ON LARGE TEMPORAL
LOCAL-STRUCTURE-BASED SCALE
IN 2D LENNARD–JONES LIQUID*

R. Orlik, A.C. Mituś

Institute of Physics, Wrocław University of Technology
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

A.Z. Patashinski and M. Ratner

Department of Chemistry and Materials Research Center
Northwestern University, Evanston, 60208 IL, USA

Dedicated to Professor Andrzej Fuliński on the occasion of his 70th birthday

In a two-dimensional (2D) equilibrium Lennard–Jones (LJ) liquid, coarse-grained time-averaged spatial distribution of local solid-like structures is studied in order to estimate the hypothetical local-structure-based long time scale. Standard NVE molecular dynamics simulation method is used. Time-averaged distributions indicate a structural slow mode with a characteristic time-scale at least two orders of magnitude larger than the local oscillation period.

PACS numbers: 61.20.Ja, 64.70.Dv

1. Local structure and its fluctuation in liquids and glasses

Hypothesis of a relatively long-living (solid-like) local structure in dense equilibrium liquids appeared at the beginning of XX-th century as an attempt to explain the Bragg scattering experiments. Since then, multiple qualitative and semi-quantitative formulations were proposed, see, *e.g.*, Refs. [1, 2]. The kinetic theory of liquids, formulated by Frenkel [3] (see also works of Eyring [4]), has put forward an intuitively clear physical picture of locally ordered clusters that resemble a crystal-like type of ordering but do not constitute nuclei of a solid phase in the thermodynamic sense.

A statistical-mechanics formulation based on a coarsened description assumes introduction of a local-order parameter field $\psi(\boldsymbol{r})$. Both crystalline (Hess [5], Mitus and Patashinskii [6]) and non-crystalline (Nelson, Toner, Steinhardt and Ronchetti [7, 8]) local order and corresponding fields $\psi(\boldsymbol{r})$ were introduced. These ideas were used to formulate a phenomenological theory of melting [6] and its generalization for a fluctuation theory of locally ordered liquids [9, 10].

In a system with long-living local structure, the thermal motions in equilibrium and super-cooled liquids is treated in terms of two components (see, *e.g.*, Refs. [11, 12] and references therein). The first component, vibrational motion of particles, conserves the local structure, while the second component, rearrangements in small clusters, changes the local structure in a cluster and correspondingly the local value $\psi(\boldsymbol{r})$ of the order parameter field. Both components of the motion result in fluctuations of microscopic characteristics. A widely accepted assumption states that the rearrangement component constitutes a slow mode of structural relaxation. Under this assumption, short-time averages (measurements) can be interpreted as thermodynamic properties at constant structure. This, in turn, leads in a natural way to the concept of short-time thermodynamics [11]. The short-time susceptibilities (bulk modulus $K_T\{\psi(\boldsymbol{r})\}$, heat capacity $c_V\{\psi(\boldsymbol{r})\}$ or thermal coefficient of pressure $\alpha_P\{\psi(\boldsymbol{r})\}$) are related to structure fluctuations at constant volume and temperature in a way that resembles relations between thermodynamic fluctuations and susceptibilities in classical statistical mechanics (see, *e.g.*, in Ref. [13]). The difference in short and long time susceptibilities gives a practical measure of structure fluctuations [12, 14, 15].

This approach offers a coarsened statistical-mechanics description of local-structure-driven effects both in equilibrium and non-equilibrium liquids and glasses. At limited experimental times, the glass transition can be treated as a crossover between short- and long-time behavior: upon super-cooling, the relaxation times grow and may exceed the characteristic times of an experiment. When the structurally frozen clusters become dominant, only the short-time regime can be realized. However, validation of the suggested physical picture of two-component motion, in particular in application to equilibrium liquids, remains a challenge. The crucial point here is the condition of structure conservation during short-time measurements. This condition means that the time of life of the local structure has to be significantly larger than a typical particle vibration period.

A test of the concept, and a quantification of an appropriate local-structure parameter ψ is a non-trivial task. The arguably simplest system to study the existence life-time of local structure is a 2D computer-generated liquid. The probabilistic analysis of local structure (LSA) revealed important static properties of 2D liquids close to the two-phase region, including

a high concentration of local solid-like structure, dramatic changes in ensembles of local structure fluctuations upon cooling, and a freezing criterion based on these changes [17, 18]. Then, the local structure in 2D equilibrium liquids may be characterized by an order parameter (see, *e.g.*, a review paper [16]). However, the study in Refs. [16–18] was limited to the statistics of snapshots. So far no time-dependent phenomena were studied using local structure approach. A direct observation of the lifetime of local structure assumes studying the history of particle arrangements and analyzing possible structure memory effects.

The aim of the current paper is to propose a simple approach for an analysis of structure memory effects. We apply this approach to a computer-simulated 2D equilibrium liquid, to provide arguments in favor of a long, local structure-based, temporal scale in this system.

The paper is organized as follows. The next section deals with molecular dynamics simulation of 2D Lennard–Jones system. Section 3 introduces the concept of time-averaged spatial distribution of local solid-like structures in 2D computer-simulated liquids. Those distributions are presented in Section 4. A general discussion is given in Section 5.

2. Simulation

We have simulated a 2D system of $N = 2500$ atoms interacting via Lennard–Jones potential $v_{\mathrm{LJ}}(r)$

$$v_{\mathrm{LJ}}(r) = 4\,\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right], \tag{1}$$

at reduced temperature $T^* \equiv k_{\mathrm{B}}T/\varepsilon = 0.7$ and reduced density $\rho^* \equiv \rho\,\sigma^2 = 0.8$ (k_{B} stands for Boltzmann constant). At this temperature the liquidus line was found (using LSA approach) at reduced density $\rho^* \simeq 0.82$ [17]. The critical temperature reads approximately $T^* \simeq 0.55$. A standard NVE molecular dynamics method with velocity Verlet algorithm was used [19]. The time step was $\Delta t = 0.0064\,\tau_0$. To relate this to a physical time, one uses argon atom parameters, to obtain $\Delta t = 2 \times 10^{-15}$ s. The total time of simulation was 10^{-10} s $\simeq 80\,\tau_{\mathrm{LJ}}$, where τ_{LJ} denotes the oscillation period in a harmonic regime of LJ potential: $\tau_{\mathrm{LJ}} \simeq 1.2 \times 10^{-12}$ s. The equilibrium characteristics were sampled after 5×10^4 equilibration steps.

It is important to keep in mind that 2D systems exhibit some peculiarities due to large (as compared to 3D) long-wavelength fluctuations [20]. For historical reasons we describe the system in terms of melting and liquid-solid coexistence between liquidus and solidus lines, although the solid phase may be actually a hexatic phase [21, 22]. In finite and not too large systems used for computer simulations, differences between the hexatic and the true crystalline phases are negligibly small [17].

3. Time-averaged spatial distribution of solid-like atoms

3.1. Local-structure analysis

An analysis of local solid-like structures in an instantaneous configuration of atoms is done using a probabilistic approach to structure recognition. Below, we present its main concepts; an interested reader can find more information in a review paper [16].

The local order in a 2D system in the neighborhood of an atom located at the point r is described by 2D local version of bond-order parameter of Nelson *et al.* [7, 8, 23]

$$Q_{6m}(\boldsymbol{r}) = \frac{1}{N_0} \sum_{i=1}^{N_0} Y_{6m}(\pi/2, \phi_i) , \qquad (2)$$

where $Y_{6m}(\theta, \phi)$ ($m = -6, \ldots, 6$) denotes the spherical harmonic function, the sum is taken over the $N_0 = 6$ metrically defined nearest-neighbors of the atom located at the point r and the pair of polar and azimuthal angles (θ_i, ϕ_i) describes the direction between the central atom r and its i-th nearest neighbor. The invariant $Q(\boldsymbol{r})$ for $(N_0 + 1)$-atom cluster with central atom at r is defined as [8, 23]

$$Q_6^2(\boldsymbol{r}) = \frac{4\pi}{13} \sum_{m=-6}^{6} |Q_{6m}(\boldsymbol{r})|^2 . \qquad (3)$$

The statistics of invariant Q_6 in an instantaneous configuration is described by a probability density function (PDF) $\rho(Q_6)$. This function is approximated by an empirical PDF, constituting a histogram of random variable Q_6, calculated from the set $\{Q_6(\boldsymbol{r}_i)\}$, $i = 1 \ldots N$, where N denotes the number of atoms. Furthermore, we assume that $\rho(Q)$ can be decomposed into PDFs $\rho_k(Q)$ describing fluctuating patterns of structure Γ_k

$$\rho(Q) = \sum_k c_k \, \rho_k(Q) . \qquad (4)$$

We use two patterns as the candidates for the local structure in the system. Pattern Γ_6 is a 2D hexagon, *i.e.* a $N_0+1 = 7$-atom cluster from 2D triangular lattice. Pattern Γ_5 is a 7-atom cluster centered around a 5-coordinated atom (disclination in 2D triangular lattice). The PDFs for patterns depend on the choice of an ensemble of the atoms' fluctuations. The "best" decomposition (4) is obtained by maximizing the significance level calculated from χ^2-test verification of the hypothesis which states that the data corresponding to the left-hand side and the right-hand side of (4) are drawn from the same distribution.

Local structure analysis, performed for various 2D liquids, has lead to a physical picture of 2D liquids as locally solid-like ordered systems [16]. In particular, the concentration of solid-like component constitutes, close to the liquidus line, approximately 0.5. It remains constant during simulations, up to thermodynamic fluctuations.

On the other hand, this analysis yields no information about the spatial distribution of solid-like part of the system, crucial for studies of its temporal evolution. Spatial distribution is a central object of interest in this paper and is found using a simple probabilistic approach worked out in Refs. [23, 24]. Namely, each 7-atom cluster can be classified as a fluctuation either of the pattern Γ_5 or Γ_6 using a Maximal Probability Decision Rule (MPDR). It states that a trial cluster with invariant Q_6 is a fluctuation of pattern Γ_6 when $Q_6 > Q_6^{(0)}$. $Q_6^{(0)}$ is a solution of an equation $\rho_6(Q_6^{(0)}) = \rho_5(Q_6^{(0)})$, where the PDFs for patterns are calculated from the decomposition (4). The value of $Q_6^{(0)}$ depends on temperature and density. Close to the liquidus line, for $T^* = 0.7$, $Q_6^{(0)} = 0.555$ [17]. The central atom of a cluster classified as a fluctuation of pattern Γ_6 is called a solid-like atom (SLA); the remaining atoms in the liquid are called liquid-like.

In Fig. 1 we present a typical spatial distribution of SLA atoms in an instantaneous configuration at $T^* = 0.7$ and $\rho^* = 0.80$, calculated using MPDR with $Q_6^{(0)} = 0.555$; liquid-like atoms are not shown. An analysis of the time evolution of this distribution is a challenge because of a highly irregular form of SLA clusters, and requires rather sophisticated tools. Those topics are at progress now and will be presented elsewhere. Instead of a direct calculation of characteristic time scales related to typical times of life of those clusters, in this paper we use an indirect approach and study only
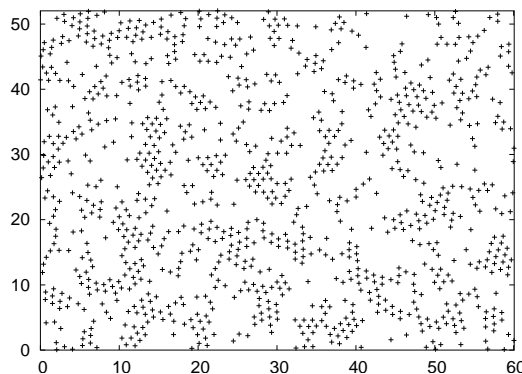

Fig. 1. Solid-like atoms (crosses) in a configuration of LJ liquid of 2500 atoms at $T^* = 0.7$, $\rho^* = 0.80$. Liquid-like atoms are not shown.

the coarse-grained time-averaged distributions of SLA atoms. As a result, a detailed information about important features of time evolution of small and large SLA clusters is lost. Nevertheless, even this simple approach provides a measure of structural memory and clearly indicates an existence of a time scale much larger than τ_{LJ}.

3.2. Coarse-grained time-averaged distributions

Coarse-grained time-averaged distributions of solid-like atoms are defined as follows. We chose a set of M configurations, spanning the time interval of length t. In each of the configurations the solid-like-atoms are found. The coarse-graining procedure is done in the following way. We divide the simulation box into $N_1 \times N_2 = N$ rectangles, *i.e.*, one atom on average per one rectangle. The cells are labeled with indices $i = 1, \ldots, N_1$, $j = 1, \ldots, N_2$. The occupation $p_{i,j}(t_k)$ of a cell (i,j) at a moment of time t_k ($k = 1, \ldots, M$, $t_M = t$), *i.e.*, in k-th configuration, is defined as a number of SLA atoms in this cell. As a rule, $p_{i,j}(t_k) = 0$ or 1. In general, it is possible that two SLA atoms occupy the same rectangle, but in dense systems those events are rare. The time-averaged coarse-grained spatial distribution of SLA clusters $p_{i,j}(t)$ is an average over configurations of $p_{i,j}(t_k)$

$$p_{i,j}(t) = \frac{1}{M} \sum_{k=1}^{M} p_{i,j}(t_k) \,. \tag{5}$$

Parameter $p_{i,j}(t)$ gives the probability of an occupation of rectangle (i,j) in a time interval of length t. However, because of the fluctuations discussed above, the notion of the probability has to be treated with some care. For an ideal lattice $p_{i,j}(t) \equiv 1$. The plots of $p_{i,j}(t)$ yield important information about the stability of SLA clusters in a time interval t. For sufficiently large time intervals, an average coarse-grained distribution of SLA clusters smears out and $p_{i,j}(t)$ becomes a constant p_∞ that is independent on i, j and t. Moreover, this constant is equal to an average (equilibrium) concentration of SLA atoms $c_6(T^*, \rho^*)$

$$p_{i,j}(t) \rightarrow p_\infty = c_6(T^*,\, \rho^*) \quad (t \rightarrow \infty) \,. \tag{6}$$

This property of $p_{i,j}(t)$ plays an important role in the further analysis. Namely, the decay of spatial heterogeneity of $p_{i,j}(t)$ with increasing time interval t gives information about local structure-based time-scales in the system. If the plot of $p_{i,j}(t)$ displays spatial heterogeneity, then memory effects exist in the corresponding time interval t, leading to spatial correlations between SLA clusters.

4. Results

In Fig. 2 we present the time-averaged probabilities $p_{i,j}(t)$ for time interval $t = 10^{-10}$ s $\simeq 80\,\tau_{\rm LJ}$, calculated for the reduced density $\rho^* = 0.8$ at reduced temperature $T^* = 0.7$. The equilibrium concentration of solid-like structures reads $c_6 = 0.42 \pm 0.01$. Instead of a 3D plot we present a few 2D cross-sections, constituting of those areas in (i,j) plane where $p_{i,j}(t) \geq p$, for the following values of p: $p = 0.3$, 0.4, 0.5 and 0.6. We find that the cross-sections are not spatially homogeneous. In Fig. 2(a) there are a few patches where the time-averaged local solid-like structures occur with low probability $p < 0.3$. The size of those patches grows with increasing value of probability p. In the case of $p = 0.4$, *i.e.* close to the value $p_\infty = 0.42$, they occupy a large part of (i,j) plane, see Fig. 2(b). For a higher probability $p = 0.5$, noticeably larger than p_∞, one still finds patches where SLA atoms tend to stay during the simulation (Fig. 2(c)). Some traces of this inhomogeneity are still seen for $p = 0.6$, see Fig. 2(d). Clearly, the spatial distribution of time-averaged solid-like structures has not
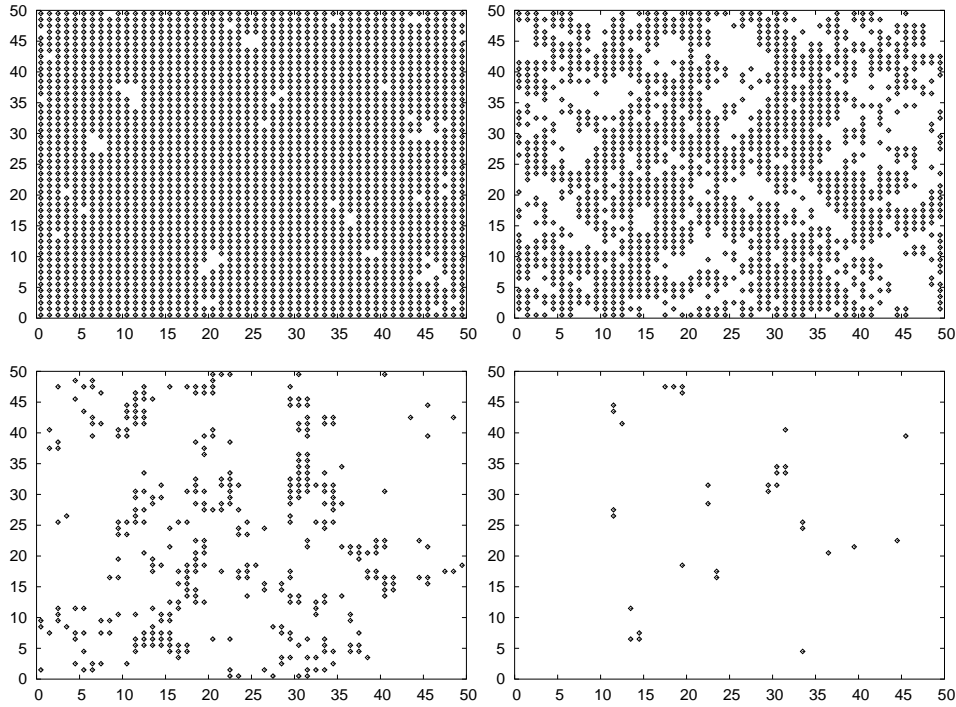

Fig. 2. Cross-sections of time-averaged probabilities $p_{i,j}(t)$ with plane $p = {\rm const.}$ for time interval $t = 10^{-10}$ s $\simeq 80\,\tau_{\rm LJ}$, calculated for the reduced density $\rho^* = 0.8$ at reduced temperature $T^* = 0.7$, for (a) $p = 0.3$, (b) 0.4, (c) 0.5 and (d) 0.6.

reached the homogeneous long-time form discussed in the previous section, in which case the cross-sections for $p = 0.3$ and 0.4 should consist of only black points, while those corresponding to $p = 0.5$ and 0.6 should be white.

5. Discussion and conclusions

In this paper, we have introduced an indirect measure for memory effects related to local structures in 2D computer simulated liquids, namely the time-averaged coarse-grained distributions of solid-like atoms. The main result of our study is the observation that in the time interval two orders of magnitude larger than the oscillation period τ_{LJ} , the averaged SLA distribution is not uniform. The plots display the islands in (i, j) plane occupied by SLA atoms with a relatively high probability during the simulation run. And vice versa, the regions exist where the SLA appear with a noticeably lower probability than its average value, the last being equal to the equilibrium concentration of SLA atoms. We conclude that in a 2D LJ liquid, memory effects exist due to a local solid-like structure, which becomes a good candidate for a slow mode.

We expect that in super-cooled liquids the difference between short and long-time scales is more distinct than in an equilibrium liquid. The time scales $t > 10^{-10}$ s are sufficiently large for (local) phonon-like modes in compact condensed matter, and for a short-time, local-structure-based thermodynamics in glass-forming liquids [15].

More studies are necessary to quantify the concept of large time scales. This includes a detailed analysis of the dependence of results on the averaging period. Our preliminary results show that some heterogeneity in time-averaged distributions persists for times much larger than those used in the present work. Studies for other values of thermodynamic parameters should also be done. Finally, let us point out that the real (*i.e.*, not averaged over time) dynamics of SLA clusters should be studied in order to cast more light onto structural processes that define the time scales in liquids. Those studies are in progress now.

REFERENCES

[1] A.R. Ubbellohde, *The Molten State of Matter*, J. Wiley & Sons Ltd., NY 1978.

[2] J.M. Ziman, *Models of Disorder*, Cambridge Univ. Press, Cambridge 1979.

[3] J. Frenkel, *Kinetic Theory of Liquids*, Clarendon Press, Oxford 1946.

[4] H. Eyring, *J. Chem. Phys.* **4**, 283 (1936); H. Eyring, Mu Shik Jhon, *Significant Liquid Structures*, Willey & Sons Ltd., NY 1969.

[5] S. Hess, *Z. Naturforsch.* **A35**, 69 (1980).

[6] A.C. Mitus, A.Z. Patashinskii, *Sov. Phys. JETP* **53(4)**, 798 (1981); *Phys. Lett.* **A87**, 79 (1982).

[7] D.R. Nelson, J. Toner, *Phys. Rev.* **B24**, 363 (1981).

[8] J.P. Steinhardt, D.R. Nelson, M. Ronchetti, *Phys. Rev. Lett.* **47**, 1297 (1981).

[9] A.Z. Patashinskii, B.I. Shumilo, *Sov. Phys. JETP* **62**, 177 (1985).

[10] A.Z. Patashinskii, L.D. Son, *Sov. Phys. JETP* **76**, 534 (1993).

[11] A.Z. Patashinski, M. Ratner, *J. Chem. Phys.* **120**, 2814 (2004).

[12] A.Z. Patashinski, V.L. Pokrovskii, *Fluctuation Theory of Phase Transitions*, 2nd ed., Pergamon Press, Oxford 1979.

[13] L.D. Landau, E.M. Lifshitz, *Statistical Physics*, Part 1, 3rd ed., Pergamon Press, Oxford 1980.

[14] A.Z. Patashinski, M. Ratner, *Physica A* **314**, 526 (2002).

[15] A.Z. Patashinski, M. Ratner, *J. Chem. Phys.* **121**, 4711 (2004).

[16] A.Z. Patashinski, A.C. Mitus, M. Ratner, *Phys. Rep.* **288**, 409 (1997).

[17] A.C. Mitus, A.Z. Patashinski, A. Patrykiejew, S. Sokolowski, *Phys. Rev.* **B66**, 184202 (2002).

[18] A.C. Mitus, R. Orlik, A.Z. Patashinski, A. Patrykiejew, S. Sokolowski, O. Riefert, *Acta Phys. Pol. B* **34**, 3751 (2003).

[19] M.P. Allen, D.J. Tildesley, *Computer Simulations of Liquids*, Clarendon Press, Oxford 1987.

[20] K.J. Strandburg, *Rev. Mod. Phys.* **60**, 161 (1988).

[21] K. Binder, S. Sengupta, P. Nielaba, *J. Phys.: Condens. Matter* **14**, 2323 (2002).

[22] M. Kosterlitz, P.J. Thouless, *J. Phys.* **C6**, 1181 (1973); V.L. Berezinskii, *Sov. Phys. JETP* **32**, 493 (1971); *Sov. Phys. JETP* **34** , 610 (1972); B.I. Halperin, D.R. Nelson, *Phys. Rev. Lett.* **41**, 121 (1978); D.R. Nelson, B.I. Halperin, *Phys. Rev.* **19**, 2457 (1979); A.P. Young, *J. Phys.* **C11**, L453 (1978); *Phys. Rev.* **B19**, 1855 (1979).

[23] A.C. Mitus, A.Z. Patashinskii, S. Sokolowski, *Physica A* **174**, 244 (1991).

[24] H. Gades, A.C. Mitus, *Physica A* **176**, 297 (1991).