also that due to a limited number of experimental data on the self-diffusion coefficient of liquid argon, especially, under pressure for temperatures from a “normal range”, i.e. sufficiently below the critical point [3–4], there isotherm 90 K provides a most data-rich choice in a vicinity of the boiling point.

The potential’s cut-off was chosen as $r_{\text{cut}} = 4.5\sigma$ that is twice of the conventional choice $r_{\text{cut}} = 2.25\sigma$ to assure possible long-ranged interaction in a high-density compressed liquid: the chosen value corresponds to 8 van der Waals radii $r_W = 1.88$ Å of the argon atom, i.e. to the forth coordination sphere (although comparative studies showed that the results does not differ significantly, i.e. nearest-neighbor interactions between atoms prevails, as expected). The time step of simulations was equal to $dt = 10^{-14}$ s.

Before measurements, the system was equilibrating during 40.96 ps; the equilibration was controlled by the plots of the pressure and the temperature of the system. The co-ordinates of all atoms were recorded for the subsequent 4096 time iterations (40.96 ps). To exclude effects of periodization, all trajectories were corrected via the shift of co-ordinates on $L_{\text{box}}$ when a particle reached the box’s side and the respective co-ordinate jumps occurred.

The time-averaged mean square displacement (tMSD) for each trajectory was calculated as

$$
\delta f^2(\tau = mdt) = \frac{1}{N - m} \sum_{i=1}^{N - m} \left[(f_x(t_i + mdt) - x(t_i))^2 + (f_y(t_i + mdt) - y(t_i))^2 + (f_z(t_i + mdt) - z(t_i))^2\right],
$$

where $f_{x,y,z}$ are components either of the displacement $\mathbf{r}$ or the velocity $\mathbf{v} = (\mathbf{r}(t_i + mdt) - \mathbf{r}(t_i))dt^{-1}$.

**B. Results**

To check consistency of the simulation method and get a reference state for further considerations of the self-diffusion under elevated pressure, plots of the mean square displacement (MSD) and the mean square velocity change (MSV) are obtained, see Fig. 1. One can note ergodicity of the process, time- and ensemble-averaged MSD and MSV coincide with a high accuracy: the respective curves for tMSD for all individual particles are well concentrated around their averaged value.

This ergodicity as well as a transition from the ballistic motion on small times to the Gaussian diffusion on large times that reflect a usual crossover from from the under- to the overdamped regime for a motion of a massive particle a thermal bath. Fig. 1(B) demonstrates the respective thermalization of the velocity during the time interval around 1 ps. An estimation of the characteristic distance traveled during this time shows the it corresponds to the radius of the first coordination sphere, i.e. the mean distance between nearest atoms. The diffusion coefficient determined from the slope of MSD (equally, time- or ensemble- averaged) in the diffusive regime is found as $D_{\text{sat}} = 2.3 \times 10^{-9}$ m$^2$ · t$^{-1}$ that corresponds to the values obtained other authors for L-J system mimicking liquid argon at the same temperature [10] and belong to the middle of the interval of its experimental values determined in different sources: $D_{\text{sat}}^{\exp} = (1.89 \pm 0.08) \times 10^{-9}$ m$^2$ · t$^{-1}$, $D_{\text{sat}}^{\exp} = (2.10 \pm 0.10) \times 10^{-9}$ m$^2$ · t$^{-1}$ [17], $D_{\text{sat}}^{\exp} = 2.43 \times 10^{-9}$ m$^2$ · t$^{-1}$ [18].

Now let us consider the simulated self-diffusion under the pressure 20 MPa. In this case, the situation changes drastically, see Fig. 2. First of all, the time averaged MSD over each individual trajectory has a larger scattering during the first 0.1 ps the walk registering. Further the bunch of trajectories is compressed into same range as in Fig. 2(A) that occurs in a vicinity of the leaving first coordination sphere and, after the characteristic relaxation time of the order 1-2 ps, the motion is a normal diffusion. In contrast to the saturated case, this phenomenon is detected for the ensemble averaged MSD too. While the black dashed line in Fig. 2(A) is one and the same for any starting time chosen from the the whole sample, thin black dashed lines in Fig. 2(A) show the initial splitting during the first 0.1 ps too. They were computed for a set of independent sub-samples of $10^3$ time records, the starting positions of which were separated by the time intervals of 2 ps, i.e. of the order of auto-correlation decay. Thus, one can hypothesize an existence of the instant short-living ensemble non-equivalences in the compressed liquid, which, however fast thermalize.

The mean-square displacements averaged over the whole ensemble of MSDs, both time- and ensemble-computed, demonstrate ergodicity. But there is a difference between Figs. 2(A) and 2(A): the initial slope of the log-log plot in the case of the applied pressure 20 MPa is equal to 1.85 not 2, i.e. formally corresponds to a superdiffusive motion instead of a ballistic one. However,
FIG. 1. (Color online) Mean square displacements for the displacement (A) and the velocity (B) in saturated liquid argon at \( T = 90 \) K: ensemble averaged \( \langle \Delta r(\tau)^2 \rangle \) (black dashed line), time-averaged over each trajectory \( \delta r(\tau)^2 \) (cyan lines), and ensemble averaged over the latter \( \langle \delta r(\tau)^2 \rangle \) (red solid line); the same with a replacement “\( r \)” by “\( v \)” in the notation for velocities.

It should be pointed out that it is not “an averaged motion faster then diffusive walks”, but “an averaged walk slower than ballistic flights”. This claim is supported by an analysis of the velocity variances shown in 2(B).

The velocity variances determined via the time averaging method for trajectories of all particles separately clearly split into two sub-populations. The first one exhibits a narrow-localized power-law growth (linear in the double logarithmic scale, with the same slope as for the MSD) with the subsequent crossover to a constant. The second one consists of a set of lines varying from straight one to the smooth transition between straight lines. Such picture characterizes an ensemble of velocities thermalised to different values. The overall (over the both sub-populations) time-averaged velocity variances, shown as the solid red line in 2(B), reduces to the similar shape: average thermalised motions within the time interval corresponding to the movements within the first coordination sphere, an interaction with the nearest-neighbor shell’s atoms (at the moments about the characteristic relaxation time of orders 0.1-1 ps) and the further diffusive walk for larger times and distances (compare with 2(B)). Note also, that the instantly short-time trapped sub-population (cyan in 2(B)) may creates additional obstacles for the second (cyan in 2(B)) sub-population that results in slowing ballistic flights within the first coordination sphere down to superdiffusion.

This conclusion can be supported by the behaviour of a set of ensemble-averaged MSDs for different starting
times shown in (3B) as green dashed lines connecting theirs subsequent points. All these lines are not smooth, in contrast to Fig. (4B) but have zigzags bounded by lines of the time-averaged velocity variances. This means that for such not so large ensemble of particles, ensemble averaged evolution of velocities variance “feels” instant locking of moving particles, which, however, does not take more than one time step. The time-moment distribution of such jumps differs between different realizations, nad the resulting averaging shown in Fig. (4B) as the dashed black line converges to the same as for the mean time-averaged variance dynamics for individual trajectories. But it should be pointed out that this ergodicity fulfills for the global averaging only, which destroys more fine resolution of sub-populations.

III. REDUCED DENSITY FLUCTUATIONS AND SELF-DIFFUSION

A. Density and self-diffusion along an isotherm

To analyze the pressure/density-dependent behavior of the self-diffusion in the considered LJ-fluid simulating liquid argon, it is worthy to address the relative density fluctuations

\[ \nu^{-1} = \frac{\langle (\Delta \rho)^2 \rangle}{\rho} = \frac{\mu_0}{\rho RT} \kappa_T, \]  

(1)

which allows for analysis of an interplay between microscopic liquid structure and thermodynamics since \( \kappa_T \) is a practical linear dependence on the density, \( \log(\nu) = k\rho + b \), where \( k \) and \( b \) are substance-dependent parameters, the same for both liquid-vapor coexisting parameters and in the single phase region that make possible to derive the so-called Fluctuation Theory-based Equation of State (FT-EoS)

\[ \rho = \rho_0 + \frac{1}{k} \log \left[ \frac{k \mu_0}{\nu RT} (P - P_0) + 1 \right], \]  

(2)

that makes available predicting the density of liquids, from simple to quite complex substances, see [20] and references therein, using the data measured at normal conditions only.

In particular, Fig. 3(A) shows the predicted density of argon along the isotherm \( T = 90 \) K from the liquid-vapor coexistence curve to the vicinity of the freezing point (25 MPa) at this temperature; the average absolute deviation between them is equal to 0.0065 %. Experimental data for the density under pressure as well as the saturated density, speed of sound and the heat capacity ratio used for computing \( \nu \) and \( k \) (see the description of the algorithm in Ref. [21]) are taken from the database of the National Institute of Standards and Technology (NIST) [21] based on the high-accurate equation of state fitting a wide compilation of different experimental data [22].

The dimensionless reduced coefficient of self-diffusion in liquids in a majority of cases exhibit a universal exponential behavior [13, 23–25]

\[ \left( \rho^{1/3} \sqrt{\mu_0/RT} \right) D \propto e^{-A \frac{-S_{ex}}{N k_B}}, \]  

(3)

where \( S_{ex}/N k_B \) is the excess entropy per particle, which defines the difference between the entropy of the system under study and the entropy of an equivalent ideal gas at the same temperature and density, and \( A \) is a positive constant, which may vary for different substances.

It should be pointed out that the excess entropy is not a quantity, which can be determined straightforwardly in experiment and its value depends on fitting to a chosen model [14]. The simplest possibility is a usage of purely thermodynamic quantities, namely the compressibility factor \( Z = \mu_0 P/\rho RT \) and its isochoric derivative

\[ \frac{S_{ex}}{N k_B} = - \int_0^\rho \left[ T \left( \frac{\partial Z}{\partial T} \right)_V + Z(\rho) - 1 \right] \frac{dp}{\rho}. \]  

(4)

Using the standard thermodynamic definition of the internal pressure

\[ P_T = T \left( \frac{\partial P}{\partial T} \right)_V - P, \]

the derivative mentioned above can be easily calculated and Eq. (4) rewritten as

\[ \frac{\Delta S_{ex}}{k_B} = - \int_0^\rho \left[ \frac{\mu_0 P_T}{\rho RT} + \mu_0 P(\rho)/\rho RT - 1 \right] \frac{dp}{\rho}, \]  

(5)

if one considers a difference between excess entropies of two states with the densities \( \rho_0 \) and \( \rho \) placed on one isotherm. After substituting into the integrand the pressure expressed from FT-EoS (2) as an explicit function of the density, the integral (5) is taken analytically that results in

\[ \frac{\Delta S_{ex}'}{k_B} = - \left[ \frac{\mu_0 (P_T + P_0)}{RT \rho} + \frac{\nu}{k \rho} \log(k \rho) + \nu e^{-k \rho} \left( \text{Ei}(k \rho) - \frac{e^{k \rho}}{k \rho} \right) \right]^{\rho}_{\rho_0}, \]  

(6)
where $E_i(k\rho)$ is the exponential integral, and $P_i = \text{const}$ as it follows from the basic construction of FT-EoS \cite{2}; although it fulfills only approximately in average, the actual changes of $P_i$ with respect to its value within the considered range of pressures can be neglected. An accuracy of the density prediction shown in Fig. 3(A) confirms this.

Fig. 3(B) shows the curve of the relative coefficient of self-diffusion change calculated using Eqs. (6), (3) with $A = 3.2$ in comparison with the raw experimental ratio of the coefficient of self-diffusion under pressure to its saturated value taken from \cite{18}. One can see that the proposed density fluctuation-based model quite accurately reproduces the non-linear character of the self-diffusion coefficient’s diminishing with the growing pressure.

### B. Particle number distribution as a generalized linear model

Now let us consider this model from the point of view of the probability density functions (p.d.f.) distributed within a small volume surrounding some chosen particle. This analysis can be done following the approach called an exponential dispersion model (EDM) \cite{27}, within of which the p.d.f. written with respect to the number of particles $n$ is represented as

$$w(n, \theta) = a(n) \exp[n\theta - \kappa(\theta)],$$

(7)

where $\theta$ is the canonical parameter and $\kappa(\theta)$ is called the cumulant function, since the moments of distribution are determined as

$$\bar{n} = \frac{d\kappa}{d\theta}$$

(8)

and

$$\text{var}(n) = \langle (\Delta n)^2 \rangle = \frac{d^2\kappa}{d\theta^2} - \frac{dn}{d\theta}$$

(9)

As the first step, consider the volume as small but sufficiently large that the mean particle density $\bar{n}$ can be associated with the thermodynamic density and the inverse reduced fluctuations satisfies the dependence revealed by the thermodynamic data:

$$\nu = \frac{\bar{n}}{\langle (\Delta n)^2 \rangle} = e^{k\bar{n}} + b = \nu_0 e^{k\bar{n}},$$

i.e. the variance has a form satisfying the conditions of the EDM:

$$\langle (\Delta n)^2 \rangle = \nu_0^{-1} \bar{n} e^{-k\bar{n}}.$$  

Therefore, the mean value satisfies the ordinary differential equation

$$\frac{d\bar{n}}{d\theta} = \nu_0^{-1} \bar{n} e^{-k\bar{n}},$$

which can be easily solved by the variable separation method:

$$\theta = \nu_0 E_i(k\bar{n}) + c_1.$$  

(10)

Within the same way, it is possible to find the cumulant function using (8):

$$\frac{d\kappa}{dn} = \nu_0^{-1} \bar{n} e^{k\bar{n}},$$

i.e.

$$\frac{d\kappa}{dn} = \nu_0 \bar{n} e^{k\bar{n}}$$

with the solution

$$\kappa(\bar{n}) = \nu_0 k^{-1} e^{k\bar{n}} + c_2.$$  

(11)

Note that $c_1$ and $c_2$ are additive constants, and a substitution of the expressions (10), (11) into (7) will change the latter by a constant factor $\exp(c_2)$ and the $n$-only dependent multiplier, which can be incorporated into the still indefinite function $a(n)$. Therefore, one can put the both $c_1 = 0$ and $c_2 = 0$ without loss of generality.

Thus, the conclusion is that the cumulant function in this case is the derivative of the reduced bulk modulus with respect to the density: with the solution

$$\nu(\bar{n}) = \nu_0 k^{-1} e^{k\bar{n}} + \frac{d\nu}{dn}.$$  

The resulting p.d.f. has a form

$$w(n, \bar{n}) = a(n) \exp[\nu_0 E_i(k\bar{n}) - \nu_0 k^{-1} e^{k\bar{n}}],$$

(12)

which can be associated with the thermodynamic entropic contribution into the self-diffusion \cite{5} after a transition to the mass density.
At the same time, Eq. (12) allows for a more general interpretation. Let us consider the case of extremely small number densities, i.e. $|k|\bar{n} \ll 1$. This may be achieved considering the vapor branch at almost ideal gas conditions, when $n_0 \approx 1$, and $k < 0$, see [19], where the inverse reduced density fluctuations under such conditions were studied basing on actual experimental data for gaseous argon.

In the considered case $\exp(k\bar{n}) \approx 1 + k\bar{n}$, and the cumulant function

$$\kappa = k^{-1}e^{k\bar{n}} \approx k^{-1} + \bar{n}.$$  

The series representation of the exponential integral function in this case is

$$\text{Ei}(k\bar{n}) = \log(\bar{n}) + [\log(k) - i\pi] + \gamma + \sum_{j=1}^{\infty} \frac{(k\bar{n})^j}{j!j},$$

where $\gamma$ is Euler’s constant, and $[\log(k) - i\pi] = \text{Re} \log(k)$ is a real number.

Whence,

$$n\text{Ei}(k\bar{n}) = n\log(\bar{n}) + n[\gamma n + \text{Re}\{\log(k)\}] + n\sum_{j=1}^{\infty} \frac{(k\bar{n})^j}{j!j}.$$  

The exponential of the first term is equal to

$$\exp(n\log(\bar{n})) = \bar{n}^n,$$

the last term can be neglected as small, the second term does not depend on $\bar{n}$ and, therefore, can be combined with $a(n)$. Thus, the resulting p.d.f.:

$$w(n) = \left\{ a(n)e^{(\gamma + \text{Re} \log(k))n - k^{-1}} \right\} \bar{n}^n e^{-\bar{n}}.$$  

Taking the first factor as $1/n!$ (it is possible since $a(n)$ is a still indefinite function), this expression reduces to the Poisson distribution

$$w(n) = \frac{\bar{n}^n}{n!} e^{-\bar{n}}$$

that is known for the ideal gas (or in the case of small volumes containing an extremely small number of particles inside) [28, 29].

Thus, the revealed non-trivial dependence on the liquid density, which can be connected with average inter-particle distances, may serves for a future microscopic probabilistic background for the studying transport processes in liquids under pressure, which exhibit a non-trivial behavior.

**IV. DISCUSSION**

To analyze and discuss step-wise specificity of the processes, which take place in overdamped liquid argon that results in the particles population splitting seen in Fig. 2(B) and in the replacement of an average ballistic flight by a superdiffusive walk during short times, it is possible to apply the wavelet variance approach [30, 31].

For a discrete sample $f_n = f_n^{(0)}$, where $t_n = n\Delta t$, the Haar wavelet transform operates for the scales $j$ with sequential averaging

$$f_n^{(j+1)} = \frac{f_n^{(j)} + \overline{f_n^{(j)}}}{\sqrt{2}},$$

and computing wavelet coefficients

$$d_{j+1}[n] = \frac{f_n^{(j)} - \overline{f_n^{(j)}}}{\sqrt{2}}.$$  

The dependence of the binary logarithm of the latter function $\log_2 \{\text{var}(d_{j+1}[n])\} = (\alpha + 1)j + \text{const}$ on the scales numbers $j$ corresponding to the time intervals $\tau = 2^j \Delta t$ is connected with the index of a generalized diffusion process, $(\Delta f)^2 = 2D\tau^\alpha$.

Fig. 4(A) demonstrates plots of the wavelet variances for two sample trajectories belonging particles from two sub-populations revealed in Fig. 2(B). These variances are computed for the full 3D trajectories of the velocity as

$$\sum \text{var}(dv_j) = \text{var}(dv_x) + \text{var}(dv_y) + \text{var}(dv_z).$$

The values are shown as markers connected by lines for a visual guidance. One can see that the way of the wavelet variances is the same as for the conventional time-averaged mean square displacements. But two dimensional step(time)-scale output of the wavelet transform has an advantage in the possibility to trace wavelet coefficients squared during the time course of the process for different scales as shown in Figs. 4(B)–(E).

The most important difference is observed for the scale $j = 3$ (the time window $\tau = 0.08$ ps), which falls into the regime of a non-Brownian motion with the population splitting (the respective states are denoted Fig. 4(A) by the black large circle and the blue square). The difference between Figs. 4(B) and (C) provides a natural physical explanation for the difference between molecular motions in two sub-populations: while Figs. 4(C), which gives the wavelet variance growing superdiffusively contains “a continual forest” of step-wise existing jumps that is typical for such processes, Figs. 4(B) demonstrates a kind of random point process. This means that a particle is caged within the first coordination sphere for a long time, oscillated there (its mean velocity is equal to zero) during a random time interval, then instantly jumps through the shell of surrounding particles (each this velocity jump is time-localized and has one and the same magnitude), and then continues to be caged in the next cell formed by nearest neighbors up to the next jump.

At the next stage, i.e. after the characteristic relaxation time, when the averaged motion is purely diffusive (the respective scale $j = 8$ corresponding to $\tau = 1.28$ ps) are denoted by the red large circle and the green square.
FIG. 4. (Color online) Average wavelet coefficients variance of velocities for two sample trajectories, which belong to each of two sub-populations (A). The sequences of the wavelet coefficients squared for two scales are shown in subplots (B)–(E), where they are highlighted by the same colors as large doubled markers indicating the respective scales of the wavelet variances.

Note that the behavior revealed for the short-time range of the process is quite close to the microscopic processes typical to supercooled and glass-forming liquids \[6, 32\]. They exhibit subdivision of particle configuration into jammed regions, where molecular motion is hindered and regions, where these motions are still long-ranged. The principal difference is in a persistence of such jamming. While regions of particle caging are growing with supercooling, and an amorphous solid is formed via the glass phase transition, there is no any phase transition in the case of overdamped argon, it remains a normal liquid under the pressure 20 MPa. The observed caging due to the high density particle packing at the temperatures of a “normal temperature range” is a transient effect but of the same physico-geometrical origin.

This conclusion on the similarity between molecular motions in supercooled and overdamped simple liquids has an additional independent confirmation, which refers to the reduced density fluctuations \[1\]. Fig. 5 shows the logarithm of this quantity as a function of the density simultaneously calculated along the saturation curve up to the triple point and along the isotherm \(T = 90\) K up to the vicinity of the freezing pressure at this temperature. The experiment-based database \[21\] was used as a source of thermodynamic data, i.e. they are completely independent of simulations.

At the first, one can see that all dots are placed along one straight line. This illustrates the assumption made for the derivation of Eq. \(2\) and the origin of accuracy of the density predictions shown in Fig. \(3\) (A).

At the second, the sequence of blue circles corresponding to the simultaneous change of the density and the temperature along the saturation curve and the black squares corresponding to the pressure change along the isotherm overlap up the the density corresponding to the triple point, i.e. to the normal freezing density. But further, the set of squares continues this sequence along the same straight line calculated using the saturated data. Thus, form the point of view of such continuation, the isothermal fluctuations at high pressures should correspond to the fluctuations in metastable liquid argon under normal saturated vapor, when argon it is accurately kept in fluid non frozen state, i.e. it represents a supercooled liquid.
V. CONCLUSION

The main results of this work can be summarized as follows. Although the self-diffusion in simple liquids in the thermodynamic limit behaves as a normal diffusion process even at high pressures, its detailed picture for time ranges less than the characteristic equilibration time is more complex and exhibits properties of instant trapping and population splitting that bring it closer to anomalous processes found in metastable media.

In addition, the discussed short-time behavior of the velocity fluctuations for a particle moving within a cage formed by the first co-ordination shell, which exhibits properties of anomalous diffusion, can be associated with the recent topic of non-stationary transient modes in Ornstein-Uhlenbeck and related stochastic processes [33–35].

Finally, it should be pointed out that non-trivial response of the density fluctuations on the growing particles packing under elevated pressures results in their description within a frame of the generalized linear model that makes available an analytic predictive expression for calculating the density and the self-diffusion coefficient of argon with accuracy corresponding to the experimental one.

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